Designing efficient TiO₂-based photoelectrocatalysis systems for chemical engineering and sensing

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Abstract

Photoelectrocatalysis (PEC) incorporates electrochemical techniques with photocatalysis (PC) to facilitate the separation of the photoelectron-hole produced at semiconductor nanoparticles, leading to enhanced photocatalytic efficiency for various applications. Due to its inherently low cost, non-toxicity and chemical stability, titanium dioxide (TiO₂) based PEC devices are considered the most promising system for chemical engineering such as pollution degradation and fuel generation, and PEC sensing. In an attempt to bridge fundamental research and practical applications in chemical engineering and sensing, we herein systematically review recent advances in these PEC systems of different scales. More importantly, we offer a series of rational strategies including cell design, application of electric field photoelectrode morphology manipulation and bandgap engineering to enhance the performance of TiO₂-based PEC devices and accelerate the commercialization of the TiO₂-based PEC technology in chemical engineering.

Keywords: TiO₂, photoelectrocatalysis, Material engineering, PEC engineering, PEC sensing.

1. Introduction

It is well-recognized that sustainable energy conversion, utilization and storage are the ultimate solutions to global energy challenges. Solar energy is an ideal renewable energy source as it is abundant and readily available ¹. Photoelectrocatalysis (PEC) is a powerful and efficient process based on the combination of photocatalysis (PC) and electrochemical technology for the utilization of solar energy. Since breakthrough of PEC water splitting process on a TiO₂ electrode, the TiO₂ photoelectrode has been the dominant and most promising candidate due to its strong PEC oxidation power, low-cost, non-toxicity and strong chemical stability in various environments. ² To date, successful fundamental research of TiO₂-based photocatalysis systems has resulted in the development of a wide range of PEC devices for application in PEC fuel generation, PEC water purification and PEC sensing ³⁻⁴. However, to meet the requirements of practical applications in chemical engineering, the overall efficiency of current PEC devices need to be further improved, which requires optimization of all components in PEC devices, including electrochemical bias, PEC cell and photoelectrode.

In order to bridge the gap between fundamental research and practical applications in chemical engineering, we systematically review modification strategies (including electrochemical bias, cell design and photoelectrode manipulation) and various application developments (including pollution degradation, fuel generation and sensors) on TiO₂-based PEC devices as shown in Fig. 1. The electrochemical bias is applied to achieve effective separation of photoelectrons and photoholes and allow synergetic oxidation of organics. The PEC cell design aims to not only improve the mass transport at the interface of photoelectrodes and bulk solution, but also maximize light intensity at the surface of photoelectrodes. The photoelectrode manipulation enhances light absorption efficiency, charge transport to the catalyst surface and subsequently improves the PEC efficiency. This involves the morphology fabrication, the band gap engineering and surface modification of TiO₂ photoelectrode. Nevertheless, various successful PEC devices, including PEC pollution degradation, PEC fuel generation and PEC sensors, have demonstrated in attempt to inspire more advancements of PEC system for chemical engineering in the future.

Fig. 1 The efficiency of PEC devices can be commonly enhanced by three strategies including PEC cell design, electrochemical bias control and photoelectrode manipulation for chemical engineering (pollutant degradation and fuel generation) and chemical sensing (PEC sensors).

2. Fundamentals of TiO₂ Photoelectrocatalysis

2.1 TiO₂ Photocatalysis

The photocatalytic reactions at the surface of TiO₂ are commonly interpreted by the energy band model of semiconductors (see Fig. 2). The valence band (E_{VB} , the highest occupied energy band) and conduction band (E_{CB} , the lowest empty energy band) are separated by an energy band gap (E_{BG} , region of forbidden energies). Once the photoexcitation process is triggered under suitable light irradiation (where the light energy $h\nu$ is equal to or greater than E_{BG}), electrons are excited and promoted to the E_{CB} , leaving holes in the E_{VB} as shown in Eqn. 1:

The separated electrons and holes then migrate through the semiconductor to the semiconductor/electrolyte interface, where reduction of electron acceptors (i.e. A) and oxidation of electron donors (i.e. D) occur at the conduction band and valence band, respectively (Eqns. 2 and 3).

However, the opposite process, i.e. the recombination reaction of the electron e^- and hole h^+ pair always takes place, producing unwanted heat and greatly limiting the photocatalytic efficiency. PC systems, e.g. slurry PC devices, usually require complicated post-separation processes before the TiO_2 photocatalyst can be recovered/separated from the products and reaction medium. This results in both high cost and low re-usability of the catalyst.

Fig. 2 A typical photocatalysis process: an n-type semiconductor produces photoelectrons and photoholes under effective illumination. The photoelectrons are captured by the electron acceptor (A) while the photoholes seize electrons from the electron donor (D).

2.2 TiO_2 Photoelectrocatalysis

Charge recombination - the recombination of photoelectrons and photoholes (i.e. the back reaction of Eqn. 1), is a critical factor limiting the solar-to-chemical energy conversion efficiency of semiconductor photocatalysts. It is well-established that the incorporation of PC systems with electrochemical systems could markedly improve the efficiency of the PC processes, resulting in a wide range of PEC cells and devices. As shown in Fig. 3, the reduction and oxidation

reaction occur separately at the cathode and anode, respectively ⁵⁻⁶. Subsequently, the redox reactions can be controlled and the reaction products collected individually, removing the need for separation in PC systems. This brings inherent advantages and facilitates PEC application in chemical engineering (organic degradation and fuel generation) and sensing.

Fig. 3 A typical set up of a PEC system: the potential bias imposed by the electrochemical station allows the separation of charge carriers under a potential bias (in this case positive). The porous separator facilitates the oxidation reaction in the left chamber while the reduction reaction occurs in the right chamber.

2.2.1 PEC degradation and mineralization

The PEC system is widely considered as an environmentally friendly and efficient method for pollution degradation in aqueous solution. Under ideal conditions, efficient PEC degradation can mineralize organic pollutants in water bodies to CO₂ and H₂O, without producing the toxic and detrimental intermediates. During PEC degradation, the photo-generated electrons (e⁻) and holes (h⁺) are transferred onto the surface of the photocatalyst initiating the degradation reaction. Photogenerated electrons (e⁻) could react with electron acceptors, such as dissolved O₂ in aqueous solution, generating the superoxide radical anion ·O₂⁻ (Eq. 4).

