



Review Article

The role of emerging photoactive nanostructures in electrochemical sensor construction: Synthesis, properties, challenges, and perspectives

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ABSTRACT

Functional characteristics with high photoactive and electroactive properties have been emerging as the subject of advanced analytical applications. Recently, significant research has been augmenting the development of photoactive nanomaterials that can be utilized for both qualitative and quantitative determination of analytes for environmental, food, and healthcare applications. This review focuses on recent advancements in photoactive nanostructures for photoelectrochemical (PEC) sensing applications, emphasizing their preparation, functionalization, and electrode construction strategies. Key developments include the rational design of photoactive materials with enhanced photoelectrochemical performances and signal-amplification techniques for improved sensitivity and selectivity. The review highlights the application of PEC sensors for detecting various analytes, such as insecticides, antibiotics, pathogens, carcinogenic compounds, and metabolic disorder markers in environmental, food, and healthcare settings. Current challenges, including material stability, selectivity, and real-world applicability, are critically discussed, along with future research directions for designing next-generation PEC sensors with superior functional properties.

Introduction

Engineered nanomaterials are chemically synthesized substances that are designed at angstrom scale levels, typically 1–100 nm, and exhibit distinct dimensional properties [1]. These materials are renowned for their unique characteristics, such as high surface area, mesoporous structures, superior thermal and mechanical stability, remarkable electrical conductivity, and dynamic optical properties [2,3]. These attributes make engineered nanomaterials highly versatile, enabling their application across various sectors, including energy conversion and storage [4–7], catalysis [8,9], sensors [10,11], biochemical analysis [12–14], bioimaging [15,16], clinical diagnostics [17,18], and therapeutic treatments [19,20]. Among these applications, sensors stand out due to their critical role in everyday life, particularly in current technological contexts [10,21]. Sensors are devices designed to detect minimal environmental changes at the micro or macro levels even at the attomole/gram level and convert these variations into measurable signals through a transducer [22,23]. These detection methods can vary based on the type of change detected—be it color [24,25], electrical resistance [26,27], conductivity [28,29], and signal ratio [30–32], are

leading to classifications such as optical, electrical/electrochemical, chemiresistive/impedimetric, conductometric, and ratiometric sensors. Electrochemical/impedimetric sensors have shown significant promise, especially in applications related to environmental monitoring, food safety, and healthcare [33–36]. Electrochemical analysis encompasses a variety of techniques, including voltammetry, conductometry, diffusion pulse voltammetry, linear sweep voltammetry, amperometry, chronopotentiometry, and impedimetric methods [37,38]. The increasing industrialization and urbanization worldwide have escalated the presence of environmental contaminants, which pose significant threats to human health and ecosystems. The World Health Organization (WHO) identifies air pollution (both indoor and outdoor) [39,40], electronic waste (e-waste) [41], and pollutants in water, food, and biological waste as leading environmental concerns [42–44]. Industrial activities contribute significantly to the release of heavy metals, pesticides, dyes, pharmaceutical, and personal care products residues into the environment, leading to bioaccumulation and increased toxicity in water and soil, thereby disrupting ecological balance and threatening public health [6,45]. To mitigate these toxic particulates, various methods such as adsorption [46,47], filtration [48,49], conversion and storage [50,51],

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and degradation [52] have been developed, often transforming harmful substances into valuable, eco-friendly products [53–56]. However, the persistent presence of residual toxicants remains a concern, especially in industrial effluents and synthetic waste, which directly or indirectly impact environmental and human health [57]. This underscores the need for improved monitoring and detection methods. Recent advancements in electrochemical approaches have led to the development of photoelectrochemical (PEC) methods, which combine photo-irradiation with electrochemical techniques [58]. The PEC method is particularly advantageous due to its higher stability, low energy consumption, rapid response, and ease of operation [59–64]. In PEC detection, light irradiation on the electrode surface generates a redox potential, enhancing the sensitivity of the detection process [65]. The standard PEC setup typically involves a three-electrode configuration comprising a photoelectrode (working), platinum wire (counter), and Ag/AgCl or SCE (reference) [66]. This technique, known as a photo-electric conversion approach, has been a significant innovation in sensor technology [67]. The miniaturization of detection devices, facilitated by advances in nanomaterial technology, has made these techniques more user-friendly and accessible. PEC techniques have been proven to be powerful tools for detecting various analytes [68]. Traditional methods like high-performance liquid chromatography, mass spectrometry, fluorescence, titration, and conventional electrochemical techniques are used for analyte identification and quantification [69]. However, PEC techniques, which employ photoactive nanomaterials as transducers, have emerged as a superior alternative due to their higher sensitivity and selectivity [70]. In PEC detection, light irradiates the interface where the analyte, photoactive material, and electrode interact, resulting in enhanced current response and minimal background noise [58,65,71–73].

The past few decades have witnessed significant advancements in the development and application of nanostructured materials for environmental, food, and healthcare detection [6,74]. Nanostructured materials with tunable properties are ideal for developing detection systems. These nanostructured are crucial in enhancing the sensitivity and selectivity of PEC sensors due to their high surface area, catalytic activity, and rapid electron transfer rates [75,76]. Recent research has focused on the nanoarchitected advanced photoactive materials as sensing platforms, particularly in PEC techniques for environmental, food, and healthcare applications. By modifying substrates with these photoactive nanomaterials, researchers have achieved significant improvements in the sensitivity and selectivity of PEC sensors due to their responsive to visible light. These photoactive nanomaterials can absorb photons with adequate energy to generate an electron-hole pairs that are transferred to the active electrodes to amplify the electrical signal [77]. To improve absorption capability of visible light, the electrode can be employed to construct a heterostructure/junction strategies to enhance absorption properties in the occurrence of photoactive nanomaterials [78]. These photoactive nanomaterials are emerging platforms for analytical applications in agriculture, industry, environmental monitoring, pharmaceuticals, and clinical diagnostics [6,76,79,80]. Fig. 1, the bar chart displays number of published records on PEC sensor including for the applications of bacterial, pharmaceutical, food, environmental, biosensor and sensor fields. In addition, photoactive nanostructures are exceptionally able to cause functional activities in response to irradiation. Given their promising roles and increasing applications, it is significant to analyse their potential impact on human health and the safety of surrounding environments. At the cellular level, these photoactive nanostructure impacts are classified based on two primary mechanisms as follows: (i) the induction of reactive oxygen

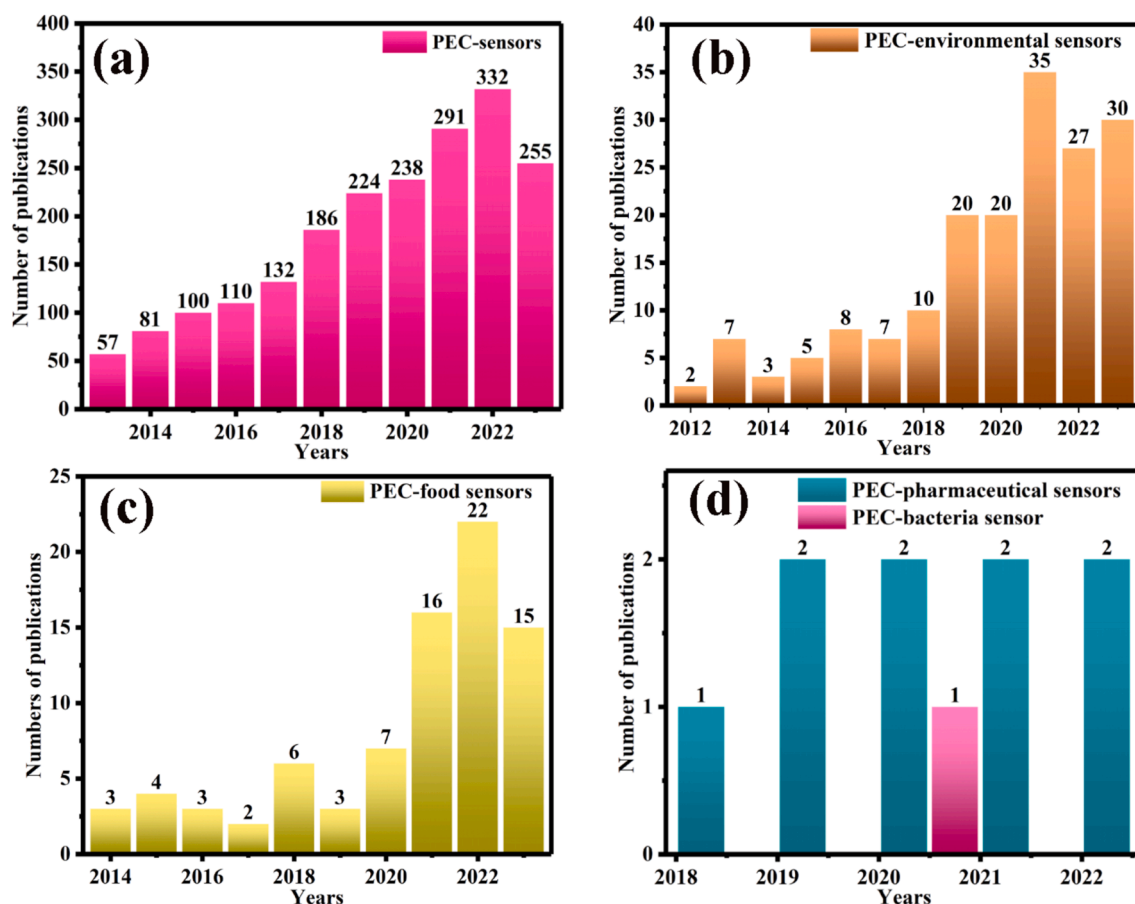


Fig. 1. Shows the bar chart of the number of publications relating to web of science-indexed keywords such as photoelectrochemical (PEC)-based sensors for environmental, food, pharmaceutical, and bacterial sensor applications.

species (ROS) and (ii) the development of plasmonic photothermal heat that has been observed. Despite their widespread use and continuous exposure, the potential impacts of these nanomaterials at the cellular level and their surrounding environment need to be adequately assessed. Further research is essential for a comprehensive understanding of these photoactive nanostructure impacts and for a more precise assessment of their safety and health impacts [81].

This review aims to comprehensively overview the recent improvements based on the photoactive nanostructures with their emphasized features and construction strategy based on photoactive electrodes for PEC sensor applications. In particular, the PEC sensor for environment, food, and healthcare remains limited. This comprehensive review strives to bridge the gap by offering essential principles of PEC sensing. Additionally, it thoroughly evaluates the pros and cons of construction strategies utilized in PEC sensors, making it an invaluable resource for identifying this field. Moreover, a collective review of PEC sensors for detecting various analytes, such as insecticides, antibiotics, pathogens, carcinogenic compounds, and metabolic disorder markers in environmental, food, and healthcare fields. The comprehensive overview concludes by describing the challenges encountered and highlighting the implied opinion for future research. Furthermore, highlighted the exciting potential of innovative PEC sensing strategies to propel remarkable advancements and new milestones in this field.

Nanomaterials as PEC sensors in healthcare, environmental, and food monitoring applications

Nanomaterials are demonstrating their pivotal role in the development of PEC sensors, particularly in crucial fields like healthcare, environmental monitoring, and food safety [82]. The integration of nanotechnology into PEC sensors has significantly expanded the boundaries of sensitivity, specificity, and overall performance, marking a substantial advancement across a range of applications. In healthcare, the incorporation of nanomaterial-based PEC sensors is revolutionary [83]. These sensors, with exceptional sensitivity and specificity, are ideal for detecting a wide array of biomarkers at extremely low concentrations, which is crucial for primary diagnosis and therapy [84]. For instance, in cancer diagnostics, PEC sensors enhanced with nanomaterials can detect specific cancer biomarkers in blood or tissue samples, providing valuable information for early detection [85,86]. Similarly, in managing chronic conditions like diabetes, these sensors offer more precise monitoring of glucose levels, which is essential for effective disease management [87–89]. Environmental monitoring is another domain where nanomaterial-based PEC sensors are making a significant impact. The growing concern over environmental pollution demands highly accurate methods for detecting and measuring contaminants [90]. The addition of nanomaterials to PEC sensors enhances their sensitivity, enabling the detection of trace amounts of hazardous substances in water, air, or soil [91]. These sensors are crucial in identifying pollutants such as heavy metals, organic contaminants, and other toxic compounds, thereby playing a vital role in environmental protection and pollution control efforts [92]. In the realm of food safety, the use of nanomaterial-enhanced PEC sensors is critical for food safety. These sensors are capable of identifying a wide range of foodborne pathogens, toxins, and chemical residues like pesticides [93]. The ability to detect such contaminants at low levels is essential for preventing foodborne illnesses and maintaining public health standards. Additionally, these sensors can be used to monitor food freshness and quality, aiding in effective supply chain management and quality assurance [60,94,95]. The integration of nanomaterials into PEC sensors represents a significant leap forward in various fields, offering unparalleled sensitivity, specificity, and efficiency in applications ranging from healthcare to environmental protection and food safety. The ongoing research and development in this area continue to push the boundaries of what these sensors can achieve, promising even greater advancements in the future.

