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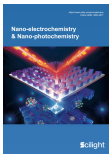

*Review*

# Nanozyme-Based Photoelectrochemical Analysis

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**Abstract:** To achieve the goal of trace analysis in photoelectrochemical (PEC) sensing technology, the rational design of interface function materials to perform efficient target conversions and signal carrier transformations is an urgent need. As promising enzyme mimics, nanozymes enable the reproduction of the enzyme-induced catalytic amplification behaviors and have attracted much interest in sensing applications. Inheriting the merits of nanomaterial science, nanozymes overcome the limitation of poor electroconductivity and fragility of enzymes, showing enhanced and stable signal carrier transduction. More importantly, it brings more opportunities to regulate the carrier transport pathways to improve the signaling. Based on the pace of development in this field, this review provides an in-depth discussion of the signal amplification strategies according to the different functions of nanozymes, including catalyzing signal transduction and tuning carrier migrations. Then, combined with various analytic strategies, high-performance sensing applications were introduced. Furthermore, the challenges and future perspectives were proposed. We hope this review provides valuable information for researchers in related fields regarding the selection and modification strategies of nanozymes, thereby offering new insights for the development of advanced systems.

**Keywords:** photoelectrochemical sensing; nanozyme; signal amplification; interface reaction; carrier migration

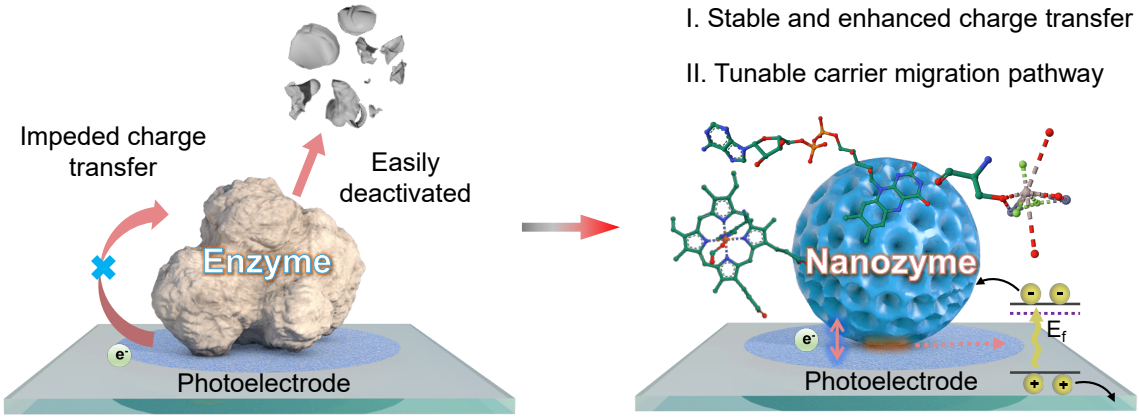
## 1. Introduction

With increasing emphasis on health, safety, and the environment, the requirement for new detection techniques with high sensitivity and universality is strongly demanded [1–4]. In this regard, researchers are dedicated to developing advanced signal amplification strategies to integrate with various signal output models, including colorimetric, fluorescent, electrochemical, and so on, for achieving the goal of high-performance assay of trace analytes. Among them, the fluorescence-based detection method with high sensitivity is commonly limited by a high background signal, leading to reduced accuracy. Notably, photoelectrochemical (PEC) integrates the advantages of the electrochemical and fluorescent methods, and features the separation between the sources of excitation (light) and detection (photocurrent), showing a promising sensitivity and low-background signal [5–9].

Since the inception of PEC analysis, enzymatic reactions have played a crucial role in the construction of photoelectrode transducers, owing to the interface microenvironment changes induced by the transformation of their substrate into products [10]. Typically, enzymes incorporated within the photoelectrode interact with photoactive compounds to induce the direct or indirect quantification of targets. Importantly, due to the superior bioactivity, enzymes are often employed as signal amplification units in PEC sensing platforms, widely employed for target assay in various scenarios [11–13]. However, most natural enzymes are faced with some intrinsic disadvantages, including high cost, poor stability, and rigorous storage conditions [14–16]. Meanwhile, a critical obstacle in the advancement of a proficient enzyme-photoelectrode for biosensing is the poor electron transfer

kinetics between the electrode and the redox cofactor nestled within the enzyme [17,18]. The sophisticated structure of enzymes poses a great challenge in the regulation of the carrier transport. These shortcomings limit the further development and application of the enzyme-based PEC sensors in practice.

Since the discovery of $Fe_3O_4$ nanoparticles with peroxidase-like activity in 2007, research on nanozymes has been steadily advancing. Nanozymes represent a new paradigm capable of replicating the catalytic functions of enzymes [19,20]. Although there is still room for improvement in mimicking enzymes, nanozymes have indeed served as a bridge between materials science and biocatalysis [14,21]. In the field of PEC sensing platforms, the integration of nanozymes has propelled the application of enzyme catalysis on photoelectrodes, fostering the development of innovative electrodes and sensing systems. Skillfully combining nanozymes with optical and electrical properties into the framework of PEC sensing technology not only overcomes limitations in natural enzyme research but also brings more opportunities to regulate the carrier migration pathways [22,23]. In short, nanozymes show higher catalytic stability, improved electron-transfer efficiency, and simpler operability in comparison with natural enzymes. These qualities provide a fresh vision to design efficient signal-amplification strategies of PEC sensors for accessing the goal of trace target analysis (Scheme 1) [24].




**Scheme 1.** Schematic illustration of nanozymes substituting natural enzymes for advantages in PEC sensors.

Given the pace of advances in nanozyme-based PEC sensors, this review will make a thorough discussion and survey on the fundamentals, sensing strategies, applications, and the state of the art in PEC nanozyme sensors. The nanozyme-enabled catalytic signal amplification mechanisms and various methods for regulating carrier migrations were highlighted. Besides, the challenges and prospects in this area are discussed. This work will serve as a useful source to inform the interested audience of the developments in PEC nanozyme sensors.

## 2. PEC Sensing Principle

As depicted in Figure 1, the work mechanism of PEC sensors is based on chemical or biological probing for analyte recognition and PEC-active species for inducing signal transduction [8,9,25]. Similar to a traditional electrochemical device, a three-electrode system in the PEC sensing platform is used to take part in the photoelectric conversion process, thereby generating the photocurrent/photovoltage as a detection signal [26–28]. Specifically, photoactive materials are illuminated by solar light with an energy equal to or greater than their band gap, thus resulting in the separation and transfer of electron-hole pairs (the source of the detection signal) [29–31]. The direct or indirect interaction between the receptors and analytes offers to change the carrier transport efficiency at the photoelectrode/electrolyte interface, thereby enabling quantitative or qualitative target assay [32–34].

