

Nanomaterials for molecular recognition: specific adsorption and regulation of nanozyme activities

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Abstract

Biosensors use biomolecules to recognize target analytes and many biosensors employ nanomaterials for signal transduction. In this review, the reverse design for biosensors is described. These sensors rely only on nanomaterials for target recognition; and in some sensors, biomolecules are employed only for signal transduction. The first type relies on fluorescent nanomaterials and the specific binding of target analytes which can lead to a fluorescence change in nanomaterials. The second type is based on the regulation of the catalytic activity of nanozymes. The third type relies on an additional signal transduction molecule, such as a DNA oligonucleotide, adsorbed on the surface of nanomaterials. In this case, biomolecules are only used for signal transduction but do not play a role in target recognition. In the end, we also discuss some challenges associated with such designs including limited selectivity and susceptibility to interference. Future research opportunities include further mechanistic studies, the development of new ways to boost selectivity, and testing real samples.

1. Introduction

A biosensor contains at least two components: target recognition and signal transduction. Usually, antibodies, enzymes or aptamers are used for target recognition, since such biomolecules can achieve excellent specificity and detect a broad range of analytes. To convert biological recognition events to physically detectable signals, nanomaterials are often coupled to these biomolecular probes for signal transduction. One example of this is the use of gold nanoparticles, which have strong extinction coefficients, distance-dependent color shifts, Raman enhancement and fluorescence quenching properties.¹⁻³ Another commonly used nanomaterials for signal transduction are quantum dots (QDs). QDs are nanometer-sized semiconductor particles which have superior optical properties compared to traditional organic fluorophores.⁴ They possess wide absorption bands, narrow emission spectra, high luminescent efficiency and large Stokes shift. Furthermore, metal-organic frameworks (MOFs) are notable for their diversity in composition and structure as their metal centers and organic ligands can be adjusted. This allows the design of MOFs with various functions, providing opportunities to develop novel sensing modalities.⁵ In particular, fluorescent MOFs have rich luminescence sites, adjustable luminescence range and various pore structures. They have been widely used to construct fluorescent probes and used for specific molecular recognition and fluorescence sensing of metal cations, inorganic anions, biomolecules and other analytes.^{6,7} Magnetic nanoparticles allow sample enrichment, separation and magnetic resonance based detection.⁸ For traditional biosensors that rely on antibodies or aptamers coupled with nanomaterials, they are susceptible to instability of biomolecules. In addition, antibodies suffer from batch-to-batch variation problems, and many reported aptamers cannot bind to their intended targets.^{9,10}

Interestingly, it has been demonstrated in some examples that nanomaterials alone can also achieve highly specific sensing for various analytes based on adsorption or surface reactions.¹¹⁻¹³ For example, molecular recognition based on the regulation of nanozyme activities.¹⁴ Nanozymes are nanomaterials that can convert enzyme substrates into enzyme products, although the catalytic mechanism can be different from their enzyme counterparts.¹⁵⁻¹⁸ Owing to the diversity of surface properties of nanozymes and chemical reactions that mainly occur on the surface of nanoparticles, the catalytic activity of nanozymes may be regulated when they interact with analytes such as small molecules, ions or biomacromolecules. For instance, the specific recognition of tetracycline (TC) by Cu-g-C₃N₄ nanozyme was achieved by inhibiting the catalytic ability of the Cu-g-C₃N₄

nanozyme.¹⁹ In addition, the interaction between targets and MOFs may lead to the enhancement or quenching of MOFs fluorescence for target recognition. Moreover, a few metal oxides also exhibit unique molecular recognition properties. Fe₃O₄ can specifically recognize and detect As(V),²⁰ while CeO₂ shows selective recognition ability to H₂O₂.²¹ Currently, nanomaterials have shown excellent performance in identifying and detecting chemical hazards,²² high-energy explosives,²³ small biological molecules,²⁴ proteins,²⁵ and heavy metal ions.²⁶ Such recognition abilities were often discovered accidentally during experiments instead of by rational design. An advantage of such sensors is that they are likely to have higher stability compared to traditional biosensors since no specific biomolecules are required.

In this article, we aim to review such examples of using nanomaterials for target recognition. The first type is made solely on nanomaterials, where target binding can induce a signal change and most of them are based on the intrinsic fluorescence of the nanomaterials (Figure 1A). The second type is based on the modulation of the catalytic (nanozyme) activity of nanomaterials by target molecules (Figure 1B). The third type relies on an additional signal transduction molecule since target binding alone cannot give any signal (Figure 1C). In this case, the signal transduction molecule could be a biomolecule, but the biomolecule is only used for signal transduction and plays no role in target recognition. Our discussion is limited to the native surface of inorganic nanomaterials and does not include molecularly imprinted polymers.²⁷

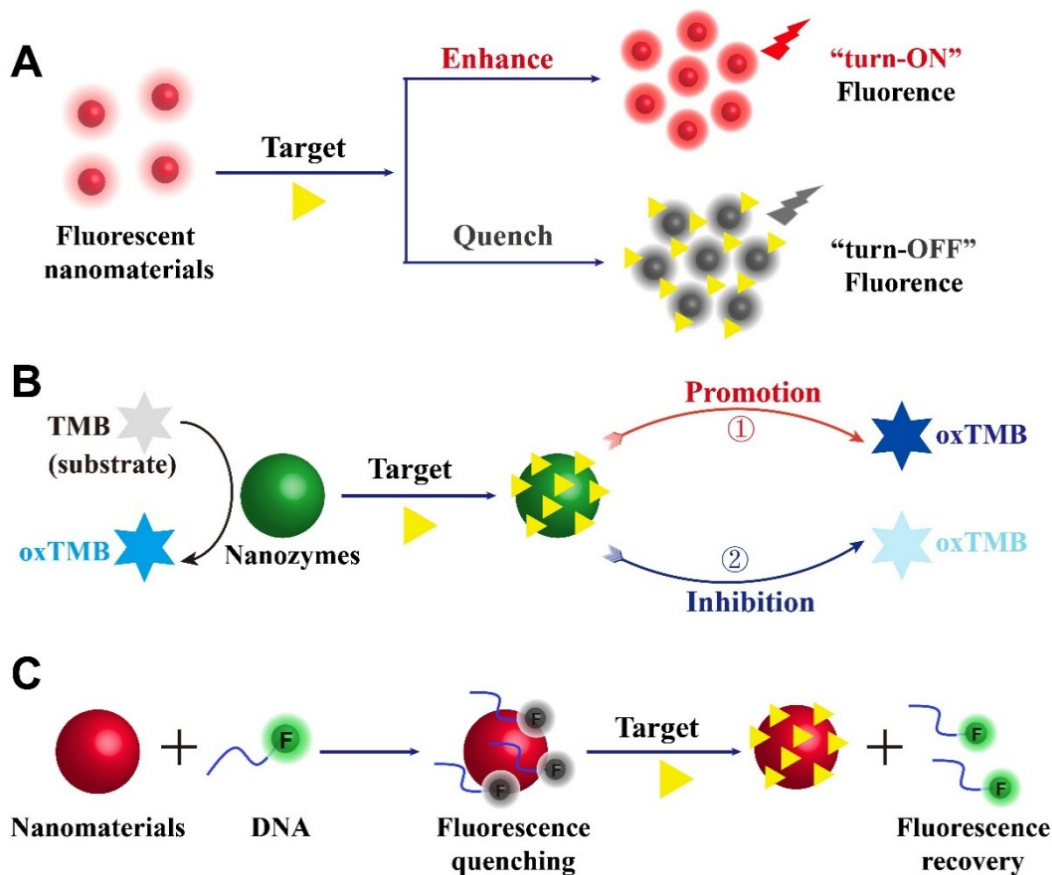


Figure 1. Schemes of the three types of nanomaterial-based sensors are reviewed in this paper. (A) The fluorescence of nanomaterials is changed by interactions with target molecules. (B) Detection based on the modulation of nanozyme activities. (C) Using an additional molecule such as a fluorescently labeled DNA for signal generation.

2. Target recognition based on fluorescent nanomaterials

Fluorescent nanomaterials are attractive sensing elements due to their highly sensitive fluorescence properties. The main recognition mechanism is based on intermolecular interactions between fluorescent nanomaterials and analytes (such as biological small molecules, proteins, and heavy metal ions), resulting in a change in the emission wavelength or fluorescence intensity of nanomaterials.²⁸ The above fluorescent nanomaterials mainly involve quantum dots,^{29,30} noble metal nanoclusters,³¹ and lanthanide containing MOFs.²³

2.1 Detection of anions

Phosphate anions play a very important role in both the biological systems and aquatic environment. However, excessive phosphate concentration is harmful to the ecological environment causing problems such as eutrophication. Therefore, specific recognition and detection of phosphate-containing molecules is of significance. A wide variety of phosphate-containing molecules exist such as PO_4^{3-} , pyrophosphate (PPi) and adenosine triphosphate (ATP). Their structural similarity makes highly selective recognition and determination more challenging.