Preparation of photoactive nanomaterials

Nanomaterials can be synthesized using a variety of strategies, broadly categorized into top-down and bottom-up approaches. The top-down method involves reducing larger particles, at the macro or micro scale, to nanoscale dimensions, typically through techniques like milling [96]. However, this method presents certain limitations, such as the inability to precisely control the shape, size, and uniform distribution of the resulting nanomaterials [1,97]. In contrast, the bottom-up approach begins at the atomic level, where precursor salts form atomic nuclei that grow into nanomaterials. This method offers greater control over factors such as seeding and growth, influenced by various agents, including oxidizing and reducing agents, ligands, surfactants, and growth inhibitors. Additionally, the characteristics of the nanomaterials can be finely tuned by adjusting parameters like the choice of solvent, pH, type of precursor, stirring speed, temperature, gradual addition of reactants, pressure, the use of ambient or inert gas conditions, and aging time [98,99]. Among the most common techniques for nanomaterial synthesis are wet chemical methods, which include sol-gel processes, precipitation, co-precipitation, reduction, solution combustion, and hydrothermal or solvothermal methods [2,100]. Other approaches like microwave-assisted synthesis, probe sonication, and the polyol method are also widely used, offering distinct advantages depending on the specific requirements of the nanomaterial being synthesized [96,101]. The recent advancements in nanomaterial fabrication have introduced a variety of innovative approaches, each offering distinct advantages and limitations. Among the electrical methods, techniques like electrochemical anodization and deposition, as well as electrospinning, have gained prominence [102]. These methods are particularly valued for their precision and control in creating nanostructures. In the realm of photochemical approaches, photochemical reduction (PR) and photochemical deposition (PD) are commonly employed, leveraging light to initiate and control the formation of nanomaterials [103,104]. Chemical coating techniques such as in-situ seed and growth methods [105], template-assisted synthesis [106], layer-by-layer (LBL) growth [107], and spin- or dip-coating [108] are extensively used for their ability to produce well-ordered and uniform nanostructures. Physical coating methods, including sputtering, pulsed-laser deposition (PLD), molecular beam epitaxy (MBE), and atomic layer deposition (ALD), are notable for their precision in material deposition and structural control at the nanoscale [109]. Laser-based techniques, such as laser ablation, melting, and engraving, are also critical in nanofabrication, enabling the precise patterning and structuring of materials [110]. Additionally, advancements in printing technologies, including 2D, 3D, and even 4D printing, have opened new possibilities for fabricating complex nanostructures with high precision and versatility [111]. In lithography, cutting-edge techniques such as photolithography, UV and/or deep UV, X-ray, e-beam, focused ion beam (FIB), nanoimprint, and quantum lithography have become foundational in nanofabrication, each offering unique capabilities in patterning and material structuring at the nanoscale [112]. These diverse methods—ranging from electrical and photochemical approaches to coating, laser techniques, printing technologies, and lithography—are essential for the synthesis, preparation, and fabrication of nanomaterials. Each technique has its strengths and limitations, making them suitable for different applications in environmental monitoring, food safety, and healthcare detection. This review will delve into the preparation and application of photoactive nanomaterials and their composites, offering a concise overview of the techniques used in their development. Recently, Soomro et al. developed a novel saw-blade-like NiWO_4 nanocomposite, which was directly grown in situ on an ITO substrate using a template-controlled, low-temperature-assisted co-precipitation method. The detailed characterization of this structure, including FE-SEM images and XPS spectra, is revealed in Fig. 2 (a and b) [113]. In another study by the same group, they reported the in-situ growth of TiO_2 over partially oxidized $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, combined with BiVO_4 nanoparticles through a

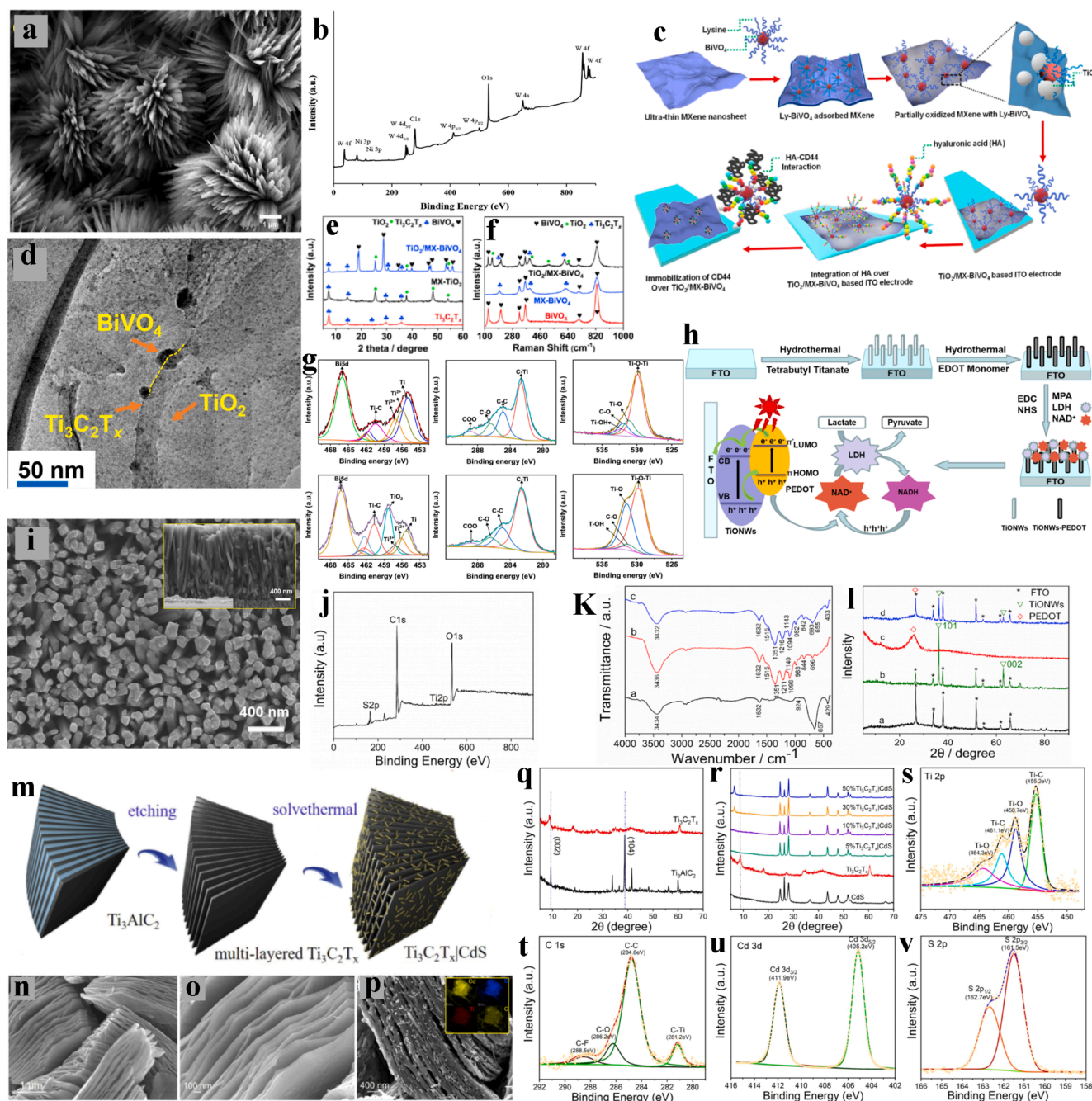


Fig. 2. (a) The FE-SEM analysis was performed on the ITO/NiWO₄ nanostructure, (b) the XPS analysis involved conducting a survey spectrum that indicated peaks corresponding to Ni, W, and O, reprinted with permission from ref. [113]; (c) The schematic synthesis and assembly of the PEC-based biosensor for detecting CD44 protein (d) TEM image, (e) PXRD patterns, (f) Raman spectrum, and (g) conducting high-resolution XPS profiling for TiO₂/MX-BiVO₄, reprinted with permission from ref. [114]; (h) demonstration of synthesis and detection mechanism, (i) PEDOT-TiONWs composite (Inset: Side view comparing bare TiONWs (left) to TiONWs-PEDOT composite (right)) (j) XPS survey spectrum, (k) FTIR, (l) XRD, reprinted with permission from ref. [115]; (m) SEM image of multi-layered Ti₃C₂T_x and Ti₃C₂T_x/CdS, alongside (q-r) XRD pattern, and (s-v) XPS spectra, were obtained for the Ti₃C₂T_x/CdS nanocomposites, reprinted with permission from ref. [116].

hydrothermal process. The process involved washing the nanostructures in ethanol and drying them under a nitrogen atmosphere. Fig. 2(c) provides a schematic representation of the step-by-step development of the TiO₂/MX-BiVO₄ photoactive heterojunction and the assembly of the sensor. Fig. 2(d-g) illustrate the physio-chemical and structural characteristics of the material, including TEM, XRD, Raman, and XPS spectra, showcasing the thin-sheet morphology with hybrid nanostructures, the anatase phase of TiO₂, and the monoclinic phase of BiVO₄ [114]. These results justify the surface-bound interactions formed through in-situ growth, as demonstrated in their work. Zheng et al.

reported the efficient development of rutile-type TiO₂ nanowire arrays on an FTO substrate using a hydrothermal method. The process was followed by washing with double-distilled water, drying under inert nitrogen conditions, and calcinated at 500 °C for 2hrs. The construction of the sensor and its mechanism is depicted in Fig. 2(h). The TiO₂ NW/FTO substrate was thoroughly characterized using SEM, XPS, FTIR, UV-Vis, and XRD, as shown in Fig. 2(i-l) [99]. In another study, Sun et al. reported the preparation of both photoanode and photocathode materials, represented by Ti₃C₂T_x/CdS and CuInS₂, respectively. These materials were synthesized via etching, hydrothermal, and solvothermal

techniques. The structural, morphological, and elemental compositions of these materials are presented in Fig. 2(m-v) [100]. Tables 1–3 provide a comprehensive overview of various photoactive nanomaterial preparations, the resulting nanostructures, and their corresponding nanocomposites, specifically for PEC-based detection applications.

Morphology of nanomaterials in PEC sensors

Morphology is pivotal in the development of nanomaterials for diverse applications, particularly in the realm of photo-electrochemical (PEC) sensors, which are utilized in healthcare, environmental monitoring, and food safety. The unique and customizable properties of nanomaterials, influenced by their size, shape, and structure, make them excellent candidates for sensor technologies [2,117,118]. In PEC sensors, the morphology of these nanomaterials is crucial as it affects key

factors such as light absorption, charge transport, and catalytic activity, all of which are essential for the sensor's efficiency [10,119]. For effective in vitro diagnostics, it is essential to design PEC sensors using nanomaterials with varying dimensions. However, relying on a single type of nanomaterial often presents limitations due to inherent constraints. Issues such as low photoelectric conversion efficiency may arise from factors like a brevity absorption threshold, wide bandgap, high charge carrier recombination rate, and inadequate solar energy utilization [120,121]. These drawbacks make it challenging to advance PEC sensing technologies using only a single semiconductor material. To address these limitations, researchers have explored various strategies, including the development of heterogeneous nanostructures. These structures are formed by combining multiple nanomaterials with distinct band structures, allowing for bendable arrangements and the creation of various types of heterojunctions. As illustrated in Fig. 3a,

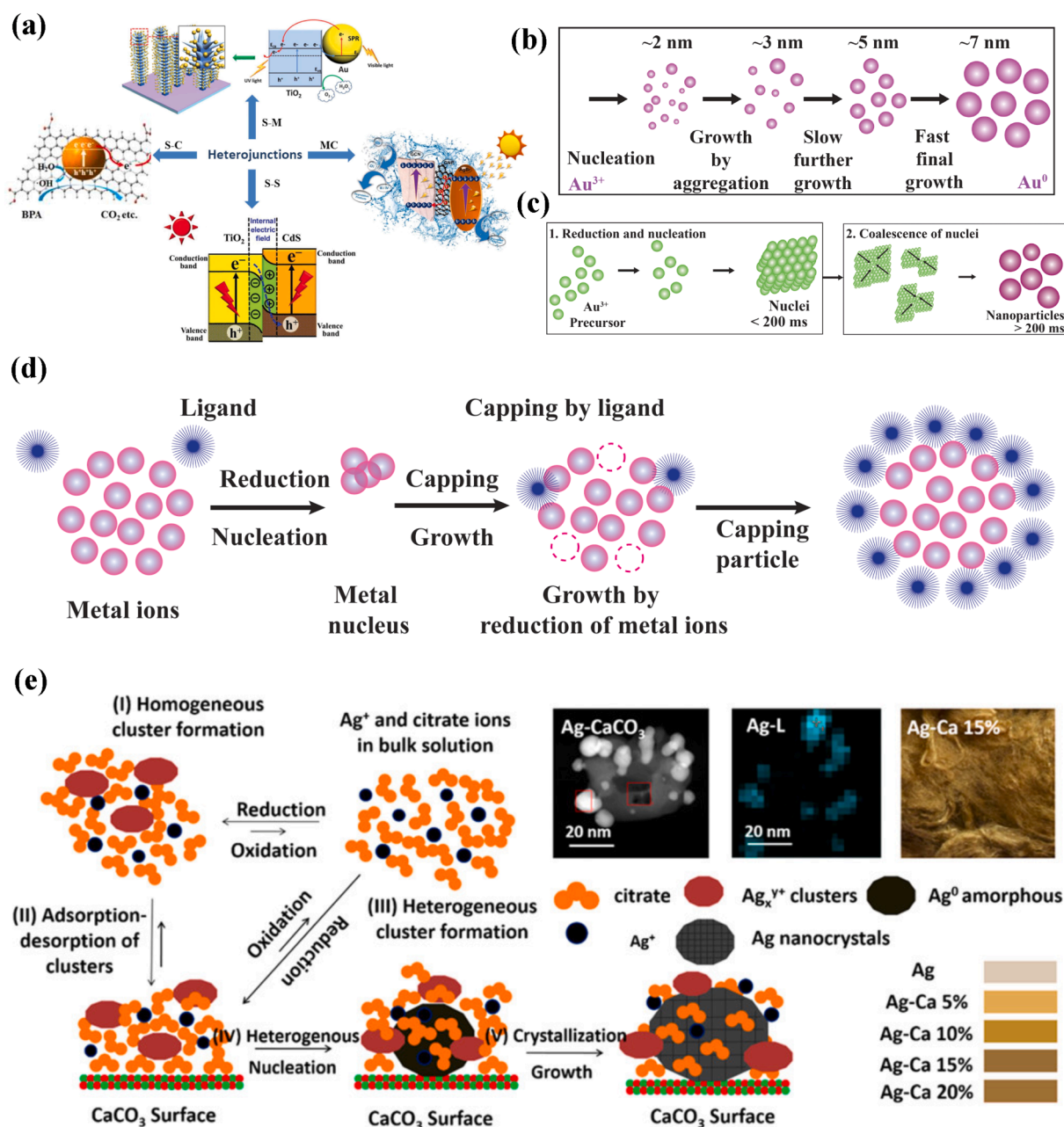


Fig. 3. (a) The mechanism of charge separation and transfer, reprinted with permission from ref. [164]; (b-c) a schematic illustration detailing the growth mechanism of gold nanoparticle, including the deduced process, Adapted from ref. [133,136]; (d) a schematic diagram outlining the ligand-based growth process, adopted from ref. [147], and (e) the homogeneous growth of Ag crystal on the CaCO_3 surface, reprinted with permission from ref. [149].

these include metal–semiconductor (M–S), semiconductor–semiconductor (S–S), semiconductor–carbon (S–C), and multicomponent (MC) heterojunctions [122,123]. Each type of heterogeneous nanostructure offers unique advantages over single-component nanomaterials. For instance, M–S heterojunctions, which consist of metal and metal oxide nanostructured particles, create a Schottky barrier at the interface, which reduces electron-hole recombination. This configuration enhances visible light absorption and improves catalytic oxidation performance due to the quantum effects of the metal nanoparticles [124]. S–S heterojunctions, on the other hand, facilitate efficient electron-hole separation through the alignment of energy bands between the two semiconductors. The incorporation of organic semiconductors in these junctions further enhances their extinction coefficient and photostability, leading to better photoelectric conversion efficiency [125]. S–C heterojunctions, which integrate semiconductors with carbon-based materials, provide several benefits, including large surface area, lower toxicity, flexibility, excellent electrical conductivity, and superior electron transfer capabilities. These junctions also act as scaffolds for the consistent immobilization of functional materials, addressing polymerization issues and enhancing the sensitivity of PEC sensors [79]. Finally, MC heterojunctions capitalize on the synergistic effects of spatial energy levels for robust photoelectric responses, better carrier separation, and substantially improved conversion efficiency [126]. These innovative PEC sensors, derived from heterogeneous nanostructures combine the strengths of various nanomaterials, resulting in improved synthesis, assembly, and performance. Consequently, they hold great potential for in vitro diagnostics, offering enhanced sensitivity and efficiency for detecting a larger type of analytes.