In this regard, the construction of high-performance sensing platforms not only requires the rational design of the PEC-active materials for efficient photoelectron conversion but also integrates the efficient interface catalytic reaction for signal amplification [35–37]. As promising enzyme mimics, nanozymes have been widely employed in PEC sensors to perform the function of enzymes for target recognition and catalytic signal amplification. Importantly, the unique physicochemical property endows nanozymes with PEC activity for engineering the signal carrier transports. Such excellent functions bring more opportunities to improve the signal transduction of nanozyme-involved PEC sensing platforms. Therefore, the various signal amplification strategies will be introduced to move toward the goal of trace analysis.

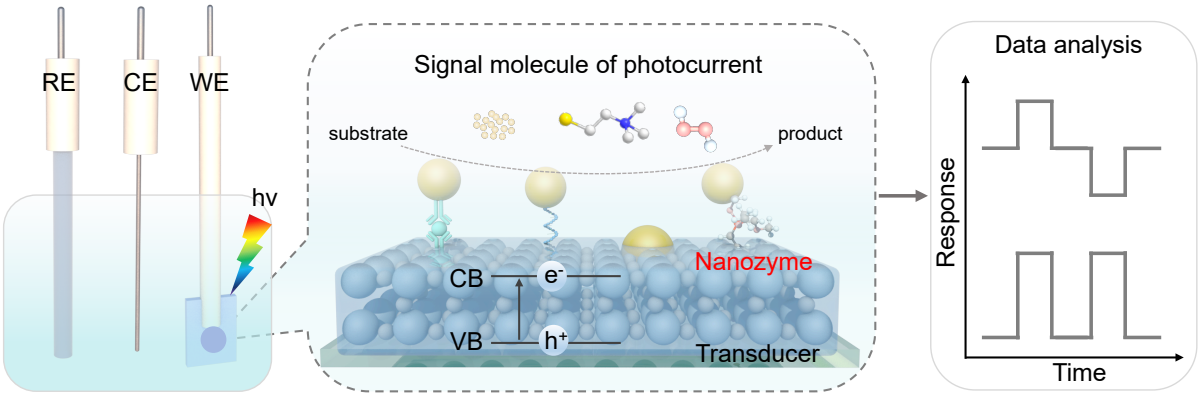



**Figure 1.** Schematic illustration for the general device and working principle of nanozyme-based PEC sensors.

### *2.1. Regulating Interface Catalytic Reactions*

As mimics of enzymes, the key function of nanozymes is the reproduction of the catalytic signal transformations and amplifications. For achieving a high-performance sensing application, the development of nanozymes with excellent catalytic activity and selectivity is of great importance. To date, diverse nanomaterials with different morphologies and dimensions have been explored, including mesoporous-based metal-organic frameworks (MOFs) [38,39], metallic oxide and metal nanoparticles (NPs) [40], carbon-based materials [41,42] and so on. They presented efficient catalytic activity in sensing applications. Notably, single-atom catalysts (SACs) with maximum atom utilization and strong metal-support interfacial interaction enable vivid mimicking of the active centers of enzymes, showing superior catalytic performance. With the development of nanotechnology, nanozymes have reproduced the various catalytic performances of natural enzymes, including oxidase, peroxidase, catalase, superoxide dismutase, hydrolase, lyase, and so on [43–48]. Importantly, they inherit the physicochemical property of nanomaterials, which endows sensing platforms with novel functions to meet the challenging chemical transformations in practice. Motivated by these, nanozymes have been widely employed to engineer PEC sensing platforms to perform the signal transduction function. Briefly, the reactants or products in nanozyme-mediated catalytic reactions can impact the charge transfer efficiency of the photoelectrode/electrolyte interface through electron/hole scavenging or steric hindrance effects. Such effects are capable of enhancing or inhibiting the carrier transports, and thus conversion of target substance information (e.g., concentration) into PEC signals [49–52].

Applying nanozymes with high catalytic activity in PEC sensing systems is akin to using a key that unlocks highly sensitive quantitative and qualitative analysis of various target molecules by modulating the interfacial catalytic reaction. In the current nanozyme-mediated PEC sensing, there are four main kinds of enzymatic reactions involved: oxidase-like reactions, peroxidase-like reactions, catalase-like reactions, and hydrolase-like reactions (Figure 2a). Among them, redox enzymes involve the generation and reaction of hydrogen peroxide ($H_2O_2$), which serves as a typical electron/hole scavenger to facilitate the carrier transfers for achieving the signal amplifications [53,54]. Moreover, the relative redox products can interact with the photoelectrode, becoming critical factors in changing the PEC sensing signal through electron exchange. Similarly, other nanozyme-enabled catalytic reactions can induce more transductions of target molecules for broadening the range of the analytes. Combined with diverse detection strategies to induce changes in catalytic reactions, nanozyme-based PEC sensors have realized efficient analytical applications. The construction strategies and analytical cases of PEC sensors based on nanozymes will provide a detailed introduction in part of sensing applications based on the diversity interaction between the targets and the PEC interface.

### *2.2. Regulating Photogenerated Carrier Migration*

In addition to performing the enzyme-like activity, nanozymes featuring metallic and semiconductor properties play a significant role in improving the inherent photoelectron conversion ability of PEC-active materials. First, as the supporting units, nanozymes enable the formation of Schottky/Ohmic junctions and heterojunctions with semiconductor materials [55–57]. On the one hand, nanozymes with semiconductivity refer to nanomaterials in which electrons in the valence band (VB) can transition to the conduction band (CB) under light excitation. These nanozymes come into contact with semiconductor-modified photoelectrodes and form a strong built-in electric field, which can suppress the recombination of charge carriers and enhance the efficiency of photoelectric conversion (Figure 2bI). On the other hand, the metallic nanozymes were modified on the semiconductor-based photoelectrode, enabling regulation of the energy band structure of semiconductors.

Typically, noble metal NPs, such as gold, palladium, and platinum NPs, and their hybrids [58–61], were introduced and formed a barrier (Schottky junction or Ohmic contact) due to the energy difference between the metal Fermi level and the semiconductor CB or VB (Figure 2bII). It helps to promote the separation of charge carriers in the semiconductor. Apart from this, noble metal NPs with pH-dependent enzyme-like activity hold a crucial position in nanozyme-based PEC sensors. Additionally, the inherent localized surface plasmon resonance effect of noble metal NPs manifests itself at the metal-semiconductor interface, enabling efficient photoelectric conversion at lower voltages and enhancing the efficiency of interface redox reactions [62,63]. Furthermore, some single-atom nanozymes supported on graphite or conductive carbon black substrates form interface potential barriers similar to Schottky junctions when in contact with semiconductors [64–66]. These nanozymes exhibit remarkable capabilities in augmenting the extraction of minority carriers at the solid-solid interface and enhancing the charge injection efficiency at the solid-liquid interface within PEC sensors. Prominent instances encompass single-atom nanozymes harboring metal active centers such as Fe-N-C, Co-N-C, and Ni-N-C, which offer higher cost-effectiveness in the application of nanozyme-enhanced PEC sensing signals [67–70].