Fluorescent MOFs have rich luminescence sites, adjustable luminescence range and various pore structures. The metal nodes in MOFs enable them to selectively recognize certain species *via* specific interactions, and their porosity can promote mass transport to make the recognition process occur quickly. Generally, the mechanism of fluorescent MOFs used for molecular recognition is that analytes specifically interact with metal ions or ligands in MOFs, thereby affecting the fluorescence intensity of MOFs (enhancement or quenching). For phosphate detection, the MOFs often contain metal ions that have strong affinities to phosphate.

For example, zirconium-based MOFs (Zr-MOFs) exhibit high affinity towards phosphate groups, thereby serving as specific binding sites for phosphate. Some typical MOFs include PCN-222, PCN-224, MOF-525, NU-1000 and UiO-66, wherein the fluorescence signal is usually enhanced after the addition of PO_4^{3-} . Ma et al.³² utilized a porphyrin-based MOF (PCN-224) as a highly selective fluorescent probe for the determination of PO_4^{3-} . PCN-224 was synthesized using zirconium as metal nodes and tetrakis(4-carboxyphenyl) porphyrin (TCPP) as a fluorescent ligand. In the presence of PO_4^{3-} , ZrO clusters in PCN-224 can strongly bind PO_4^{3-} by forming Zr-O-P bonds, resulting in enhanced fluorescence of the TCPP ligand at 650 nm for specific PO_4^{3-} recognition. Based on this principle, the limit of detection (LOD) of PCN-224 for phosphate was 54 nM. Similarly, Cheng et al.³³ proposed a fluorescent/colorimetric “signal-on” nanoprobe based on PCN-222 nanorods (NRs) for PO_4^{3-} . As shown in Figure 2A, due to the high affinity of the zirconium nodes in PCN-222 NRs for PO_4^{3-} , the structure of the PCN-222 NRs collapsed upon adding PO_4^{3-} . This will lead to the release of TCPP ligands from PCN-222 NRs as well as the enhancement of fluorescence and absorbance signals. Compared with other potential interfering species (Figure 2E), PO_4^{3-} detection was achieved with a wide concentration range from 0.25 to 100 μM , and the LOD was estimated to be 23 nM. In addition, a luminescent Tb-MOF was also reported for PO_4^{3-} response, which used nitric heterocyclic carboxylic acid as a ligand.³⁴ The addition of PO_4^{3-} selectively quenched the fluorescence of Tb-MOF and the mechanism may be

attributed to the binding of Tb^{3+} by PO_4^{3-} . Since phosphate cannot effectively serve as an antenna to absorb light for Tb^{3+} , the Tb^{3+} luminescence was quenched. In these studies, most of the tested competing anions do not interact strongly with head metals such as Zr^{4+} and Tb^{3+} . Depending on the scenario of application, other anions such as PPi , arsenate and ATP might exist and they may also generate a similar signal response as phosphate.

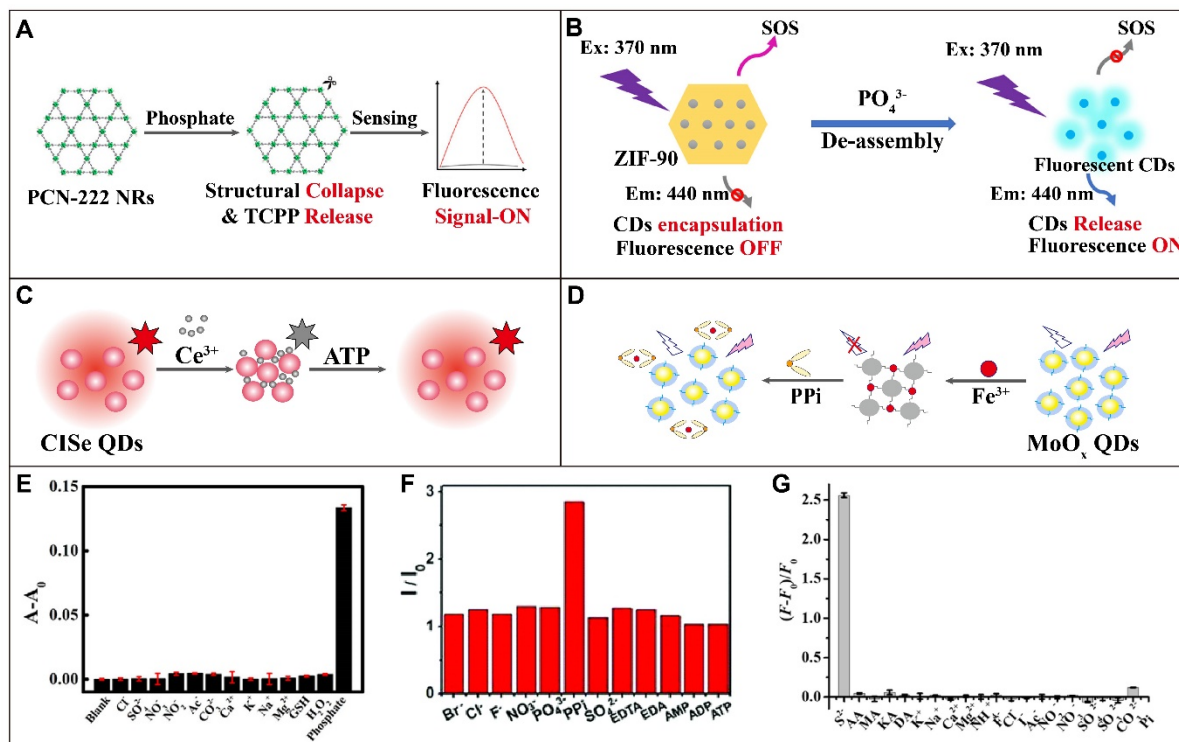


Figure 2. Examples of sensors for anion detection. (A) PCN-222 NRs are used for PO_4^{3-} specific recognition with fluorescence enhancement, and the selectivity data are shown in (E). Reprinted with permission from [33] American Chemical Society, Copyright 2020. (B) CDs@ZIF-90 for PO_4^{3-} detection based on the competitive coordination between PO_4^{3-} and the metal nodes in ZIF-90. Reprinted with permission from [35] American Chemical Society, Copyright 2020. (C) CISE QDs are employed for ATP detection with fluorescence quenching. Reprinted with permission from [36] American Chemical Society, Copyright 2021. (D) PPI sensing by Fe^{3+} - MoO_x QDs using Fe^{3+} as a quenching agent and the selectivity data are shown in (F). Reprinted with permission from [40] Royal Society of Chemistry, Copyright 2018. (G) KA-Cu NCs/MIL-53 (Fe) for selective detection of S^{2-} . Reprinted with permission from [43] Springer Nature, Copyright 2022.

Quantum dots (QDs) are another kind of fluorescent nanomaterials, which have also been developed for the detection of phosphate-containing molecules. In most cases, molecular recognition is based on the competition between analytes and the surface modification group of

QDs, resulting in the enhancement or quenching of fluorescence. As shown in Figure 2B, Wu et al.³⁵ synthesized fluorescent carbon dots (CDs) and developed a method for PO_4^{3-} detection using CDs@ZIF-90. The fluorescence of CDs was suppressed after encapsulation into ZIF-90. Then, the competitive coordination between PO_4^{3-} and the metal node of ZIF-90 led to the decomposition of the structure of ZIF-90, thus releasing the CDs and recovering the fluorescence. This method shows a linear range from 1.0 to 50.0 $\mu\text{mol L}^{-1}$ with a LOD of 0.23 $\mu\text{mol L}^{-1}$.

ATP recognition has been widely reported using QDs. In general, the fluorescence of QDs is first quenched by modification with transition metal ions (such as Ce^{3+} , Fe^{3+} , or Zn^{2+}). Subsequently, when ATP was added, the binding between ATP and metal ions was stronger than that between metal ions and QDs, releasing the metal ions from the QDs and restoring the QD fluorescence. As shown in Figure 2C, Chen et al.³⁶ developed a “turn-on” fluorescent copper indium selenide QD (CISE QDs) based sensor for ATP detection with a LOD of 56 nM. Ce^{3+} was selected as a fluorescence quenching agent and in the presence of ATP, its triphosphate strongly coordinated with Ce^{3+} on the surface of CISE QDs- Ce^{3+} , leading to fluorescence recovery. Based on the strong coordination of triphosphate, a series of fluorescent biosensors using QDs as ATP recognition elements were reported, such as MoS_2 QDs- Fe^{3+} ,³⁷ CdTe QDs- Zn^{2+} ,³⁸ and CDs- Fe^{3+} .³⁹

PPi is an important anion in multiple biological and metabolic processes, and monitoring PPi is essential for physiological functions. As shown in Figure 2D, PPi sensing by MoO_x QDs was developed using Fe^{3+} as a quenching agent.⁴⁰ Fe^{3+} was pre-added in the MoO_x QDs solution, leading to the aggregation of MoO_x QDs to obtain initially quenched fluorescence. In the presence of PPi, the high formation constants between Fe^{3+} and PPi led to the formation of Fe^{3+} -PPi complex which was then detached from the surface of MoO_x QDs, resulting in the disaggregation of MoO_x QDs and recovery of fluorescence. The authors claimed very high PPi selectivity was achieved without interference from other phosphate analogues or anions including EDTA (Figure 2F). This was a very intriguing result, and it would be interesting to test the response to these anions at different concentrations. Meanwhile, the mechanism of nanoclusters (NCs) acting as recognition elements to detect PPi is similar to that for QDs. Xu et al.⁴¹ proposed a PPi sensor integrating Cu^{2+} as the fluorescence quencher on DNA-stabilized silver nanoclusters (DNA-AgNCs). Due to the strong affinity of PPi towards Cu^{2+} , the fluorescence of AgNCs can be restored, the LOD was 0.28 μM .

