

Low-Dimensional Nanostructured Catalysts of Copper Oxides and Nickel Oxides Supported on Graphene and Their Applications in Biosensing and Photoelectrochemical Hydrogen Evolution

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Statement of Contributions

This thesis contains material from one published journal paper and two submitted journal papers that I authored or coauthored.

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W. Y. Gao conducted the primary architect of the research design, data collection, and analysis. X. J. Zhou proposed the original idea of substrate and material selection. N. F. Heining, J. P. Thomas, L. Zhang provided technical support. K. T. Leung discussed the results and contributed to correcting the manuscript. All the authors revised the manuscript.

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Abstract

Cuprous oxide (Cu_2O) nanomaterials provide a versatile platform for building non-enzymatic glucose sensors. In particular, Cu_2O nanocubes with controllable sizes and distributions can be deposited electrochemically on a conductive graphene strip as a soft substrate under different conditions, including overpotential, temperature, copper ion electrolyte concentration, and deposition time. The graphene substrate provides a promising condition for sensing because of its high conductivity, high specific surface area, and unique thermal and mechanical properties. A more negative overpotential is found to produce smaller nanocubes with a large number density, while the deposition temperature could affect the morphology of nanocubes. The size of the nanocubes increases with increasing copper ion concentration and deposition time. Using an optimal condition of -1.0 V vs Ag/AgCl, 1 mM $[\text{Cu}^{2+}]$, and 100 s deposition time at room temperature, we obtain a near-homogeneous monolayer of Cu_2O -shell Cu-core nanocubes, ~ 50 nm in size, on a graphene strip substrate. The Cu_2O nanocubes/graphene is used as a high-performance sensor with a wide detection range of 0.002 - 17.1 mM and a high sensitivity appropriate for saliva-range glucose sensing. It is also used to test saliva glucose in the real sample with 95% accuracy. This non-enzymatic glucose sensor is considerably better in performance than other non-enzymatic sensors, including those based on bare graphene, and graphene sputter-coated with a Cu film, and conventional enzymatic sensors such as glucose oxidase immobilized on graphene. For the glucose oxidase/graphene sensor, the addition of the enzyme increases the resistance of the graphene substrate, which leads to poorer performance. Even with an added Nafion film, the glucose oxidase/Nafion/graphene sensor only has a slightly increased detection range. In addition to being an excellent catalyst, Cu_2O nanocubes have a large specific surface area and a large number of active sites. These nanomaterial properties, along with the use of a high-conductivity substrate like graphene, make the Cu_2O nanocubes/graphene sensor among the best saliva-range glucose sensors reported to date.

Photoelectrochemical hydrogen evolution (HER), a half reaction of water splitting, is crucial to the low-cost, environmentally friendly production of clean H_2 fuel as part of the solution for transitioning away from a fossil fuel economy. Electrodeposition of a controllable Cu film on graphene followed by thermal oxidation at 200 - 400 °C has been used to produce copper oxide (Cu_xO , $x=1,2$) nanowires. The relative compositions of CuO and Cu_2O layers in Cu_xO -Cu/graphene system form a heterojunction structure enabling high efficiency for electron-hole separation and a fast charge transfer rate, where the CuO layer with a proper thickness enhances light absorption, improves the charge separation, and serves as a protective layer for Cu_2O photocorrosion while graphene serves as a flexible high conductive substrate. A high-performance dual Z-scheme heterojunction photocatalyst to greatly improve charge carrier separation, increase carrier density, and reduce electron-hole recombination is obtained by

decorating this $\text{Cu}_x\text{O-Cu/graphene}$ system with an efficient co-catalyst based on Cu-based ternary CuFe_2O_4 nanoparticles, obtained by a solvothermal method. The addition of CuFe_2O_4 nanoparticles on the best optimized $\text{Cu}_x\text{O-Cu/graphene}$ is found to nearly double the photocurrent from -2.64 mA cm^{-2} to -4.91 mA cm^{-2} , making this dual heterojunction catalyst the best catalyst system for HER reported to date.

Electrodeposition of nickel nanoparticles, achieved through potentiostatic amperometry, followed by thermal annealing at 200-400 °C has produced nickel oxide nanoparticles on flexible graphene substrates. Using transmission electron microscopy and depth-profiling X-ray photoelectron spectroscopy, we show that the resulting NiO_x nanoparticles exhibit several Ni oxidation states and a core-shell heterostructure, with a metallic Ni crystalline core and a NiO crystalline shell with a mixed crystalline-amorphous NiOOH/Ni(OH)_2 skin. The composition of NiOOH/Ni(OH)_2 redox couple relative to NiO is found to vary with the annealing temperature and annealing time. Besides, the high conductive graphene substrate enhances the electron transfer. The NiO_x nanoparticle samples obtained with selected annealing temperature-time combinations are used for lactate detection, with the best sample showing an excellent linear range of 0.02-65.1 mM, a high sensitivity of $80.0 \mu\text{A mM}^{-1} \text{ cm}^{-2}$, and an impressive limit of detection of 0.00015 mM. NiO_x nanoparticle sample is also tested for lactate sensing in an artificial sweat electrolyte, and it exhibits a reduced linear range of 0.02-53.1 mM and a lower limit of detection of 0.00013 mM, but the same high sensitivity of $80.0 \mu\text{A mM}^{-1} \text{ cm}^{-2}$. This sensing performance can be optimized by controlling the $\text{NiOOH} + \text{Ni(OH)}_2$ relative composition to NiO, with the sample obtained with a higher relative content at a lower annealing temperature found to provide more reactive sites for sweat-range lactate detection and therefore higher sensitivity.

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Dedication

To my supportive parents, Jinglan Zhang and Xianhua Gao,

To my lovely little family, Pei Li and Muxue Li,

To my respective mother-in-law, Yubao Ye.

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Chapter 1

Introduction

1.1 Nanostructured Transition Metal Oxides

Nanomaterials are materials with at least nanometer-scale dimension and represent the crucial connection between individual atoms and molecules and the bulk systems. The science and technology of nanomaterials have ignited tremendous enthusiasm and expectations over the past few decades because unique mechanical, optical, magnetic, electrical, catalytic, and other properties emerge at this length scale. The properties of nanomaterials can be systematically modulated through precise control of such parameters as size and shape, their synthesis conditions and appropriate functionalization. One of the common classifications for nanomaterials is based on dimensionality or the number of dimensions that are not on the nanoscale (but are on the bulk scale), including zero-dimensional (nanoclusters, nanoparticles, nanocubes), one-dimensional (nanowires, nanorods, nanotubes), two-dimensional (nanosheets, nanowalls), and three-dimensional materials (powders, fibers, multilayer films).

Transition metal oxide (TMO) represents one of the most interesting categories of solids due to their various structures and properties arising from the distinctive characteristics of the outer d-electrons. This unique electron configuration gives TMO a broad spectrum of electrical behavior, ranging from metallic conductivity at one end of the range to high level of insulation at the other.¹ TMO is also considered as one of the most promising functional materials because of its low cost, unique electrical, magnetic, and optical properties. Most TMOs are semiconductors with a fairly wide range of bandgap energy that enables the transmittance of light up to the ultra-violet region. The optical bandgap of TMO can be adjusted through controlling the thickness and particle size,² while the electronic properties of TMO are highly sensitive to defects leading to a degradation of work function and instability.³ Therefore, TMO nanostructures are more attractive than bulk-phase structures because of their high specific surface areas, and the availability of a great number of active sites. To introduce defects in nanostructured TMO, many methods have been developed, such as heteroatom doping, solution treatment, annealing treatment, template synthesis, and plasma etching.⁴ As a result, nanostructured TMOs are considered excellent material candidates used in numerous applications, including lithium-ion batteries,⁵ supercapacitors,⁶ gas sensors,⁷ biosensors,⁸ solar cells,⁹ photocatalysts,¹⁰ enhancers of thermal conductivity of nanofluid,¹¹ nanoenergetic materials,¹² superhydrophobic surfaces,¹³ and removal of organic pollutants from wastewater.¹⁴ In

the present work, we will focus on copper oxide, nickel oxide and copper ferrite nanomaterials as electrocatalysts or photocatalysts that can be produced by simple fabrication processes.

1.1.1 Copper Oxide Nanomaterials

Copper oxides have long enjoyed extensive applications across multiple disciplines, owing to their low cost and unique properties, particularly their inherent conductivity. Three p-type semiconductors of copper oxides are commonly identified by their binary phases: cupric oxide (CuO), cuprous oxide (Cu₂O) and paramelaconite (Cu₄O₃).¹⁵ Among these, CuO is the most stable phase. On the other hand, Cu₄O₃ is an intermediate copper oxide compound, which is difficult to synthesize because of stabilization issues between mixed valence Cu⁺ and Cu²⁺ ions, and is therefore not considered in the present work.¹⁶ CuO has a direct bandgap of 1.2-1.7 eV.¹⁷ CuO typically displays a distinctive monoclinic crystal structure, in which Cu²⁺ is bonded in a square coplanar geometry to four equivalent O²⁻ atoms. It is well-known that the properties of CuO nanostructures such as optical, electrical, antimicrobial, magnetic, and catalytic properties are size- and shape-dependent.¹⁸⁻²⁰ CuO nanostructures can be synthesized using a variety of methodologies, yielding diverse shapes and dimensions. As illustrated in Figure 1.1, these include nanoparticles and low-dimensional structures such as nanowires,²¹ nanorods,¹⁰ nanotubes,⁶ nanocubes,²² and nanoflakes,⁷ as well as nanowhiskers²³. A variety of fabrication techniques for CuO nanostructures, including solution-based methods such as hydrothermal synthesis,²⁴ co-precipitation,²⁵ and electrodeposition,²⁶ and solid-state methods such as magnetron sputtering are available.²⁷

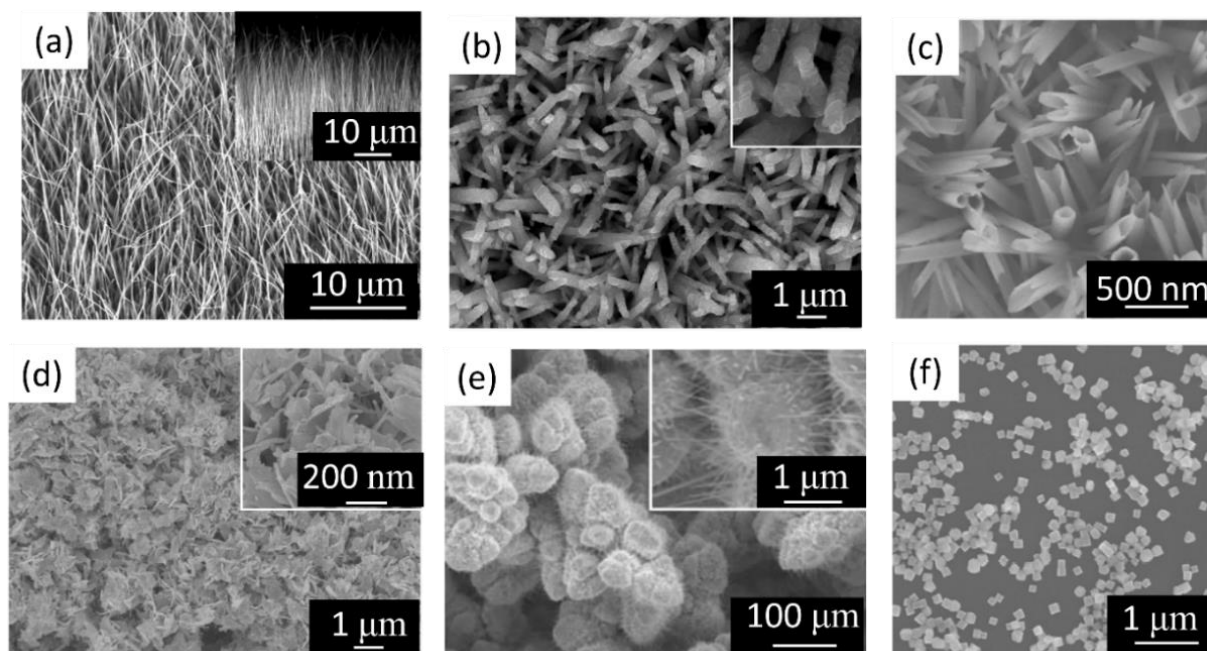


Figure 1.1 Morphologies of various CuO nanostructures, (a) nanowires,^{*} (b) nanorods,[†] (c) nanotubes,[‡] (d) nanoflakes,[§] (e) nanowhiskers,^{**} and (f) nanocubes^{††}.

Cu₂O has a larger direct bandgap of 2.0-2.4 eV²⁸ than CuO. Cu₂O features a cubic crystal structure, with copper and oxygen atoms occupying distinct yet interrelated positions. Within this structure, copper atoms reside in a face-centered cubic sublattice, while oxygen atoms are situated in a body-centered cubic sublattice.²⁹ Cu₂O has attracted a lot of attention due to its electrical, catalytic, and optical properties. In particular, the facet-dependent properties of Cu₂O have been widely studied. Cu₂O nanomaterials can be fabricated by using many synthesis methods, including wet chemistry (hydrothermal synthesis,³⁰ solvothermal synthesis,³¹ sol-gel method³² and electrodeposition³³), magnetron sputtering³⁴ and irradiation technique,³⁵ enabling the fabrication of nanowires,³⁶ nanotubes,³⁷ nanocrystals,³⁸ nanocubes,³⁹ cuboctahedra⁴⁰ and thin films⁴¹. Among these synthesis methods, the wet-chemistry approach is the most popular for manipulating the exposed facets of Cu₂O because of its exceptional flexibility in adjusting the nucleation and growth

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[†] Zheng, Z., Zhou, W. L., *RSC Adv.* **2023**, 13, 3487-3493. Copyright 2023 by Royal Society of Chemistry.

[‡] Lan, W., Xie, E. Q., *Chem. Eng. J.* **2019**, 374, 191-188. Copyright 2019 by Science Direct.

[§] Bai, H. N., Zheng, Y. D., *Sens. Actuators B Chem.* **2021**, 337, 129783. Copyright 2021 by Science Direct.

^{**} Mukherjee, N., Mondal, A., *Mater. Lett.* **2011**, 65, 3248-3250. Copyright 2011 by Science Direct.

^{††} Zhao, J., Wang, B., *CrystEngComm.* **2021**, 23, 6107. Copyright 2021 by Royal Society of Chemistry.

rates along distinct orientations. Theoretically, the Gibbs-Wulff law determines the equilibrium shape of a crystal, with high-energy facets typically diminishing under equilibrium.⁴² In practice, the final shape of the crystal and its exposed facets are determined by the dynamic balance between thermodynamic forces and kinetic processes. Indeed, our group has demonstrated cubic, cuboctahedral, and octahedral Cu-Cu₂O core-shell nanoparticles with different average sizes and number densities deposited on Si substrate by controlling the electrolyte concentration and deposition time through electrodeposition.⁴³ By changing the electrolyte concentration, the growth rates in the [111] and [100] directions that produce the (111) and (100) facets can be controlled, leading to shape change from cube to truncated cube, cuboctahedron, and finally truncated octahedron as shown in Figure 1.2.⁴³ With the wide variety of nanostructures, both cuprous oxide and cupric oxide are found to be important to and indeed widely used in multiple applications, both individually and in combination.

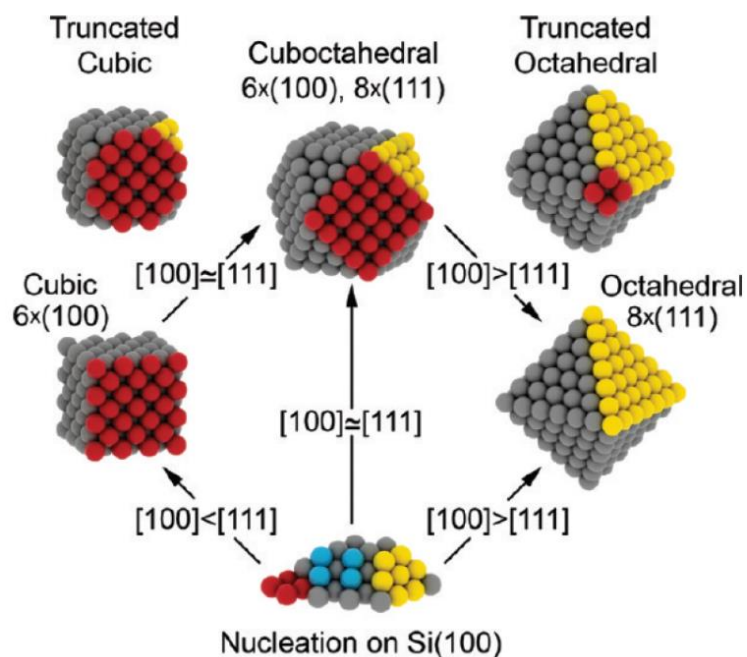


Figure 1.2 Schematic diagram of the shape evolution of Cu nanoparticles at different relative growth rates along the [100] and [111] directions.^{††}

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1.1.2 Nickel Oxide Nanomaterials

Nickel oxide (NiO) is an intrinsic p-type semiconductor with a wide band gap of 3.6-4.0 eV.⁴⁴ NiO nanomaterials have attracted increasing attention due to not only their cost-effectiveness and ease of synthesis and isolation, natural abundance and environmental friendliness, but also their ferromagnetic properties, high chemical stability, and unique electrical and optical properties. NiO has a wide variety of nanostructures, including nanoflowers, nanospheres, nanorods, nanosheets, nanohexagons and nanopyramids.⁴⁵ Fabrication of NiO nanomaterials has been extensively investigated, and includes wet-chemistry methods such as hydrothermal synthesis,⁴⁶ electrochemical synthesis,⁴⁷ sol-gel process,⁴⁸ microwave-assisted method,⁴⁹ chemical bath deposition⁵⁰ and chemical precipitation,⁵¹ and dry synthesis methods such as thermal decomposition,⁵² magnetron sputtering,⁵³ and electrospinning⁵⁴. In addition, green synthesis methods of NiO nanomaterials that are based on plant extracts,⁵⁵ dead biomass,⁵⁶ and bacteria⁵⁷ are available.

One notable drawback of NiO semiconductor is its low electrical conductivity that is insufficient to support fast electron transport during reaction. It is possible to increase the conductivity of NiO by annealing in air or doping with noncovalent atoms to increase the concentration of Ni²⁺ vacancies and thus reduce the resistivity of NiO.⁵⁸ Annealing in air is a simple and effective strategy to obtain the nickel hydroxide (Ni(OH)₂) and nickel oxyhydroxide (NiOOH) redox couple (collectively termed NiO_x) offering the potential for rapid electron transport and ultimately leading to enhanced electrochemical performance.⁵⁹ Bode *et al.* have illustrated through X-ray diffraction analysis that NiO_x is composed of four main phases: β-Ni(OH)₂, α-Ni(OH)₂, β-NiOOH, and γ-NiOOH.⁶⁰⁻⁶¹ As is shown by the Bode's diagram in Figure 1.3, the β-NiOOH phase develops during the initial charge, followed by γ-NiOOH phase under the overcharging conditions. The difference between the two phases is attributed to the distinct oxidation states of Ni and the intercalated species involved, where the number and position of the hydrogen atoms (protons) in both structures remain undefined. NiOOH can be used as reaction sites, due to the presence of active –OOH intermediate, for electrocatalytic oxidation of electrocatalytic alcohol, aldehyde and water,⁶² solar cell application,⁶³ oxygen evolution reaction,⁶⁴ and biosensors⁶⁵.

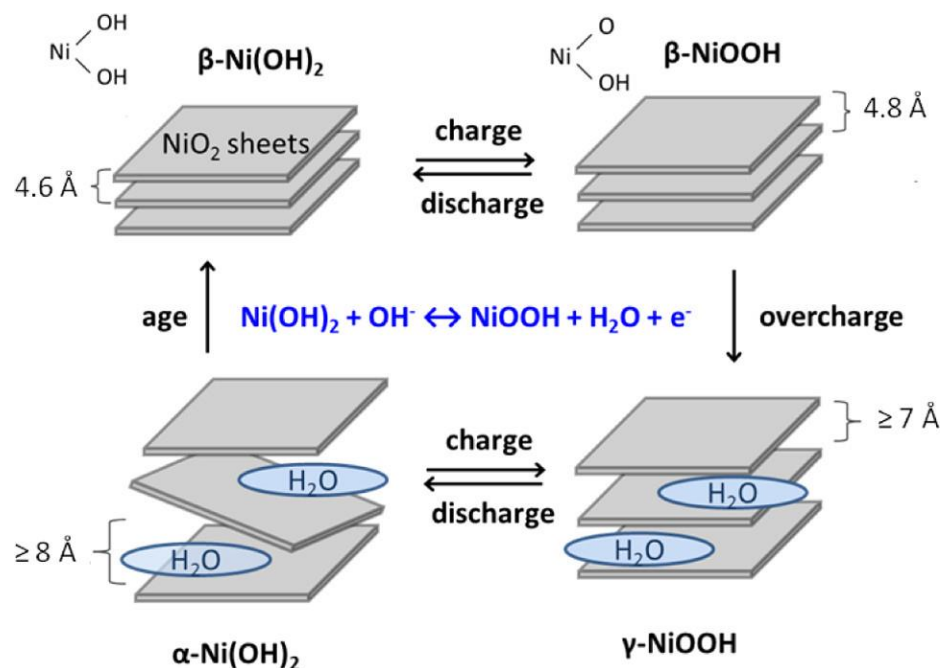


Figure 1.3 Bode scheme for $\text{Ni(OH)}_2/\text{NiOOH}$ redox transformation.^{§§}

1.1.3 CuFe_2O_4 Nanomaterials

Spinel is a ternary transition metal oxide with the general formula AB_2O_4 , where A is a divalent cation (M^{2+}) and B is a trivalent cation (M^{3+}). A and B atoms can be group 2, group 13, and first-row transition metals. Two crystallographic sites: octahedral and tetrahedral sites exist in this structure.⁶⁶ Among these AB_2O_4 spinel nanomaterials, spinel ferrite is one of the most promising soft magnetic materials with high saturation magnetization and coercivity, as well as good thermal and electrical properties.⁶⁷

Copper ferrite, CuFe_2O_4 , is a ferrimagnetic material with a spinel structure. It is a semiconductor with a narrow direct bandgap (1.5-1.7 eV).⁶⁸ The exceptional mechanical strength, high thermal stability, outstanding electrical conductivity have made copper ferrite an excellent candidate for use in catalysis and energy storage devices. CuFe_2O_4 can crystallize either in a face-centered cubic phase or body-centered tetragonal phase as shown in Figure 1.4 based on the synthesis conditions according to the Jahn-Teller effect.⁶⁹ It can be synthesized by solid-state reaction,⁷⁰ co-precipitation,⁷¹ and solution-based reactions such as those used in sol-gel method,⁷² hydrothermal synthesis,⁷³ and solvothermal synthesis⁷⁴. During the last five years, CuFe_2O_4 has

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been reported to contribute to the fabrication of dual Z-scheme heterojunction photocatalyst with two other kinds of semiconductor to enhance the photocatalytic activity through efficient electron-hole separation.

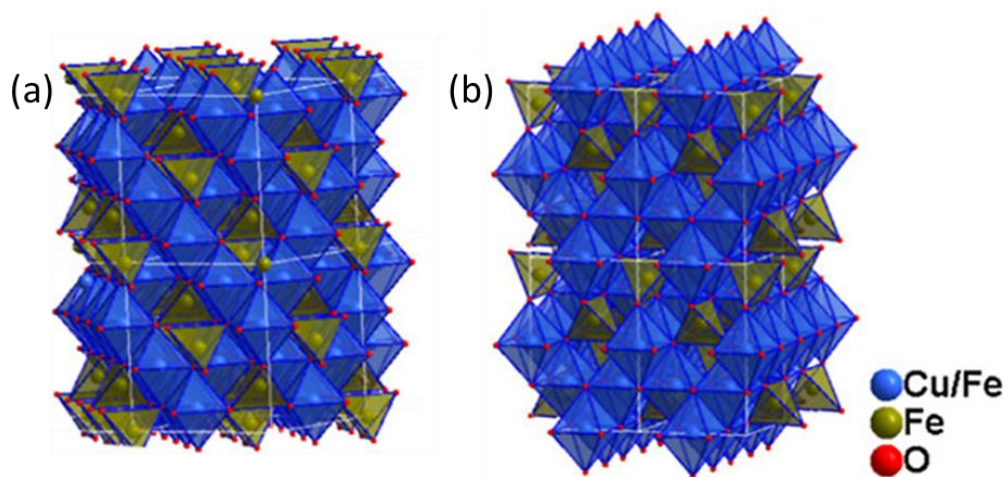


Figure 1.4 Crystal structure of (a) face-centered cubic phase and (b) body-centered tetragonal CuFe₂O₄.^{***}

1.2 Substrate Selection

Since the main application in this work is focused on catalysis in electrochemistry, appropriate choice of the substrate (used as the electrode) is critically important. The commonly used substrates for electrodeposition are glassy carbon electrode (GCE), gold electrode, indium tin oxide (ITO) or fluorine tin oxide (FTO), and silicon wafer. Different substrates have different properties. For instance, GCE is carbon-based electrode that is widely used in electrochemical studies. GCE exhibits excellent chemical stability and resistance to corrosion, low background current, wide potential window, and reproducibility, but GCE is also fragile and has limited conductivity. Other than GCE, gold electrodes are also widely used because of their chemical stability, low background current, easy surface modification, and high electrical conductivity, but gold electrodes are expensive and relatively soft and malleable, which make them more prone to physical damage and scratching. Furthermore, both GCE and gold electrodes must be polished by hand every time after use, which makes them cumbersome for reuse. It is therefore beneficial to find disposable low-cost

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alternative electrodes. Another class of widely used electrodes in electrochemistry is ITO and FTO. ITO has high transparency, low electrical resistivity, and compatibility with lithography and patterning processes,⁷⁵ but its high cost, limited supply, brittleness and environmental impact limit the application of ITO. Compared with ITO, FTO has higher transparency, lower cost, better stability, and higher electrical resistivity, but it is not compatible with certain materials and more challenging for material deposition. Both ITO and FTO cannot cover all the common substrate requirements. Silicon wafer has also been used as electrode because it has high electrical conductivity with appropriate doping and excellent potential for large-scale production and is easily integrated with other semiconductor components. However, silicon wafers, such as the gold electrode and ITO, are expensive. Apart from these common electrodes, some novel electrodes have also been developed based on the achievements of nanotechnology. As flexible electrodes are required for some applications such as lithium-ion batteries, flexible energy storage systems, and flexible supercapacitors,⁷⁶ carbon-based films such as carbon nanotubes⁷⁷ and graphene⁷⁸ are used as conductive substrates, while conventional paper,⁷⁹ textile,⁸⁰ polymer,⁸¹ and plastic films⁸² are used as non-conductive substrates.

Among the novel flexible substrates, graphene, discovered in 2004,⁸³ has attracted a lot of interest in many areas of fundamental research and technological applications. Graphene is a two-dimensional material consisting of a single layer of carbon atoms arranged in a hexagonal lattice. Graphene was initially dissolved in suspension to work as 2D nanomaterials. Later, some researchers started to use graphene as substrates for immobilizing and enhancing the activity of other catalysts.⁸⁴ Work has also been done to make graphene paper that is mechanically strong, highly electrically conductive, and biocompatible. Graphene sheets are stacked layer by layer through both intralayer and interlayer crosslinks that lead to highly ordered structures.⁸⁵ With the development of manufacturing technology for graphene, graphene paper has become a readily available commercial product, similar to ITO and silicon wafer.

1.3 Experimental Details

1.3.1 Electrochemical Synthesis and Characterization

In the present work, a three-electrode electrochemical cell connected to an electrochemical workstation (CH Instruments 660E) has been used for all the electrochemistry experiments (Figure 1.5a). The three electrodes consist of the working electrode, an Ag/AgCl electrode filled with a 1 M KCl solution used as the reference electrode, and a platinum wire as the counter electrode. The working electrode is typically a conductive substrate such as a graphene chip used for

electrodeposition of nanomaterials. The aqueous solution used for the electrochemical reaction consists of a primary electrolyte and, where appropriate, a supporting electrolyte to control the pH.

To deposit nanomaterials on a graphene substrate, potentiostatic amperometry in an aqueous solution is used in the present work. In potentiostatic amperometry, the current is measured as a function of time at a constant applied potential.⁸⁶ When an electric potential is applied to the substrate (served as the working electrode), electrons are drawn from the surface of the working electrode, resulting in the reduction of the metal ions in the solution to form a metallic coating on the electrode surface. The electrolyte solution typically contains metal ions that are positively charged. In addition to the electrolyte concentration, other experimental parameters such as deposition time, over-potential, and pH could also influence the electrodeposits. The details of these experimental conditions are given in the experimental parts of Chapters 2-4. In the present work, we also use cyclic voltammetry to study the redox behavior of chemical compounds and the electrochemical properties of materials.⁸⁶⁻⁸⁷ It involves measuring the resulting current over a range of applied potentials on the working electrode in a cyclic fashion. The potential is typically varied linearly with time, first increasing from an initial potential to a final potential (forward scan) and then decreasing from the final potential back to the initial potential (reverse scan), forming a cyclic sweep. Cyclic voltammogram can be used to provide information on the catalytic properties of nickel oxides in the presence of lactate by altering the various scan rates. The details about these specific experiments are given in Chapter 4.

Electrochemical impedance spectroscopy (EIS) is a powerful technique used for the analysis of interfacial electrode reactions and the electrical properties of electrodeposited materials.⁸⁸ According to Ohm's law, the resistance R of an ideal resistor is given by $R = E/I$, where E is the voltage, and I is the current. However, in practical scenarios, the impedance is used to measure the resistance to electrical flow in more complex systems. Typically, the calculation of electrochemical impedance involves the current passing through the cell when an AC potential is applied at different frequencies. The most common approach to interpret the data is the use of Randle's simplified equivalent circuit model⁸⁹ to infer a number of important parameters, including the solution resistance (R_s), double-layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), and the Warburg impedance element (Z_w). In the present work, the details of the EIS experiment are given in Chapter 3.

In materials science, thermal annealing is often used as an important post-synthesis treatment that can significantly impact not only the nature of the product but also the mechanical, thermal, and electrical properties of the product, which can make the product more suitable for a targeted

application. This procedure often involves heating a material at a high temperature, maintaining it at that temperature for a specified duration, and subsequently cooling it to allow for grain growth. More importantly, a lower yet sufficiently high annealing temperature can induce surface oxidation of the material. Annealing can also be conducted in various ambient environments (at different partial pressure of gases of interest) to achieve specific products or properties. A tube furnace connected to a temperature controller and a gas flow system used to anneal samples in oxygen or dry air is shown in Figure 1.5b. In the present work, the annealing process is carried out under various gas flow conditions at selected temperatures after electrodeposition as discussed in Chapters 3-4.

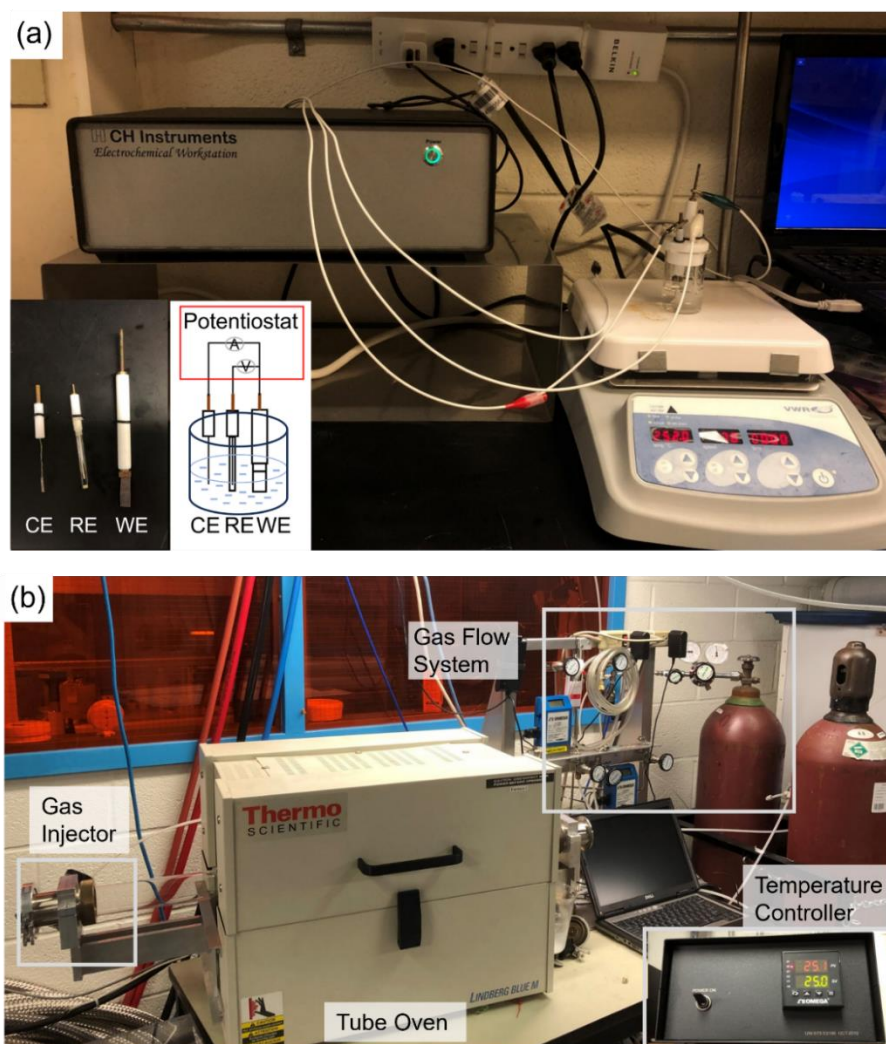


Figure 1.5 (a) Photograph of an electrochemical workstation (CHI 660E) and a standard three-electrode electrochemical cell setup. The graphene substrate is used as the working electrode (WE),

a Pt wire is used as the counter electrode (CE), and an Ag/AgCl is used as the reference electrode (RE). (b) A tube furnace connected to a gas flow system and a computer-controlled temperature controller.

The photocatalytic properties of copper oxides and CuFe_2O_4 nanoparticles are studied by linear sweep voltammetry (LSV) in the three-electrode electrochemical cell connected to the CHI 660E electrochemical station (discussed above) under simulated sunlight illumination. The illumination system is a 300 W solar simulator that includes a 300 W Xenon lamp (Newport-Oriel Instruments, Model 68811) coupled with an AM 1.5 G filter, along with its power supply shown in Figure 1.6. A power meter (Molelectron, EPM 100e) is used to calibrate the light intensity to 1 sun ($100 \text{ mW}\cdot\text{cm}^{-2}$). A typical photoelectrochemical water splitting reaction setup in a quartz beaker (enlarged inset) is shown in Figure 1.6. LSV is a simple technique, in which the current at the working electrode is measured while the potential between the working electrode and the reference electrode is linearly varied over time. LSV has been widely used to investigate the photoelectrochemical water splitting reaction and measure the photocurrent of hydrogen evolution.

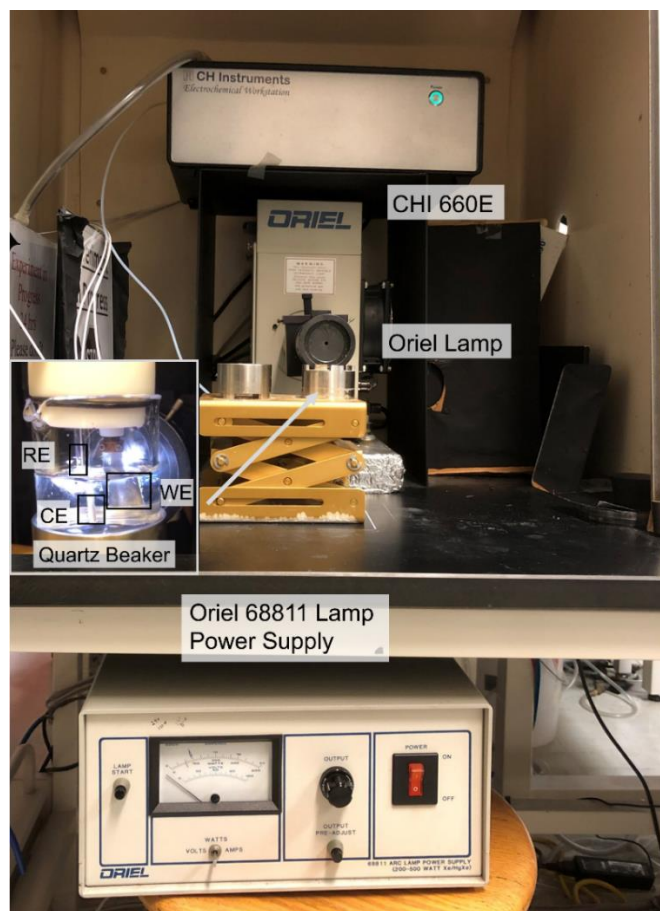


Figure 1.6 Photographs of a 300 W solar simulator (Newport-Oriel Instruments, Model 68811) used to provide the AM 1.5 G solar light with 1-Sun intensity, along with its power supply, and an electrochemical workstation (CHI 660E), and an enlarged inset of a three-electrode electrochemical cell in a typical photoelectrochemical water splitting reaction setup in a quartz beaker. The graphene substrate with the nanostructured materials is used as the working electrode, a Pt wire is used as the counter electrode, and an Ag/AgCl is used as the reference electrode.

1.3.2 Solvothermal Method

The solvothermal method refers to reactions or processes used for synthesis of nanomaterials in a solvent contained in a specially sealed reaction vessel under elevated temperature (usually 100-1000 °C) and pressure (1-10,000 atm).⁹⁰ In solvothermal processes, the non-aqueous solvent contains the reagents for material synthesis. Elevated temperature and pressure are used to amplify the reactivities of both the solvent and the solutes, often accelerating the reactions and enabling the formation of new compounds. Solvothermal synthesis serves as a facile “one-pot” method to

produce novel materials such as the CuFe_2O_4 spinel nanoparticles discussed in Chapter 3⁹¹ and to promote crystal growth,⁹² relying on the ability of reactants to dissolve in the solvent. The solution (and its ingredients) is put inside a Teflon reaction cell placed in a stainless-steel high-pressure reaction vessel, known as the autoclave (Figure 1.7b). The sealed autoclave is then placed inside an oven. In the present work, a non-aqueous solution (ethylene glycol) containing the reactants such as copper, iron salts, sodium acetate and poly-vinylpyrrolidone is stirred vigorously before being transferred into the Teflon reaction cell inside the autoclave. The autoclave is then heated in a muffle furnace (Figure 1.7a) in a controlled manner following a heating and cooling program over a period. Once the heat treatment is completed and the autoclave is allowed to cool, the precipitates are collected and washed with deionized HPLC grade ethanol and isopropanol and suspended in ethanol.

