J. Meas. Sci. Instrum., 2026, 17(1): 16-35. http://jmsi.publish.foundersss.cn
DOI: 10.62756/jmsi.1674-8042.2026002 jmsi@nuc.edu.cn

A brief review of photoactive materials for photoelectrochemical biosensors

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Received: November 17, 2025 **Revised:** January 19, 2026 **Accepted:** January 22, 2026

Abstract: Photoelectrochemical (PEC) biosensors have drawn growing interest due to their capability to detect biomolecules with the help of generating photocurrent during oxidation reactions, followed by their high sensitivity, minimal background interference, cost-efficiency, and portability. This review provides an extensive summary of the photoactive materials that power PEC biosensor performance. We start by outlining the basic ideas and signal-generating processes of PEC biosensing, highlighting the crucial role of charge-carrier dynamics in photocurrent production. The article's main body thoroughly examines several categories of photoactive materials, such as metal oxides, quantum dots, organic materials, plasmonic nanostructures, and two-dimensional nanomaterials. We go over the special qualities, charge-transfer methods, light-harvesting capacities, and effects on biosensor performance of each material type, all supported by current experimental research. To improve sensitivity and selectivity, we also examine key design techniques, including heterojunction formation, surface functionalization, and hot-electron injection. We also discuss the main issues in PEC biosensors, including interference reduction, biocompatibility, material stability, and reproducibility. Lastly, we discuss future directions, emphasizing new materials, innovative device designs, and potential applications in food safety, environmental monitoring, and point-of-care diagnostics. The goal of this thorough overview is to assist researchers in choosing and creating cutting-edge photoactive materials for high-performance PEC biosensors of the future.

Key words: photo electrochemistry; biosensors; immunodetection; sensor technology

0 Introduction

Novel photoelectrochemical (PEC) sensors utilize the principles of photoelectric chemistry to analyze and detect biological and chemical molecules. They generate current by transferring valence electrons within the photo-excited material, initiating a chemical reaction upon exposure to a light source. Light and photocurrent are used in PEC sensors as excitation sources and determination signals, which lowers background noise and increases sensitivity compared to other technologies. An electronic reader makes PEC instruments easy to operate, cheap, and portable[1]. The evident attributes render PEC sensors viable candidates for the swift and precise detection of environmental toxins and illicit substances.

The sensitivity of PEC sensors is greatly affected by how well photoelectric conversion works, which is mostly governed by the properties of photoactive materials[2]. When light hits the photoactive materials, they help separate and move charges, which makes photocurrent, the signal that detects the light. This is usually the conversion layer that turns photons into electrical energy[3]. An applied bias or internal electric field separates these charge carriers, causing electrons to flow toward the electrode and holes toward the electrolyte. At the electrode surface, the electrons participate in redox processes that produce a detectable current correlated with the target analyte's concentration. The signal generation efficiency depends on charge carrier dynamics, such as their generation, separation, transport, and minimization of recombination. Enhanced carrier transport and optimized light-absorption materials are key to improving the performance of PEC biosensors. In this paper, various photoactive materials are reviewed, offering suggestions for the researchers.

1 Concept and basic principles of photoelectrochemical biosensors

1.1 Concept of photoelectrochemical biosensors

Through photon absorption under light, molecules,

ions, and semiconductor materials are excited, resulting in charge transfer and the transformation of light energy into electrical energy. PEC biosensors are a type of sensors that use light to generate an electrochemical response for detecting biological substances. Food safety analysis, environmental monitoring, and medical diagnostics frequently use these sensors. PEC biosensors represent an innovative detection technology that integrates photoelectrochemistry with biosensing, leveraging the conversion capabilities of photoelectrochemically active materials[4]. PEC biosensors can quantitatively detect the target analyte by looking at how the photocurrent or photovoltage changes before and after the biomolecular recognition process and seeing how these changes relate to the intensity of the target marker. In PEC detection, light works as an excitation source to activate photoelectrochemically active materials, which makes it easier for charge to move from one place to another. The electrical signal that results is then used for detection[5]. PEC biosensors are superior to traditional analytical methods in a number of important ways. By reducing background noise, their combination of photo-excitation and electrochemical detection greatly increases sensitivity. Better signal-to-noise ratios are achieved by precisely controlling signal creation through the decoupling of excitation and detection modalities. The ability to fine-tune photoactive materials, including semiconductors, heterojunctions, and tailored nanostructures, to customize light absorption, charge separation, and interfacial charge transfer, as well as comparatively easy assay settings, are further advantages of PEC platforms. These attributes result in devices that are affordable, adaptable to a wide variety of analytes, and possibly portable—qualities that are ideal for applications involving food safety, environmental monitoring, and point-of-care diagnostics.

1.2 Basic principles of photoelectrochemical biosensors

The basic PEC biosensor detection mechanism and principle are depicted in Fig. 1[6]. The electrochemical workstation conducts a normal three-electrode setup that comprises a working, a counter, and a reference electrode. In a suitable electrolyte solution, the tri-electrode system operates. To stimulate and modify the PEC active material on the electrode surface of the biosensor, PEC biosensors usually work by using a light source with a visible-band wavelength. When the target recognition element on the surface of the electrode bonds to the specimen, it starts a new oxidation or reduction reaction that moves charge and electrons to make the photocurrent. There is a corresponding relationship between the response signal picked up by the PEC biosensor and the change in analyte concentration. The biological response is recorded and detected by the electrochemical workstation. As a result, quantitative biomarker detection is made easier by using PEC biosensors to track changes in signals. This allows for the assessment and computation of current biomarker concentrations. This outlines the basic idea behind how PEC biosensors work.

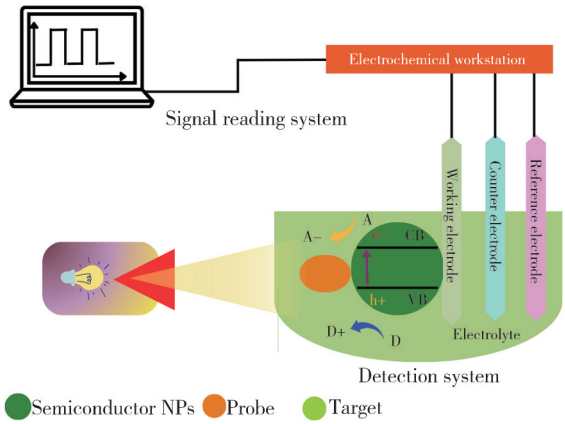

Fig. 1 Schematic illustration of the basic three-electrode PEC biosensing system, which consists of a working electrode (WE), a counter electrode (CE), and a reference electrode (RE), submerged in an electrolyte solution. Under light illumination, photoactive materials on the WE surface generate electron–hole pairs, leading to photocurrent signals that correlate with target analyte concentration. This fundamental setup enables highly sensitive detection of biological molecules through PEC reactions[6]

When light hits photoelectrochemically active materials, they absorb energy that is greater than their bandgap width. This creates photo-produced electron-hole pairs as the energized electrons migrate between the valence and conduction bands. There are two different situations in which electron transfer can occur.

1) When the p-type semiconductor used to modify the photoelectrochemically active material on the electrode of the PEC biosensor transfers electrons to the conductive substrate from its conduction band, the electrolyte fills the valence band with electrons, creating an anodic photocurrent, as displayed in Fig.2 (a).

2) Conversely, when the PEC active material is a p-type semiconductor, electrons are transferred to the electrolyte solution from the conduction band, and the conductive substrate provides electrons to fill the holes in the valence band, resulting in the generation of a cathodic photocurrent, as displayed in Fig.2 (b). At present, the majority of PEC biosensors can produce visible signals based on this principle.

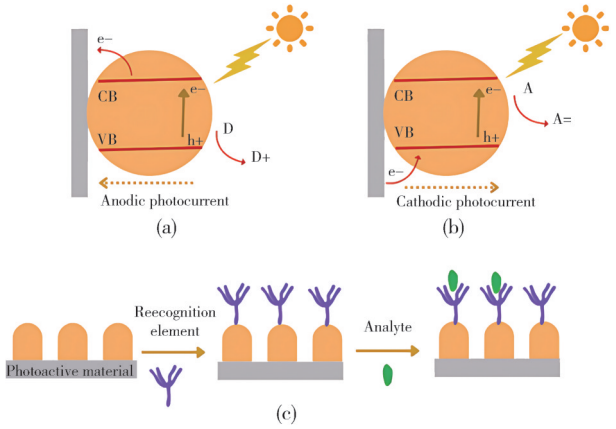

Fig. 2 Mechanism of photocurrent generation in n-type and p-type semiconductors and biofunctionalization strategy for PEC biosensor. (a) In n-type semiconductors, photoexcited electrons transfer to conductive substrate while holes migrate to electrolyte, generating anodic photocurrent, (b) In p-type semiconductors, electrons move to electrolyte and holes are filled by electrons from substrate, producing cathodic photocurrent, and (c) Biofunctionalization strategy where photoactive materials are modified with specific recognition elements (antibodies, aptamers) for selective target analyte detection[7]

2 Signal generation and charge carrier dynamics in PEC biosensors

Photoexcitation is an essential mechanism for PEC sensing. An electrical signal is produced by the created electron-hole pairs taking part in electrochemical processes at the electrode/electrolyte contact. A detection method is provided by the correlation between the signal's strength and the target analyte's concentration.

The efficiency of signal generation depends heavily on the charge carrier dynamics, which refers to how the electrons and holes behave after their generation. After photoexcitation, the electrons (which carry negative charges) and holes (which carry positive charges) must stay apart so that recombination does not happen, which would impair the sensor's overall efficiency. An intrinsic electric field in the semiconductor material or a bias supplied at the electrode usually makes this separation easier.

After separation, the electrons move toward the electrode, where they are involved in reduction reactions, such as the electrochemical reduction of an analyte (e.g., hydrogen peroxide, glucose, or heavy metals). Conversely, the holes migrate toward the electrolyte, where they can participate in oxidation reactions, such as the oxidation of the target analyte. The photo-response of the sensor changes when charge carriers move and recombine. A greater photocurrent and a more sensitive sensor happen when charge carriers separate well and recombine as little as possible.

The interface in the lower portion of Fig. 2(c) demonstrates the construction of the sensing surface. The basic layer is created by the photoactive substance and is subsequently altered to give selectivity by adding recognition components (such as aptamers or antibodies). The target analyte attaches itself selectively to the recognition element upon introduction. Charge transport between the photoactive layer and the electrolyte is impacted by this binding, which also modifies the interfacial environment. Consequently, the amount of analyte present is directly correlated with the photocurrent generated under light irradiation. Therefore, the crucial location where biological recognition is transformed into a quantifiable PEC signal is this interface.