Other anions, such as F^- and S^{2-} can also be selectively recognized by nanomaterials. Yang

et al.⁴² prepared a dual-emission Eu-MOF using boric acid ligand as the specific recognition unit for F^- . Because of the strong covalent interaction between boron and F^- , this Eu-MOF detected F^- with high selectivity and showed a low LOD (2 μM). Moreover, Hu et al.⁴³ employed MIL-53 (Fe)/kójic acid (KA)-Cu NCs complex for selective detection of S^{2-} in many other different ions based on the Fe-S bonds between S^{2-} and MIL-53 (Fe), thus generating a “turn-on” fluorescence signal (Figure 2G). This S^{2-} sensor displayed a low LOD of 18.6 nM and a wide linear detection range from 0.05 to 5 μM .

Based on the current literature, these sensors can achieve high sensitivity due to the strong binding affinity between target anions (phosphates, F^- and S^{2-}) and certain metal ions. While high specificity was often claimed in the papers, the use of such sensors in real samples needed to be further verified. Such inorganic binding reactions may suffer from competition by similar anions (e.g. by different phosphate species), or from interference by cationic species. For example, if both Fe^{3+} and Cu^{2+} have very high affinities to PPI, then the presence of these anions in a sample can mask PPI. Thus, extra care needs to be taken to ensure that samples are free of such potential interferences.

2.2 Detection of cations

Hg^{2+} is one of the most toxic heavy metal pollutants. So, the development of highly selective nanomaterials to identify and detect Hg^{2+} is needed for environmental protection. Numerous biosensors and small molecular ligands were reported for Hg^{2+} detection.^{44,45} Here, we only review examples using nanomaterials. Hg^{2+} monitoring based on GMP-Tb-luminol fluorescent nanomaterials was reported by Lv et al.²⁶ As shown in Figure 3A, both GMP and luminol are synergistically linked to Tb^{3+} as ligands. When Hg^{2+} was added, the higher coordination strength between Hg^{2+} and GMP inhibited energy transfer from GMP to Tb^{3+} and decreased Tb^{3+} luminescence. Meanwhile, the fluorescence of luminol increased because of the aggregation-induced emission phenomenon. This Hg^{2+} sensor exhibited an excellent linear range from 5 nM to 130 μM with a low LOD of 1.3 nM. Lu et al.⁴⁶ also designed a fluorescent assay for rapid detection of Hg^{2+} using $CH_3NH_3PbBr_3$ perovskite QDs based on a surface ion-exchange mechanism. The presence of Hg^{2+} caused fluorescence quenching of the $CH_3NH_3PbBr_3$ QDs and a blue shift with increasing concentrations of Hg^{2+} , which was attributed to a partial replacement of Pb^{2+} on the surface of $CH_3NH_3PbBr_3$ QDs by Hg^{2+} . This method showed excellent sensitivity and a low LOD down to 0.12 nM in the detection range up to 100 nM. Other metal ions including Cd^{2+} , Pb^{2+} , and

Cu^{2+} had no effect on the fluorescence of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QDs, indicating high selectivity for Hg^{2+} detection. In addition, Zhang et al.⁴⁷ developed a bifunctional strategy for highly selective and sensitive determination of Hg^{2+} using cytidine stabilized AuAg NCs as fluorescent “turn-off” probes (Figure 3B). The sensing mechanism was based on high-affinity metallophilic Hg^{2+} - Ag^+ interactions, which effectively quenched the fluorescence of the AuAg NCs. The AuAg NCs showed high selectivity and a rapid response for Hg^{2+} recognition over other metal ions, and the LOD was 30 nM. The US EPA defined toxic level of Hg^{2+} is 10 nM in water and to be practically useful, sensors need to have a LOD in the ~ 1 nM range.

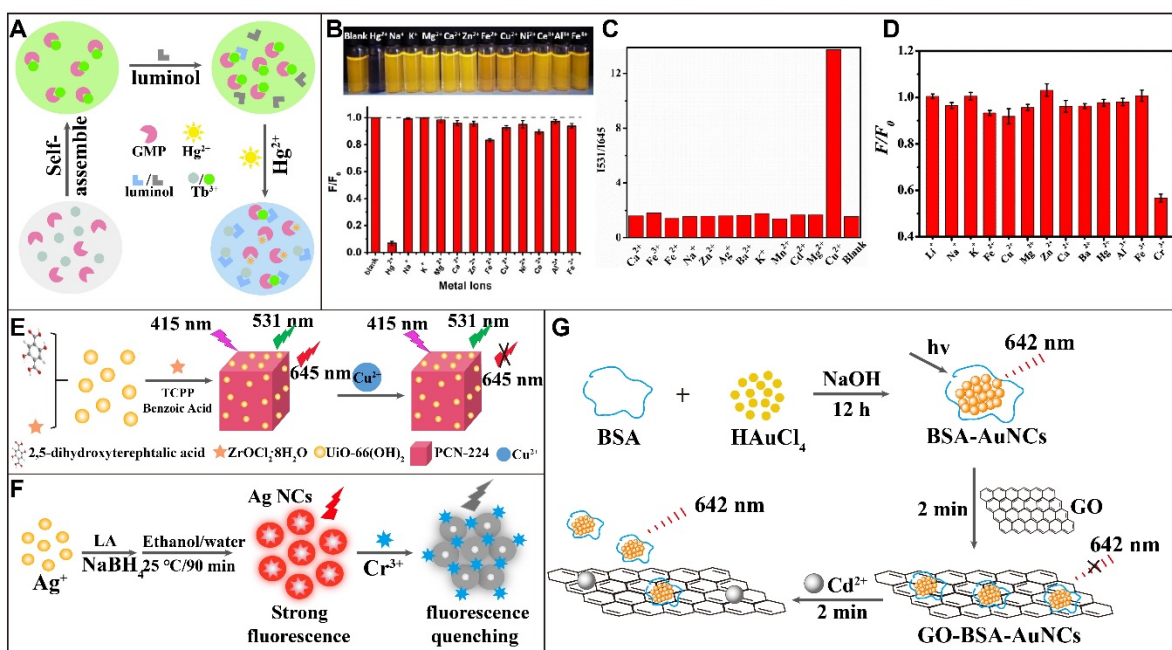


Figure 3. Examples of sensors for cations detection. (A) Hg^{2+} monitoring based on the GMP-Tb-luminol fluorescent nanomaterials. Reprinted with permission from [26] Royal Society of Chemistry, Copyright 2020. (B) AuAg NCs as a fluorescent “turn-off” probe for highly selective determination of Hg^{2+} . Reprinted with permission from [47] Elsevier, Copyright 2015. (C) (E) Fluorescent PCN-224 for Cu^{2+} recognition based on fluorescence quenching. Reprinted with permission from [49] American Chemical Society, Copyright 2019. (D) (F) Fluorescence AgNCs are used for selective sensing of Cr^{3+} . Reprinted with permission from [53] Springer Nature, Copyright 2019. (G) BSA-Au NCs-GO as a “turn-on” fluorescent probe for specific detection of Cd^{2+} . Reprinted with permission from [54] John Wiley and Sons, Copyright 2018.

Cu^{2+} is a very important element in all living things, and it is used by many enzymes as a cofactor. However, excessive Cu^{2+} in the body is harmful and can lead to a series of diseases such

as Wilson's disease, Alzheimer's disease, and Menkes syndrome.⁴⁸ Fluorescent MOFs for Cu^{2+} recognition usually relied on fluorescence quenching. As shown in Figure 3E, Chen et al.⁴⁹ fabricated a ratiometric fluorescent MOF probe by encapsulating green-emission UiO-66(OH)_2 into the red-emission porphyrin MOF (PCN-224). The recognition mechanism was that Cu^{2+} can selectively quench the fluorescence of PCN-224 (Figure 3C), showing the excellent performance in detecting Cu^{2+} with a LOD as low as 0.07 nM. Similarly, Zhou et al.⁵⁰ synthesized CDs-PCN-224 fluorescent probes for monitoring Cu^{2+} with a LOD of 44 nM. Furthermore, Ma et al.⁵¹ reported a Ag(I)-Ln(III)-MOF for selective Cu^{2+} detection. A possible mechanism is that the interaction between Cu^{2+} and the oxygen atoms in the ligand reduced the antenna effect of the ligand, leading to quenching of the luminescence.