Meanwhile, photogenerated holes (h⁺) could oxidize OH⁻ and H₂O into ·OH radicals (Eq. 5 and 6).

The organic compounds in the water body could be oxidized by the hydroxyl radicals ($\cdot\text{OH}$), oxygen peroxide radicals ($\cdot\text{O}_2$) and photogenerated holes (h^+) into CO_2 and soluble degradation products. Due to their strong oxidation power (see Eq. 7), photocatalysts are able to degrade most organic pollutants in water bodies under illumination, especially persistent organic pollutants (e.g. Aldrin ⁷, chlorophenols ⁸, polybromodiphenyl ethers ⁹ and decabromodiphenyl ethers ¹⁰) and antibiotics (e.g. chlortetracycline ¹¹, tetracyclines ¹² and triclosan ¹³).

2.2.2 PEC generation of fuel

Unlike PEC degradation, photoelectrode generated electron/hole pairs (e^-/h^+) can also drive oxygen evolution, hydrogen and CO_2 reduction reactions. Thermodynamically, for water splitting reactions to occur in a PEC system, the photo-excited electrons at E_{CB} levels need to have sufficient energies to reduce H^+ ions into H_2 while photogenerated holes at E_{VB} levels can oxidise H_2O to form O_2 . Subsequently, oxidation of H_2O to O_2 can occur at the TiO_2 photoelectrode (usually as photoanode). At the cathode side (electrocatalyst or/and photocatalyst as a cathode), the photoelectrons can be used to reduce hydrogen ions and produce hydrogen gas and/or induce the reduction of CO_2 to hydrocarbon fuels in aqueous electrolyte as shown in equations 8 to 15:

E^0 is the value of standard reduction potentials at 298.15 K (25 °C) and at a pressure of 101.325 kPa (1 atm)¹⁴.

It is well-recognized that the photocatalytic reduction of CO_2 to hydrocarbon fuels is more challenging than the production of pure H_2 because the former involves complicated photophysical and photochemical processes. For instance, the products in

photocatalytic conversion of CO₂ are commonly a mixture of many organic compounds including HCOOH, HCHO, CH₃OH, CO, H₂, and CH₄.

2.2.3 PEC sensing

The photocurrent produced in PEC devices can be utilized for analytical purposes. The applications of TiO₂-based PEC sensors can be classified into two categories: PEC sensors for monitoring organic content in water¹⁵⁻²⁵, and signal transducers for chemical sensors and biosensors²⁶⁻²⁷. Both applications have been intensively researched over the past decade.

a. PEC COD sensor

Upon light irradiation, the continuous charge separation or recombination of photogenerated electron-hole pairs yields a stable photocurrent in aqueous solution at the photoelectrode. This photocurrent can be measured to quantify the aggregated organic compounds present in water samples—the corresponding sensors are named PEC sensors (see Fig. 4a).

Fig. 4 Elements and sensing processes of the typical TiO₂-based PEC sensor (a) and PEC biosensor (b).

Chemical oxygen demand (COD) reflects the overall amount of aggregated organic compounds in water¹⁹. Zhao et. al invented a thin-layer photoelectrochemical device to rapidly and accurately analyse COD values in water²⁵, namely PeCOD technology. The COD values measured by the

photoelectrochemical method are also termed PeCOD^{20, 28}. The PeCOD analysers take advantage of the superior oxidation power of the TiO₂ photoanode under UV irradiation. The TiO₂ electrodes can photocatalytically oxidize and electrochemically quantify the exhaustive degradation of organic compounds in waterbodies. In other words, PEC devices can literally “wet-burn” the organic compounds in aqueous solution. (Eq. 16):

where X represents a halogen atom and the coefficients y , m , j , k , and q stand for the stoichiometric ratio of elements in the organic compounds. Therefore, the number of electrons captured in this process is the oxidation number ($n = 4y - 2j + m - 3k - q$). The achievement of this mineralization reaction is a pre-requisite for the determination of the overall amount of organic compounds and the COD of a water sample.

b. PEC biosensors

The principle of sensing mechanism for the PEC biosensor is based on monitoring the biological interactions between various recognition elements and their corresponding targets by PEC electrode as a signal transducer²⁹. As shown in Fig. 4b, the continuous charge separation or recombination of photogenerated electron-hole pairs yields a stable photocurrent which can be utilized to monitor biological processes. The incorporation of the biological interactions provides invaluable selectivity to the analysis as the PEC sensor is a universal transducer. In PEC biosensor, the biological recognition elements, such as enzymes, antibodies, nucleic acids and DNA are immobilized on TiO₂ nanostructured electrodes. The biological recognitions strong interact with target compounds *via* specific binding affinity. Therefore, the target analytes in solution could be electron donors or acceptors to inhibit (or facilitate) the recombination rate thereby generating higher (or lower) photocurrent which can be seen as bioanalytical signals³⁰. To date, PEC biosensors can selectively analyse various compounds (e.g. DNA, protein, cell, biomolecules, ions, etc.)³¹⁻³³.

3. Rational Strategies for High-Performance PEC Devices

The usefulness of the PEC devices and application depends on the efficiency of the PEC systems. The overall PEC efficiency (η) at the TiO₂ surface of a PEC system could be described by the following equation:

$$\eta = \eta_{light\ trans.} \times \eta_{light\ abs.} \times \eta_{charge\ sep.} \times \eta_{mass\ trans.} \quad (17)$$

Where $\eta_{light\ trans.}$, $\eta_{light\ abs.}$, $\eta_{charge\ sep.}$ and $\eta_{mass\ trans.}$ represent the efficiency of light transmitted through the reaction media to the catalyst surface, light absorption by the catalyst, charge separation, and mass transport of reactants, respectively. The improvement of the overall efficiency of a PEC device requires optimization of these individual efficiencies. In particular, when light is directed into a PEC reactor, some light energy is inevitably absorbed by the reaction media, such as water, leading to the loss of light energy. The shorter the light path in the media, the more light energy reaches the surface of the catalyst, the higher the $\eta_{light\ trans.}$. PEC cell design can facilitate high $\eta_{light\ trans.}$ as well as $\eta_{mass\ trans.}$. The photoelectrode manipulation could increase the $\eta_{light\ abs.}$ and $\eta_{charge\ sep.}$ to maximize the utilization of light irradiation and to facilitate the chemical reaction at the surface of photoelectrodes.