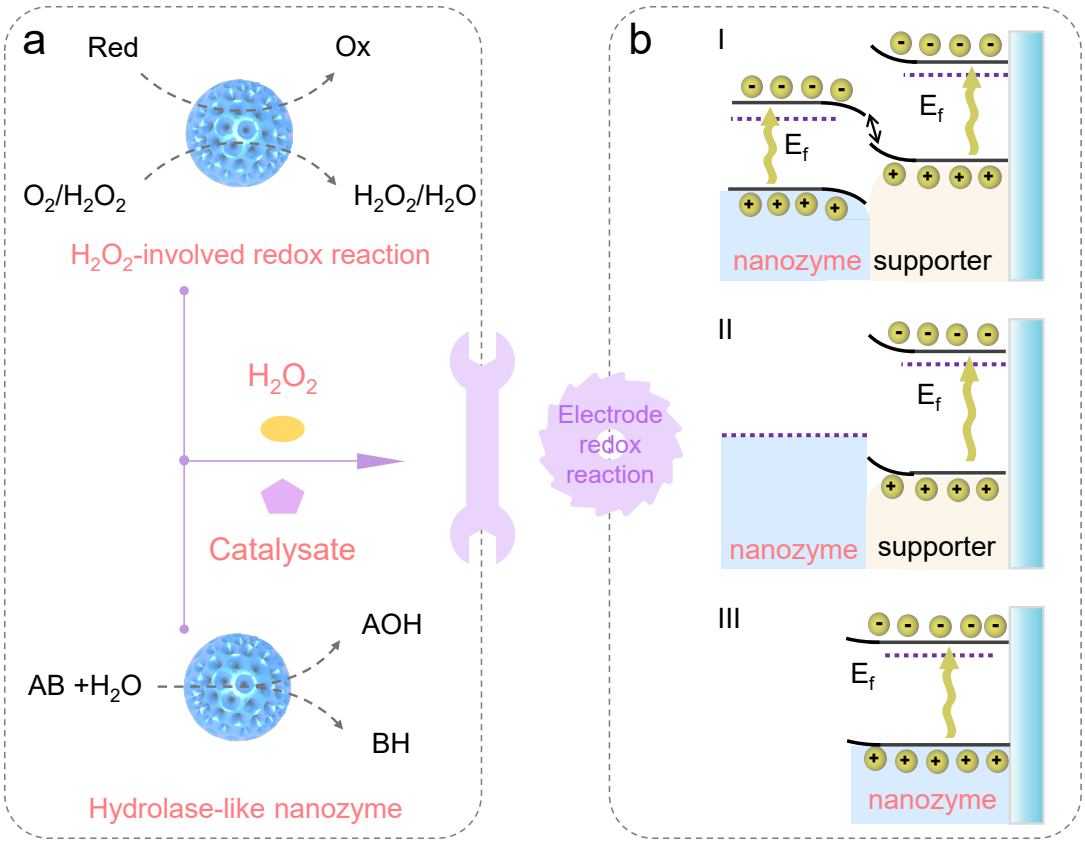



**Figure 2.** (**a**) Nanozyme-induced catalytic reactions for signal transduction; and (**b**) three types of nanozyme-involved photoelectrodes.

Second, by virtue of the semi-conductivity, nanozymes can be directly modified on bare photoelectrodes to generate PEC signals for target analysis, without the help of other photoactive materials (Figure 2bIII). Numerous efforts have been made to engineer semiconductive nanozymes through size and morphology control, surface modification, crystal phase, and defect engineering, etc. [71,72]. These nanozymes can form heterojunctions on photoelectrodes to enhance PEC detection signals, such as the Z-scheme, S-scheme, and P-N junction. Currently, the research of these nanozymes in PEC sensors covers various metal oxides, metal compounds of chalcogenide elements, carbon-nitride materials, and MOFs [73]. Particularly noteworthy are MOFs composed of inorganic and organic modules, which exhibit both molecular and non-molecular dual properties and hold immense potential in mimicking enzymatic functions. Moreover, their band gap theory extends beyond conventional semiconductor physics, as it can be regulated by ligand molecules. This strong adaptability not only improves the PEC efficiency of the photoelectrode but also broadens the range of surface reaction types [74]. In short, nanozyme-enabled PEC materials offer to rationally regulate the carrier migration pathway, resulting in efficient carrier transport on the electrode interfaces. Combining with the superior enzyme-like activity, nanozyme-based PEC sensors realized excellent chemical conversions and signal transduction, affording high-performance analytical applications.

## 3. Nanozyme-Based PEC Sensing Applications

### *3.1. Direct Type*

$H_2O_2$, as the key substrate or product, participates in various analyte transformations. It can work as an electron/hole scavenger to influence carrier transport (Figure 3a). Motivated by these, researchers have yearned to construct nanozyme-involved catalytic systems for inducing the transformation of $H_2O_2$, thus achieving a series of target assays. For instance, Luo's group assembled a Z-scheme composite of polyimide/CdS and showed a peroxidase-like performance [75]. Such properties motivated researchers to integrate the xanthine oxidase (XOD) for building a cascade sensing system. The target molecule (hypoxanthine) is oxidized by XOD, accompanied by the $H_2O_2$ generation. It can be transferred to the superoxide anion free radical ($O_2^{\bullet-}$) based on the peroxidase-like activity of polyimide/CdS. They work as scavengers to promote the separation of carriers, resulting in an enhanced photocurrent response. Coupling with the excellent catalytic performance of natural enzymes, the obtained PEC sensor has realized a sensitive and selective serum hypoxanthine assay with a limit of detection (LOD) of 5.28 μM. Similar to this strategy, various natural oxidases, such as glucose oxidase (GOx), uricase, acetylcholinesterase (AChE), and so on, have been integrated with peroxidase-like nanozymes to construct cascade systems. The constructed sensing platforms enable the realization of a series of small biological molecules and corresponding enzyme activity assays (Figure 3b). For example, Liu et al. synthesized 2D/2D dual-metalloporphyrin MOFs (CuTCPP(Cu)/CuTCPP(Fe)) to fabricate the S-scheme heterojunction [76]. Owing to the improved built-in electric field, the obtained CuTCPP(Cu)/CuTCPP(Fe) exhibits boosted carrier separation and migration ability, resulting in a superior PEC response. Moreover, the CuTCPP(Fe) with enzyme-like active centers shows good peroxidase-mimicking activity. Based on these, the uricase was introduced to construct a cascade catalytic amplification sensor for sensitive detection of uric acid (Figure 4a). Different from the above-mentioned enhancement mode, the CuTCPP(Fe) can oxidize 3,3′-diaminobenzidine into brown precipitation on the photoelectrode surface in the presence of $H_2O_2$, decreasing the PEC signaling. Therefore, the inhibited photocurrent is positively related to the concentration of uric acid, achieving high-performance applications. Notably, Zhu's group reported an AgCu@CuO aerogel, which integrates the photoactive property and peroxidase-like activity [77]. Based on the XOD-peroxidase cascade reaction, the AgCu@CuO-enabled PEC sensor has achieved sensitive evaluation of XOD activity by using a similar inhibition mode. Leveraging the enzyme-nanozyme integrated methods, a series of biological small molecules and corresponding enzyme activity assays have been realized.