Recognition of other metal ions such as Pb^{2+} , Cr^{3+} and Cd^{2+} by fluorescent nanomaterials has also been reported. For example, Ali and co-workers⁵² developed fluorescence GSH-QDs for selective sensing of Pb^{2+} . In the presence of Pb^{2+} , the QDs aggregated and the fluorescence was quenched, which was attributed to competitive GSH binding of Pb^{2+} , changing both the surface and photophysical properties of the QDs. Ren et al.⁵³ found that Cr^{3+} can interact with AgNCs and quench its fluorescence quickly (Figure 3F). Since paramagnetic Cr^{3+} can be adsorbed on the surface of AgNCs through electrostatic interactions, it triggered a conformational change of the ligands on the surface of the AgNCs and its aggregation, resulting in fluorescence quenching (Figure 3D). The fluorescent AgNCs probe had a linear range from 2 to 40 μM and the LOD was reported to be 0.71 μM .

In addition, Ju et al.⁵⁴ reported the BSA-Au NCs-GO as a "turn-on" fluorescent probe for selective detection of Cd^{2+} . The recognition mechanism is related to the adsorption of GO to Cd^{2+} . As shown in Figure 3G, due to the chelation of Cd^{2+} with the oxygen atom of GO, Cd^{2+} formed a more stable complex on the GO surface than with the BSA-Au NCs, displacing the BSA-Au NCs from the GO surface and recovering the fluorescence of the Au NCs. Furthermore, Xie et al.⁵⁵ fabricated a sensing platform for As(V) determination employing $\text{NH}_2\text{-MIL-88(Fe)}$ as a fluorescent probe. Owing to the specific interactions between As(V) and $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ clusters inside $\text{NH}_2\text{-MIL-88(Fe)}$, the fluorescence of $\text{NH}_2\text{-MIL-88(Fe)}$ was significantly enhanced with a fast response time (<1 min). This sensor had a broad linear range (0.1-50 μM) and a high sensitivity (LOD 4.2 ppb) along with excellent anti-interference ability against a series of competing ions.

2.3 Detection of other analytes

In addition to the specific recognition of anions and cations, the selective detection of other analytes including biomacromolecules, small molecules and stereoisomers have also been explored. For instance, as shown in Figure 4A, He and co-workers⁵⁶ fabricated Ni^{2+} -AuNCs for turn-on fluorescence response of histidine. This sensor exhibited excellent selectivity against other amino acids. The fluorescence of AuNCs was first quenched by Ni^{2+} , and then histidine can recover the fluorescence of AuNCs by binding with Ni^{2+} which then removes it from the surface of the AuNCs.

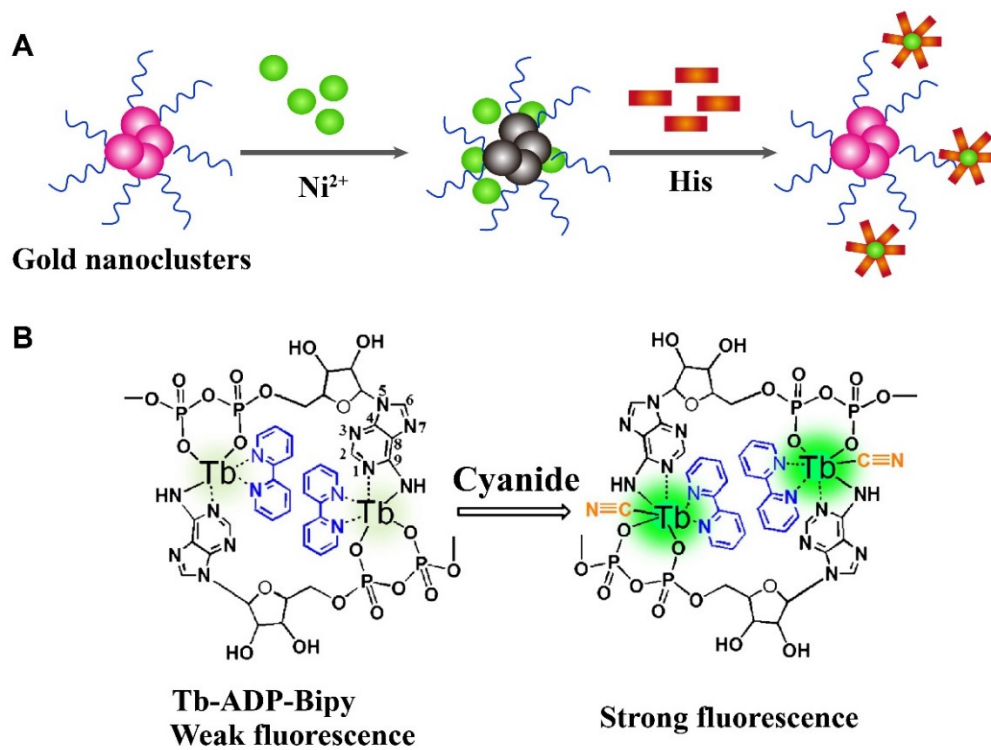


Figure 4. Examples of sensors for the detection of other analytes. (A) Ni^{2+} -AuNCs for fluorescence turn-on response of histidine. Reprinted with permission from [56] Royal Society of Chemistry, Copyright 2012. (B) Tb-ADP-Bipy MOF as a fluorescent probe for the specific identification of cyanide. Reprinted with permission from [58] Springer Nature, Copyright 2017.

Recently, MOFs were proposed for the specific detection of stereoisomers. Han et al.⁵⁷ proved that chirality can be introduced into a Zn-MOF *via* a cation exchange strategy, thus endowing chiral centers in the pore of Zn-MOF. The Zn-MOF showed enantioselective luminescence sensing for stereoisomers, and it was further verified in cinchonine and cinchonine epimers and amino alcohol enantiomers.

Furthermore, small molecules of catecholamines such as dopamine (DA) are also selectively recognized by nanomaterials. Specifically, Ma et al.²⁴ synthesized cysteine-stabilized MnO₂ QDs (Cys-MnO₂ QDs) for selective DA detection. In the presence of DA, Cys-MnO₂ QDs catalyzed the self-polymerization of DA to form polydopamine nanoparticles (PDA NPs). The fluorescence resonance energy transfer (FRET) between MnO₂ QDs and PDA NPs led to the fluorescence quenching of the MnO₂ QDs. This DA sensor showed a wide detection range from 0.1 to 200 μ M with a low LOD of 28 nM.

Moreover, the specific identification of cyanide with fluorescent MOF was reported by Wang et al.⁵⁸ As shown in Figure 4B, they designed Tb-ADP-Bipy MOFs as a fluorescent probe. Cyanide can strongly increase the fluorescence of the Tb-ADP-Bipy MOFs due to extended π -conjugation between the MOFs and cyanide. This assay exhibited excellent selectivity and sensitivity to quantify cyanide with a LOD of 30 nM.

3. Target recognition based on regulation of nanozyme activities

Enzymes are a major class of biosensing molecules and they are commonly used to detect their substrates. The most famous example is probably the detection of glucose by glucose oxidase.⁵⁹ Other analytes such as lactate and cholesterol can also be detected using their enzymes. In recent years, nanozymes have been discovered to show molecular recognition performance.⁶⁰⁻⁶² Generally, molecular recognition is achieved by the regulation of nanozyme activity by target analytes. Owing to the diversity of surface properties of nanozymes, there may be various interactions between nanozymes and different analytes such as small molecules, ions or biomacromolecules. Inhibition or promotion of catalytic activity of nanozymes will lead to a change in signal, thus indicating different concentrations of analytes.¹⁴ Nanozymes as recognition elements have great prospects, and a large number of studies on colorimetric sensing are emerging. To date, such sensing nanozymes can be broadly classified into the following categories: (1) carbon-based nanozymes, such as fullerenes and their derivatives, graphene and its derivatives, carbon nanotubes and other carbon-based nanomaterials; (2) noble metal based nanozymes, including gold, silver, platinum and palladium; (3) metal oxide-based nanozymes, such as CeO₂, Fe₃O₄, and MoO₃; and (4) MOF nanozymes.

3.1 Carbon-based nanozymes

In recent years, carbon-based nanozymes have served as novel molecular recognition elements for different analytes.⁶³ Carbon-based nanozymes show unique interactions and chemical reactions with various molecules, which can change the surface states of nanozymes, affected their activity, and allowed them to be used as recognition elements.^{64,65} A common recognition mechanism is analytes induced inhibition of nanozyme activity. As shown in Figure 5A, Huang et al.⁶⁶ prepared peroxidase-like activity of carbon dots (CDs), which can catalyze the oxidation of chromogenic substrate 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H₂O₂ to produce a blue product (oxTMB). In the presence of ATP, the catalytic activity was significantly inhibited leading to a colorless solution. This colorimetric assay of ATP realized a broad linear range (0.05–2.0 μM) and a low LOD of 34 nM. The authors believed that ATP can inhibit the production of hydroxyl radicals catalyzed by CDs. However, the exact molecular mechanism was unclear since ADP and GTP showed much lower responses.

