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ARTICLE

Recent progress of heterostructure-based photoelectrode in photoelectrochemical biosensing: A mini review

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Photoelectrochemical (PEC) biosensing has received increasing attention due to its great potential in the biomarkers analysis. The performance of PEC biosensor depends largely on the photosensitive materials. The photoactive materials with excellent properties are of great importance to realize advanced PEC bioassay. As a special class of nanocomposites, the heterostructure consisted of different kinds of semiconductors with potential application in PEC system has witted the rapid development to improve the performance of PEC biosensors recently. In this review, the research progress on the promising heterostructure is introduced and summarized, and the applications of such heterostructure in PEC bioassay are provided. The future development of heterostructures pertaining to PEC biosensing system is also briefly discussed.

1. Introduction

Photoelectrochemical (PEC) biosensing, a newly analytical method, relates to the charge transfer reaction among a photoactive substance, an analyte and an electrode under light radiation.[1-3] In PEC detection, the totally separated and different energy forms of the excitation source (light) and detection signal (current) lead to potentially high sensitivity and reduced background signals for target analysis.[4-6] Moreover, PEC method also owns other features such as low cost, simple equipment and easy miniaturization.[7,8] The fast-growing PEC bioassay has attracted great interest among the community.[9-11] In general PEC bioassay, as shown in Fig. 1, the quantitative analysis of target is realized through the analyte-induced photocurrent change on photoactive materials-decorated electrode. Therefore, the photosensitive materials are of great importance for enhancing the photon-to-electricity conversion of photoelectrode and improving the analytical performance of biosensor, which are also a key to construct a more advanced PEC biosensing platform.[12-14]

With the fast development of nanotechnology, semiconductor nanomaterials have been utilized in preparation of photoelectrode in PEC area, significantly boosting the stability, repeatability and sensitivity of biosensors.[15,16] Among many semiconductors, metal oxides, such as TiO_2 and ZnO, have been widely studied due to their highly chemical stability and fine PEC properties;[17,18] Bi-containing nanomaterials have attracted much attention with remarkable advantages of excellent photocatalytic properties, non-toxic, high-efficient and stable properties.[19,20]

However, the shortcomings of single nanomaterial-based photoelectrode have limited its application in PEC bioassay, such as poor absorption of visible light, severe recombination of photogenerated electron-hole pairs and low charge transfer rate. In order to solve these problems, many efforts have been made to explore new materials.

Heterostructure, a special class of nanocomposites, possesses outstanding coupling ability, and can regulate the spectral absorption range as well as promote charge transfer, thus significantly enhancing the photocurrent.[21,22] Owing to band matching, the combination of different kinds of semiconductors brings out the production of heterostructure with excellent performances, which has been recognized as an effective pathway in solving the above-mentioned problems. A large number of studies have also proved that the heterostructure-based photoelectrode can greatly improve the performance of PEC biosensor.[23-25]

In this review, we mainly concern with recent research progress of the promising heterostructure nanocomposites in PEC biosensors. This review classifies several types of heterostructure photoelectrode and introduces their applications in current PEC system, aiming to emphasize the importance of the heterostructure-based photoelectrodes for advanced PEC biosensors. The future prospects for the development of heterostructure-based photoelectrodes are discussed.

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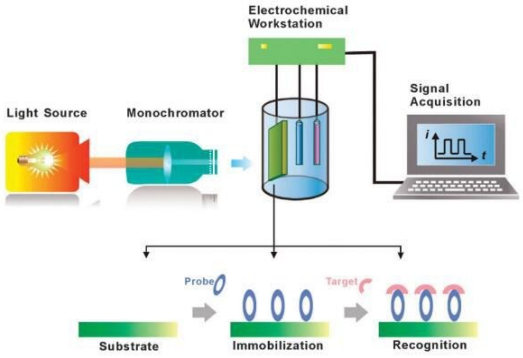

Fig. 1. Schematic of the working principle of PEC bioanalysis. (Reprinted with permission from ref. 2. Copyright 2014, Royal Society of Chemistry.)