Anisotropic nanoparticle growth

The reducing metal salts typically form spherical nanoparticles, as spheres represent the lowest-energy shape configuration [127]. However, by carefully manipulating reaction conditions experimental parameters can tune the morphology of nanoparticles. Despite progress in this area, the precise ways in which these factors influence nanoparticle shape are not yet fully understood. It's believed that the collective impact of these variables significantly determines the final shape of nanocrystals. Anisotropic nanoparticles, which have non-spherical shapes, can be synthesized using both top-down and bottom-up methods. However, the bottom-up methods are more prevalent due to the limitations of top-down techniques, which often result in nanoparticles with a broad size distribution, diverse shapes, and geometries. Additionally, top-down methods tend to be costly and difficult to scale for industrial applications. One of the most effective bottom-up techniques for producing anisotropic nanoparticles is wet chemical synthesis, which allows for the creation of nanoparticles with a variety of sizes, shapes, structures, compositions, and surface chemistries, all with high yield and structural purity. Nanoparticle growth can be controlled either kinetically or thermodynamically [128]. Thermodynamically controlled growth typically results in uniform development of crystal facets, leading to spherical or near-spherical structures. In contrast, kinetically controlled growth often leads to anisotropic structures, where growth is preferentially directed along certain crystallographic directions. The final shape of nanoparticles is largely determined by the interplay between thermodynamic and kinetic factors, though a comprehensive understanding of the process remains elusive. Capping agents, which can preferentially adsorb onto specific crystal facets, play a key role in controlling the development of anisotropic nanoparticles. These agents can either promote or inhibit growth on certain facets, leading to anisotropic shapes. Structural defects or the formation of surfactant micelles can also physically direct the anisotropic growth of nanoparticles [129]. However, the role of capping agents alone cannot fully explain experimental outcomes, as similar shapes can form without them, such as in vapor phase synthesis [130]. Anisotropic growth can also be induced by factors like the control of nucleation and oxidative

etching. Research by Lofton and Sigmund suggests that twin planes in seed particles creates anisotropic nanoparticle growth [131]. By employing twin-plane nucleation techniques, it is possible to control the kinetics and promote the formation of desired nuclei, thereby enhancing the efficiency of anisotropic nanoparticle production. The development of anisotropic structures is also influenced by energetic factors. At the nanoscale, surface energy plays a dominant role, driving the formation of anisotropic shapes. Even though anisotropic nanoparticles might exhibit facets with lower surface energies, they typically have a large surface related to spherical particles, resulting in more energy per atom, particularly in face-centered cubic (fcc) metals [132]. This energetic consideration is crucial in understanding why anisotropic structures form and how they can be controlled during synthesis.

Metal nanoparticle

Polte et al. explored the process of gold nanoparticle formation in an aqueous solution using tetrachloroauric acid and trisodium citrate as the starting materials. Their study employed both batch reactor and continuous flow methods with a static mixer. In the batch reactor experiments, they collected samples that were then analyzed using techniques such as X-ray absorption near edge structure (XANES), small-angle X-ray scattering (SAXS), and UV–visible spectroscopy [133]. The researchers identified a four-step mechanism during the formation of gold nanoparticles. The initial phase, nucleation, involves the conversion of about 20 % of the gold salt into nanoparticles within the first 20 s, resulting in particles with an average radius of less than 2 nm. This is followed by coalescence, which occurs over 20 min and leads to the formation of larger particles with an average radius of 4 nm and a polydispersity of around 45 %. The increase in size from 2 to 4 nm is attributed to either Ostwald ripening or coalescence processes [134,135]. In the second step, particle growth continues until the nanoparticles reach an average size of 5.2 nm, with a notable reduction in dispersity, suggesting a diffusion-controlled growth process. This growth phase, typically rapid, extends unusually from 25 to 50 min in this case, likely due to the ongoing reduction of gold in the solution, where the concentration of gold metal is the limiting factor. The third step of the process is characterized by a stabilization of particle size at around 5.2 nm, marking a balance between growth and dissolution that persists from 50 to 70 min. During this time, the gold concentration in the solution remains constant. In the final step, there is a rapid depletion of the remaining gold salt in the solution, causing a swift increase in particle size from 5.2 nm to 7.7 nm (Fig. 3b), while polydispersity drops to 10 %. This rapid size increase is believed to result from autocatalytic reduction occurring on the nanoparticle surfaces. In the continuous flow experiments, where a static mixer was used, tetrachloroauric acid was reduced by sodium borohydride, a potent reducing agent. This reduction and nucleation happened in less than 200 ms, which was the detection limit for SAXS measurements. Following this, coalescence was evidenced by a quick decrease in the number of particles in the solution, as shown in Fig. 3c. The growth process continued for up to 24 h due to the absence of stabilizing agents like citrate in the solution, which would normally prevent further growth [136].

Metal oxides

The growth mechanism of metal oxides is a complex process influenced by various factors that are critical for tailoring the properties and optimizing the applications of metal oxide materials in areas such as catalysis, energy storage, and electronics. **Nucleation:** The growth process generally begins with nucleation, where individual metal atoms or clusters attach to a substrate surface. This initial phase is pivotal, as it dictates the size, shape, and density of the resulting metal oxide nanoparticles. Nucleation can proceed through different pathways, including homogeneous nucleation, where metal atoms aggregate in the solution before settling on the substrate, and heterogeneous nucleation, where

metal atoms directly adhere to the substrate. After nucleation, the metal atoms or clusters undergo oxidation to form metal oxide nuclei, which involves reacting with oxygen molecules from the environment or a precursor source. The oxidation state of the metal and the availability of oxygen are key factors that influence the rate and extent of oxide formation. As the metal oxide nuclei form, they continue to grow by incorporating more metal atoms or clusters from the surrounding environment. This growth can occur via several mechanisms, including surface diffusion, where atoms move along the surface to join existing nuclei, and bulk diffusion, where atoms migrate through the bulk material to reach the growing nuclei. Additionally, coalescence may occur as these nuclei grow, where smaller nuclei merge to form larger particles. Coalescence can lead to the formation of irregularly shaped particles, influencing the final morphology of the metal oxide. **Ostwald ripening:** Ostwald ripening is a crucial process in the growth of metal oxide nanoparticles. It involves the preferential growth of larger particles at the expense of smaller ones due to differences in surface energy. Smaller particles, having higher surface energy, tend to dissolve, and the dissolved atoms then redeposit onto larger particles. This process can lead to changes in the particle size distribution over time, resulting in more uniform or larger particles. For example, Titanium dioxide (TiO_2) is a widely studied semiconductor material, with over forty thousand published articles in the past decade. TiO_2 is valued for its low cost, stability, and strong oxidizing capability of photogenerated holes, making it an essential material in solar energy systems. For instance, TiO_2 -based dye-sensitized solar cells have shown enhanced efficiency in converting sunlight into electrical power. The photogenerated electron-hole pairs in TiO_2 facilitate water splitting to generate hydrogen, a potential future fuel source. Additionally, TiO_2 can act as a photocatalyst to break down organic pollutants into environmentally benign products like carbon dioxide and water. The efficiency of these applications is significantly influenced by the material's specific surface area, leading to the preference for nanoparticulate TiO_2 . However, TiO_2 nanoparticles have low electron transport coefficients due to defects, grain boundaries, and surface states [137,138]. To overcome these limitations, researchers have developed one-dimensional TiO_2 nanostructures such as nanotubes [139,140], nanorods [141,142], and nanowires [143], which offer a higher specific surface area and improved electron transport behavior. 1D TiO_2 structures are produced using hydrothermal, electrochemical synthesis, and template methods [144,145]. **Hydrous Fe (III) oxide precipitation:** Similar to TiO_2 , the growth of hydrous Fe (III) oxides involves multiple mechanisms that influence the size and quantity of primary nanoparticles. Nucleation, defined as the formation of stable nuclei, increases primary particles while maintaining their size. During growth, iron oxide compounds adhere to existing particles, increasing their size without changing their number. Ostwald ripening plays a role by causing larger particles to grow at the expense of smaller ones, reducing the number of primary particles while increasing their size. Heterogeneous nucleation on quartz surfaces, as opposed to homogeneous nucleation in solution, may occur for several reasons. Firstly, heterogeneous nucleation requires less energy than homogeneous nucleation [146]. Secondly, at $\text{pH} = 3.7 \pm 0.2$, quartz surfaces become negatively charged with the presence of nitrate and chloride, while iron oxide surfaces are positively charged, creating electrostatic attraction between the two. This attraction may lead to the accumulation of iron oxide clusters on the quartz surface, resulting in a more supersaturated local solution and promoting nucleation on the quartz surface. Compared to growth, Ostwald ripening, and aggregation, nucleation as the dominant process produces a greater hydrous iron oxide surface area once a specific volume of oxides precipitates.

Growth mechanism

The importance of controlling the morphology of nanoparticles, which is crucial for achieving consistent manufacturing outcomes. This

has control hinges on a thorough understanding of the growth mechanisms of nanoparticles. Growth typically proceeds by adding atoms to the developing crystal, perpetuating the growth cycle. LaMer burst nucleation and Ostwald ripening have long been used to describe nanoparticle formation and the resulting changes in particle size (Fig. 3d) [147]. Ostwald ripening occurs because the atoms, molecules, or ions on the nanoparticle surface are more energetically unstable than those in the bulk. This instability causes these surface species to dissolve into the solution, where they gradually reduce the size of larger particles and redeposit onto smaller ones, thereby influencing the overall growth dynamics. Nanoparticle formation is governed by several factors, including the synthesis method, reactant concentration, stirring, pH, temperature, duration, pressure, and the surrounding environment [148]. The pH of the medium crucially influences nanoparticle size and morphology. While chemical synthesis techniques typically operate at temperatures below 350°C , physical methods often require higher temperatures exceeding 350°C . When plant extracts are used for nanoparticle synthesis, the incubation time of the reaction medium significantly impacts the final product. In various environments, a single nanoparticle can quickly transform into a core-shell structure by reacting with or absorbing materials from the surrounding medium (Fig. 3e) [149,150]. The use of surface-active molecules, such as surfactants, is particularly effective in controlling crystal growth and directing it to achieve desired shapes and sizes. Proper selection of surfactants like CTAB, or stabilizers such as PVP, citrate, thiols, and polymers, along with careful management of parameters like pH and temperature, can significantly minimize or prevent particle aggregation [151].

Thin films and nanocoatings for PEC sensors

The incorporation of nanomaterials into PEC sensors may be accomplished via the use of nanocoatings and thin films, which are both flexible and efficient substrates [82,152]. Spin coating, sputtering, chemical vapour deposition (CVD), and electrodeposition are some of the processes that are routinely used to produce these coatings. These techniques allow for exact control over the material thickness, homogeneity, and orientation [153]. Through improvements in charge transfer, light absorption, and overall structural stability, this regulated assembly guarantees that the performance of the PEC is completely maximized [109]. Thin films of titanium dioxide (TiO_2) that has been functionalized with quantum dots (QDs) or graphene oxide (GO) have the potential to considerably increase the sensitivity of the photoelectric converter [154,155]. A high density of active sites for photocatalysis is provided by quantum dots, which enables efficient charge transfer. Graphene oxide, on the other hand, improves charge separation and electron mobility owing to its superior conductivity and vast surface area. Similarly, thin films based on zinc oxide (ZnO) nanorods have been the subject of much research for use in PEC applications [156]. In addition to lowering the rate of charge recombination, the well-aligned, one-dimensional structure of these materials makes it easier for electrons to move more quickly, which ultimately results in enhanced photocurrent responses. Additionally, hybrid nanocoatings that are made up of metal-organic frameworks (MOFs) and semiconductor materials have a great potential for use in PEC sensing [157]. MOFs are known for their large surface area and adjustable porosity, whereas semiconductors are known for their light-harvesting and charge-separation capabilities. These hybrid systems combine the two features. The photocurrent generation, charge dynamics, and catalytic activity of these materials are all enhanced as a result of the synergistic interaction between the components. As a result, these materials are perfect for the sensitive detection of target analytical substances [158,159].