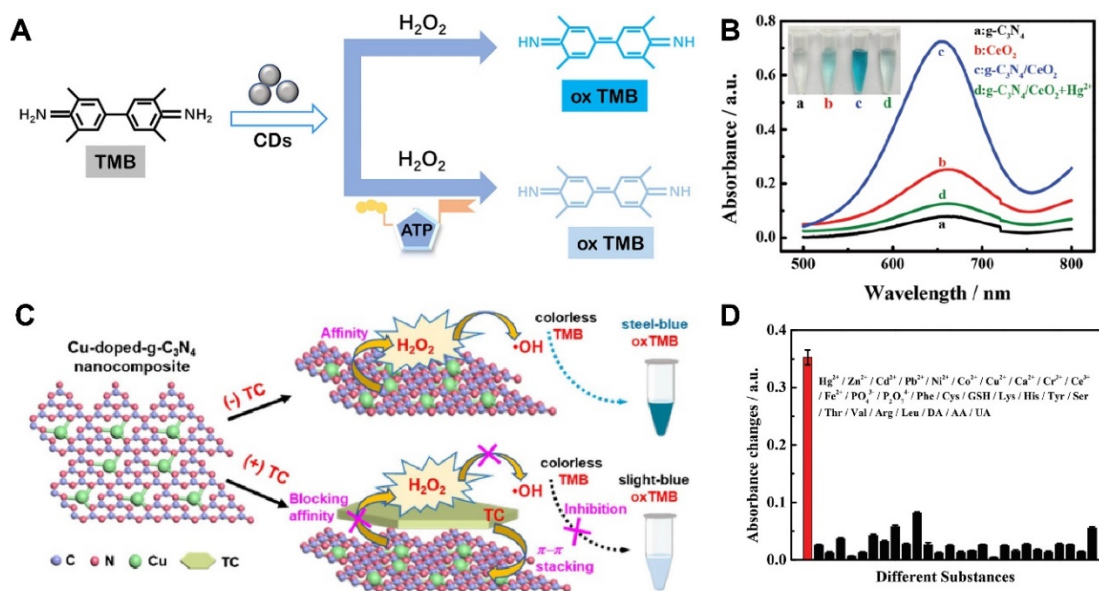


Figure 5. Examples of sensors based on carbon-based nanozymes. (A) Peroxidase-like activity of CDs as recognition elements for ATP detection. Reprinted with permission from [66] Elsevier, Copyright 2022. (B) Comparative experiment on the inhibitory effect of Hg²⁺ on the activity of g-C₃N₄/CeO₂ nanozyme. (D) The selective response of g-C₃N₄/CeO₂ nanocomposites to Hg²⁺ in the presence of other interfering substance. Reprinted with permission from [67] Royal Society of Chemistry, Copyright 2020. (C) Cu-g-C₃N₄ nanozyme for specific identification of tetracycline by the blocking effect. Reprinted with permission from [19] Springer Nature, Copyright 2022.

Zhao et al.⁶⁷ synthesized g-C₃N₄/CeO₂ nanocomposites for selective colorimetric analysis of Hg²⁺ in blood and in wastewater. In the presence of Hg²⁺, due to the strong interactions between Hg²⁺ and the nitrogen atoms in g-C₃N₄, the g-C₃N₄/CeO₂ nanozyme was aggregated and its activity was inhibited (Figure 5B). The selective response of g-C₃N₄/CeO₂ nanocomposites to Hg²⁺ was further verified in the presence of other interfering substance (Figure 5D). Shen et al.¹⁹ employed Cu-g-C₃N₄ nanozyme for specific identification of tetracycline (TC) residues in milk. As shown in Figure 5C, Cu-g-C₃N₄ shows excellent peroxidase-like activity. Owing to the blocking effect caused by the π - π stacking interaction between the TC tetraphenyl skeleton and the Cu-g-C₃N₄ nanozyme, the catalytic activity was inhibited and the color of the solution faded with the increase of TC concentration, and the LOD reached 86 nM.

3.2 Noble metal-based nanozymes

Gold nanoparticles (AuNPs) have intense red color visible to the naked eyes. At the same time, AuNPs can easily adsorb proteins, bacteria, cells and other biological molecules,⁶⁸ making AuNPs a good candidate for molecular recognition and visual detection. When an analyte interacts with AuNPs, it may cause aggregation of AuNPs, resulting in a color changing from red to blue or purple. In recent years, molecular recognition based on this mechanism has been widely reported.^{69,70}

AuNPs have also been widely reported as a nanozyme with glucose oxidase⁷¹ and peroxidase like activities.⁷² When it recognizes analytes, the catalytic activity of AuNPs is either enhanced or suppressed, thus realizing selective detection. For example, Zhao et al.⁷³ found that SO₄²⁻ can induce aggregation of cysteamine-modified AuNPs (cyst-AuNPs) through hydrogen bonding and electrostatic interaction, thus suppressing the peroxidase-like activity of cyst-AuNPs (Figure 6A). The specific interaction between SO₄²⁻ and cyst-AuNPs provides excellent selectivity for SO₄²⁻ recognition (Figure 6B). Based on this principle, the LOD reached 0.16 μ M SO₄²⁻. Singh et al.⁷⁴ reported a colorimetric assay for malathion sensing using palladium-gold nanorods (Pd@AuNRs) as nanozymes. The peroxidase activity of Pd@AuNRs was selectively inhibited by malathion. The specific recognition mechanism was proposed to be the sulfanyl group of malathion interacting with AuNRs, which disturbed the surface charge of the AuNRs and inhibited the peroxidase activity. This malathion sensor displayed a LOD of 60 ng mL⁻¹.

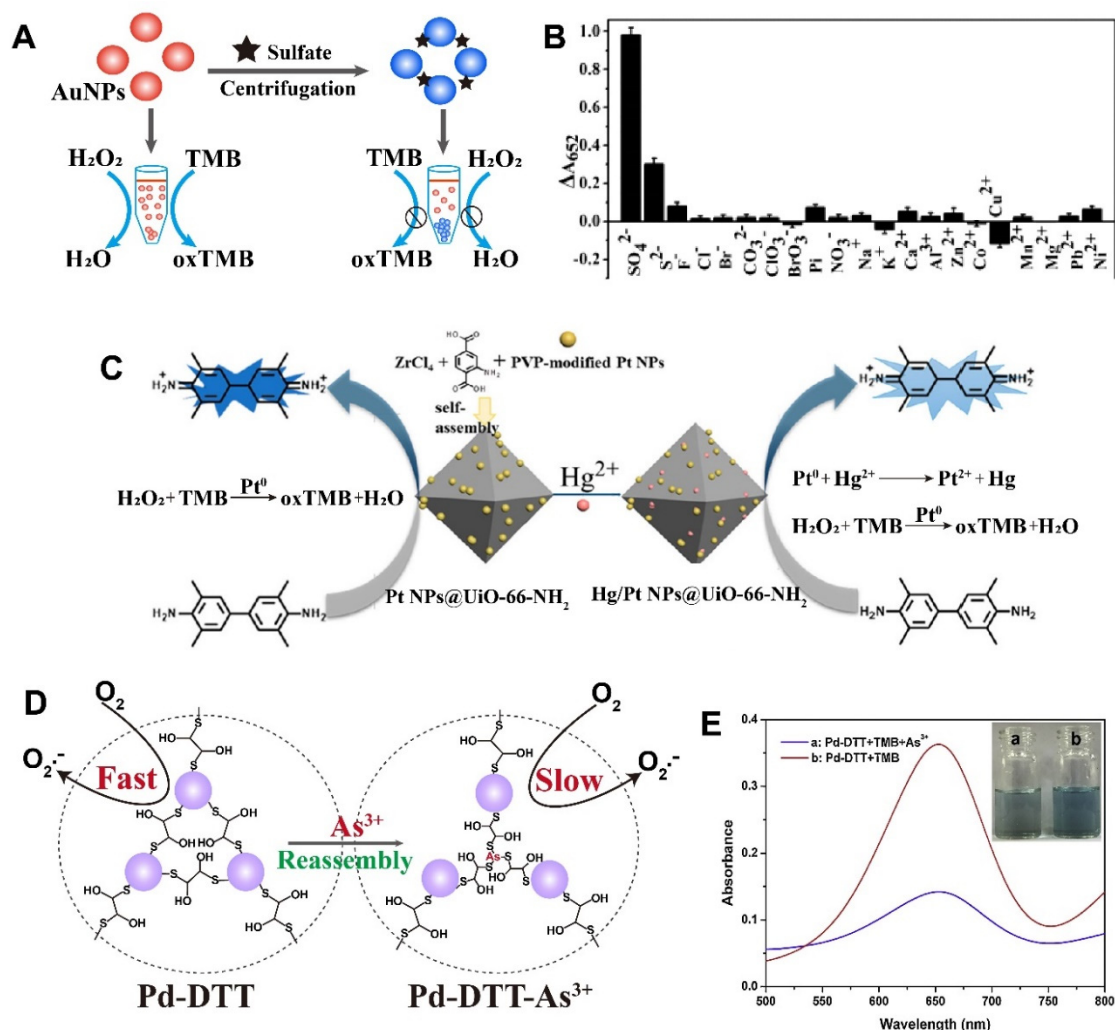


Figure 6. Examples of sensors based on noble metal nanozymes. (A) (B) Selective recognition of SO_4^{2-} based on the specific interaction between SO_4^{2-} and cyst-AuNPs. Reprinted with permission from [73] Elsevier, Copyright 2015. (C) PtNPs@MOF composites for selective Hg^{2+} identification. Reprinted with permission from [75] American Chemical Society, Copyright 2017. (D) (E) Pd-DTT performs As^{3+} detection with suppressed oxidase-like activity. Reprinted with permission from [77] Elsevier, Copyright 2019.