2. Heterostructure photoelectrodes and the applications in PEC biosensing

Nowadays, the heterostructure formed by integrating different kinds of photoactive materials has been paid great attentions in PEC system, the related reports are constantly emerging. The formation of heterojunction increases the electron-hole mobility through the interface between the materials, which in turn shorten the distance and time of charge transport to hinder the recombination of electron-hole pairs, thus greatly improving the PEC activity. Hence, the heterostructures possess more excellent PEC properties that couldn't be fulfilled by single material.[22,26] In this section, we divide the heterostructure-based photoelectrode into four categories: TiO_2-based, ZnO-based, CdS-based and Bi-containing heterostructure photoelectrode, and focus on their applications in PEC biosensing system.

2.1 TiO_2-based heterostructure photoelectrode

As a quintessential semiconductor, the research of TiO_2 materials has expanded tremendously in view of their inherent features such as photoelectric activity, chemical inertness, and biocompatibility in PEC area.[27] However, the PEC performance of the bare TiO_2 is far from satisfactory due to its main absorption of ultraviolet light and severe recombination of the photogenerated electron-hole pairs. One strategy to solve the problems is to form the heterostructure consisted of TiO_2 and narrow band gap semiconductors via band matching.[28] The addition of the narrow band gap semiconductors on TiO_2 could accelerate electron transfer, restrain electron-hole recombination and increase the photoelectric conversion efficiency. A series of work has also proven that this effective means could improve the PEC performance of TiO_2-based photoelectrode.[29,30]

For example, Gao et al.[31] proposed a facile synthetic method of TiO_2-CdSe heterostructure based on the dentate binding of TiO_2 nanoparticles (NPs) to carboxyl functionalized CdSe quantum dots (CF-CdSe QDs). This heterostructure exhibited significantly enhanced photocurrent response of about 10 times than that of TiO_2 NPs under light irradiation (Fig. 2A), and the absorption in the visible light region was obviously increased (Fig. 2B), which meant that the chemically bonded TiO_2-CdSe heterostructure had an excellent PEC property. Moreover, Fig. 2C vividly revealed that the integration of TiO_2 NPs and CF-CdSe QDs could promote the charge separation and transfer, and thus improving the PEC performance of TiO_2 NPs. Furthermore, using TiO_2-CdSe heterostructure as versatile labels, the fabricated PEC/electrochemical immunosensing platform for human immune globulin G detection displayed a wide linear range from 0.05 pg/mL to 100 ng/mL and a low limit of detection (LOD) of 16.7 fg/mL, which also obtained the acceptable results in human serum samples analysis.

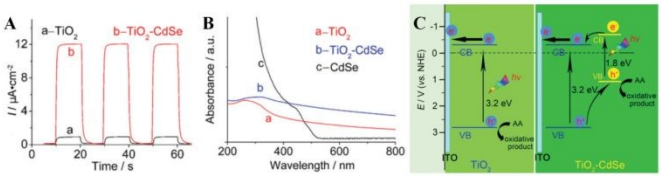

Fig. 2. (A) Photocurrent response and (B) UV-vis spectra of TiO_2 NPs (curve a), TiO_2-CdSe (curve b) and CdSe QDs (curve c); (C) Energy band diagram of TiO_2 NPs and TiO_2-CdSe heterostructure hybrids. (Adapted with permission from ref. 31. Copyright 2015, Royal Society of Chemistry.)

Wang et al.[32] prepared TiO_2/g-C_3N_4 heterojunction by a solvothermal method. As shown in Fig. 3, thanks to the unique electronic band structure between g-C_3N_4 and TiO_2, effective electron transfer process on heterojunction could suppress the recombination of electron-hole pairs, thus enhancing the PEC performance. With the combination of TiO_2/g-C_3N_4 heterojunction photoelectrode and alkaline phosphatase (ALP)-based enzymatic hydrolysis reaction, the designed PEC biosensor showed excellent performance of ALP activity detection with a LOD of 0.03 U/L, which also had a good practicability for ALP determination in human serums.

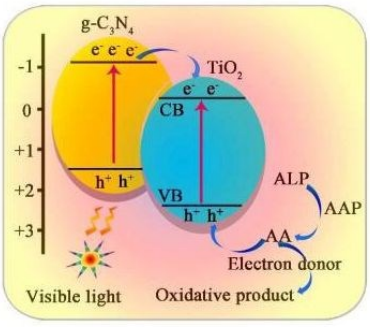

Fig. 3. The scheme for visible light-driven electron-hole excitation, separation and transfer mechanism of the TiO_2/g-C_3N_4 composite. (Reprinted with permission from ref. 32. Copyright 2017, Royal Society of Chemistry.)