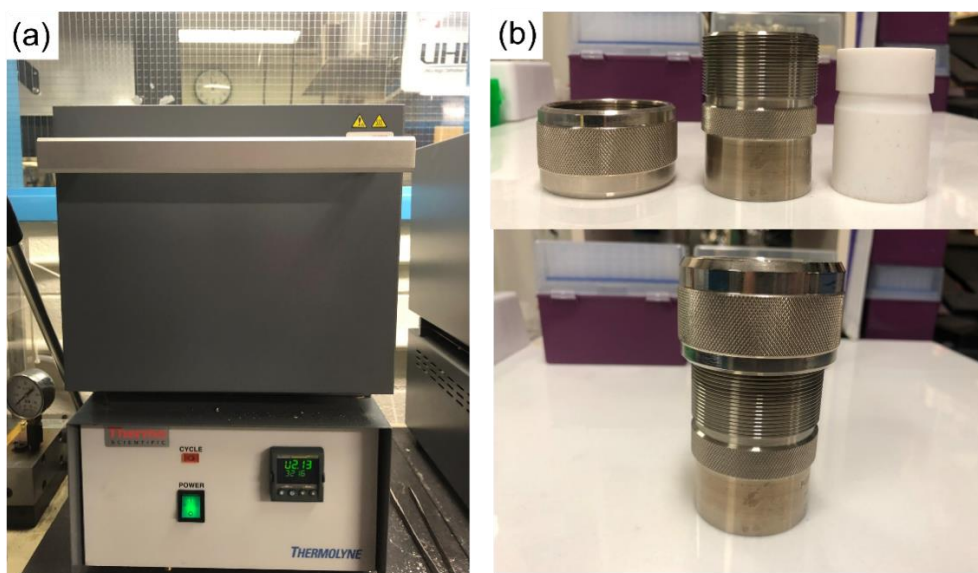


Figure 1.7 Photographs of (a) a Thermolyne muffle furnace and (b) a typical solvothermal setup of Teflon reaction vessel and the stainless-steel autoclave.

1.4 Characterization

1.4.1 Scanning Electron Microscopy, Helium Ion Microscopy and Transmission Electron Microscopy

Scanning electron microscopy (SEM) is used to obtain important information about the material surface, including topography, morphology, grain composition and orientation, and other

crystallographic information.⁷⁴ Shown in Figure 1.8a, the Zeiss Merlin microscope is equipped with a Gemini II electron optics column with a double condenser lens system and a field emission electron source, which provides state-of-the-art performance at an extremely low acceleration voltage (down to 100 V) and at normal acceleration voltage 20 kV (with an ultrahigh spatial resolution of 0.8 nm). The microscope is equipped with a number of detector systems for comprehensive analysis of diverse sample types, a charge compensation system, and a plasma sample cleaner. The in-lens and secondary electron 2 (SE2) Everhart-Thornley detectors for low-energy secondary electrons (with kinetic energy < 50 eV) are used to obtain fine topographical images of the specimen structure. These two detectors contain unique surface information because the in-lens detector is located inside of the electron column for detecting secondary electron 1 (SE1) electrons while the SE2 detector is appropriately positioned outside the column for collecting secondary electron (SE2) electrons. The energy-filtered backscattered (EsB) detector is used to capture inelastically backscattered electrons (with high kinetic energy > 50 eV), which provide information about the electronic excited states and contrast identification based on inelastic electron energy loss transitions. The angle-selected backscattered (AsB) detector is used to collect backscattered electrons emitted at low and high angles to enhance topographical contrast. The Merlin microscope is also equipped with an energy dispersive X-ray spectroscopy (EDS) system (EDAX Octane, Ametek, Inc.), which provides elemental composition quantification by detecting X-ray emission at element-specific characteristic photon energies from the sample excited by the high-energy incident electron beam of the SEM.

Helium ion microscopy (HIM) is based on the same principle of a traditional charged particle beam microscope such as the SEM, and has similar applications. Instead of a high energy electron beam in the SEM, HIM employs a high energy helium ion beam, which provides a different image contrast mechanism and interaction with the sample. A Zeiss Orion Plus HIM, shown in Figure 1.8b, can achieve an ultrahigh resolution of 0.35 nm because of the considerably shorter de Broglie wavelength of the helium ions than electrons at the same kinetic energy (30 kV). A gas field ionization ion source consists of a finely sharpened single-crystal tungsten trimer tip maintained at a high bias (25 kV) and low temperature (approximately 80 K) to effect field ionization of the helium gas. Precise control of the helium pressure near the as-formed trimer tip allows for easy management of the intensity of the He⁺ ions generated from the apex atoms (trimer) of the ionization disc. These He⁺ ions can be subsequently accelerated and focused, with collimation adjustment achievable through an aperture and the use of appropriate focus and extraction voltages. The resulting ion beam provides high brightness (4×10^{-9} A/cm²sr) and a small energy spread ($\Delta E/E \sim 3 \times 10^{-5}$), allowing the beam to be focused into a probe size as small as 0.25 nm.⁹³ In addition to

high-resolution imaging with not only superior spatial resolution but also significantly larger depth of focus (than SEM, due to the strong forward scattering of the considerably heavier He^+ ion than the electron), HIM can also be used to selectively remove material from a surface by sputtering with the helium ions. Despite the notably slower sputtering rate, HIM can be used for shaping, machining and patterning materials on the nanoscale, including, for example, performing circuit-edit of a nanodevice.⁹⁴ In Chapter 2, HIM is used to remove the material from and carve into a Cu_2O nanocube to expose its core-shell structure.

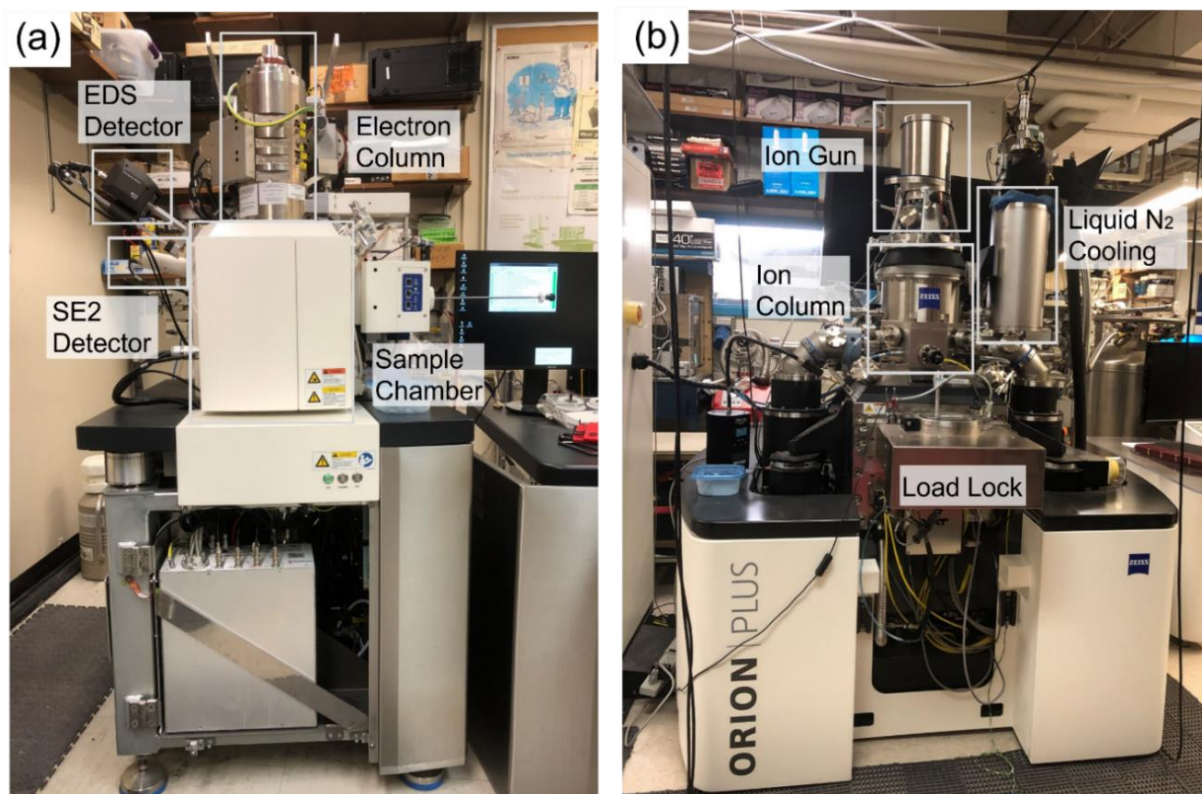


Figure 1.8 Photographs of (a) a Zeiss Merlin field-emission scanning electron microscope, equipped with in-lens and SE2 detectors, an energy-selective (EsB) and an angle-selective (AsB) backscattered detectors, and an energy-dispersive X-ray spectroscopy (EDS) system, and (b) a Zeiss Orion Plus helium ion microscope.

Transmission electron microscopy (TEM) is one of the most powerful tools for crystal structure investigation, phase determination, and surface plane identification of an individual structure on the atomic scale. In the present work, a Zeiss Libra 200 MC microscope, shown in Figure 1.9, is used

to collect high-resolution TEM images and selected area electron diffraction (SAED) information of individual CuFe_2O_4 (Chapter 3) and nickel oxide nanoparticles (Chapter 4). The Libra system is equipped with Zeiss' proprietary electron gun monochromator (MC), Kohler illumination system, and double-corrected in-column omega energy filter technology. This TEM is also equipped with a high-angle annular dark field (HAADF) detector and an energy dispersive spectroscopy (EDS) system. The electrostatic omega-type imaging element in the MC employs symmetric hexapole fields to cancel second-order aberrations, thus minimizing brightness loss and ensuring a non-dispersive source image at the MC exit. This design enables the operator to reduce the energy width of the primary electron to less than 0.2 eV and to preserve the original spot size, making it ideal for MC-STEM (Scanning TEM) and electron energy loss spectroscopy. In TEM mode, a high-energy electron beam operated at 200 kV is transmitted through a thin specimen, with a typical thickness less than 100 nm. In the mid column region, the electron beam interacts with the specimen, and the transmitted electrons are collected and precisely focused for the subsequent image magnification. Upon careful interpretation, these atomic resolved images can be used to identify crystal structures, determine their growth orientations, quantify crystal properties, and investigate defects or textures in the specimen. One common analysis approach evaluates whether the measured SAED diffractogram (or a simulated diffractogram obtained from fast Fourier transform (FFT) of a high-resolution TEM image) exhibits a ring or spot diffraction pattern allowing the crystal orientation of the sample to be determined.⁹⁵ Sample handling and preparation for TEM measurement require extreme care. The sample itself must meet certain basic requirements, including uniform thinness, generally being conducting and not strongly magnetic, while a stable electron beam must be maintained and free from noise pickup and temperature fluctuation in the ambient laboratory environment.

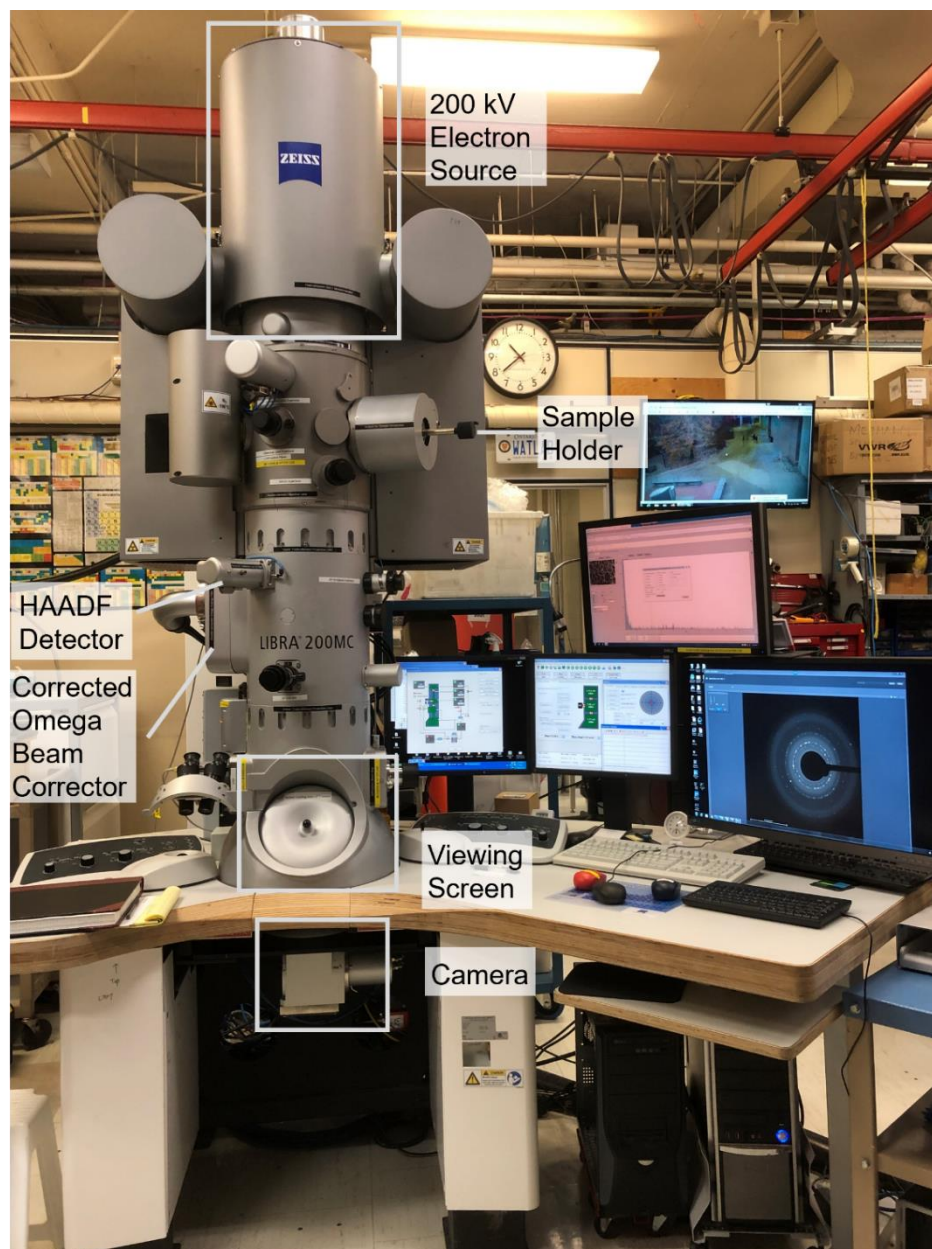


Figure 1.9 Photograph of a Zeiss Libra 200MC transmission electron microscope operating at 200 kV.

1.4.2 X-ray Diffraction

X-ray diffraction (XRD) is a technique used for identification and characterization of the crystalline structure of materials at the atomic level. It involves shining an X-ray beam onto a sample and analyzing the pattern of X-rays that are scattered or diffracted by the atoms in the material. In the present work, a PANalytical X'Pert Pro MRD diffractometer, shown in Figure

1.10, is used to determine the crystalline structure. A Cu anode upon high-energy electron-impact excitation is used to generate Cu K α radiation (1.54 Å). A number of advanced optics and diffraction geometries, along with a high-precision 4-circle goniometer, are available for this system. Due to the often-small quantity of nanomaterials deposited on a substrate and the nanometer length scale of the crystallites, the signals emanating from these nanostructured materials are usually quite weak and overwhelmed by the strong signal from the substrate. To concentrate on the signal coming from the nanomaterials, glancing incidence X-ray diffraction (GIXRD) is employed to investigate the crystal structure of the deposited nanostructures. In the GIXRD technique, the incident X-ray beam is kept at a very shallow incidence angle (ω) while the X-ray detector is scanned over the 2θ angular range to collect the diffracted beams. This specific incidence angle is chosen to generate an evanescent wave that has a limited penetration depth (typically less than 100 nm) and it predominantly travels along the surface of the sample. The shallow interaction of this wave with the material surface and the nanostructured deposit amplifies the signals from the near surface region and not the bulk.⁹⁶ For this purpose, we employ a parallel beam geometry with an X-ray mirror on the incident beam optics side and a parallel-plate collimator on the diffracted beam optics side. This setup enables GIXRD measurements for most of the samples in the present work with an incidence angle as small as 0.6°.

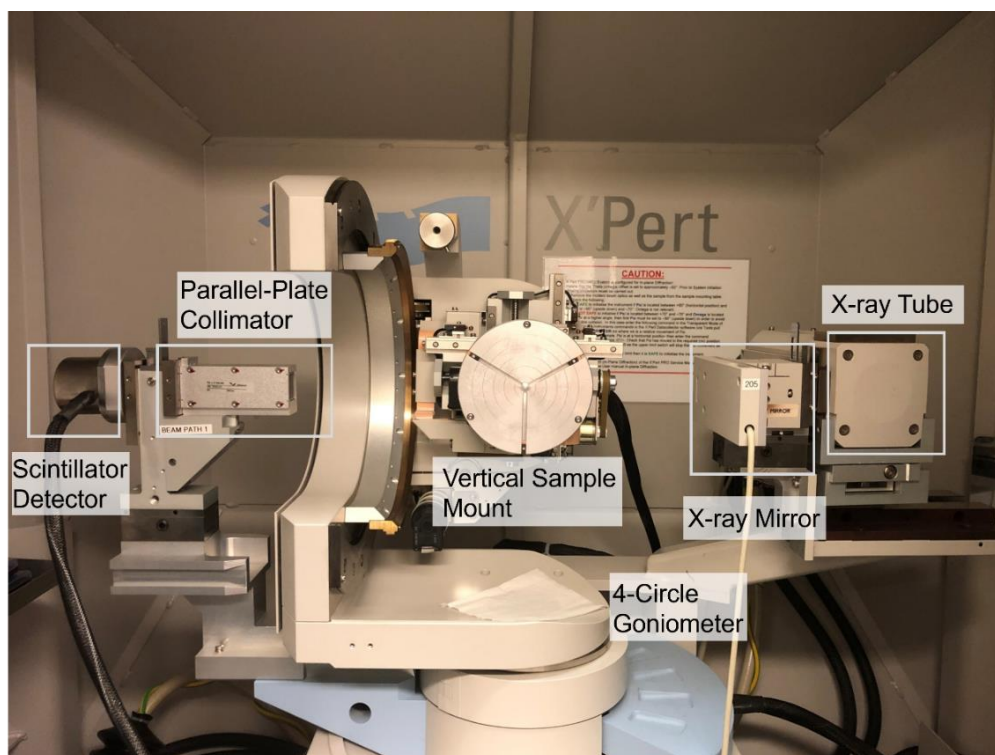


Figure 1.10 Photograph of Panalytical X'pert Pro MRD X-ray diffractometer (XRD), which is set up in the parallel beam optical geometry, employing a 4-circle goniometer used to automatically the shape and symmetry of the unit cell of a crystal, an X-ray mirror as the incident beam optics and a parallel plate collimator as the diffracted beam optics.

1.4.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is employed to examine the elemental composition, empirical formula, chemical and electronic states of the nanomaterials. This analytical technique is performed in two separate instruments: the Thermo-VG Scientific ESCALab 250 Microprobe shown in Figure 1.11a and the recently installed Thermo Scientific Nexsa G2 surface analysis system shown in Figure 1.11b. Both the ESCALab 250 Microprobe and the Nexsa G2 system are equipped with a monochromatic Al K α source and are capable of a typical energy resolution of 0.5 eV full width at half maximum. A focused X-ray beam is directed onto the sample, inducing the emission of photoelectrons. The kinetic energy (E_K) of these photoelectrons is determined by employing a hemispherical energy analyzer. The corresponding binding energy (E_B) of the sample is calculated by using the Einstein equation, $E_B = h\nu - (E_K + \phi)$, where $h\nu$ is the photon energy of

the X-ray (i.e. 1486.6 eV for Al K α in the ESCALab 250 and Nexsa G2), h is the Planck's constant, ν is the light frequency, and ϕ is the work function.⁹⁷

XPS provides chemical-state analysis with exceptional surface sensitivity, due primarily to the limited inelastic mean free path of the photoelectrons (within the selected kinetic energy range) (typically <10 nm). This surface sensitivity allows for comprehensive examination of individual chemical states of the surface region through the identification of characteristic photopeaks at specific binding energies. Comparing these binding energy positions to established reference standards provides invaluable insights into the local chemical environments, commonly manifested as core-shell chemical shifts. Moreover, the energies and intensities of these photopeaks offer the means to quantify all surface elements present in the material, except for hydrogen. By using an argon ion source to sputter the specimen layer-by-layer during the XPS measurements, we can obtain depth profiles that depict the changes in the chemical states as functions of sputtering depth, thus enabling us to follow the chemical-state composition change in the near-surface region of the material. These depth profiles are particularly useful in determining compositional changes during material growth, e.g., in a core-shell nanocube.

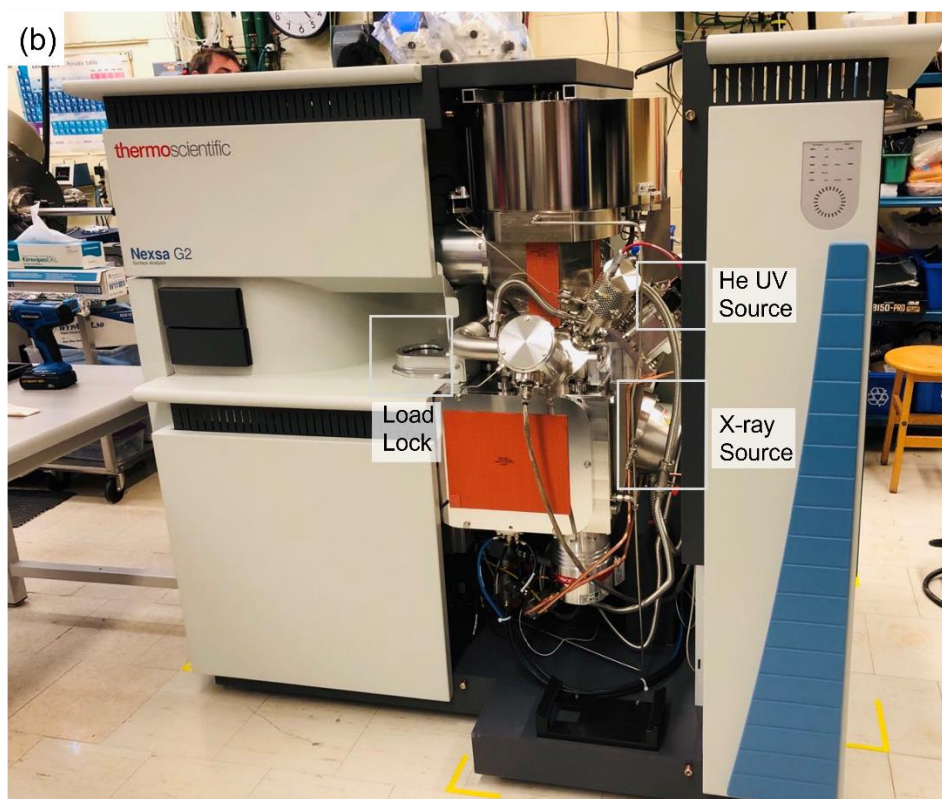
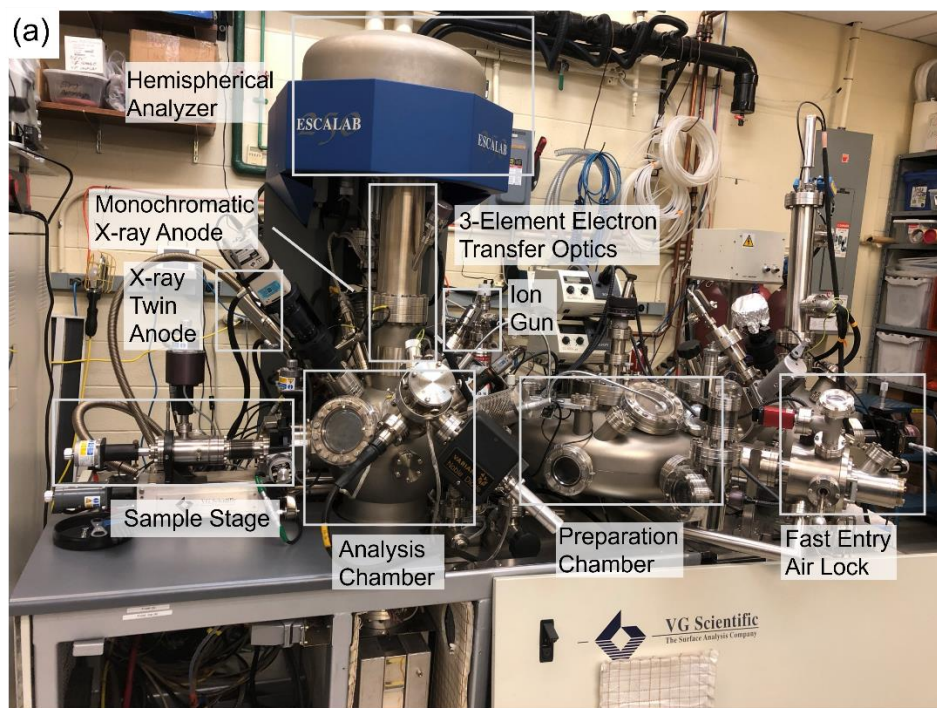


Figure 1.11 Photograph of (a) a Thermo-VG Scientific ESCALab 250 Microprobe and (b) a Thermo Scientific Nexsa G2 surface analysis system.

1.5 Applications of Transition Metal Oxides

As many TMO nanomaterials possess unique semiconducting properties, they have been used in a wide range of applications including supercapacitors,⁹⁸ lithium-ion batteries,⁹⁹ electrocatalysts,¹⁰⁰⁻¹⁰¹ and photocatalysts¹⁰². Among these applications, TMO nanomaterials have attracted a lot of attention as high-performance electrocatalysts and photocatalysts. Their unique electronic structures, surface properties and multiple redox couples facilitate efficient catalytic reactions, promote redox processes, and greatly increase electrocatalytic performance. Additionally, TMO photocatalysts also play an essential role in harnessing solar energy for chemical transformation, e.g. from water to hydrogen. Their semiconducting properties allow them to absorb light and generate charge carriers, initiating photoelectrochemical reactions. Indeed, these distinctive properties make them excellent candidates for various electrochemical or photoelectrochemical processes used in biosensors¹⁰³ and photoelectrochemical water-splitting reactions¹⁰⁴.

1.5.1 Glucose Sensing

As a crucial metric for monitoring diabetes, glucose has been the focus of biomedical research for decades. A tremendous amount of work has been undertaken using TMO nanomaterials for both enzymatic and non-enzymatic glucose sensing. Among the popular approaches to glucose sensing, electrochemical glucose sensing is straightforward, direct and in real-time, offers rapid response and high specificity, affordability and user friendliness. Over the past decades, various electrochemical sensing technologies have been developed to monitor glucose levels in diabetics, but most of them are invasive. In contrast, non-invasive saliva glucose analysis presents several advantages over traditional blood glucose testing. It allows for the easy collection of samples and alleviates stress for the patient who requires frequent testing throughout the day. Currently, this has led to a significant increase in research and development focusing on non-invasive glucose sensors specifically designed for saliva analysis. These innovations include enzymatic solutions such as on-chip electrochemical devices,¹⁰⁵ color pH indicator paper strips,¹⁰⁶ and glucose-sensing electrodes integrated into mouth guards with wireless measurement capabilities,¹⁰⁷ as well as non-enzymatic electrochemical glucose sensors¹⁰⁸⁻¹⁰⁹. Among these non-enzymatic electrochemical glucose sensors, porous CuO electrodes have been fabricated using ZnO nanorods as a template and they have been found to provide high sensitivity, stability, and selectivity for saliva glucose.¹⁰⁹ The enhancement of glucose sensing relies on the redox activation of electrode materials in electrocatalytic processes, which greatly influences the sensitivity of electrochemical glucose detection. During the reaction between copper oxide and glucose, multiple redox couples facilitate reactions due to the multiple oxidation states of copper. The final reaction step involves CuOOH, in

which –OOH offers the crucial reaction site for glucose oxidation.¹¹⁰ In the present work (Chapter 2), we fabricate Cu₂O nanocubes for use as electrodes for saliva glucose sensing.

1.5.2 Lactate Sensing

Lactate (C₃H₆O₃) concentration is considered a key parameter in areas such as food safety and quality control, cell culture monitoring, athlete performance, and medical diagnostics, as shown in Figure 1.12. Specifically, lactate concentration represents a primary metrics for monitoring tissue oxidation in clinical diagnostics, assessing patient health, studying diseases, and providing continuous surveillance in surgery, sports performance, and shock/trauma treatment. Many techniques for lactate detection have been reported and including high-performance liquid chromatography, liquid chromatography-mass spectrometry, spectrophotometry, colorimetry, and fluorometry.¹¹¹⁻¹¹⁵ However, many of these analytical techniques are expensive, time-consuming, and require sample pre-treatment, making them generally incompatible with in-situ analysis. Electrochemical enzymatic and non-enzymatic lactate sensing offer a more straightforward and direct alternative. Nonetheless, the majority remain enzyme-based sensors that suffer from disadvantages such as high cost, short lifetime, and poor stability. Non-enzymatic biosensors based on nanomaterials have therefore been developed with the goal of resolving this problem. TMO nanomaterials, including NiO, CuO, and Co₃O₄,¹¹⁶⁻¹¹⁸ have been studied as potential candidates for lactate sensing due to their electrochemical catalytic properties, high sensitivity, environmental friendliness, and low cost. In particular, NiO and Ni(OH)₂ have been widely used as catalysts for non-enzymatic lactate sensing due to their participation in a hopping mechanism via electron transfer between Ni³⁺ and Ni²⁺.^{63, 119-120} In the present work (Chapter 4), we fabricate NiO_x nanoparticles by electrodeposition on graphene followed by thermal oxidation at selected annealing temperatures over different amounts of time, and compare their performance for lactate detection based on the concentration of NiOOH/Ni(OH)₂ redox couple.

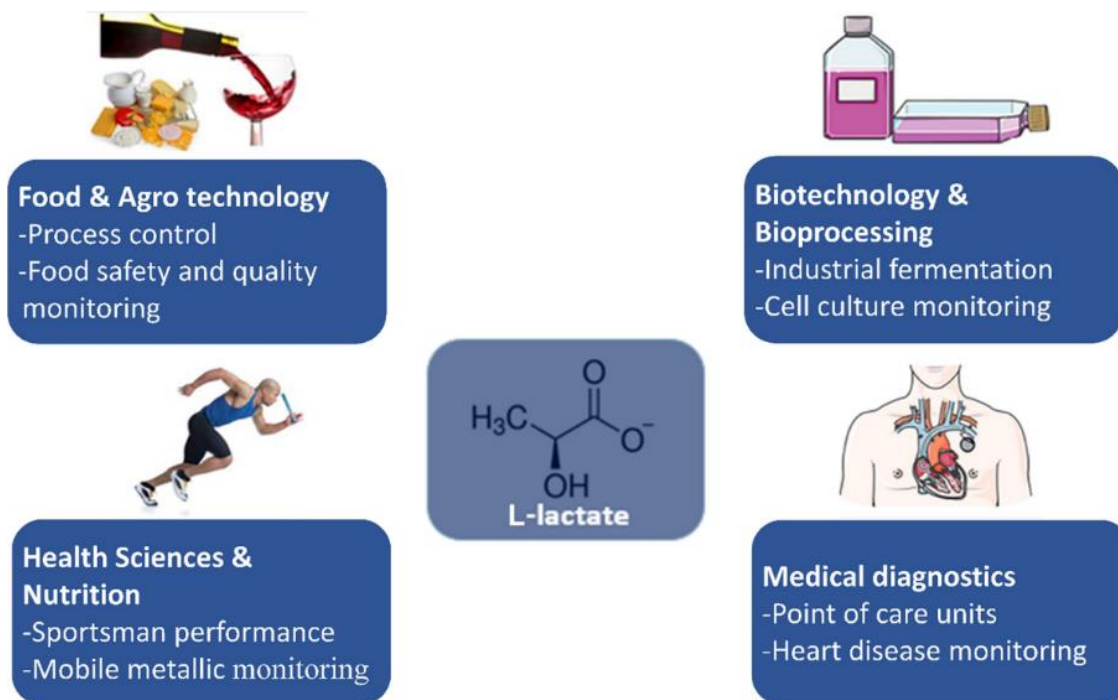


Figure 1.12 L-lactate applications in food processing, biological, and medical sectors.^{†††}

1.5.3 Photoelectrochemical Water Splitting

With the ever increasing consumption of fossil fuels and the associated negative impact on global climate change, hydrogen has attracted global attention as an ideal clean energy source. Among all the chemical fuels, hydrogen (H_2) stands out with its superior gravimetric energy density (142 MJ/kg, upper heating value), making it the ultimate clean energy carrier that offers substantial environmental benefits by eliminating carbon emission. The photoelectrochemical method is a viable approach for the hydrogen evolution reaction (HER) facilitating solar-to-hydrogen conversion. Fujishima and Honda first utilized TiO_2 as catalyst for the photoelectrochemical water splitting reaction, which has significantly advanced solar energy conversion research.¹²¹ This work has since inspired scientists to pursue a wide spectrum of photocatalysts to further the development of solar energy conversion technologies.

The overall water splitting reaction is an energetically uphill process that includes both a hydrogen evolution reaction (HER) and an oxygen evolution reaction (OER), leading to a positive shift in the Gibbs free energy. Specifically, the free energy change for converting a water molecule

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to H_2 and $\frac{1}{2}\text{O}_2$ is $\Delta G^0 = 237.3 \text{ kJ/mol}$. According to the Nernst equation that relates the Gibbs free energy and electrochemical reduction potential, $\Delta G = -zFE$, where z is the number of electrons transferred, F is the Faraday constant, and E is the standard reduction potential. For the water splitting reaction, $E = 1.23 \text{ V}$ per electron transferred. For a semiconductor to facilitate this reaction using light, it needs to absorb photons with energies greater than 1.23 eV , corresponding to wavelengths of approximately 1000 nm or shorter. This absorbed energy is then converted into hydrogen and oxygen gases. To facilitate solar water splitting, the bandgap of the semiconductor should be wide enough to cover the required energy and the band-edge energies of the conduction and valence bands should straddle the electrochemical potentials for both (H^+/H_2) and $(\text{O}_2/\text{H}_2\text{O})$, which are 0 eV and 1.23 eV vs. the standard hydrogen electrode, respectively, at a pH of 0.¹²²

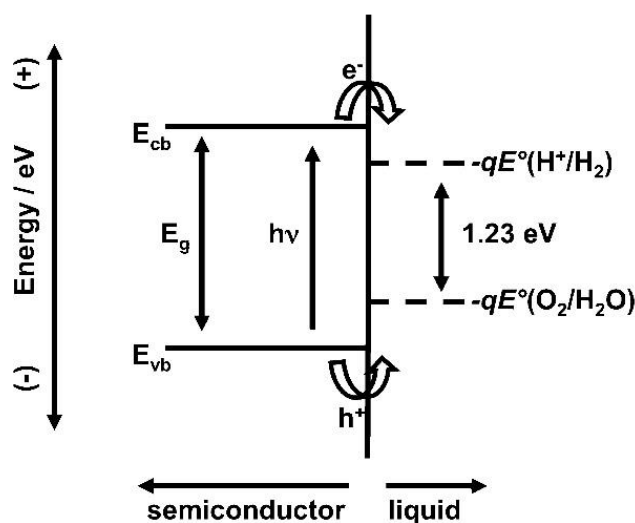
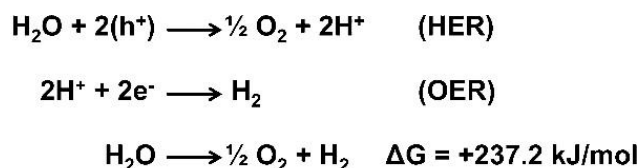


Figure 1.13 The overall water splitting includes oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) under acid conditions. An ideal semiconductor material enables this process under illumination, where the energy dynamics are illustrated on a vertical axis (–) and (+) showing the conduction band edge (E_{cb}) and valence band edge (E_{vb}) and the electrochemical

potentials given by $-qE^0$, representing the reduction potentials for both (H^+/H_2) and (O_2/H_2O) redox couples.^{†††}

It is well established that the efficiency of water splitting greatly depends on the activity of the photocatalyst. To increase efficiency, the primary strategy is to improve the light absorption properties of photocatalysts, especially in the visible light region. This effort has not only broadened the horizon of photocatalysis, but also led to new innovations in the field.¹²³ The band diagrams of common TMOs including such basic information as conduction band position, valence band position, bandgap and work function are shown in Figure 1.14. The positions of the Fermi level determine whether these oxides belong to p-type semiconductor (close to valence band) or n-type semiconductor (close to conduction band).¹²⁴ The role of minority carriers have been clearly demonstrated as electrons for p-type semiconductors and holes for n-type semiconductors by Gerischer,¹²⁵ Pleskov,¹²⁶ and Memming¹²⁷. Because of their large bandgaps, most TMOs are active as a catalyst only under ultraviolet (UV) light. However, to harness the full solar energy spectrum, the catalyst must exhibit strong photo-response within the visible light range, which constitutes approximately 43% of solar energy compared to the modest 5% contributed by UV light. Therefore, an ideal photocatalyst should have a bandgap below 3 eV, in order to enable efficient utilization of visible light in the 420-800 nm range.¹²³ Extensive research has been conducted on various TMOs, such as TiO_2 ,¹²⁸ Fe_2O_3 ,¹²⁹ WO_3 ,¹³⁰ CuO ,¹³¹ and ZnO ,¹³² for use as potential photocatalysts in this spectral region. In addition, ternary TMOs including $CuFe_2O_4$,¹³³ $ZnFe_2O_4$,¹³⁴ $MgFe_2O_4$,¹³⁵ $CuMn_2O_4$,¹³⁶ and $ZnMn_2O_4$ ¹³⁷ can also be used as photocatalysts by themselves or in combination with other nanomaterials.