In addition, other noble metal nanozymes (such as Pt, Pd) have also been explored for molecular recognition. For instance, Li et al synthesized PtNPs@MOF composites and applied it for sensitive and selective Hg^{2+} measurement (Figure 6C).⁷⁵ In this system, the MOF was only used as a carrier for the PtNPs. The PtNPs possessed high peroxidase-like activities, enabling the composites to oxidize TMB and generate a colored signal in the presence of H_2O_2 . Interestingly, due to the specific interaction between Hg^{2+} and PtNPs, the nanozyme activity was effectively

suppressed, which endowed excellent selectivity for Hg^{2+} adsorption over the interfering metal ions. This Hg^{2+} colorimetric sensor showed a linear detection range from 0 to 10 nM with a LOD of 0.35 nM. Similarly, Gao et al.⁷⁶ showed a novel Pt nanocubes as an artificial peroxidase for specific colorimetric detection of Ag^+ . The strong binding between Ag^+ and the surfaces of Pt nanocubes inhibited the peroxidase-like activity, thereby achieving Ag^+ detection with a wide dynamic range of 0.01-10 nM. Moreover, Pd nanoparticles with nanozyme activity were also studied. Xu et al.⁷⁷ reported oxidase-like dithiothreitol-capped Pd nanoparticles (Pd-DTT) for As^{3+} identification. As shown in Figure 6D and 6E, Pd-DTT can trigger the oxidation of colorless TMB with the participation of O_2 thus forming blue colored oxTMB. After adding As^{3+} , it can strongly chelate the sulfhydryl groups in DTT, resulting in the reassembly of Pd-DTT and the significant suppression of oxidase-like activity, leading to the discoloration of TMB to realize the specific monitoring of As^{3+} . The assay can detect hypertoxic As^{3+} in environmental samples, showing a wide linear range from 33 ng L^{-1} to 333.3 $\mu\text{g L}^{-1}$ and the LOD was reported to be 35 ng L^{-1} .

In all the abovementioned examples, the catalytic activities were suppressed by the addition of target metal ions. From an analytical standpoint, such signal-off sensors are less desirable compared to signal-on sensors. Some early examples of signal-on detection also existed. For example, Hg^{2+} can significantly enhance the catalytic activity of AuNPs,⁷⁸ resulting in the oxidation of colorless TMB to blue oxTMB. Since the interactions are mostly based on the adsorption of heavy metals such as Hg^{2+} , Ag^+ or As^{3+} to noble metal species, selectivity can be an issue in practical samples when a high concentration of such metals co-exist, especially for sensors based on inhibited activities.

3.3 Metal oxide-based nanozymes

Many nanozymes are metal oxides (such as CeO_2 , Fe_3O_4 , Co_3O_4 , V_2O_5 , CeO_2 , MnO_2).⁷⁹ It was reported that some simple inorganic ions such as PO_4^{3-} can affect the surface charge and catalytic activity of metal oxide nanozymes. Based on this, colorimetric sensors can be constructed to realize the recognition of inorganic ions.

Recently, Yang and co-workers⁸⁰ established a simple colorimetric assay for PO_4^{3-} recognition based on PO_4^{3-} -induced shielding of Fe_3O_4 NPs peroxidase-like activity. As shown in Figure 7A, PO_4^{3-} can be adsorbed on the surface of Fe_3O_4 NPs by coordination with Fe^{3+} , thus blocking the catalytic active site of Fe_3O_4 NPs and inducing a reduced colorimetric signal. Finally, the Fe_3O_4 NPs nanozyme probe exhibited highly selectivity toward PO_4^{3-} over other ions, and the LOD was

as low as 0.11 μM .

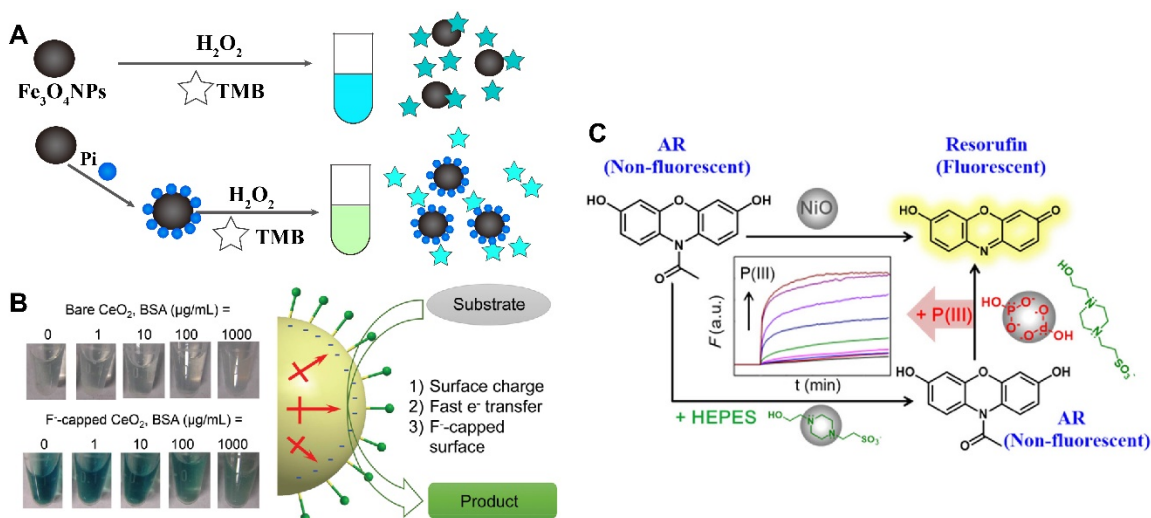


Figure 7. Examples of sensors based on metal oxide nanozymes. (A) Fe_3O_4 NPs are used for PO_4^{3-} selective recognition. Reprinted with permission from [80] Royal Society of Chemistry, Copyright 2015. (B) F^- detection based on promoting the oxidase activity of CeO_2 . Reprinted with permission from [81] Royal Society of Chemistry, Copyright 2019. (C) NiO performs selective recognition of phosphite. Reprinted with permission from [84] American Chemical Society, Copyright 2020.

In addition, F^- can selectively enhance the oxidase activity of CeO_2 nanoparticles in our previous study.⁸¹ The adsorption of F^- effectively alters the surface charge of CeO_2 , thus promotes the substrate adsorption affinity, and electron transfer between substrates, oxygen, and CeO_2 (Figure 7B).^{82,83} Therefore, this mechanism endows a selective assay for F^- determination over other common anions, and the LOD was 0.64 μM .

While most research studies focused on the detection of phosphate, few studied the detection of phosphite, which is also an environmentally important analyte. A few commonly used buffers were screened as inhibitors for the oxidase-like activity of NiO nanoparticles using Amplex red (AR) as a substrate (Figure 7C).⁸⁴ HEPES was found to be an effective inhibitor. Interestingly, phosphite was the only anion that could restore the catalytic activity, likely due to its stronger affinity with the NiO surface and it is not an inhibitor. Under the optimum condition, the sensor detected phosphite up to 1 mM with a LOD of 1.46 μM .

3.4 MOF-based nanozymes

MOFs can also serve as peroxidase mimics due to multivalent metal sites (such as $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Cu}^+/\text{Cu}^{2+}$) in their nanostructures. In addition, the porosity of MOFs is conducive to the enrichment of substrate, thus promoting the interaction between substrate and catalytic active center. By adjusting the types of metal centers and organic ligands, MOFs with different functions can be designed, which provides an opportunity to develop new molecular recognition elements. A mechanism of using MOF nanozymes as recognition elements is that analytes form coordination interactions with metal ions or ligands, thus affecting the nanozymes activity of MOFs.

Based on this principle, a large number of Zr-based MOFs nanozymes have been developed for specific PO_4^{3-} recognition. This type of sensors typically utilizes Zr metal center in MOFs as the PO_4^{3-} binding site, thereby achieving molecular recognition by forming a stable Zr-O-P bonds. For example, Li et al. prepared the UiO-66(Fe/Zr)- NH_2 MOF nanozyme for colorimetric sensing of PO_4^{3-} .⁸⁵ The presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ nodes offer intrinsic mimetic enzyme activity to catalyze the substrate, while the Zr^{4+} nodes act as selective sites for PO_4^{3-} recognition, showing high selectivity and sensitivity, decreasing the LOD down to 85 nM in the concentration range of 0.2-266.7 μM . Similarly, UiO-66(Ce/Zr)⁸⁶ shows oxidase-like active due to $\text{Ce}^{4+}/\text{Ce}^{3+}$ and provides Zr^{4+} sites to specifically recognize PO_4^{3-} . When PO_4^{3-} was present, it rapidly adsorbed onto the oxidized UiO-66(Ce/Zr) and changed the surface chemical properties, leading to different changes in the enzyme-like activity of the oxidized UiO-66(Ce/Zr) on TMB and ABTS (Figure 8A). MOF-808(Zr/Ce)⁸⁷ nanozymes were also reported for selective PO_4^{3-} determination.