Advantages of nanomaterials in PEC sensors

Nanomaterials exhibit unique attributes, such as an exceptionally high surface area, enhanced electrical and thermal conductivity, and remarkable chemical stability, which collectively contribute to the superior performance of PEC sensors. The high surface area of nanomaterials provides a greater number of active sites for chemical reactions, facilitating more efficient electron transfer processes. This efficiency is crucial in PEC sensors, where rapid and effective electron movement is needed for accurate signal detection. Moreover, the enhanced electrical and thermal conductivity of nanomaterials ensures that the generated charge carriers—electrons and holes—are swiftly transported to the sensor's electrode, minimizing recombination losses,

and thereby improving the overall sensitivity and responsiveness of the sensor. The chemical stability of these materials also plays a pivotal role, as it ensures the durability and longevity of the sensor, even under harsh operating conditions. Another significant advantage of nanomaterials is their ability to improve light absorption. Due to their small size and unique optical properties, nanomaterials can absorb light more effectively than bulk materials, leading to a higher generation of charge carriers when exposed to light. This characteristic is particularly important for PEC sensors, which rely on light-induced electron-hole pairs to detect analytes. The versatility of nanomaterials further enhances the functionality of PEC sensors. By altering the size, shape, and composition of nanomaterials, scientists can customize the sensor's properties to target specific analytes or adapt to particular applications.

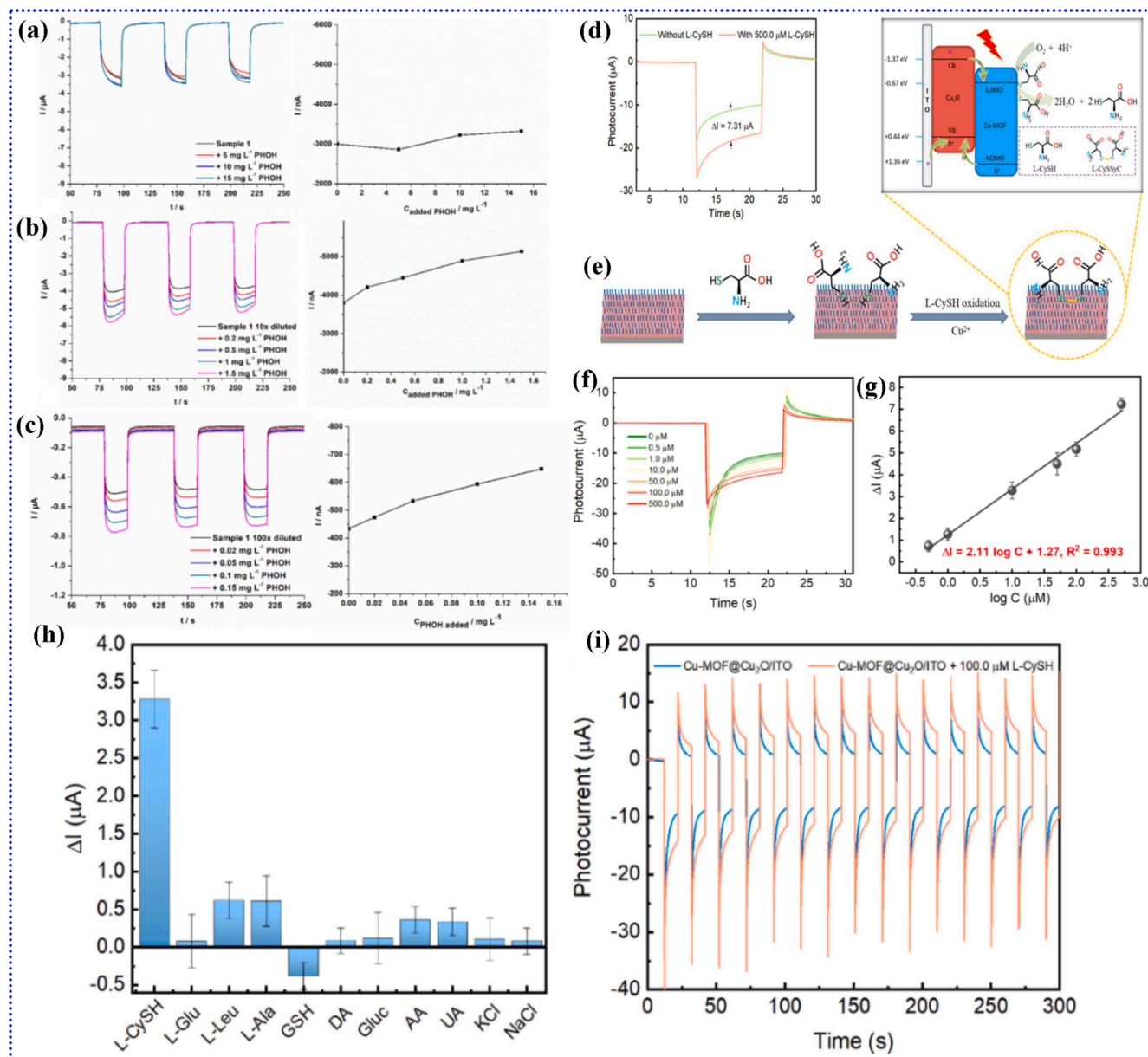


Fig. 4. Spiking sample 1 with PHOH standard resulted in photocurrents on the left and corresponding photoresponse values on the right for different spiked PHOH concentrations and calculated their average response time for PEC sensor measurements. In (a) sample 1 was completely undiluted, while in (b) was deteriorated with 10 folds, and in (c) by a factor of 100 ($N = 1$) with pH 9 borate buffer, reprinted with permission from ref. [165]. (d) The photocurrent responses of this sensor in a pH 5.0 and 0.1 M phosphate buffer solution at 0 V potential (e) Schematic illustrating the “signal-on” PEC reaction mechanism based on the Cu-MOF@Cu₂O/ITO electrode (f) The photocurrent responses of Cu-MOF@Cu₂O/ITO after the addition of 0.5, 1.0, 10.0, 50.0, 100.0 and 500.0 μM L-CySH; (g) The corresponding linear relationship (h) The selectivity of this PEC sensor for L-CySH detection (i) The stability of this PEC sensor before and after react with 100.0 μM L-CySH, reprinted with permission from ref. [166].

For example, by integrating different nanomaterials into the sensor design, it is possible to create sensors with selective sensitivity to certain chemicals or biological molecules, making them highly effective for use in diverse fields such as environmental monitoring, healthcare diagnostics, and food safety [4,65,160–163].

Heterostructure nanocomposite-based PEC sensor for environmental detection applications

Plausible mechanism

Neven et al. have successfully developed an innovative PEC sensor specifically designed to lower phenol concentrations during industrial processes. This sensor was capable of analyzing industrial samples directly, without requiring any pre-treatment like buffer solution dilution, which underscores its potential to operate effectively within a process stream. To estimate phenol (PHOH) concentrations, the method of standard addition was employed, using PHOH as the standard, and the results were then expressed in terms of the sensor's sensitivity to PHOH. As illustrated in Fig. 4a, adding PHOH did not significantly increase in photocurrents, suggesting that changes in PHOH concentration during production might not be readily detected by this PEC sensor. To address this issue, sample 1 was diluted using pH 9 borate buffers at 10x and 100x dilutions, allowing for a more detailed examination of the sensor's performance across different PHOH concentration levels. The introduction of pH 9 buffer enhanced the sensor's performance and increased the oxidation rate of PHOH in the presence of compound 1, which is pH-dependent. As shown in Fig. 4 (b and c), dilution significantly improved the sensor's sensitivity to incremental increases in PHOH concentrations, enabling it to detect smaller changes in concentration and restoring linearity in the sensor's response as concentrations rose. Despite expected differences in photocurrent values between diluted and undiluted samples (Fig. 4 (a and b)), the results were surprisingly similar, likely due to the varying pH levels affecting PHOH oxidation rates. Additionally, the performance of the PEC sensor was observed to decline when detecting high concentrations of PHOH, suggesting its limitations under certain conditions [165].

In a related study, chlorophenols, which are highly toxic organic pollutants in water, were also explored. Chlorophenols donate electrons, continuously consuming holes and reducing the recombination of photogenerated charge carriers. Xu et al. created a PEC sensing platform for detecting 4-chlorophenol using a nanocomposite of Au/g-C₃N₄, formed by reducing Au(III) on protonated g-C₃N₄ in a single step. The introduction of 4-chlorophenol, which serves as a hole oxidant, reduced the recombination of carriers and led to an increase in photocurrent intensity [167]. Similarly, Wang et al. developed an I-BiOCl/N-GQDs heterostructure nanocomposite via a one-pot precipitation method at room temperature (RT), leading to a distinct interface that facilitated charge separation and demonstrated excellent photoactive electrochemical properties. The proposed mechanism for detecting chlorpyrifos, where visible light induces the separation of photo-induced carriers in I-BiOCl and N-GQDs. This heterojunction enhances carrier movement and extends electron lifetimes, thereby improving PEC efficiency. When chlorpyrifos is present, its sulfur and nitrogen components bind to the surface of Bi (III), hindering effective carrier transfer and leading to a decreased photocurrent signal. The I-BiOCl/N-GQDs-0.5-modified electrode exhibited a cathodic photocurrent of −455.9 nA in a solution 0.10 M Na₂SO₄. The presence of 30 ng mL^{−1} chlorpyrifos, which chelates with Bi (III), further impedes electron transfer, as indicated by the observed decrease in photocurrent to −152.8 nA. The open circuit photovoltage decay (OCPD) method assessed photogenerated carrier's lifetimes, with V_{oc} decay indicating carrier recombination. The electron lifetime was longer without chlorpyrifos, confirming that its presence accelerates carrier recombination. Furthermore, the I-BiOCl/N-GQDs-0.5 photocathode's broad linear detection range for chlorpyrifos, from 0.3 to 80 ng mL^{−1}, with a limit of detection (LOD) of 0.01 ng mL^{−1}. The

sensor exhibited high selectivity for chlorpyrifos, as other tested substances did not quench the PEC signal, which can be attributed to the specific interactions between chlorpyrifos and Bi(III) due to the presence of P=S and C=N bonds. The sensor also showed remarkable stability, retaining 97.5 % of its initial photocurrent signal after two weeks of storage at RT, and demonstrated reproducibility with a 5.4 % relative standard deviation across five tests [168]. In another study, Shen et al. developed a signal-on cathodic PEC using a Cu-MOF@Cu₂O heterostructure, achieving high sensitivity in detecting L-CySH. The sensor's photocurrent response peaked after five hours of exposure to 500.0 μM L-CySH, as shown in Fig. 4d. The detection mechanism involves the bonding of L-CySH to the electrode through Cu–S interactions and its subsequent oxidation to L-CyssyC in the presence of Cu²⁺, which acts as an electron acceptor as depicted in Fig. 4e. This process enhances the photocurrent response, correlating with L-CySH concentration over a wide range 0.5–500.0 μM with a LOD of 0.32 μM as shown in Fig. 4 (f and g). Fig. 4h shows the sensor revealed excellent selectivity and stability, with negligible interference from other compounds lacking –SH groups. As illustrated in Fig. 4i, the sensor maintained consistent photocurrent responses during continuous testing, indicating its robustness and reliability for L-CySH detection, with only a minimal decrease in performance after four weeks [166].

Metal oxides and their nanocomposites

Wang et al. introduced a cutting-edge biosensor for detecting Bisphenol A (BPA) using a PEC platform that integrates molecular imprinting (MI) technology with a TiO₂/CdS heterostructure. This innovative MI-TiO₂/CdS heterostructure significantly enhances the separation of photogenerated charge carriers, boosts PEC conversion efficiency, and provides specific recognition sites for BPA. The study focused on evaluating the efficiency of photoinduced electron-hole pair separation in different samples, including TiO₂, MI-TiO₂, TiO₂/CdS, and MI-TiO₂/CdS, using transient photocurrent response, photoluminescence (PL) spectroscopy and electrochemical impedance spectroscopy (EIS). Results showed that both TiO₂ and MI-TiO₂ alone had the lowest photocurrent responses due to rapid recombination of charge carriers in phosphate buffer solution (PBS). In contrast, the TiO₂/CdS and MI-TiO₂/CdS heterostructures exhibited significantly higher photocurrent values, indicating enhanced separation of electron-hole pairs. Notably, MI-TiO₂ and MI-TiO₂/CdS showed even greater photocurrents with BPA, demonstrating the effective creation of BPA-specific recognition sites on their surfaces. The ΔI values (I_{sample} – I_{blank}) for MI-TiO₂/CdS were found to be 1.45, 1.93, and 2.17 times greater than those of MI-TiO₂, TiO₂/CdS, and TiO₂, respectively, underscoring the superior performance of MI-TiO₂/CdS in detecting BPA. To further validate the transient photocurrent results, the effectiveness of charge carrier transfer was analyzed using EIS under light exposure. The charge transfer resistance (R_{ct}) values for TiO₂, MI-TiO₂, TiO₂/CdS, and MI-TiO₂/CdS were determined to be 261.5, 252.5, 124.5, and 122.5 Ω, respectively. The lower R_{ct} value observed in the MI-TiO₂/CdS composite indicates a more efficient charge carrier transfer pathway to the electron acceptor, resulting in higher overall charge transfer efficiency. Additionally, PL spectroscopy was employed to assess the recombination efficiency and migration of photogenerated charge carriers. The MI-TiO₂/CdS composite exhibited a lower emission intensity compared to TiO₂, MI-TiO₂, and TiO₂/CdS, indicating that the unique heterostructure effectively enhances photogenerated electron-hole pair separation and transport. These findings demonstrate that the MI-TiO₂/CdS binary heterostructure offers a distinct internal electron transfer mechanism that significantly reducing photogenerated electron-hole pair recombination [169]. Another study, toxins like aflatoxin B1 (AFB1), ochratoxin A (OTA), and microcystin-LR (MC-LR), which are hazardous substances produced by organisms, were also targeted for detection. MC-LR, the most toxic and predominant form of microcystin, is a stable heptapeptide released by cyanobacteria in various water environments.