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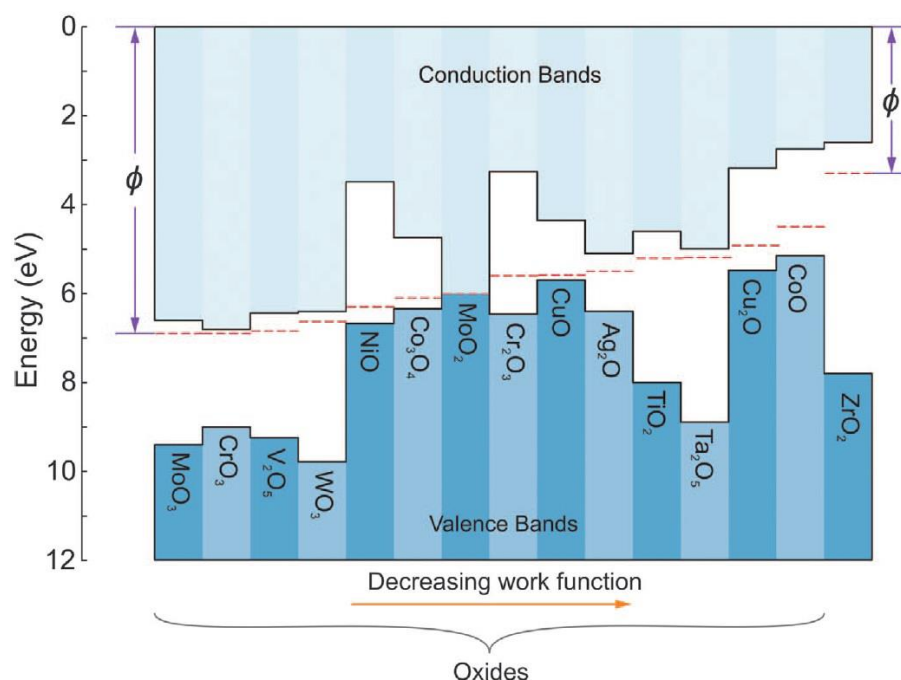


Figure 1.14 Illustration of basic band structures in common transition metal oxides with their conduction bands (upper shaded regions), valence bands (lower shaded regions), and band gaps (shown as white area). The dashed red lines in these diagrams represent the Fermi levels for the oxides.¹²⁴ The arrangement of these oxides is in left-to-right sequence, corresponding to a decrease in work function.^{§§§}

To improve the photocatalytic reaction efficiency, the existing challenges such as high over-potential, wide bandgap, fast electron-hole recombination, and low light utilization must be addressed. A variety of strategies including suitable textural design, doping, and the construction of semiconductor heterojunctions have been employed. Incorporation of semiconductor heterojunction is a widely used approach for effectively separating the electron-hole pairs. Three types of semiconductor heterojunctions exist: type I with straddling-gap, type II with staggered-gap, and type III with broken-gap, as shown in Figures 1.15a-c. While type-II heterojunction has shown the most impressive photoactivity, due to its enhanced ability to facilitate charge separation, it does have some drawbacks, such as reduced overall redox ability and limited light absorption. The Z-scheme heterojunction strategy has emerged as a popular approach by separating electron-hole pairs effectively and maximizing the redox capability of a photocatalyst. In 1979, Bard first

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introduced the concept of Z-scheme photocatalysis.¹³⁸ Tada *et al.* later advanced the notion by proposing an all-solid-state Z-scheme¹³⁹ while Yu *et al.* further extended the idea with a direct Z-scheme.¹⁴⁰ This method proved instrumental in elevating the overall efficiency of photocatalysts while effectively addressing the limitations commonly associated with conventional heterojunction photocatalysts. Under light irradiation, photogenerated electrons are effectively transported from the conduction band (CB) of SC-II to the valence band (VB) of SC-I in the direct Z-scheme heterojunction. The respective charge transfer and reaction mechanisms of type II and direct Z-scheme photocatalysts are shown in Figures 1.15d and 1.15e. The direct Z-scheme photocatalyst ensures efficient separation of photocarriers and improves the redox capability of the photocatalyst. The concept of dual Z-scheme photocatalyst system involving three semiconductors was introduced by Li *et al.* in their review article¹⁴¹ and later discussed by Singh *et al.*¹⁴² The alignments of band edges of SC-II are lower than those of SC-I and SC-III. The internally generated electric field among the semiconductors enables the conduction band electrons of SC-II to recombine with the valence band holes in both SC-I and SC-III. In this work (Chapter 3), we fabricate Cu_xO nanowires by electrodeposition with further thermal oxidation, without and with the addition of CuFe_2O_4 nanoparticles obtained by solvothermal synthesis. The composition of $\text{Cu}_x\text{O}/\text{CuFe}_2\text{O}_4$ works as a remarkably efficient dual Z-scheme heterojunction photocatalyst system for hydrogen evolution.

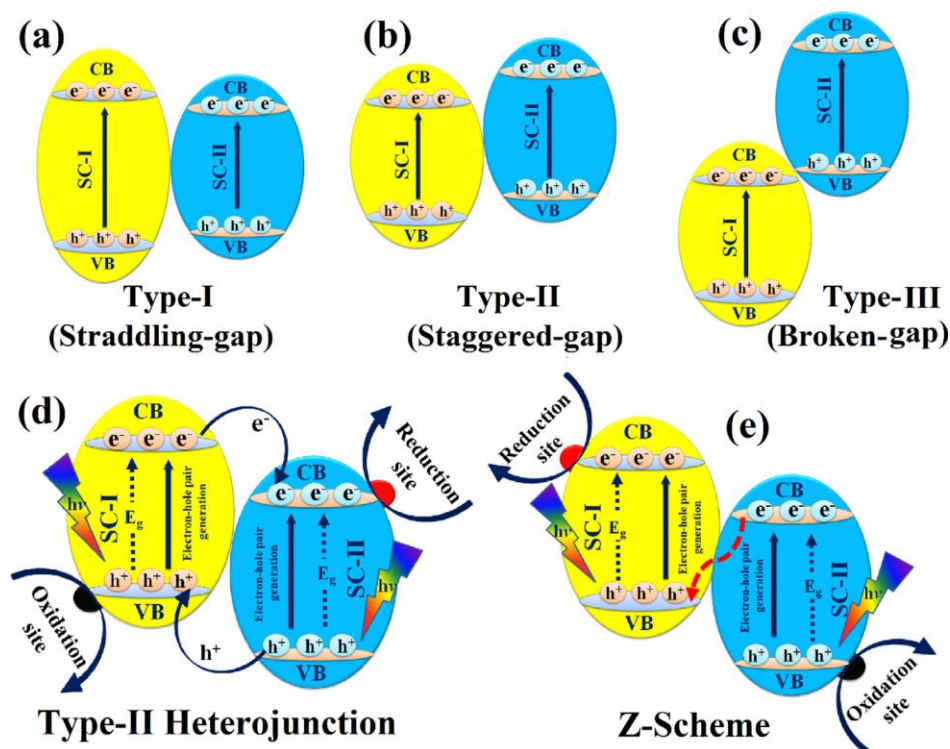


Figure 1.15 Pictorial representations of three types of heterojunctions: (a) Type I straddling gap, (b) Type II staggered gap and (c) Type III broken gap. (d) Schematic illustrations of the charge transfer mechanisms in (d) Type-II heterojunction and (e) direct Z-scheme heterojunction photocatalyst systems****

1.6 Scope of Thesis

The primary objective of the present work is to develop transition metal oxide nanomaterials with different nanostructured morphologies and to investigate their potential as electrocatalysts and photocatalysts. After a brief introduction to transition metal oxides, we present a brief review of the synthesis methods (i.e. electrodeposition, and solvothermal synthesis) used to produce Cu_xO , NiO_x , and CuFe_2O_4 nanostructured materials as catalysts in Chapter 1. A description of the experimental procedures to fabricate TMO nanomaterials along with the characterization techniques employed to analyze their morphologies, crystalline structures, and chemical compositions is also given above in Chapter 1.

We present our data in the next three chapters. In Chapter 2, we describe the facile, one-step electrochemical synthesis of Cu_2O nanocubes, with controllable sizes and uniform distributions, on

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a flexible graphene strip. We provide a detailed study of the growth parameters, including different deposition voltages, deposition temperatures, electrolyte concentrations, and deposition time, used to optimize the morphology and size of Cu₂O nanocubes. Our data from depth-profiling XPS and helium ion microscopy show that these Cu₂O nanocubes have a core-shell-skin structure, with a small metallic Cu core, a prominent Cu₂O shell, and a thin CuO skin (as the outermost layer). We compare the performance of the Cu₂O nanocubes/graphene sensor with other sensors, including a bare graphene strip, a graphene strip coated with a copper film by magnetron sputtering, and an enzymatic sensor based on glucose oxidase immobilized on a graphene strip without and with Nafion. The Cu₂O nanocubes/graphene sensor is found to be among the best saliva-range glucose sensors reported to date. Furthermore, our Cu₂O nanocubes/graphene sensor is fabricated in an aqueous electrolyte on a commercially available graphene substrate, which is considerably simpler than the multistep fabrication methods employed for other sensors with comparable saliva-range glucose sensing performance.

In Chapter 3, photoelectrochemical hydrogen evolution (HER), a half reaction of water splitting, is identified as crucial to the low-cost, environment-friendly production of clean H₂ fuel as part of the solution for transitioning away from a fossil fuel economy. Electrodeposition of a controllable Cu film on graphene by using potentiostatic amperometry followed by thermal oxidation at 200-400 °C has been used to produce copper oxide (Cu_xO, x=1,2) nanowires. The relative compositions of CuO and Cu₂O layers in Cu_xO-Cu/graphene system form a heterojunction structure enabling high efficiency for electron-hole separation and a fast charge transfer rate. The CuO layer with a proper thickness has been found to enhance light absorption, improve the charge separation, and serve as a protective layer against photocorrosion for Cu₂O, while graphene is used as a flexible high-conductive substrate. A high-performance dual Z-scheme heterojunction photocatalyst system is developed to greatly improve charge carrier separation, increase carrier density, and reduce electron-hole recombination. This dual Z-scheme heterojunction system is obtained by decorating the Cu_xO-Cu/graphene system with an efficient co-catalyst based on Cu-based ternary CuFe₂O₄ nanoparticles, obtained by a solvothermal method. The photoelectrochemical hydrogen evolution performance using Cu_xO-Cu/graphene without and with the addition of CuFe₂O₄ nanoparticles as the photocathodes are compared. The addition of CuFe₂O₄ nanoparticles on the best optimized Cu_xO-Cu/graphene is found to nearly double the photocurrent from -2.64 mA cm⁻² to -4.91 mA cm⁻², making this dual heterojunction catalyst the best Cu-based catalyst system for HER reported to date.

In Chapter 4, we fabricate nickel oxide nanoparticles by potentiostatic amperometry followed by thermal annealing at temperatures ranging from 200 to 400 °C. Using transmission electron microscopy and depth-profiling X-ray photoelectron spectroscopy, we show that the resulting nickel oxide nanoparticles exhibit a core-shell-skin heterostructure, with a Ni metal core and a NiO shell and a mixed amorphous-crystalline Ni(OH)₂/NiOOH skin. The quantity of the NiOOH/Ni(OH)₂ redox couple is found to vary with the annealing temperature and annealing time. The nickel oxide nanoparticle samples obtained with selected annealing temperature-time combinations are used for lactate detection. The sample with the best performance shows an excellent linear range of 0.02-65.1 mM, a high sensitivity of 80.0 $\mu\text{A mM}^{-1} \text{cm}^{-2}$, and an impressive limit of detection of 0.00015 mM. This sensing performance can be optimized by controlling the NiOOH/Ni(OH)₂ redox couple composition relative to NiO. The sample obtained with a higher relative NiOOH/Ni(OH)₂ content by annealing at a lower temperature is found to provide more reactive sites for lactate detection and therefore higher sensitivity.

In Chapter 5, we summarize the present work and offer some suggestions for the future work.

Chapter 2

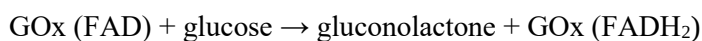
Non-Enzymatic Saliva-Range Glucose Sensing Using Electrodeposited Cuprous Oxide Nanocubes on a Graphene Strip^{†††}

2.1 Introduction

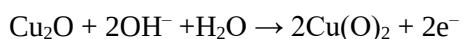
Metal and metal oxide nanoparticles have attracted a lot of attention for decades because of their special electronic, mechanical and catalytic properties.¹⁴³ One prominent example is cuprous oxide nanoparticles, which have been used as a catalyst for biosensors,¹⁴⁴⁻¹⁴⁵ an antifouling coating,¹⁴⁶ an essential component in optoelectronics,¹⁴⁷ and other applications (such as amination coupling reactions,¹⁴⁸ antimicrobial coating,¹⁴⁹ food packaging¹⁵⁰ and drug delivery applications¹⁵¹) due to their high conductivity, low toxicity, environmental friendliness, and low cost. Compared to other metals, copper has outstanding catalytic properties, and copper-based biosensors have superior performance in sensitivity (with a wide dynamic range), detection limit, stability and interference-free selectivity.¹⁵² Earlier studies have focused on non-enzymatic glucose biosensors based on copper materials, such as metallic Cu,¹⁵³ cupric oxide (CuO),¹⁵⁴ cuprous oxide (Cu₂O),¹⁵⁵ and their composite oxides.¹⁵⁶ Among the many approaches to fabricate copper and copper oxide nanoparticles, such as nanosphere lithography,¹⁵⁷ hydrothermal synthesis,¹⁵⁸ laser annealing,¹⁵⁹ and sonochemical reduction,¹⁶⁰ electrochemical deposition¹⁶¹ offers a quick, low-cost and reproducible fabrication method for these nanoparticles. Furthermore, a large variety of substrates is readily available for electrodeposition, including silicon,¹⁶² indium tin oxide,¹⁶³ and glassy carbon electrode.¹⁶⁴ In addition to these hard substrates, flexible soft substrates are becoming more accessible for depositing copper and copper oxide nanoparticles. Among these, two-dimensional materials such as graphene have been recently used in many areas, including electronics, photonics, and biomedical applications.¹⁶⁵ Several metal and metal oxide nanoparticles (e.g., Pt,¹⁶⁶ Au,¹⁶⁷ Pd,¹⁶⁸ TiO₂¹⁶⁹, and Co₃O₄¹⁷⁰) have been fabricated on graphene sheets. Indeed, the graphene sheet itself has attracted a lot of commercial interests because of their high electrical conductivity, high specific surface area, unique thermal and mechanical properties.⁸⁵ The graphene sheet is therefore a versatile flexible substrate with exceptional conductivity for electrodeposition of copper oxide nanoparticles.

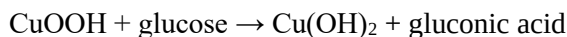
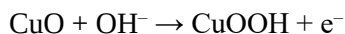
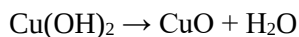
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According to the International Diabetes Federation, the number of diabetes patients is expected to increase from 382 million in 2011¹⁷¹ to 422 million in 2020 to 642 million in 2040 globally.¹⁷² To monitor the glucose level in a diabetes patient, numerous products have been developed for glucose sensing in the marketplace and even more literature about further improvement to these products have been reported. However, most of these products require a blood test from a fingertip, which is an invasive procedure, especially when the patient needs continuous monitoring.¹⁷³ Consequently, interest has grown in developing a totally painless method, other than just changing the blood sample acquisition site from the forearm, thigh, and hand to the finger.¹⁷⁴ Compared to a blood glucose test, saliva glucose analysis has many advantages, including easy-to-collect test samples, and less stress for the patient requiring frequent testing throughout the day.¹⁷⁵ While normal glucose concentration in saliva is very low, a significant increase of glucose in saliva in a diabetes patient has been reported.¹⁷⁶ The concentration of glucose in saliva ranges from ~20 μM in normal subjects to as high as 200 μM in diabetes patients.¹⁷⁶⁻¹⁷⁷ Recently, an upsurge in efforts to develop non-invasive saliva-range glucose sensors for both enzymatic and non-enzymatic sensing has been reported.¹⁷⁸ These include the enzymatic on-chip electrochemical device,¹⁷⁵ paper strip-based color pH indicator,¹⁷⁹ and glucose sensing electrodes attached on the surface of a mouth-guard with a wireless measurement system,¹⁰⁷ as well as the non-enzymatic electrochemical glucose sensor.¹⁸⁰ The mechanism of glucose detection in an enzymatic sensor is different from that of a nonenzymatic one. Generally the enzymatic glucose monitor depends on the oxidation reaction between the enzyme glucose oxidase (GOx) and glucose through the movement of electrons that generate the current or voltage measured by the electrodes.¹⁸¹ The overall mechanism follows the well-known reaction of glucose oxidase:



where GOx (FAD) is the oxidized form of GOx while the GOx (FADH₂) is the reduced form.¹⁸² In the case of a metal oxide nanoparticle non-enzymatic sensor, the metal oxide nanoparticle serves as an electrocatalyst to transfer the electrons arising from oxidizing glucose. For instance, the nonenzymatic sensor based on Cu₂O nanoparticles by amperometric method involves transferring electrons from the metal nanoparticles to glucose through the following mechanism. Cu(I) of Cu₂O is electro-oxidized to Cu(II) species, namely Cu(OH)₂, which is further oxidized to Cu(III) species, namely (CuOOH), in the alkaline solution. Glucose is then oxidized to gluconic acid while Cu(II) and Cu(III) are reduced back to Cu(I). During this process, Cu(III) works in effect as an electron-transfer mediator.¹⁸³⁻¹⁸⁴





In the present work, we fabricate a high-performance non-enzymatic glucose sensor for non-invasive saliva-range glucose testing by taking advantage of the novel properties of Cu₂O nanocubes and the flexible graphene substrate. The Cu₂O nanocubes are deposited by using a facile electrochemical method, and the optimum electrodeposition conditions are selected by changing the deposition voltage, electrolyte concentration, deposition time and temperature.

2.2 Experimental Details

All the chemicals, including copper sulphate, sodium perchlorate, sodium hydroxide, glucose, glucose oxidase, and Nafion were used as purchased from Sigma-Aldrich. Filtered high-resistivity (18.2 MΩ·cm) deionized water was used for preparing all the solutions. Conductive graphene sheets (25 μm thick), with a sheet resistance of 28 mΩ/square, were purchased from Graphene Laboratories Inc. and used as the substrates. The saliva samples were collected from volunteers based on the requirement of saliva collection, and then centrifuged at 14,000 rpm for 10 min to obtain the supernatants, which were collected and stored at 4 °C until use.

2.2.1 Fabrication of Cu₂O Nanocubes

All the electrochemical experiments were conducted in a three-electrode system connected to a CH Instruments 660E electrochemical station, with an Ag/AgCl reference electrode and a platinum wire counter electrode. The working electrode used for electrochemical deposition of Cu₂O nanoparticles was a graphene strip (10×5 mm²), cut from a graphene sheet. Cuprous oxide was deposited over a typical 5×5 mm² area of the graphene strip by potentiostatic amperometry for 100 s in a 1 mM copper sulphate (CuSO₄·5H₂O) electrolyte with 10 mM sodium perchlorate (NaClO₄) as the supporting electrolyte. The resulting Cu₂O/graphene sample was then used as the working electrode for non-enzymatic glucose sensing. As a comparison of the Cu₂O/graphene sensing performance, we also prepared three other electrodes: (a) a bare graphene strip, (b) a graphene strip coated with copper for 60 s in a magnetron sputterer, and (c) a graphene strip coated with glucose oxidase (GOx) by adding 40 μL 5 μM glucose oxidase solution and allowing to dry overnight (GOx/graphene). We also added 20 μL 0.5% wt. Nafion to the GOx/graphene sample and allowed it to dry for 3 h at 4 °C (GOx/Nafion/graphene) in an attempt to improve its sensing performance. Details of the testing procedure for glucose are given below.

2.2.2 Characterization Methods

A Zeiss Merlin field emission microscope was used to characterize the surface morphologies by scanning electron microscopy (SEM). Glancing-incidence X-ray diffraction (XRD) to determine the crystal structures was performed in a PANalytical X'Pert Pro MRD diffractometer with Cu K α (1.542 Å) radiation at an incidence angle of 0.6°. X-ray photoelectron spectroscopy (XPS) conducted in a Thermo-VG Scientific ESCALab 250 microprobe with monochromatic Al K α radiation (1486.6 eV) and a typical energy resolution of 0.5 eV full width half maximum was used to characterize the chemical-state composition. A Zeiss Orion plus helium ion microscope operated at 40 kV was used to dissect a single Cu₂O nanocube to confirm the core-shell structure. Finally, a commercial blood glucose monitoring system (ACCU-CHEK Aviva, Roche Diagnostics) for capillary, whole blood, amperometric testing using glucose dehydrogenase coated test strips was used to determine the blood glucose concentrations of human subjects. These results were used as reference to compare with results obtained from our salvia-range sensors.

2.3 Results and Discussion

2.3.1 Optimization of Cu₂O Nanocubes

The cuprous oxide nanocubes are synthesized on a soft high-conductive substrate graphene strip by one-step, templateless, and capping-agent-free electrodeposition. Cyclic voltammetry shows in Figure S2.1 (Supporting Information) two reduction peaks at -0.3 V (Figure A) and -0.6 V (Figure B) and two oxidation features at +0.28 V (Figure A') and +0.68 V (Figure B'), all with respect to Ag/AgCl, at room temperature. Deposition performed at an overpotential more negative than -0.3 V is found to produce small metal nanoparticles. In accord with the nucleation mechanism, the nucleus number density tends to be higher with increasingly more negative overpotential.¹⁸⁵⁻¹⁸⁶ Figures 2.1a-f show the typical morphologies of nanocubes obtained by potentiostatic amperometry at different overpotentials in a 1 mM Cu²⁺ electrolyte solution for 100 s deposition time (all conducted at room temperature). Evidently, the deposited Cu₂O nanocubes are found to be nearly of the same size and uniformly distributed on the conductive graphene substrate. The size of Cu₂O nanocubes becomes smaller while the number density becomes larger when more negative overpotentials are employed. For the 100 s deposition, Cu₂O nanocubes with the largest number density are obtained at -1.2 V and they appear to have the smallest size (20 nm side length, Figure 2.1f), while the Cu₂O nanocubes obtained at -0.2 V have the largest size (220 nm side length) with the least density (Figure 2.1a).

2.3.2 Morphology and Chemical Analysis of Cu₂O Nanocubes

The morphology and size of the nanocubes also depend on other parameters, including the deposition temperature, electrolyte concentration, and deposition time, and substrate. The deposition temperature influences the electrochemical thermodynamics and kinetics.¹⁸⁷ Figure S2.2 (Supporting Information) shows that the nanocubes appear to increase in size with increasing deposition temperature, from 20 nm at 4 °C to 30 nm at 40 °C to 80 nm at 70 °C. The temperature of the electrolyte solution directly affects the viscosity of the solution and consequently the diffusion coefficient and the thickness of the diffusion layer.¹⁸⁸ The electrolyte concentration also has an important effect on the morphology of the nanocubes. A higher Cu²⁺ concentration leads to a larger nucleus size and to larger nanocubes at the expense of the number density. Since the size of the nucleus determines the extent of its diffusion zone, the size of a nanocube is proportional to the size of the nucleus. The size of the nanocubes is found to increase with increasing Cu²⁺ concentration at the same overpotential (Figure S2.3, Supporting Information). Among the possible nanoparticle shapes, such as cubic, cuboctahedral, and octahedral, that could be obtained on a graphene substrate, a low Cu²⁺ concentration (about 10 mM) tends to favour nanocubes.¹⁸⁹ As graphene is more conductive than the Si substrate, nanocubes with a size range of 15-250 nm can be deposited with an even lower Cu²⁺ concentration (below 10 mM). Figure S2.4 (Supporting Information) shows the morphology change of the nanocubes obtained at -1.0 V in a 5 mM Cu²⁺ solution with increasing deposition time from 1 s, 10 s, 50 s, 100 s, to 200 s. Cu₂O nanocubes generally increase in size with a longer deposition time because of the increase in the amount of electron transfer. Figure S2.5 (Supporting Information) shows the morphology change of the nanocubes obtained in a 1 mM Cu²⁺ solution, in which the increasing trend in size with the increasing time is not as obvious as shown in Figure S2.4. In addition to the growth in the nanocube size, the emergence of nanodendrites is evident at a larger deposition time with the present (Figure S2.4, Supporting Information) and higher electrolyte concentrations (Figure S2.3, Supporting Information). As the Cu₂O nanocubes become larger, they are in contact with one another, forming linear chains.¹⁹⁰⁻¹⁹¹ These studies enable us to synthesize and deposit Cu₂O nanocubes on a graphene substrate without the need for employing templates and capping agents by simply using potentiostatic amperometry.¹⁸⁹ As shown in our XRD and XPS data below, the Cu₂O nanocubes so produced are found to be core-shell particles. The nature of the electrode material and the crystallographic orientation of the surface determine the value of zero-charge potential. The conductive graphene strip used as the substrate in the present work provides notable advantages for electrodeposition including high charge carrier mobility, excellent thermal conductivity, mechanical flexibility, and large specific surface area. For glucose sensing,

nanocubes of 50 nm in size are used because a uniformly distributed, near-monolayer coverage of Cu₂O nanocubes can be obtained on a graphene substrate, by the aforementioned facile electrodeposition at -1.0 V in 1 mM CuSO₄·5H₂O and 10 mM NaClO₄ for 100 s at room temperature (Figure 2.1e).

The corresponding glancing-incidence X-ray diffraction profiles of Cu₂O nanocubes deposited at different overpotentials are shown in Figure 2.1g. The strongest peak at 54.72° corresponds to the graphene substrate, and all the XRD profiles are normalised to this graphene peak. The primary peaks corresponding to Cu and Cu₂O are marked by triangles and circles, respectively. For the nanocubes deposited at -1.0 V vs Ag/AgCl, the prominent peaks at 36.50° and 42.40° are in good accord with the respective (111) and (200) planes of the Cu₂O face-centered cubic phase, while the weaker features at 61.52° and 73.69° correspond to the (220) and (311) planes (JCPDS#03-065-3288). The discernibly weaker features at 43.34°, 50.47° and 74.17° can be attributed, respectively, to the (111), (200) and (220) planes of the Cu face-centered cubic phase (JCPDS#01-070-3039). The presence of both Cu₂O and Cu features suggests a core-shell nanostructure for the nanocube, which is also supported by the depth-profiling X-ray photoelectron spectra discussed below. As the relative diffraction intensities of the Cu₂O features appear higher than those of the Cu features, the Cu₂O shell could therefore be quite substantial relative to the Cu core. The XRD profiles for nanocubes with different sizes obtained at different overpotentials (not shown) are found to be similar, which suggests similar crystallography for these core-shell nanocubes with different sizes.

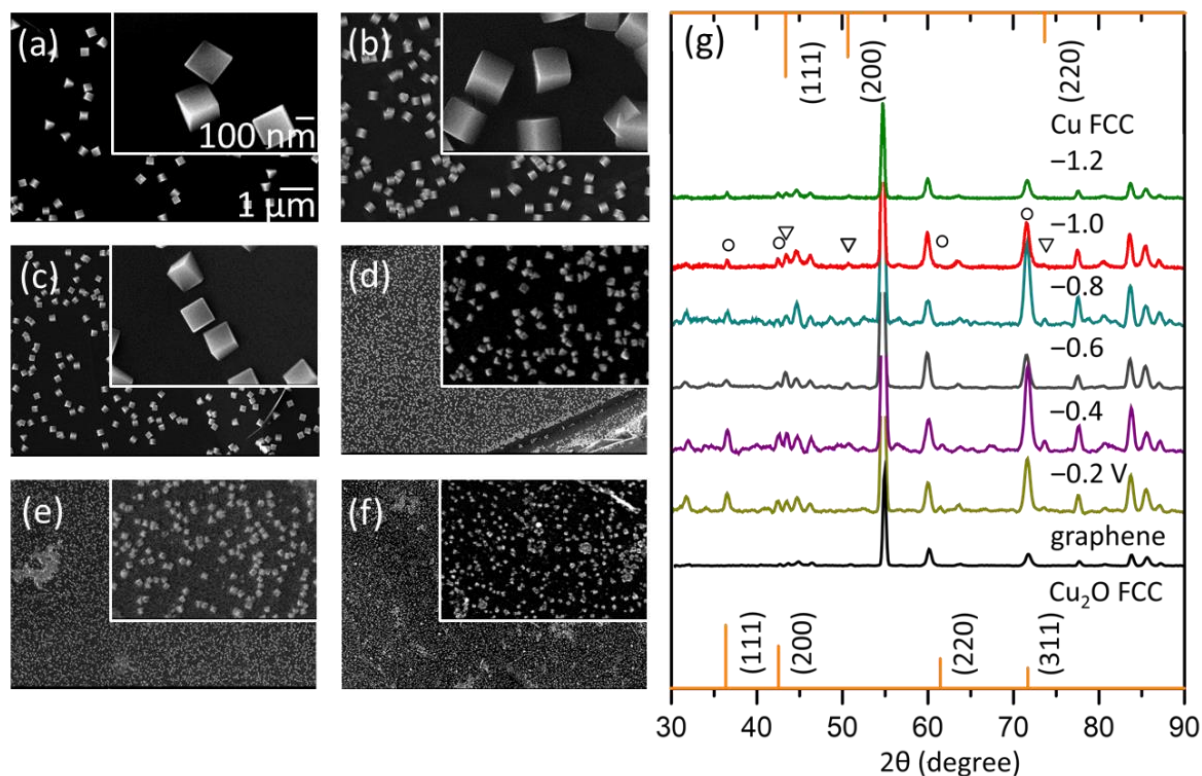


Figure 2.1 SEM images of Cu_2O nanocubes electrodeposited at (a) -0.2 V, (b) -0.4 V, (c) -0.6 V, (d) -0.8 V, (e) -1.0 V, and (f) -1.2 V (all with respect to Ag/AgCl) in $1 \text{ mM } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $10 \text{ mM } \text{NaClO}_4$ at room temperature for 100 s . All the SEM images employ the same scale. (g) The corresponding glancing incidence X-ray diffraction profiles are assigned in accord with the reference profiles for the Cu face-centered cubic (FCC) phase (JCPDS#01-070-3039), marked by triangles, and Cu_2O FCC phase (JCPDS#03-065-3288), marked by circles, along with the measured profile for a pristine graphene substrate.

Figure 2.2a shows the corresponding XPS spectra of the Cu $2p$ and O $1s$ regions of the Cu_2O nanocube samples presented in Figure 2.1. In addition to the prominent Cu $2p_{3/2}$ (Cu $2p_{1/2}$) peak at 932.3 eV (952.1 eV) attributed to Cu_2O or Cu,¹⁹²⁻¹⁹⁴ a weaker Cu $2p_{3/2}$ (Cu $2p_{1/2}$) feature at 934.2 eV (954.3 eV) and its shake-up satellite features at 940.0 - 943.5 eV can be assigned to CuO.¹⁹⁵⁻¹⁹⁷ The relative intensity of the Cu $2p_{3/2}$ peak for $\text{Cu}_2\text{O}/\text{Cu}$ with respect to that for CuO appears larger for the Cu_2O nanocubes obtained at -1.0 V (and -1.2 V) than those for nanocubes deposited at less negative overpotentials. This indicates that the relative proportion of $\text{Cu}_2\text{O}/\text{Cu}$ in the smaller nanocubes obtained at -1.0 V (and -1.2 V) is more than the larger nanocubes obtained at the less negative overpotentials. The two O $1s$ peaks at 530.5 eV and 531.9 eV in the corresponding O $1s$

spectra are assigned to Cu₂O/CuO and –OH bond, respectively. The presence of CuO is consistent with the easy oxidation of Cu₂O nanoparticles to CuO in water or in air.¹⁹⁸ The –OH bond feature can be attributed to the presence of hydroxyl group on the graphene substrate after electrodeposition because of water adsorption.

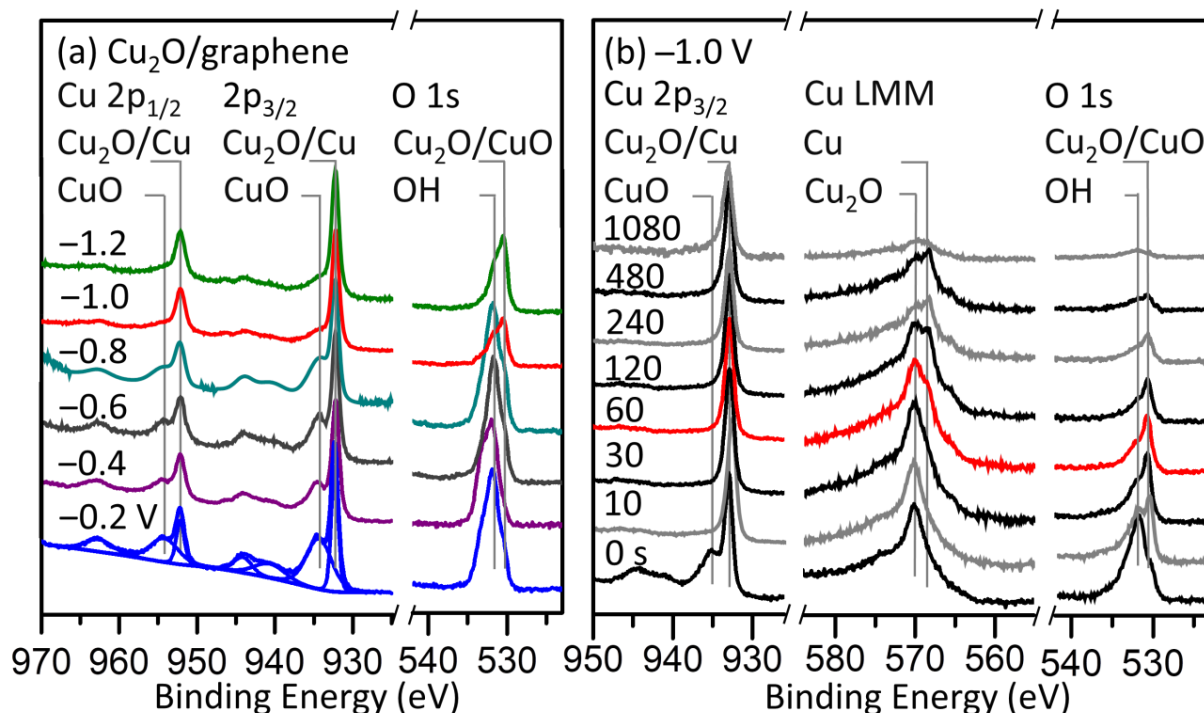


Figure 2.2 XPS spectra of (a) Cu 2p_{3/2} and Cu 2p_{1/2}, and O 1s regions of Cu₂O nanocubes electrodeposited on graphene at different overpotentials in 1 mM CuSO₄·5H₂O and 10 mM NaClO₄ at room temperature for 100 s. (b) Corresponding depth-profiling XPS spectra of the Cu 2p_{3/2} photopeak, Cu LMM Auger peak and O 1s regions of the Cu₂O nanocubes obtained at -1.0 V vs Ag/AgCl in (a).

While the Cu 2p photopeaks for CuO and Cu₂O/Cu can be easily discerned in Figure 2.2a, the relative locations of the CuO and Cu₂O/Cu components in the nanocube is less clear. Furthermore, it is difficult to identify the presence of metallic Cu because the metallic Cu feature (at 932.8 eV) is separated in binding energy from the Cu₂O feature at 932.9 eV by only 0.1 eV (i.e. considerably smaller than the instrumental resolution of our XPS system). In Figure 2.2b, we show the depth-profiling XPS spectra of the Cu 2p_{3/2} photopeak, Cu L₃M₄₅M₄₅ Auger peak, and O 1s photopeak regions of the nanocubes/graphene sample obtained at -1.0 V as a function of argon sputtering

time. The CuO Cu 2p and –OH O 1s features appear to be easily removed by brief sputtering. After 10 s sputtering of the Cu₂O nanocubes, the weaker CuO Cu 2p_{3/2} feature at 934.2 eV appears to have been removed completely, which indicates that CuO exists as a thin outermost layer on the surface of the nanocubes. After 60 s sputtering of the Cu₂O nanocubes, a weak Cu LMM peak at 568.6 eV corresponding to metallic Cu emerges at the low binding energy side of the prominent Cu₂O Cu LMM peak at 570.1 eV. The relative intensity of this metallic LMM feature becomes stronger upon further sputtering for a total of 240 s, confirming the presence of the metallic core in the nanocubes. In addition, the Cu 2p_{3/2} peak at 932.3 eV and Cu LMM peak at 570.1 eV for Cu₂O remain prominent upon further sputtering. This suggests that Cu₂O is the main component of the nanocubes. As depicted in a schematic diagram in Figure 2.3b, these depth-profiling XPS data therefore show that the Cu₂O nanocube consists of a small metallic Cu core, a prominent Cu₂O shell and a thin CuO skin (as the outermost layer). Similarly, the strong O 1s peak at 531.9 eV is greatly reduced after sputtering for a 10 s and it becomes totally diminished after 60 s of sputtering, which suggests that this –OH feature is on the surface of the graphene substrate. The O 1s shoulder remaining after further sputtering corresponds to water adsorption of graphene substrate where is not covered by Cu₂O nanocubes.

To confirm the core-shell model of an individual Cu₂O nanocube, we take advantage of the nanoscale probing capability of helium ion microscopy. Figure 2.3a1 shows a helium ion micrograph of a group of nanocubes on graphene before sequential raster-sputtering of one of the nanocubes with the helium ion beam, as marked by the open square in Figures 2.3a2-a4. After the first scanning of the area inside the open square, removal of about half the nanocube is evident and a T-shape object appears in Figure 2.3a2, which indicates that the shell/perimeter of the nanocube is removed more efficiently than its core portion. This suggests that the material on the perimeter and the core are chemically different, with the former, likely softer, material appearing to be more easily sputtered away than the harder core material during the scanning with the high energy helium ion beam. Continued scanning (and sputtering) of the same area with the helium ion beam ultimately removes the harder core material, as shown in Figures 2.3a3 and 2.3a4. While these helium ion images do not identify the chemical nature of the components, they illustrate the material difference between the shell and the core of a single nanocube. Combining with the depth-profiling XPS data shown in Figure 2.2b, this therefore supports our proposed model of the Cu₂O nanocube to consist of a Cu core, a Cu₂O shell and a CuO skin, shown in Figure 2.3b. For comparison, we also show a schematic model of a sputter-coated Cu film on graphene in Figure 2.3c, which consists of a Cu film on top of graphene with a Cu₂O overlayer and a CuO outermost layer.

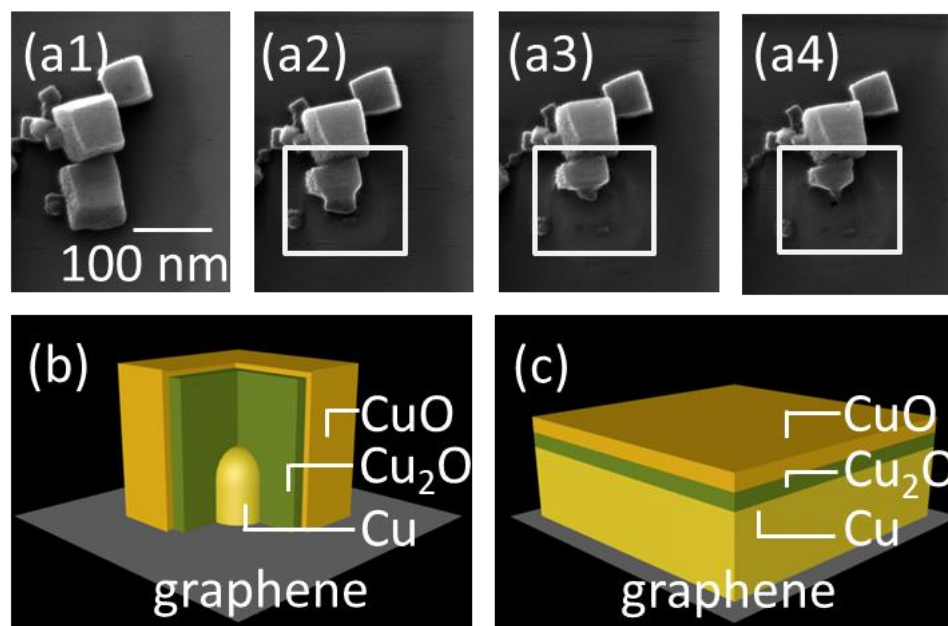


Figure 2.3 (a1-a4) Helium ion micrographs of an individual nanocube (marked by an open square) in a cluster of Cu₂O nanocubes (electrodeposited on a graphene substrate at -1.0 V in a 1 mM CuSO₄ · 5H₂O and 10 mM NaClO₄ solution for 100 s at room temperature) upon sequential scanning (and sputtering) with a helium ion beam. Schematic models of the proposed structures of (b) a Cu₂O nanocube on graphene and (c) a Cu film sputter-coated on graphene.