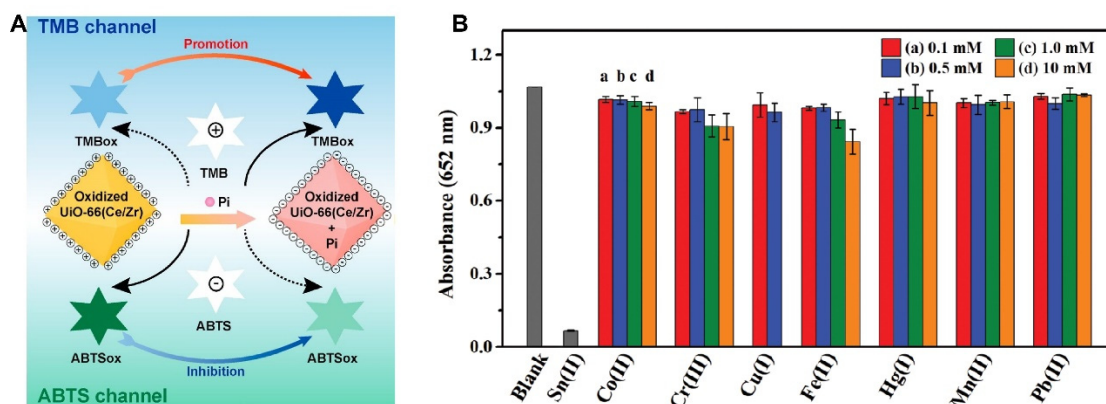


Figure 8. Examples of sensors based on MOF nanozymes. (A) UiO-66(Ce/Zr) shows specific recognition of PO_4^{3-} using Zr^{4+} metal node as the PO_4^{3-} binding site. Reprinted with permission from [86] Elsevier, Copyright 2020. (B) The selectivity of the Fe-Ni-MOF nanozyme for Sn^{2+} detection. Reprinted with permission from [88] Royal Society of Chemistry, Copyright 2020.

In addition, MOF nanozymes have also been used for metal ion recognition. Hu et al.⁸⁸ reported a Fe-Ni-MOF nanozyme with peroxidase-like activity that can perform specific determination of Sn^{2+} . It was proposed that Sn^{2+} can reduce the catalytic activity of Fe-Ni-MOF based on redox interactions, which decreases the color of oxTMB (Figure 8B). The selectivity of the Fe-Ni-MOF nanozyme for Sn^{2+} detection was further evaluated using other interfering ions, and the LOD was 0.36 μM .

4. Sensors based on nanomaterials and extra signaling molecules

In recent years, biosensors based on nanomaterials and fluorescent labeled-DNA have received extensive attention.⁸⁹ The main idea is based on the strong fluorescence quenching performance of nanomaterials and the difference in adsorption capacity of the nanomaterial surface to single strand DNA/unstructured DNA and double strand/folded DNA. These sensors are favored by many researchers⁹⁰⁻⁹² due to their simplicity and low cost. Interestingly, biosensors were also constructed using nanomaterials for target recognition, while DNA only served for signal generation. In some cases, it has also been proved that only nanomaterials can achieve highly specific sensing of various analytes by replacing the pre-adsorbed DNA on the surface of nanomaterials.

4.1. Sensors based on metal oxides

The variety of metal oxide surface properties provides opportunity for molecular recognition. In the past decade, our lab focused on the DNA adsorption/desorption on the surface of various nanomaterials. For example, a fluorescently labeled-DNA is used as a probe, we found that H_2O_2 can specifically displace the adsorbed DNA from CeO_2 nanoparticle.²¹ Further research shows that, H_2O_2 acts as a capping ligand and it is quickly released DNA from the particle surface, generating fluorescence signal for H_2O_2 . The effect of DNA length, sequence, salt concentration, and pH has been systematically studied. Furthermore, the displacement mechanism instead of oxidative DNA cleavage is confirmed by denaturing gel electrophoresis and surface group pK_a measurement. Based on the interaction between H_2O_2 and CeO_2 , we further developed a highly sensitive sensor for H_2O_2 .

Since DNA is a polyanion, DNA-based methods have not been very successful in detecting anions, possibly due to charge repulsion. On the contrary, we discovered that Fe_3O_4 NPs could be used for arsenate detection.²⁰ In this study, Fe_3O_4 NPs adsorb fluorescently labeled-DNA *via* the

backbone phosphate and quench fluorescence, Arsenate displaces adsorbed DNA to increase fluorescence, allowing detection of arsenate down to 300 nM. This is a new way of using DNA for analyte recognition that relies on its phosphate instead of the bases.

It needs to be pointed out that in some cases, even though a specific biomolecule probe is used, the detection could still be due to nanomaterial-based recognition. For example, our lab adsorbed FAM-labeled adenosine aptamer to CeO₂ nanoparticles and found that fluorescence enhancement was observed only with ATP but not adenosine (Figure 9A), although adenosine has even stronger affinity to the aptamer.⁹³ This suggested that the signal was generated due to adsorption of ATP to CeO₂, displacing the aptamer strand. Similar observation was also made with a non-aptamer sequence, where only ATP produced the fluorescence enhancement (Figure 9B). The reason was attributed to the very high adsorption affinity between DNA and CeO₂, and aptamer binding cannot compete with the adsorption. Only when ATP with a triphosphate group was added, ATP can displace the adsorbed aptamer. For surfaces like graphene oxide, its adsorption to the aptamer was weaker and specific aptamer binding related DNA desorption can be observed.⁹⁴

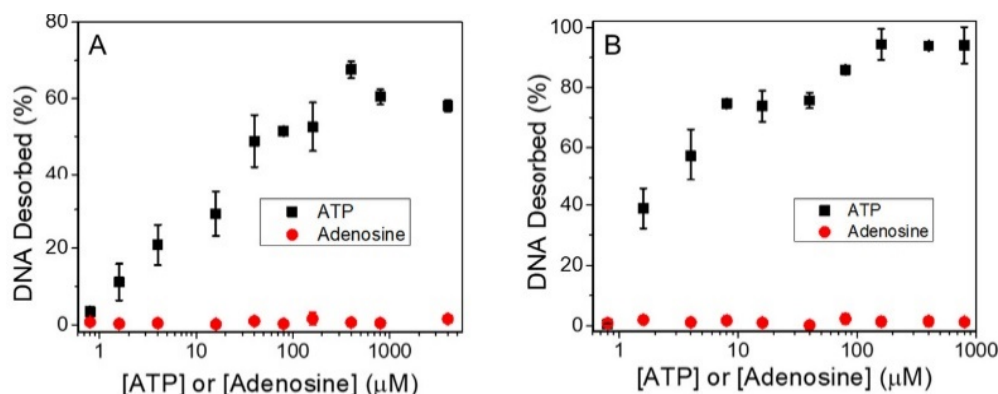


Figure 9. Titration of ATP and adenosine to CeO₂ adsorbed with 50 nM (A) FAM-aptamer or (B) FAM-A₁₅. Reprinted with permission from [93] American Chemical Society, Copyright 2021.

4.2 Sensors based on MOFs

Currently, most ATP biosensors relied on an aptamer, which can hardly differentiate ATP from adenosine diphosphate (ADP), adenosine monophosphate (AMP) or adenosine.⁹⁵ In our previous work,⁹⁶ we found that zeolitic imidazolate framework (ZIF)-67 has exceptional selectivity for recognizing ATP, allowing a fluorescently labeled-DNA to be used for signal

generation (Figure 10A and 10B). Surprisingly, the selectivity of ZIF-67 is much better than that of the ATP aptamer. By comparing other materials such as ZIF-8, ZnO and CoO, we supposed that both ligand (2-methylimidazole) and Co^{2+} are required for the selective recognition of ATP. Furthermore, we partially substituted Zn^{2+} in ZIF-8 with other transition metal ions and prepared a series of bimetallic M/ZIF-8 ($\text{M} = \text{Ni}, \text{Mn}, \text{Cu}$).⁹⁷ Interestingly, Cu/ZIF-8 exhibited an ultrahigh selectivity for recognizing pyrophosphate (PPi) among various competing molecules (Figure 10D). The excellent selectivity of PPi was attributed to the higher binding affinity between PPi and divalent copper ion (Cu^{2+}) on the surface of Cu/ZIF-8. It was reported that PPi preferentially binds to Cu^{2+} with a high stability constant (K) ($\log K_{\text{Cu-PPi}} = 12.45$), while orthophosphate has a low affinity to Cu^{2+} .