3.1 Applied Potential Bias

Applying potential bias on the working electrode can seize photogenerated electrons from the conduction band²⁸. The electric potential serves two purposes in this photoelectrocatalytic system: first, to suppress the recombination of the photo-induced holes and electrons and therefore achieve high photocatalytic oxidation efficiency; second, to quantify the extent of the photoelectrocatalytic oxidation reaction by quantifying the amount of electrons originating from the oxidation reaction and subsequently determine the amount of organic compounds in the sample. For TiO₂ semiconductor photoanodes in particular, the applied potential bias collects the electrons made available by the interfacial photocatalytic reactions. Maximum (100%) photoelectron collection efficiency can be achieved only when the applied potential bias is sufficiently positive²¹. Fig. 5 shows the effect of potential bias on both photocurrents in the absence and presence of organic compounds. The current initially increases with potential increasing from -0.4 to 0.1 V. The photocurrents became constant when the

applied potential bias was more positive than 0.1 V vs. Ag/AgCl, indicating 100% photoelectron collection efficiency.

Fig. 5 Effect of potential of a nanostructured TiO₂ electrode on the photocurrents in the presence of 0.2 mM glucose and blank electrolyte solution ²¹.

When sufficient potential bias is applied onto the TiO₂ photoanode, the photoelectrocatalytic reaction is insensitive to O₂ concentration because the PEC system configuration involves a three-electrode system that allows the physical separation of the two half-reactions ²⁸. The oxidation half-reaction takes place at the TiO₂ working electrode and always determines the overall reaction rate regardless of the type of reduction half-reaction occurring at the auxiliary electrode. This is because the rate of the reduction half-reaction at the auxiliary electrode will inevitably keep up with the oxidation half-reaction at the working electrode by automatically adjusting the auxiliary electrode potential according to the available species (including, but not limited to O₂, as the O₂ solubility in water is low at room temperature).

Besides external potential bias into the system, a built-in electric field at the interface of semiconductors could facilitate the separation of electron-hole at the TiO₂ photoanode. The built-in electric field can be established at a heterojunction or p-n junction between different semiconductors³⁴.

In the degradation of persistent organic compounds (e.g. landfill leachate) using PEC, a much higher potential (e.g. 20V) could be used to assure fast reaction rates of the mineralization of organics. The potential variation from 5 to 20 V leads to an increase of landfill leachate degradation efficiency from 30.6% to 70.2% ³⁵. In this case, often, the reaction occurs rapidly due to the synergetic

effect of electrocatalysis and photoelectrocatalytic reactions, e.g. it facilitates the production of the free radical $\cdot\text{OH}$.

For PEC fuel generation, although the high bias potential would suppress the recombination of photoelectron-holes, the overloaded bias potential could induce the extra energy loss³⁶⁻³⁹. Therefore, there is an optimal external potential of the PEC system (e.g. PEC solar cell) to balance PEC fuel reduction and organic oxidation to further improve solar-to-fuel (STF) efficiency⁴⁰⁻⁴¹.

3.2 PEC Cell Design

In a typical slurry PC system, the catalyst has a large surface area to absorb light and catalyse the targeted reactions. In contrast, slower mass transfer can be expected due to the PEC electrode having a much smaller surface area to absorb light and fewer reaction sites. The PEC system also suffers from a larger light energy loss in reaction media (such as aqueous solution) due the cell geometry that must facilitate light illuminating the surface of the electrode. These issues need to be addressed *via* the design of PEC systems. To maximize the efficiency of the PEC reaction, a well-designed PEC device could promote catalytic efficiency *via* maximizing the utilization of light energy and facilitating mass transfer in aqueous electrolyte. Accordingly, the optical system configurations and reactor design are considered in the following sections.

3.2.1 The optical system

In the optical system, we need to be able to control wavelength and intensity of light as it directly affects the PEC reaction²¹. When designing PEC devices, we need to consider the shape, size, weight and cost of the optical system.

For large-scale applications, solar light is an ideal source for PEC systems due to the low cost. However solar irradiation is intermittent, and its light intensity varies with time, therefore, it is generally not suitable for some research applications such as sensing and evaluation of catalyst performance. Artificial light sources such as Xenon lamps, Mercury lamps, Tungsten lamps and light emission diodes (LED) are better alternatives for different-scale PC and PEC systems, especially in small-scale research applications, because these light sources allow us to control light intensity, and incorporate it into PEC systems of different sizes, shapes and scales to suit our needs. In some cases, e.g. small-scale pollution treatment and PEC sensors, the operating cost of the artificial UV light

sources can be acceptable for the PEC device due to the excellent stability and energy conversion efficiency provided ⁴².

Solar light contains consistent wavelengths of light, among them only c.a. 4% is UV irradiation which could be directly utilized by TiO₂ (see Fig. 6a) ⁴³. If other wavelengths (visible and infrared regions) of light could interfere with the targeted reactions, optical filters are an effective option to remove this interference. It is much easier, however, to use artificial light sources to control light wavelengths. Mercury lamps emit strong UV light in comparison with xenon light and tungsten light. As shown in Fig. 6a, the mercury light is characterized by its line spectrum from 200 nm to 365 nm. Therefore, the mercury lamp is technically suitable for TiO₂-based PC and PEC devices. In fact, mercury light sources have been incorporated into PC systems for wastewater treatment at a commercial scale ⁴⁴⁻⁴⁵. However, mercury lamps, especially high-power mercury lamps (e.g. 500W), produce significant amounts of ozone and cannot provide light irradiation of continuous wavelengths. Consequently, they are not as common as xenon light sources in lab applications.

Fig. 6 Spectra of light sources and filters: (a) light spectra of mercury lamp, xenon lamp, halogen lamp and solar light; (b) transmission spectra of different visible light cut-off filters, and (c) emission spectra of various light-emitting diodes with different peak emission wavelengths.

Xenon light is a popular light source for lab applications, such as incident photon conversion efficiency (IPCE) measurement, UV light source (after removal of visible light), visible light (after removal of UV) and solar light simulators, based on the light emission of a continuous spectrum from UV to visible to infrared range (see Fig. 6a). The xenon lamp can emit with high luminance and high colour temperature. In the laboratory, solar simulators simulate the spectrum of natural sunlight to evaluate the applicability and performance of the

photocatalyst under specific optical conditions. To simulate the solar light spectrum, an air mass (AM) filter must be used to shape the spectral output of xenon arc light to match the specific natural solar conditions (AM 1.5G). Under this optical condition, the PEC efficiencies of the various PEC devices or solar cells are measured. The use of monochromators or optical filters can remove the unwanted segments of the light to meet desired needs. For example, in PEC sensing applications, the heat generated by the visible and infrared light can interfere with accurate measurements by heating up the reaction medium. Zhang et. al used the UV band pass filter to block visible and infrared radiation and subsequently block heat injection in the PEC sensor ²⁸. The UG5 filter was chosen from among several filters due to its better blockage of visible and infrared light and transmission of UV light (see Fig. 6b) ²⁸. In some PEC based biosensors, UV light causes severe damage to labile biomolecules. To overcome this problem, UV cut filters were used to filter out the UV light ⁴⁶.