Similar to native enzymes, the catalytic performance of nanozymes is pH-dependent. In this regard, the proton concentration has also been employed as the signal transduction factor for establishing a linear relationship between target molecule concentration and the PEC signal [76]. Therefore, researchers have dedicated themselves to combining the enzymatic reaction that can induce substrate conversion and the generation of acidic or basic products. The changed buffer environment can regulate the activity expression of nanozyme for further affecting the PEC signal. A detailed study has been conducted on the Fe SACs as classical peroxidase-like mimics adsorbed on semiconductor photoelectrodes ($Cu_2O/Ti_3C_2T_x$) [50]. Upon photoexcitation, a strong charge transfer mechanism exists between the nanozyme and the semiconductor, greatly enhancing the generation of photocurrent signals, as shown in Figure 4b. The improved signal transduction ability is expected to enable sensitive sensing applications. Here, the acetylcholinesterase (AChE) has been used to hydrolyze acetylcholine (ACh) and generate acetic acid, leading to an increase in solution acidity. It promotes the expression of the peroxidase-like activity of Fe ASCs to oxidize 4-CN for producing the insoluble 4-CD, and thus hinders the PEC signaling. Consequently, the Fe SACs/$Cu_2O/Ti_3C_2T_x$ PEC sensing platform has realized sensitive AChE activity assay in the range from 2 to 500 mU/mL with a limit of detection (LOD) of 0.22 mU/mL (Figure 4c). Furthermore, inspired by the organophosphorus pesticides (OPs) can greatly inhibit the AChE activity for recovering the photocurrent response, the proposed sensor achieved efficient quantification of OPs with an LOD of 0.08 ng/mL (Figure 4d).

Apart from redox enzymes, nanozymes have been reported to reproduce the hydrolase-like catalytic performance. For example, Tan et al. reported that the specific expression of alkaline phosphatase-like activity can be enhanced by controlling the crystal shape of $CeO_2$ [78]. Based on this pH-dependent enzyme-like property and PEC activity of $CeO_2$ (Figure 5a), Zhu's group applied it to evaluate the AChE activity by regulating the pH value in the nanozyme reaction environment (Figure 5b) [79]. Notably, to improve the PEC response, the signal Zn atom was introduced to tune the Fermi level of $CeO_2$. As a result, the doping of Zn enables conversion of the $CeO_2$/g-$C_3N_4$ heterostructure from an inferior type-II to an advanced S-scheme, showing a significantly enhanced photocurrent. The proposed Zn-$CeO_2$/g-$C_3N_4$ achieved a sensitive and selective AChE activity assay in the range of 5–1600 mU $mL^{-1}$.

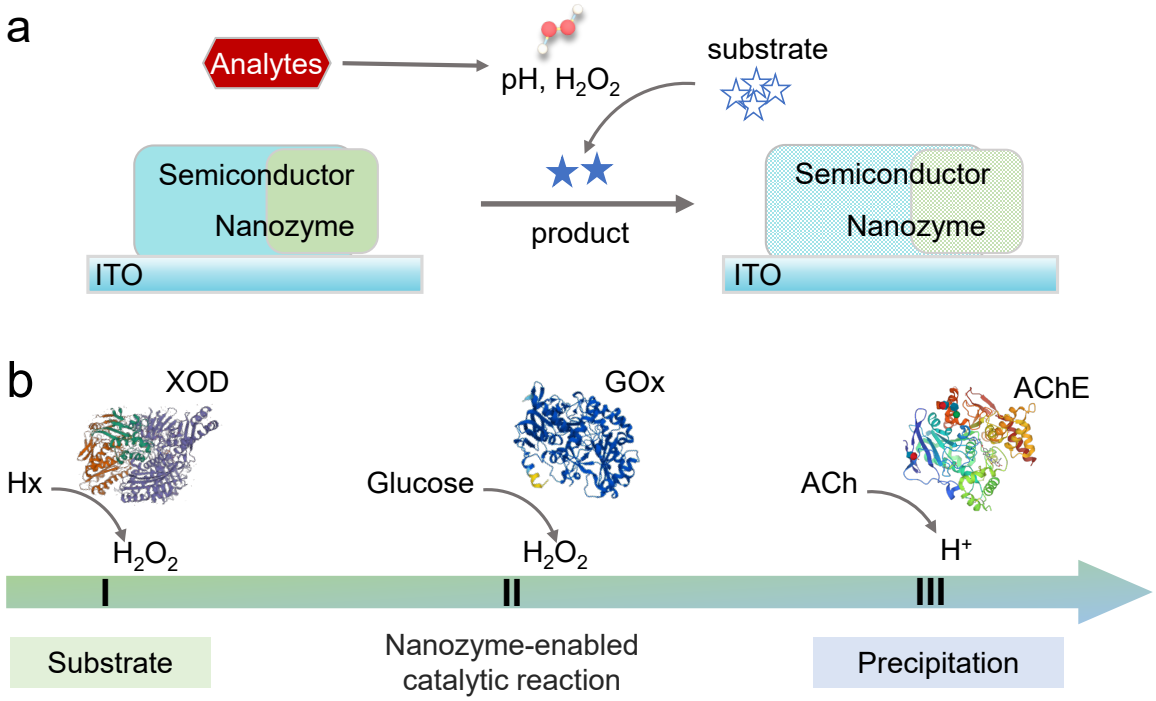



**Figure 3.** (**a**) Schematic diagram of a semiconductor surface adsorbed nanozyme as a photoelectrode transducer; (**b**) Schematic illustration of enzyme-nanozyme cascade reaction for signal transduction.