2.3.3 Glucose Sensing Performance of Cu₂O Nanocubes/Graphene and Related Graphene Sensors

To date, the most common commercial products for glucose detection in the marketplace are enzymatic sensors. Generally, this type of commercial sensor is popular because of its high selectivity to the target molecule, glucose. Enzyme immobilization can be commonly achieved by direct adsorption, sol-gel adsorption, and cross-linking.¹⁹⁹ One major challenge for enzymatic biosensors is the stability of the enzyme over long-term storage because the activity of the enzyme is affected by the temperature, pH, humidity, and ionic strength.²⁰⁰ This potential issue provides an opportunity for non-enzymatic biosensors, in which glucose is oxidized on the surface of the electrode to generate the current directly without the need for enzyme immobilization. The entire process occurs at the active sites of the electrode where the glucose molecules are adsorbed. In addition to low cost and good stability, copper oxides work as the electrocatalysts in a glucose

sensor because of their high electro-oxidation activity and their propensity for electron-transfer reactions at low overpotential.²⁰¹⁻²⁰² In the present work, the active sites of the glucose sensor are provided by the Cu₂O nanocubes electrodeposited on the graphene substrate at -1.0 V in a 1 mM CuSO₄·5H₂O (electrolyte) and 10 mM NaClO₄ (supporting electrolyte) solution for 100 s at room temperature. The average size of these Cu₂O nanocubes so produced is 50 nm (Figure 2.1e). These deposition conditions provide on graphene a large density of Cu₂O nanocubes of a small size of a near-monolayer coverage that is optimal for use as a catalyst.

To investigate the efficacy of this Cu₂O nanocubes/graphene sensor, we compare its glucose sensing performance with three other sensors: a bare graphene strip (graphene), a graphene strip coated with a copper film by magnetron sputtering for 60 s (Cu/graphene), and an enzymatic sensor based on glucose oxidase (GOx) immobilized on a graphene strip without (GOx/graphene) and with Nafion (GOx/Nafion/graphene). With the increase of glucose concentration (0 to 2.4 mM), distinct enlargements of the redox current signal are obtained and the potential for current vs time curves is selected at +0.6 V vs Ag/AgCl as shown in Figure S2.6. Figure 2.4 shows the characteristic current vs time (or i-t) curves at +0.6 V vs Ag/AgCl upon stepwise addition of an aliquot of 20 μ L glucose (of 10 mM concentration), with constant stirring, to these sensors immersed in a 10 mL 0.1 M NaOH solution. The reason why Cu₂O nanocubes/graphene sensor needs to operate in NaOH solution is due to the catalytic mechanism of Cu₂O as mentioned above, in which Cu(I) is oxidized to Cu (II) forming Cu(OH)₂, and further to CuOOH. For this reason, the detection should be performed under alkaline conditions. We have also attempted the detection in PBS (with pH 7) and confirm that Cu₂O nanocubes do not work as a catalyst for glucose if NaOH is not added. The corresponding SEM images of the sensors before the addition of glucose are also shown. For the bare graphene sensor, the current jump is small upon glucose addition and its linear range is 0.02-1.10 mM with sensitivity 1.90 μ A mM⁻¹ cm⁻² (Figure 2.4a1). Even though the graphene substrate has good conductivity, graphene itself does not produce a large electrical current after glucose addition, making graphene more appropriate as a catalyst support material and not the catalyst itself.

For the Cu/graphene sensor, the corresponding XRD and XPS data in Figure S2.7 (Supporting Information) show that the sputtered-coated Cu film on graphene undergoes ambient oxidation in air. In Figure S2.7a, the prominent XRD peaks at 43.31°, 50.44° and 74.12° correspond to the (111), (200) and (220) planes, respectively, of the Cu face-centered cubic phase (JCPDS#01-089-2838). The Cu film does not exhibit any discernible features of Cu₂O FCC phase (JCPDS#03-065-3288) and CuO monoclinic phase (JCPDS#01-089-2529) because Cu₂O and CuO resulting from

oxidization in air might be amorphous or poorly crystalline. In contrast, since Cu₂O nanocubes/graphene have a more crystalline structure with better active sites for electron transfer, the sensor performance is expected to be better. Using the more surface-sensitive XPS technique, we show in Figure S2.7b (Supporting Information) the presence of Cu₂O/Cu and CuO in the Cu-coated graphene, with photopeaks at their respective binding energy positions as those indicated for the Cu₂O nanocubes/graphene sample in Figure 2.2b. Depth-profiling XPS spectra of the Cu LMM Auger region further reveals the presence of metallic Cu (Figure S2.7b, Supporting Information), the intensity of which increases with increasing sputtering time. On the other hand, the Cu₂O Cu LMM feature is found to decrease with further sputtering for 480 s, which indicates that only the surface of the sputter-coated Cu film reacts with oxygen forming the Cu₂O/CuO overlayer. After sputtering for 1080 s, the prominent composition of Cu/graphene is metallic Cu. In addition, we also anneal the Cu₂O nanocubes sample at 300 °C for 3 h to obtain predominantly CuO. The corresponding XRD profiles and i–t curves for Cu₂O nanocubes and the annealed (i.e., CuO) sample are compared in Figure S2.8, Supporting Information.

As with the structural composition of the Cu₂O nanocubes on graphene, the Cu₂O/CuO overlayer of the Cu film on graphene works as a catalyst in the oxidation reaction with glucose. The resulting detection range of the Cu/graphene sensor (Figure 2.4b1) is greatly extended by nearly tenfold (with respect to the graphene substrate, Figure 2.4a1) to 0.02–11.10 mM with sensitivity 9.56 $\mu\text{A mM}^{-1} \text{cm}^{-2}$. For the Cu₂O nanocubes deposited on graphene (Figure 2.4c1), the dynamic range for linear detection is found to be even wider and significantly extended over five decades to 0.002–17.1 mM. The linear range of the CuO sample (obtained by annealing) is found to be 0.02–14.66 mM, which is less than that of the Cu₂O nanocubes (Figure S2.8, Supporting Information). Unlike the sputter-coated Cu film, the Cu₂O nanocubes provide increased catalytic effects through their active sites over a large specific surface area. Finally, the detection range of the enzymatic sensor GOx/graphene without Nafion (Figure 2.4d1) is found to be quite limited at 0.2–1.0 mM with sensitivity 2.86 $\mu\text{A mM}^{-1} \text{cm}^{-2}$, but it can be extended to 0.02–11.10 mM with sensitivity 5.60 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ by adding 20 μL 0.5% Nafion. In Figure S2.9 (Supporting Information), we compare the Nyquist plots and the relevant resistances determined for the four sensors. Figure S2.10 (Supporting Information) provides the corresponding linear curves for these substrates. Evidently, the charge-transfer resistance is found to be the smallest for the Cu/graphene system, followed by those of Cu₂O nanocubes/graphene, graphene, and GOx/graphene. Since the sputter-coated Cu film and electrodeposited Cu₂O nanocubes are considered metallic contact points on graphene, the charge transfer resistance is smaller than on the bare graphene. The presence and

availability of reactive sites on Cu₂O nanocubes appear more important for the sensing performance although Cu/graphene has a lower charge-transfer resistance.

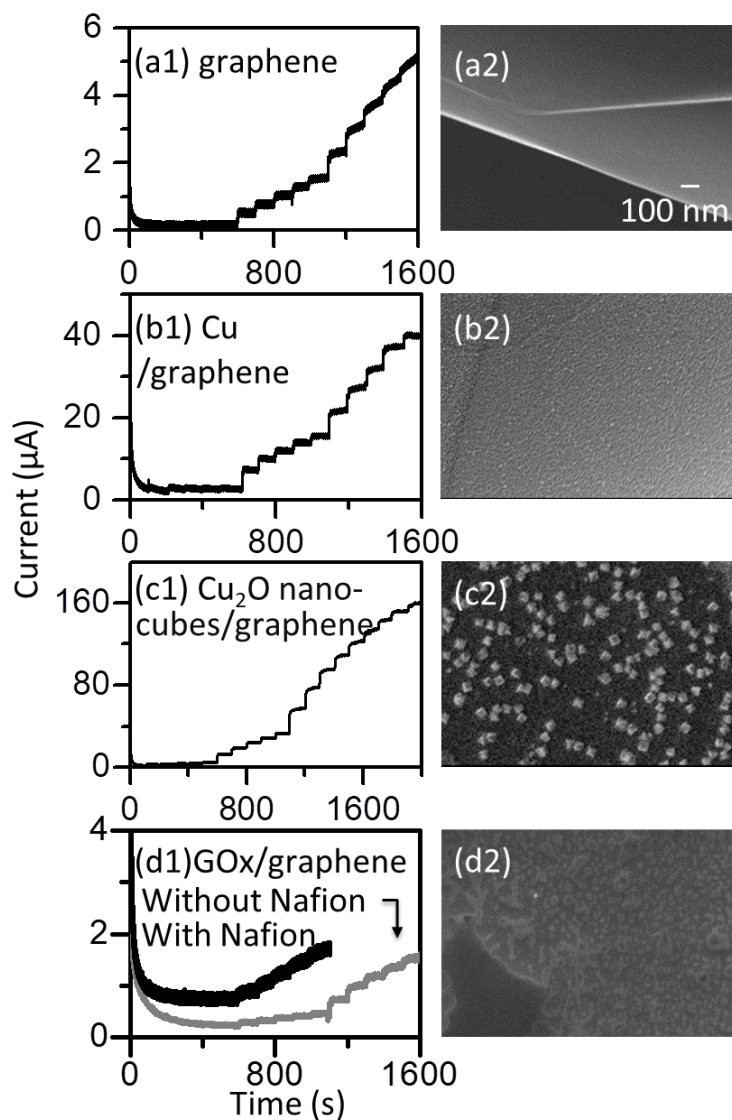


Figure 2.4 i-t curves (left column) obtained upon sequential addition of aliquots of glucose to 0.1 M NaOH at 0.6 V vs Ag/AgCl and the respective SEM images (right column) of (a1, a2) graphene, (b1, b2) Cu/graphene, (c1, c2) Cu₂O nanocubes/graphene, and (d1, d2) GOx/graphene without and with Nafion. The scale bars are the same for a2 to d2.

As the glucose sensor is designed for saliva-range glucose sensing, the linear range should be high enough to cover the glucose range for saliva. Figure 2.5a clearly demonstrates the current

jumps upon addition of a sufficiently low concentration of glucose from 2 μM to 210 μM , which is comparable to the glucose concentration of saliva (20-200 μM) found in normal individuals and diabetes patients.¹⁷⁶⁻¹⁷⁷ Figure 2.5b shows the linear calibration curve of current vs glucose concentration appropriate for saliva-range glucose sensing. The regression equation for the low concentration of glucose detection gives an R^2 of 0.994. The sensitivity of glucose for the Cu_2O nanocubes/graphene sensor is $36.40 \mu\text{A mM}^{-1} \text{cm}^{-2}$ in this linear range of 2-210 μM , well above that required for saliva-range glucose sensors.

We also examine the effects of possible interfering species to evaluate the selectivity of the Cu_2O nanocubes/graphene sensor. The physiological level of glucose (3-8 mM) is much higher than those of common interferents such as ascorbic acid ($\sim 0.1 \text{ mM}$), uric acid ($\sim 0.02 \text{ mM}$).²⁰³ Furthermore, saccharides such as sucrose and fructose could also be considered as interferents. As sucrose is a disaccharide, it must be broken down into glucose and fructose before the human body can use it. The serum concentration for fructose in diabetes patients has been reported to be $12.0 \pm 3.8 \mu\text{M}$ while that of glucose is above 11 mM.²⁰⁴ The difference in the relative concentrations of fructose and glucose is therefore about 1000 times in human body, which allows us to safely neglect the presence of sucrose and fructose as interferents. Using the Cu_2O nanocubes/graphene electrode as the working electrode for amperometry at +0.6 V vs Ag/AgCl, we add a 0.1 mM glucose followed by those of other interferents, including ascorbic acid, citric acid, uric acid, all with 0.1 mM concentration (i.e. at least 10 times higher than the expected level), and dopamine at 0.01 mM, into 20 mL 0.1 M NaOH. Evidently, ascorbic acid and dopamine yield less than 10% change in the current response compared with the current of second addition of glucose, while the other interferents (citric acid and uric acid) do not register a response in the i-t curve (Figure 2.5c).

The stability of the sensor is another important performance metric of a glucose sensor. To observe the relationship between the performance of the Cu_2O nanocubes/graphene sensor over time, we plot the i-t curve after storing a freshly made sensor under ambient conditions for 90 and 180 days and the overlapping linear fitting graph, shown in Figures S2.11c, d (Supporting Information), respectively. Evidently, the Cu_2O nanocubes/graphene sensor remains functional and stable for at least 180 days. We have also used the same sensor and repeated the detection experiments multiple times. We find that the currents in repeated consecutive tests (using the same sensor) appear to become smaller after each test. We therefore believe that the first test result is the most reliable and our sensor should therefore be considered for one-time detection and not reusable.

To demonstrate the application of our Cu₂O nanocubes/graphene sensor under real biomedical conditions, we obtain blood and saliva samples following Ethics Protocol (approved Application #43115) from five volunteers, four of whom are normal subjects while the fifth is considered prediabetic. Using a commercial amperometric blood glucose testing system with blood deposited on glucose dehydrogenase coated test strips, we determine the blood glucose concentrations of our human subjects. A regression relation $[\text{serum glucose (mg/dL)}] = 95.607 + 27.710 [\text{saliva glucose (mg/dL)}]$ ²⁰⁵ is then used to convert the serum or blood glucose concentration to saliva glucose concentration. These reference values of saliva glucose concentrations are shown in Figure 2.5d. We also collect saliva samples from our human subjects and use our Cu₂O nanocubes/graphene sensor to obtain the respective saliva glucose concentrations by making use of the calibration curve shown in Figure 2.5b. After centrifuged in 12,000 rpm for 10 min, an aliquot of 200 μL saliva supernatant is added into 10 mL 0.1 M NaOH at +0.6 V vs Ag/AgCl. These results are compared with our reference values in Figure 2.5d. For our prediabetic subject (Subject #1) with a blood glucose concentration of 10.8 mM, corresponding to a derived saliva glucose concentration of 195 μM , our Cu₂O nanocubes/graphene sensor provides a value of 186 μM . For our normal subjects, with blood glucose concentrations of 7.0 mM (Subject #2), 6.5 mM (Subject #3), 5.8 mM (Subject #4) and 5.5 mM (Subject #5), saliva testing using our Cu₂O nanocubes/graphene sensor gives saliva glucose concentrations of 60.6 μM , 42.8 μM , 17.6 μM and 7.5 μM , respectively. Evidently, a clear correlation exists between blood glucose concentration and saliva glucose concentration. Furthermore, our Cu₂O nanocubes/graphene sensor results are in excellent agreement (better than 95%) with our reference values (derived from blood glucose measurement). The present human subject study (Figure 2.5d) therefore confirms the high accuracy of saliva glucose testing provided by our Cu₂O nanocubes/graphene sensor. It is also of interest to note that the present saliva glucose sensor results appear to magnify the minor difference in the blood glucose concentrations found in our normal subjects. The saliva glucose sensor results are therefore more sensitive to changes in the blood glucose concentration.

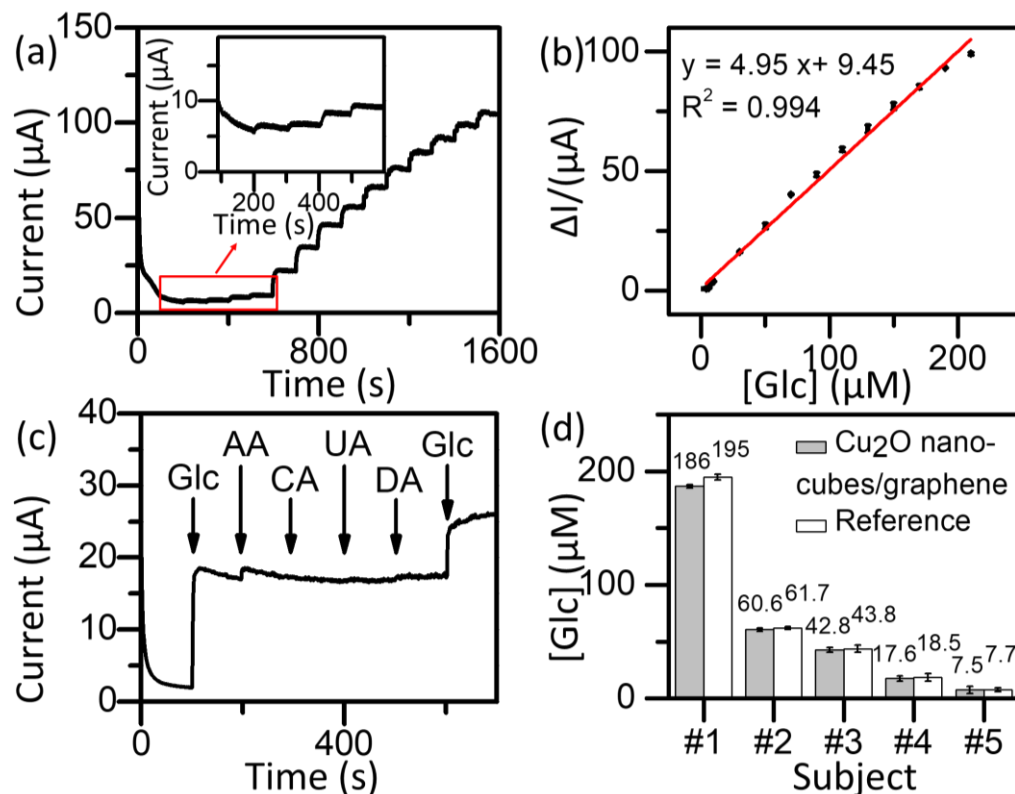


Figure 2.5 (a) i-t curve upon sequential addition of aliquots of glucose (glc) with increasing concentration from 2 to 210 μM to the Cu₂O nanocubes/graphene sensor held at +0.6 V vs Ag/AgCl in 0.1 M NaOH and inset image from 2 to 10 μM , and (b) the corresponding linearity response curve. (c) i-t curve illustrating minimal current jumps due to interference upon adding aliquots of 0.1 mM ascorbic acid (AA), 0.1 mM citric acid (CA), 0.1 mM uric acid (UA) and 0.01 mM dopamine (DA) solutions to 0.1 M NaOH at +0.6 V vs Ag/AgCl. An aliquot of 0.1 mM glucose solution is also added before and after the interference test. (d) Comparison of saliva glucose concentrations derived from blood glucose measurements (right bars) with those obtained by using Cu₂O nanocubes/graphene sensor (left bars) for five human subjects.

Table 2.1 summarizes the performance of these four sensors and compares them with other nonenzymatic and enzymatic glucose sensors that are mostly based on Cu₂O nanomaterials. Given that our target linear range of detection for glucose should be 0.02-0.2 mM, all three of our nonenzymatic graphene sensors appear viable for saliva-range glucose detection. Not only is the linear range the widest, the sensitivity of the Cu₂O nanocubes/graphene sensor is also higher than the other two nonenzymatic sensors. The enzymatic GOx/graphene sensor (with and without Nafion) appears less competitive in both sensitivity and linear range performance than even the

nonenzymatic Cu/graphene sensor. Several sensors shown in Table 2.1 have very high sensitivity, such as $2143 \mu\text{A mM}^{-1} \text{cm}^{-2}$ for nanospindle-like Cu_2O /straight multi-walled carbon nanotube hybrid nanostructures,²⁰⁶ $1210 \mu\text{A mM}^{-1} \text{cm}^{-2}$ for $\text{Cu}_x\text{O}/\text{Cu}$ nanowire array,²⁰⁷ and $1950 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ for sandwich nanoporous framework decorated with vertical CuO nanowire arrays²⁰⁸. The higher sensitivities found for these nanostructures are not unexpected because they all have much higher number densities and therefore much higher amount of material per unit area. Of the other sensors reported in the literature, only two cover the linear dynamic range of interest. The sensors based on Cu_2O nanoparticles on reduced graphene oxide and on Cu_2O nanospindles on straight multiwalled carbon nanotubes appear to cover the glucose range in saliva and have higher sensitivities. The methods to prepare these sensors are, however, quite elaborate. For instance, Cu_2O nanoparticles are anchored on reduced graphene oxide by using an ionic liquid crystal (1-hexadecyl-2, 3-dimethylimidazolium bromide) as a template, while Cu_2O nanospindles are fabricated with straight multiwalled carbon nanotubes by a series of (ultra)sonication and heat treatment steps (at different temperature) before drop-casting onto a glassy carbon electrode to use as a working electrode. The $\text{Cu}(\text{OH})_2$ nanograss arrays on uniform nanoporous copper substrate sensor and the sandwiched nanoporous framework decorated with vertical CuO nanowire array sensor have a high sensitivity and a wide range, but they do not cover the range for saliva glucose detection. In our case, Cu_2O nanocubes can be obtained on a commercial graphene strip by facile electrodeposition in an aqueous electrolyte. The resulting Cu_2O nanocubes/graphene sensor provides a wide linear detection range of 0.002-17.1 mM that is comparable to those achieved by other much more complex, less stable or difficult-to-fabricate sensors. Our graphene strip offers a flexible substrate with good conductivity to transfer electrons, while the near-homogeneous monolayer of Cu_2O nanocubes provides a large specific surface area and numerous reactive sites for nonenzymatic reaction to take place. The present sensor also has good sensitivity and a low limit of detection. The Cu_2O nanocubes/graphene sensor is therefore an excellent candidate for use as a practical and more sensitive saliva-range glucose sensor.

Table 2.1 Comparison of saliva-range glucose sensors.

Electrode matrix	Sensitivity ($\mu\text{A mM}^{-1}\text{ cm}^{-2}$)	Limit of Detection (LOD) (μM)	Linear range (mM)	Applied potential vs Ag/AgCl (V)	Reference
Bare graphene sheet	1.90	N/A	0.02-1.00	0.6	This work
Cu-coated graphene	9.56	N/A	0.02-11.1	0.6	This work
Cu ₂ O nanocubes on graphene sheet	36.40	0.23	0.002-17.1	0.6	This work
Glucose oxidase on graphene sheet	2.86	N/A	0.2-1.0	0.6	This work
Nanospindle-like Cu ₂ O/straight multi-walled carbon nanotube hybrid nanostructures	2143	0.2	0.0005-2.5	0.4	206
Cu/Cu ₂ O hollow microspheres	33.63	0.05	0.22-10.89	0.45	209
Coral-like PtAu-MnO ₂ binary nanocomposites on graphene paper	58.54	20	0.1-30.0	0	210
Graphene wrapped Cu ₂ O nanocubes	N/A	3.3	0.3-3.3	0.6	211
Filter paper strip for salivary analysis	N/A	1230	0.50-74.9	N/A	179
Cu ₂ O nanoparticles on reduced graphene oxide	185	0.05	0.01-6	0.6	183
Single-walled carbon nanotubes and multilayers of chitosan, gold nanoparticles and glucose oxidase on chip saliva nano-biosensor	26.6	5	0.1017-1.11	0.2	105
Three-dimensional Cu foam-supported single crystalline mesoporous Cu ₂ O nanothorn arrays	97.9	0.005	N/A	0.55	212
Cu _x O/Cu nanowire Array	1210	10	0.01-7	0.6 V	207
Sandwich nanoporous framework decorated with vertical CuO nanowire arrays	1950	1	0.1-6	0.58	208

2.4 Conclusion

The size and number density of Cu₂O nanocubes on a graphene substrate have been optimized for use as a saliva-range glucose sensor by changing the electrodeposition overpotential, Cu²⁺ electrolyte concentration, and deposition time at room temperature. The Cu₂O nanocube is found to have a metallic copper core and a Cu₂O shell with a CuO skin as the outermost layer. The glucose sensing performance of this Cu₂O nanocubes/graphene sensor is enhanced by the high conductivity of the graphene substrate and is found to be superior in sensitivity and linear range to other sensors including graphene, graphene sputter-coated with a Cu film, and graphene functionalized with glucose oxidase (with and without Nafion). This Cu₂O nanocubes/graphene sensor exhibits a wide detection range of 0.002-17.1 mM covering the appropriate glucose range found in the saliva in diabetes patients. The sensor is also stable in air and remains functional even after storing for 180 days. This sensor has also been tested favorably by using real saliva samples. The Cu₂O nanocubes/graphene glucose sensor therefore offers a sensitive non-invasive option for saliva-range glucose monitoring, with minimal interference, for diabetes patients.

Chapter 3

Copper Oxide Nanowires Decorated with CuFe_2O_4 Nanoparticles as High-Performance Dual Heterojunction Photocatalyst for Photoelectrochemical Hydrogen Evolution

3.1 Introduction

Global energy consumption has increased rapidly with the growth of population and economic development in the past century. The demand for renewable clean energy in the world has risen dramatically because of the rapid depletion of conventional energy sources and the recognition of their detrimental environmental effects and their contributions to global warming and climate change. Hydrogen has become one of the more promising renewable energy sources because H_2 has the highest gravimetric energy density and its combustion yields a pollution-free by-product, water. With the use of an appropriate catalyst, a photoelectrochemical (PEC) water splitting reaction provides a popular approach to produce hydrogen as a clean, low cost, and environmentally friendly energy source.²¹³ As the appropriate choice of catalysts in a PEC cell for the half-cell hydrogen evolution reaction (HER) is crucial, the catalysts should broadly satisfy the following requirements: (1) a proper band gap compatible with the solar electromagnetic spectrum (1.6-2.2 eV); (2) appropriate band edge alignment that spans the water redox potentials; (3) high energy conversion efficiency; (4) stability in the operating environment; and (5) a naturally abundant material source with a low cost of production that is compatible with large-scale applications.²¹⁴ Transition metal-based materials constitute one type of promising HER catalyst candidates not only because of their high abundance in the Earth's crust, low cost, and generally benign toxicity to the environment, but also because of their outstanding electrical conductivity, and superior chemical and thermal stability.²¹⁵ Among the transition metal oxides, cupric oxide (CuO) and cuprous oxide (Cu_2O) have direct bandgaps of 1.2-1.7 eV²¹⁶ and 2.0-2.4 eV²¹⁷, respectively, which cover the solar electromagnetic spectrum. Their small bandgaps also enable CuO and Cu_2O to strongly photoabsorb, making them attractive photocatalysts for HER under sunlight irradiation. However, their main challenge of becoming high-efficient photocathodes for HER is the high electron-hole recombination rate.²¹⁸

A promising strategy to alleviate this issue is to construct heterojunction structures of $\text{CuO}/\text{Cu}_2\text{O}$ composite to facilitate efficient separation of photogenerated electron-hole pairs. The $\text{CuO}/\text{Cu}_2\text{O}$ heterojunction can improve PEC energy conversion efficiency by facilitating such electron-hole separation. In addition, the presence of CuO on top of Cu_2O can also serve as a

protective layer against Cu_2O photocorrosion.²¹⁹ The relative compositions of CuO and Cu_2O , especially the thickness of the CuO layer, have significant effects on optical, structural, morphological, and (photo)catalytic properties. As the thickness of the CuO layer increases, it enhances light absorption, especially in the longer wavelength region, and improves charge separation due to reinforced band bending. However, a thicker CuO layer can also impede efficient charge transport, leading to a reduction in the overall performance of the PEC system.²²⁰ Therefore, attaining the appropriate thickness of the CuO layer plays a vital role in realizing a high-performance $\text{CuO}/\text{Cu}_2\text{O}$ heterojunction photocatalyst.

An even more promising strategy is to build a dual Z-scheme heterojunction structure¹⁴² by introducing a third semiconductor connected with $\text{CuO}/\text{Cu}_2\text{O}$, thus offering a longer lifetime of charge carriers, higher charge carrier concentration, and enhanced light absorption. Several dual Z-scheme photocatalyst systems containing $\text{CuO}/\text{Cu}_2\text{O}$ with other semiconductors such as ZnO ,²²¹ TiO_2 ,²²² WO_3 ,²²³ reduced graphene oxide,²²⁴ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ ²²⁵ have been reported. Other than transition metal oxides, stoichiometric-composition mixed metal oxides with the spinel (AB_2O_4) structure are also found to be efficient catalysts. Spinel oxide materials combine two mixed metals into a AB_2O_4 chemical composition, with A^{2+} divalent metal ion, B^{3+} trivalent metal ion, and O^{2-} anions.²²⁶ However, only a limited amount of work has focused on the combination of $\text{CuO}/\text{Cu}_2\text{O}$ with spinel oxide materials. Among the spinel materials, the Cu-based ternary material such as CuFe_2O_4 with a compatible bandgap (1.5-1.7 eV)²²⁷ has been considered as an efficient co-catalyst with other semiconductors because of its low cost, abundant sources, ferromagnetic properties, high electrical conductivity, effective catalytic activity, and high photochemical stability and visible light response.²²⁸ CuFe_2O_4 can also be synthesized by a variety of methods including solid-state reaction,⁷⁰ co-precipitation,²²⁹ sol-gel method,²³⁰ hydrothermal synthesis,²³¹ and solvothermal synthesis²³².

In this work, we fabricate $\text{Cu}_x\text{O}-\text{Cu}$ on a flexible graphene strip substrate for use as a heterojunction photocatalyst for PEC water splitting for hydrogen evolution. The high conductivity of graphene is particularly attractive for electron transfer in electrochemistry. We further show that the addition of spinel CuFe_2O_4 nanoparticles on $\text{Cu}_x\text{O}-\text{Cu}/\text{graphene}$ to produce a dual Z-scheme heterojunction photocatalyst, for the first time, can lead to a significant increase in the photoconversion efficiency for hydrogen evolution. A plausible mechanism based on the charge transfer pathways of a multi-component Z-scheme photocatalytic system reported earlier²³³ is found to be consistent with the observed increase in performance.

3.2 Experimental Methods

3.2.1 Chemicals and Electrochemical Methods

Analytical grade copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), lactic acid (CH_3CHCOOH), sodium hydroxide (NaOH) and sodium sulfate (Na_2SO_4) were purchased from Sigma and used without further purification. The graphene strip was purchased from Graphene Supermarket (USA). Ultra-pure, filtered, high-resistivity ($18.2 \text{ M}\Omega \cdot \text{cm}$) water was used to prepare all the solutions. An electrochemical workstation CH Instruments 660E was used for all the electrodeposition and electrochemical characterization experiments. Copper films were electrochemically deposited on the graphene strip, and then post-annealed in O_2 to form copper oxide films. The PEC performance of the resulting copper oxide/graphene photoelectrode was evaluated by using a three-electrode configuration, with the photoelectrode as the working electrode, an Ag/AgCl electrode as the reference electrode, and a Pt wire as the counter electrode. The reference electrode potential for hydrogen evolution was converted to RHE (reversible hydrogen electrode) according to the Nernst equation ($E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + 0.0591\text{pH} + 0.2046$, where E_{RHE} and $E_{\text{Ag}/\text{AgCl}}$ are the potentials obtained with RHE and Ag/AgCl reference electrodes, respectively). The electrolyte used for electrodeposition was a mixture of copper sulfate and lactic acid prepared at a selected pH adjusted by using sodium hydroxide. For PEC measurements, the electrolyte was 1 M Na_2SO_4 solution buffered at pH 6.5. The photocurrent spectra was obtained for an illuminated photoelectrode with a sample area of $10 \times 10 \text{ mm}^2$ under simulated sunlight exposure at $100 \text{ mW} \cdot \text{cm}^{-2}$ (i.e., 1 sun) from a 300 W Xenon lamp (PLS-SXE 300, Newport Corporation) equipped with an AM 1.5G filter.

3.2.2 Synthesis of $\text{Cu}_x\text{O}-\text{Cu}/\text{Graphene}$

Different concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 0.3 M lactic acid, adjusted to different pH by adding 4 M NaOH , were used to prepare the 10 mL electrolyte solutions. The colour of the solution turned from light blue to dark blue upon addition of NaOH . The graphene strip was cut into chips ($10 \times 20 \text{ mm}^2$) and (denoted as G) to be used as the substrates for electrodeposition of the Cu films. Various conditions including overpotential, deposition time, CuSO_4 concentration and pH were used to optimize electrodeposition. The migration of positively charged copper ions to the cathode resulted in the formation of a reddish orange-colored copper film on the graphene substrate upon each copper ion gaining a pair of electrons at the cathodic surface [according to the reaction: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$]. At the anode, OH^- was discharged first, as confirmed by the evolution of oxygen gas at the Pt (counter electrode) surface [in accord with the reaction: $4\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{e}^-$]. Nanostructured Cu films were deposited by using potentiostatic

amperometry under optimized conditions (see below) at a constant voltage of -1.2 V vs Ag/AgCl for 20 min in 40 mM CuSO_4 at pH 12. After electrodeposition, the Cu film was annealed in O_2 in a tube oven to facilitate thermal annealing at selected temperatures: 200, 300, and 400 $^\circ\text{C}$ for 30 min, resulting in samples that we denoted as $\text{Cu}_x\text{O-Cu/G-200-30}$, $\text{Cu}_x\text{O-Cu/G-300-30}$, $\text{Cu}_x\text{O-Cu/G-400-30}$, respectively. In this sample notation of $\text{Cu}_x\text{O-Cu/G-X-Y}$, X is the annealing temperature in $^\circ\text{C}$ and Y is the amount of annealing time in min. We also annealed the Cu film at a fixed temperature of 300 $^\circ\text{C}$ for selected amounts of time of 30, 60 and 180 min, to produce samples denoted as $\text{Cu}_x\text{O-Cu/G-300-30}$, $\text{Cu}_x\text{O-Cu/G-300-60}$, and $\text{Cu}_x\text{O-Cu/G-300-180}$, respectively.

3.2.3 Synthesis of CuFe_2O_4 Nanoparticles

A wide range of methods are available to obtain spinel materials, including ball-milling, sol-gel, co-precipitation, solvothermal, and combustion syntheses. As the preparation method employed greatly affects the crystal structure and specific surface area of the product, the appropriate choice of preparation method is therefore vitally important to the resulting catalytic activity.²³³ In this work, CuFe_2O_4 was fabricated by using a solvothermal method. A mixture of 0.002 mol of copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), 0.004 mol of iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 0.006 mol of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ and 0.1 g of poly-vinylpyrrolidone was dissolved in 30 mL of ethylene glycol with constant stirring at room temperature for 1 h. The solution was then transferred into a teflon-lined autoclave (50 mL) and heated at 180 $^\circ\text{C}$ for 24 h. CuFe_2O_4 precipitates were collected and washed by HPLC grade ethanol and isopropanol and suspended in 5 mL ethanol. 0.040 mL of the resulting CuFe_2O_4 solution was drop-casted on top of a bare graphene chip (G) or to a $\text{Cu}_x\text{O-Cu/G}$ sample, and the resulting samples were thoroughly dried in a nitrogen box overnight.

3.2.4 Characterization

A Zeiss Merlin field emission microscope was used to image the morphologies by scanning electron microscopy (SEM). The crystalline structure of an individual CuFe_2O_4 NP was determined by transmission electron microscopy (TEM) in a Zeiss Libra 200 MC microscope with a double-corrected Omega filter operated at 200 kV. The TEM specimen was prepared by drop-casting the NPs suspended in ethanol directly on a 300-mesh lacey carbon-coated copper TEM grid. The crystal phases of the nanostructured films were determined by glancing incidence X-ray diffraction (XRD) in a PANalytical X'Pert Pro MRD diffractometer with $\text{Cu K}\alpha$ (1.5406 $\text{\AA}$) radiation at an incident angle of 0.6° . The chemical-state composition was characterized by X-ray photoelectron spectroscopy (XPS) in a Thermo-VG Scientific ESCALab 250 microprobe with monochromatic $\text{Al K}\alpha$ radiation (1486.6 eV) and a typical energy resolution of 0.5 eV full width at half maximum.

3.3 Results and Discussion

3.3.1 Optimization of Copper Oxide Nanomaterials

Similar to electrodeposition of Cu films in an alkali solution with further oxidization on Cu foil,²³⁴ ITO²³⁵ and FTO,^{220, 236} we obtain a Cu film on the graphene substrate. As the deposition conditions can greatly affect the morphology, size, and shape of the copper deposits, several voltages (−0.4 V, −0.6 V, −0.8 V, −1.0 V and −1.2 V, all vs Ag/AgCl), CuSO₄ concentrations (4 mM, 10 mM, 20 mM, and 40 mM), deposition times (1.5 min, 5 min, 10 min, 20 min, and 60 min), and pH (4, 6, 8, 10 and 12) are used for the optimization. To produce copper oxide, we further anneal the Cu film in a tube oven with oxygen flow at several selected temperatures for selected amounts of annealing time. The effects of different deposition parameters on the morphology, size and distribution of the Cu film deposited on graphene (denoted as Cu/G) have been examined by using SEM. The morphologies of the Cu films prepared by electrodeposition at different overpotentials (all vs Ag/AgCl) are shown in Figure S3.1. The morphology of the Cu film appears to change significantly with increasingly more negative overpotential. Obtained with an overpotential of −0.4 V, the resulting cauliflower-like Cu nanostructures are composed of irregular massive Cu petals. With increasingly more negative overpotential, more cauliflower-like Cu features appear at −0.6 V and they aggregate into larger networks at −0.8 V and form a continuous Cu film at −1.2 V. Evidently, the overall film thickness and surface roughness of the Cu film increase with increasing negative overpotential. As expected, the cauliflower-like nanostructures also appear to grow in number and size, and they connect with one another with increasing CuSO₄ concentration (Figure S3.2) and with increasing deposition time (Figure S3.3). Isolated cauliflower-like Cu nanostructures with irregular Cu petals are observed with the lowest CuSO₄ concentration at 4 mM (Figure S3.2a) or for the shortest deposition time of 1.5 min (Figure S3.3a). The surface roughness of the Cu film also increases with increasing CuSO₄ concentration to 40 mM (Figure S3.2e). The graphene substrate is fully covered by the Cu film upon deposition for 20 min (Figure S3.3d). The morphology of the copper deposits also varies with the pH of the electrolyte (Figure S3.4) because it is greatly influenced by the chemical potential of OH[−] ions. At a low pH level, Cu²⁺ move together to nucleate and random aggregation appears. At a high pH level, the increased amount of OH[−] ions more readily neutralize the positive charges, and the Cu nuclei therefore grow slowly and orderly on the existing nuclei.²³⁷⁻²³⁸ When the concentration of OH[−] ions is further increased to provide a pH of 12 (Figure S3.4e), growth becomes enhanced on specific crystal faces of the structure, creating diffusion layers on certain surfaces of the Cu film. From these studies, we determine that the optimum electrodeposition conditions for producing a complete Cu thin film

(fully covering the substrate) with high surface roughness are -1.2 V in 40 mM CuSO_4 at pH 12 for 20 min. It should be noted that thicker films obtained by more negative overpotential, higher CuSO_4 concentration, or more time than the values considered here would become detached from the substrate.

After securing the condition for optimal electrodeposition of a Cu film on the graphene substrate (Cu/G), we anneal the optimized Cu film in O_2 to obtain a more robust catalyst film consisting of copper oxides (Cu_xO) for photoelectrochemical water splitting studies. Both the annealing temperature and the amount of annealing time can affect the composition and structure, as well as the thickness of the Cu_xO film. We have considered annealing temperatures of 200, 300 and 400 °C for 30 min and of 300 °C for 30, 60 and 180 min for the Cu/G sample. The morphologies and crystal structures of the Cu/G and Cu_xO -Cu/G samples are shown in Figure 3.1. For the Cu film on graphene (without any post-annealing), cauliflower-like structures (3-5 μm in size) are found (Figure 3.1a). Upon post-annealing Cu/G in O_2 at 200 °C for 30 min, the surfaces of the microcrystallites of the resulting Cu_xO -Cu/G-200-30 sample have evidently become smoother (Figure 3.1b). Remarkably, post-annealing Cu/G in O_2 at a higher temperature of 300 °C for 30 min produces nanowires for the Cu_xO -Cu/G-300-30 sample (Figure 3.1c), while increasing the annealing time to 60 min in Cu_xO -Cu/G-300-60 (Figure 3.1d) and 180 min in Cu_xO -Cu/G-300-180 (Figure 3.1e) lead to longer nanowires with a higher density. However, annealing at a higher temperature of 400 °C in Cu_xO -Cu/G-400-30 leads to shorter but thicker nanowires with a reduced density (Figure 3.1f).