As one of the incandescent lamps, halogen lamps produce a continuous spectrum of light from near UV to infrared as shown in Fig. 6a (e.g. 330-2500 nm). The halogen lamp provides excellent black body radiation in the infrared but lacks sufficient intensity of UV light. It is a convenient and low cost light source for PEC applications in the visible light region ⁴⁷.

Recent advances in light emitting diodes (LED) technology have made high-power LED of different wavelengths (including UV LEDs) available at low or acceptable cost as a promising alternative light source. As shown in Fig. 6c, the LED can deliver narrow-spectrum or close to single wavelength light from UV to visible light. Therefore, the need for optical filters and cooling devices are no longer necessary. Additionally, LEDs are also famous for their long operation life (tens to hundreds of thousands of hours). Due to their high wavelength flexibility, UV-LEDs could be mounted onto thin-layer PEC cells on the reactor and simulate UV lamp's parallel illumination instead of solar light ⁴⁸. Its stable and adjustable UV light intensity and monochromatic light make the LED a perfect light source for PEC sensors ¹⁹. Moreover, UV-LEDs hardly generate heat in photocatalytic processes which avoids unnecessary heat impacts on photocatalytic efficiency and system stability, saving costs of optical filters, cooling systems and electricity ⁴⁹. Though the use of UV-LEDs in PC and PEC

are mainly at the lab-scale stage, with the cost of UV-LEDs continuously dropping ⁵⁰, it is highly feasible that LEDs will be applied at an industrial scale. In fact, LED arrays ⁴⁸⁻⁴⁹ and LED panels ⁵¹⁻⁵² have already been used in small-scale to medium-scale PC and PEC applications. In summary, the inherent advantages and low costs of LEDs have resulted in more and more PEC devices incorporating modern LED technologies. Incorporation of LEDs into the development of new generation of PEC devices is a promising research direction

3.2.2 PEC reactors

Properties such as light harvesting, mass transfer and cell structure can be enhanced through cell design. Light absorption must be considered in the design of PEC cells as the efficiency of photocatalytic reactions is determined by light energy utilization ⁵³⁻⁵⁵. According to Beer's Law, light energy is consumed in aqueous electrolyte (Eqn.18).

$$A = \varepsilon bc \quad (18)$$

Where A is the absorbance; ε is the molar absorptivity; b is the path length of sample and c is the concentration of solution. Therefore, it is crucial to suppress the light energy loss *via* decreasing the path length of light irradiation in the electrolyte.

Mass transfer is another major parameter in practical application of PEC devices. In comparison with the PC system, especially slurry reactors, a lower mass transfer can be expected in PEC systems because the reactants must be transported to the surface of the photoelectrode ^{19, 51-52, 56}. Therefore, enhancing the surface-area-to-volume ratio is effect way to improve the mass transfer in the practical PEC system. Commonly, PEC cells have been designed into one and two compartment reactors for different applications.

a. One-compartment PEC cell

In one-compartment PEC cells, the photoelectrode and counter electrodes (and reference electrode in three-electrode systems) are placed in the same compartment. This design is simple and convenient and one-compartment PEC cells have been widely applied in the laboratory to measure the performance of photocatalysts. PEC degradation devices are commonly designed as single-compartment rather than double-compartment cells since they can facilitate the oxidation of organic compounds with a higher production rate of $\cdot\text{OH}$ ⁵⁷. To

minimise light path length and increase the absorption of light irradiation, the light source is inserted into the PEC cell as shown in Fig. 7 a. In this case, the PEC devices are designed into cylindrical shapes with annular parallel electrodes placed around the artificial lamp irradiation (tubular shape)⁵⁸⁻⁵⁹. The cylindrical PEC cell is a promising design as it has the potential to be scaled-up.

Fig. 7 Schematic design of the one-compartment reactors of (a) PEC cylindrical reactors; (b) the thin-layer PEC cell.

The thin-layer reactor is developed not only to sufficiently receive the collimated light (see Fig. 7b), but also to increase the mass transfer. In the thin-layer PEC cell, the electrolyte is confined into a thin film on the surface of the photoelectrode resulting in enlarged ratios of TiO_2 electrode area and organic solution volume. The design could effectively decrease the energy loss in the pathway from lamp to electrode and enhance the mass transfer⁵³. With these advantages, the thin-layer PEC system is widely adopted in PEC pollution degradation and PEC sensors. It should be noted that the oxidation reaction chamber and reduction reaction chamber can be relatively separated—commonly bridged by a narrow and thin channel to avoid cross-interference and obtain stable analytical signals in PEC sensing. It can also be considered as a desired “two-compartment PEC device” although there is no porous separator between the two compartments.

b. Two-compartment PEC cell

PC technology has been intensively investigated for fuel generation, as the PC cell (a common single-compartment reactor) is considered, at first glance, a low-

cost and convenient system for fuel generation . However, a series of post-separation processes, including the separation of photocatalyst as well as the mixed products, has to be introduced for practical application. This increases the operating cost remarkably. In PEC devices, photo-oxidation and reduction reactions can be separately controlled in two individual electrodes in a PEC cell, avoiding the mixing of oxidation and reduction products. This is an inherent advantage of a PEC system over a corresponding single compartment PC system where the reduction and oxidation reactions occur on the same TiO_2 nanoparticles. To separate the oxidation and reduction reactions, a porous separator (i.e. porous glass and membrane) divides the reaction system into two compartments and separates the oxidation products from the reduction reaction product. The balance of charge and reactants are also achieved through this separator. For instance, hydrogen and oxygen can be generated simultaneously at the photocathode and photoanode, respectively, for PEC water splitting which also avoids the safety issue of H_2 - O_2 explosion in industrial processes (see Fig. 8a) ⁶⁰⁻⁶¹. For most PEC systems to convert CO_2 to fuels, the electrodes are mostly separated by a proton conducting membrane, e.g. Nafion (see Fig. 8b).⁶² Although the two compartment PEC cell can be adapted in fuel generation devices, the membrane-less PEC cell can reduce overall system cost and avoid the high concentration overvoltage across the photoelectrodes.⁶³ This stepped-up development requires optimization of the whole cell configurations, including simple and safe collection of products (O_2 , H_2 and hydrocarbons), continuous operation, easily scalable, stable temperature, minimizing bias potential and maximizing light illumination .