Recognized as a possible hepatotoxin, neurotoxin, and tumor promoter, the WHO has set a maximum permissible level of $1 \mu\text{g/L}$ for MC-LR in drinking water [170]. OTA and AFB1, on the other hand, are powerful mycotoxins often found in improperly stored food items [171]. Liu et al. developed a molecularly imprinted polymer (MIP)-modified 1D S-C heterojunction using TiO_2 nanoparticles (NPs) and multi-walled carbon nanotubes (MWCNTs) to identify MC-LR in water. The incorporation of MWCNTs significantly enhanced the photoinduced charge transfer capability, promoting the separation of electron-hole pairs and improving the oxidation capacity for MC-LR. This sensor exhibited a low LOD of 0.4 pM and successfully used to accurately determine MC-LR in water, achieving recovery rates between 96.4% and 113.0% . This study highlighted the possibility and advantages of 1D heterojunctions, using carbon nanotubes (CNTs) as a supportive scaffold over traditional 2D graphene-based heterojunctions [172]. Continuing this research, Liu et al. developed a sacrificial agent for capturing photoexcited holes from BiOBr nanoflakes (NFs), using aptamers to separate photoinduced electron-hole pairs bound to MC-LR molecules. The BiOBr NFs/N-GR heterojunction achieved efficient detection of MC-LR with a 0.03 pM LOD, as the remaining electrons rapidly transferred to the electrode through N-GR. In a further development, a Z-scheme heterojunction using CdTe quantum dots (QDs) and Bi_2S_3 nanorods (NRs) was created for PEC aptasensing of MC-LR, demonstrating PEC activity 13 times greater than CdTe QDs alone and twice that of Bi_2S_3 NRs. This heterojunction displayed a strong PEC response under visible light, a peak at 470 nm within the $430\text{--}630 \text{ nm}$ wavelength range. The binding of MC-LR at the hetero-interface impeded electron transfer, reducing the photocurrent and enabling ultrasensitive MC-LR detection with a 5.0 fM LOD [173]. Table 1. summarizes PEC results from various nanomaterials and nanocomposite electrodes for detecting prominent contaminants in environment.

Heterostructure nanocomposite-based PEC sensor for food detection applications

Toxins such as insecticides [174], antibiotics [175–178], husbandry [179], fungicides [180], pathogens [181], carcinogenic agents [182], and endocrine disruptors [183] often persist as residues in food products, leading to various food-borne diseases. These harmful agents find their way into frequently consumed products like preserved foods, fruits, lentils, vegetables, crops, and dairy products, either directly or indirectly. Despite their prevalence, the full extent of their toxicological effects remains largely unexplored. Several detection methods have been employed to identify these contaminants, with PEC detection emerging as a particularly promising analytical approach in recent years. The PEC technique has garnered significant attention owing to its advantages, including rapid operation, ease of use, and very low background noise [184]. The advancement of photoactive nanomaterials has further enhanced detection capabilities by improving photo conversion efficiency, thus narrowing the gap between detection technologies and achieving higher-quality performance [185]. Traditionally, enzyme-based biosensors have been utilized across various fields; however, their practical applications are often limited by certain constraints. In response, the development of nanozyme-based biosensors has gained considerable interest as a potential alternative, offering promising applications in biosensing [186]. For instance, gold (Au) and platinum (Pt) nanodendrites have demonstrated impressive peroxidase-like activity, leading to significant signal amplification, making them highly effective in enhancing the sensitivity and reliability of detection methods [187].

Metal oxides and their nanocomposites

Wang et al. have introduced a novel development in PEC detection using $\text{CdIn}_2\text{S}_4/\text{SnO}_2$ heterojunctions, which efficiently prevent the recombination of photogenerated electrons and holes. Additionally, hollow PtCu nanocages (PtCu NCs) were incorporated into the design

due to their peroxidase-mimicking catalytic properties (Fig. 5a). Upon irradiation with visible light, this configuration induces electron-hole pair formation, with electrons transferring from the conduction band (CB) of CdIn_2S_4 to SnO_2 , while holes from valence band (VB) are scavenged by ascorbic acid (AA) (Fig. 5b). The performance was optimized at a concentration of 7 mg/mL , and the incubation time for PtCu NCs was found to be crucial for their peroxidase-like activity towards the oxidation of 3,3'-diaminobenzidine (DAB), which influences the sensitivity of the sensor. The oxidation of DAB leads to the formation of a non-conductive precipitate in the presence of hydrogen peroxide, hindering electron transfer and decreasing the photocurrent. The optimal incubation time was determined to be 30 min . The PEC signal was observed to increase with higher concentrations of streptomycin (STR), as illustrated by a linear calibration plot in Fig. 5 (c and d), indicating a reduction in PtCu-Apt on the electrode surface and resulting in less precipitation at the active sites. Fig. 5 (e and f) the developed PEC platform demonstrated a broad dynamic range, lower LOD, high sensitivity, excellent selectivity, and strong anti-interference capability, offering a cost-effective method for detecting antibiotics in food samples, with potential applications in detecting other targets [188]. In another study, Zheng et al. enhanced signal amplification by developing a hybrid nanostructured poly(diphenylbutadiene) nanofiber-immobilized BiOBr flower-like microsphere heterojunction on an ITO substrate. This hybrid structure facilitated high visible light absorption and excellent separation of photogenerated charge carriers, key features for PEC sensors. The organic-inorganic heterojunction, with well-matched energy levels, improved the separation of these charge carriers. The presence of $\text{CeO}_2\text{-Au}$ nanozyme, which acts as a peroxidase-like enzyme, further regulated the signal, quenching the photocurrent response. The $\text{CeO}_2\text{-Au}$ nanozyme, combined with PDPB-BiOBr on the aptasensor, reduced light absorption and led to a diminished PEC signal. The addition of 4-chloro-1-naphthol (4-CN) and hydrogen peroxide resulted in the catalytic conversion of 4-CN to benzo-4-chlorohexadienone (4-CD), which precipitated on the sensor surface, further impeding electron transfer and decreasing the photocurrent by $\sim 43\%$. This setup allowed for the detection of acetamiprid with an ultrasensitive PEC aptasensor, demonstrating significant signal changes that were easy to measure [189]. In addition to that Dashtian et al. presented a simple yet highly sensitive MIP CdS/CdSe/Zn heterojunction with polydopamine on a titanium substrate. This selective type II heterojunction structure was designed to operate at a low work function. The CdS/CdSe/Zn heterojunction on the Ti substrate acted as an opal electrode, enhancing light absorption and improving charge carrier separation and collection. The electrode, modified with L-Phe-IPDA, showed superior light absorption, attributed to effective polymerization and π -plane conjugation, which facilitated the separation of photogenerated charge carriers (Fig. 5g). Upon light irradiation, the excited electrons in the CB of CdSe transferred to the CB of CdS, generating an anodic photocurrent, while L-Phe-IPDA acted as the sensing layer. The holes moved in the opposite direction, effectively separating carriers, and the addition of ascorbate ions scavenged the photogenerated holes, enhancing the photocurrent signal. The electrode demonstrated a decreased R_{ct} and increased electron lifetime, making it a superior candidate for PEC applications [190]. In the realm of food safety, rapid and selective detection of food-borne pathogens like *Escherichia coli* (E. coli) is critical. Wang et al. developed a defect-rich, bimetallic-confined mesoporous N-doped carbon (mNC) platform for detecting such pathogens. As shown in Fig. 5 (h and i). Utilizing a heterojunction of CeO_2 and In_2O_3 , known for their optimal band gap energy and photoactive performance, the constructed Apt/ $\text{In}_2\text{O}_3/\text{CeO}_2@m\text{NC700}/\text{GCE}$ electrode exhibited lower photocurrent response upon aptamer modification due to the blocking of photogenerated charge carriers. The large surface area and pore size of the hybrid structure allowed for the tight adsorption of aptamer strands, which enhanced the sensitivity for E. coli detection. The porous structure, multiple active sites, and superior photoharvesting ability of the electrode junction contributed to the significant amplification of the PEC

Table 1

Nanostructured materials as a photo-electrochemical sensors in environmental applications.

S. NO.	Mechanism of action	Nanomaterials	Approaches	Morphology	Light wavelength (λ), or power density (P)	Linear range and LOD	Type of analytes	Real samples	Ref.
1	PEC	Bi ₂ S ₃	electro polymerization and SILAR	Spherical	>420 nm (300 W)	0.5–70 pM and 0.1 pM	Dioctyl phthalate (DOP)	Spiked water	[203]
2	MIP-PEC	N, S-CDs/CuPc	Hydrothermal and electrostatic adsorption	Spherical	>365 nm	0.01–1000 ng mL ⁻¹ and 0.51 pg mL ⁻¹	Ochratoxin A (OTA)	—	[204]
3	PEC	CdS ₁₁ /ZnO-GE@NF	Hydrothermal and chemical bath deposition	Nanorod	250 W and 10 cm	0.2–1000 μ M and 0.03 μ M	Cu ²⁺	Industrial wastewater and sea water	[205]
4	PEC	LiTCNE/TiO ₂ /ITO	Sonication	—	20 W LED	0.4–500 μ mol L ⁻¹ and 0.10 μ mol L ⁻¹	Tert-butylhydroquinone (TBHQ)	Biodiesel	[206]
5	PEC	Aptamer-Gr/MCT/Au NPs/TiO ₂ NTs	Anodization	Nanotube	150 W (>430 nm)	50.0 fM to 0.3 nM and 12.0 fM	Atrazine (ATZ)	Water	[207]
6	PEC	aptamer/CS/VOPc/CN/ITO	Chemical modification	Nanosheet	250 W (<400 nm) and 15 cm	1.0 $\times$ 10 ⁻¹⁰ – 5 $\times$ 10 ⁻⁷ M and 3.3 $\times$ 10 ⁻¹¹ M	Diclofenac (DCF)	Tap water	[208]
7	PEC	BiVO ₄ /2D-C ₃ N ₄ /DNA	Electrodeposition	Twisted rod		5 $\times$ 10 ⁻⁷ ~ 10 μ g/L and 4.191 $\times$ 10 ⁻⁸ μ g/L	DNA	water	[209]
8	PEC	ITO/CuInS ₂ /chitosan/glutaraldehyde/ aptamer/MCH	Hydrothermal	Nanorod	450 nm	10 fg/mL-1 μ g/mL and 3.65 fg/mL	17 β -estradiol (E2)	Tap and lake water	[210]
9	PEC	Nitrogen doped BiVO ₄	Hydrothermal	Fern	300 W	0.1 nM-100 μ M and 0.025 nM	Bisphenol A (BPA)	Tap water, lake water and sewage	[211]
10	PEC	Bi ₂ WO ₆ /N-GQDs	Solvothermal	Nanosheet	250 W	0.2 pM to 1000 pM and 0.06 pM	pentachlorophenol (PCP)	River water	[212]
11	PEC	Bi/BiOI-0.1 composites	Solvothermal	Nanosheet	450 W	4 ng mL ⁻¹ to 2600 ng mL ⁻¹ and 1.3 ng mL ⁻¹	Phenol	Water	[213]
12	PEC	BiPO ₄ /BiOCl heterojunction	Hydrothermal	Nanosheet	UV light	20 to 3.38 $\times$ 10 ⁴ ng/mL and 6.78 ng/mL	4-Chlorophenol (4-CP)	River water	[214]
13	PEC	CS/WO ₃ /FTO	Hydrothermal	Plate	150 W	1.0 to 60.0 μ mol L ⁻¹ and 0.3 μ mol L ⁻¹	Co ²⁺	Water	[215]
14	PEC	WO ₃ /CdS	Chemical bath deposition	Nanoplate	300 W (100 mW/cm ²)	0.5 – 1000 and 0.06 μ M	Cu ²⁺	Tap water	[216]
15	PEC	N-deficient graphitic carbon nitride (ND-g-CN)	Hydrothermal	Lamellar	IR lamp	60 to 19090 ng L ⁻¹ and 20 ng L ⁻¹	Ciprofloxacin (CIP)	Swage water	[217]
16	PEC	PtNi NWs	Precipitation	Nanowire	300 W with 420 nm filter	0.1 pM–100 nM and 26 fM	chloramphenicol (CAP)	River water	[218]
17	PEC	Fe ₃ O ₄ @C@TiO ₂ /MI-PPy/MGCE	Electrochemical polymerization	Nanosphere	500 W (375 nm or 5 mW/cm ²)	5.00 to 50.00 μ M and 0.05 to 5.00 μ M and 0.03 μ M	bisphenol A (BPA)	Tap, reiver, and sewage water	[219]
18	PEC-Aptasensors	Gr@BP nanocomposite	Solvothermal	Nanosheet	405 nm, 530 nm, 660 nm	0.01–1000 nM and 0.0031 nM	bisphenol A (BPA)	Wastewater	[220]
19	PEC	2,4-D-imprinted WO ₃ ·H ₂ O	Hydrothermal	Nanosheet	30 W (320 nm to 2500 nm)	1 $\times$ 10 ⁻¹³ to 1 $\times$ 10 ⁻⁸ M and 1 $\times$ 10 ⁻¹⁵	2,4-dichlorophenoxyacetic acid (2,4-D)	Tap and natural water	[221]
20	PEC	rMIP/NPC/FTO	Electrodeposition	Wedge	250 W	0.1–107 nM and 0.047 nM	Levofloxacin(LEV)	River water	[222]
21	PEC	3D-CN	Thermal condensation	Microspheres		1.6–3200 μ g L ⁻¹ and 0.53 μ g L ⁻¹	4-Chlorophenol (4-CP)	water	[223]