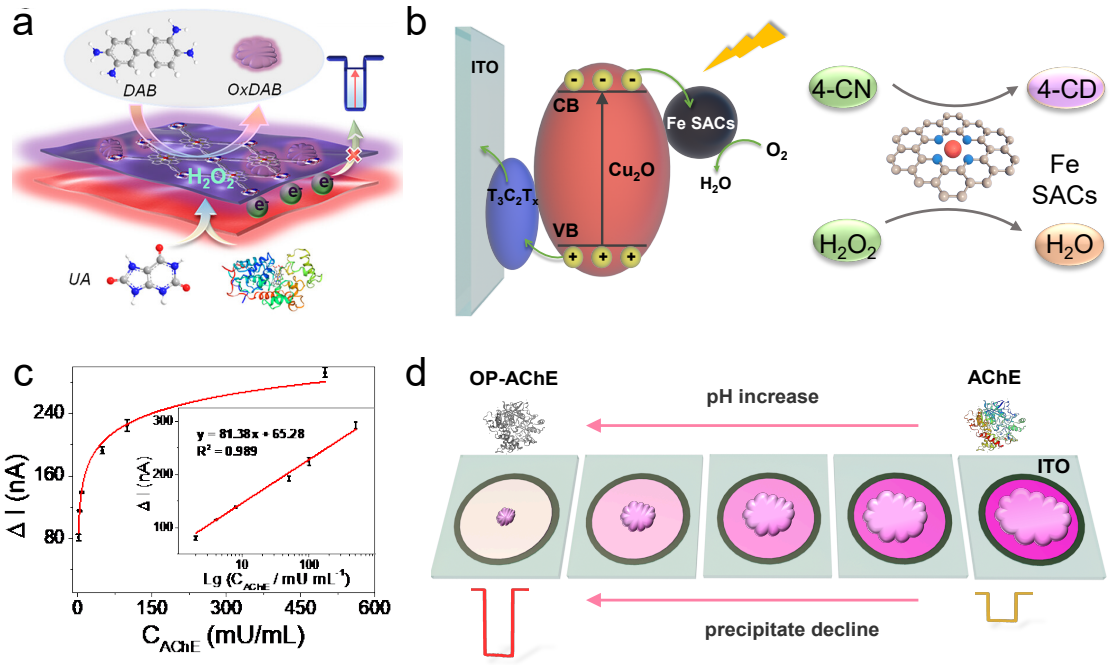



**Figure 4.** (**a**) Illustration of the CuTCPP(Cu)/CuTCPP(Fe)-based sensor for urea acid detection. (**b**) Schematic illustration of the band structure and peroxidase-like activity in nanozyme-photoelectrodes. (**c**) The photocurrent responses of Fe SACs/$Cu_2O$/$Ti_3C_2T_x$-based sensor in different AChE amounts. (**d**) Schematic illustration of the PEC sensing mechanism for OPs.

It should be pointed out that the natural fragility of enzymes limits applications in extreme conditions. To this end, immobilizing enzymes within stable nanomaterials has been recognized as an efficient strategy for improving performance in practice. MOFs with diverse and spatially isolated metal sites have emerged as promising candidates for nanozymes. Meanwhile, their applications have experienced significant growth in the PEC field due to semiconductor-like properties [80,81]. For example, Zhao's group reported the Fe/Co-MIL-88 nanozyme enabling dual-functional photo-induced charge transfer and biomimetic precipitation (BMP) for such a

hypothesis. The presence of the model target adenosine triphosphate (ATP) could lead to the release of GOx labeled aptamer from a magnetic bead, which would enable the GOx production of $H_2O_2$ for the BMP by Fe/Co-MIL-88 [82]. Due to the inhibitive effect of BMP on the PEC signal, the constructed sensing platform realized highly sensitive detection of ATP with the LOD of 125 fmol/L.

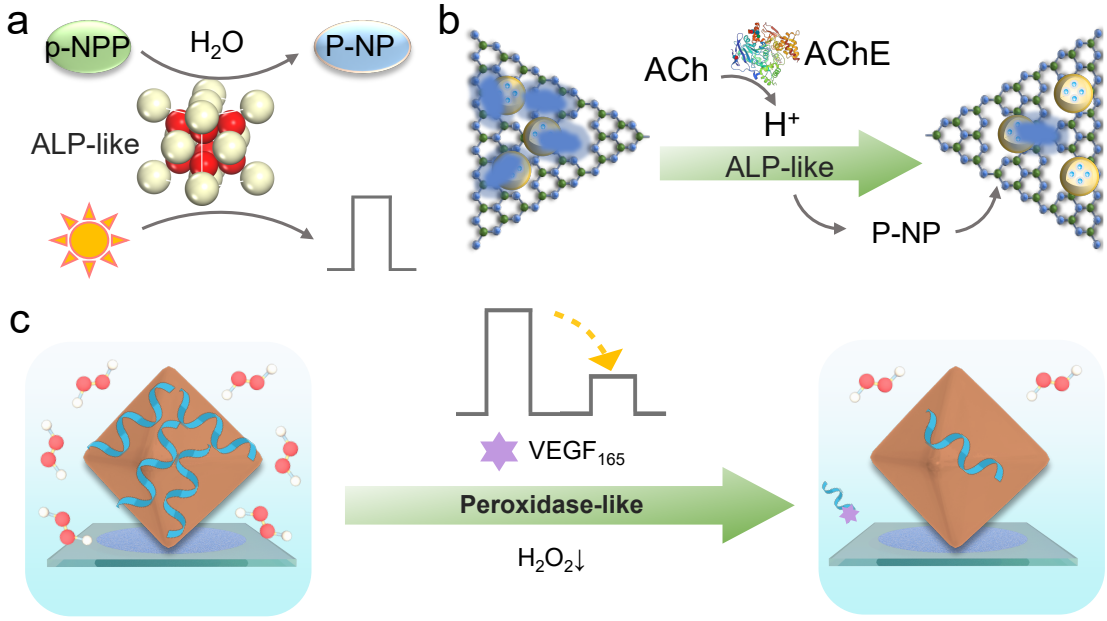



**Figure 5.** (**a**) $CeO_2$ as an ALP mimics to perform a hydrolytic reaction. (**b**) Illustration of Zn-$CeO_2$/g-$C_3N_4$-based sensor for cascade detection of AChE activity. (**c**) The MOF-based nanozyme for a label-free homogenous PEC aptasensing strategy for $VEGF_{165}$ detection.

Additionally, benefiting from the good carrier function of MOFs, Hou and coworkers synthesized PDDA@Fe-MIL-88 nanozymes for immobilization of the aptamer on the surface [83]. The target molecules bind to the aptamers, and the active sites on the MOF surface are exposed, leading to a decrease in the concentration of $H_2O_2$ in the PEC cell. This results in sluggish electrode/electrolyte interfacial reaction kinetics, thereby reducing the generation of photocurrent (Figure 5c). However, this direct method of aptamer analysis has some inherent limitations. $H_2O_2$ serves as both a sacrificial agent on the photoelectrode surface and a substrate in the peroxidase-like reaction. The simultaneous occurrence of these two reactions in the PEC cell can confound the effects of the target molecule, leading to a decrease in the accuracy of detection. Therefore, the following introduces a method of indirectly modifying nanozymes to photoelectrode surfaces using aptamer molecules for quantitative analysis.

### *3.2. Indirect Type*

The utilization of biological/chemical recognition reactions to indirectly establish a connection between nanozymes and photoelectrodes has become an important strategy in current PEC bioanalytical techniques (Figure 6a). Based on the different characteristics of linkers, they can be categorized into three types: nucleic acid-based reaction, nanozyme-linked immunosorbent, and chemical adsorption reaction.