Fig. 8 Schematic two-compartment PEC reactors for (a) water splitting; (b) the CO_2 reduction.

3.3 Photoelectrode manipulation

The manipulation on photoelectrode is aim to enhance light absorption, suppress the recombination of photogenerated charge carriers, facilitate the chemical reaction and subsequently improve PEC efficiency.

3.3.1 Nanostructured TiO₂ photoelectrode

TiO₂-based catalysts are often designed and made with various nanostructures. The nanostructured TiO₂ photoelectrodes shorten diffusion length and maximise light harvest within the nanostructure and therefore improve the PEC efficiency⁶⁴. Also, by exposing high energy facets, the photocatalyst can facilitate the PEC reaction to further improve energy conversion efficiency. Many factors including size, shape, morphology, and porosity can greatly affect the PEC performance of TiO₂ electrodes. To optimise PEC performance, various morphologies of nanostructured TiO₂ electrodes from zero to one, two and three-dimensional have been developed (see Fig. 9).

Fig. 9 Schematic and corresponding SEM images of different nanoscale structures of TiO₂ photoelectrodes: (a) 0D nanocrystals, (b) 1D nanostructures, (c) 2D nanosheets/films, and (d) 3D nanostructures^{17, 65-67}.

As shown in Fig. 9, a nanoparticle film as the photoelectrode provides a large surface area and effective optical path length to promote light absorption and shorten the charge diffusion pathway. However, the assembled nanoparticles are also isolated from each other, which limits the effective transfer of photogenerated charges through inter-particles to the conductive substrate as

current collector. This process increases the probability of charge carrier recombination at the inter-particle boundary. The 1-dimensional nanostructures, i.e. nanorods and nanotube arrays, can provide a “high-speed” pathway along the longitudinal direction for single-crystalline nanostructures and shorten the charge diffusion length (see Fig. 9b). The 2-dimensional nanostructure film can expose highly reactive facets and also shorten the charge diffusion length (see Fig. 9c). The 3-dimensional ordered nanostructures possess unique properties, such as light guiding, trapping and scattering, to enhance PEC efficiency.⁶⁶

The 1D TiO₂ nanostructured photoelectrodes (e.g. nanorod arrays³⁶⁻³⁸, branched nanorods^{39, 68-69} and nanotube arrays⁷⁰⁻⁷³) have been intensively developed and employed due to the high PEC efficiency and facile fabrication. The nanorod/nanowire structures are commonly synthesised by hydrothermal^{19, 38}, template growth⁷⁴, electrospinning⁷⁵ and chemical/physical vapor deposition⁷⁶, while the synthesis of TiO₂ nanotube photoelectrodes are demonstrated by templating⁷⁰, hydrothermal⁷⁷, and anodic self-organization approaches⁷⁸ methods. Cho et al.⁶⁸ compared the PEC performance of nanoparticles, nanorods and branched nanorods of TiO₂ electrodes (see Fig. 10 d and g). The high recombination of photogenerated charges within the nanoparticle film is responsible to the low PEC efficiency. The branched TiO₂ nanorods with enhanced surface-to-volume ratios could enhance light absorbance. It is established that the ideal nanostructure of photoelectrode requires to well construct the charge pathway from catalyst to current collector and maximize the capability of light absorption. For instance, the TiO₂ nanorod@nanobowl arrays reported by Wang et al. combined the features of nanorods and 3D ordered nanostructures (see Fig. 9h and i). This TiO₂ nanorod@nanobowl array photoelectrode, consisting of rutile TiO₂ nanorods grown on the internal surface of patterned anatase TiO₂ nanobowls, was fabricated for PEC water splitting³⁹. The nanobowl nanostructure had a strong light scattering ability that enhanced light harvesting. The TiO₂ nanorods radially aligned on the internal surface of the TiO₂ nanobowls, increased the photoanode/electrolyte contact area offering fast transport pathways of holes.

Fig. 10 (a) Schematic and corresponding SEM images of (b, e) TiO₂ nanoparticles, (c, f) nanorods, (d, g) branched nanorods and (i) TiO₂ nanorod@nanobowl. (b, d) represent the cross-sectional view, (e, g, i) the top view, the insets in (c, d) show high-magnification SEM images of nanorods and branched-nanorods, (h) is an SEM image of TiO₂ nanobowls ^{39, 68}.

3.3.2 Faceted TiO₂

Faceted TiO₂ photoelectrode is to expose high energy facets (e.g. at anatase 0.90 J m⁻² for {001}, 0.53 J m⁻² for {100}; at rutile 1.05 J m⁻² for {101}, 1.38 for {001}). This energy-level difference drove the separation of photogenerated electron and hole to the {101} and {001}, respectively, and therefore enhance the efficiency of the PEC process. Meanwhile, surface atomic structures of photocatalysts can greatly affect the adsorption/desorption of reactants. For instance, the chemical reactivity of water splitting on anatase TiO₂ surfaces decreases in the order (001) > (103)_f > (100) > (110) > (103)_s > (101), which is obtained by theoretical calculation of water molecule adsorption and dissociative adsorption on TiO₂ surface ⁷⁹. In the other word, the proper faceted TiO₂ photoelectrode could improve the efficiency of PEC water splitting ⁸⁰. For the PEC degradation application, the adsorption of organic molecules also was strongly affected by different TiO₂ facets ⁸¹. Sun et al. reported that the adsorption capability of the rutile TiO₂ (111) surface towards aldehyde was greater than alcohol and carboxylic acid using in-situ PEC measurements ⁸². Using the same method to measure intrinsic degradation kinetics of oxalic acid

on oriented anatase TiO₂ films, the anatase TiO₂ with exposed {001} facets demonstrated a higher PEC degradation reactivity than that of {101} faceted anatase TiO₂ ⁸³.