In conclusion, the dynamics of charge carrier generation, separation, and transport, along with the incorporation of techniques like surface plasmon resonance (SPR) and hot electron injection, are crucial for optimizing signal generation in PEC biosensors. These processes directly impact the sensor's sensitivity, detection limits, and overall performance, making them essential considerations in PEC sensor design.

3 Materials & design strategies of PEC biosensors

3.1 Photoelectrode materials-metal oxides function as semiconductors

Titanium dioxide (TiO_2) is a well-studied nanomaterial that is known for having very good chemical and physical properties. Since 1972, when it was first used to divide water with light, TiO_2 has been employed in photocatalysis, solar cells, batteries, sensors, medication delivery, and bio-coatings. On account of its identical properties, like as weight-to-strong strength ratio, low density, photochemical stability, high catalytic efficiency, biocompatibility, and resistance to corrosion, it is a strong choice for photocatalytic applications[8-10].

Unmodified TiO_2 has certain problems in bioanalysis, though, because it has a wide bandgap that makes it absorb ultraviolet (UV) light. This is hard since a lot of biomolecules break down when exposed to UV light. When TiO_2 is exposed to light, the photo holes that form become more active, which can be harmful to biomolecules. To get around these problems, researchers have focused on adding photo absorbers to TiO_2 surfaces. This makes them more active in visible light and better at sensing biological signals[10].

As showed that dopamine molecules could bind to TiO_2

and make it easier to detect nicotinamide ademine dinucleotide (NADH)[11]. This change creates a dopamine-Ti charge transfer complex that can excite molecules in a wider range of wavelengths, even those that can be seen. Synthesized functionalized TiO_2 nanoparticles utilize porphyrin molecules, resulting in a stable PEC response attributed to effective electron transport[12]. These examples show that attaching organic molecules to metal oxides greatly increases the activity of TiO_2 in visible light and lowers the harmful effects of UV light and photogenerated holes. This makes it easier to make stable TiO_2 nanoparticles for PEC biosensors.

A paper in ACS Omega detailed a PEC biosensor consisting of branched TiO_2 (B-TiO_2) enhanced with carbon dots (CDs) and glucose oxidase (GOx). The photocurrent density exhibited a linear rise with glucose concentrations up to 9 mmol. The sensor's stability and selectivity were assessed, revealing negligible variations in photocurrent during numerous on/off cycles and commendable anti-interference characteristics. Fig. 5 of the study presents the graphs depicting the photocurrent response.

Similar to TiO_2 and SnO_2 have also been applied for PEC applications by adding some visible band response materials. Tin dioxide (SnO_2) is being used more and more in PEC biosensing because of its excellent electron mobility, low toxicity, affordability, and chemical and thermal stability. Researchers have built a very sensitive PEC sensor that uses SnO_2 nanoparticles to find adenosine triphosphate in lysates from cancer cells.

Iron oxide (Fe_2O_3), especially in its hematite form, has become quite popular as a semiconductor material in PEC biosensors because it is very stable, not poisonous, and has strong photocatalytic characteristics. Fe_2O_3 is a better choice for practical sensing applications than TiO_2, which only responds to UV light.

Fe_2O_3-based PEC biosensors have been widely explored for detecting biomolecules, pollutants, and environmental toxins. Studies have demonstrated its effectiveness in sensing glucose, hydrogen peroxide, and heavy metals. For instance, research on Fe_3O_4 nanoparticles for glucose detection has shown promising results in enhancing sensor sensitivity and stability[13]. The use of Fe_2O_3-modified electrodes in glucose biosensors improves electron transfer efficiency, leading to higher photocurrent responses, which is crucial for bio-electrochemical applications. The development of enzymatic and non-enzymatic electrochemical glucose sensors is also covered in a review by MDPI *Biosensors* (2022). Additionally, it discusses how charge carrier dynamics and sensor performance are impacted by Fe_2O_3 and other nanomaterials[14].

These findings demonstrate that Fe_2O_3 is a valuable material for PEC biosensors, providing efficient charge transport, stability, and the ability to operate under visible light. Adding biomolecules like glucose oxidase or enzyme-based recognition elements to it makes it even more selective and sensitive, which makes it a good choice for biomedical and environmental monitoring.

Bright yellow, n-type semiconductor bismuth vanadate ($BiVO_4$) has attracted much interest due to its photocatalytic qualities, especially in PEC water-splitting applications. Tetragonal zircon, tetragonal scheelite, and monoclinic scheelite are the 3 primary crystal forms. The monoclinic scheelite phase exhibits the maximum photocatalytic activity when exposed to visible light because it has a bigger structural distortion and a shorter bandgap, which helps with optical absorption and separating electrons and holes[15]. Recent research has shown beyond a doubt that monoclinic $BiVO_4$ has an indirect bandgap of roughly 2.4 eV and a straight transition that is about 200 meV greater. This imperceptible nature gives $BiVO_4$ a relatively long excited-state lifetime, which makes it a good material for converting solar energy into electricity[16].

Tungsten trioxide (WO_3) is a flexible n-type semiconductor that is often employed in PEC biosensors because it has fantastic optical and electrical properties. It has a bandgap of about 2.6 — 3.0 eV, which lets it absorb visible light well; hence it is good for PEC applications. For example, by adding protoporphyrin IX (PPIX) ($C_{34}H_{34}N_4O_4$) and decreased graphene oxide (rGO) to an electrode named indium tin oxide (ITO, a new PEC sensor was made that can detect cysteine very well, with a limit of 25 nmol[17]. Furthermore, it has been demonstrated that adding plasmonic gold nanoparticles to WO_3 improves its PEC characteristics, enabling non-enzymatic ethanol detection in liquors with a 0.5 μmol detection limit[18]. These investigations demonstrate how WO_3-based nanocomposites can be used to create sensitive and specific PEC biosensors for a range of analytes.

With band gaps of roughly 2.0 eV and 1.7 eV, respectively, copper oxides—more especially, cuprous oxide (CuO) and cupric oxide (CuO) —are p-type semiconductors that can be used in PEC applications to absorb visible light. Cu_2O, in particular, has garnered attention for its potential in PEC biosensors due to its favorable electronic properties and abundance. For example, research has demonstrated, doping n-type Cu_2O thin films improves their optical, structural, and PEC

properties, building them a great aspirant for use in biosensors[19], as shown in Fig. 3. To further enhance the performance of PEC devices, the integration of CuO and ZnO nanorods has been investigated to design the electrical structure at their interface[20]. The co-existence of Cu_2O and CuO phases can also be beneficial, as CuO often co-synthesizes with Cu_2O, potentially enhancing the overall PEC activity[21]. These characteristics underscore the potential of copper oxides in developing efficient and cost-effective PEC biosensors.

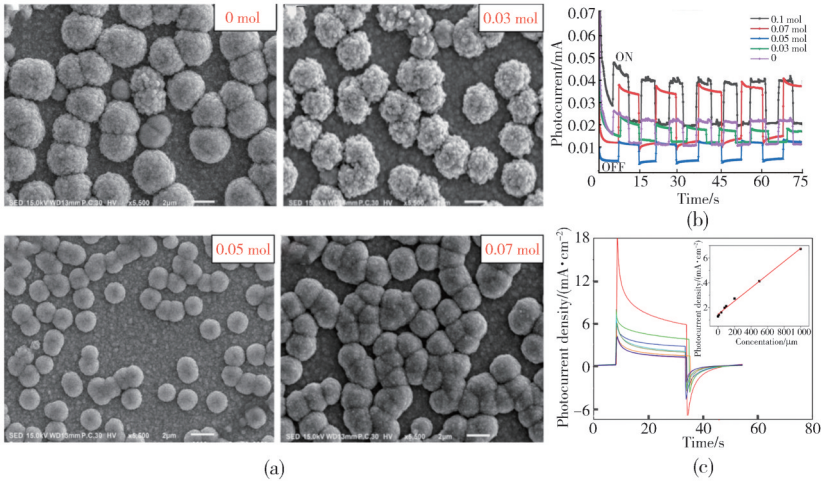

Fig. 3 Morphological and photoelectrochemical characterization of K-doped Cu_2O thin films and Cu_2O/ZnO heterostructure. (a) K-doped n-Cu_2O thin films electrodeposited as n-type at varying concentrations are shown in SEM images, (b) K-doped Cu_2O thin-film photocurrent measurements at varying dopant concentrations produced by n-type electrodeposition, and (c) Cu_2O/ZnO heterostructure-based photoanode photocurrent responses at 0 V (vs. Ag/AgCl) under illumination in 0.1 mol phosphate buffered saline (PBS) with 0, 10, 40, 80, 100, 200, 500, and 1 000 mmol GSH present (from bottom to top)[19]

Recent progress includes a multimodule PEC stage that combines iridium oxide (IrO_2)-hemin-TiO_2 nanowire layouts to find glutathione (GSH) very accurately[22]. IrO_2 speeds up charge transfer happens faster, and haemin speeds up light absorption strongly and only occupies GSH molecules. This combined system improves both light absorption and charge transfer at the same time. It also uses IrO_2's catalytic properties to find functional biomolecules more accurately. Fig. 4 details the design and performance of this advanced nanowire-based biosensor for GSH detection.