The specific recognition and hybridization reactions of nucleic acid molecules play a crucial role in the signal amplification strategy mediated by nanozymes. They serve as the medium connecting nanozymes and photoelectrodes, forming two types of relationships, promoting and impeding the linking, in target detection. This enables the achievement of signal enhancement or attenuation in the PEC biosensors. Single-stranded DNA (ssDNA) aptamer probes have received considerable attention because of their high specificity, affinity, stability, synthetic availability, and batch-to-batch uniformity [84–86]. As shown in Figure 6b, nucleic acid aptamers with different terminal modifications were successfully connected through the addition of the target substance, effectively immobilizing the nanozyme on the surface of the photoelectrode [52,87,88]. Luo et al. utilized Cu-$C_3N_4$ nanozyme-modified aptamers, Staphylococcus aureus, and aptamers immobilized on the surface of the photoelectrode to form a sandwich structure, enabling quantitative analysis of Staphylococcus aureus [89]. Another method, where the target substance promotes the linking of DNA molecules modified with nanozymes, is also widely applied in PEC sensing. As depicted in Figure 6c, the target substance initiates a chain reaction of nucleic acid hybridization, resulting in the release of additional single or double-stranded DNA molecules capable

of binding to the nanozyme. Subsequently, these DNA molecules, labeled by nanozymes, are immobilized on the photoelectrode through DNA hybridization [90–92]. As an example, Jiang et al. utilized a target microRNA to construct a bipedal DNA walker, enabling the activation of the S1 hairpin probe that had been modified on the photoelectrode. This interaction facilitated the binding of the photoelectrode with the S2 probe, which possesses the ability to adsorb Au@Ag@CDs nanozymes [93].

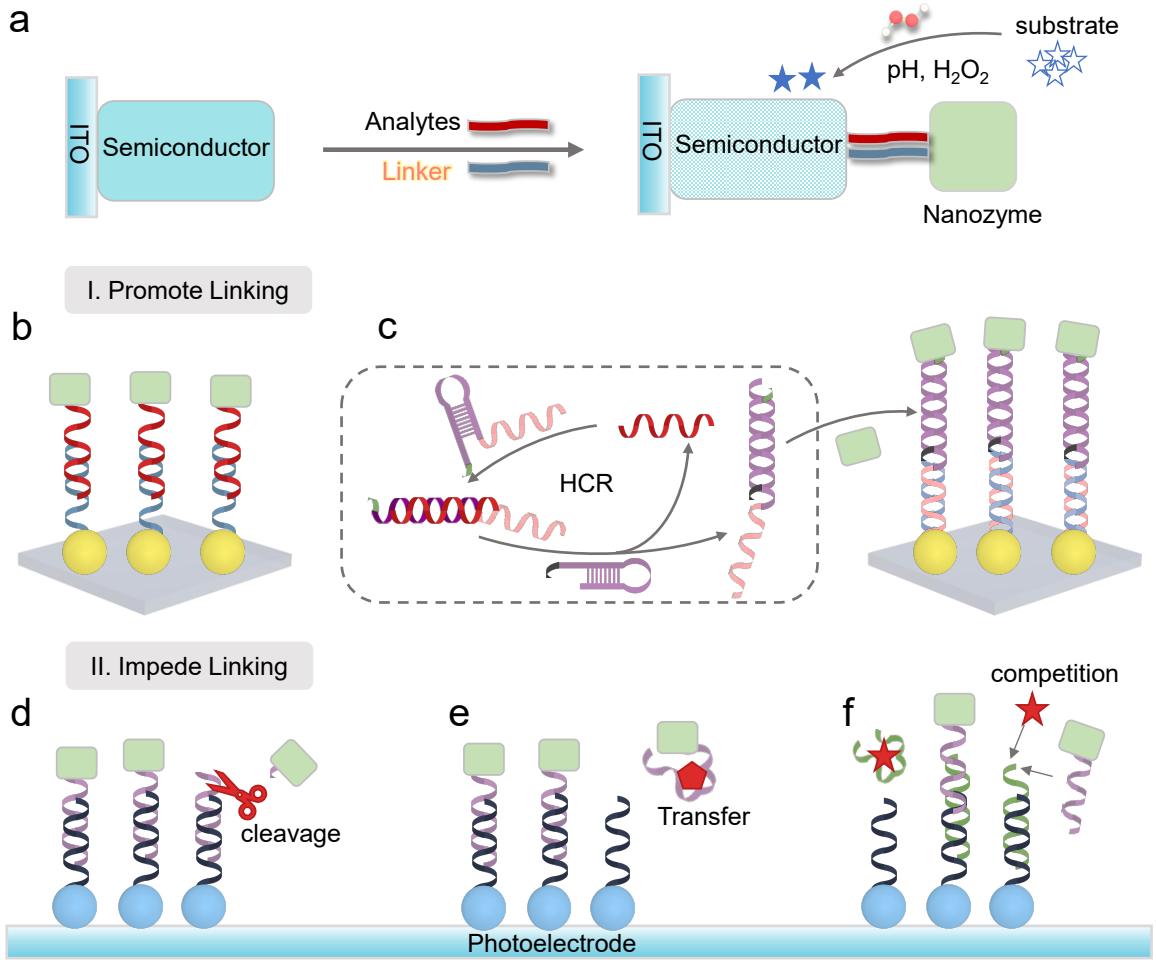



**Figure 6.** (**a**) Schematic diagram of nanozymes immobilized on the surface of a photoelectrode through linkers. When the nucleic acid reaction is employed as a linker, two types of nanozyme-PEC sensors emerge: target-induced (**b**,**c**) promote linking and (**d**–**f**) impede linking.

Regarding the impediment relationship between the target and the linking behavior, three strategies were identified, namely cleavage, transfer, and competition. The common feature shared by these strategies is the initial modification of the photoelectrode surface by the nanozyme through a DNA hybridization reaction, followed by the disruption of their linking upon the presence of a target object. The case study of detecting boromycin (BLM) using the Au/$WS_2$ photoelectrode-$DNA_1$-$DNA_2$-Ag/ZnMOF nanozyme sensing structure constructed by Lu's group successfully exemplified the cleavage strategy (Figure 6d). In the presence of BLM, an oxidation reaction occurs, leading to the irreversible cleavage of $DNA_2$ with $Fe^{2+}$ as a cofactor. This cleavage event results in a decrease in electrode surface precipitation and the generation of an enhanced PEC signal [94,95]. The second strategy, transfer, is based on the specific recognition of the target molecule by the linker between the nanozyme and the photoelectrode, resulting in the subsequent detachment of the nanozyme from the photoelectrode (Figure 6e) [96–98]. Hu et al. constructed PtCu nanocages nanozyme-labeled aptamers, which formed a double-stranded DNA complex with complementary DNA on the photoelectrode. Upon the addition of streptomycin, the nanozyme-labeled aptamer specifically recognizing streptomycin was displaced, resulting in a new detection signal [99]. The last inhibitory connection strategy is the competition between the target molecule and the nanozyme for modification on the photoelectrode, as shown in Figure 6f [100–102]. For example, the streptomycin-labeled $Co_3O_4$-Au nanozyme competes with the ssDNA related to the target for binding to the ITO/$TiO_2$/$Bi_2S_3$ surface with the H1 probe, thereby achieving PEC detection of microRNA [103].