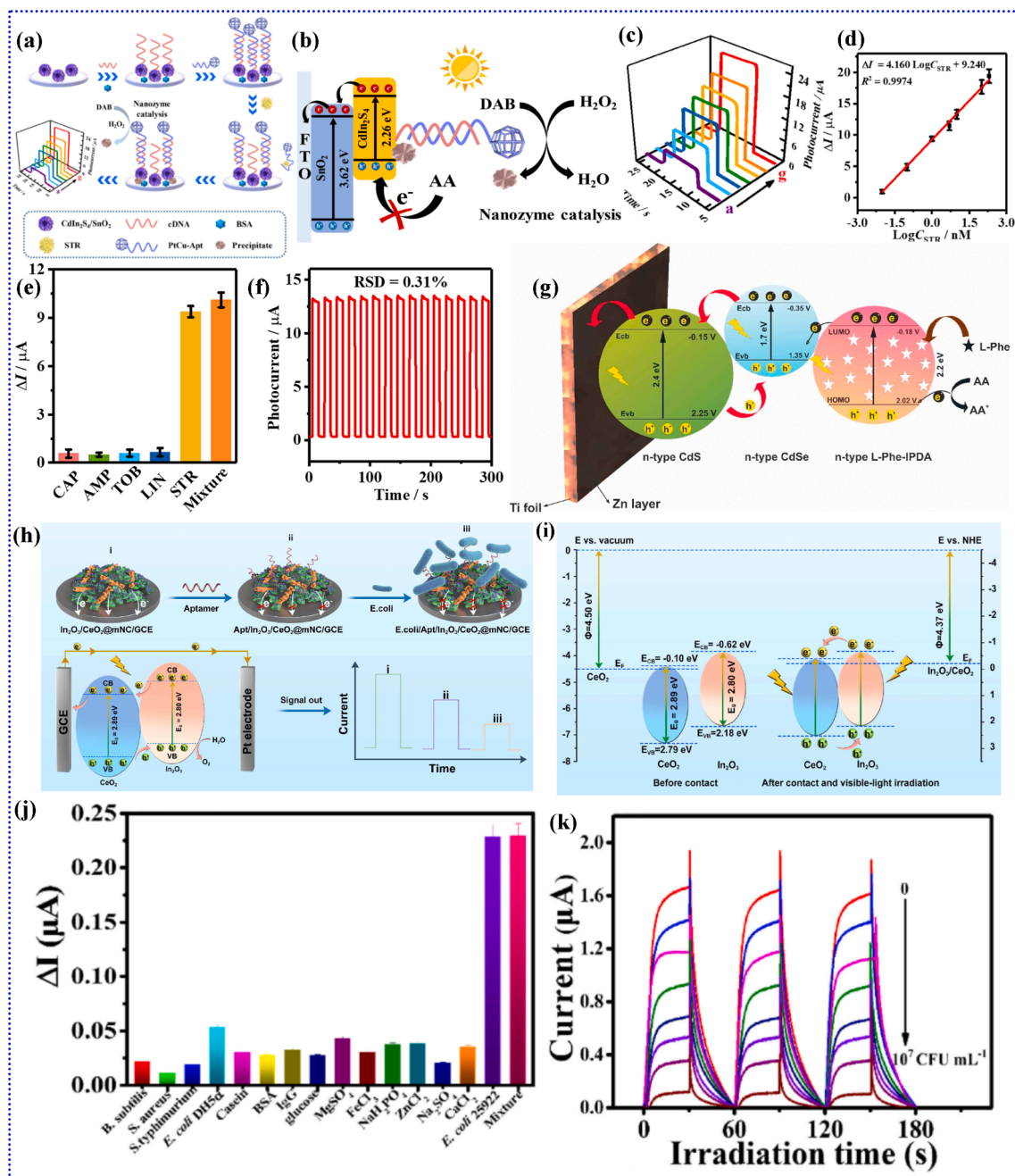


Fig. 5. (a, b) Schematic illustration of the preparation of a PEC biosensor utilizing $\text{CdIn}_2\text{S}_4/\text{SnO}_2$ heterojunctions for STR bioanalysis and the corresponding electron transfer mechanism in the PEC aptasensor; (c–f) Photocurrent responses of the PEC biosensor at different STR concentrations (curves a–g: 0.01–200 nM) with the associated calibration curve, along with an anti-interference test showing stability over 300 s, reprinted with permission from ref. [188]. (g) Mechanism of charge separation and the L-Phe response in the L-Phe-IPDA-CdSe/CdS–Zn/Ti heterojunction, reprinted with permission from ref. [190]. (h) Diagram of the $\text{In}_2\text{O}_3/\text{CeO}_2$ @mNC-based PEC aptasensor protocol for E. coli detection. (i) Energy band structure and electron-hole migration pathway in the $\text{In}_2\text{O}_3/\text{CeO}_2$ heterojunction. (j, k) Enhancement of the photocurrent signal, selectivity, and photocurrent response of the $\text{In}_2\text{O}_3/\text{CeO}_2$ @mNC700-based aptasensor for E. coli detection across varying concentrations, reprinted with permission from ref. [191].

signal, making it an effective tool for real-time detection of E. coli with high selectivity, sensitivity, and the photocurrent response with respect to different concentration, as shown in Fig. 5 (j and k) [191]. Table 2. summarizes PEC results from various nanomaterials and nanocomposite electrodes for detecting prominent harmful agents in food.

Heterostructure nanocomposite-based PEC sensor for healthcare applications

Metal oxide and their nanocomposites

Recently, Zheng et al. developed a multifunctional nanocomposite of PEDOT-TiONWs heterostructure on an FTO substrate, which was further immobilized with LDH and NAD^+ via an amide bond for the detection of lactate and NAD^+ . The fabricated electrode, $\text{NAD}^+/\text{LDH}/\text{PEDOT-TiONWs}/\text{FTO}$, was subjected to visible light irradiation, illustrating the

Table 2

Nanostructured materials as a photo-electrochemical sensors in food applications.

S. No	Mechanism of action	Nanomaterials	Approches	Morphology	Light wavelength (λ), power density (P), or light dose (LD) and distance btw. the electrode	Linear range and LOD	Type of analytes	Real samples	Ref.
1	PEC	g-C ₃ N ₄ /Au/WO ₃	Precipitation	Wrinkled sheet	300 W	1.0 pg mL ⁻¹ to 100 ng mL ⁻¹ and 0.33 pg mL ⁻¹	AFB1	Peanut	[224]
2	PEC	Bi ₂ S ₃ /BiOI/ZnO/ITO and modified p DNA@Ag ₂ S	Electrodeposition	Nanosheet	mW/cm ² (LED)	0.01 pg/mL to 200 ng/mL and 0.0035 pg/mL	Ochratoxin A (OTA)	Wheat flour	[225]
3	PEC	FeCdS@FeIn ₂ S ₄	Precipitation	Ball-flower	5 W LED (450 nm)	0.01 pg mL ⁻¹ to 10 ng mL ⁻¹ and 3.3 fg mL ⁻¹	Enrofloxacin (ENR)	—	[226]
4	PEC	CdIn ₂ S ₄ /SnO ₂	Hydrothermal	Microspheres	5 W LED	0.01–200 nM and 7.50 pM	Streptomycin (STR)	Milk	[188]
5	PEC	PDPB-BiOBr	Hydrothermal	Microspheres	300 W (420 nm)	0.1 pM–10 μ M and 0.05 pM	Acetamidiprid	Cucumber and apple	[189]
6	PEC	In ₂ O ₃ /CeO ₂ @mNC700	Freeze drying	Nanosheet	300 W	1.12 CFU mL ⁻¹	E. coli	Milk and bread	[191]
7	PEC	Pd NPs/CdS	Precipitation and photoreduction	Microspheres	250 W	1.0 $\times$ 10 ⁻¹² to 1.0 $\times$ 10 ⁻⁶ mol/L and 3.3 $\times$ 10 ⁻¹³ mol/L	Carbendazim (CBZ)	lettuce	[227]
8	PEC	L-Phe-IPDA-CdS-CdSe-Zn/Ti	Electrodeposition	Marigold flower	LED	0.005–2.5 and 2.5–130 μ M and 0.9 nM	L-phenylalanine (L-Phe)	UrineApple juiceGrape juice	[190]
9	PMFC sensor	MoS ₂ -Ti ₃ C ₂ Tx	Hydrothermal		465 nm	0.01 – 1000 ng/mL and 0.73 pg/mL	aflatoxin B1 (AFB1)	Milk, groundnut oil, maize	[228]
10	PEC	Cu-BTC MOF/g-C ₃ N ₄ nanosheet	Solvothermal	Nanosheets	9 W LED	1.0 $\times$ 10 ⁻¹² –1.0 $\times$ 10 ⁻⁸ mol L ⁻¹ and 1.0 $\times$ 10 ⁻⁸ ~ 1.0 $\times$ 10 ⁻³ mol L ⁻¹ and 1.3 $\times$ 10 ⁻¹³ mol L ⁻¹	Glyphosate	Soybean	[229]
11	PEC	BiOI/AR-TiO ₂	Solvothermal	Nanosheet	300 W	1 pg mL ⁻¹ –200 ng mL ⁻¹ and 0.24 pg mL ⁻¹	Chlorpyrifos (CPF)	watersamples, lettuce and pitaya	[230]

proposed PEC reaction mechanism shown in Fig. 6a. Upon illumination, excited electrons from the HOMO of PEDOT were transferred to the LUMO. This occurs because the CB of TiONWs is lower than that of PEDOT, allowing electrons to transfer to the CB of TiONW. Applying a positive voltage attracts electrons to the electrode substrate, reducing photo-generated electron-hole recombination and enhancing the photocurrent response. Concurrently, LDH converts lactate to pyruvate with the help of the coenzyme NAD⁺, which accepts electrons and hydrogen to form NADH. Photo-generated holes (h⁺) on the VB of TiONWs transfer to the HOMO of PEDOT to remove electrons from NADH, converting it back to NAD⁺ and completing the cycle. As shown in Fig. 6b, increasing the analyte concentration generates more NADH, consuming more photo-generated holes and enhancing the photocurrent response. This results in highly sensitive performance and quantitative determination of lactate in food, clinical, and fermentation industries. EIS was used to confirm heterojunction formation in the fabricated electrodes. Uniform PEDOT deposition on TiONWs/FTO showed a 62 % reduction in electron transfer resistance (R_{et}) compared to TiONWs/FTO alone, indicating effective heterojunction formation facilitating electron transfer to the electrode surface. However, after immobilizing LDH and NAD⁺, the EIS spectrum diameter increased due to the adsorption of larger biomolecules, which hinder the electron transfer process. These significant changes in R_{et} values demonstrate the effective construction of the PEC biosensor for lactate detection [115]. Sun et al. have developed a self-powered PEC molecular imprinted sensor designed for the specific and sensitive detection of sarcosine (SAR), a significant indicator for prostate cancer as shown in Fig. 6c. This sensor integrates a photoanode composed of Au@TiO₂ and a photocathode made of Cu₂O,

both constructed on an FTO substrate using the MIP technique. The Au@TiO₂ generates photoelectrons when exposed to light. These photoelectrons are attracted to the light-induced holes at the photocathode and are transferred to the Cu₂O through the circuit. The remaining holes in the Au@TiO₂ are reduced, leading to the generation of a substantial number of photoelectrons by oxidizing the Cu₂O. This self-powered system eliminates the need for additional electron acceptors or donors. When comparing the photocurrents, the Cu₂O/MIP exhibits a lower photocurrent than the Cu₂O alone due to the steric hindrance effect of the MIP, which hampers the electron transfer process. However, when the MIP is removed from the photocathode (Cu₂O/rMIP), the photocurrent increases significantly, nearly matching that of the non-imprinted polymer photocathode (Cu₂O/NIP). This behaviour is termed the self-powered cathodic sensing process. EIS was performed on the photocathode with and without the MIP. The MIP-modified photocathode showed an increased R_{et} , attributed to poor conductivity, and hindered electron transfer. After the MIP was eluted, the R_{et} decreased, suggesting that the Cu₂O/rMIP electrode configuration is highly effective for biomedical diagnostic applications [192]. Wang et al. have investigated a perovskite-type heterostructure nanocomposite composed of SrTiO₃/TiO₂/PDA, configured as an electrode on FTO, as illustrated in Fig. 6d. This electrode exhibited a progressive increase in photocurrent with the addition of glucose. The increase in photocurrent is attributed to the conversion of glucose into gluconic acid, followed by the oxidation of hydrogen peroxide by the electrode holes, thereby generating photocurrent. The rapid photocurrent response time of less than 200 ms, combined with a stable and uniform growth response, suggests that this electrode configuration holds promise for sensor