The corresponding glancing-incidence X-ray diffraction profiles for these Cu_xO -Cu/G samples are shown in Figure 3.1g. The strongest peak of the graphene substrate is located at 54.72° . For the as-deposited copper film in Cu/G (Figure 3.1a), the prominent peaks at 43.19° and 50.30° are in good accord with the respective (111) and (200) planes of Cu face-centered cubic (FCC) phase, while the weaker features at 73.89° and 89.62° correspond to the (220) and (311) planes, respectively (JCPDS#01-070-3038). For Cu_xO -Cu/G-200-30 (Figure 3.1b), new features corresponding to Cu_2O FCC phase are evident, with the Cu features remaining prominent. For the Cu_xO -Cu/G-300-30 sample, the Cu_2O features become more intense, with additional features corresponding to CuO monoclinic phase emerging at 35.25° , 38.53° , and 48.71° . The strong Cu_2O peaks at 36.52° and 42.42° and the weaker features at 61.55° and 73.73° can be attributed, respectively, to the (111) and (200) planes, and the (220) and (311) planes of the Cu_2O FCC phase (JCPDS#01-077-0199). For samples obtained with longer annealing times (60 min, 180 min) at 300 °C, the intensities of Cu_2O and CuO peaks appear barely changed, and the intensities of Cu metal

appear to fade with the longer annealing times. For $\text{Cu}_x\text{O-Cu/G-400-30}$, the CuO features are found to become more intense. The features at 35.25° , 38.53° , and 48.71° can be attributed, respectively, to the (-111) , (111) and (-202) planes of the CuO monoclinic phase (JCPDS#01-089-2530), and the peaks of Cu metal can be barely observed. The presence of largely Cu_2O features after annealing at 200°C indicates that part of Cu has been oxidized to Cu_2O . Further annealing at 300°C leads to additional CuO features while the relative diffraction intensities of Cu_2O remain much higher than those of the CuO features, which suggests that the main composition of the copper oxide nanomaterial is still Cu_2O . After annealing at 400°C , the relative diffraction intensities of CuO become larger, which indicates that a greater amount of Cu_2O is further oxidized to CuO. While the phase composition remains relatively stable within the temperature range of $300\text{--}400^\circ\text{C}$, notable transformations occur in the morphology of the material.

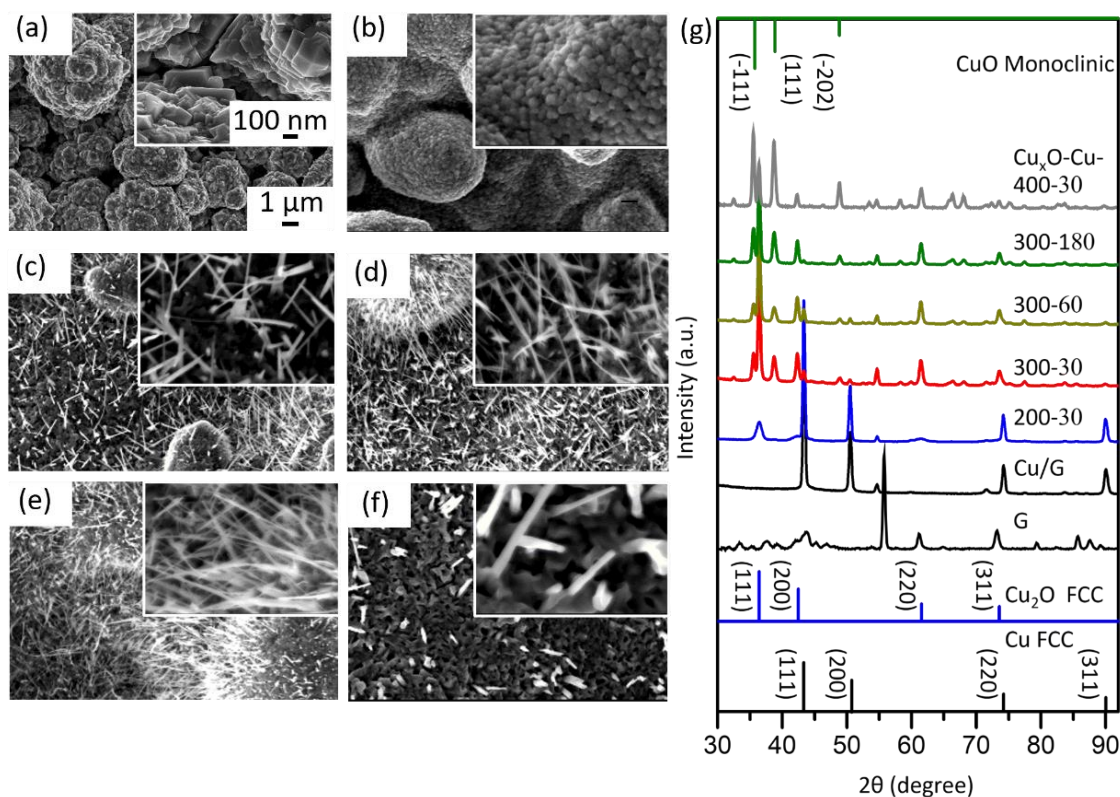


Figure 3.1 SEM images of (a) a Cu film as electrodeposited on graphene (Cu/G), and of $\text{Cu}_x\text{O-Cu/G}$ upon annealing (b) at 200°C for 30 min ($\text{Cu}_x\text{O-Cu/G-200-30}$), at 300°C for (c) 30 min ($\text{Cu}_x\text{O-Cu/G-300-30}$), (d) 60 min ($\text{Cu}_x\text{O-Cu/G-300-60}$), and (e) 180 min ($\text{Cu}_x\text{O-Cu/G-300-180}$), and (f) at 400°C for 30 min ($\text{Cu}_x\text{O-Cu/G-400-30}$), and (g) their corresponding glancing incidence

XRD profiles, along with the measured profile for a pristine graphene substrate and reference profiles for Cu FCC (JCPDS#01-070-3038), Cu₂O FCC (JCPDS#01-077-0199), and CuO monoclinic phases (JCPDS#01-089-2530). All the SEM images employ the same scale.

Figure 3.2a shows the corresponding XPS spectra of the Cu 2p_{3/2} and O 1s regions of selected Cu_xO-Cu/G samples. The dominant Cu 2p_{3/2} peaks of Cu/G at 932.3 eV and post-annealed Cu_xO-Cu/G (at 200, 300, and 400 °C) at 933.9 eV are assigned to Cu/Cu₂O and CuO, respectively. The shake-up satellite structures at the higher binding energy side of the Cu 2p_{3/2} peak are characteristic of the Cu(II) states.²³⁹ The formation of these satellites can be attributed to shake-up transitions by ligand to metal 3d charge transfer that cannot occur in Cu(I) compounds or metallic Cu because their 3d shells cannot be filled completely. The O 1s peaks at 529.9 eV and 531.3 eV correspond to the Cu₂O/CuO and –OH group, respectively.

While the Cu 2p peaks for CuO can be easily discerned in Figure 3.2a, the relative chemical state distribution in the nanodeposit is less clear. Figure 3.2b shows the depth-profiling spectra of Cu 2p_{3/2} peak, Cu L₃M₄₅M₄₅ Auger peak, and O 1s photopeak regions of the Cu_xO-Cu/G-300-30 sample as a function of argon sputtering time. Upon sputtering for 10 s, the dominant peak has evidently shifted from 933.9 eV, attributable to CuO, to 932.4 eV that can be assigned to Cu₂O, which confirms the presence of a thin CuO layer on the surface of the nanowires. A small shift in the Cu LMM peak position from 569.3 eV to 569.9 eV also occurs, the latter of which is close to the reported value of 570.0 eV for Cu₂O.²⁴⁰ Further sputtering for a total of 240 s causes the broad Cu 2p_{3/2} peak to become sharper, while the intensities of the satellites appear to be substantially reduced. The Cu 2p_{3/2} peak at 932.4 eV and Cu LMM peak at 569.9 eV for Cu₂O remain prominent upon further sputtering, which suggests that Cu₂O is the main component of Cu_xO-Cu/G-300-30. For O 1s, two component peaks centered at 529.9 eV and 531.3 eV appears, which correspond to CuO and –OH, respectively. After sputtering, the lower binding energy peak at 529.9 eV shifts to 530.2 eV, while the higher binding energy component at 531.3 eV is reduced in intensity and has completely disappeared after 1080 s of sputtering. This suggests that the adsorbed –OH group is part of the near-surface and can be completely removed by sputtering.

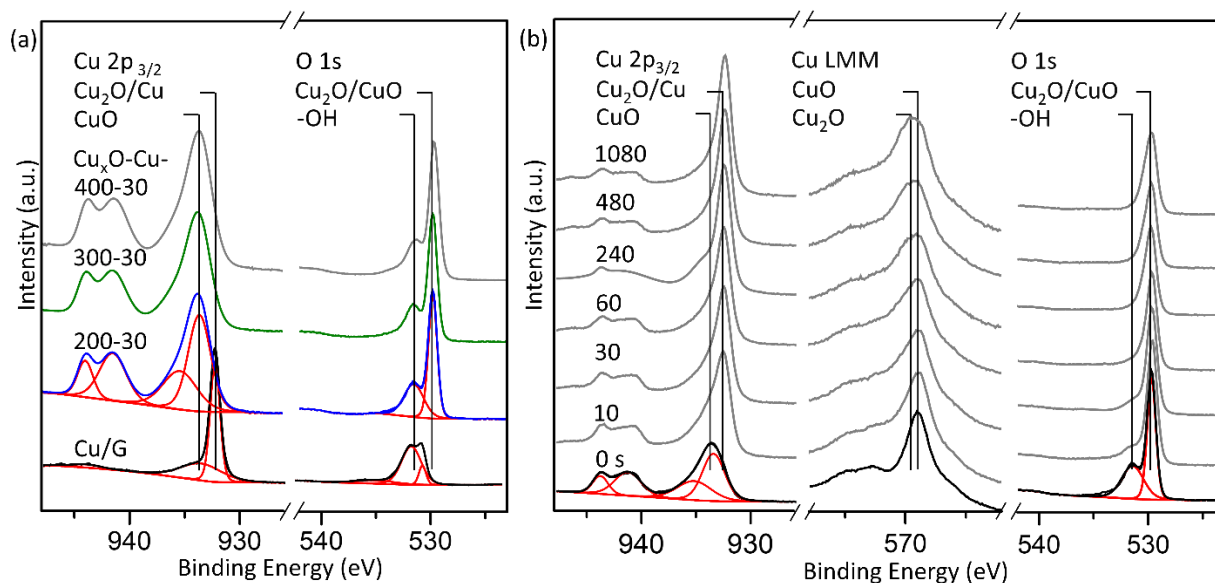


Figure 3.2 XPS spectra of Cu 2p_{3/2} and O 1s regions of Cu/G, Cu_xO-Cu/G-200-30, Cu_xO-Cu/G-300-30 and Cu_xO-Cu/G-400-30 and depth-profiling spectra of Cu 2p_{3/2}, Cu LMM and O 1s regions of Cu_xO-Cu/G-300-30.

The cross-sectional SEM image in Figure 3.3a shows the side view of the nanowires in the Cu_xO-Cu/G-300-30 sample. Based on these SEM, XRD and XPS data, we show plausible schematic models of Cu_xO-Cu-200-30, Cu_xO-Cu/G-300-30, and Cu_xO-Cu/G-400-30 in Figures 3.3b-d. The composition of Cu_xO-Cu-200-30 (Figure 3.3b) consists mainly of a Cu base and a thin Cu₂O layer, with a thinner CuO layer observed on top. For the samples obtained with a higher post-annealing temperature, the Cu_xO-Cu/G-300-30 sample (Figure 3.3c) consists of a thin Cu base, a thick Cu₂O layer, and a CuO skin with CuO nanowires shown as an aerial view in Figure 3.1c. The Cu_xO-Cu/G-400-30 sample (Figure 3.3d) consists of a minimal Cu base, a thin Cu₂O layer and a thicker topmost CuO skin with CuO nanowires shown as an aerial view in Figure 3.1f. In the post-annealing process, Cu is thermally oxidized to Cu₂O and further to CuO. Initially, a layer of Cu₂O is generated at the vapour-solid interface, which is characterized by high porosity and formation of defects caused by significant compressive stress.²⁴¹ To undergo further oxidation, Cu atoms are believed to migrate to reach the expanding interface by lattice diffusion and/or grain-boundary diffusion. Lattice diffusion leads to the continuous growth of the Cu₂O layer, while grain-boundary diffusion contributes to the formation of the nanowires.²⁴² In this work, CuO nanowires become an important part of the CuO layer that provides the photocathodic reactivity.

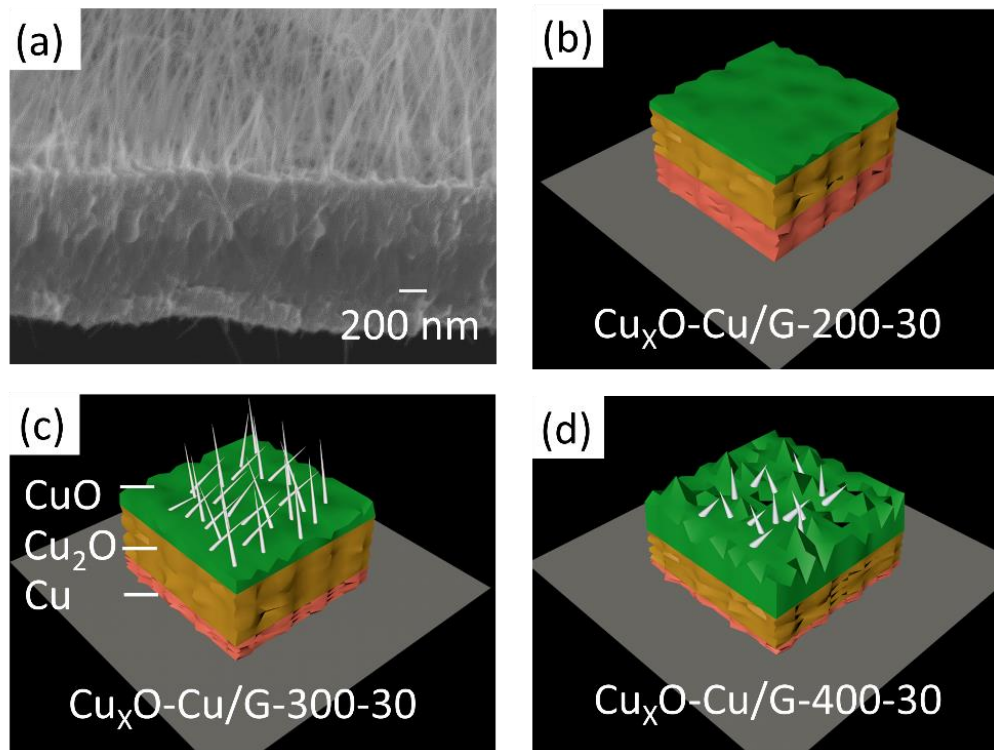


Figure 3.3 (a) Cross sectional SEM image of $\text{Cu}_x\text{O-Cu/G-300-30}$ and schematic representations for (b) $\text{Cu}_x\text{O-Cu-200-30}$, (c) $\text{Cu}_x\text{O-Cu/G-300-30}$, and (d) $\text{Cu}_x\text{O-Cu/G-400-30}$, illustrating the change in the relative compositions of CuO (topmost layer or skin), Cu_2O (middle layer) and Cu (base) in the respective nanostructured films on graphene.

3.3.2 Characterization of CuFe_2O_4

The CuFe_2O_4 nanoparticles prepared by a solvothermal method are drop-casted on top of a graphene substrate for detailed analyses. The SEM image in Figure 3.4a shows aggregation of CuFe_2O_4 nanoparticles with an average particle size of ~ 20 nm. In the glancing incidence XRD profile (Figure 3.4d), the most prominent feature at 35.54° corresponds to the (311) plane, which suggests oriented growth of the sample along the (311) direction. The weaker peaks at 30.17° , 43.20° , 53.59° , 57.13° , and 62.74° can be attributed, respectively, to the (220), (400), (422), (511), and (440) planes, all of the face-centered cubic phase of CuFe_2O_4 (PDF#01-077-0010). In the high-resolution TEM image shown in Figure 4b, the nanoparticle is found to have an interplanar spacing of $2.52 \text{ \AA}$, which is in good accord with that of the (311) planes of CuFe_2O_4 . Figure 3.4c shows the selected area electron diffraction (SAED) pattern with concentric diffraction rings. The identification of phases is achieved by comparing the measured distance from SAED with the

diffraction patterns of the reference phases from the ICDD database (PDF#01-077-0010). The interplanar distances are calculated to be 0.298, 0.252, 0.209, 0.170, 0.161 nm, which can be assigned to the characteristic planes of (220), (311), (400), (422), and (511), respectively, of the cubic phase. The corresponding XPS spectra of the Cu $2p_{3/2}$ and Fe $2p_{3/2}$ regions of CuFe_2O_4 nanoparticles on a graphene substrate are shown in Figure 3.4e. The prominent Cu $2p_{3/2}$ feature at 933.1 eV can be attributed to Cu^0 or Cu^+ , while the weaker Cu $2p_{3/2}$ feature at 934.5 eV is assigned to Cu^{2+} and is further confirmed by the shake-up satellite features at 941.4-943.9 eV. The prominent Fe $2p_{3/2}$ feature at 710.5 eV can be assigned to Fe^{2+} , while the peak at 712.3 eV are attributed to Fe^{3+} bonded to a hydroxyl group ($-\text{OH}$).²⁴³

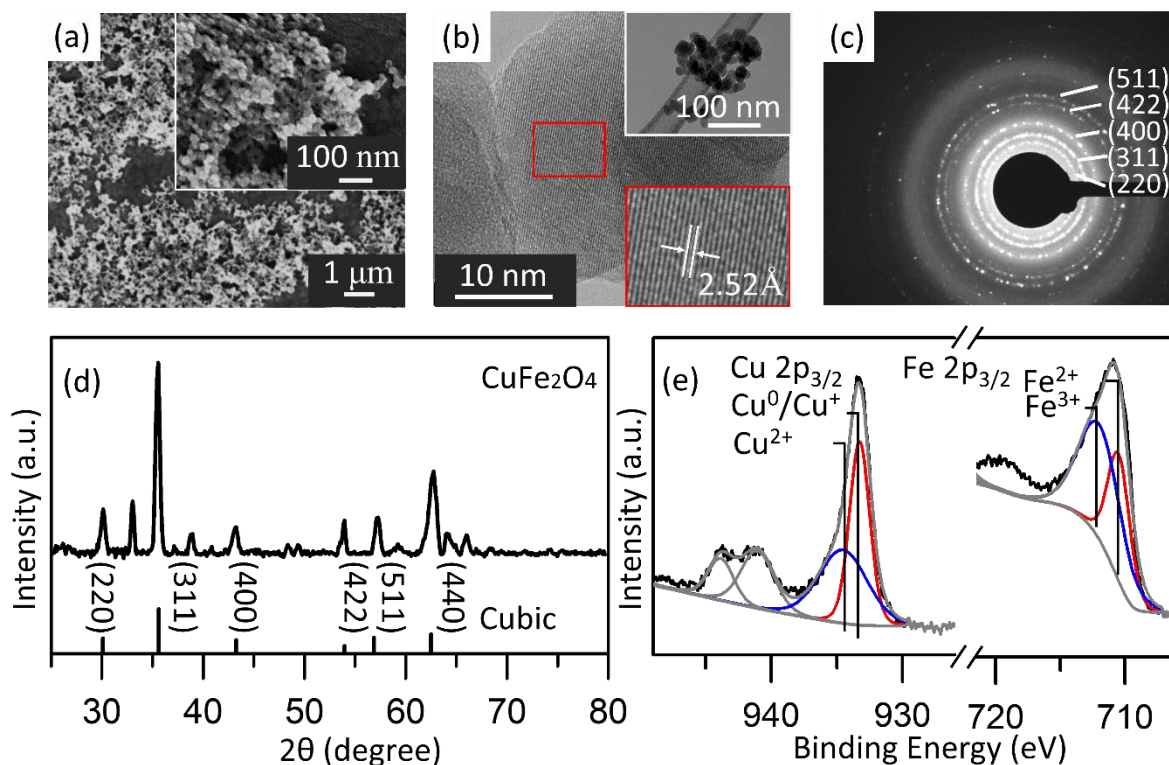


Figure 3.4 (a) SEM image of the CuFe_2O_4 nanoparticles drop-casted on a graphene chip substrate. (b) Low-resolution (top inset) and high-resolution TEM images of individual CuFe_2O_4 nanoparticles, with an expanded view depicting the interplanar spacing of the (311) planes in the bottom inset. (c) Selected Area Electron Diffraction (SAED) rings obtained from individual CuFe_2O_4 nanoparticles. (d) Corresponding glancing-incidence XRD profile along with the reference profile of the cubic phase of CuFe_2O_4 (PDF#01-077-0010). (e) XPS spectra of Cu $2p_{3/2}$ and Fe $2p_{3/2}$ regions of CuFe_2O_4 nanoparticles.

3.3.3 Photoelectrochemical Properties

To evaluate the PEC water splitting activity of the prepared photocathodes, linear sweep photovoltammetry is used under 0.2 Hz chopped illumination with an intensity of 100 mW cm^{-2} (i.e. 1 Sun). A 1 M Na_2SO_4 buffer solution at pH 6 is used as the electrolyte in all PEC water splitting experiments. To compare the photocatalytic properties, photovoltammetric profiles of the $\text{Cu}_x\text{O-Cu/G}$ samples obtained with different post-annealing temperatures are shown in Figures 3.5a1, 3.5b1, and 3.5c1. Evidently, the $\text{Cu}_x\text{O-Cu/G-300-30}$ photocathode exhibits a photocurrent density of -2.64 mA cm^{-2} at 0 V vs reversible hydrogen electrode (RHE) (Figure 3.5b1), which is much higher than those found for other photocathodes obtained with a different post-annealing temperature: -0.50 mA cm^{-2} for $\text{Cu}_x\text{O-Cu/G-200-30}$ (Figure 3.5a1), and -0.44 mA cm^{-2} for $\text{Cu}_x\text{O-Cu/G-400-30}$ (Figure 3.5c1). The hydrogen evolution result therefore indicates that 300 °C appears to be the best annealing temperature to produce the $\text{Cu}_x\text{O-Cu/G}$ photocathode with the highest PCE water splitting activity.

The PEC water splitting activities of $\text{Cu}_x\text{O-Cu/G}$ samples obtained with post-annealing temperature of 300 °C for different amounts of time, $\text{Cu}_x\text{O-Cu/G-300-30}$, $\text{Cu}_x\text{O-Cu/G-300-60}$, and $\text{Cu}_x\text{O-Cu/G-300-180}$, are shown in Figure S3.5a. Evidently, only minor differences in the photocurrent densities are observed for these photocathodes. Therefore, among these three conditions, $\text{Cu}_x\text{O-Cu/G-300-30}$ is selected for coating with CuFe_2O_4 NPs. In addition, Figure S3.5b shows the photocurrent density of CuFe_2O_4 NPs on graphene ($\text{CuFe}_2\text{O}_4 \text{ NP/G}$). Evidently, discernibly smaller photocurrent is observed under chopped illumination of the AM 1.5G light, which is consistent with the fast recombination rate of electron-hole pairs. To compare the changes in the PEC water splitting performance as a result of the addition of CuFe_2O_4 NPs, the photocurrent of $\text{Cu}_x\text{O-Cu/G-300-30}$ with CuFe_2O_4 NPs is also shown in Figure 3.5b1, along with its SEM image and its schematic model (in lower inset) in Figure 3.5b2. Remarkably, the addition of CuFe_2O_4 NPs appears to nearly double the photocurrent densities of $\text{Cu}_x\text{O-Cu/G-300-30}$ from -2.64 mA cm^{-2} to -4.91 mA cm^{-2} at 0 V vs RHE. The corresponding Nyquist plots of $\text{Cu}_x\text{O-Cu/G-300-30}$ and $\text{CuFe}_2\text{O}_4+\text{Cu}_x\text{O-Cu/G-300-30}$ (i.e. $\text{Cu}_x\text{O-Cu/G-300-30}$ with the addition of CuFe_2O_4 NPs) under simulated sunlight illumination of the AM 1.5G light obtained by potentiostatic electrochemical impedance spectroscopy is shown in Figure S3.6a. In a Nyquist plot, a semicircle at high frequencies is characteristic of the charge transfer process and the diameter of the semicircle corresponds to the charge transfer resistance in the Helmholtz layer (R_H). We use Z-view to calculate the resistances of $\text{Cu}_x\text{O-Cu/G-300-30}$ and of $\text{CuFe}_2\text{O}_4+\text{Cu}_x\text{O-Cu/G-300-30}$ assuming an integrated equivalent model circuit in Figure S3.6b. The addition of CuFe_2O_4 NPs to the $\text{Cu}_x\text{O-Cu/G-300-30}$ sample reduces the resistance from 37.54Ω to 12.65Ω under illumination, making

the resulting $\text{Cu}_x\text{O-Cu/G-300-30}$ more conductive. The lower charge transfer resistance found in $\text{CuFe}_2\text{O}_4+\text{Cu}_x\text{O-Cu/G-300-30}$ therefore confirms the presence of CuFe_2O_4 NPs as the main contributor for the observed better PEC performance shown in Figure 3.5b1.

We also show the effects on the photocurrents of the other samples: $\text{Cu}_x\text{O-Cu/G-200-30}$, and $\text{Cu}_x\text{O-Cu/G-400-30}$ upon addition of the CuFe_2O_4 NPs, along with their SEM images and schematic models (lower insets), in Figures 3.5a2 and 3.5c2 respectively. The CuFe_2O_4 NPs are found to aggregate on the surface of $\text{Cu}_x\text{O-Cu/G-200-30}$ but are well dispersed on the $\text{Cu}_x\text{O-Cu/G-300-30}$ and $\text{Cu}_x\text{O-Cu/G-400-30}$ samples that contain CuO nanowires. This suggests that the nanowires provide an ideal framework for loading CuFe_2O_4 NPs by separating the nanoparticle aggregates into smaller groups leading to better charge transport properties. Not surprisingly, the addition of CuFe_2O_4 NPs also increases the photocurrent density slightly from -0.50 mA cm^{-2} to -0.61 mA cm^{-2} for $\text{CuFe}_2\text{O}_4+\text{Cu}_x\text{O-Cu/G-200-30}$ and almost three times from -0.44 mA cm^{-2} to -1.35 mA cm^{-2} for $\text{CuFe}_2\text{O}_4+\text{Cu}_x\text{O-Cu/G-400-30}$.

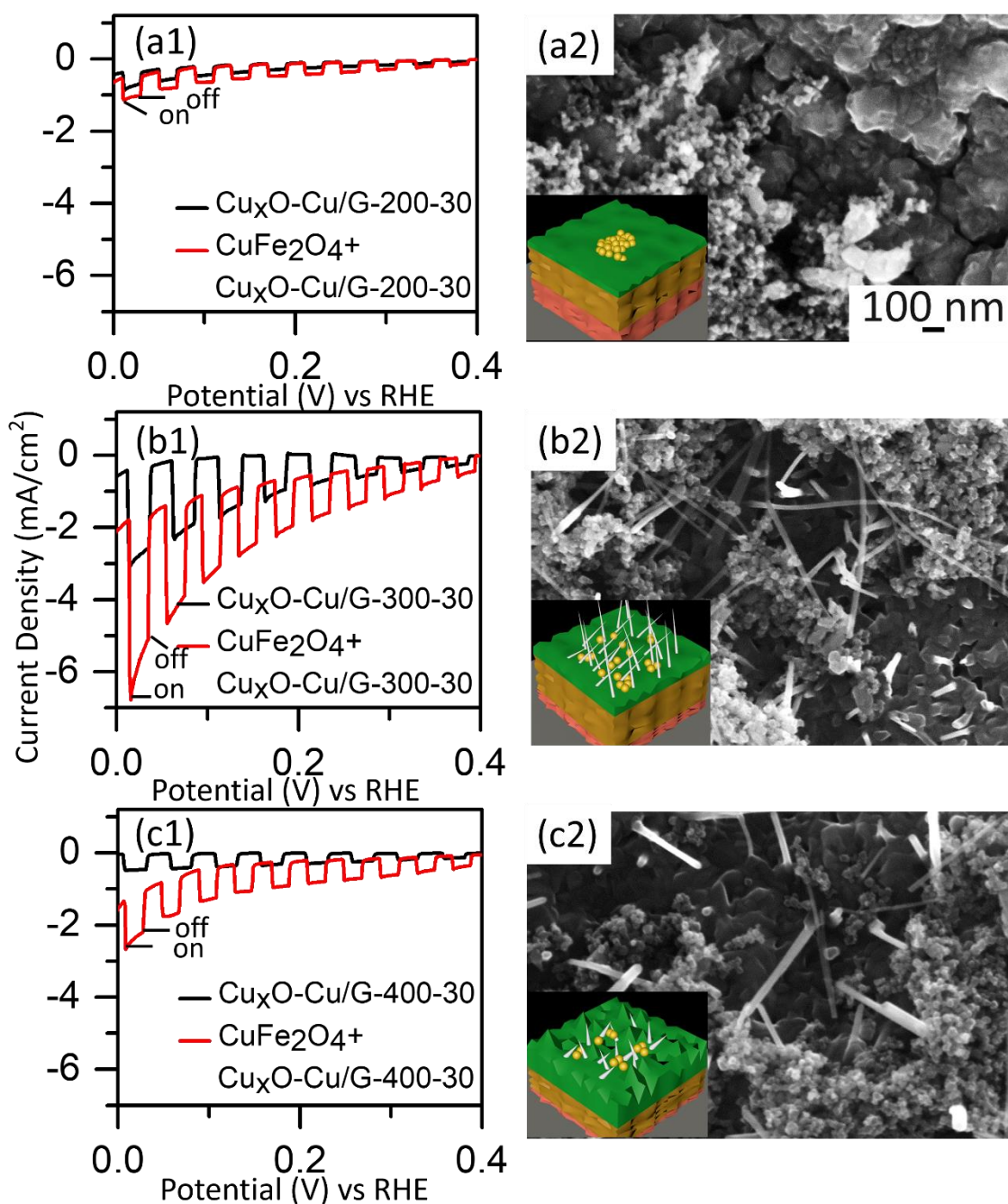


Figure 3.5 Photocurrents of (a1) $\text{Cu}_x\text{O-Cu/G-200-30}$, (b1) $\text{Cu}_x\text{O-Cu/G-300-30}$ and (c1) $\text{Cu}_x\text{O-Cu/G-400-30}$ without (black profiles) and with addition of the CuFe_2O_4 NPs (red profiles) measured as a function of applied potential by linear sweep voltammetry in 1 M Na_2SO_4 at pH 6, and the respective SEM images and schematic models (lower insets) of the latter samples (with NP addition) are shown in (a2), (b2) and (c2). All the SEM images employ the same scale.

3.3.4 Mechanism of Photoelectrochemical Water-Splitting Reaction

Based on the band energy level diagrams shown in Figure 3.6, we propose plausible single and dual heterojunction mechanisms involving charge migration between the electrolyte and the respective photocathode systems: Cu_xO -Cu/G and Cu_xO -Cu/G with CuFe_2O_4 NP addition and the electrolyte solution. As the Cu_xO -Cu/G-200-30 mainly consists of a Cu base and a thin Cu_2O layer (Figure 3.3a), its poor PEC water splitting performance (Figure 3.5a1) could be attributed to two notable drawbacks of Cu_2O as a photocathode: fast photogenerated electron-hole recombination²⁴⁴ and self-photo corrosion in an aqueous solution.²⁴⁵ The Cu_xO -Cu/G-300-30 shows better PEC water splitting performance with enhanced photocurrent density because the presence of the CuO layer with an appropriate thickness (Figure 3.3c) offers protection for the Cu_2O layer from photocorrosion. In addition, the CuO/ Cu_2O heterojunction extends the absorption range of the visible spectrum, improves the electron-hole separation efficiency and reduces the photoexcited electron-hole recombination.²¹⁸ Since both the conduction band (CB) and valence band (VB) of Cu_2O are located above the respective CB and VB of CuO, the transfer of photogenerated electrons starts from the CB of Cu_2O to that of CuO while the transfer of holes occurs from the VB of CuO to that of Cu_2O (Figure 3.6a). For Cu_xO -Cu/G-400-30 (Figure 3.3d), the excessive thickness of the topmost CuO layer leads to poor electron migration and lower photocurrent response.

In the case of Cu_xO -Cu/G with CuFe_2O_4 NP addition, we propose a direct dual Z-scheme heterojunction mechanism, given that three semiconductors Cu_2O , CuO and CuFe_2O_4 are involved during the photocatalytic reaction. Three categories of direct dual Z-scheme photocatalysts exist: arrow-up direct dual Z-scheme, arrow-down direct dual Z-scheme, and cascade direct dual Z-scheme.¹⁴² The arrangement of the three semiconductors in this work belongs to the arrow-down direct dual Z-scheme, shown in Figure 3.6b. The band edge positions of CuO are lower than those of the corresponding edges of Cu_2O and CuFe_2O_4 . Under illumination, electron-hole pairs are formed at the VB and CB of the different semiconductors. Electron and hole diffusion continues until the system achieves Fermi-level equilibrium, resulting in the formation of a charged region with an internal electric field. With the formation of the internal electric field, the photogenerated electrons in the CB of CuO recombine with the holes in the VBs of Cu_2O and CuFe_2O_4 . The recombination provides enhanced charge separation, higher redox ability, and longer charge carrier lifetime. In the arrow-down dual Z-scheme of the Cu_2O /CuO/ CuFe_2O_4 heterojunction photocatalyst system, electrons remain unutilized in the CBs of Cu_2O and CuFe_2O_4 while the holes stay in the VB of CuO. This arrangement facilitates effective charge separation and enhances the redox capability of the photocatalyst. Moreover, it promotes the generation of reactive oxidative species, thereby enhancing the overall efficiency of hydrogen production. The dual Z-scheme

heterojunction in $\text{CuFe}_2\text{O}_4+\text{Cu}_x\text{O}-\text{Cu}/\text{G}$ therefore provides a viable pathway for the charge transfer among these three semiconductors.

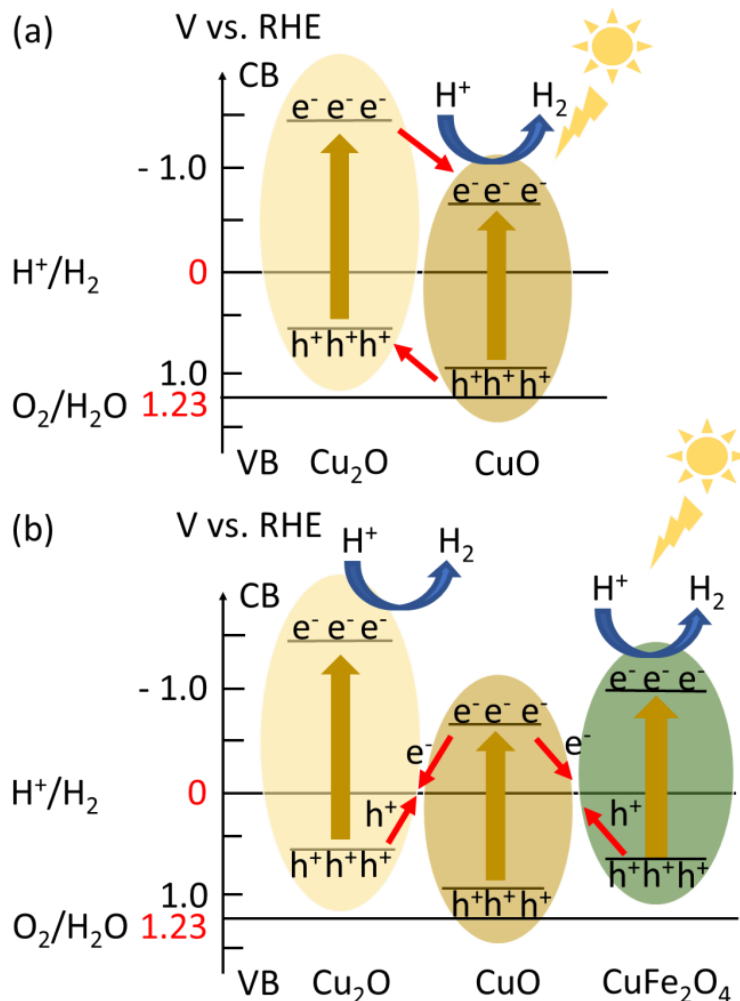


Figure 3.6 Schematic representations for reaction mechanisms of (a) $\text{Cu}_2\text{O}/\text{CuO}$ single heterojunction and (b) $\text{Cu}_2\text{O}/\text{CuO}/\text{CuFe}_2\text{O}_4$ dual heterojunction photocatalyst systems.

To compare the PEC water splitting performance of $\text{Cu}_2\text{O}/\text{CuO}$ based photocatalysts without and with addition of other nanomaterials, such as CuFe_2O_4 nanoparticles employed in this work, we compare the performance of recently reported CuO -based composite materials in Table 3.1. It should be noted that the present work is the first report of the use of $\text{Cu}_x\text{O}-\text{Cu}/\text{G}$ with CuFe_2O_4 as dual heterojunction photocatalyst for photoelectrochemical hydrogen evolution. The reported CuO -based nanomaterial electrodes are mainly prepared by electrodeposition with further thermal

annealing. While binary oxides of copper (CuO and Cu₂O) represent promising materials for hydrogen production, ternary oxides of copper offer better prospect than binary oxides because of easier tuning of the band structure and the optoelectronic properties. Among the Cu-based ternary oxides, CuBi₂O₄²⁴⁶ and CuFe₂O₄²⁴⁷ are promising materials because of their favorable band edges for solar water splitting. A core-shell CuO@CuFe₂O₄ as photocatalyst has been reported for hydrogen evolution with the photocurrent reaching -1 mA cm⁻² under relatively positive potentials. The mechanism of charge transfer for CuFe₂O₄ can be attributed to the typical small polaron hopping of semiconductor conduction band “d”.²⁴⁸ The present CuFe₂O₄+Cu_xO-Cu/G dual heterojunction photocatalyst system therefore offers the best PEC water splitting performance at 0 V vs RHE among all the Cu-based composite catalysts reported to date.

Table 3.1 Summary of CuO-based nanomaterials used as heterojunction photocatalysts for hydrogen evolution.