To expose more oxidative (reductive) facets is an important parameter for maximizing PEC activities for the photoanode (photocathode). Many synthesis methods including hydrothermal or solvothermal routes, crystallization transformation, oxidation from Ti metal and epitaxial growth, have been used to synthesize TiO₂ particles with different facets exposed (see Fig. 11a) ⁸⁴⁻⁸⁷. Commonly, the high-energy facets of TiO₂ diminish quickly, during the crystal growth process under equilibrium conditions. For instance, the surface of anatase TiO₂ single crystal is dominated by energetically favourable {101} facets (see Fig. 11a) ⁸⁸⁻⁸⁹. Lai et al. ⁸⁴ experimentally and theoretically demonstrated a key role of Ti-F-Ti species in the synthesis of faceted TiO₂. As shown in Fig. 12b, {101} facets with low surface energy usually dominate the surface anatase TiO₂ crystals (see Fig. 11b1 and b2). Density function Theory (DFT) results also show that surface fluorine coverage leads to the decrease of surface energy of {001} and {100} facets (see Fig. 11b2). According to theoretical studies, the exposure of dominant facets of anatase TiO₂ is controllable by additive F⁻ ions.

Although many studies have synthesized various free-standing TiO₂ particles with different facets exposed, the fabrication of faceted TiO₂ photoelectrode is still difficult due to the random dopited orientation of the TiO₂ particles onto films. The Van et al. ⁹⁰ developed a way of fabricating {100} oriented thin films of anatase TiO₂ nanocrystal arrays on a transparent conductive substrate (fluorine-doped tin oxide, FTO) by a combination of manual assembly and secondary growth. The TiO₂ film with exposed {100} facets showed a photocurrent density of 0.3 mA cm⁻², compared to 0.075 mA cm⁻² for randomly oriented TiO₂ films. However, TiO₂ photoelectrode fabricated by nanoparticles results in a serious charge recombination as discussed before. It is important to further develop the synthetic method which can directly grow faceted TiO₂ photocatalyst on current collectors.

Fig. 11 (a) Morphological growth of anatase TiO_2 crystals. (b) DFT calculated surface energies (J m^{-2}) and structures for different stages of HF interaction with single crystal anatase TiO_2 {101} {001} {100} surfaces: (b1) clean surfaces; (b2) full HF-covered surfaces; (b3) complete fluorinated surfaces ⁸⁴.

3.3.3 Band gap Engineering

The electronic structure governs many properties of semiconductors, such as light absorption, charge mobility and thermodynamic potential for PEC reactions. Extensive availability of TiO_2 nanostructures, however, cannot alter the fact that TiO_2 can only utilize UV light due to the inherent band gap of TiO_2 . This band gap limits TiO_2 from harvesting photons of visible light. Specifically, the electronic band structure determines that TiO_2 can only absorb <5% of total solar radiation, which in turn decreases the efficiency and increases the cost of practical PEC devices including solar water treatment and solar fuel generation. The design of the electronic structure, commonly entitled band gap engineering, of TiO_2 is therefore proposed to extend the harvesting of visible and infrared wavelengths of solar light.

a. Doping

Doping is the most common way to modify the electronic structure of TiO_2 by the introduction of foreign atoms. The improvement in visible-light absorption

enhances the ability of TiO₂ to capture more solar energy, and therefore extends the PEC application to a wider wavelength region ⁹¹. Doping can increase the visible light absorption of TiO₂ in two ways. (1) introducing additional local states in the band gap to allow the absorption of low energy light (see Fig. 12a and b); (2) narrowing the band gap achieved by lowering the E_{CB} band edge and/or elevating the E_{VB} band edge (see Fig. 12c) ⁹².

As the E_{CB} minimum of TiO₂ mainly consists of Ti *d* states, the metal ion can be considered as doping elements for Ti to lower the energy levels of *d* states to narrow the band gap. It shows great potential for decreasing the band gap of TiO₂, and therefore widens the light absorption range, making it more efficient in the degradation of pollutants, water splitting, sensors and many other PEC applications under solar light. Transition ions, rare metal ions, noble or poor metals (such as Zn ⁹³, Cu ⁹⁴, W ⁹⁵, Fe ⁹⁶, Co ⁹⁶, Ni ⁹⁷, Sn ⁹⁸, La ⁹⁹, Mn ⁹⁶, B ¹⁰⁰, Zr ¹⁰¹, etc.) have been used to dope the TiO₂ lattice due to its unique *d* electronic configuration ¹⁰².

Fig. 12 Schematic electronic band structure modification of doped TiO₂: (a) band gap of pristine TiO₂, (b) introducing local states in the band gap of a doped TiO₂, (c) band gap narrowing of a doped TiO₂, and (d) representative absorption spectra of the pristine and doped TiO₂.

Over the last 10 years, non-metals (such as nitrogen, carbon, boron, fluorine, sulphur, phosphorus) have been used to dope TiO₂ for visible light activities ⁹². Non-metal doping can produce band gap narrowing for the redshift of light absorption edge by modifying the E_{VB} of TiO₂. Asahi et al. ⁹² indicated that substitutional N doping was the most effective in band gap narrowing. The N-

doped TiO₂ photoelectrode performed water splitting with a maximum photoconversion efficiency of 8.35% at 0.3 V bias potential illuminated by xenon lamp illumination at an intensity of 40 mW cm⁻² ¹⁰³. Many other reports came to similar conclusions that their N-doped TiO₂ absorbed both UV and visible light and showed improved PEC performance ¹⁰⁴⁻¹⁰⁶.

Many intrinsic point defects (i.e. oxygen vacancies, Ti vacancies, Ti³⁺ and Ti⁴⁺ interstitials) can be used to modify the electronic structure of TiO₂ for a wide visible light absorption range ¹⁰⁷. The “black TiO₂” (or hydrogenated, reduced TiO₂) was synthesized at 20 bar hydrogen atmosphere by Chen et al. (see Fig. 13a) ¹⁰⁸. The surface disordered layer model was proposed to explain the visible and near-infrared light absorption in the hydrogenated TiO₂. At the electronic level, the disordering induced the up-shift of the valence band edge (see Fig. 13b, c and d) ¹⁰⁸. The “black TiO₂” can fully harvest solar light to enhance the photocatalytic efficiency for water splitting.