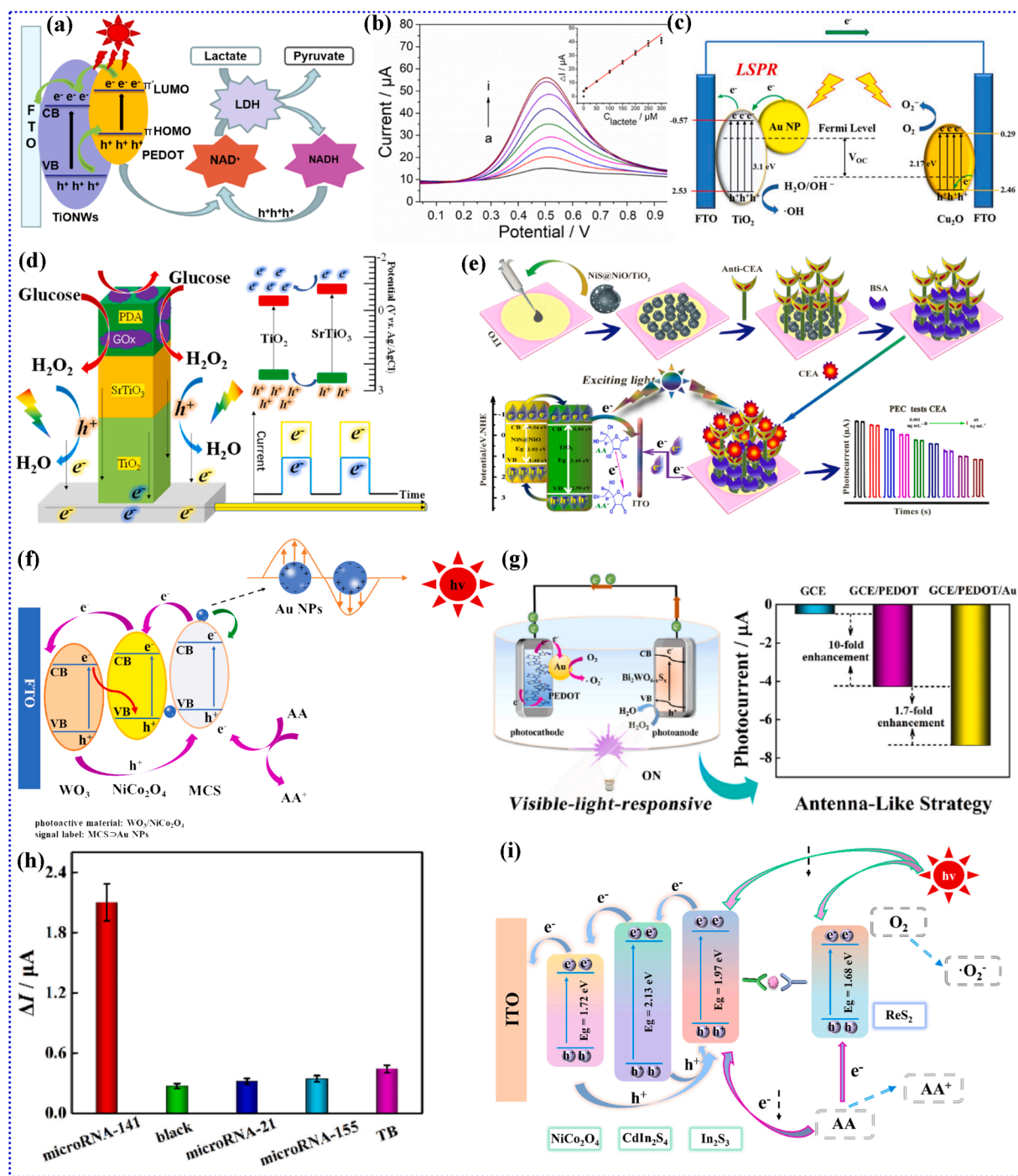


Fig. 6. (a) Reaction mechanism of the PEC biosensor; (b) Depicts the DPV response of NAD^+ [LDH|PEDOT-TiONWs|FTO] with varying concentrations of L-lactate, with Linear calibration plot in the inset, reprinted with permission from ref. [115]. (c) Mechanism of electron transfer in self-powered photoelectrochemical system, reprinted with permission from ref. [192]. (d) Sensing mechanism of $TiO_2/SrTiO_3$ heterojunction and $TiO_2/SrTiO_3/PDA/GO_x$ biosensor, reprinted with permission from ref. [193]. (e) The fabrication processes of PEC biosensors for CEA detection, reprinted with permission from ref. [194]. (f) Probable mechanism of the PEC immunosensor for the detection of NSE; reprinted with permission from ref. [193]. (g) Developed an antenna-like strategy; (h) Selectivity of the cathodic PEC for the interferences (100 pmol/L): the blank, microRNA-21, microRNA-155 and TB, reprinted with permission from ref. [198]. (i) Shown reasonable electron and hole transfer mechanism, reprinted with permission from ref. [199].

systems and clinical applications [193]. To further enhance PEC performance, Zheng et al. developed a heterostructure configuration of $NiS@NiO/TiO_2/ITO$ for the recognition of carcinoembryonic antigen (CEA), a tumor marker, as shown in Fig. 6e. The flat band potentials for $NiS@NiO$, TiO_2 , and $NiS@NiO/TiO_2$ were determined, revealing that the $NiS@NiO/TiO_2$ nanocomposite had an attractive heterostructure with CB and VB potentials lower than those of the other electrodes. Under

irradiation, photoelectrons generated in the CB of $NiS@NiO$ are shifted to the CB of TiO_2 , while holes in the VB of TiO_2 are shifted to the $NiS@NiO/TiO_2$. These are subsequently collected by the electron donor, AA, enhancing the photocurrent. Three key factors contribute to the enhanced photocurrent: the hollow and thin-shell structure of the $NiS@NiO$ composite increases the surface area, improving light absorption; the heterostructure forms a p-n junction with numerous active

sites, increasing charge carrier magnitude and enhancing separation and migration; and the reduced interface distance between connections accelerates the charge transfer rate. Additionally, the EIS spectrum for the NiS@NiO/ITO electrode shows a lower R_{et} value compared to other fabricated electrodes, due to the hollow spheres in the NiS@NiO electrode that facilitate electronic transit at the electrode interfaces. However, the introduction of analytes such as anti-CEA and BSA increases the R_{et} values, indicating that these substances hinder the electron transfer process due to poor conductivity. This proposed sensor demonstrates significant potential in PEC sensing applications, including clinical diagnosis, environmental monitoring, and food analysis [194]. Yan et al. investigated the fabrication and sensing performance of a TiO₂ nanotube array (TiONTA) nanocomposite that incorporated electro- and photo-deposited polyaniline (PANI) and gold nanoparticles (AuNPs). This resulted in an Au/PANI/TiONTA heterostructure nanocomposite. This composite demonstrated several advantages: (i) enhanced light absorption due to the presence of PANI and AuNPs; (ii) effective separation of photo-induced electrons through the heterostructure; and (iii) an increased surface area that boosts surface reaction kinetics, thereby improving the photo-induced electrocatalytic properties. The photoelectric conversion efficiency was compared among TiONTA, PANI/TiONTA, and Au/PANI/TiONTA electrodes. The Au/PANI/TiONTA heterostructure nanocomposite showed a significant increase in photocurrent under visible light illumination, with a photoresponse exceeding 10 %, compared to less than 6 % for the other electrodes. The inclusion of PANI helps to prevent the recombination of electron-hole pairs, while AuNPs enhance light absorbance and facilitate electron migration, improving electrode conductivity. This improved electron transfer property was further confirmed by EIS measurements. The Nyquist plot of the Au/PANI/TiONTA heterostructure nanocomposite electrode, characterized by a small semi-circular shape, indicates an increased electron transfer rate at the electrode interfaces and a reduced charge-transfer resistance. For glucose detection, glucose oxidase (GO_x) was immobilized on the Au/PANI/TiONTA heterostructure nanocomposite electrode. GO_x oxidizes glucose to gluconic acid and reduces oxygen to hydrogen peroxide. Under visible light illumination, the free electrons generated on the AuNPs are shifted to the LUMO of PANI. Subsequently, excited electrons in the HOMO of PANI are transferred to the CB of TiO₂, while the holes in the VB of TiO₂ migrate to the HOMO of PANI, producing a photocurrent through the cyclic oxidation of hydrogen peroxide to oxygen. This proposed PEC platform shows potential for fabricating different substrates for the exposure of nucleic acids and proteins [195]. Li et al. have developed a feasible method for forming a Z-scheme heterostructure, significantly improving photoelectric conversion efficiency. Traditional heterostructures often suffer from rapid reverse-recombination of photoelectrons, leading to reduced redox potential. In contrast, the Z-scheme heterostructure, utilizing a “Z” pathway, effectively isolates photogenerated electrons and holes, reducing electrostatic repulsion and increasing redox potential due to overlapping band potentials. The ZnIn₂S₄/Ag₂CO₃ Z-scheme heterostructure facilitates carrier transit, accelerating photogenerated charge carriers and enhancing light-harvesting capability through surface plasmon resonance (SPR). The bandgap (E_g) values for ZnIn₂S₄ and Ag₂CO₃ were determined, revealing n-type properties from the positive slope of the Mott-Schottky plot. The Fermi level (E_f) of Ag₂CO₃ is lower than that of ZnIn₂S₄, forming a staggered band structure. Under visible light, ZnIn₂S₄ and Ag₂CO₃ generate electron-hole pairs. Photogenerated electrons in the CB of Ag₂CO₃ transfer to Ag nanoparticles (acting as an electron mediator) and combine with holes in the VB of ZnIn₂S₄. During this process, electrons in the CB of ZnIn₂S₄ are transferred to the ITO substrate electrode, while holes in the VB of Ag₂CO₃ are absorbed by AA. The PEC sensor electrode with the Z-scheme heterostructure shows a 60-fold enhancement in photocurrent, attributed to this configuration. This biosensor exhibits ultrahigh sensitivity and stability, with an ultra-low detection limit for neuron-specific enolase (NSE) detection. Optimal conditions were identified (2.0 mg/mL concentration and pH 7.4), with

maximum photocurrent observed under these conditions. EIS measurements confirmed the PEC sensing response, showing a gradual increase in R_{et} value with NSE modification, indicating excellent performance for biomarker detection [196]. In another study, Zhang et al. fabricated a Z-scheme WO₃/NiCo₂O₄ nanoarray p-n heterojunction with cactus-like structures for sensitive neuron-specific enolase detection. The nanoarrays acted as a photoanode matrix, with MnxCd1-xS ⊃ Au NPs (MCS ⊃ Au NPs) as signal antibody markers, forming a single-on-type PEC sensor. The p-n heterojunction was grown on an FTO substrate using the hydrothermal method. The metal oxides in WO₃/NiCo₂O₄ provided a high surface area for polydopamine (PDA) film deposition. The energy levels between WO₃/NiCo₂O₄ and MCS ⊃ Au NPs were well-matched, enhancing PEC performance. The WO₃/NiCo₂O₄ electrode was modified with PDA and capture antibody Ab1. Under light, photogenerated electrons in WO₃ transfer to the VB of NiCo₂O₄, and photogenerated holes combine at the VB as shown in Fig. 6f. The Z-scheme mechanism efficiently separates charge carriers and enhances redox potential. The PDA film increases light harvesting and bridges the gap between Ab1 antibodies. Introducing MCS ⊃ Au NPs significantly enhances photocurrent intensity, attributed to the localized surface plasmon resonance (LSPR) effect of Au NPs. EIS and Nyquist plots showed increased R_{et} values after immobilization, confirming the PEC performance for NSE detection. The PEC immunosensor exhibited excellent selectivity, sensitivity, and reproducibility, making it promising for real sample detection [197]. Besides, Ai et al. studied an antenna-like strategy for developing cathodic PEC-based biosensors, which showed significant interest due to intrinsic hole conduction in p-type semiconductors and reverse recombination issues (Fig. 6g). The antenna-like strategy resulted in a 10-fold increase in photocurrent without using hole-conducting semiconductors. Instead, PEDOT was used to generate cathodic photocurrent, facilitating photoelectron migration to the n-type S-doped Bi₂WO₆ photoanode. The high electrical conductivity of PEDOT enabled efficient charge separation from S-doped Bi₂WO₆. Different S doping ratios (1 %, 5 %, and 10 %) were tested, with the highest photocurrent signal at 1 % S, indicating defect sites responsible for higher recombination. The self-powered dual-photoelectrode cathodic fabrication of PEDOT and Bi₂WO_{6-x}S_x demonstrated enhanced PEC performance. Photogenerated electrons from Bi₂WO_{6-x}S_x were neutralized by hydrogen peroxide, while electrons migrated via the PEDOT photocathode in a self-powered system. Electrons transferred to Au NPs, generating superoxide anion (O₂⁻) from dissolved oxygen as shown in Fig. 6h. The optimized self-powered antenna-like strategy significantly amplified the cathodic photocurrent, showing highly sensitive and selective PEC sensing for miRNA-141, opening a potential path for accurate disease diagnosis [198]. According to the report by Zhang et al. has utilized NiCo₂O₄/CdIn₂S₄/In₂S₃ heterostructure nanocomposite as a sensing platform with ReS₂@Au NPs as a secondary antibody label. NiCo₂O₄/CdIn₂S₄ was prepared by the hydrothermal method and sensitized with In₂S₃ to improve the PEC signal. PDA film deposition enhanced electron biosorption on the electrode surface. ReS₂@Au NPs amplified the PEC signal, creating a “signal-off” immunosensor as shown in Fig. 6i. Light irradiation resulted in photogenerated electrons reaching the electrode surface CB, while holes migrated to the VB, inhibiting charge carrier recombination. Parameters such as pH 7.4, composition, and proportion of photoactive materials (50 %), and incubation time (1 h) were optimized. ReS₂@Au NPs-Ab2 bioconjugate electrode surfaces absorbed light, reducing light-capturing properties but increasing ReS₂ conductivity and improving biocompatibility. Photogenerated electrons reacted with dissolved oxygen species, generating superoxide radicals. Holes generated by ReS₂ competed with AA, reducing matrix cavity removal efficiency. Double inhibition effectively quenched the signal. EIS analysis confirmed the charge transfer process, with a gradual increase in R_{et} value due to steric hindrance and protein insulation. The proposed sensor platform showed hypersensitivity, specificity, stability, and reproducibility, making it promising for serum sample detection [199]. This comprehensive discussion compares heterostructure

nanocomposites strategies and semiconductor band alignment-based approaches for PEC detection in healthcare applications. Table 3. summarizes PEC results from various nanomaterials and nanocomposite electrodes for detecting prominent biomolecules in healthcare.