Composite	Synthesis methods	Photocurrent density for HER	Mechanism	Reference
Cu ₂ O/CuO	Electrodeposition followed by thermal annealing	-3.15 mA cm ⁻² at 0.4 V vs. RHE	Heterojunction	218
Cu ₂ O/CuO	Electrodeposition followed by thermal annealing	-1.2 mA cm ⁻² at 0 V vs. RHE	Heterojunction	220
Cu ₂ O/CuO /Cu(OH) ₂	Electrodeposition followed by thermal annealing	-2.3 mA cm ⁻² at 0 V vs. RHE	Heterojunction	249
Cu ₂ O/CuO	Magnetron sputtering followed by thermal annealing	-1.9 mA cm ⁻² at 0 V vs. RHE	Heterojunction	250
Cu ₂ O/CuO/Pt	Electrodeposition followed by thermal annealing	-2.74 mA cm ⁻² at 0 V vs. RHE	Heterojunction	236
CuO/CuFe ₂ O ₄	Electrodeposition followed by thermal annealing	-1 mA cm ⁻² at 0.3 V vs. RHE	small polaron hopping of SC conduction band “d”	248
Cu _x O-Cu/G-300-30	Electrodeposition followed by thermal annealing	-2.64 mA cm ⁻² at 0 V vs. RHE	Heterojunction	This work
CuFe ₂ O ₄ +Cu _x O-Cu/G-300-30	Electrodeposition followed by thermal annealing, with hydrothermal NP decoration	-4.91 mA cm ⁻² at 0 V vs. RHE	Dual z-scheme Heterojunction	This work

3.4 Conclusion

In summary, copper oxide nanomaterials have been obtained by electrodeposition on graphene in a high pH solution (pH 12) followed by annealing at temperatures up to 400 °C. Different annealing temperatures (200, 300, and 400 °C) and amounts of annealing time (30, 60 180 min) are used to control the CuO layer thickness and relative compositions of CuO and Cu₂O, which are found to greatly affect the PEC water splitting performance. The Cu_xO-Cu/G-300-30 nanowire sample appears to provide the best photocatalyst performance when compared with Cu_xO-Cu/G-200-30 and Cu_xO-Cu/G-400-30, while Cu_xO-Cu/G-300-30, Cu_xO-Cu/G-300-60, and Cu_xO-Cu/G-300-180 offer minor difference in their PEC performance. Appropriate thicknesses of CuO and Cu₂O layers are the key to provide the best photocatalytic properties. Among the CuO/Cu₂O photocathodes, our best performing sample is obtained at a lower temperature (300 °C) for a shorter annealing time (30 min), while the PEC water splitting performances of the other samples remain competitive. Furthermore, the addition of a Cu-based ternary material such as CuFe₂O₄ nanoparticles on Cu_xO-Cu/G-300-30 significantly improves the photocatalyst activity (that nearly doubles the photocurrent from -2.64 mA cm⁻² to -4.91 mA cm⁻² at 0 V vs RHE), which is consistent with the dual Z-scheme heterojunction mechanism. Upon electron-hole pair formation on the VBs and CBs of Cu₂O, CuO and CuFe₂O₄, electrons remain unutilized in the CBs of Cu₂O and CuFe₂O₄ while holes stay at the VB of CuO. This arrow-down dual Z-scheme mechanism highlights the importance of two heterojunctions in the CuFe₂O₄+Cu_xO-Cu/G photocatalyst system, which provides improved charge separation and redox ability to overcome the limitation of pristine photocatalysts. As both Cu_xO and CuFe₂O₄ nanomaterials are non-noble metal oxides that are low cost and have low toxicity and good chemical and thermal stability, their facile fabrication procedure offers potential for cost-effective scale-up of these high-performance photocatalysts for commercialization.

Chapter 4

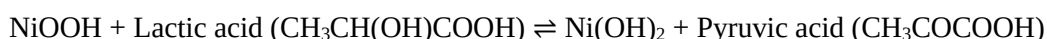
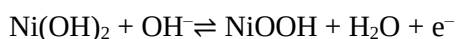
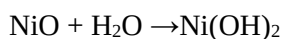
Supported NiO_x Nanocatalysts on Graphene for Non-Enzymatic Lactate Sensing

4.1 Introduction

Lactate ($\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$) concentration is one of the key metrics for monitoring tissue oxidation in clinical diagnostics, providing continuous surveillance in surgery and managing shock/trauma treatment. Sweat lactate sensors have been proposed as a promising solution to overcome the typical drawbacks of most blood tests. Variations in sweat lactate composition have been observed across five common sampling body sites (torso, face, thigh, axilla, and arm), with reported concentrations ranging from 16 mM on the face to over 30 mM on the thigh.²⁵¹ Elevated lactate levels in the body (>5 mM) could indicate metabolic acidosis, hypoxia, sepsis, acute respiratory distress, myocardial infarction, and skeletal muscle fatigue. Abnormal increase in lactate concentration resulting from oxygen deficiency increases the risk of lactate acidosis and causes pulmonary and circulatory problems.²⁵² Additionally, monitoring lactate levels can also maximize training efficiency for general workouts and professional sports, as muscle cells switch to anaerobic metabolism. Various methods are available for detecting lactate, such as high-performance liquid chromatography,²⁵³ fluorometry,²⁵⁴ colorimetry,²⁵⁵ chemiluminescence,²⁵⁶ and nuclear magnetic resonance spectroscopy.²⁵⁷ However, these methods are generally time-consuming, labor-intensive as they require sample pre-treatment, and costly due to the need for expensive instrumentation and trained personnel. In contrast, electrochemical biosensors are simple, direct, essentially in real-time, and without any need for sample preparation. These sensors also combine rapid response with high specificity, and while being economical and user-friendly. Most lactate biosensors are enzyme-based sensors with notable limitations, such as loss of enzyme activity and storage stability. These challenges can be alleviated with the development of non-enzymatic lactate biosensors.

Several types of nanomaterials, including metal nanoparticles, metal oxides, metal-organic frameworks,²⁵⁸⁻²⁵⁹ conducting polymers,²⁶⁰⁻²⁶¹ molecularly imprinted polymers,²⁶²⁻²⁶³ carbon,²⁶⁴ and composite materials,²⁶⁵ are potential material candidates for non-enzymatic lactate sensors. Among these materials, metal oxide nanomaterials, especially transition metal oxides, offer several important advantages, such as easy synthesis, high stability, tunable morphology, adjustable porosity, and versatile functionalization. Nanostructures of notable metal oxides, such as NiO,¹¹⁶ CuO,¹¹⁷ and Co₃O₄,¹¹⁸ have been studied as potential candidates for lactate sensing due to their

electrochemical catalytic properties, high sensitivity, environmental friendliness, and low cost. Nickel oxide (NiO) also behaves as a p-type semiconductor due to a hopping mechanism via electron transfer between Ni^{3+} and Ni^{2+} . The coexistence of these Ni oxidation states suggests that NiO_x species could contain NiO, NiOOH and $\text{Ni}(\text{OH})_2$. The Ni^{3+} state exists as nickel oxyhydroxide (NiOOH) which serves as an active site for oxygen evolution reaction (OER) due to the presence of the active $-\text{OOH}$ species.²⁶⁶ In other applications, nickel oxide has also been found to have electrocatalytic properties attributed to the generation of NiOOH species, an electrochemical active site well known for facilitating the oxidation of organic compounds and the oxidation of lactate. The mechanism of NiO for lactate detection^{120, 267-268} involves the following steps:



Various physical and chemical methods, including co-precipitation,²⁶⁹ sol-gel,²⁷⁰ hydrothermal synthesis,²⁷¹ electrospray synthesis,²⁷² laser ablation,²⁷³ and electrodeposition⁴⁷, have been employed for the synthesis of NiO. Among these methods, electrodeposition stands out as a fast, cost-effective, and straightforward approach to obtain NiO. Since NiO is a “charge-transfer insulator”,²⁷⁴ the existence of NiOOH/ $\text{Ni}(\text{OH})_2$ on the surface of NiO is essential for a working redox couple electrocatalyst. The formation of NiOOH/ $\text{Ni}(\text{OH})_2$ redox couple can enhance the catalytic activity. The NiOOH/ $\text{Ni}(\text{OH})_2$ redox couple is commonly produced by potential cycling of nickel electrodes in robust alkaline electrolytes, such as KOH or NaOH. It has been widely reported that the controllable formation of two distinct layers can be achieved when Ni undergoes oxidation in the presence of air.^{267, 275} The two layers are a shell of NiO resulting from Ni reacting with oxygen and a skin (outermost layer on top of the shell) of NiOOH/ $\text{Ni}(\text{OH})_2$ arising from the adsorption of and reaction with water molecules. Rožman *et al.* have reported the controllable formation of a structurally disordered NiOOH/ $\text{Ni}(\text{OH})_2$ redox pair on Ni-nanowire electrodes. This was achieved by cyclic voltammetry employing different scan rates in KOH to convert inactive NiO to the surface-catalytic-active NiOOH/ $\text{Ni}(\text{OH})_2$.²⁷⁵ Another potential method to obtain the NiOOH/ $\text{Ni}(\text{OH})_2$ redox couple is thermal annealing of NiO, as the calcination temperature can influence the NiOOH content on the NiO surface. A higher calcination temperature is found to lead to a decrease in the concentration of NiOOH.²⁷⁶ Additionally, annealing in air leads to a slightly higher NiOOH content when compared with annealing in oxygen.⁶³ On the other hand, $\text{Ni}(\text{OH})_2$ could exist in both amorphous and crystalline forms,

depending on the synthesis and preparation conditions. The amorphous form of $\text{Ni}(\text{OH})_2$ can be obtained under less controlled or rapid synthesis conditions, unlike the crystalline form which requires, for instance, the presence of certain additives, elevated temperatures, or certain electrochemical processes. The amorphous form has attracted a lot of attention because of its superior catalytic activity compared to its crystalline counterpart, which is attributed to the inherent flexibility and the abundance of defect sites in the amorphous form.²⁷⁷⁻²⁷⁹ Moreover, the use of core-shell heterostructures, with a combination of crystalline and amorphous components, has gained popularity. Its phase-dependent properties typically result in encouraging catalytic performance, with the amorphous component providing high catalytic activity and the crystalline component providing high electrical conductivity.²⁸⁰⁻²⁸¹

In this work, graphene is selected as the substrate due to its many attractive features, and its flexibility, and remarkable electrical conductivity has made it especially suitable for improving electron transfer in electrochemical processes. The soft graphene substrate offers a new prospect for lactate sensing. We have successfully produced nickel oxide on a graphene substrate through electrodeposition and manipulated the content of the $\text{NiOOH}/\text{Ni}(\text{OH})_2$ redox couple relative to NiO with core-shell heterostructures through post-annealing at different temperatures for selected durations in an air environment. The synthesized samples are found to show excellent electrocatalytic performance for non-enzymatic sweat-range lactate sensing.

4.2 Experimental Methods

4.2.1 Chemicals

Analytical grade chemicals including nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), boric acid [$\text{B}(\text{OH})_3$], sodium hydroxide (NaOH), sodium L-lactate, glucose (Glc), ascorbic acid (AA), citric acid (CA), uric acid (UA), and dopamine (DA) were purchased from Sigma-Aldrich and used without further purification. Artificial eccrine perspiration was purchased from Pickering Laboratories, Inc. (USA). The conductive graphene sheet (150 μm thick, sheet resistance: $1 \times 10^{-5} \Omega \cdot \text{cm}$) was purchased from Graphene Supermarket (Graphene Laboratories Inc., USA). Filtered high-resistivity (18.2 $\text{M}\Omega \cdot \text{cm}$) ultra-pure water was used for preparing all the solutions.

4.2.2 Synthesis of NiO_x/G

All the electrochemical experiments were conducted in a three-electrode electrochemical cell connected to a CH Instruments 660E electrochemical station, with an Ag/AgCl reference electrode and a platinum wire counter electrode. The working electrode used for electrochemical deposition

of Ni nanoparticles was a graphene substrate ($20 \times 10 \text{ mm}^2$), cut from a graphene sheet. Nickel oxide was deposited over a typical $10 \times 10 \text{ mm}^2$ area of the graphene substrate by potentiostatic amperometry for 120 s in a 5 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ electrolyte with 0.2 M boric acid as the supporting electrolyte. Different concentrations of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 0.2 M boric acid were used to prepare the 10 mL electrolyte solution. Various conditions, including the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentrations, overpotentials and deposition time, were used for the electrodeposition of Ni nanoparticles (NPs). The Ni NPs electrodeposited at -1.4 V vs Ag/AgCl for 120 s in 5 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were further annealed in a tube oven to facilitate thermal oxidation at different temperatures (200°C , 300°C , and 400°C) for different amounts of time (30 min, 180 min) to obtain the nickel oxide NPs.

4.2.3 Characterization of Materials

A Zeiss Merlin field emission microscope was used to characterize the surface morphologies by scanning electron microscopy (SEM). Glancing-incidence X-ray diffraction (XRD) was carried out to determine the crystal structures in a PANalytical X'Pert Pro MRD diffractometer with Cu K α ($1.542 \text{ \AA}$) radiation at an incidence angle of 0.6° . X-ray photoelectron spectroscopy (XPS) conducted in a Thermo Scientific Nexsa G2 surface analysis system with monochromatic Al K α radiation (with a photon energy of 1486.6 eV) and a typical energy resolution of 0.5 eV full width at half maximum was used to characterize the chemical-state composition. The crystalline structure of individual NiO_x NPs was determined by transmission electron microscopy (TEM) in a Zeiss Libra 200 MC microscope, equipped with a double-corrected Omega energy filter, operated at 200 kV . The TEM specimen was prepared by drop-casting the nanoparticles suspended in ethanol directly on a 300-mesh lacey carbon copper TEM grid. For sensing performance evaluation, a 0.01 to 1 M lactate solution was used, with interferent detection of Glc, AA, CA, UA, or DA set at concentrations of 0.1 M in a 0.25 M NaOH electrolyte. For lactate sensing performance evaluation in artificial sweat, a 0.02 to 65.1 mM lactate solution was used in $1:1 \text{ v/v}$ artificial sweat and 0.5 M NaOH.

4.3 Results and Discussion

4.3.1 Characterization

Ni NPs are deposited on a graphene substrate by amperometry at selected overpotentials (-1 V , -1.2 V , -1.4 V , and -1.6 V , all vs Ag/AgCl), electrolyte concentrations (1 mM , 2 mM , 5 mM , and 10 mM), and deposition time (20 s , 60 s , 120 s , 240 s , 300 s , and 600 s). Their corresponding SEM images are shown in Figures S4.1-S4.3, respectively. Evidently, these Ni NPs generally have a

spherical shape with a narrow size distribution. The average size of the Ni NPs appears to increase with more negative overpotentials (Figure S4.1), higher electrolyte concentrations (Figure S4.2), and longer deposition time (Figure S4.3). The number density is found to increase with longer deposition time and start to decrease above 120 s. At -1.2 V and -1.4 V, Ni NPs are apparently obtained with uniform coverage, while Ni NPs electrodeposited at -1.4 V appear to have a slightly higher number density. For potential more negative than -1.4 V, the coverage is found to be less uniform with lower number density. The number density of Ni NPs appears less uniform when the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentration is higher than 5 mM. The Ni NPs selected for the subsequent studies are obtained at -1.4 V in 5 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with 0.2 M boric acid for a deposition time of 120 s. These deposition conditions result in well dispersed Ni NPs, with the highest number density, uniformly covering the entire substrate surface.

After obtaining Ni NPs uniformly covering on the graphene substrate (denoted here as G) with the highest number density (in a monolayer), the Ni/G sample is annealed in air in a tube oven at different temperatures (200 °C, 300 °C, and 400 °C) for different amounts of time (30 min, 180 min), as shown in Figure 4.1. We designate the resulting NiO_x NP samples as $\text{NiO}_x/\text{G-XXX-YY}$, where XXX denotes the annealing temperature in °C and YY represents the annealing time in minutes. Evidently, annealing the Ni NPs for a longer time and at a higher temperature produces larger NiO_x NPs with rough surfaces and consequently larger specific surface areas. For Ni NPs and $\text{NiO}_x\text{-200-30}$, the strongest XRD feature is the graphene peak at 54.72° (Figure 4.1g). Evidently, the electrodeposited Ni NPs correspond mainly to Ni metal, with the prominent XRD peaks at 44.50° , 51.84° , and 76.37° (Figure 4.1g) found to be in good accord with the respective (111), (200) and (220) planes of Ni faced-centered cubic phase (PDF#00-004-0850). For the samples annealed at different temperatures for 30 min, the strongest peaks still correspond to the Ni (111) plane. For the samples annealed for 180 min, especially the sample $\text{NiO}_x\text{-400-180}$, the dominant peaks belong to rhombohedral NiO. The remaining weaker XRD peaks at 43.28° , and 62.83° can be attributed to the (202) and (220) planes of NiO rhombohedral phase (PDF#01-089-3080). The weak features at 37.57° and 58.19° are in good accord with (011) and (220) planes of orthorhombic NiOOH (PDF#00-027-0956). No sign of features that correspond to Ni(OH)_2 , suggesting that Ni(OH)_2 if present is likely amorphous appears.

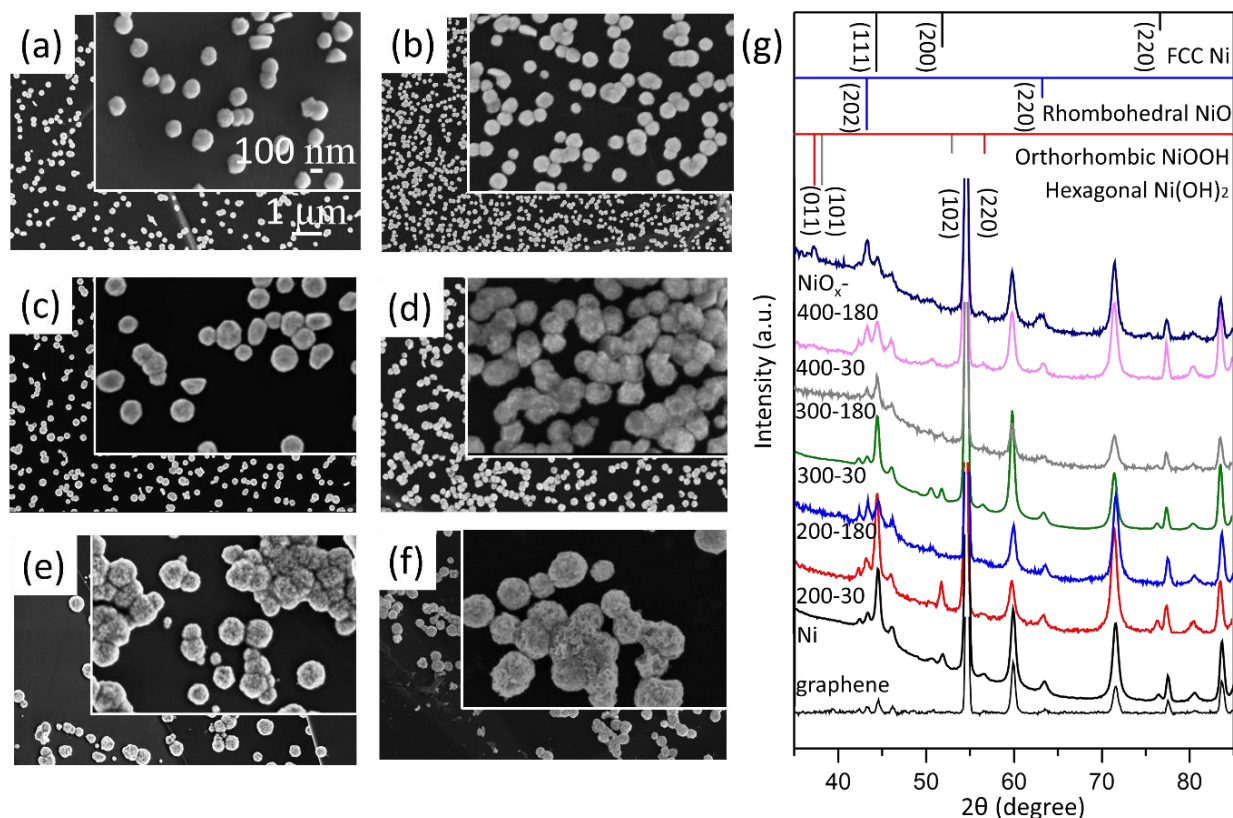


Figure 4.1 SEM images of NiO_x NPs obtained by annealing electrodeposited Ni NPs in air at different temperatures for different time, (a) 200 °C for 30 min, (b) 200 °C for 180 min, (c) 300 °C for 30 min, (d) 300 °C for 180 min, (e) 400 °C for 30 min, and (f) 400 °C for 180 min. All the SEM images employ the same scale. (g) The corresponding glancing incidence XRD profiles of NiO_x NP samples, along with that of Ni NPs electrodeposited at -1.4 V in 5 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with 0.2 M boric acid for 120 s, and the reference profiles for Ni face-centered cubic phase (PDF#00-004-0850, black lines), NiO rhombohedral phase (PDF#01-089-3080, blue lines), and orthorhombic NiOOH (PDF#00-027-0956, red lines), and hexagonal Ni(OH)_2 (PDF#00-014-0117, grey lines) as well as the measured profile for a pristine graphene substrate.

To determine the relative chemical-state composition and shell structure of NiO_x NPs, XPS spectra for Ni NPs and the NiO_x NP samples obtained with different post-annealing conditions and depth-profiling XPS profiles of NiO_x -200-30 are shown in Figure 4.2. Previous elemental analysis studies have revealed that low-temperature calcination induces more active reaction sites on NiO_x , of which NiOOH is strongly involved in the electrocatalytic reaction to form lactate.^{116, 276} The high content of the NiOOH/ Ni(OH)_2 redox pair relative to NiO is one of the key factors in increasing the

sensitivity of the electrode for lactate detection. As shown in Figure 4.2a, the dominant Ni 2p_{3/2} peak at 852.6 eV found for Ni NPs is assigned to metallic Ni.²⁸² This metallic Ni feature remains even after annealing at 200 °C, indicating that the metallic core represents a major component. Except for the Ni/G sample, all the NiO_x/G samples exhibit Ni 2p_{3/2} peaks at 853.7 eV, 855.3 eV and 856.5 eV, which are attributed to NiO, Ni(OH)₂ and NiOOH, respectively.²⁸³⁻²⁸⁷ The Ni 2p_{3/2} peaks of NiO, Ni(OH)₂, and NiOOH for these samples obtained with higher annealing temperature and longer annealing time are found to have a discernible shifts of 0.3 eV toward higher binding energies. The broad peak centered at 861 eV in NiO can be observed.²⁸⁸⁻²⁸⁹ In Figure 4.2a, the O 1s spectra of the NiO_x NPs can be fitted with four peaks at 529.3, 530.7, 531.8 and 533.3 eV, which correspond to NiO, Ni(OH)₂, NiOOH and physisorbed H₂O, respectively.^{287, 290-291} The broad O 1s feature at 532.6 eV found for the Ni NP sample can be assigned to the hydroxide group of physisorbed H₂O while the weak NiO O 1s feature at 533.3 eV indicates surface oxidation. The trend found for the O 1s peak area of NiOOH + Ni(OH)₂ relative to that of NiO clearly shows that the NiO_x NPs obtained by annealing at lower temperatures contain much more NiOOH + Ni(OH)₂ than those obtained at higher annealing temperatures, which supports the facile generation of reactive sites (NiOOH) by post-annealing especially at a lower temperature. The ratio of NiOOH + Ni(OH)₂ to NiO is obtained by comparing the respective Ni 2p_{3/2} peak areas for NiOOH, Ni(OH)₂ and NiO. The highest NiOOH + Ni(OH)₂ to NiO peak area ratio is found to be 1.28 for the NiO_x/G-200-30 sample. The NiOOH + Ni(OH)₂ to NiO ratio follows the decreasing trend: NiO_x/G-200-30 > NiO_x/G-200-180 > NiO_x/G-300-30 > NiO_x/G-300-180 = NiO_x/G-400-30 = NiO_x/G-400-180.

In Figure 4.2b, we show the depth-profiling XPS spectra of the Ni 2p_{3/2} and O 1s regions of the NiO_x/G-200-30 sample. After 10 s sputtering of the NiO_x NPs, the NiOOH and Ni(OH)₂ peak have become weaker. Further sputtering for a total of 60 s has effectively removed NiOOH, Ni(OH)₂ and NiO peaks, revealing only the prominent Ni metallic peak, which indicates that the NiO_x NP has a core-shell structure. Similarly, the strong O 1s peak at 531.8 eV for NiOOH is greatly reduced after sputtering for 30 s. While the O 1s peak at 530.7 eV for Ni(OH)₂ has become prominent after 30 s sputtering followed by intensity decrease upon further sputtering, the O 1s peak at 529.4 eV for NiO has become even more prominent after 30 s of sputtering but then all the O 1s peaks become generally weakened with further sputtering. The present XPS data confirm the existence of Ni(OH)₂, as part of the NiOOH/Ni(OH)₂ redox pair. These depth-profiling XPS data therefore show that the NiO_x NP consists of a metallic Ni core and a NiO shell with a Ni(OH)₂/NiOOH skin.

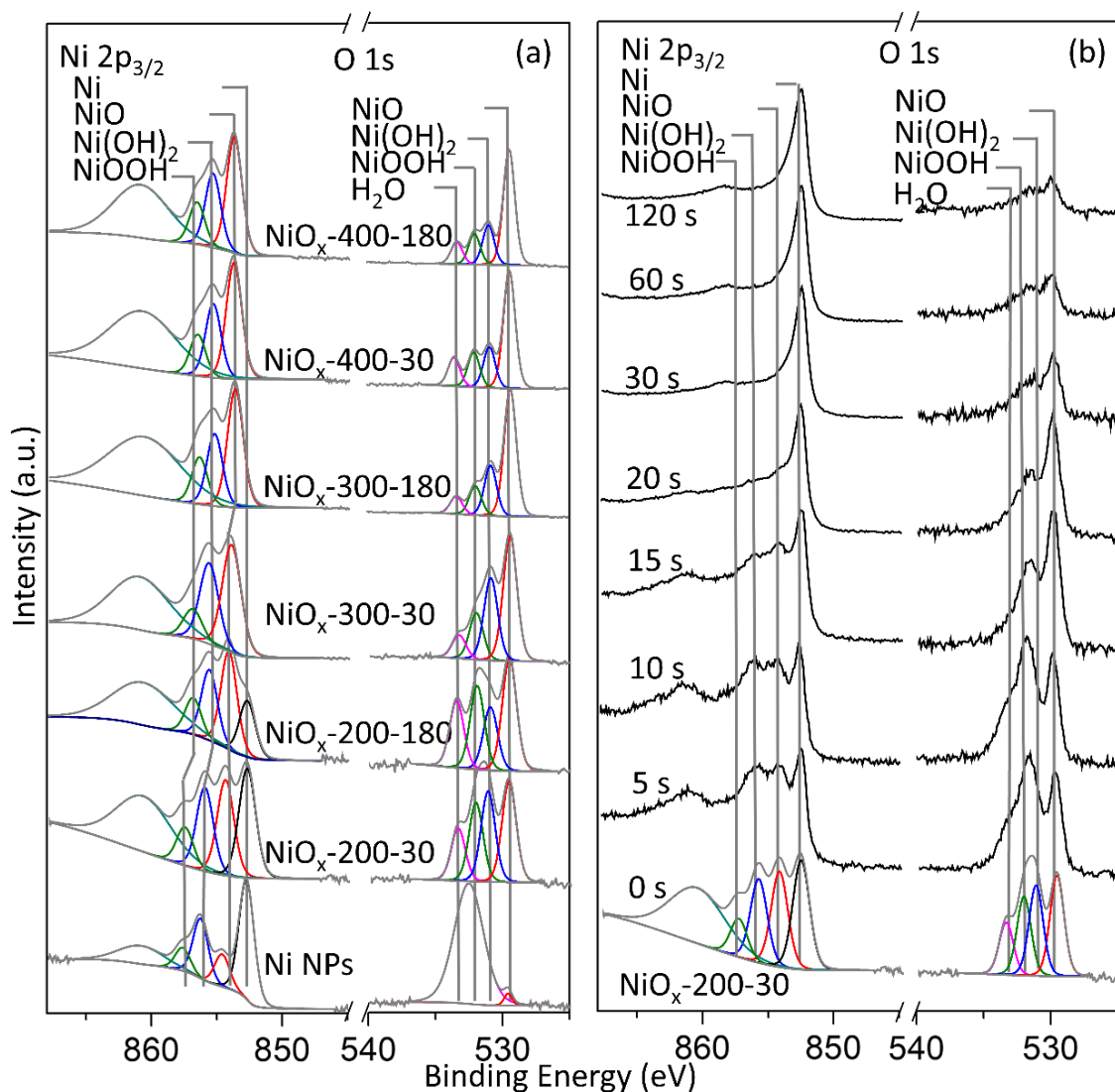


Figure 4.2 (a) XPS spectra of Ni 2p_{3/2} and O 1s regions of Ni NPs and NiO_x NPs obtained by annealing at selected combinations of annealing temperature and time. (b) Corresponding depth-profiling XPS spectra of the Ni 2p_{3/2} and O 1s regions of for the NiO_x-200-30 sample.

Figures 4.3a1 and 4.3b1 show the low-resolution TEM images of Ni NPs and NiO_x-200-30 NPs scraped off from the respective samples and appropriately dispersed on lacey carbon Cu TEM grids. Evidently, spherical nanoparticles with approximate sizes of 150 nm and 230 nm are observed for the Ni NP and NiO_x NP, respectively. Their corresponding high-resolution TEM images shown in Figures 4.3a2 and 4.3b2 reveal the highly crystalline nature of these nanoparticles. In Figure 4.3a2, the observed lattice fringe spacing of 1.76 Å is in good accord with

the interplanar spacing of the (111) planes of FCC Ni, consistent with our XRD data. The corresponding selected area electron diffraction (SAED) pattern for the Ni NP in Figure 4.3a1, shown in Figure 4.3a3, is found to consist of rings of bright spots, indicating a single crystalline structure, with the rings corresponding to the (111), (200), and (220) reflexes of the FCC structure of Ni (PDF#00-004-0850). In Figure 4.3b2, the same lattice fringes of Ni (111) plane can be observed, which confirms that the NiO_x NP contains a metallic Ni core. The FFT pattern of the selected area near the edge (perimeter) of the NiO_x-200-30 NP (Figure 4.3b2, bottom left inset) exhibits a spot pattern characteristic of a crystalline shell. In Figure 4.3b3, the measured SAED pattern for the NiO_x NP shown in Figure 4.3b1 also reveals consecutive rings of spots. Evidently, the (111), (200) and (220) planes marked in white belong to Ni (PDF#00-00-004-0850) and the (202) and (220) planes marked in red belong to NiO (PDF#01-089-3080) while the (011) and (011) planes marked in yellow belong to NiOOH (PDF#00-027-0956). This confirms the presence of the Ni core and that the outer region of the NiO_x NP contains both crystalline NiO (shell) and NiOOH (skin). The present result also shows that Ni(OH)₂ does not appear to have any corresponding SAED spots and therefore any crystalline structure. In summary, Ni forms the crystalline core of the nanoparticle while NiO forms the crystalline shell. The outermost skin consists of both amorphous Ni(OH)₂ and crystalline NiOOH.

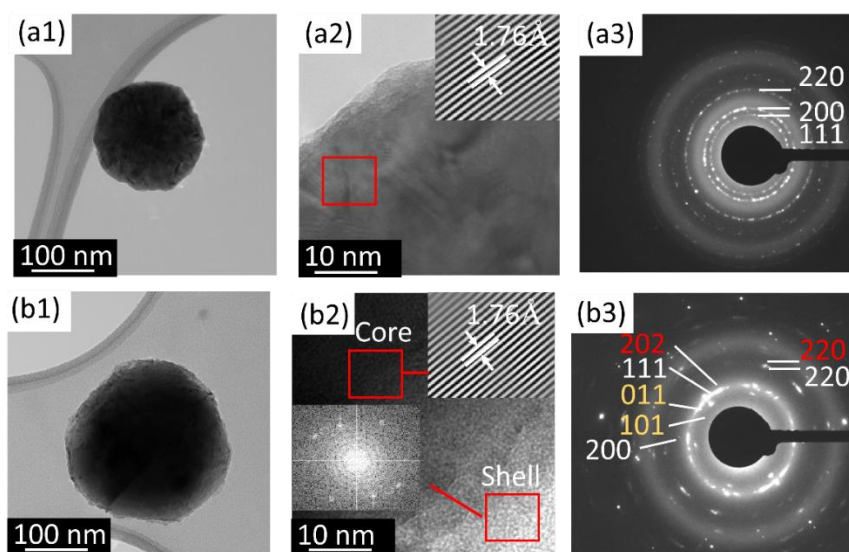


Figure 4.3 (a1, b1) Low-resolution and (a2, b2) high-resolution TEM images and (a3, b3) selected area electron diffraction (SAED) patterns of (a1-a3) Ni NP and (b1-b3) NiO_x NP, with top insets in (a2, b2) depicting the interplanar spacing of the Ni (111) planes and the bottom inset in (b2)

showing a simulated diffraction pattern generated by FFT for the marked shell region. In a3, white labels refer to Ni while in b3, white, red, and yellow labels refer to Ni, NiO and NiOOH, respectively.

4.3.2 Lactate Sensing

The NiOOH/Ni(OH)₂ redox pair is known to provide the crucial reaction site for lactate detection. Our data show that a greater NiOOH/Ni(OH)₂ composition can be obtained when annealed at a lower temperature. To demonstrate the lactate sensing performance, the NiO_x-200-30 sample is selected as the working electrode. Figure 4.4a shows cyclic voltammograms collected from 0 to +0.7 V vs Ag/AgCl at different scan rates ranging from 0.02 V/s to 0.4 V/s in steps of 0.02 V/s in a 0.25 M NaOH solution containing 2 mM sodium L-lactate. Evidently, the cathodic-peak current is found to increase linearly with the scan rate v with a regression coefficient of 0.998, while the anodic-peak current likewise increases linearly with a regression coefficient of 0.996 (Figure 4.4b). The direct current proportionality to the scan rate (not $v^{1/2}$) therefore indicates that electron transfer between the NiO_x electrode and lactate is a surface-controlled oxidation process (and not diffusion control).²⁹² With increasing scan rate, the anodic-peak current for lactate oxidation becomes larger while the peak potential also shifts to a higher voltage (Figure 4.4a). The voltage separation between the anodic peak and the cathodic peak is also found to increase gradually with increasing scan rates, indicating a charge-transfer kinetics limitation that is characteristic of a typical quasi-reversible system.²⁹³

It is evident that the NaOH concentration has a significant influence on the performance of the NiO_x/G electrode. If the concentration of NaOH is too low, reaction (2) would shift to the left and thus lower the electrocatalytic ability of NiOOH toward lactate. If the concentration of NaOH is too high, the ions in the solution may interact with one another strongly and disturb the electrocatalytic reaction for lactate. Therefore, selecting an appropriate concentration of NaOH is crucial. The current response of the NiO_x-200-30/G electrode for 2 mM lactate detection operated at +0.55 V vs Ag/AgCl in selected NaOH concentrations (0.05 M, 0.15 M, 0.25 M, 0.35 M and 0.55 M) is shown in Figure S4.4a. From this result, a 0.25 M NaOH solution is selected. In addition, it is also essential to determine the optimal applied potential. The optimization process aims to identify the potential at which the lactate oxidation current reaches its maximum value. Figure S4.4b illustrates the change in the current response for selected applied voltages (0.35, 0.45, 0.5, 0.55, 0.6, and 0.65 V) while maintaining a fixed concentration of 0.25 M NaOH solution. The

lactate oxidation current exhibits a continuous increase with increasing applied potential until it reaches +0.55 V vs Ag/AgCl, which we identify as the optimum.

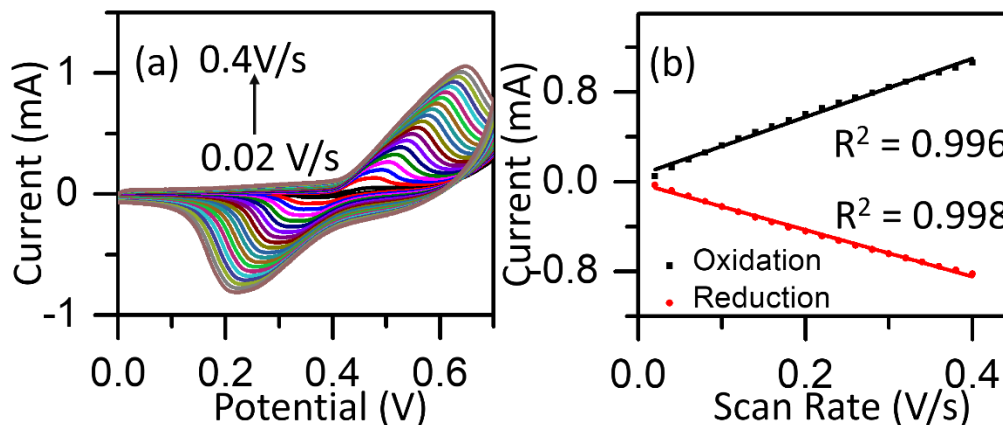


Figure 4.4 (a) Cyclic Voltammograms obtained from 0 to +0.7 V vs Ag/AgCl at different scan rates from 0.02 V/s to 0.4 V/s in steps of 0.02 V/s in a solution of 2 mM sodium L-lactate and 0.25 M NaOH, and (b) the corresponding linear relations of anodic-peak current (black) and cathodic-peak current (red) vs. the scan rate.

Six NiO_x samples obtained with different combinations of annealing temperature (200 °C, 300 °C and 400 °C) and time (30 min and 180 min) have been used to evaluate the lactate detection performance at +0.55 V vs Ag/AgCl in 0.25 M NaOH, and the corresponding i-t curves and linearity response curves are shown in Figure 4.5 and Figure S4.5, respectively. The results for these six samples, including the relative composition ratio of Ni(OH)₂ + NiOOH to NiO, linear range, sensitivity, and limit of detection (LOD), are summarized in Table 4.1. The NiO_x-200-30 sample (NiO_x NPs obtained by post-annealing Ni NPs at 200 °C for 30 min) is found to exhibit the best overall performance, with the highest sensitivity (80.0 μA mM⁻¹ cm⁻²), the lowest detection of limit (LOD) (0.00015 mM), and a wide detection range of 0.02-65.1 mM (with R² = 0.996). The anodic-peak current response in the voltammogram is in direct correlation with the lactate concentration present in the reaction solution (Figure 4.5b). The NiO_x-400-30 and NiO_x-400-180 samples both show a wider detection range, likely due to their larger size with more NiO to initiate the reaction, despite a low NiOOH + Ni(OH)₂ content. In this situation, the nanoparticle needs more electrons to convert NiO to NiOOH and Ni(OH)₂ before reaction with lactate, which consequently gives rise to a low current response for the lactate analyte. The present results

demonstrate that the surface reactivity of the NiO_x electrodes decreases due to the reduction in the number of reactive sites obtained at elevated post-annealing temperature.

We also examine the effects of possible interfering species to evaluate the selectivity of the NiO_x sensors in Figure 4.5c. The physiological level of lactate is normally ten to twenty times higher than those of common interferents such as ascorbic acid, citric acid, uric acid, and dopamine. Using the NiO_x-200-30/G sample as the working electrode for amperometry at +0.55 V vs Ag/AgCl, we first add a 2 mM sodium L-lactate into 10 mL 0.25 M NaOH and then follow by those of other interferents: glucose, ascorbic acid, citric acid, and uric acid, all with 0.1 mM concentration (i.e. at least ten times higher than the expected level to greatly amplify the interference effect), while that for dopamine is 0.01 mM. Evidently, glucose, ascorbic acid and dopamine yield less than a 3% change in the current response, while the other interferents (uric acid, and citric acid,) do not register a response in the i-t curves at all (Figure 4.5c). To confirm that NiO_x NPs can indeed be used to detect lactate in sweat, the effect of chloride needs to be considered as well. Figure S4.5d shows that i-t curve of NiO_x-200-30 at +0.55 V vs Ag/AgCl upon addition of 2 mM lactate in 0.25 M NaOH without and with 0.25 M NaCl in the electrolyte. No notable difference can be observed in the responses obtained in these solutions, indicating that the NiO_x sample offers strong resistance to chloride poisoning. NiO_x is therefore an excellent electrocatalyst for sweat lactate sensing. Finally, to further verify that the NiO_x sample is indeed capable of detecting lactate in a sweat sample, the electrolyte is mixed with 1:1 v/v ratio of artificial sweat and 0.5 mM NaOH. The linearity response curve with sequential addition of aliquots of lactate with increasing concentration is shown in Figure 4.5d. The artificial eccrine perspiration includes metabolites (uric acid, lactic acid, urea, and ammonia), minerals (sodium, calcium, magnesium, zinc, iron, copper, potassium, chloride, nitrate, and sulphate), and all kinds of amino acids (glycine, L-alanine, L-asparagine, L-histidine, L-lysine, and taurine, etc.). It is found that the current flow of NiO_x-200-30 in artificial sweat is not as smooth, and the detection range is slightly reduced to 0.02-53.1 mM (with $R^2 = 0.994$), and the LOD is 0.00013 mM. Nevertheless, the sample maintains its high sensitivity at 80.0 $\mu\text{A mM}^{-1} \text{cm}^{-2}$.