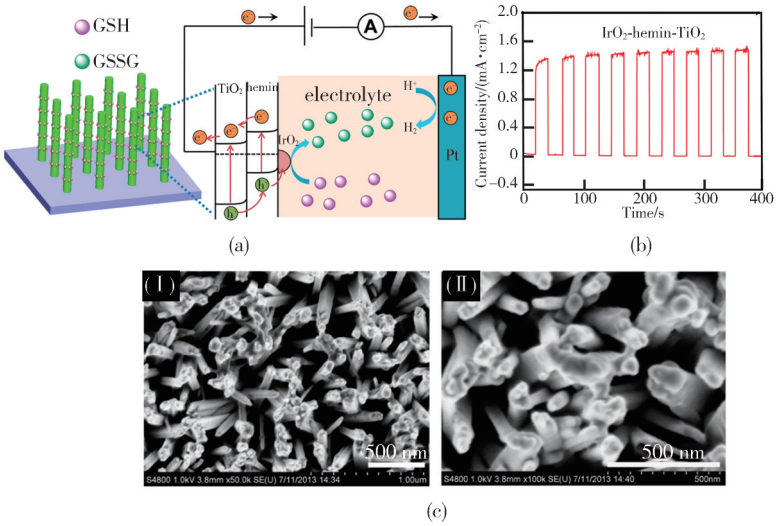

Fig. 4 Design and performance of IrO_2-hemin-TiO_2 nanowire-based PEC biosensor for glutathione detection. (a) A schematic representation of the PEC procedure for an IrO_2-hemin-TiO_2-Wire biosensor to detect GSH, (b) IrO_2-hemin-TiO_2 nanowire photoanode's time-dependent photocurrent density at repeated on/off cycles of simulated sunshine illumination, and (c) SEM pictures of IrO_2-hemin-TiO_2 nanowire arrays on an fluorine-doped tin oxide (FTO) glass substrate are shown in (I, II)[22]

The comparative study reported in Table 1 underlines the fundamental trade-offs inherent in selecting metal oxide semiconductors for PEC biosensing applications. Beyond fundamental bandgap considerations, the choice of material significantly affects charge-carrier dynamics, interfacial properties, and long-term stability. For

instance, whereas TiO_2 demonstrates outstanding chemical stability and photocatalytic activity, its UV-limited absorption needs sensitization techniques for practical biosensing in biological conditions. Conversely, Fe_2O_3 offers visible-light responsiveness and environmental friendliness but suffers from low charge-carrier mobility and recombination losses. WO_3 provides a balanced choice, with moderate visible-light absorption and good electron-transport properties, though its photocatalytic activity often requires co-catalyst integration. Cu_2O exhibits intense visible-light harvesting but suffers from stability issues due to photo-corrosion and oxidation susceptibility. $BiVO_4$ exhibits near-ideal bandgap alignment for visible light use, although it requires doping to overcome innate restrictions in electron mobility. These material-specific features directly influence biosensor design parameters, including detection sensitivity, operating lifetime, and application to specific analytes or environmental conditions. These intrinsic constraints are being addressed by new techniques, including heterojunction formation, nanoscale structuring, and surface functionalization, enabling more effective and adaptable PEC biosensing platforms.

Table 1 Comparative analysis of metal oxide semiconductors for photoelectrochemical biosensing applications, showing band gaps, advantages, limitations, and suitable applications.

Material	Bandgap range/eV	Light absorption	Advantages	Limitations	Best applications	Cost	Ref.
TiO_2	3.0－3.2	UV region only	Excellent chemical stability High photocatalytic activity Biocompatible Non-toxic	UV-based biosensing Medical implants Low water purification	UV-based biosensing Medical implants Water purification	Low	[7,9-11]
Fe_2O_3 (Hematite)	2.0－2.2	Visible light	Visible light active Low cost Abundant Environmentally friendly	Environmental monitoring Glucose detection Heavy metal sensing	Environmental monitoring Glucose detection Heavy metal sensing	Very low	[12-13]
WO_3	2.6－3.0	Visible light	Good electron mobility High stability in acidic conditions Strong absorption in visible region	Limited photocatalytic activity Requires co-catalysts Moderate cost	Gas sensing Ethanol detection	Moderate	[16-17]
Cu_2O	2.0－2.2	Visible light	Strong visible light absorption Suitable band positions Low toxicity	Poor stability (easily oxidizes) Photo-corrosion issues Requires protective layers	Glucose biosensors Photocathodes Heterojunction devices	Low	[18-20]
$BiVO_4$	2.4－2.5	Visible light	Ideal bandgap for visible light Good charge separation High photocatalytic efficiency	Low electron mobility Requires dopants for better performance Moderate stability	Water splitting Pharmaceutical detection Environmental analysis	Moderate	[14-15]
ZnO	3.2－3.3	UV region	High electron mobility Easy synthesis Various nanostructures possible	UV-limited absorption Dissolution in acidic conditions Photo-corrosion	UV biosensors Hybrid composites Gas sensing Low	Low	[30-42]

3.2 Photoelectrode materials-quantum dots

Here, Fig. 5 illustrates a typical quantum dot-based PEC biosensor for glucose detection, covering its design, material characterization, and sensing performance. There has been a lot of research on semiconductor quantum dots (QDs) and their unparalleled light-emitting characteristics, notably those made from Fig. 5 semiconductors like CdS and CdSe. Their size-dependent fluorescence and adaptable surface chemistry make them ideal for biological applications. Research has demonstrated QD-based electrochemical detection systems for multiple analytes. CdSe/ZnS QDs, coupled with glucose oxidase (GOx), have enabled oxygen and glucose.

Fig.5(a) gives a diagrammatic representation of PEC approach for detecting glucose at the GOx/CdTe/FTO electrode, and CdTe QDs and GOx/CdTe QDs on an FTO based electrode in SEM pictures, Fig.5(b) shows a sensor's photocurrent response when (0, 0.1, 1.1, 3.1, 5.1, 7.1, 9.1, 11.1, and 13.1 mol glucose (0.1 mol pH 7.0 Tris - HCl), Fig. 5(c) displays morphological and compositional characterization (SEM, EDX spectrum, elemental mapping of Ti, S, Cd, Se), and Fig.5(d) shows CdTe QDs' UV-vis absorption and fluorescence spectrum[22] detection, while near-infrared QDs have facilitated highly sensitive glucose measurement. CdS nanoparticles have also shown promise in direct glucose sensing. Additionally, a hybrid acetylcholinesterase (AChE)/CdS QD system has been developed for photocurrent-based biosensing of AChE inhibitors. These results demonstrate how semiconductor QDs can be used to create extremely sensitive and adaptable electrochemical sensors for use in biomedicine[23-25].

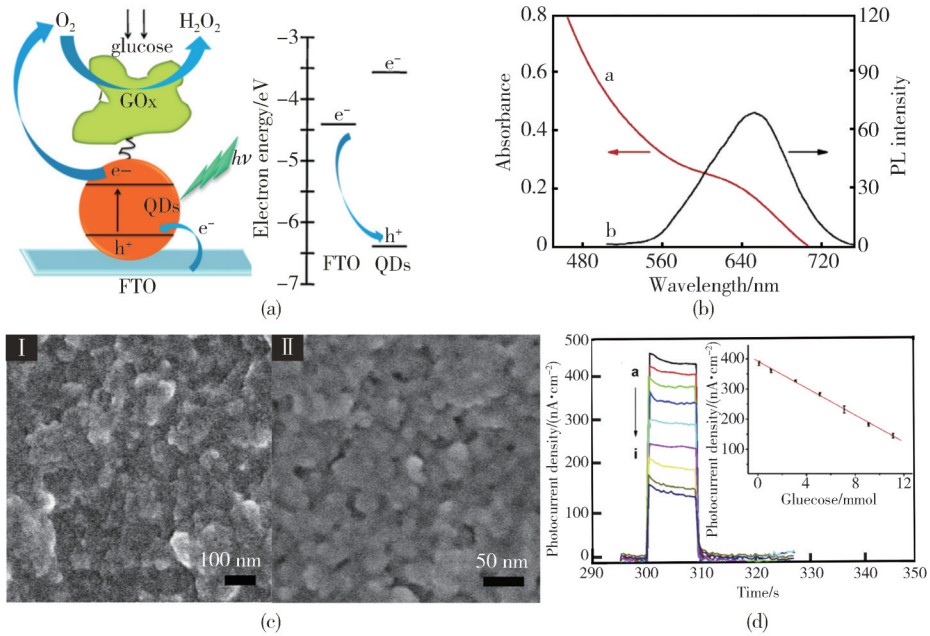

Fig. 5 Quantum dot-based PEC biosensor for glucose detection using CdTe QDs. (a) Diagrammatic representation of PEC approach for detecting glucose at GOx/CdTe/FTO electrode, (b) CdTe QDs' ultraviolet-visible absorption and fluorescence spectrum, (c) CdTe QDs and GOx/CdTe QDs on an FTO based electrode in SEM pictures, and (d) Sensor's photocurrent response when 0, 0.1, 1.1, 3.1, 5.1, 7.1, 9.1, 11.1, and 13.1 mmol glucose (0.1 mol pH 7.0 Tris-HCl) is present[23]

Some other kinds of QDs, like carbon quantum dots (CQDs) and silicon quantum dots (SiQDs), are also used in PEC biosensors. As shown in Fig.6, CQDs are favored for their strong luminescence, biocompatibility, and ease of functionalization, enabling applications in bioimaging and as fluorescent probes for detecting various analytes[26]. SiQDs, on the other hand, are utilized in PEC sensors due to their photoluminescence properties, allowing for the detection of substances like pesticides and antibiotics through quenching mechanisms[27].

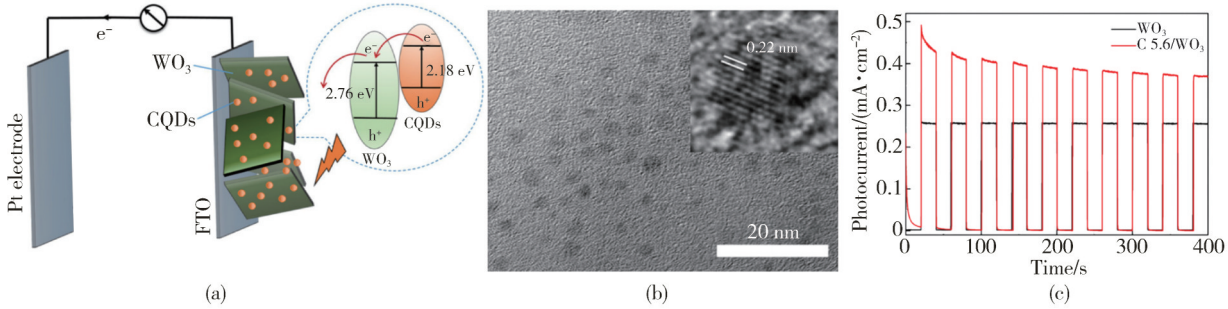

Fig. 6 CQDs/WO_3 composite structure and enhanced PEC performance. (a) CQDs/WO_3 composites schematic diagram in PEC system, (b) HRTEM pictures of CQDs at low and high magnification as they were prepared, and (c) Under simulated solar illumination, the transient photocurrent responses of WO_3 and the CQDs/WO_3 composites at 1.23 V (vs. reversible hydrogen electrode)[28]

The integration of QDs into PEC biosensors enhances light exploitation and charge isolation efficiency, leading to improved sensitivity and performance in detecting biological targets.