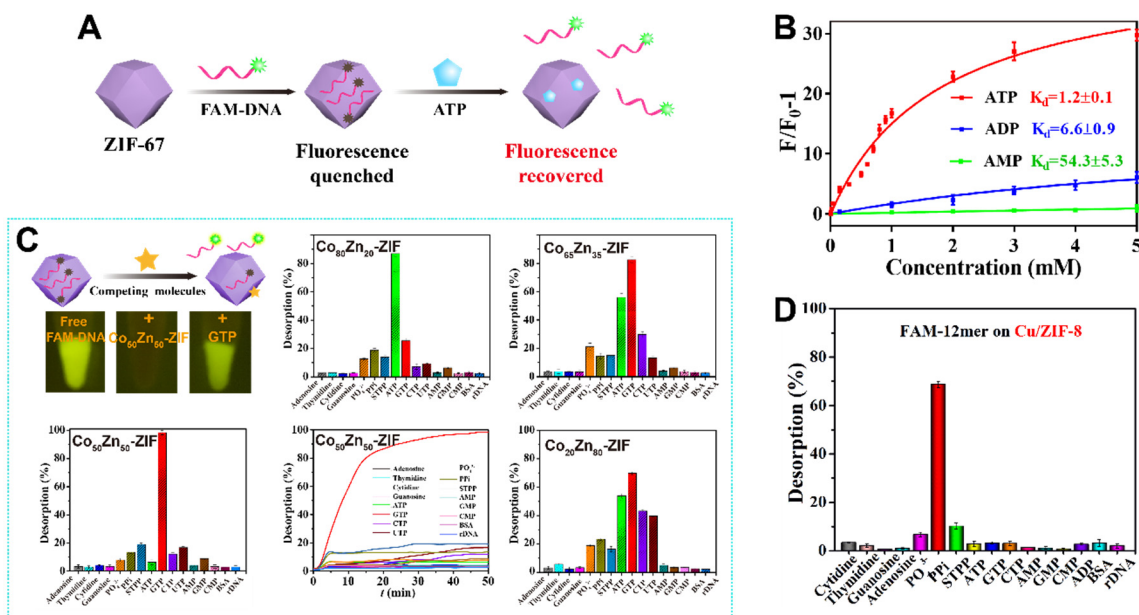


Figure 10. (A) and (B) represent ZIF-67 for ATP selective recognition. Reprinted with permission from [96] American Chemical Society, Copyright 2021. (C) Fluorescently-labeled DNA desorbed from $\text{Co}_x\text{Zn}_{100-x}$ -ZIFs. Reprinted with permission from [98] Elsevier, Copyright 2022. (D) Cu/ZIF-8 for PPi response. Reprinted with permission from [97] Royal Society of Chemistry, Copyright 2022.

Moreover, in another study,⁹⁸ we synthesized a series of homobimetallic $\text{Co}_x\text{Zn}_{100-x}$ -ZIF ($x = 0-100$) by tuning the contents of Co and Zn. Using a fluorescently-labeled DNA as probe, we found that guanosine triphosphate (GTP) can readily displace the adsorbed DNA from $\text{Co}_{50}\text{Zn}_{50}$ -ZIF, while this phenomenon was not found in CoZn-ZIFs with other metal ratios (Figure 10C).

Although we have observed that some MOFs have different molecular recognition behaviors for a variety of analytes, we believe that the selection of changing metal centers, ratios and ligands has an important impact on the properties of the obtained MOFs, and further exploration is still needed in the future.

4.3 Sensors based on metal nanoparticles

Compared to MOF, GO and metal oxides, noble metal nanoparticles such as AuNPs adsorb DNA much more strongly.³ While the sensing scheme in Figure 11A has been used, very few DNA strands can be desorbed by this mechanism due to the very strong affinity of AuNP adsorption.⁹⁹ Given the discussion above, we demonstrated that many of such sensors generated signals due to target adsorption to AuNPs instead of binding to aptamers (Figure 11B). In this case, desorption of DNA was due to competitive target adsorption. For example, adding As(III) to a FAM-DNA/AuNP conjugate can lead to fluorescence enhancement due to competitive adsorption of As(III).¹⁰⁰ For many other analytes, the amount of desorbed DNA was less than 1%.⁹⁹

Similarly, many colorimetric sensors were designed based on the reaction schemes shown in Figure 11C and 11D, where forming aptamer/target complex was believed to inhibit aptamer adsorption. In practice, the mechanisms in Figure 11C and 11D are hard to realize due to adsorption of target analytes by AuNPs. In reality, the major effects were from the adsorption of target analytes to AuNPs (Figure 11E). In some cases, the stability of the AuNPs was not improved or even decreased by the adsorbed target such as adenosine and dopamine.^{101,102} In some other cases, it is also possible to observe enhanced AuNP stability due to the adsorbed target molecules, such as ATP.¹⁰¹ Work has been published on the use of the catalytic activity of AuNPs based on the desorption of aptamers.^{103,104} The main purpose of including these examples here is to articulate that although some sensors were designed to use aptamers for target recognition, the real mechanism could be due to interactions between target molecules and AuNPs, and aptamers played little to no role in signal generation. Of course, such sensors are not really specific, since they were only based on the adsorption affinity and sometimes charge of target molecules, and many other molecules could exhibit even stronger absorption (although they were not tested together).

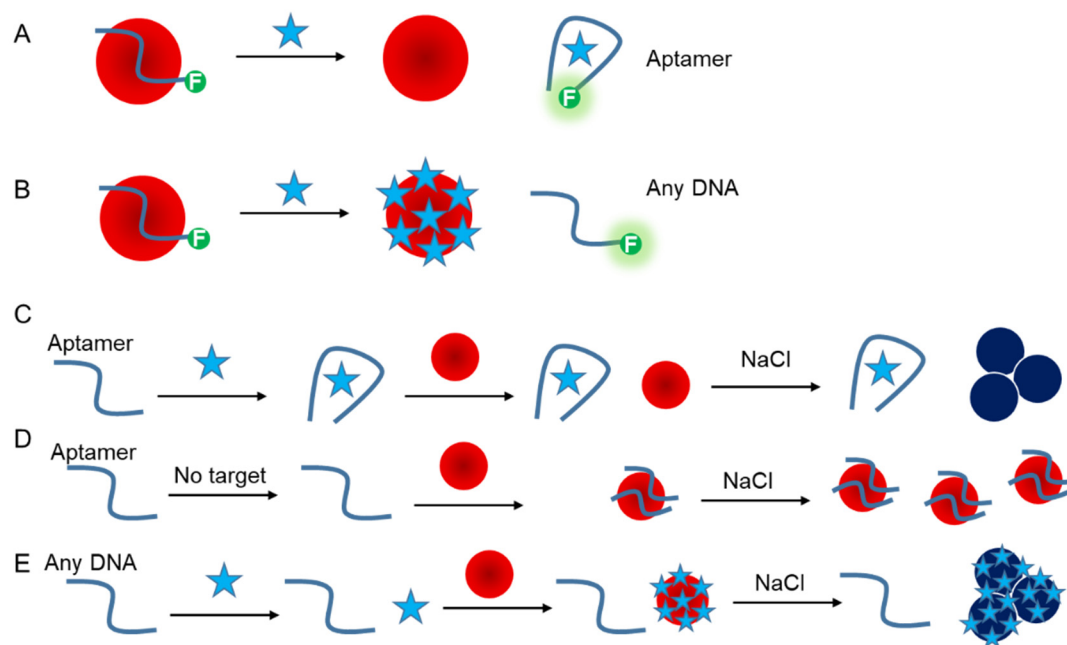


Figure 11. Different types of sensing schemes based on DNA adsorption on AuNPs. (A) The specific binding of target and FAM-aptamer leads to desorption of fluorophore-labeled aptamer from AuNPs for signal recovery. This mechanism is difficult to realize on AuNPs due to very strong adsorption of DNA by AuNPs. (B) The competitive adsorption between target and the pre-adsorbed FAM-DNA on the surface of AuNPs for signal generation. Colorimetric sensors based on (C) aptamer adsorption to protect AuNPs from salt-induced aggregation, and (D) target inhibition of aptamer adsorption. (E) Colorimetric responses based on the aggregation of AuNPs caused by the adsorption of target on the surface of AuNPs, inhibiting the adsorption of DNA.

Summary and future perspectives

We herein reviewed sensors using nanomaterials for target recognition. This is in sharp contrast to biosensors, in which target recognition is achieved using biomolecules. Based on the current literature, nanomaterial-based sensors can take place in at least three forms. First, nanomaterials can specifically adsorb target molecules or react with some components in nanomaterials, resulting in a change in the optical properties of the materials. Second, target analytes can modulate the catalytic activity of nanomaterials. Finally, a signaling probe can be added such as a fluorescently labeled DNA.

So far, most of the studies are for proof of concept. To achieve practical applications of such sensors, interference is a major issue. For most of the detections, selective recognition was

achieved by metal binding by ligands such as phosphate. The relative selectivity of such reactions is well known based on simple inorganic chemistry. Better selectivity might be achieved by tuning the nanozyme activity since in addition to binding affinity, other properties of target molecules such as charge, electronegativity and size might also come into play.

We hope this review has articulated this direction of developing sensing nanomaterials. In future studies, better mechanistic studies are needed to understand the selectivity in affecting nanozyme activities. For example, studying the effect of phosphite on NiO nanozymes, and the effect of fluoride on CeO₂ nanozymes, both of which mimicked oxidase activities. It is intriguing that some MOFs had excellent selectivity for ATP and such understanding can only be achieved via computer simulation. It is also interesting to explore whether better selectivity can be achieved by combining molecular imprinting and incorporating target molecules during the synthesis of the nanomaterials. For example, using molecular imprinting technology to specifically recognize template molecules and preparing specific recognition elements have been demonstrated.¹⁰⁵⁻¹⁰⁷ Furthermore, it is important to fully test promising nanomaterials in real samples. Finally, an interesting idea is to combine sensing nanomaterials with bioprobes for the same target to see if even better selectivity can be achieved.

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