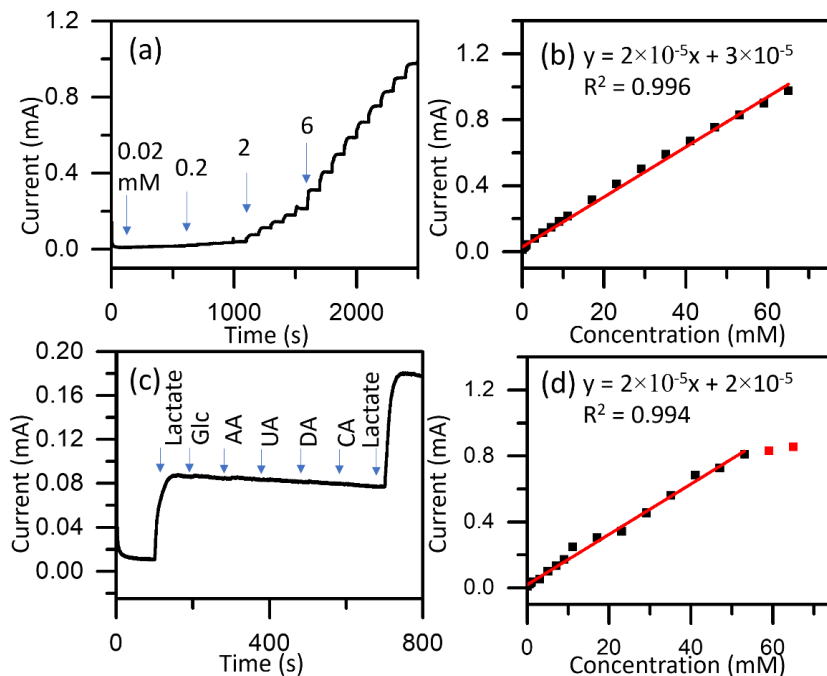


Figure 4.5 (a) i-t curve upon sequential addition of aliquots of lactate with increasing concentration (0.02, 0.2, 2 (5 times), 6 mM (9 times), 65.1 mM) to the NiO_x-200-30 sensor held at +0.55 V vs Ag/AgCl in 0.25 M NaOH and (b) the corresponding linearity response curve. (c) i-t curve collected at +0.55V vs Ag/AgCl illustrating minimal current jumps due to interference upon adding aliquots of 0.1 mM glucose (Glc), ascorbic acid (AA), uric acid (UA), dopamine (DA), and citric acid (CA) solutions to 0.25 M NaOH. (d) Linearity response curve upon sequential addition of aliquots of lactate with increasing concentration (0.02, 0.2, 2 (5 times), 6 mM (9 times), 65.1 mM) to the NiO_x-200-30 sensor held at +0.55 V vs Ag/AgCl in 1:1 v/v artificial sweat and 0.5 M NaOH. For the linearity response, R^2 is regression coefficient, y is the current (in mA) and x is the concentration (in mM), and the units of slope and intercept are mA/mM and mA respectively.

Table 4.1 summarizes the performance of the six NiO_x sensors evaluated in the present work and compares them with other nonenzymatic lactate sensors that are based on nickel nanomaterials. As the targeted linear range of detection for sweat lactate should be 1-30 mM or higher, all six of our nonenzymatic NiO_x sensors appear viable for sweat-range lactate detection. The nickel nanomaterials used in the sensors reported in the literature can be classified into different categories, NiO, Ni metal-organic framework (MOF), Ni-based layered double hydroxide, and nickel spinel nanomaterials. Among these materials, nickel spinel nanomaterials (NiCo₂O₄) on nickel foam have been reported for lactate sensing with the highest sensitivity of 430 $\mu\text{A mM}^{-1} \text{cm}^{-2}$

and a linear range with a high low concentration limit of lactate (5-50 mM). Ni MOF modified platinum electrode has been reported with a high sensitivity of $106.61 \mu\text{A mM}^{-1} \text{cm}^{-2}$, but with a smaller linear range (0.01-0.9 mM and 1-4 mM). Among the NiO, Ni(OH)₂, and NiO_x samples, NiO@Au has the widest detection range but low sensitivity. In addition, most works listed in table 1 is using hard substrates including glassy carbon electrode (GCE), platinum electrode, nickel foam, and there is also some lactate sensing based on plastic substrates, such as screen-printed carbon electrode and inject printed Ag conductive electrode. In the present work, NiO_x-200-30 based on flexible conductive graphene substrate exhibits a wide linear range, lowest limit of detection with high sensitivity. The NiO_x-200-30 is therefore an excellent candidate for use as a practical sweat-range lactate sensor.

Table 4.1 Summary of nickel nanomaterials for lactate sensing.

Electrode Matrix	Linear range (mM)	Limit of detection (μM)	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Reference
NiO and Ni(OH) ₂ /GCE	7.76-32.76	530 and 590	9.08 and 35.76	120
Ni-MOF/Platinum Electrode	0.01-0.9 and 1-4	5	106.61 and 29.53	259
NiO NPs/GCE	0.005-5	5.7	–	119
NiCo ₂ O ₄ /Ni Foam	5-50	–	430	294
NiS nanoclusters@NiS microsphere/Ni Foam	0.0005-0.0855	0.5	0.39	295
NiO@Au/GCE	0.1-500	11.6	8.0	296
NiO, NiO ₂ 50, NiO ₃ 50, NiO ₄ 50/GCE	Up to 25	95, 27, 42, 72	3.30, 62.35, 38.88, 9.50	116
Ni layered double hydroxides/Screen -Printed Carbon Electrode	5-25	30.59 $\pm$ 0.34	23.51 $\pm$ 0.45	268
NiCo layer double hydroxides/Screen -Printed Carbon Electrode	2-26	399	83.98	297
NiO _x /NiO _x -Nafion nanocomposite/Inject-Printed Ag Conductive Electrode	–	270	0.021	298
Au@NiO nanodendrites microarrays/Ni Microelectrodes	0.1-10	8.2	11.89	299
NiO _x -200-30/Graphene	0.02-65.1	0.15	80.0	This work
NiO _x -200-30/Graphene in artificial sweat condition	0.02-53.1	0.13	80.0	This work
NiO _x -200-180/Graphene	0.02-53.1	0.16	21.0	This work
NiO _x -300-30/Graphene	0.02-35.1	0.18	18.2	This work
NiO _x -300-180/Graphene	0.02-59.1	0.25	10.5	This work
NiO _x -400-30/Graphene	0.02-107.1	0.34	5.63	This work
NiO _x -400-180/Graphene	0.02-95.1	0.68	8.94	This work

4.4 Conclusion

In the present work, we have prepared NiO_x nanoparticles on flexible conductive graphene substrate by amperometry at –1.4 V for 120 s in 5 mM NiCl₂·6H₂O with 0.2 M boric acid, followed

by thermal annealing. Different annealing temperatures (200, 300 and 400 °C) and annealing time (30 and 180 min) are found to significantly affect the $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio. XPS and TEM data confirm that the NiO_x nanoparticles so obtained have a core-shell structure with a Ni metal crystalline core and a crystalline NiO shell with an outermost skin consisting of crystalline NiOOH and amorphous $\text{Ni}(\text{OH})_2$. The higher NiOOH + $\text{Ni}(\text{OH})_2$ composition (relative to NiO) provides crucially more reaction sites for lactate detection. Among the six samples evaluated here, NiO_x -200-30 is found to show the best performance with a wide linear span (0.02-65.1 mM) amply sufficient to cover the lactate range in human bodily fluid, a high sensitivity of $80.0 \mu\text{A mM}^{-1} \text{cm}^{-2}$, and a low limit of detection of 0.00015 mM. When tested with an artificial sweat solution, the NiO_x -200-30 sample exhibits a reduced linear range (0.02-53.1 mM) and a lower limit of detection of 0.00013 mM, while maintaining a high sensitivity of $80.0 \mu\text{A mM}^{-1} \text{cm}^{-2}$. By carefully manipulating the relative composition of NiOOH/ $\text{Ni}(\text{OH})_2$ in NiO_x along with morphology optimization of the nanoparticle size and distribution on a flexible graphene substrate, a lactate sensor with excellent performance appropriate for use in human sweat can be obtained. The synthesized NiO_x nanoparticles also have potential to work as catalyst for oxygen evolution reaction.

Chapter 5

Concluding Remarks and Future Work

5.1 Summary of Contributions

In the present work, we have succeeded in developing the facile, one-step electrochemical synthesis of Cu₂O nanocubes, with controllable sizes and uniform distributions, on a soft graphene substrate, and in demonstrating their application in nonenzymatic glucose sensing. The flexible graphene substrate offers good conductivity for electron transfer, while the near-homogeneous monolayer of Cu₂O nanocubes provides a large specific surface area and numerous reactive sites to facilitate the nonenzymatic reaction. The high electro-oxidation activity of Cu₂O nanocubes has enabled electron transfer at low overpotential and made these nanocubes an excellent electrocatalyst. Selected deposition voltages, deposition temperatures, electrolyte concentrations, and deposition amounts of time have been used to optimize the morphology and size of the Cu₂O nanocubes that are appropriate for use as electrocatalysts for glucose sensing. Our depth-profiling XPS and helium ion microscopy data show that these Cu₂O nanocubes (~50 nm in size) have a core-shell structure that consists of a small metallic Cu core, a prominent Cu₂O shell and a thin CuO skin (as the outermost layer). We also compare the performance of the Cu₂O nanocubes/graphene sensor with other sensors, including a bare graphene chip, and a graphene chip coated with a copper film obtained by magnetron sputtering, as well as an enzymatic sensor based on glucose oxidase immobilized on a graphene chip without and with Nafion. The Cu₂O nanocubes/graphene sensor provides not only the widest linear range from 0.002 to 17.1 mM with high sensitivity, but also high selectivity and exceptional stability and indeed without any discernible degradation in performance even after ambient storage for over 180 days. Its glucose sensing performance is considerably better than those of other nonenzymatic and enzymatic sensors considered here. The Cu₂O nanocubes/graphene sensor is also among the best saliva-range glucose sensors reported to date. Furthermore, our Cu₂O nanocubes/graphene sensor is fabricated in an aqueous electrolyte on a commercial graphene substrate, which is considerably simpler than the multistep fabrication methods employed for other sensors with comparable saliva-range glucose sensing performance.

To further explore the applications of Cu-based nanomaterials, we also synthesize copper oxide nanowires (Cu_xO-Cu/G) by using the quick, low-cost, and reproducible electrochemical deposition method followed by further thermal oxidation. Instead of common hard substrates, such as silicon, indium tin oxide, and glassy carbon electrodes, we again use the flexible graphene substrate to take

advantage of its high electrical conductivity, high specific surface area, unique thermal and mechanical properties for this work. For CuFe_2O_4 nanoparticles, a simple, one-step solvothermal synthesis is used. We then study the effect of these CuFe_2O_4 nanoparticles on the photoelectrochemical hydrogen evolution performance of the supported copper oxide nanowires. Different deposition voltages, electrolyte concentrations, deposition time and pH have been used to optimize the Cu film, with further selected annealing temperatures and time to obtain the optimized Cu_xO -Cu/G that are appropriate for use as photocathodes for water splitting. Our depth-profiling XPS data show that the supported Cu_xO -Cu nanowire consists of a Cu base, a Cu_2O layer and a CuO skin with different thickness controlled by annealing temperature. The addition of CuFe_2O_4 nanoparticles onto the best optimized Cu_xO -Cu nanowires supported on graphene is found to nearly double the photocurrent from -2.28 mA cm^{-2} to -3.93 mA cm^{-2} . A direct dual Z-scheme heterojunction mechanism involving the three semiconductors: Cu_2O , CuO and CuFe_2O_4 is proposed. The dual heterojunction architecture provides improved charge separation and redox ability to overcome the limitation of pristine photocatalysts, making the copper oxide nanowires decorated with CuFe_2O_4 nanoparticles an excellent photocatalyst system. The facile fabrication procedure offers potential for cost-effective scale-up of these high-performance photocatalysts for hydrogen production.

As a third demonstration of the powerful applications of metal oxide nanomaterials, we deposit nickel oxides on a graphene substrate by amperometry, and manipulate the relative content of $\text{Ni(OH)}_2/\text{NiOOH}$ redox couple and NiO in the amorphous/crystalline core-shell heterostructures by post-annealing in air. Our XRD, depth-profiling XPS and TEM-SAED data show that the NiO_x nanoparticle has a core-shell structure consisting of a crystalline Ni core, a crystalline NiO shell, and an outermost skin of amorphous Ni(OH)_2 and crystalline NiOOH with different ratio that can be controlled by appropriate annealing temperature and annealing time. With the highest Ni(OH)_2 or NiOOH to NiO ratio, the NiO_x nanoparticles obtained by post-annealing at 200°C for 30 min show the best performance for lactate detection with an excellent linear range of 0.02-65.1 mM, a high sensitivity of $80.0 \mu\text{A mM}^{-1} \text{ cm}^{-2}$, and an impressive limit of detection of 0.00015 mM. This sensor therefore provides excellent performance for lactate detection under artificial sweat condition. The facile fabrication avoids the alkaline condition and offers the potential for cost-effective high-performance catalysts for lactate sensor commercialization.

5.2 Future Work

In the present work, we have demonstrated that Cu_2O nanocubes and NiO_x nanoparticles supported on graphene substrates are high-performance catalysts for glucose and lactate sensors, respectively, while copper oxide nanowires and CuFe_2O_4 nanoparticles are excellent co-photocatalysts for photoelectrochemical hydrogen evolution. The potential applications for these nanomaterials can be further explored in the future work listed below.

In Chapter 2, we have studied Cu_2O nanocubes as electrocatalyst for non-invasive saliva glucose sensing for diabetes, but commercialization of these sensors remains challenging since saliva samples need to be collected and pretreated. An even more convenient sensing approach (than saliva sampling) is breath-based gas sensors for diabetes monitoring since breathalyzers for alcohol detection have been widely used for decades. Acetone is chosen for its high abundance among the various volatile organic compounds present in human breath and its concentration has been reported to have a relatively high correlation with that of blood glucose.³⁰⁰ Due to the ppb level of acetone in exhaled breath, a gas sensor with a high sensitivity and moisture resistance is required. CuO -based nanomaterial is an excellent active gas-sensitive material due to its excellent stability and high catalytic activity toward various reduction and oxidation reactions. We expect that the synthesized CuO nanowires reported in Chapter 3 can also be used as a sensitive layer for acetone gas sensing application. Further investigation will therefore be of great interest.

In Chapter 3, we study Cu_xO nanowires in conjunction with the CuFe_2O_4 nanoparticles as dual Z-scheme photocatalysts for hydrogen evolution. The positions of the conduction band and valence band, and bandgap of the third semiconductor in the dual Z-scheme heterojunction system play a crucial role in the charge transfer pathways that could greatly affect the photocatalytic performance for hydrogen evolution. In addition to CuFe_2O_4 , other materials can be studied for use as the third semiconductor in the dual heterojunction system. Possible candidates include other spinel ferrites, such as CoFe_2O_4 , ZnFe_2O_4 , NiFe_2O_4 , and MgFe_2O_4 , and rare earth metal ferrites, such as LaFe_2O_4 , LaCu_2O_4 , and ErFe_2O_4 . The photoelectrochemical water splitting performance of co-catalyst systems incorporating these new ferrites will be of great interest. We will determine the bandgaps of these ferrites samples by using our newly installed Nexsa G2 XPS system (along with UV-vis data) and study the electron transfer processes in the dual Z-scheme heterojunction system. In addition, a computational study based on the Density Functional Theory will provide calculated electronic structures of these ferrites that may offer new insight into the electron transfer mechanism.

In Chapter 4, the $\text{Ni(OH)}_2/\text{NiOOH}$ redox couples present in the skin of the NiO_x core-shell-skin nanoparticles are found to provide the active sites for lactate sensing and the redox couple content can be judiciously controlled by post-annealing. While the NiO shell offers slower reaction, we might be able to enhance the activity of NiO by doping with a rare earth metal to provide nickel vacancies and oxygen vacancies, and to increase surface defects. Europium is a good choice for doping due to its unique optical properties. In addition to lactate sensing, another potential application of europium- (and other rare earth transition metals) doped NiO nanomaterials is the removal of the organic dyes from water by photocatalytic degradation. By manipulating conditions of fabrication process including different combination, concentration, pH of electrolytes, and temperature, europium doped NiO nanomaterials with different crystalline structures and photophysical properties can be obtained. Their performance for rhodamine B degradation will be of great interest. Finally, while we have focused the present work on biosensing and photoelectrochemical water splitting application, the CuO, Cu_2O , NiO and spinel ferrites nanomaterials investigated here can also be extended to other applications, such as CO_2 reduction, cholesterol detection, and solar cells.

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Author:

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Author:

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Nonenzymatic Saliva-Range Glucose Sensing Using Electrodeposited Cuprous Oxide Nanocubes on a Graphene Strip



Author: Wenyu Gao, Xiaojing Zhou, Nina F. Heinig, et al

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Appendix A

Supporting Information

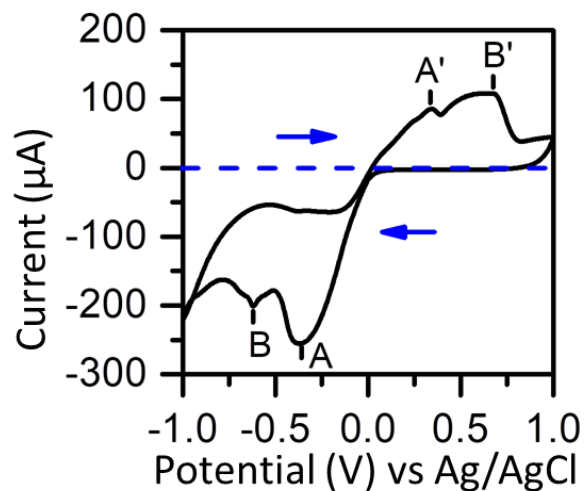


Figure S 2.1 Cyclic voltammogram of nanoparticle electrodeposition on a graphene substrate in 1 mM $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ and 10 mM $[\text{NaClO}_4]$ at a scan rate 0.1 V/s at room temperature.

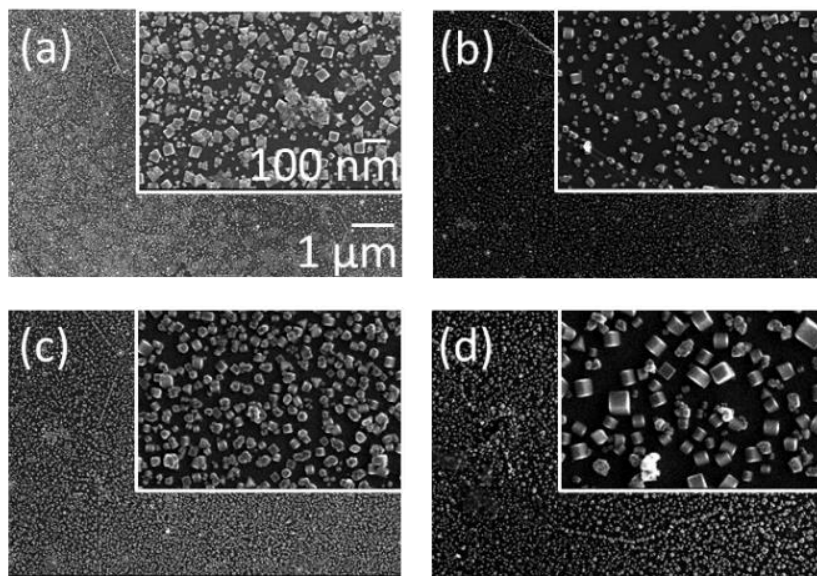


Figure S 2.2 SEM images of Cu_2O nanoparticles electrodeposited in 1 mM $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ and 10 mM $[\text{NaClO}_4]$ for 100 s at -1 V vs Ag/AgCl at different temperatures: (a) 4 $^{\circ}\text{C}$, (b) 40 $^{\circ}\text{C}$, (c) 60 $^{\circ}\text{C}$ and (d) 70 $^{\circ}\text{C}$. The scale bars are the same for all images.

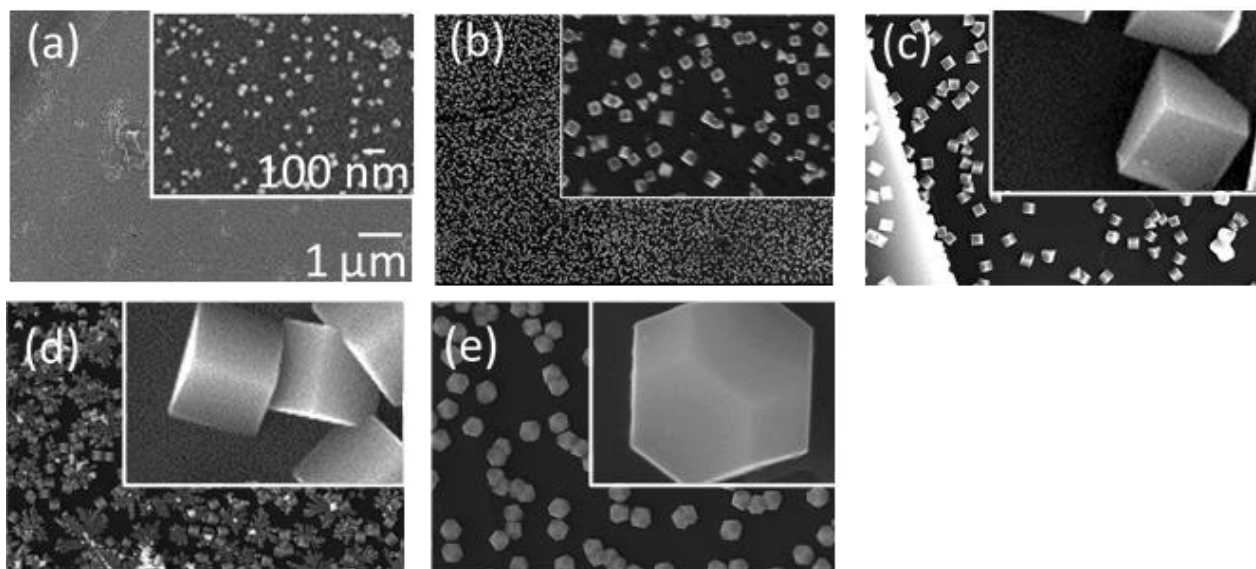


Figure S 2.3 SEM images of nanoparticles electrodeposited on graphene substrates at -1.0 V vs Ag/AgCl at room temperature for 100 s in different electrolyte concentrations of $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$: (a) 0.5 mM, (b) 1 mM, (c) 3 mM, (d) 5 mM and (e) 10 mM, all with a 10 mM $[\text{NaClO}_4]$ supporting electrolyte. The scale bars are the same for all images.

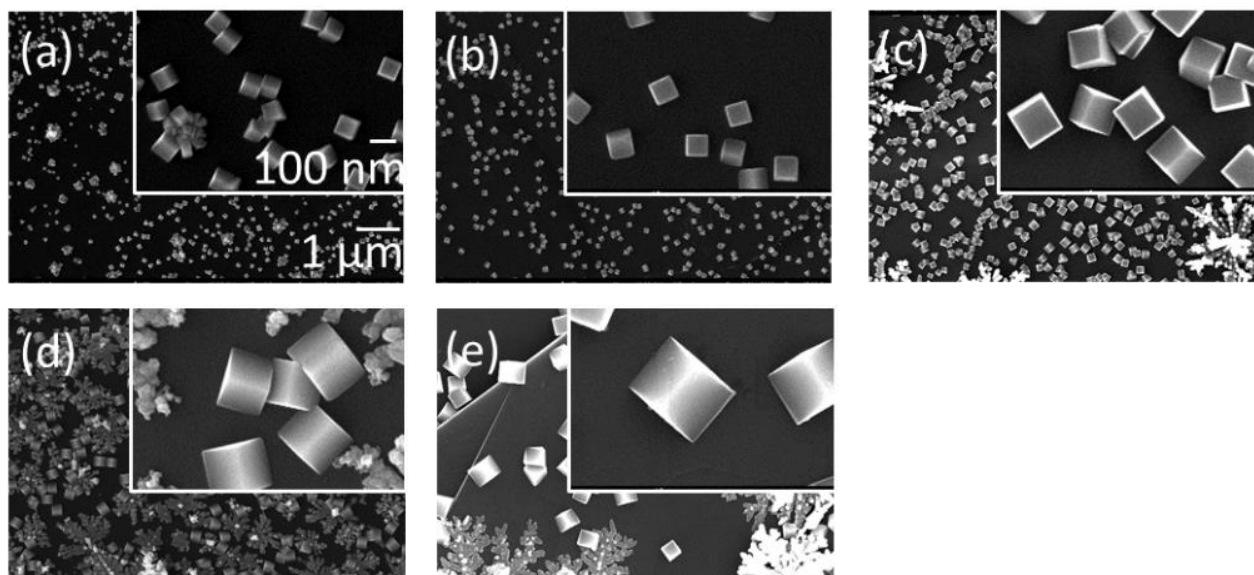


Figure S 2.4 SEM images of nanoparticles electrodeposited on graphene substrates at -1.0 V vs Ag/AgCl at room temperature in a 5 mM $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ and 10 mM $[\text{NaClO}_4]$ solution for different deposition times: (a) 1 s, (b) 10 s, (c) 50 s, (d) 100 s, and (e) 200 s. The scale bars are the same for all images.

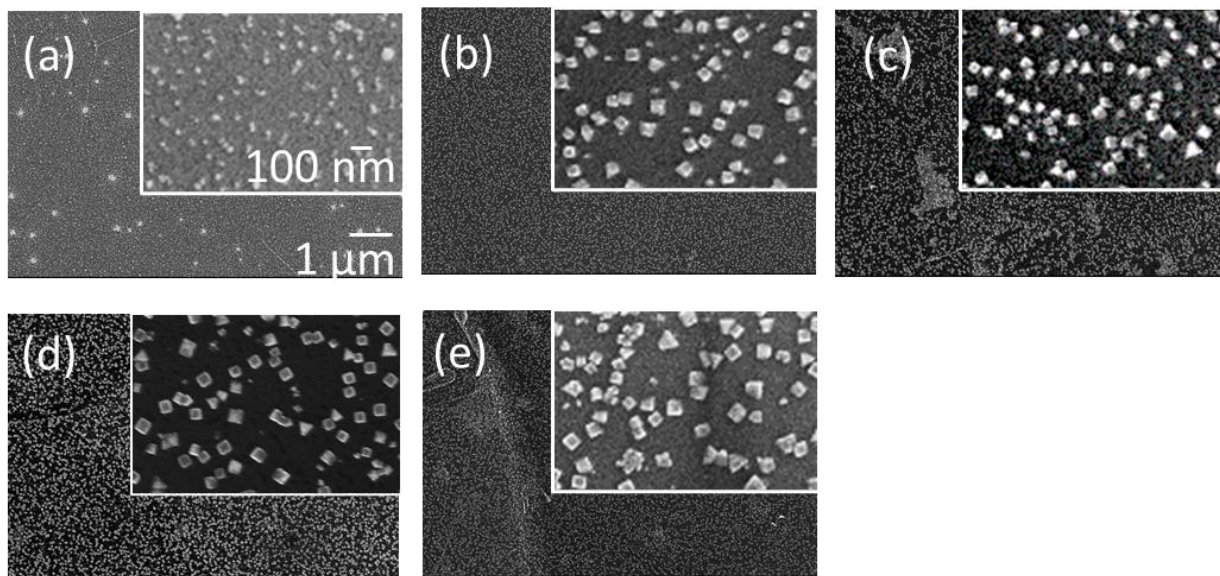


Figure S 2.5 SEM images of nanoparticles electrodeposited on graphene substrates at -1.0 V vs Ag/AgCl at room temperature in a 1 mM $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ and 10 mM $[\text{NaClO}_4]$ solution for different deposition times: (a) 1 s, (b) 10 s, (c) 50 s, (d) 100 s, and (e) 200 s. The scale bars are the same for all images.

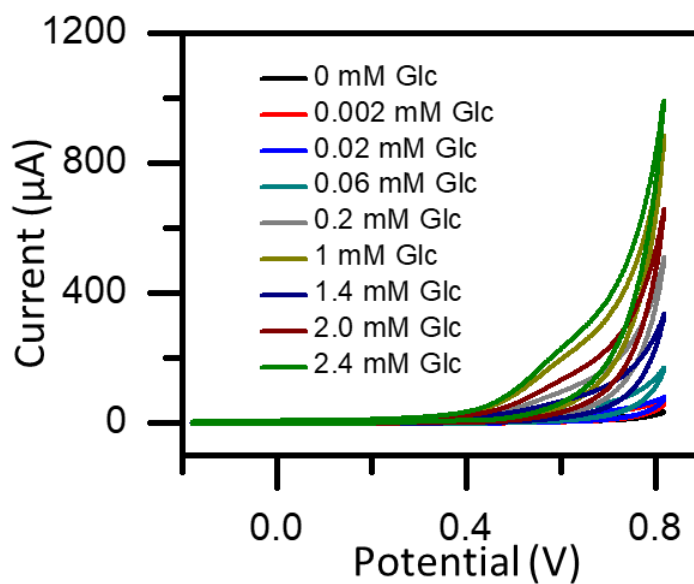


Figure S 2.6 Cyclic voltammograms of Cu_2O nanocubes/graphene at different glucose (Glc) concentrations.

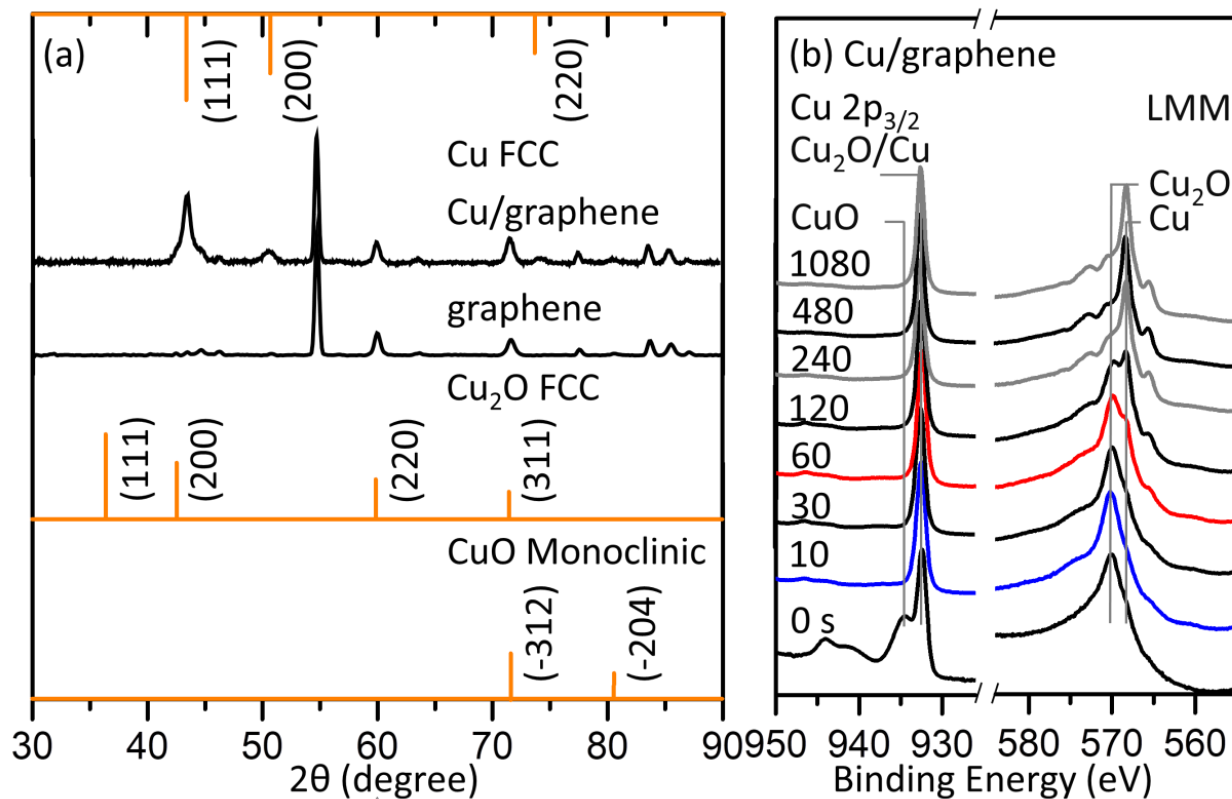


Figure S 2.7 (a) Glancing incidence XRD profiles for graphene sputter-coated with a Cu film (Cu/graphene) and for a pristine graphene substrate (graphene), along with the reference profiles for the Cu face-centered cubic (FCC) phase (JCPDS#01-089-2838), Cu₂O FCC phase (JCPDS#03-065-3288), and CuO monoclinic phase (JCPDS#01-089-2529), and (b) Depth-profiling XPS spectra of the Cu 2p_{3/2} and LMM regions for Cu/graphene.

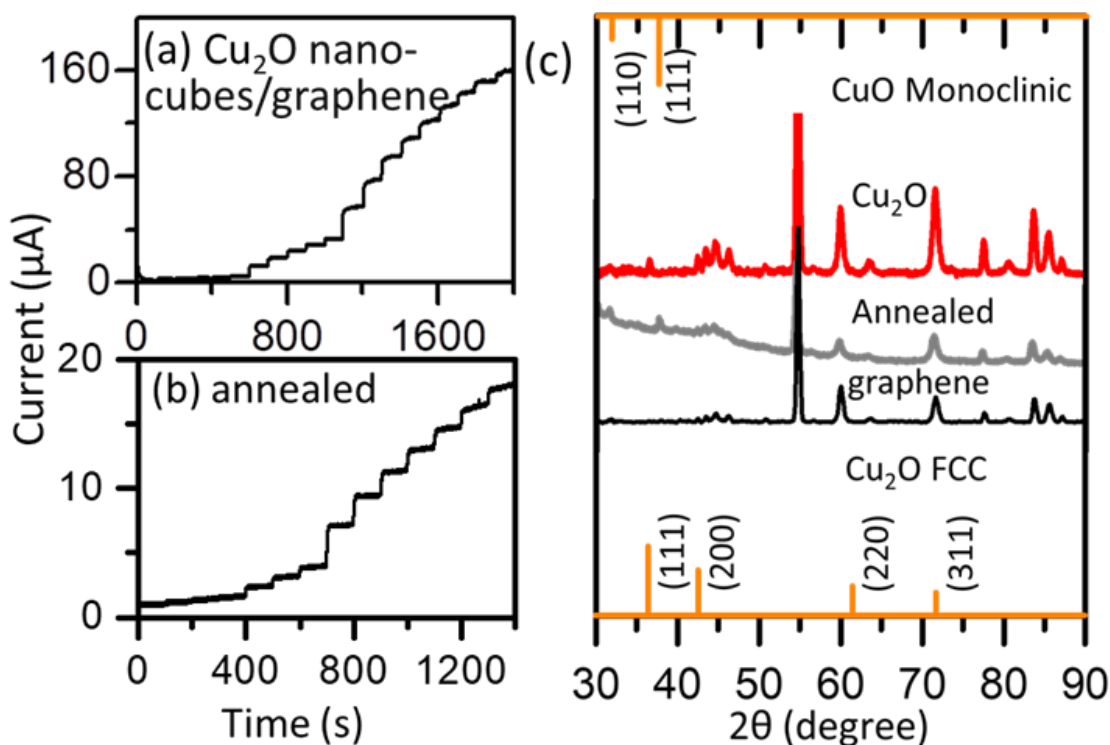


Figure S 2.8 I-t curves of (a) Cu_2O nanocubes/graphene sensor and (b) annealed CuO /graphene sensor, and (c) corresponding glancing incidence X-ray diffraction profiles assigned in accord with the reference profiles for the and CuO monoclinic phase (JCPDS#01-089-2529), and Cu_2O FCC phase (JCPDS#03-065-3288), along with the measured profile for a pristine graphene substrate.

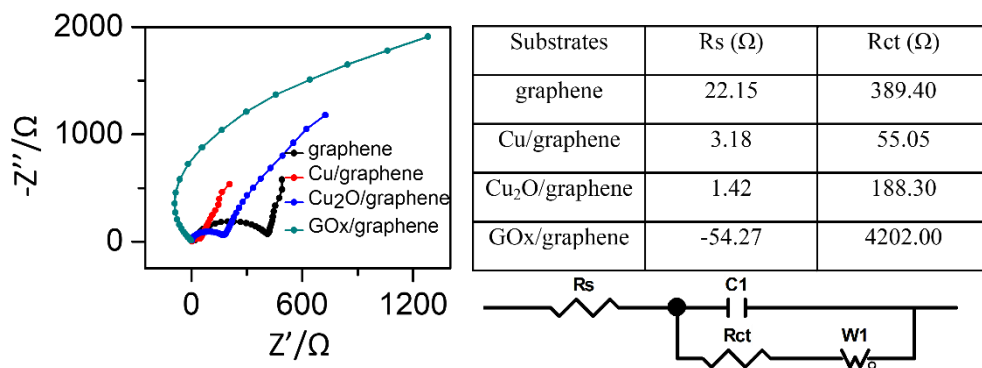


Figure S 2.9 Nyquist plots of four glucose sensors in 1 M Na_2SO_4 solution, where R_s is the resistance of solution, and R_{ct} is the charge transfer resistance of the substrate, $C1$ is the capacitance and $W1$ is the so-called Warburg element, which accounts for the diffusion processes.