Lead-based PbS QDs are recognized for their small bandgap and robust absorption in the near-infrared spectrum, rendering them appropriate for photoelectrochemical applications. A study showed how to use PbS QDs and TiO_2 nanoparticles together to make a PBC aptasensor that can measure kanamycin. In this setup, PbS QDs/TiO_2 nanoparticles acted as the photosensitive composite, with a kanamycin-appointed deoxyribonucleicacid (DNA) aptamer as the acknowledgement element. The sensor can only detect 0.161 nmol·L^{-1}, however, it worked well for measuring kanamycin in honey and milk samples[29].

A different method entailed the integration of PbS QDs onto nanoporous NiO sheets to fabricate a self-sustaining cathodic photoelectrochemical biosensor. This hybrid nanostructure enabled effective charge separation and had commendable photoelectrochemical activity, indicating promise for glucose detection[30]. The structural and operational details of this hybrid system are presented in Fig.7.

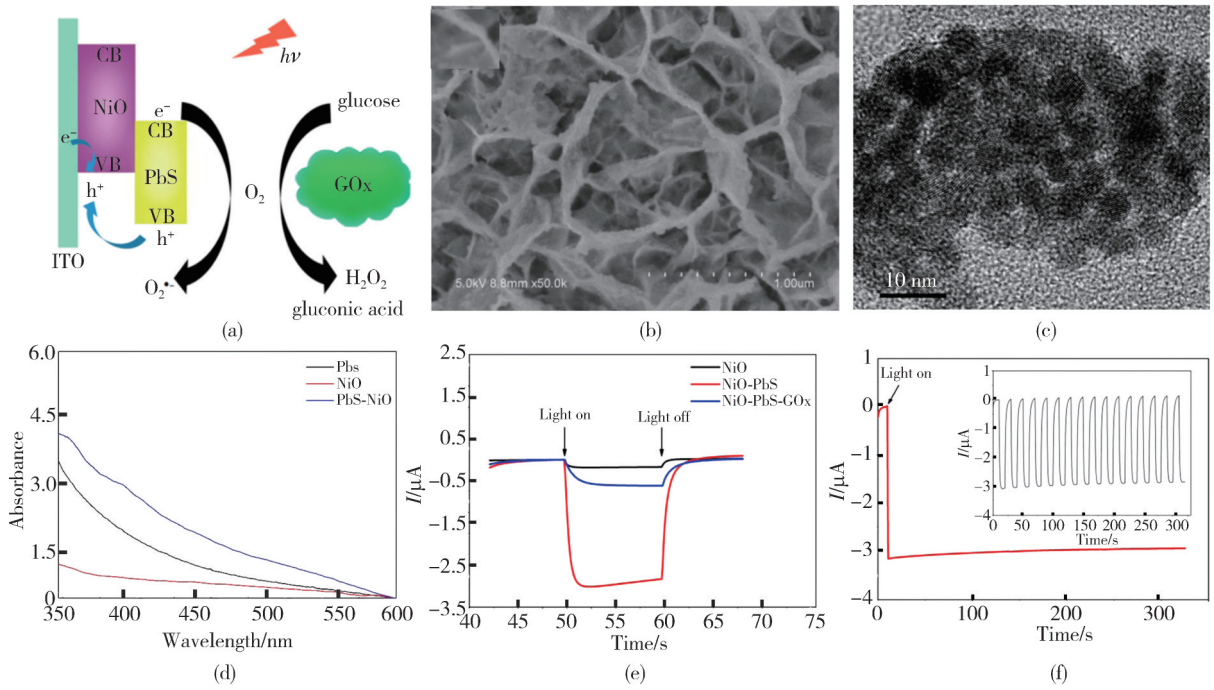

Fig. 7 PbS QD/NiO heterojunction-based PEC biosensor for glucose detection. (a) PEC glucose detection mechanism using NiO/Pbs heterojunction with GOx, (b) SEM image of PbS QD/NiO, (c) TEM pictures TEM of PbSQD, (d) Absorption, (e) PbS (black), NiO (red), and the hybrid (blue) ultraviolet-visible absorption or diffuse reflectance spectra, in an air-saturated 0.1 mol Tris-HCl solution (pH 7.0) at 0 V vs Ag/AgCl, the photocurrent responses of NiO nanofilm/ITO (black), PbS QD/NiO nanofilm/ITO (red), and GOx/PbS QD/NiO nanofilm/ITO (blue) electrodes correspond to 1.0×10^{-6} mol glucose when exposed to visible light, and (f) The PbS QD/NiO nanofilm/ITO electrod's time-based photocurrent response as it was manufactured, the operational durability test using repeated cycles of on and off illumination is displayed in the inset[30]

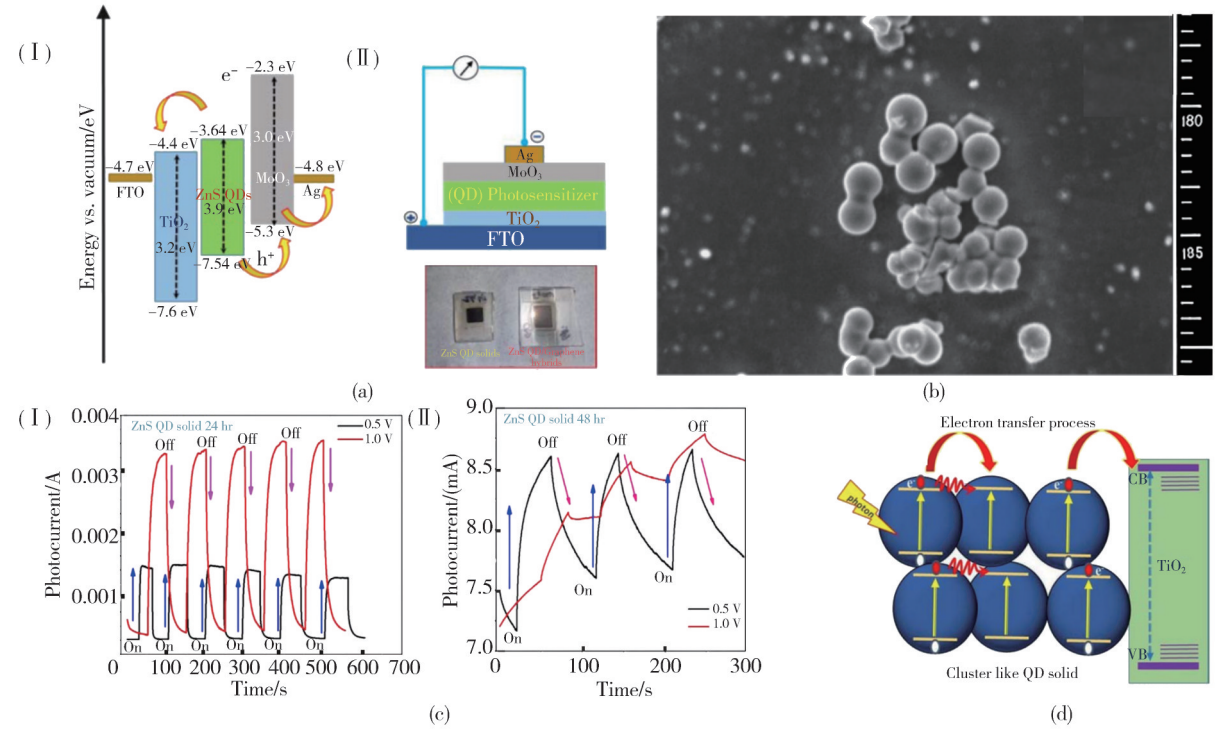

Fig. 8 ZnS quantum dot solid: energy alignment, morphology, and photocurrent characteristics. (a) (Ⅰ) Diagrammatic illustration of ZnS QDs solid's relative energy level position and (Ⅱ) Photocurrent device structure, (b) SEM photo of ZnSQDs, (c) Properties of photocurrent for produced ZnS QD solid at (Ⅰ) 24 hrs, (Ⅱ) 48 hrs, samples filed at various biasing voltage (0.5 V and 1.0 V), and (d) Diagrammatic illustration of the electron transfer procedure between a QD solid cluster and a TiO_2 film that decreases electron recombination as electron transfer rate increases[32]

QDs made of zinc have become promising element for PEC applications, especially for making solar cells work better. QDs made of Zn-Cu-In-Se that are about 4 nm in size have been shown to have a certified power conversion efficiency (PCE) of 11.6% in quantum dot-sensitized solar cells (QDSCs). This improvement is due to their better conduction band alignment and less charge recombination on the interface within the photoanode and the electrolyte. Fig. 8 explores zinc-based quantum dot systems for photocurrent generation, focusing on their energy alignment and charge-transfer mechanisms. Furthermore, ZnO QDs have been employed to sensitize hematite (α-Fe_2O_3) thin films, leading to increased visible light absorption and greater charge separation efficiency, thereby augmenting the overall efficacy of PECdevices[31].

A lot of researchers are interested in using CQDs to improve PEC biosensors since they have great optical properties, are safe for living things, and are good for the environment. These nanomaterials work as both electron acceptors and photosensitizers, which can improve the performance of PEC sensor significantly.

Fig.9 completely displays the development and performance of a carbon dot-modified TiO_2-based photoelectrochemical biosensor for glucose detection. The figure visually encapsulates the design rationale and experimental validation of this enhanced sensing platform, illustrating the core detection mechanism where carbon dots (CDs) and glucose oxidase (GOx) are integrated with branched TiO_2 (B-TiO_2) to facilitate visible-light-driven electron transfer. Key performance assessments, such as the photocurrent response at low bias and the stable photocurrent density under operating circumstances, are presented along with morphological confirmation of the synthesized nanomaterials. Collectively, this figure demonstrates how nanomaterial hybridization extends light absorption into the visible range and increases charge separation, thereby promoting the creation of low-cost, efficient PEC biosensors[33].