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Liu et al.[33] designed a TiO_2-$BiVO_4$ heterostructure with enhanced PEC response by a solvothermal method, in which $BiVO_4$ NPs were deposited on TiO_2 nanospheres. The formation of TiO_2-$BiVO_4$ heterojunction not only extended the absorption of TiO_2 into the visible region, but also the band match made it easy to transfer electrons from the conduction band of $BiVO_4$ to TiO_2, thereby obtaining the photocurrent of ~ 1.8 times stronger than that of TiO_2. On this basis, a visible-light driven PEC aptasensor was constructed, and the sensitive determination of 17β-estradiol had also been realized in the range from 0.1 to 250 pM with LOD of 0.022 pM. Moreover, the proposed system had been applied in the determination of 17β-estradiol in human urine samples, the recoveries were in the range from 96.4 to 103.2%.

2.2 ZnO-based heterostructure photoelectrode

The properties of heterostructures dominate the behavior of photogenerated carriers, which ultimately determine the PEC performance. As a typical photoanode material, ZnO has been extensively investigated owing to its rather rich morphology, large excitation binding energy (60 meV) and excellent electron mobility.[34] However, the wide band gap of ZnO (3.37 eV) causes swift recombination of photoinduced carriers and inferior light employment. Hence, a variety of ZnO-based heterostructures have been designed by combining several functional materials to overcome these problems.

Cu_2O/ZnO p-n junctions have controllable electronic structure at interface and good energy band alignment,[35] which could effectively promote the transfer and separation of photoproduced charge carriers, thus improving the PEC performance. For example, Kang et al.[36] assembled a Cu_2O/ZnO nanorods array heterostructure by directly electrodepositing way, and acquired largest build-in interfacial electric field in heterostructures by electrodepositing of Cu_2O at pH 11. As shown in Fig. 4, the prepared heterostructure possessed the lowest recombination efficiency of photogenerated carriers, thus, obviously enhancing the PEC property. The proposed Cu_2O/ZnO heterostructure-based PEC biosensor carried out highly sensitive detection of glutathione (GSH) with a linear range from 10 to 1000 mM as well as LOD of 0.42 mM.

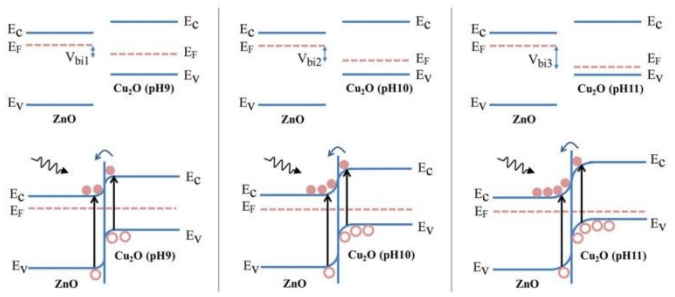

Fig. 4. Energy band diagrams for isolated ZnO and Cu_2O electrodeposited at various pH values from 9 to 11, and corresponding Cu_2O/ZnO heterostructures. (Reprinted with permission from ref. 36. Copyright 2015 Springer Nature.)

Zhao et al.[37] designed a CdS/reduced graphene oxide (RGO)/ZnO nanowire array (NWAs) heterostructure via the nanocrystal layer deposition method. In CdS/RGO/ZnO NWAs heterostructure (Fig. 5), the formed type II band alignment between CdS and ZnO NWAs plus the extraordinary charge collection and shuttle property of RGO greatly facilitated the separation of photoinduced carriers, consequently, improving the PEC activity. Such heterostructure-based self-powered PEC biosensor revealed satisfactory analytical performance of GSH with a linear range from 0.05 mM to 1 mM and LOD of 10 μM. Wang et al.[38] reported a ZnO nanorods/BiOI nanoflakes heterostructure by in situ growth of BiOI. Because of the bending of the energy bands, the formation of heterostructure greatly enhanced the PEC properties in electron transfer and carriers separation. Using G-quadruplex/Pb^{2+} as recognition system, the ZnO/BiOI heterostructure-based PEC biosensor showed rapid response and high sensitivity of Pb^{2+} with LOD of 7.5 μM.