Fig. 13 (a) A unmodified white and disorder-engineered black TiO₂ nanocrystals, (b) Schematic illustration of the density of states of disorder-engineered black TiO₂ nanocrystals, as compared to unmodified TiO₂ nanocrystals, (c, d) High-resolution TEM images of TiO₂ nanocrystals before and after hydrogenation, respectively, (e) IPCE spectra of pristine rutile TiO₂ and hydrogenated TiO₂ prepared at 350, 400, and 450 °C, collected at the incident wavelength range from 300 to 650 nm at a potential of -0.6 V vs Ag/AgCl; Inset: digital pictures of pristine rutile TiO₂ and hydrogenated TiO₂ prepared at 350, 400, 450, 500 and 550 °C ¹⁰⁸⁻¹⁰⁹.

Many studies have been devoted to hydrogenated TiO_2 due to its high PEC activity under both UV and visible light regions ¹¹⁰⁻¹¹¹. Several methods, such as hydrogen plasma ¹¹², chemical reduction (Al ¹¹³, Zn ¹¹⁴, imidazole ¹¹⁵, and NaBH_4 ¹¹⁶), electrochemical reduction ¹¹⁷ and anodization-annealing ¹¹⁰ have been developed to produce the “black (or reduced) TiO_2 ” for various PEC applications. Wang et al. ⁹³ used the hydrogenated rutile TiO_2 for PEC water splitting. The colour of the electrodes turned from white (pristine sample) to yellowish green (at 350 °C) and finally to black (450 °C or above) by annealing in ambient hydrogen atmosphere for 30 min (see Fig. 16e inset). Surprisingly, there was no shift of the valence band edge of the hydrogenated TiO_2 photoelectrodes. However, the treated photoelectrode exhibited an obvious improvement in PEC activities in the UV light region (~95 % at 370 nm), and a slight photoresponse in the visible light region (~1% at 420 nm and 0.7 % at 650 nm) based on the incident-photon-to-current-conversion efficiency (IPCE) data (see Fig. 16e). The enhancement of PEC activities is mainly due to the increase of donor density stemming from oxygen vacancies ¹⁰⁹. Naldoni et al. ¹¹⁸ indicated that the hydrogenation condition and crystallinity of TiO_2 were important parameters affecting the electronic band edges of hydrogenated or reduced TiO_2 samples. Hydrogenation has been considered a promising method to improve the PEC activities of TiO_2 photoelectrodes in both UV and visible light regions. Overall, more effort is needed to tailor the properties of TiO_2 based photocatalysts for high-efficiency PEC applications.

b. Heterostructured TiO_2 photoelectrode

Another strategy is to couple TiO_2 with a semiconductor having a smaller band gap to form a heterostructure ¹¹⁹. Enhancement of the PEC activities of the semiconductor heterostructure system is ascribed to two factors: (i) the heterojunction can promote the separation of photoexcited electron-hole pairs through various carrier-transfer pathways by keeping reduction and oxidation reactions at two different reaction sites; (ii) the coupled semiconductors can extend the light-response range. Based on the charge carrier-transfer mechanisms, different heterostructures can be classified into four different types,

the traditional charge-carrier transfer, dye-sensitized transfer, plasmonic metal coupling and Z-scheme (Fig. 14).

Fig. 14 Schematic illustration of heterostructures of (a) traditional charge-carrier transfer, (b) Z-scheme, (c) dye-sensitized transfer, and (d) plasmonic metal coupling for TiO₂-based photoelectrodes.

In traditional charge-carrier transfer mechanisms, photo-induced electrons (or holes) can be smoothly transferred from one semiconductor with a higher E_{CB} minimum (lower E_{VB} maximum) to another with a lower E_{CB} minimum (higher E_{VB} maximum) (Fig. 14a). It is commonly applied to reduce the recombination probability of electrons and holes by keeping reduction and oxidation processes in different regions. The successful demonstration is that the mixed-phase photoelectrodes of anatase/rutile TiO₂ have better PEC performance than physically mixed anatase and rutile particles⁵ due to the difference of E_{CB} between the anatase and rutile (by ~ 0.2 eV)¹²⁰. This conclusion is supported by several other studies in the literature¹²¹⁻¹²². The traditional heterostructure photoelectrodes is also established to absorb more light wavelength range by coupling an narrow band-gap semiconductors (such as CdS¹²³, PbS¹²⁴, Bi₂S₃¹²⁵, C₃N₄¹²⁶⁻¹²⁷, and CdSe¹²⁸). For instance, the introduction of CdS into TiO₂ enables visible light absorption and decreases the recombination probability of charge carriers¹²⁹.

An obvious disadvantage of conventional heterostructured photocatalysts is that the redox ability of photogenerated charges is weakened as the charges are transferred into less positive valence bands and less negative conductive bands¹³⁰. Therefore, an artificial Z-scheme photocatalytic system has been developed by combining two semiconductors with electron mediators inspired by natural photosynthesis in green plants. As shown in Fig. 17b, the photoelectrons are able to transfer to the valence band of the secondary semiconductor through the electron mediator by Z-scheme heterostructures¹³¹. The Au nanoparticles are

usually using as the electron mediator, then the CdS-Au-TiO₂ photocatalyst for exhibited high activity, far exceeding those of the single- and two-component systems ¹³². This is a result of vectorial electron transfer driven by the two-step excitation of TiO₂ and CdS. Kudo et al. ¹³³ demonstrated that metal sulfide photocatalysts (with a p-type semiconductor character) as a H₂-evolving photocatalyst can be combined with RGO-TiO₂ composite as an O₂-evolving photocatalyst, thus achieving Z-schematic overall water splitting in stoichiometric amounts. Although the separation of photoelectrons and holes has been improved by Z-scheme heterostructures, the large band gap of TiO₂ is still not reduced which limits the enhancement of photocatalytic efficiency.