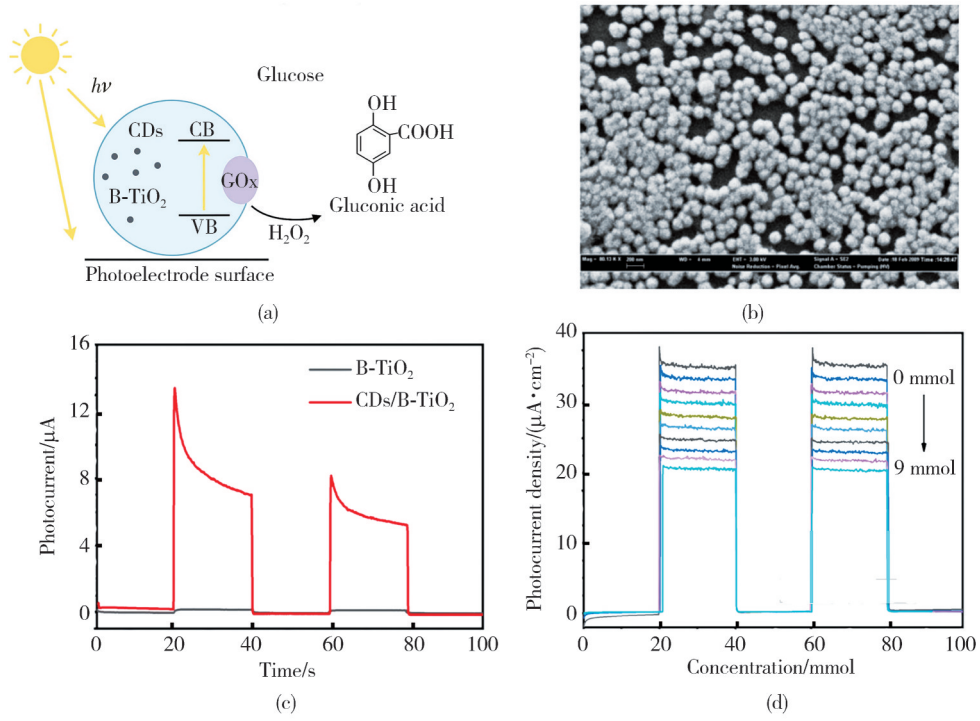

Fig. 9 Carbon dot-modified branched TiO_2 PEC biosensor for glucose detection. (a) Mechanism of PEC glucose detection by CDs/B-TiO_2/GOx, (b) SEM images of CQDs, (c) Photocurrent response at 0 V, and (d) CDs/B-TiO_2/GOx photocurrent density at 0 V in 0.100 mol PBS (pH=7.40)[33]

3.3 Organic materials in PEC biosensors

PEC biosensors employ light-sensitive and photoactive materials to produce measurable electrical signals, providing remarkable sensitivity and selectivity for detecting various analytes. The efficacy of these biosensors can be significantly enhanced by including certain chemical agents. The mechanisms by which pyridine and aromatic AZO chemicals facilitate PEC biosensing applications are outlined in below. Fig. 10 exemplifies how AZO dyes function as photosensitizers, highlighting their molecular structures and colorimetric detection capabilities.

Table 2 presents a comprehensive evaluation of several quantum dot materials applied in PEC biosensors. Optical characteristics, toxicity profiles, and application-specific needs must be carefully considered when choosing a QD

type.

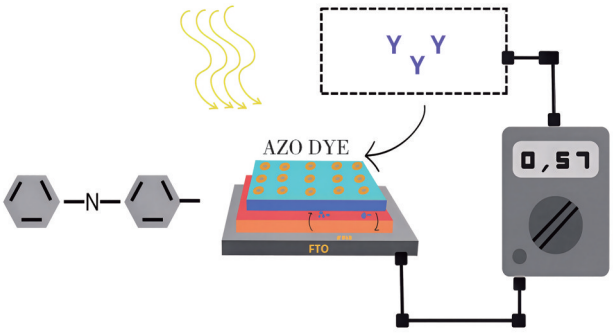

Fig. 10 Application of AZO dyes as photosensitizers in PEC biosensors. AZO dyes with characteristic −N=N− bonds absorb visible light and facilitate electron transfer processes. Their molecular structure enables selective ion detection (e. g., sulfide, S^{2-}) via colorimetric and spectrophotometric changes, demonstrating potential for visual PEC sensing applications

II-VI semiconductor QDs have excellent optoelectronic properties but raise concerns about toxicity, limiting their biomedical potential.

Carbon-based QDs are appropriate for clinical diagnostics because they solve biocompatibility concerns without sacrificing performance. Another biocompatible choice with adjustable emission properties is silicon QDs. Lead-based QDs enable near-infrared operation but are subject to regulatory limits due to their toxicity. Emerging ternary and hybrid QDs enable tailored features through composition engineering; however, at higher synthetic complexity. This comparison framework guides material selection based on target analyte, detection environment, and regulatory restrictions.

Pyridine, a heterocyclic aromatic chemical, has a complex function in PEC biosensors: Functionalizing semiconductor surfaces with pyridine moieties enhances biomolecule immobilization and facilitates efficient electron transport. Pyridine-functionalized cadmium sulfide (CdS) nanoparticles have been employed to develop the efficacy of PEC sensors by promoting effective interaction with target analytes[35]. Pyridine can either provide or take electrons, which helps charge transfer happen in the PEC system. This characteristic is very advantageous for the design of sensors with enhanced sensitivity and response times. Research has shown that pyridine-modified electrodes improve the PEC reduction of carbon dioxide, highlighting its versatility in PEC applications[35].

Table 2 Comparative analysis of QDs for PEC biosensing applications

QD type	Core composition	Bandgap range/eV	Key advantages	Primary limitations	Typical detection applications	Ref.
II-VI QDs	CdS, CdSe, CdTe	1.7−2.5	High quantum yield, size-tunable emission, and excellent electron transfer	Toxicity concerns, photobleaching, and environmental issues	Glucose, oxygen, and enzyme inhibitors	[22-24]
Carbon QDs	Carbon-based	2.0−3.0	Excellent biocompatibility, low toxicity, facile functionalization, strong luminescence	Moderate photocurrent generation, complex purification	Glucose, DNA, metal ions	[25,32,33]
Silicon QDs	Silicon-based	1.5−2.2	Biocompatibility, abundance, tunable photoluminescence	Lower quantum yield, synthesis complexity	Pesticides, antibiotics	[26]
Lead-based QDs	PbS, PbSe	0.7−1.3	Strong NIR absorption, small bandgap, high extinction coefficients	High toxicity, stability issues	Kanamycin, glucose	[28-29]
Ternary/Quaternary QDs	Zn-Cu-In-Se, etc.	1.0−2.0	Tunable bandgap, high absorption coefficients, good stability	Complex synthesis, cost considerations	Solar energy conversion	[30]
Hybrid QDs	Composite structures	Variable	Synergistic effects, enhanced charge separation, multifunctionality	Fabrication complexity, reproducibility challenges	Multiple analytes	[31,40]

Porphyrins have become essential elements in the advancement of PEC biosensors, utilizing their remarkable light-harvesting capabilities and electron transport characteristics. When 5, 10, 15, 20-tetrakis(4-hydroxyphenyl)porphyrin (THPP) is mixed with carbon nitride (CN), it makes a compound material that works much better as a PEC element in visible light. This improvement is because the material absorbs more visible light and separates charges more quickly, which makes it possible to detect glucose at very low levels, down to 0.3 mmol. By adding meso-tetrakis(4-sulfonatophenyl) porphyrin iron(III) chloride ($C_{44}H_{28}FeN_4O_{12}S_4Cl$) to TiO_2 nanoparticles, researchers were able to make PEC biosensors that can find glutathione at low potentials, with a detection boundary of 0.03 mmol·L^{-1}. Porphyrin-based covalent organic frameworks (COFs) have also been used as photocathode materials in PEC sensors to find lead ions. These sensors can find lead ions in a mass range of concentrations, from 0.05 nmol to 1 000 nmol, with a detection limit of 0.012 nmol. These changes show how flexible and useful porphyrin-based materials are for making PEC biosensors more sensitive and chosen for a broad range of biomedical and environmental uses[36-37].

Table 3 systematically compares organic materials utilized in PEC biosensors, highlighting their diverse functional roles and performance characteristics. AZO dyes

serve primarily as efficient photosensitizers with strong visible light absorption, though their stability requires optimization. Pyridine derivatives serve as interfacial modifiers, enhancing biomolecule attachment and facilitating charge transfer at electrode surfaces. Porphyrins represent versatile photoactive components with exceptional light-harvesting capabilities and catalytic functionalities, enabling sensitive detection of various analytes. Covalent organic frameworks extend these properties into ordered porous structures, offering high surface areas and tailored recognition sites. Charge transfer complexes provide innovative approaches to bandgap engineering through molecular-level interactions. The selection among these organic materials depends on the required light absorption range, desired interfacial properties, and specific recognition mechanisms, with ongoing research focusing on improving their stability, synthetic accessibility, and integration with inorganic components for hybrid PEC systems.

Table 3 Organic materials for PEC biosensing applications

Material class	Representative examples	Key functional features	Role in PEC systems	Advantages	Limitations	Detection applications	Ref.
AZO dyes	Various azo compounds	—N=N— chromophore, conjugation	Photosensitizer, electron mediator	Strong visible absorption, colorimetric response	Photodegradation, limited stability	Ion detection, colorimetric sensing	[34]
Pyridine derivatives	Pyridine, derivatives	Heterocyclic N, π-conjugation	Surface modifier, charge transfer facilitator	Enhanced biomolecule immobilization, interfacial engineering	Limited light absorption alone	CO_2 reduction, sensor surface modification	[35-36]
Porphyrins	THPP, Fe-porphyrins	Tetrapyrrole macrocycle, metal centers	Photosensitizer, catalytic center	Excellent light harvesting, tunable redox properties	Aggregation tendency, synthetic complexity	Glucose, glutathione, and heavy metals	[11,37-38]
Covalent organic frameworks (COFs)	Porphyrin-based COFs	Periodic porous structure	Photocathode material, recognition platform	High surface area, structural regularity, multi-functionality	Synthesis challenges, stability in aqueous media	Lead ions, small molecules	[38]
Charge transfer complexes	Dopamine-Ti complexes	Donor-acceptor interaction	Visible light sensitizer, charge transfer mediator	Bandgap engineering, biocompatibility	Limited library of effective pairs	NADH, neuro-transmitters	[10]

3.4 Plasmonic nanostructure

Plasmonic nanostructures are very promising for making PEC biosensors work better since they can boost light absorption and produce strong local electric fields at the nanoscale. When added to PEC systems, plasmonic materials like gold (Au) and silver (Ag) nanoparticles dramatically enhance the number of charge carriers, which makes the photocurrent responses better. The localized surface plasmon resonance (LSPR) outcome of these nanostructures may be changed to work best at certain wavelengths. This makes them better at collecting light and makes PEC biosensors more sensitive. Additionally, plasmonic nanomaterials facilitate efficient charge separation, reducing recombination losses and thereby improving sensor stability and reliability.