The enzyme-linked immunosorbent assay utilizes the fundamental immunological concept of antigen-antibody binding and has been widely employed in PEC sensing in recent years. The enzymatic reaction occurring on the labeled antibody serves as a crucial signal amplification mechanism on the photoelectrode. Therefore, nanozyme materials capable of mimicking enzymatic reactions are employed for the conjugation of secondary antibodies. Immunoassay has become the second type of linker between the photoelectrode and nanozyme [104–106]. As depicted in Figure 7a, Feng's research team synthesized PtPd/MnCo-$CeO_2$ nanozyme with peroxidase-like activity and constructed a sandwich-type PEC immunoassay. The primary antibody, CYFRA 21-1, and the second antibody can specifically recognize each other and connect on the $SnO_2$/CdS QDs/$CdCO_3$ modified FTO electrode, thereby showing feasible detection of CYFRA 21-1 [107]. Wu et al. also reported the signal amplification in PEC immunoassay using CuO nanozyme with catalytic activity for ascorbic acid (AA) oxidation (Figure 7b). With the increasing concentrations of antigen neuron-specific enolase (NSE), more CuO@CSs-$Ab_2$ were incubated on the modified electrode, and the photocurrent decreased while the fluorescence (FL) signal enhanced. The coupled FL-based PEC sensing platform exhibits high sensitivity, specificity, and stability for NSE determination [108].

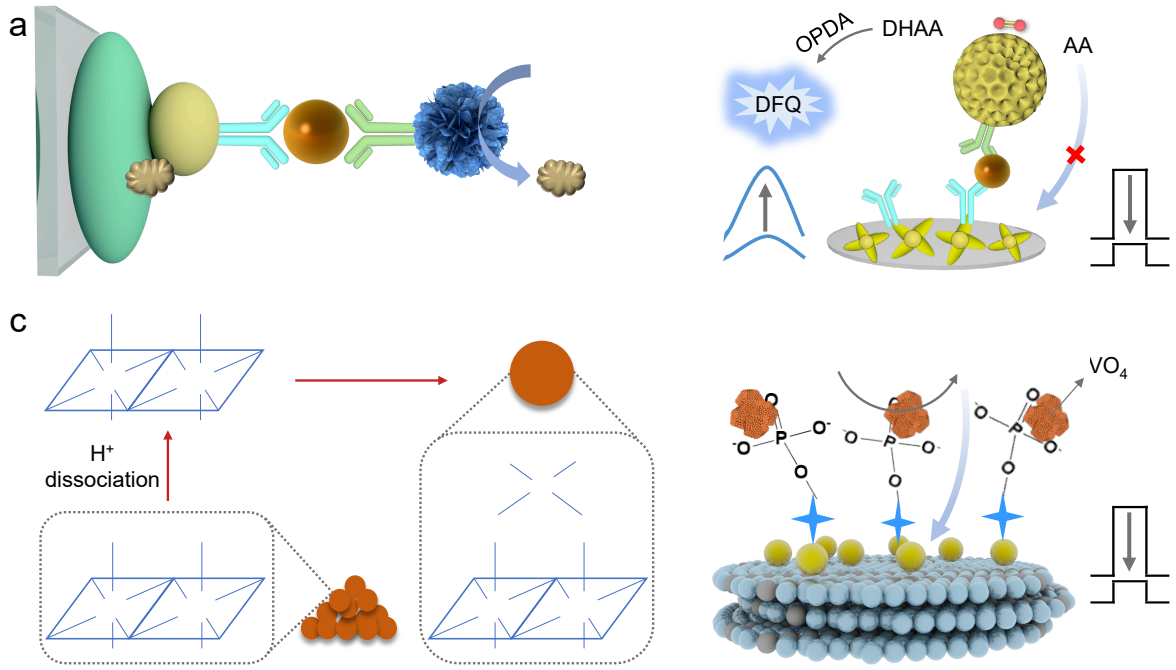



**Figure 7.** (**a**,**b**) Nanozyme-PEC sensors with an immune reaction as a linker. (**c**) Bidentate-binuclear configuration of $PO_4^{3-}$ to dihydroxo dimer of $Fe^{3+}$. (**d**) Nanozyme-PEC sensor with chemical bonding as a linker.

In many PEC sensors, the formation and breaking of chemical bonds are crucial means to achieve target detection [109,110]. Consequently, utilizing chemical absorption to graft nanozymes onto the photoelectrode surface has emerged as the third type of linker [111,112]. Currently, the bonding mechanism between Fe species and phosphate ions is being studied, which forms a dentate-binuclear configuration through Fe-O-P bonds (Figure 7c) [113]. Based on this, Ai's group achieved quantitative analysis of 5-formyl cytosine concentration in the PEC cell by utilizing the strong chelation interaction between the Fe sites on the $FeVO_4$ nanozyme and the phosphate groups on the target molecule, 5-formyl-2′-deoxycytidine-5′-triphosphate, with a wide dynamic range from 0.1 to 400 nM (Figure 7d) [114].

### *3.3. Split Type*

Among the various principles of PEC sensing, the split-type-based detection method is widely recognized for its ability to enhance sensitivity and applicability [115–117]. Therefore, researchers have divided the enzymatic reaction and the oxidation-reduction reaction on the photoelectrode surface into two separate locations, thus avoiding the potential interference between them, as illustrated in Figure 8a. In a typical study (Figure 8b), Yao et al. initially immobilized ZIF-8@Au/G nanozyme with glucose oxidation capability onto a 96-well plate. Subsequently, they utilized the hybridization reaction of the target DNA to connect another type of nanozyme, ZIF-8@Au/P, which exhibits peroxidase activity, forming a sandwich-like nanozyme catalytic platform. On this platform, the introduction of the target molecule activated a cascade reaction of the nanozymes, leading to a

decrease in $H_2O_2$ concentration. As a result, the reduction reaction kinetics at the CuO photocathode/electrolyte interface slowed down, resulting in a decline in photocurrent [118]. As a classic electron donor, AA has also been used by researchers in the design of separated nanozyme-PEC sensing platforms. In Figure 8c, a magnetically fixed nanozyme catalytic platform is depicted, where the $Fe_3O_4$ nanoparticles enriched with target molecules are attached to alkaline phosphatase-like Zr-MOF using aptamer-specific recognition. Zr-MOF in the sandwich structure can catalyze the substrate L-ascorbic acid 2-phosphate sesquimagnesium salt hydrate (AAPS) to in situ generate AA, which can be detected in the PEC system. When a mixture containing AA is transferred to the surface of the photocathode, AA acts as a hole sacrificial agent, consuming the photogenerated holes in the valence band. As a result, the photocurrent signal of the CTAB@$CH_3NH_3PbI_3$-modified photocathode is reduced [119]. Lastly, there is another approach in the field of split nanozyme-PEC systems that deserves mentioning. It enables signal amplification by utilizing a dual photoelectrode battery device (Figure 8d). In detail, the resorcinol-formaldehyde resin (RF)-$Fe^{3+}$ model nanozyme within the photocathode compartment exhibits in situ $H_2O_2$ generation under illumination and displays peroxidase-like activity, enabling the realization of a light-driven self-cascade reaction. Due to the excellent reduction capability of the photocathode, the separation efficiency of electron-hole pairs in the photoanode is enhanced, resulting in improved output signal of photocurrent and increased sensitivity in target detection [120].