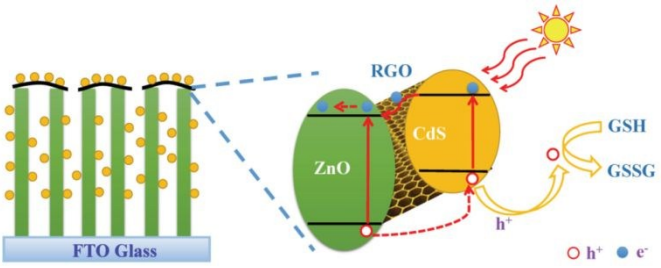

Fig. 5. Schematic illustration of the mechanism for the PEC detection of GSH. (Reprinted with permission from ref. 37. Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

2.3 CdS-based heterostructure photoelectrode

The intrinsic properties of CdS, such as narrow band gap (2.4 eV) and steerable morphology, make it a kind of important photosensitive material, having aroused increasing study interest in PEC bioanalysis.[39] Whereas, pure CdS suffers from rapid electron-hole recombination and photocorrosion problem, which causes the low photoelectric conversion and unstability under light irradiation. Combining CdS with proper cocatalyst to design the heterojunctions with excellent properties could effectively solve above problems, which greatly accelerate electron-hole separation, thereby improving the PEC performance.

Graphitic carbon nitride (g-C_3N_4), as a two-dimensional layered structure material, has the advantages of suitable band-edge position, effective photocatalytic activity and high chemical stability.[40] The heterostructures formed by the union of CdS and g-C_3N_4 have been reported to possess excellent photoelectric performance because of the large surface area

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and fast charge transfer. Our group[41] first reported a novel PEC biosensing system based on exciton-plasmon interactions (EPI) between CdS@g-C_3N_4 heterojunction and Au@Ag NPs for microRNA-21 assay (Fig. 6). In this work, we confirmed that the core/shell CdS@g-C_3N_4 nanowires obtained via a self-assembly procedure could produce an excellent PEC response owing to the formation of p-n heterojunction. Integrating effective EPI signaling mechanism and enzyme-assisted target cycle amplification, the designed PEC biosensor realized ultrasensitive detection of miRNA-21 with a low LOD of 0.05 fM, which also showed good potential of miRNA-21 determination in human serum samples. Later on, employing the CdS@g-C_3N_4 heterojunction modified dual-electrode array and the CuS QDs as signal quenchers, we further developed a general spatial-resolved PEC ratiometry for prostate-specific antigen (PSA) bioassay, exhibiting a linear range from 1.0×10^{-11} to 5.0×10^{-8} g/mL and a LOD of 4.0 pg/mL.[42]

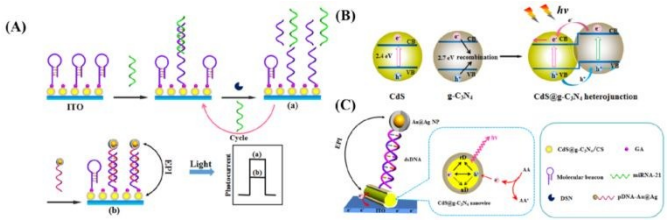

Fig. 6. (A) Schematic illustration of the fabrication process of the PEC biosensor. (B) Schematic illustration for the energy bands of CdS@g-C_3N_4 before and after coupling. (C) Charge transfer process at the formed heterojunction under light illumination. (Adapted with permission from ref. 41. Copyright 2017, American Chemical Society.)

As a typical transition metal dichalcogenide, MoS_2 has received increasing attentions owing to the unique optical, electronic and catalytic properties.[43] Integrating of CdS with MoS_2 to construct heterostructure could efficiently separate the electron-hole pairs. For instance, using CdS/MoS_2 heterojunction, Zang et al.[44] established a novel PEC DNA biosensor based on catalytic hairpin assembly (CHA) and hemin-mediated chemiluminescence (Fig. 7). In this case, by the stepwise assembly of MoS_2 and CdS QDs on the electrode, the prepared heterojunction showed the photocurrent intensity of around 280% higher than that of pure CdS QDs. The remarkable PEC activity of CdS/MoS_2 heterostructure was propitious to improve the analytical performance of the proposed method. The resulting biosensor demonstrated high sensitivity with a linear range from 1.0 fM to 100.0 pM and a LOD of 0.39 fM.