3.4.1 Enhancement performance

Recent research has demonstrated the synergistic benefits of plasmonic nanostructures in PEC biosensors for use in environmental monitoring, illness detection, and food safety. For instance, a study published by RSC *Advances* highlighted the enhancement of PEC performance in biosensors through the integration of gold nanoparticle-decorated polyaniline/TiO_2 nanotube arrays. The study demonstrated improved visible-light absorption and charge separation efficiency, leading to higher sensor sensitivity[38]. Similarly, a review by MDPI *Chemo-sensors* discussed the role of various nanostructured materials, including plasmonic nanoparticles, as transducers and signal amplifiers in PEC biosensors, further supporting their significance in bioanalysis[39].

Plasmonic nanomaterials, such as gold Au nanoparticles (AuNPs) and silver Ag nanoparticles (AgNPs), etc. are often used in PEC biosensors due to their unparalleled optical characteristics. These substances improve charge separation and light absorption, raising the sensitivity and effectiveness of PEC biosensors[40]. These results show that the field needs to improve sensitivity, selectivity, and detection efficiency by using plasmonic nanostructures in PEC biosensors in order to go forward. They are essential for next-generation biosensing applications because of their capacity to control light at the nanoscale and enable charge transfer mechanisms.

The LSPR of noble metal nanoparticles, when these are lit up by visible light. When these nanoparticles are excited, which create very strong localized electromagnetic fields near their surface. This greatly improves the ability of nearby ZnO semiconductors to absorb light, especially in the visible range. A wide-band semiconductor has a wide bandgap. Also, the Schottky barrier at the Au-ZnO

interface makes it easier for charges to separate because it lets photoexcited electrons move to the conduction band of ZnO from Au, meanwhile holes stay in Au. This breakage of charge carriers in space slows down recombination and makes carriers last longer, which improves the overall photocurrent responsiveness. Moreover, nanostructure engineering—such as creating porous or core-shell architectures—can increase the interfacial contact area, amplifying plasmonic field effects and enabling more efficient light-matter interactions. These enhancements are crucial in PEC applications, particularly in biosensing and photocatalysis, where sensitivity and efficiency depend heavily on light-harvesting capability and charge dynamics[41-42].

From a practical cost-effectiveness perspective, the 'efficiency' of plasmonic nanoparticles in PEC biosensors should be understood in terms of the net gain in photocurrent/sensitivity arising from plasmon-assisted light harvesting and interfacial charge separation, rather than material cost alone. In general, Ag nanoparticles can provide strong near-field enhancement due to relatively low optical losses, yet their susceptibility to oxidation/tarnishing often introduces stability-driven performance decay, increasing the need for protective coatings and thus the overall processing complexity. Au nanoparticles typically offer more robust chemical stability and reproducible plasmonic behavior with mature surface-functionalization chemistry, but their high material cost can limit large-scale deployment unless the target application demands high reliability and long operating lifetime. Cu nanoparticles are attractive from a raw-material cost standpoint; however, rapid surface oxidation and performance variability often necessitate passivation or core-shell engineering, which may offset the apparent cost advantage when considering long-term operation. Therefore, the practical selection of plasmonic nanoparticles should balance plasmonic enhancement strength, spectral matching to the excitation source, interfacial charge-transfer benefits, and stability-related losses to achieve an optimal efficiency–cost trade-off for a given biosensing scenario. The most commonly used plasmonic nanoparticles are summarized in Table 4.

Table 4 Comparative analysis of plasmonic nanoparticles for PEC biosensors: efficiency, cost, and applications

Material	LSPR band (peak)	Hot-electron injection efficiency	Stability	Relative cost	Key advantages	Major limitations	Recommended use case
Gold (Au)	Visible-NIR (~520–580 nm, tunable)	High (up to ~45% into TiO_2)	Excellent (chemically inert)	Very high	Strongest & most tunable LSPR, superior stability, biocompatible	High material cost	High-performance, clinical, or fundamental research sensors where sensitivity is paramount
Silver (Ag)	Visible (~400–450 nm)	Moderate to high	Moderate (prone to oxidation/sulfidation)	Medium	Strong plasmonic response in the visible range, lower cost than Au	Susceptible to degradation, requires stabilizers	Cost-sensitive applications where high visible-light enhancement is needed
Copper (Cu)	Red-NIR (~570–600 nm)	Moderate	Low to moderate (easily oxidizes)	Low	Lowest cost, decent plasmonic activity in red/NIR	Poor ambient stability requires robust passivation	Exploratory research, disposable, or cost-driven sensors for proof-of-concept
Alloys/Core-shell (e.g., Ag@Au)	Tunable (depends on composition/structure)	High (combines advantages)	High (protected core)	High	Combines advantages (e.g., Ag's cost & Au's stability), tunable properties	Complex synthesis, higher cost than single metals, reproducibility challenges	Advanced biosensors requiring specific spectral tuning, long-term stability, and balanced performance

When AgNPs are added to BiOCl composites, PEC responses improve, making it easier to detect chloramphenicol. AgNPs have also been used to make dye-sensitized solar cells work better by adding them to platinum counter electrodes, which increases power conversion efficiencies. The amalgamation of AgNPs with ZnO and Ag_2WO_4 has exhibited enhanced PEC water oxidation efficacy, ascribed to the plasmonic properties of silver. These examples highlight the crucial role of AgNPs in the advancement of PEC sensing technologies via plasmonic enhancement mechanisms. A practical example of such plasmonic enhancement is shown in Fig.11, detailing an AgNP-based aptasensor for chloramphenicol detection[43].

3.4.2 Hot electron injection

Hot electrons are highly energetic charge carriers generated when plasmonic nanostructures, such as Au or Ag nanoparticles, are illuminated by incident light through LSPR. As shown in Fig.12, these non-equilibrium electrons possess energies significantly higher than the Fermi level of the metal, enabling them to overcome the Schottky barrier at the metal-semiconductor interface and be injected into the conduction band of adjacent semiconductors (e. g., TiO_2, ZnO)[44].

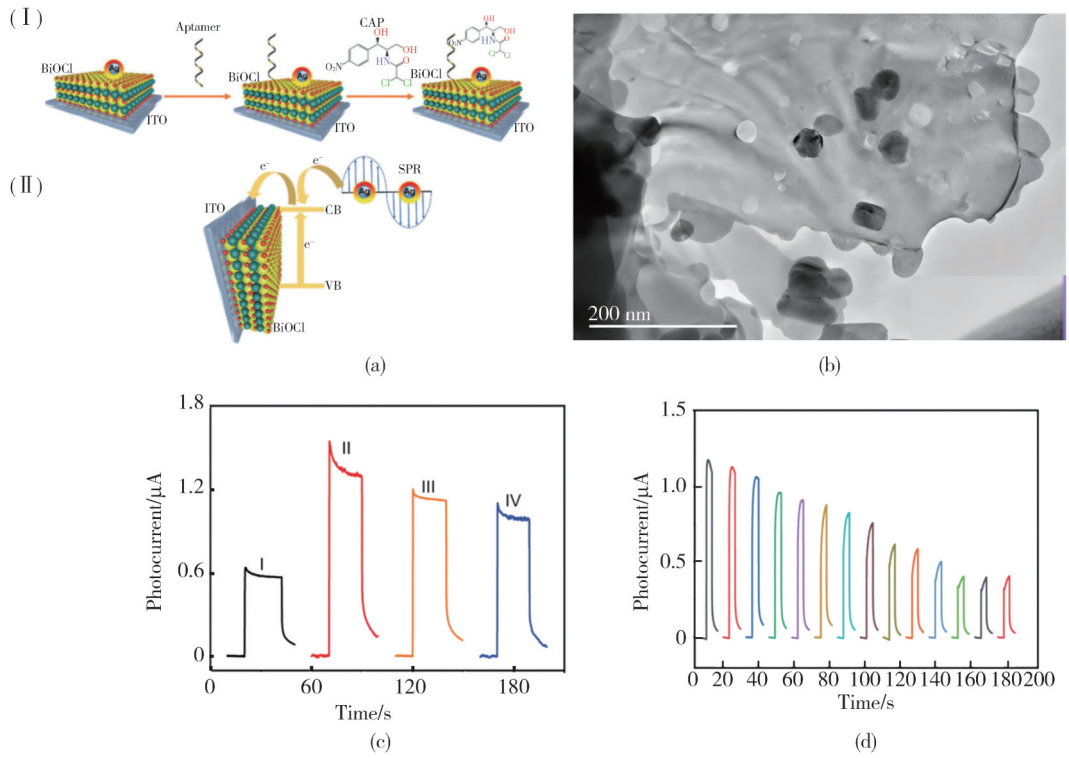

Fig. 11 AgNP/BiOCl-based PEC aptasensor for chloramphenicol detection. (a) (Ⅰ) Procedure of the built PEC aptasensor founded on aptamer/AgNP/BiOCl/ITO electrode and (Ⅱ) photocurrent improved mechanism of AgNP/BiOCl/ITO electrode, (b) SEM images of AgNPs/BiOCl, (c) Photocurrent responses of different electrodes: (Ⅰ) BiOCl/ITO, (Ⅱ) AgNP/ BiOCl/ITO, (Ⅲ) aptamer/AgNP/ BiOCl/ITO, and (Ⅳ) aptamer/AgNP/BiOCl/ITO with 0. 5 pmol chloraphenicol, and (d) Photocurrent responses of the aptamer/AgNP/ BiOCl/ITO electrode at different chloraphenicol concentrations[43]

This hot electron injection mechanism works by extending the photoresponse of the semiconductor into the visible or even near-infrared region, improving charge separation efficiency and reducing electron-hole recombination losses. For instance, Kang et al. demonstrated that Au nanoparticles decorated on ZnO nanorods efficiently injected hot electrons into ZnO under visible light, leading to enhanced photocurrent and improved biosensing sensitivity[45]. Similarly, Wang et al. reported that Au-modified TiO_2 nanotubes generated strong PEC responses due to hot electron injection coupled with Schottky junction formation, enabling highly sensitive glucose detection[46]. Moreover, defect-engineered TiO_{2-x} combined with Au nanoparticles further promoted hot electron transfer and broadened light absorption, offering a pathway toward ultrasensitive biosensing platforms[47]. Quantitative studies have shown that the proficiency of hot electron injection from Au nanoparticles into TiO_2 can reach up to 25% — 45%, confirming its vital contribution to enhanced PEC performance. Collectively, these examples demonstrate that hot electron injection is a powerful strategy for developing the sensitivity, spectral response, and overall analytical performance of PEC biosensors. In a recent study, a TiO_2/Au film photoelectrode decorated with AuNPs was engineered to enhance PEC detection of AFP through the dipole image effect. As illustrated in Fig.12, the hybrid structure significantly improves charge separation: under illumination, photogenerated electrons in TiO_2 transfer efficiently to the underlying Au layer, while the localized surface plasmon resonance of AuNPs amplifies the electric field and accelerates electron-hole separation. This synergistic effect results in a pronounced photocurrent response that decreases progressively with increasing AFP concentration, enabling highly sensitive detection. By integrating lock-in amplification to suppress background noise, the system achieves an improved signal-to-noise ratio and lower detection limits, demonstrating an effective strategy for high-performance PEC biomarker sensing[48].