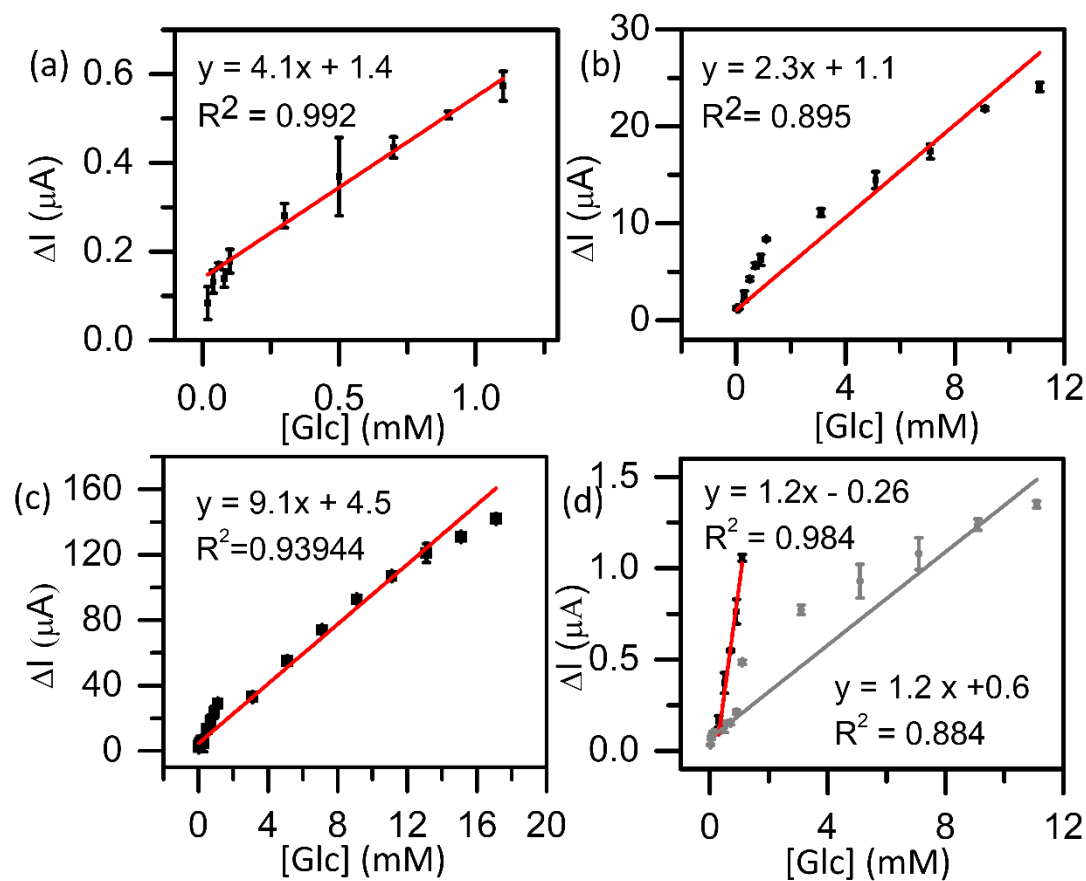


Figure S 2.10 Calibration curves of current change upon sequential addition of aliquots of glucose to 0.1 M NaOH at 0.6 V vs Ag/AgCl for (a) graphene, (b) Cu/graphene, (c) Cu_2O nanocubes/graphene, and (d) GOx/graphene without (upper curve) and with Nafion (lower curve).

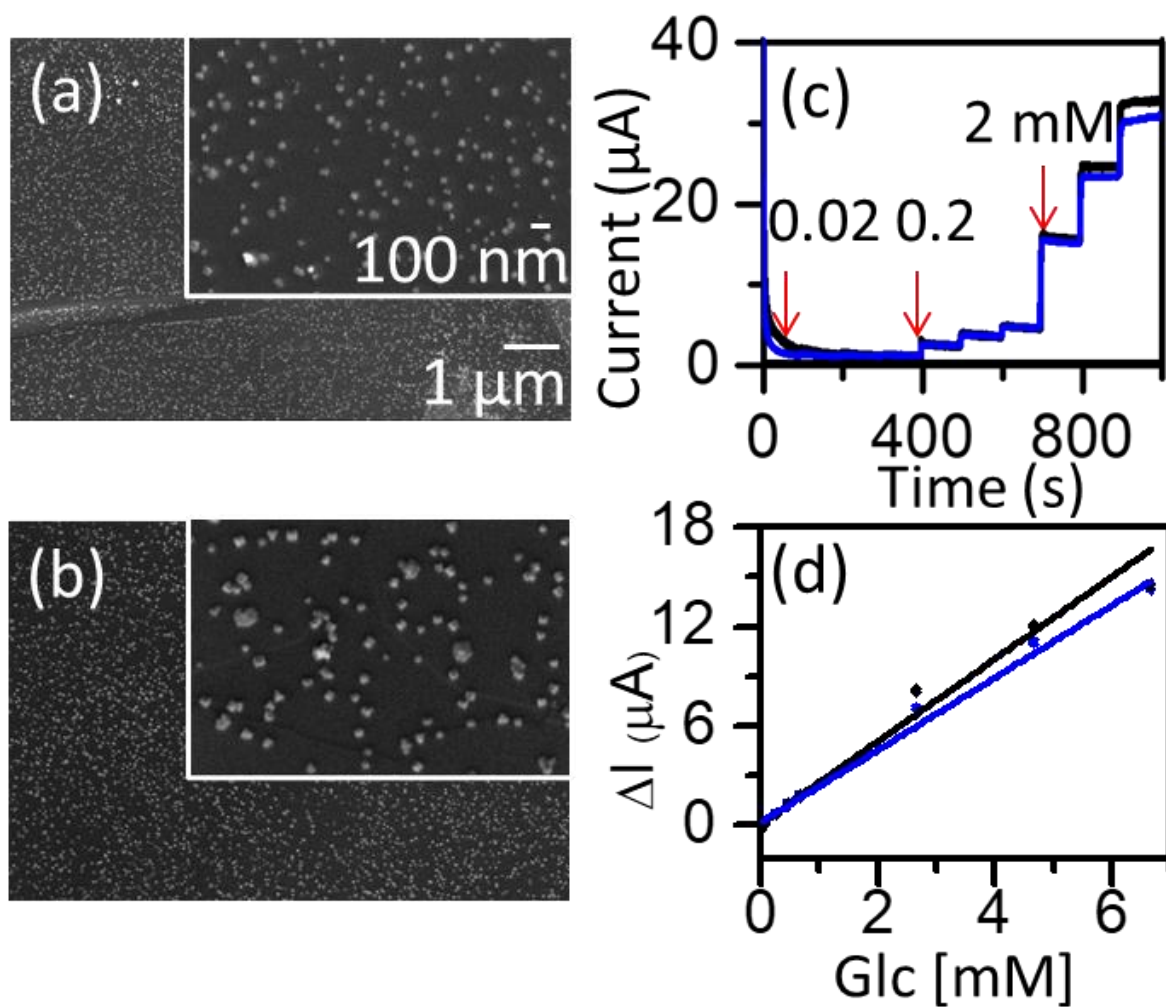


Figure S 2.11 SEM images of Cu₂O nanocubes electrodeposited on graphene substrates in 1 mM [CuSO₄·5H₂O] and 10 mM NaClO₄ at –1.0 V vs Ag/AgCl for 100 s at room temperature after storing in air for (a) 90 days and (b) 180 days. The corresponding i-t curves upon addition of aliquots of glucose with concentrations: 0.020 mM, 0.2 mM, and 2 mM thrice into 0.1 M NaOH at 0.6 V vs Ag/AgCl are shown in (c) and the current changes vs glucose concentration are shown in (d) for both the 90-day (lower curves) and 180-day samples (upper curves).

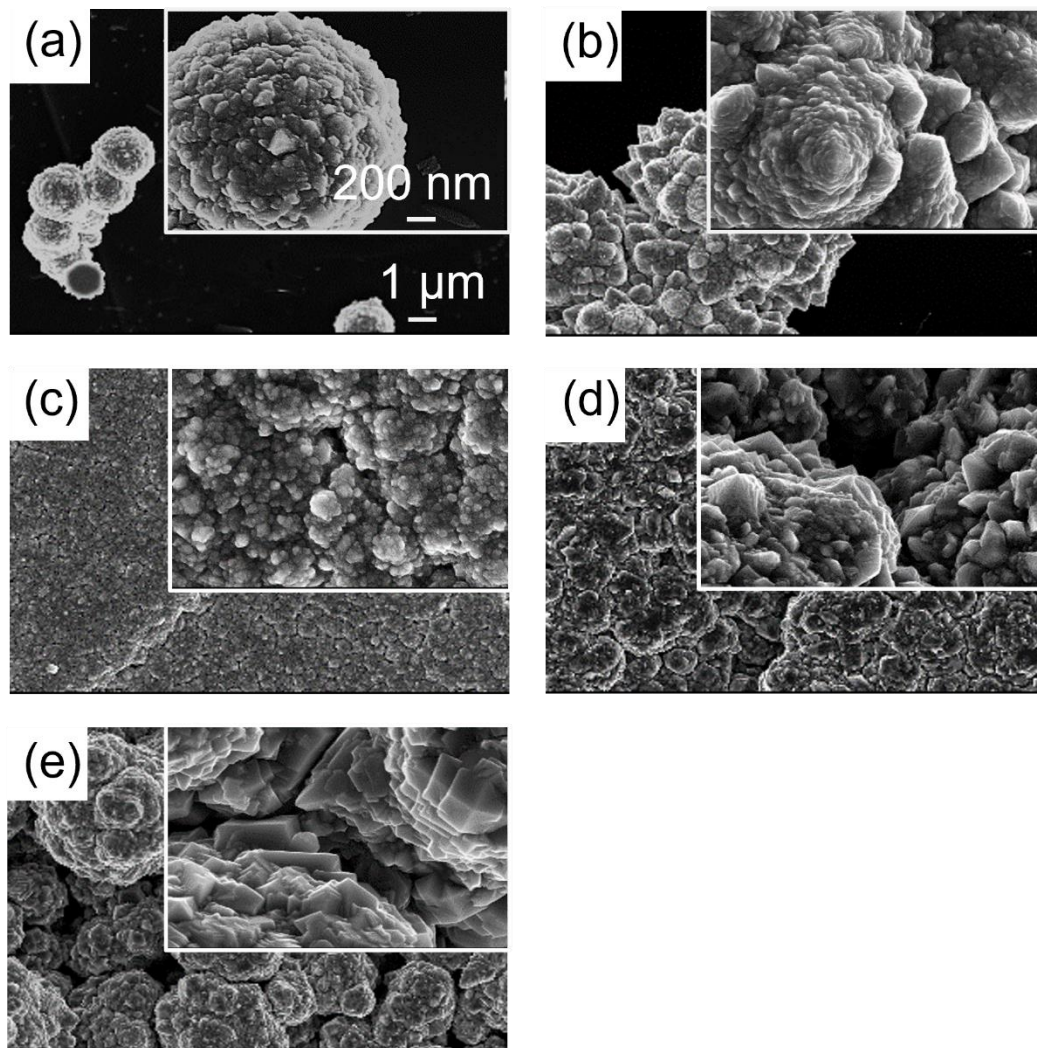


Figure S 3.1 SEM images of Cu films electrodeposited under various overpotentials: (a) -0.4 V, (b) -0.6 V, (c) -0.8 V, (d) -1.0 V, and (e) -1.2 V, all vs Ag/AgCl, in a 40 mM CuSO_4 solution at pH 12 for 20 min. All the SEM images employ the same scale.

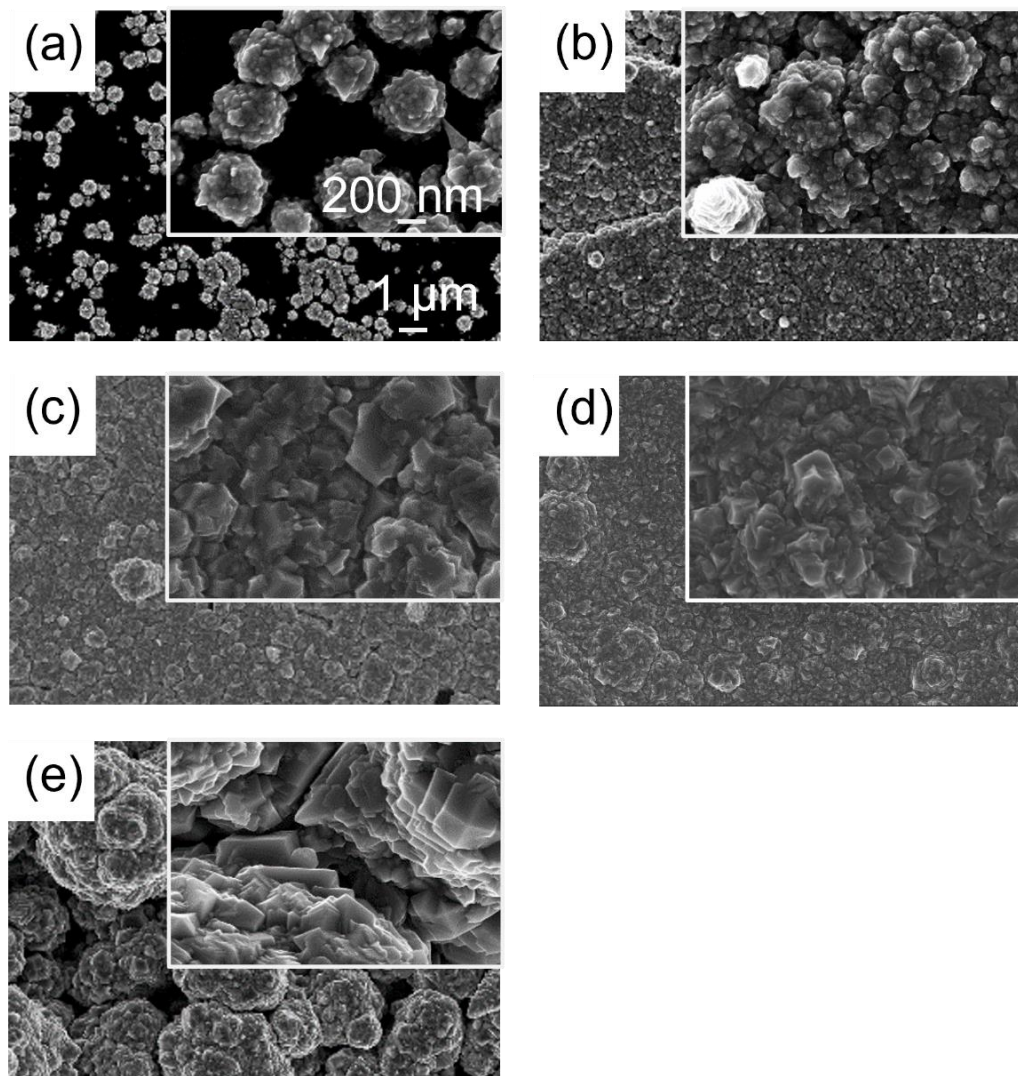


Figure S 3.2 SEM images of Cu films electrodeposited at -1.2 V (vs Ag/AgCl) with CuSO_4 concentrations of (a) 4 mM, (b) 10 mM, (c) 20 mM, (d) 30 mM, and (e) 40 mM at pH 12 for 20 min. All the SEM images employ the same scale.

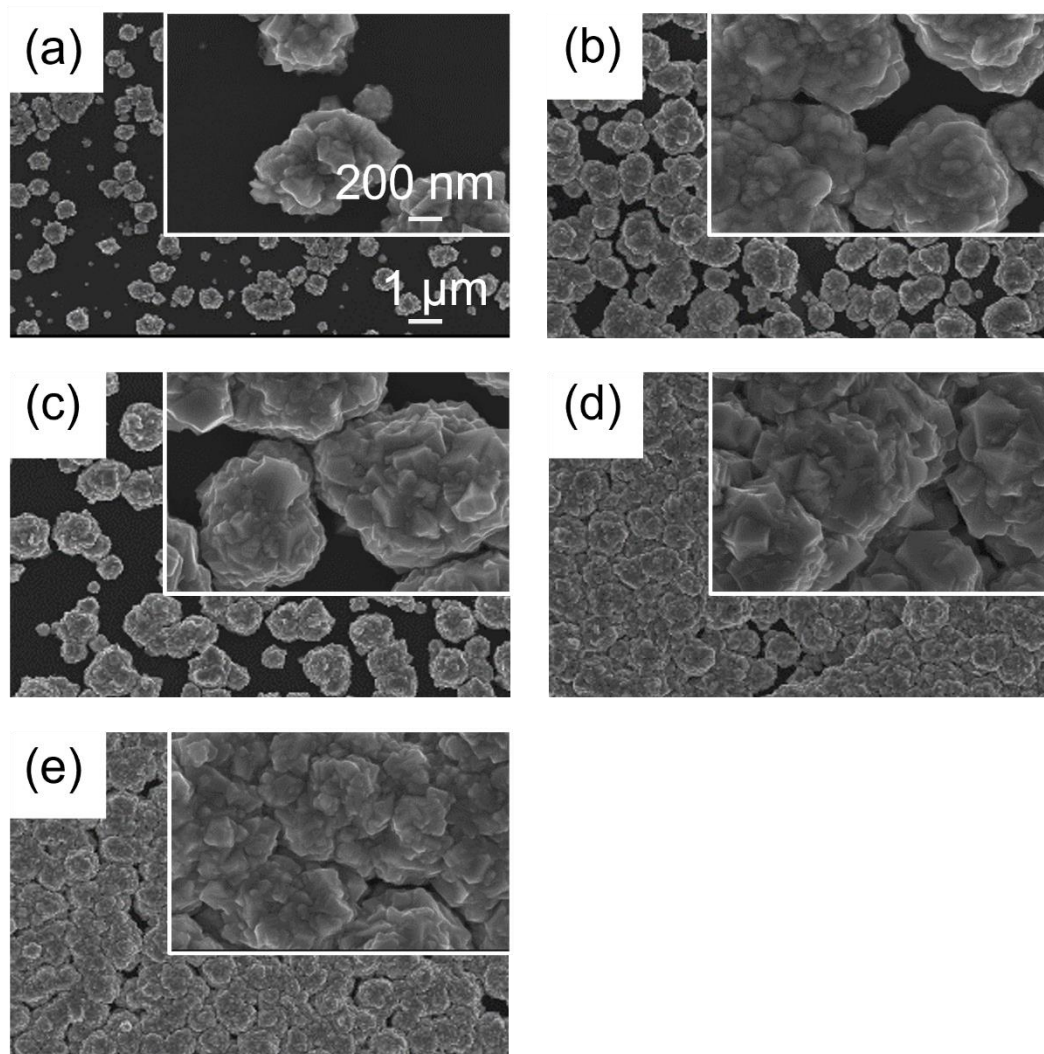


Figure S 3.3 SEM images of Cu films electrodeposited at -1.2 V (vs Ag/AgCl) in 40 mM CuSO_4 at pH 12 for (a) 1.5 min, (b) 5 min, (c) 10 min, (d) 20 min, and (e) 60 min. All the SEM images employ the same scale.

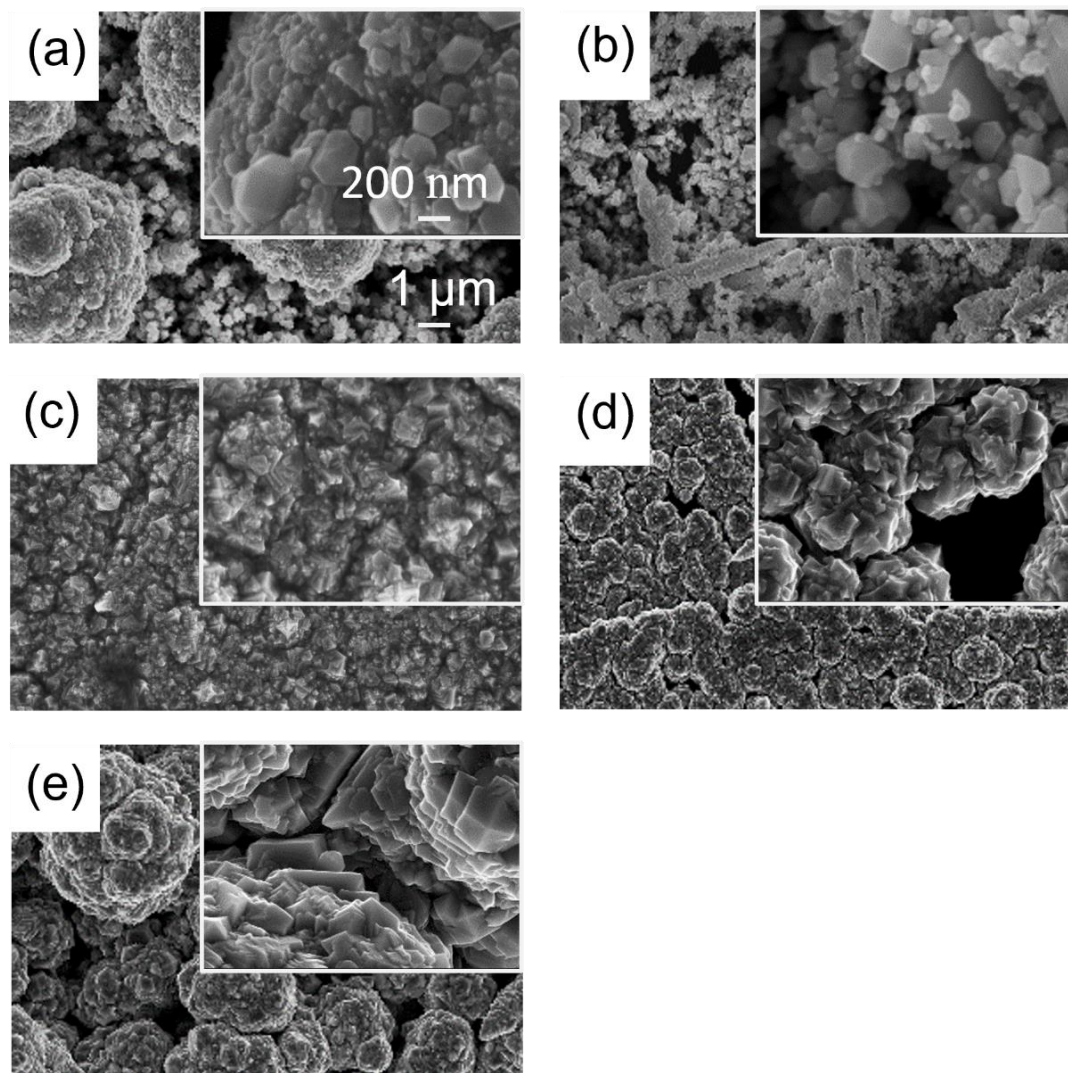


Figure S 3.4 SEM images of Cu films electrodeposited at -1.2 V (vs Ag/AgCl) for 20 min in 40 mM CuSO_4 solution with pH adjusted by sodium hydroxide from (a) 4 to (b) 6, (c) 8, (d) 10, and (e) 12. All the SEM images employ the same scale.

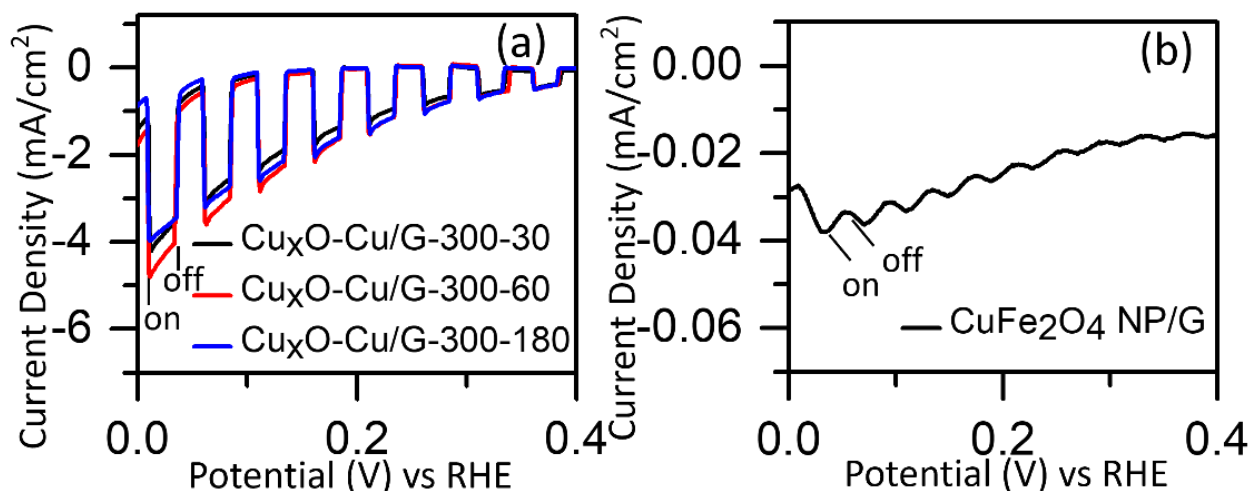


Figure S 3.5 Photocurrent density profiles measured as a function of applied potential by linear sweep voltammetry for (a) $\text{Cu}_x\text{O-Cu/G}$ annealed at 300 °C for different time (30, 60, 180 min) in 1 M Na_2SO_4 at pH 6 and for (b) CuFe_2O_4 NP/G.

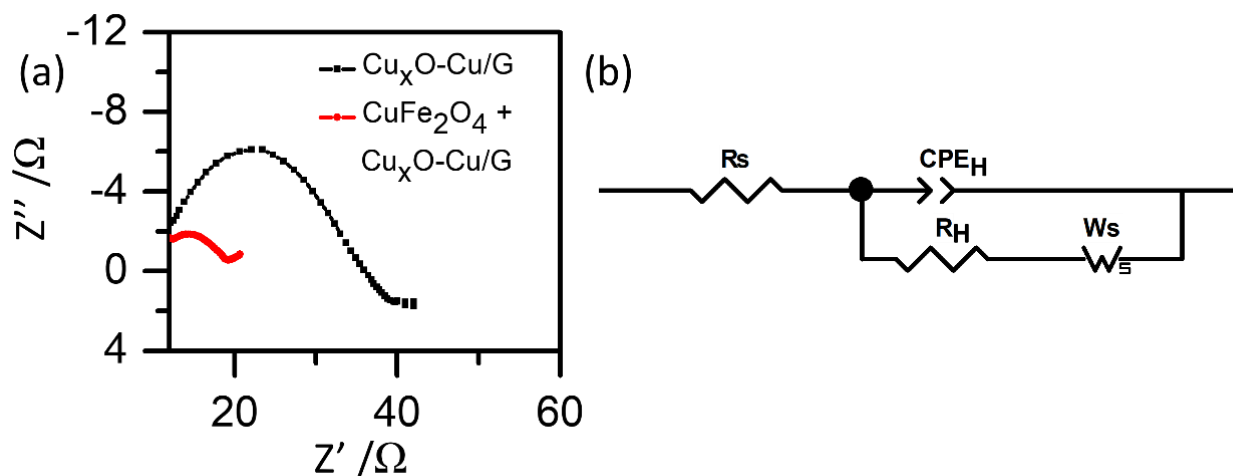


Figure S 3.6 (a) Nyquist plots of $\text{Cu}_x\text{O-Cu/G-300-30}$ as-synthesized and with the addition of CuFe_2O_4 NPs in 1 M Na_2SO_4 solution under illumination of simulated sunlight ($100 \text{ mW}\cdot\text{cm}^{-2}$). (b) A proposed equivalent circuit model, involving the series resistance (R_s), the capacitance of the electrochemical double layer (CPE_H), along with the charge-transfer resistance in the Helmholtz layer (R_H), and the Warburg diffusion impedance (W_s) in a RC circuit.

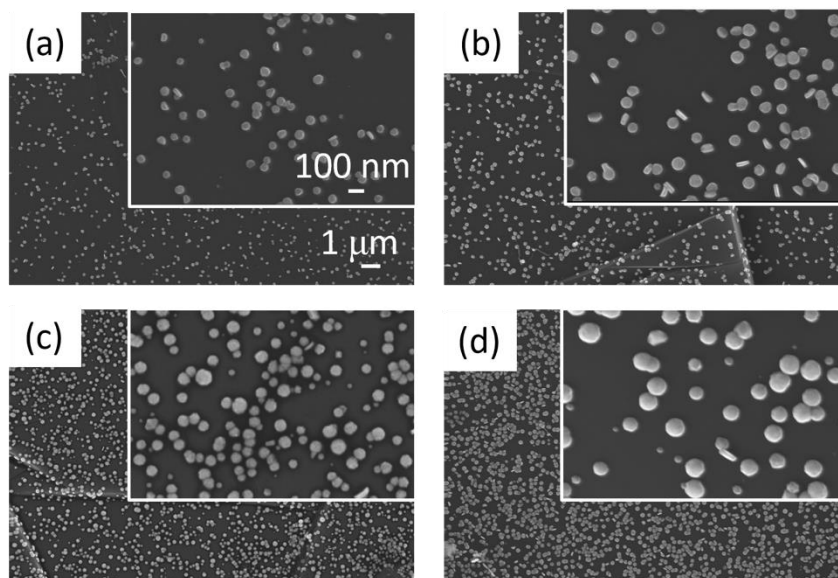


Figure S 4.1 SEM images of Ni NPs electrodeposited in 5 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for 120 s at (a) -1 V, (b) -1.2 V, (c) -1.4 V, and (d) -1.6 V, all vs Ag/AgCl. All the SEM images employ the same scale.

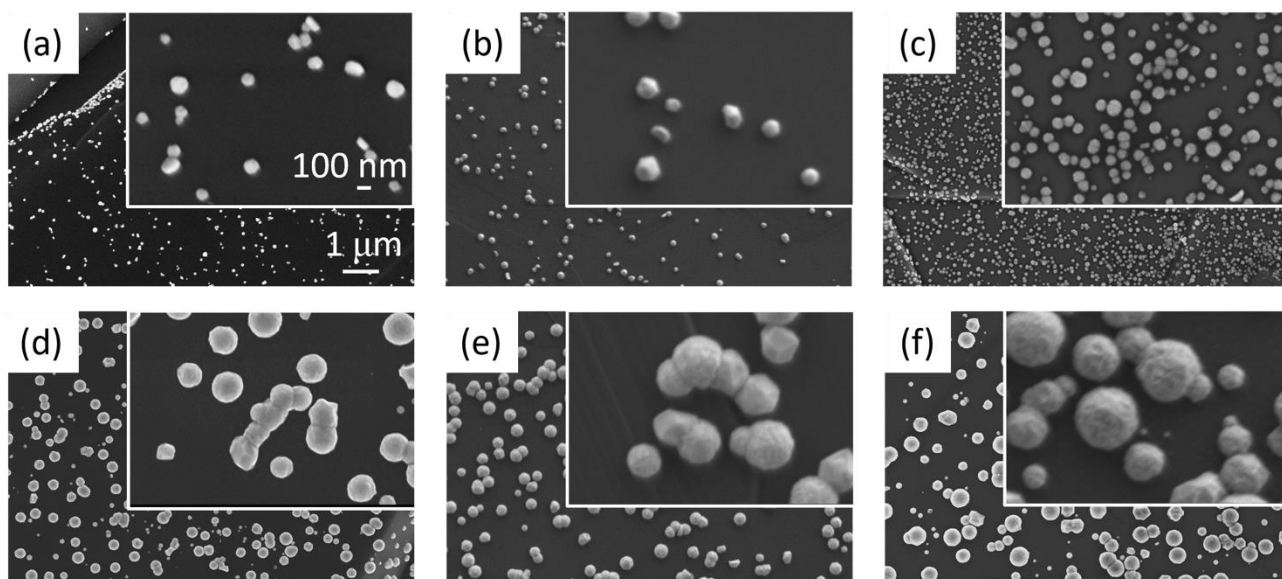


Figure S 4.2 SEM images of Ni NPs electrodeposited at -1.4 V vs Ag/AgCl in 5 mM $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for selected deposition time: (a) 20 s, (b) 60 s, (c) 120 s, (d) 240 s, (e) 300 s, and (f) 600 s. All the SEM images employ the same scale.

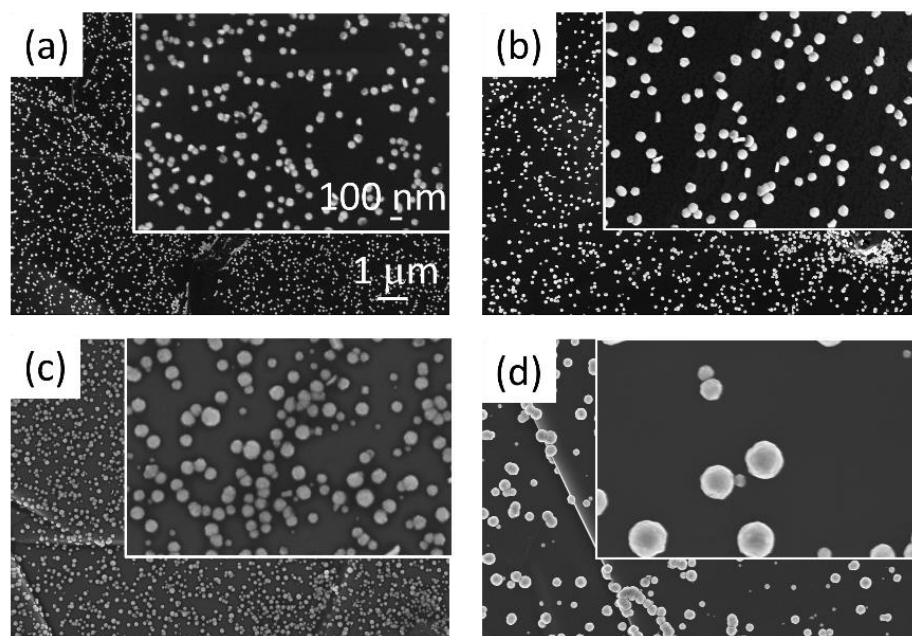


Figure S 4.3 SEM images of Ni NPs electrodeposited at -1.4 V vs Ag/AgCl for 120 s in selected $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ concentrations: (a) 1 mM, (b) 2 mM, (c) 5 mM, and (d) 10 mM. All the SEM images employ the same scale.

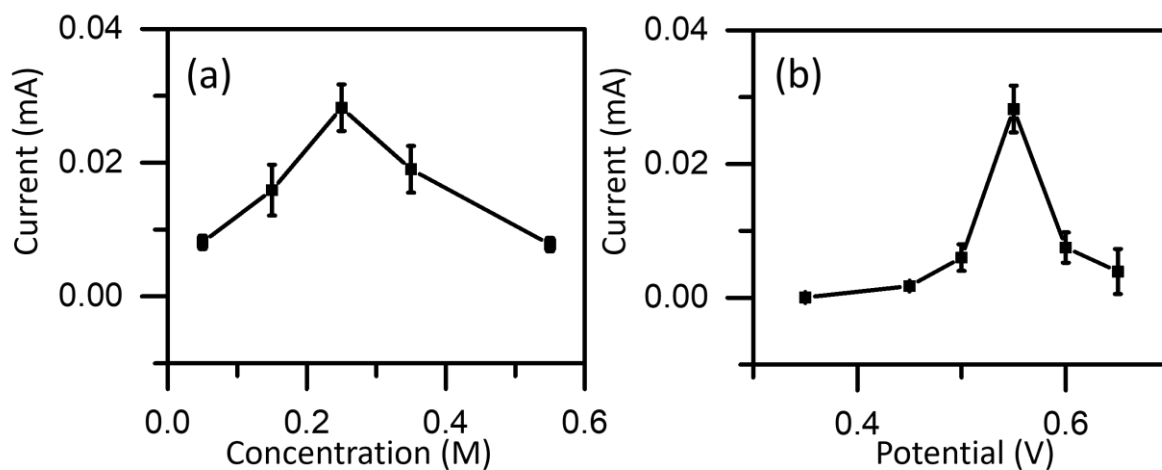


Figure S 4.4 Current response of the NiO_x -200-30 electrode for 2 mM lactate detection in 0.25 M NaOH as functions of (a) NaOH concentrations: 0.05, 0.15, 0.25, 0.35, and 0.55 M at $+0.55$ V vs Ag/AgCl, and (b) voltages: $+0.35$, 0.45 , 0.5 , 0.55 , 0.6 , and 0.65 V, all vs Ag/AgCl.

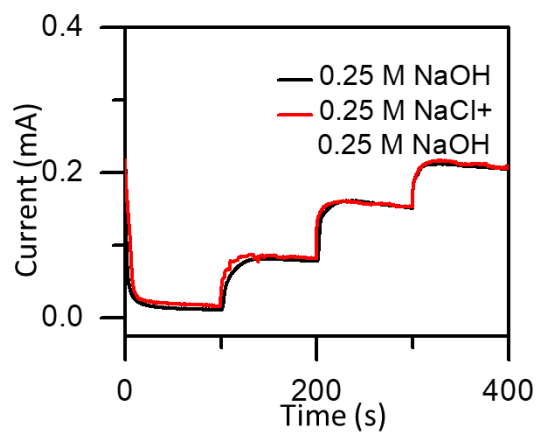


Figure S 4.5 i-t curves upon sequential addition of 2 mM lactate to NiO_x-200-30 sensor held at +0.55 V vs Ag/AgCl in 0.25 M NaOH without (black) and with 0.25 M NaCl (red).

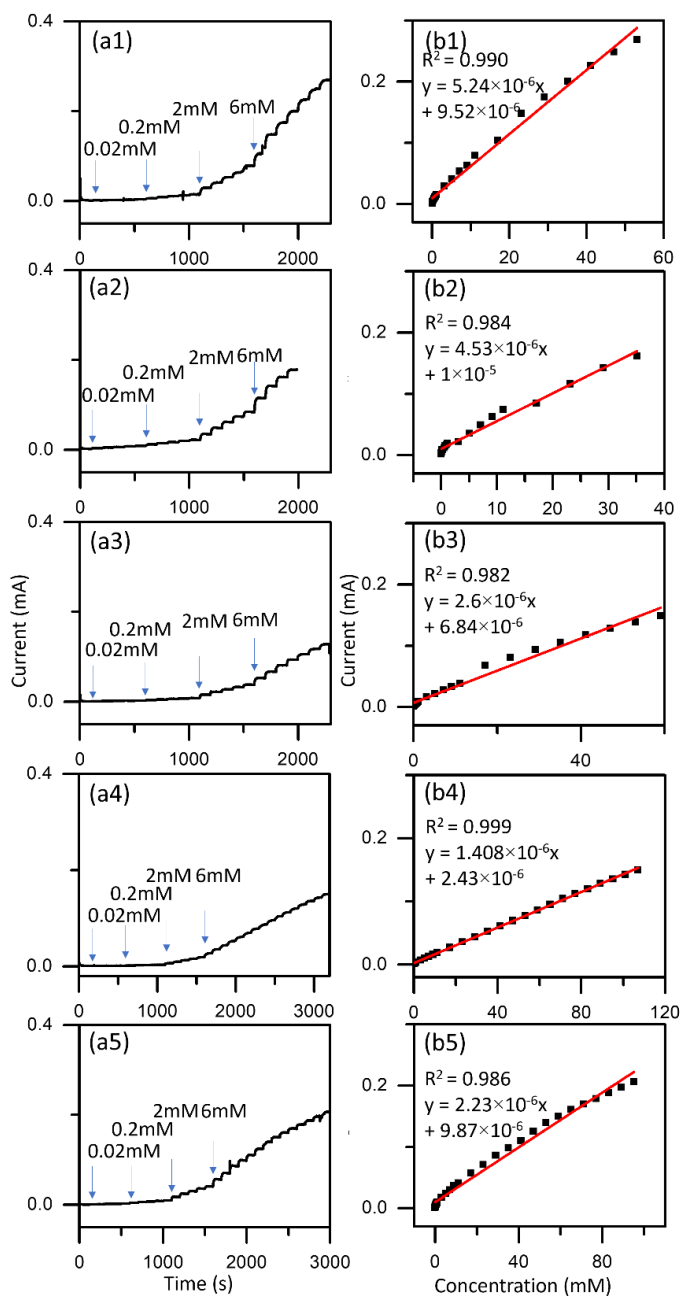


Figure S 4.6 (a1-a5) *i-t* curves and (b1-b5) the corresponding linearity response curves obtained upon sequential addition of aliquots of lactate to (a1, a2) NiO_x -200-180, (b1, b2) NiO_x -300-30, (c1, c2) NiO_x -300-180, (d1, d2) NiO_x -400-30, and (e1, e2) NiO_x -400-180), all held at +0.55 V vs Ag/AgCl in 0.25 M NaOH. For the linearity response, R^2 is regression coefficient, y is the current and x is the concentration.