Also as a transition metal dichalcogenide, the electrical conductivity of WS_2 is higher than that of layered MoS_2, due to the broad light absorption and high carrier mobility, which is preferable to form heterostructure with CdS for excellent performance.[45] In the study on WS_2 nanosheets sensitized CdS QDs heterostructure, Zang et al.[46] constructed a facile PEC immunosensor of alpha-fetoprotein (AFP) analysis by the aid of enzymatic biocatalytic precipitation. The proposed system acquired the satisfactory linear range (1.0 pg/mL – 20.0 ng/mL) and LOD (0.43 pg/mL), which also had been successfully applied to determining AFP in human serum samples. In their another report, they further developed an enhanced PEC biosensor for GSH determination.[47] In this case, due to the heterojunction effect of CdS/WS_2, the corresponding PEC signal performed about 310% increasing in respect to CdS QDs.

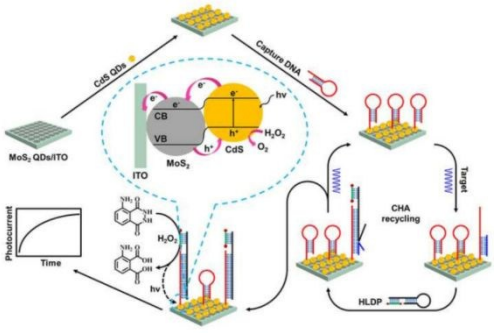

Fig. 7. Schematic illustration for CdS/MoS_2 heterojunction-enhanced PEC sensing strategy coupling with CHA and hemin-mediated chemiluminescence. (Reprinted with permission from ref. 44. Copyright 2015, Elsevier Publishing.)

2.4 Bi-containing heterostructure photoelectrode

2.4.1 Bi-containing multi-component oxides-based heterostructure To date, Bi-containing semiconductor photoactive materials with high photocatalytic ability and non-toxicity have been exploited for advanced PEC biosensing development. For example, Shu et al. took advantage of decahedral $BiVO_4$ with Au nanocrystal on {010} facets as photoanode to achieve enhanced PEC performance, designing an innovative and power-free PEC immunosensing platform for PSA detection.[48] Qian et al.[49] prepared flower-like Bi_2WO_6/Ag_2S NPs and employed as PEC matrix to construct a sandwich-type PEC immunosensor for NT-pro BNP detection. The Bi-containing multi-component oxides have inherent features including unique electronic structure, good photocatalytic performance and stability.[50-52] However, some problems existed in these multi-component oxides, such as poor light utilization, fast electron-hole recombination and slow charge transfer, are disadvantageous for application in PEC biosensing. In order to extend their applications, employing other semiconductors with suitable band gap to modify the surface of these multi-component oxides is an efficacious way, which is benefit to promoting the charge separation and enhancing the PEC performance.[53,54]

On the basis of CdS nanowires sensitized WO_3@BiOI heterostructure prepared through a sequential chemical bath deposition method, Han et al.[55] developed a label-free PEC immunosensing platform for carcino embryonic antigen assay with a LOD of 3.2 pg/mL. Later on, using cerium doped CdS modified graphene/$BiYWO_6$ heterostructure, they further

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designed a PEC aptasensor for the sensitive detection of tetracycline.[56] Ge et al.[57] synthesized a $BiFeO_3$/ultrathin g-C_3N_4 heterojunction using a simple electrostatic interaction way, and then fabricated an on-off-on PEC aptasensor for determining ampicillin (AMP) (Fig. 8). The produced p-n heterojunction not merely narrowed the band gap of materials, enhancing the utilization of visible light, but also accelerated the carriers separation, thus, the photocurrent displayed a 7.0-fold increase than that of single $BiFeO_3$. The proposed PEC aptasensor of AMP demonstrated a broad linear range of 1.0×10^{-12} mol/L to 1.0×10^{-6} mol/L with a low LOD of 3.3×10^{-13} mol/L.