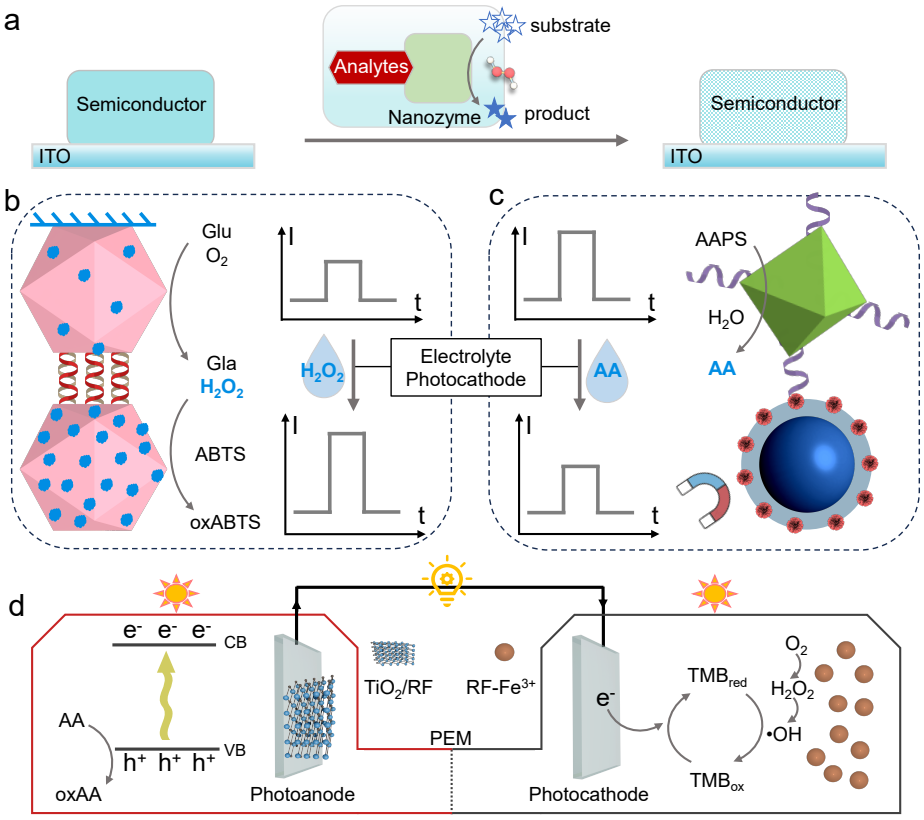



**Figure 8.** (**a**) Schematic diagram of split-type nanozyme-PEC sensing platform. (**b**,**c**) Cases of target detection achieved by introducing the products of nanozyme-cascade reactions into the PEC cell. (**d**) Nanozyme and photoelectrode together form a system of photo-fuel cells for signal amplification.

## 4. Conclusions and Perspectives

The rational design of the carrier migrations and interface catalytic reactions has been the core of PEC analysis and the key to achieving high sensitivity, selectivity, and accuracy. In this review, we have summarized the research progress of nanozyme-enabled photoelectrode platforms in PEC analytical applications. Combining the advantages of nanomaterials, nanozymes effectively avoid the problem of poor conductivity and fragility of enzymes for underpinning the excellent catalytic signal transduction functions. Notably, the metallic and semiconductor properties offer nanozymes to improve the carrier migration efficiency by regulating the energy band structure of semiconductors. Such properties bring more opportunities for engineering high-performance PEC sensing platforms to achieve the goal of trace target assay. First, we introduced nanozyme-mediated different types of enzymatic reactions to perform the substrate transformations and signal amplification functions. Then, a detailed description of the regulation strategies of the carrier migration pathway by integrating nanozymes was

provided, and the underlying mechanisms were highlighted. Finally, based on the differences in the contact modes between nanozymes and photoelectrodes, nanozyme-enabled PEC sensors are summarized, including direct type, indirect type, and split type. Although the advantages of PEC analysis involving nanozymes are obvious, there are still some challenges.

(1) Achieving high-performance analytical applications depends on the activity and specificity of nanozymes to afford sensitive and selective signal transductions. To access the efficient catalytic performance of natural enzymes, a promising strategy is to vividly mimic the enzymatically active pockets to design the appropriate active centers. Notably, the atomically dispersed catalytic sites and tunable coordination structures make SACs the ideal candidates. It is expected to precisely engineer the catalytic environments for tuning the binding and activation of substrates, realizing highly efficient and selective signal transductions. Additionally, the unique physicochemical properties offer nanozymes with optical, magnetic, and thermal response abilities, which are expected to enhance the catalytic performance by energy transformations.

(2) In the strategy of nanozyme modification of photoelectrodes, nanozymes not only need to possess enzyme-like catalytic activity but also require the ability to enhance the PEC performance through band matching with the photoactive materials on the photoelectrodes. Rational regulation of the nanozyme's energy band structure and Fermi level is paramount for creating interfaces that direct charge transfer, thereby promoting efficient electron-hole separation. Theoretical studies are crucial in providing essential guidance and predictions for this design. Computational tools, particularly Density Functional Theory, guide rational design by predicting electronic structures for optimal band engineering, simulating interfacial charge dynamics, and elucidating catalytic mechanisms. Furthermore, theoretical approaches enable performance predictions through high-throughput material screening, forecasting of key PEC metrics, and stability assessments. Thus, these studies transition the field from empirical trials to a rational, predictive paradigm, drastically improving the development efficiency of high-performance PEC systems.

Apart from efficient signal transductions, the repeatability and stability of nanozymes are also crucial considerations for accurate analytical applications. The non-specific adsorption of interfering substances and non-specific oxidation/reduction are still obstacles in the practical and industrial analysis of these sensors. Taking these into consideration, the functionality of nanozyme-based sensors needs to be enriched via rational integration of various functional moieties to meet requirements in practical applications. To continuously progress, combining the high-resolution/high-throughput elements with nanozyme-based PEC sensors is greatly needed to develop advanced analytical technology. Leveraging the micro-/nano-scale photoelectrode probes is anticipated to offer real-time monitoring and even realize single-molecule analysis. With the rapid development in recent years, we believe that nanozyme-PEC analysis will play a greater role in future sensing.

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## Data Availability Statement

The data that support the findings of this study are available from the corresponding author.

## Conflicts of Interest

The authors declare no conflict of interest.

## Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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