Other than metal oxide

Concurrently, covalent organic frameworks (COF) are innovative porous organic materials that are connected with nonmetal elements of carbon, oxygen, nitrogen, boron, etc. via covalent bonds and show great interest in PEC sensing applications [200]. An innovative S-scheme COF might tune their band gap, and optical and electrical properties through their unique structure. It is found to have effective photoactive and electroactive properties with a well-ordered nanocrystalline structure containing enormous active sites and signal-generating cavities, voids, and transitional gaps. And also, it possesses excellent thermal and chemical stability and efficient biocompatibility, thereby facilitating the platform for the adsorption of biomolecules via H-bond, electrostatic adsorption, and so on. These ideal structure-based COF materials aid in the development of PEC-based heterostructures for highly sensitive detection of biomolecules [201]. Li et al. developed an S-Scheme porphyrin-COF@p-SiNW (p-COF@p-SiNW) heterostructure was developed, where SiNW can act as a photocathode to enhance the signal response and control anti-interference capability. The p-COF modification improves electrode stability and provides numerous NH_2 groups for immobilizing anti-cardiac troponin (cTnI). In this S-Scheme heterostructure, light illumination causes electrons to flow from p-SiNW to p-COF due to the higher Fermi level of p-COF, creating a positively charged layer and an electron depletion zone at the p-COF interface. This process generates an internal electric field between p-COF and p-SiNW, facilitating electron movement from the CB of p-SiNW to the VB of p-COF, and further to oxygen and hydrogen peroxide on the electrode surface. The resulting holes remain in the VB of p-SiNW, generating a cathodic current. This S-Scheme charge-transfer pathway contributes to the enhanced cathodic photocurrent response. To determine the PEC sensing performance against the anti-cTnI, it has been observed that there is a decrease in the photocurrent density after modification of the anti-cTnI, which is responsible for the steric hindrance effect of the non-conductive nature. Therefore, the interfacial charge transfer rate is hampered via the electrode/electrolyte junction. Then increase the incubation with cTnI antigen, which further decreases the photocurrent that is ascribed to the formation of immune complexes. In addition, the R_{ct} was measured using EIS. After modification with cTnI antigen, the Nyquist plot depicts a higher R_{ct} value (27.8 k Ω) compared to that of pure and other interferences [202].

Summary and outlooks

In summary, the development of photoactive nanomaterials has been evaluated as sensing platforms for PEC methods, which has shown a new way of emerging analytical approaches. Due to their merits of low background signal, feasible accessibility of instruments, rapid response, and effective sensitivity. So far, a huge number of semiconductive photoactive nanoparticles and their nanocomposites have been prepared and explored. Utilizing these nanomaterials, the construction of heterostructure nanocomposite strategies has shown great attention for PEC sensor applications. Consequently, this review was classified from an application point of view, especially in the fields of environmental, food, and healthcare applications. To achieve better results, several strategies were employed for the preparation of photoactive nanomaterials, such as the fabrication of nanosheets, specific elemental doping, the development of heterojunctions or structures with other semiconductors, and functionalization. And also, these strategic developments have apparently shown the effective inhibition of recombination of photogenerated charge carriers, which further influences the PEC sensing performance. The predominant modifications would

greatly enhance PEC-based detection performance. To enhance sensing performance, utilizing photoactive nanomaterial-based platforms is playing a crucial role in achieving sustainable development. Despite the recent advancements in photoactive nanomaterials, many challenges remain to be addressed. The emerging field of nanoscience and nanotechnology and integrating with single/bimetallic single atoms may offer several advantages, including versatility and a portable, powerful platform that has been envisioned for wider applications. This review has also been outlined the generation of heterostructure nanocomposites for PEC-based sensing platform for advanced analytical applications, which include the preparation of photoactive nanomaterials, the fabrication of electrodes, and adequate analytical approaches for sensing performance.

PEC sensing methods have gained great attention and emerged in recent decades due to their high sensitivity, selectivity, miniaturization, excellent performance, and reliability advantages. The PEC sensing method has opened a new sensing platform that offers various prospects for the development of advanced analytical tools. With their structural design and construction, photoactive nanomaterials have been playing a vital role in advancing the PEC sensing method for various fields, including environment, food, healthcare, and so on. Nevertheless, significant development has been achieved but does not offer widespread commercial purposes. Hence, the research should be directed towards developing new photoactive materials with various nanostructures that have key characteristics, such as high photoelectric conversion and efficiency, simultaneous detection, affordability, facile preparation processes, excellent biocompatibility, environmental friendliness, and exceptional stability. In addition, structural characterization, including UV-vis, Raman, XRD, SEM, TEM, AFM, photo/electro-luminescence, and Time-correlated single photon counting (TCSPC) spectroscopy and microscopy, have been exemplified for analysis. As a result, absorption, functional group, crystallinity, morphology, topography, excitation and emission, and photon counting were to be observed using the above-mentioned methods. To maximize the potential applications of PEC sensing technology, it's essential to explore its intersection with emerging technologies, including PEC-coupled Raman spectroscopy, PEC-coupled fluorescence, PEC-coupled TCSPC, and PEC-coupled AFM has to be developed for the single or multipoint detection applications. It is crucial to adopt an interdisciplinary research approach to speed up the commercialization of PEC sensing. To meet the requirements of real-world applications, this strategy involves the creation of practical integrated detection devices that combine PEC sensing with other disciplines, focusing on reliability, stability, and throughput. Besides, the integration of internet of things (IoT) has the capability to extract quantitative information in real time, especially from remote or limited resource areas. The IoT technology is still under development in various fields, and there are many challenges involved in it, such as sensitivity, selectivity, stability and security of devices, and interferences. Much more research has to be performed in order to make it to pose to undeniable option for solve the real-time demands and monitoring applications. In the forthcoming decades, especially in chemistry, biological, food, and environmental monitoring, which will play a pivotal role in the development of wearable IoT microdevices. With the development of the Internet of Things (IoT) and artificial intelligence (AI), the trend for photoelectrochemical sensors is towards integration, intelligence, miniaturization, wireless, and portability, which is an ideal choice as a smart sensor in the forthcoming eras towards on-site industrial effluent monitoring, human-health monitoring and defense applications.

CRedit authorship contribution statement

Ravi Kumar Yohan: Writing – review & editing, Writing – original draft, Validation, Formal analysis, Conceptualization. **Mohanraj Jagannathan:** Writing – original draft, Visualization, Validation, Formal analysis, Data curation, Conceptualization. **Gopi Sivalingam:** Writing – review & editing, Methodology, Investigation,

Table 3

Nanostructured materials as a photo-electrochemical sensors in healthcare applications.

S. NO.	Mechanism of action	Nanomaterials	Approaches	Morphology	Light wavelength (λ), power density (P), or light dose (LD) and distance btw. the electrode	Linear range and LOD	Type of analytes	Real samples	Ref.
1	PEC-immunosensor	ITO/NiWO ₄ /Ab	Co-precipitation	Saw-blade	300 W and 10 cm	75–723 ng. mL ⁻¹ and 0.12 ng. mL ⁻¹	Neuron-specific enolase (NSE)	Human Serum	[113]
2	PEC	C60 NPs/MB	Sonication	Globular	460 nm (976 mW)	10 fM – 100 nM and 3.3 fM	DNA	Human Serum	[231]
3	PEC	CuO NFs/rGO	Printing	Flower		5.0 to 3.0 × 10 ³ nM and 2.1 nM	ATP	–	[105]
4	PEC	BiOI/CS	Solvothermal	Flower	500 W (>400 nm)	1.0 × 10 ⁻¹⁴ . 1.0 × 10 ⁻⁹ M and 2.2 × 10 ⁻¹⁵ M 1.0 × 10 ⁻¹⁵ . 1.0 × 10 ⁻⁹ M and 2.1 × 10 ⁻¹⁶ M	DNA miRNA-21	–	[232]
5	PEC	β-CD@CdS NRs	Solvothermal	Rod	Home build PEC system	1 × 10 ⁻¹⁴ – 1 × 10 ⁻⁹ M and 1.16 × 10 ⁻¹⁵ M	HIV-related DNA	Human Serum	[100]
6	PEC	NAD+/LDH/PEDOT-TIONWs FTO	Hydrothermal	Nanowire	400 nm	0.5–300 μM and 0.08 μM	NAD ⁺	Human Serum	[115]
7	PEC	TiO ₂ /MX-BiVO ₄	Drop casting	Sheet	300 W (100 mW cm ⁻²)	2.2 × 10 ⁻⁴ to 3.2 ng mL ⁻¹ and 1.4 × 10 ⁻⁵ ng mL ⁻¹	CD44 protein	Human Serum	[114]
8	PEC	GOx@Au–PANI–TiO ₂	Electrodeposition and photo deposition	Nanotube	500 W (>380 nm)	2–36 mM and 0.02 mM	Glucose	–	[195]
9	PEC	Ti ₃ C ₂ @ReS ₂	Hydrothermal	Nanosheet	450 nm (1 W, 92 mW/cm ⁻²)	0.1 fM to 1 nM and 2.4 aM	miRNA-141	Human Sera	[233]
10	PEC-immunosensor	MX-NiWO ₄	Low-temperature hydrothermal	Freckled on Thin sheet	300 W and 15 cm	1.2 fg.mL ⁻¹ to 0.18 mg. mL ⁻¹ and 0.15 fg.mL ⁻¹	prostate-specific antigens (PSA)	human saliva	[234]
11	PEC	P1-AuNPs/fullerenol/GCE	Precipitation	Global	460 nm	1 fM to 100 pM and 0.338 fM	DNA	–	[235]
12	PEC	PEDOT/Bi ₂ S ₃ /ZnO	Photo deposition	Columnar	150 W (500 mW/cm ²)	1 pg/mL – 100 ng/mL and 0.67 pg/mL	CEA	Human serum	[236]
13	PEC	h-BN/Au ₅ Pt ₉	–	Framework	–	0.03 ~ 100 μM and 0.406 nM	Glucose	–	[237]
14	PEC	3D Ti ₃ C ₂ T/ ₁ CdS	Hydrothermal	Accordion	300 W	1 × 10 ⁻¹⁵ – 1 × 10 ⁻⁸ M and 0.053 fM	miRNA-21	–	[116]
15	PEC	P3HT-PbS nanocomposites	Precipitation	Cube	–	0.100 pg/mL – 100 ng/mL and 0.130 fg/mL	β2-microglobulin (β2-MG)	–	[238]
16	PEC	Ag ₂ S/Ag/ZnIn ₂ S ₄ /C ₃ N ₄	Hydrothermal and Precipitation	Chrysanthemum Nanoflower	5 W LED (460 nm)	50–5 × 10 ⁵ cell mL ⁻¹ and 19 cell mL ⁻¹	Telomerase (TE)	–	[239]
17	PEC	Au@TiO ₂ nanorods	Hydrothermal	Nanorod	500 W	10 nM – 10 μM and 0.19 nM	Sarcosine (SAR)	Serum	[192]
18	PEC	n-type S doped-Bi ₂ WO ₆	Solvothermal	Nanorod	400 nm	0.3 fM	microRNA-141	Human serum	[198]
19	PEC	PM6:Y6 and Au@Ag	Hydrothermal	Spherical	500 W (420 nm or 15 mW/cm ²)	10 to 10,000 cell mL ⁻¹ and 9 cell mL ⁻¹	MCF-7	whole blood samples	[240]

(continued on next page)

Table 3 (continued)

S. NO.	Mechanism of action	Nanomaterials	Approaches	Morphology	Light wavelength (λ), power density (P), or light dose (LD) and distance btw. the electrode	Linear range and LOD	Type of analytes	Real samples	Ref.
20	PEC	NiS@NiO/TiO ₂	Precipitation	Spherical	20 mW/cm ² (420 nm)	0.001 to 45 ng mL ⁻¹ and 1.67 $\times$ 10 ⁻⁴ ng mL ⁻¹	Carcinoembryonic antigen (CEA)	Human serum	[194]
21	PEC	ZnO/CdTe/Bi	Sputtering	Nanorod	500 W mercury-xenon light	102–107 cells·mL ⁻¹ and 32 cells·mL ⁻¹	nasopharyngeal carcinoma5–8F	—	[241]
22	PEC-immunosensor	WO ₃ /NiCo ₂ O ₄	Hydrothermal	Nanosheet	100 W LED	0.1 pg/mL ~ 50 ng/mL and 0.07 pg/mL	NSE antibody	Serum	[197]
23	PEC-immunosensor	ReS ₂ @Au	Hydrothermal	Tremella	100 W LED	0.0001–50 ng/mL and 0.05 pg/mL	CYFRA 21–1	Serum	[199]
24	PEC	OVs-Bi ²⁺ xWO ₆	Hydrothermal	Nanosheet	100 W LED (430 nm)	0.01 to 500 ng/mL and 6.87 pg/mL	histone H2AX	HepG2 cells	[242]
25	PEC	TiO ₂ /Ti ₃ C ₂ Tx	Wet chemical etching	Layer	300 W	1 $\times$ 10 ² to 2 $\times$ 10 ⁷ cells/mL and 1.01 cells/mL	FR expressing breast cancer cells (MDA-MB-231) (clinical)	—	[243]
26	PEC-immunosensor	p-COFs@P-SiNWs	Metal assisted chemical etching	Nanowire	150 W (100 mW/cm ²)	5 pg/mL – 10 ng/mL and 1.36 pg/mL	Cardiac troponin I (cTnI)	Human Serum	[202]
27	PEC-immunosensor	CdS@C	Solvothermal	Pinecone	500 W	0.01 – 80 ng mL ⁻¹ and 3.6 pg mL ⁻¹	carcinoembryonic antigen (CEA)	Human Serum	[244]
28	PEC	Z- Scheme ZnIn ₂ S ₄ /Ag ₂ CO ₃	Precipitation	Flower (Petal)	—	50 fg·mL ⁻¹ ~ 200 ng·mL ⁻¹ and 4.86 fg·mL ⁻¹	neuron-specific enolase (NSE)	Human serum	[196]
29	PEC	α -Fe ₂ O ₃ NRs-Ov/Ag-Ag ₂ S	Solvothermal	Nanorod	200 W	nM to 50nM and 40.2 fM	Thrombin	Human serum	[245]
30	PEC	g-C ₃ N ₄ /CuInS ₂	Hydrothermal	Spherical flower	500 W	0.02 – 40 ng mL ⁻¹ and 5.2 pg mL ⁻¹	carcinoembryonic antigen (CEA)	Human serum	[246]
31	PEC-Aptasensors	Co ₉ S ₈ @CdS	Solvothermal	Nanoflower	500 W	0.02 to 40.0 ng mL ⁻¹ and 7.4 pg mL ⁻¹	carcinoembryonic antigen (CEA)	Human serum	[247]
32	PEC-immunosensor	BWO-PO boosted by P (Th-T3A)	Hydrothermal	Lamellar	10 W LED (420 nm)	1 pg/mL – 20 ng/mL and 0.41 pg/mL	carcinoembryonic antigen (CEA)	Human serum	[248]

Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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