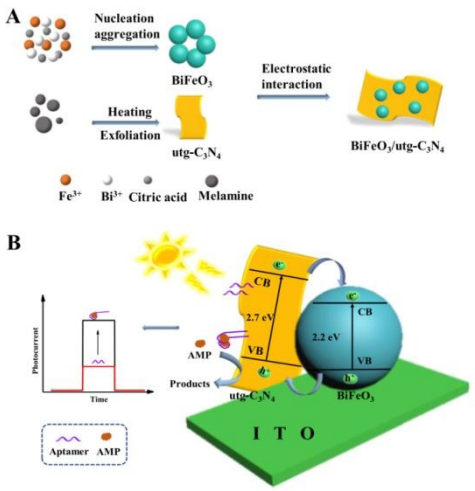

Fig. 8. (A) Schematic diagram for the formation of $BiFeO_3$/utg-C_3N_4 heterojunction and (B) The schematic drawing illustrating of the as-fabricated PEC AMP aptasensor based on $BiFeO_3$/utg-C_3N_4 heterojunction. (Reprinted with permission from ref. 57. Copyright 2018, Elsevier Publishing.)

2.4.2 Bi_2S_3-based heterostructure Bi_2S_3, an efficient semiconductor, possesses the advantages of narrow band gap, high absorption coefficient and reasonable energy conversion, which has been cited as one of the most promising photosensitive materials.[58] Meanwhile, due to good environmental compatibility, Bi_2S_3 has been used as a favourable substrate material in PEC biosensing area.[59] In addition, the narrow band gap of Bi_2S_3 also makes it ideal candidate component for preparing heterostructures.[60,61]

As exhibited in Fig. 9, Liu et al.[62] designed a Z-scheme type CdTe-Bi_2S_3 heterojunction formed by the electrostatic adsorption interaction. In the heterojunction, the photoelectric conversion efficiency of photogenerated charges separation was significantly increased, accordingly, showing higher PEC response compared to pure CdTe and Bi_2S_3 nanorods. Based on this photoactive material with fine performance, they presented a heterojunction-mediated PEC biointerface, realizing the selective detection of microcystin-LR with wide linear range (0.01 – 100.0 pM) and low LOD (0.005 pM). Nevertheless, there are few reports on such heterostructure by combining Bi_2S_3 with other matching materials in current PEC biosensing system. Given the advantageous performance, the Bi_2S_3-based heterojunction is worthy of further study in the future.

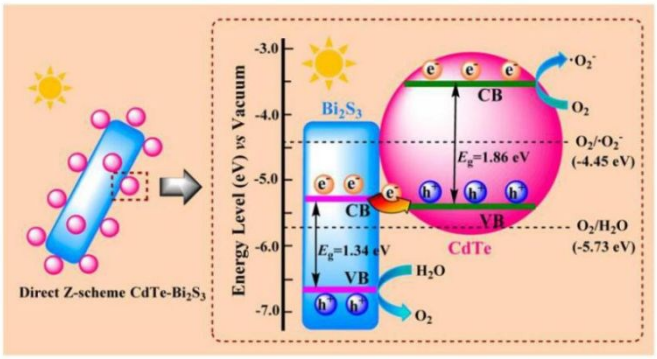

Fig. 9. Schematic diagram of enhanced photocurrent generation mechanism for direct Z-scheme CdTe/Bi_2S_3 heterojunction. (Reprinted with permission from ref. 62. Copyright 2017, American Chemical Society.)

2.4.3 Two Bi-containing heterostructure Very recently, some efforts have been devoted to the development of heterojunction consisted of two Bi-containing semiconductors in PEC biosensing. Due to the satisfying band matching, the formed dual Bi-containing heterojunction could obviously broaden the light absorption and accelerate the electron transfer. Moreover, the large heterojunction interface between two materials has the function of isolating the barrier, which reduces the possibility of the electron-hole recombination and further promotes the charge transfer. On the basis of the advantages above, the PEC activity of dual Bi-containing heterojunction is greatly boosted, and thus being beneficial to build PEC biosensor with excellent performances.