AuNPs are important for improving the efficacy of PEC biosensors because of their distinctive plasmonic characteristics. When combined with semiconductor materials such as ZnO nanorods, AuNPs promote the formation of "hot electrons" via SPR, which are subsequently injected into the semiconductor, resulting in enhanced charge separation and elevated photocurrent. This method has been efficiently employed in self-driven PEC biosensing devices for detecting biomolecules, including glutathione.

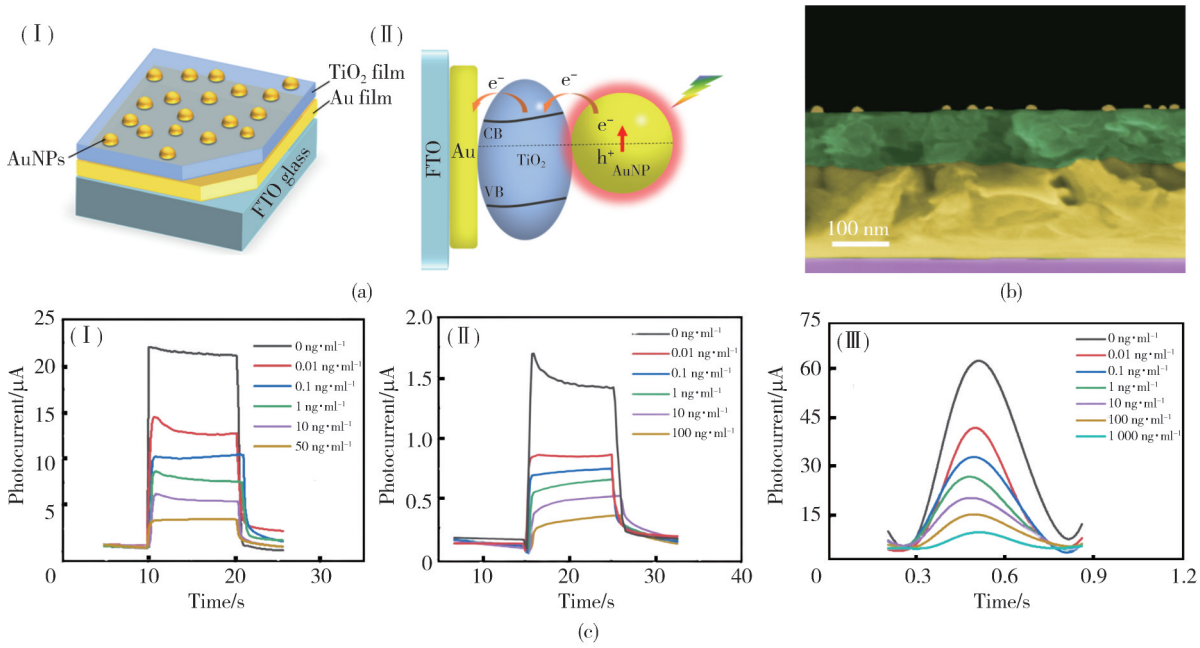

Fig. 12 TiO_2/Au film photoelectrode for enhanced PEC detection of alpha-fetoprotein using dipole image effect. (a) (Ⅰ) Sandwich structure of AuNPs/TiO_2/Au (ATA) and (Ⅱ) ATA Film's charge transfer procedure, (b) Prepared ATA-Film/FTO's cross-section, and (c) Sensors' photocurrent response based on (Ⅰ) Sandwiched structure of ATA, (Ⅱ) AuNPs/TiO_2 Structure, and (Ⅲ) Sandwiched structure of ATA using lock-in amplification (LIA) method to detect various concentration of alpha-fetoprotein (AFP)[48]

Furthermore, AuNPs have been utilized as nanozymes, emulating enzyme activity in glucose detection. In these applications, AuNPs facilitate the oxidation of glucose, utilizing oxygen and leading to a quantifiable reduction in photocurrent, thus allowing for precise glucose measurement. The SPR effect of AuNPs has increased the PEC responses of TiO_2 nanotube arrays when expounded to visible light. This makes them useful for glucose biosensing. These results highlight the crucial significance of AuNPs in the progression of PEC biosensor technologies via plasmonic enhancement mechanisms[49].

Fig. 13 presents a systematic investigation into the plasmonic enhancement of a photoelectrochemical biosensor utilizing gold nanoparticle-modified TiO_2 nanotube arrays.

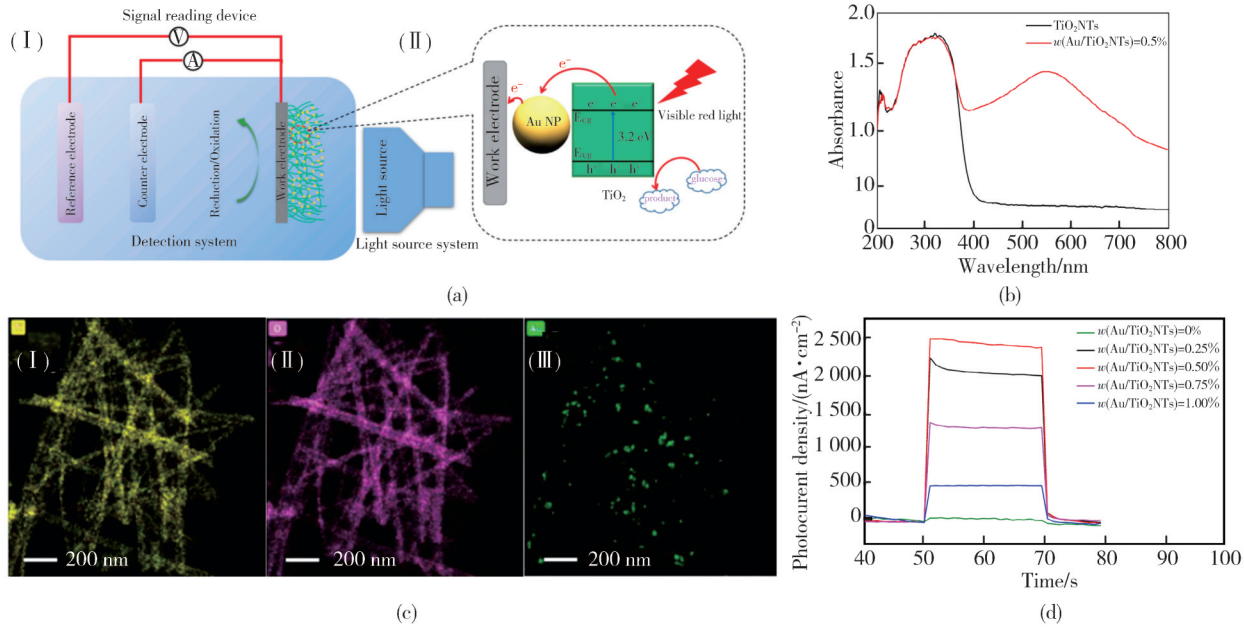

Fig. 13 Au nanoparticle-modified TiO_2 nanotube arrays for plasmon-enhanced PEC glucose sensing. (a) (Ⅰ) PEC measurement via 3-electrode system and (Ⅱ) procedure of PEC detection of glucose at Au/TiO_2NTs, (b) Ultraviolet-visible DRS of TiO_2NTs and w(Au/TiO_2NTs)=0.5%, (c) (Ⅰ) Ti, (Ⅱ) O, and (Ⅲ) Au images of w(Au/TiO_2NTs)=0.5%, and (d) Photocurrent-time responses of different gold loadings of Au/TiO_2NTs in 0.1 mol NaOH at 0.3 V[46]

The figure clearly illustrates how incorporating Au nanoparticles significantly enhances the sensor′s performance via surface plasmon resonance, amplifying visible-light absorption and facilitating efficient charge separation. The figure presents experimental evidence confirming improved optical properties via spectral analysis and validating the uniform distribution of AuNPs via elemental mapping. Furthermore, the figure demonstrates the optimization of photocurrent response as a function of gold loading, revealing a clear correlation between nanoparticle concentration and sensor sensitivity. This work visually encapsulates the key advantages of plasmonic nanostructures in PEC biosensing, including improved signal generation, extended spectral response, and the potential for highly sensitive glucose detection at low operating potentials, thereby providing a compelling case for integrating noble metal nanoparticles into next-generation photoelectrochemical plat.

Copper nanoparticles (CuNPs) have emerged as efficient materials in PEC applications, utilizing their plasmonic characteristics to improve device performance. The integration of CuNPs into PEC systems has resulted in substantial enhancements in photocurrent responses. Researchers found that adding a well organized CuNP array to a multi-layer graphenex-CdSe nanoribbon Schottky junction created a device with localized surface plasmon resonance in the 700—900 nm region. LSPR caused hot electron injection, which led to a higher switch ratio, responsivity, and detectivity[50]. Also, putting CuNPs on TiO_2 films using electrodeposition has been shown to make dye-sensitized solar cells work better. The plasmonic outcome of CuNPs made the dye load and light absorption better, which made the power conversion more efficient[51].

3.5 Enhancement of PEC performance using 2D nanomaterials

Graphene and molybdenum disulphide (MoS_2) are two-dimensional (2D) materials that have gotten a lot of attention for increasing PEC performance because of their unique structural and electrical properties. It has been shown that combining MoS_2 with graphene in PEC applications makes the catalyst more active and the charge transfer more efficient.

For instance, a study found that a graphene/MoS_2 heterojunction on indium tin oxide (ITO) substrates had a cathodic-shifted water oxidation starting potential of about 0.18 V and was almost three times more efficient at converting light into electricity than MoS_2. The vertically aligned structure of MoS_2 nanosheets, which makes it easier for electrons and holes to move and separate, as well as the heterojunction that makes it easier for photogenerated electron-hole pairs to transport and separate, were both thought to be responsible for this improvement[52]. Another study showed that a monolayer MoS_2/WSe_2 heterojunction had a 50% higher incident photo-to-current conversion efficiency and a 5.6-fold higher PEC current than monolayer WSe_2 cathodes. This research also proved the dynamics of 2D material heterostructures in PEC applications[53]. The surperior performance of such 2D heterojunction is convincingly shown in Fig.14.

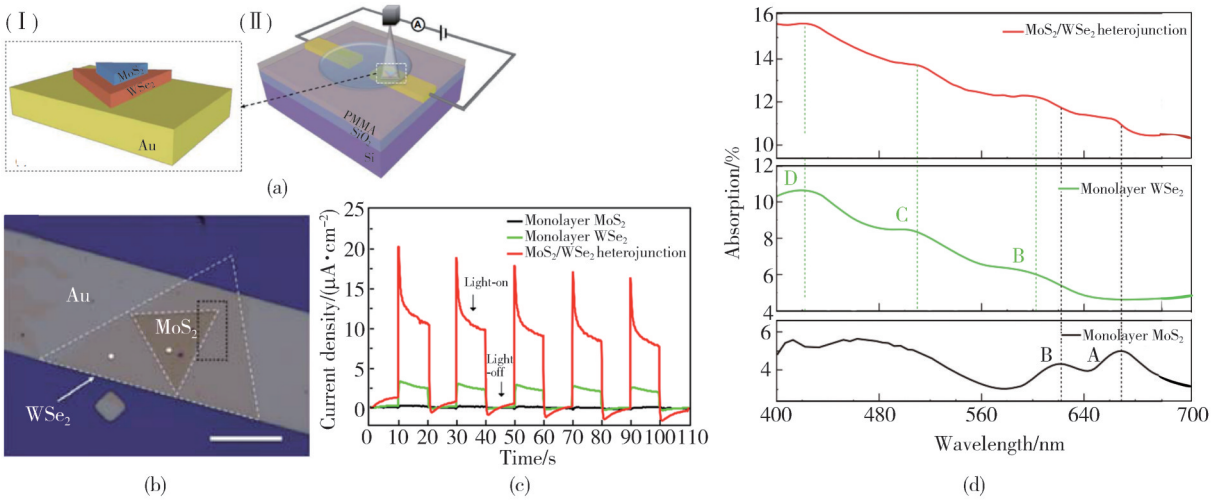

Fig. 14 Monolayer MoS_2/WSe_2 heterojunction for enhanced PEC performance. (a) Schematic diagram of (I) MoS_2/WSe_2 heterojunction and (II) PEC device & measurement, (b) Optical photo of monolayer MoS_2/WSe_2 heterojunction (dashed in white triangle), (c) Current response graph for three samples, and (d) Absorption spectra of monolayer MoS_2 (black curve), monolayer WSe_2 (green curve), and MoS_2/WSe_2 heterojunction (red curve)[53]

4 Challenges & future perspectives of PEC biosensor

4.1 Stability & reproducibility issues

For PEC biosensors to function dependably in real-world applications, stability and reproducibility must be guaranteed. Stability means that the sensor can keep working the same way throughout time, and repeatability means that it can give the same results every time it is used in the same way. Several factors can compromise these aspects.

Enzymes and antibodies are examples of biological recognition components that might degrade over time, resulting in decreased sensor effectiveness[54]. PEC biosensor stability and repeatability can be negatively influenced by external causes such as temperature swings, pH changes, and light exposure. The photoactive materials used in PEC biosensors may undergo degradation or structural changes during operation, impacting their stability and reproducibility[55]. Addressing these challenges requires the development of advanced manufacturing processes, the controlled preparation of functional nanomaterials, and the design of integrated detection components[56]. Even with these improvements, problems like long-term stability, reproducibility, and fitting into current systems still exist. Researchers are still working on these problems to make it easier to employ PEC biosensors in a wider range of fields.

4.2 Biocompatibility and real-world applications

To be able to use PEC biosensors in real-life biomedical applications, they must be biocompatible. Biocompatibility is the ability of a substance to do what it is supposed to do without creating any bad effects on the host's body or on the environment. The ISO 10993 collection of standards, which includes tests for cytotoxicity, sensitization, and implantation, gives us a way to judge how biocompatible medical devices are[57].

In practical applications, PEC biosensors have been utilized in various domains. They are employed to detect biomarkers and facilitate early disease diagnosis and monitoring. PEC biosensors aid in detecting pollutants and pathogens in water sources, contributing to public health and safety. These sensors are used to identify contaminants and ensure the quality of food products.

4.3 Enhancing selectivity and reducing interference

Enhancing selectivity and minimizing interference are pivotal challenges in the development of PEC biosensors. Several strategies have been employed to address these issues: Adding aptamers to PEC biosensors makes them more specific. Aptamers are single-stranded nucleic acids that only bind to designated compounds. When aptamers bind to their targets, they alter shape in a way that can be sensed electrically, which makes the sensor more selective[58-59]. Implementing ratio-metric PEC sensors, which utilize dual-signal responses, allows for self-calibration and correction of environmental interferences. By measuring the ratio of two signals, these sensors enhance accuracy and reduce the impact of external factors[60]. Using nanostructured materials, such as wrinkled photoelectrodes loaded with quantum dots, can greatly improve the signal-to-noise ratio and PEC current. This change makes it easier to find the target analyte and more specific[61]. Collectively, these approaches contribute to the development of PEC biosensors with improved selectivity and reduced interference, thereby enhancing their applicability in complex analytical scenarios.

4.4 Future research directions and emerging materials

Advancements in PEC biosensors are increasingly focusing on novel materials and innovative designs to enhance performance. Emerging materials such as up conversion nanoparticles and TiO_2/CdTe heterostructures are being integrated to create near-infrared (NIR) light-driven PEC sensors, offering deeper tissue penetration and reduced photodamage in biomedical applications[62]. Future studies will also focus on developing smaller PEC devices in order to produce portable, easily navigable sensors for environmental monitoring and point-of-care diagnostics[63]. Furthermore, as these materials can improve the sensitivity and selectivity of PEC sensors, research into nanomaterials with special optical, electrical, and mechanical properties is a promising direction. Moreover, integrating advanced signal amplification procedures, like as the usage of dual-signal amplification with gold nanoparticles and quantum dots, is being investigated to improve detection limits and overall sensor performance. It is anticipated that these advancements would increase the use of PEC biosensors for environmental monitoring, food safety, and medical diagnosis. After all, the sensitivity of PEC technology for detecting biomolecules depends on being able to separate and move photoexcited charge carriers. Charge recombination on the electrolyte/ electrode interface has a big influence on charge storage, which has been studied a lot in PEC water splitting and solar cell applications. Stability is still a big problem with enzyme-based PEC

sensing because of enzyme photodegradation. This shows how important it is to use non-enzymatic techniques. However, non-enzymatic PEC sensing faces challenges such as limited detection sensitivity and the requirement for biomolecular oxidation, necessitating the development of non-destructive detection methods. By increasing photocatalytic sites and analyte diffusivity, new 3D photoelectrode topologies such as fibrous membranes, inverse opals, and tree structures can improve PEC bioanalysis by increasing detection efficiency and PEC oxidation rates. These developments open the door to PEC biosensors that are more sensitive and stable[64-66].

Moreover, the operational mechanism of PEC biosensors is straightforward and cost-effective, facilitating ongoing research and application in the detection and diagnosis of early-stage cancer, with the potential for designing portable instruments for enhanced convenience in detection. Consequently, it is imperative to identify additional photocatalytic materials appropriate for PEC and biological analysis, investigate materials with enhanced external quantum efficiency, and thereby augment the sensitivity of PEC and biological sensors. Also, more research and design of nonbiological interfaces in PEC biosensors needs to be done to find better ways to hold biomolecules in place. This will make these sensors more stable and effective for commercial use over time.

5 Conclusions

In this review, we summarize the different materials and mechanisms that make PEC biosensors work, focusing on their uses in areas including food safety, environmental monitoring, and biomedical diagnostics. The paper stresses the importance of common photoactive materials, including metal oxides, quantum dots, and organic compounds for sensitive and selective analyte detection. PEC biosensors have a lot of potential for use in things like sensing glucose and finding cancer biomarkers using charge carrier dynamics and signal-generating mechanisms.

Charge recombination, stability problems with enzyme-based sensors, and the drawbacks of non-enzymatic techniques, however, continue to be barriers to further development. The sensibility and performance of these sensors can be greatly developed by combining surface plasmon resonance and hot electron injection with cutting-edge techniques like hybrid systems and 3D photo-electrode designs.

Looking ahead, the ongoing study should center upon addressing these challenges while exploring new materials and novel detection strategies. Ultimately, PEC biosensors hold great promise in revolutionizing the way we monitor and detect chemical and biological analytes, offering new solutions for health and environmental monitoring.

Acknowledgement

This work was financially supported by National Natural Science Foundation of China (Nos. 61971301, 62031022, 51975400), in part by the Central Guidance on Local Science and Technology Development Fund of Shanxi Province (No. YDZJSX2021A01), and Fundamental Research Program of Shanxi Province (No. 202303021212082).

Declaration of conflicting interests

The authors have no conflict of interests related to this publication.

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光电化学生物传感器中光活性材料简述

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摘　要： 光化学电(Photoelectrochemical, PEC)生物传感器因其在氧化反应过程中借助产生光电流来检测生物分子的能力, 以及其高灵敏度、背景干扰小、成本效益高和便携性等特点, 引起了越来越多的关注。本综述对驱动PEC生物传感器性能的光活性材料进行了全面总结。首先, 概述了PEC生物传感的基本理念和信号生成过程, 强调了电荷载流子动力学在光电流产生中的关键作用。其次, 文章主体部分详细探讨了几类光活性材料, 如金属氧化物、量子点、有机材料、等离子体纳米结构和二维纳米材料。此外, 以当前实验研究为支撑, 讨论了每种材料类型的特殊性质、电荷转移方法、光捕获能力和对生物传感器性能的影响;为提高灵敏度和选择性, 研究了关键的设计技术, 包括异质结形成、表面功能化和热电子注入;探讨了PEC生物传感器的主要问题, 包括干扰减少、生物相容性、材料稳定性和可重复性。最后, 讨论了未来的发展方向, 重点在于新材料、创新的设备设计以及在食品安全、环境监测和即时诊断方面的潜在应用。这篇全面综述旨在帮助研究人员选择和创造用于未来高性能PEC生物传感器的前沿光活性材料。

关键词： 光电化学; 生物传感器; 免疫检测; 传感器技术

引用格式： Md Hayatul Islam, XUE Yingxian, LI Min, et al. A brief review of photoactive materials for photoelectrochemical biosensors. Journal of Measurement Science and Instrumentation, 2026, 17(1): 16-35. DOI: 10.62756/jmsi.1674-8042.2026002