Our group[63] reported first use of a novel photogenerated hole-induced chemical redox cycling amplification (RCA) strategy on Bi_2S_3/$Bi_2Sn_2O_7$ heterojunction photoelectrode in PEC immunoassay (Fig. 10), achieving the sensitive immunoassay of myoglobin (Myo) with LOD of 1.0×10^{-13} g/mL. Later on, using Bi_2S_3/Bi_2WO_6 heterojunction prepared by the ultrasonic method, we presented a concept of PEC-chemical-chemical (PECCC) redox cycling as an efficient signal amplification path, and the proposed system accomplished the ultrasensitive PEC bioassay towards Myo in the range of 1.0×10^{-13} to 1.0×10^{-7} g/mL with LOD of 3.0×10^{-14} g/mL.[64] Likewise, on Bi_2S_3/$BiVO_4$ heterojunction photoelectrode, we further reported a novel $Ru(NH_3)_6^{3+}$/$Ru(NH_3)_6^{2+}$-mediated PECCC RCA strategy, realizing effective triple signal amplification for ultrasensitive interleukin-6 immunoassay with a low LOD of 2.0×10^{-15} g/mL.[65] Based on the BiOBr/Bi_2S_3 heterostructures synthesized by self-sacrificial synthesis method, Fan et al.[66] constructed a novel visible light PEC

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immunosensor for ultrasensitive detection of squamous cell carcinoma antigen with LOD of 0.3 pg/mL (Fig. 11). Employing ascorbic acid (AA) as electron donor, the $BiOBr/Bi_2S_3$ heterostructures displayed nearly 30 times enhancement of PEC signal than that of pure BiOBr.

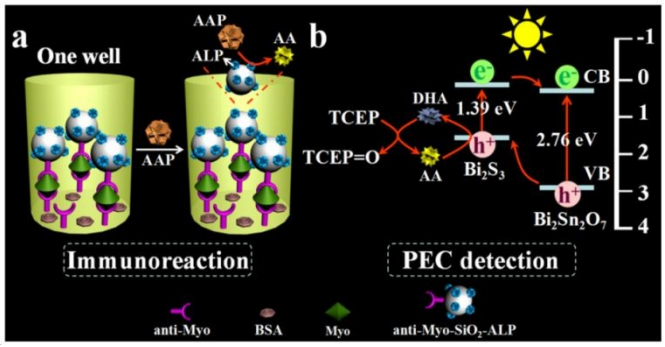

Fig. 10. Schematic illustration of (A) sandwich immunoreaction in one well of 96-well plate and ALP-catalyzed generation of AA, (B) redox cycling for signal amplification on $Bi_2S_3/Bi_2Sn_2O_7$ heterojunction. (Reprinted with permission from ref. 63. Copyright 2018, American Chemical Society.)

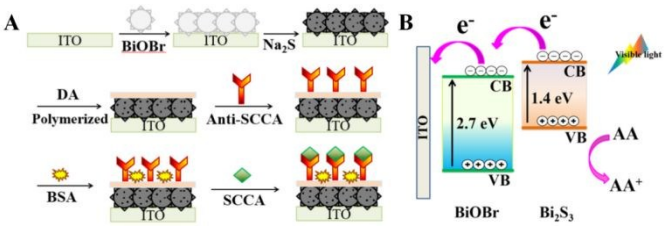

Fig. 11. (A) The schematic of the preparation process of PEC immunosensor. (B) The schematic of electron transfer of PEC immunosensor based on $BiOBr/Bi_2S_3$ in AA electrolyte. (Reprinted with permission from ref. 66. Copyright 2019, Elsevier Publishing.)

3. Conclusion and outlook

Various heterostructures such as TiO_2-based, ZnO-based, CdS-based, and Bi-containing heterostructure in PEC biosensing are reviewed. By the band matching, different kinds of semiconductors are incorporated to form different heterostructures. The production of heterojunction suppresses electron-hole recombination and promotes carriers transfer, as well as allows more light absorption. Recently, the relevant publications clearly reveal that the design and preparation of high-performance heterostructure afford great opportunities to develop the advanced PEC biosensing system. However, compared with other types of nanocomposites in PEC field, the construction and application of heterostructures are still in the infancy.

In order to pursue superior-performance heterostructure-based PEC biosensors, further efforts should focus on several aspects as follows: (1) Probing new materials suitable for forming advanced heterostructure is certainly need; (2) The interfacial electric field in heterostructure should be investigated more in detail to gain insight into the mechanism behind the improving PEC performance; (3) Few heterostructures like CdS-based and Bi-containing heterostructures yet not explored well for PEC biosensing, hence in future more works are demanded.

Conflicts of interest

There are no conflicts to declare.

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