The dye sensitizer and plasmonic metals coupling can also be used to extend the light absorption of TiO₂ to the visible light region (see Fig. 14c and d) ¹³⁴⁻¹³⁵. Most dyes have sufficiently negative excited state redox potentials to oxidize water for oxygen production, and therefore dye-sensitized TiO₂ can be used as photoanodes for PEC water splitting. The plasmonic metal (e.g. Au, Ag, and Pd) can absorb the proper visible light due to the Surface Plasmon Resonance (SPR) effect. SPR is defined as the resonance energy produced when the frequency of photons of the incident light matches the frequency of the coherent oscillation of conduction electrons confined at the surface volume of the metal nanoparticles ¹³⁶. Moskovits et al. ¹³⁷ explained this charge transfer mechanism, in which the surface plasmon decay produces electron-hole pairs in the deposited metal (gold). The resulting hot electrons are then directly injected into TiO₂ by quantum tunneling. Several studies used this mechanism to design PEC devices ¹³⁸. For instance, Zhang et al. ¹³⁹ designed a photoelectrode by rationally selecting 20 nm Au nanocrystals and assembling them with the TiO₂-based photonic crystal substrate. This was used for water splitting under visible light (> 420 nm), and produced a photocurrent density of ~150 $\mu\text{A cm}^{-2}$ ¹³⁹. By coupling with nano-sized plasmonic gold particles, tunable sensing capability is designed and achieved by modifying TiO₂ nanorod arrays and subsequent hydrogenation treatment (i.e. Au@H-TiO₂) ¹⁴⁰. Under visible light, the Au@H-TiO₂ electrode exhibits selective detection capability to labile organic compounds due to the SPR effect. Furthermore, the modified electrode can also indiscriminately detect all kinds of organic compounds in a rapid manner under UV irradiation due to the strong oxidation capability. This unique tunable oxidation capability bestows

Au@H-TiO₂ photoelectrodes as a new generation of PEC sensors for selective and collective detection of organic compounds ¹⁴⁰.

4. PEC Devices

4.1. PEC Degradation of Organics

Organic pollution is a major global issue leading to disease and death of living creatures ¹⁴¹. Over the past several decades, the use and production of chemical compounds and pharmaceutical products has resulted in the discharge of large amounts of toxic pollutants into waters and the environment.

Traditionally, common advanced oxidation processes (AOPs) are widely used in degradation of a variety of refractory organic compounds, such as ozonation, photolysis and electrocatalysis¹⁴². Ozonation process is an effective method in degradation of organic compounds due to its strong oxidative ability of ozone. The efficiency of ozonation process is usually not high due to the complexity of refractory organics, and therefore high ozone dosage is needed for satisfactory degradation efficiency.

Photolysis process is an environmental favourable way in degradation of organic pollutants by using photon's energy to break down chemical bonds. It is widely used in pollutants degradation and water disinfection. Because the efficiency of photolysis process is low when long wavelength light (including visible light and infrared) is applied. Often, in order to achieve highly efficient degradation, short wavelength irradiation (UV) and photocatalyst are adopted for large scale application.

For electrocatalysis there are two different pathways in degradation of pollutants: direct anodic oxidation and indirect oxidation¹⁴³. In the direct anodic oxidation process, the organic pollutants are oxidized by oxidative species (such as hydroxyl radicals) generated electrochemically at the electrode surface. In contrast, in the indirect oxidation, major pollutants degradation are oxidized and degraded strong oxidative mediator (such as chlorine or hypochlorite) generated from anodic oxidation. Electrocatalysis process can degrade majority of organic compounds, especially in colour removal.

PEC technologies are developing as one of the most promising water pollution degradation method given their potential for low electrical carrier

recombination rates and high efficiency under light irradiation. Despite their potential, few pilot-scale reactors have been reported and the development of PEC degradation reactor design is still at the lab-scale stage. The main obstacles in scaling up PEC reactors are the high cost and low efficiency in utilizing solar light.

4.1.1 Lab-scale PEC degradation devices

Lab-scale PEC degradation devices are most commonly used for research purposes and are normally applied to evaluate and characterize the performance of photoelectrodes using certain irradiation illuminances and concentrations of organic compounds. In the common three-electrode PEC reactor, an additional reference electrode is applied to maintain a constant potential that ensures the stability of current in the system and is beneficial for characterizing the behaviour of the working electrode. Due to its simple configuration, a lab-scaled degradation reactor is superior in its flexibility of changing induced light with different wavelengths. Consequently, the impact of illumination light source, ranging from UV lamp ¹⁴⁴⁻¹⁴⁶ to solar light ¹⁴⁷⁻¹⁴⁸, on degradation efficiency can be easily studied. In addition, a three-electrode reactor could also define the photoelectrode area by applying different shaped quartz windows, which would avoid interference with water degradation caused by varying the irradiated photocatalysts area. Table 1 shows the efficiency of organic pollutant degradation with PEC systems using different modified TiO₂ electrodes, performed in lab-scale PEC degradation reactors.

Despite the advantages of lab-scaled characterization and evaluation of photoelectrodes, the three-electrode reactor has low degradation efficiency and complicated working electrode preparation processes in practical water purification applications. For practical water pollution degradation usage, various batch PEC reactors have been studied.

To further improve the degradation efficiency approaching practical utilization, various modifications of normal lab-scale reactors have been studied, including ways to improve light harvesting efficiency, decreasing light absorption in aqueous solution and promoting the mass transfer rate on the surface of electrodes.

As most large light sources (Hg lamp and Xe lamp) are commonly made in a tubular shape, cylindrical reactors have been developed for maximum light utilization. In this design, the light tube is inserted into a PEC reactor and annular parallel electrodes are placed around the central light source (Fig. 15a). Inspired by the flat-plate electrode design in normal batch reactors, Horikoshi et al.¹⁴⁹ developed a reactor with six TiO₂/OTE plate-electrodes surrounding a UV lamp. The six TiO₂ photoelectrodes were linked together in order to harvest light from every direction and make full use of the illumination light (Fig 15b). After 1 h illumination, the benzene was degraded by approx. 35%. Similarly, Palmisano et al.⁵⁹ used six TiO₂/graphite rods as electrodes in a cylindrical PEC reactor. The degradation rate of 4- nitrophenol reached 70 % after 6.5 h.

Table 1 Modified TiO₂ electrodes for pollution degradation using PEC systems.

Photoelectrode	Illumination properties	Compounds degraded	Time for degradation of 50% pollutants (/min)	Ref.
Y-TiO ₂ film	30 W UV lamp	MO and Cr(VI) ions	130	144
Pd/C-N-S-TiO ₂	Visible light 350 W xenon lamp	Acetylsalicylic acid	80	150
Ag/TiO ₂	High-pressure mercury UV lamp 400 W	Rhodamine B	20	145
Au/TiO ₂ NTAs	Visible light 350 W xenon lamp	Methyl orange	230	151
Ag ₃ PO ₄ /TiO ₂ NWAs	Visible light 150 mW cm ⁻²	Methyl orange	16	152
Graphene/Cu ₂ O/TiO ₂ mesh	Solar light 150 W xenon lamp	Bisphenol A	25	147
Bi ₂ Ti ₂ O ₇ /TiO ₂ NWAs	Solar light 300 mW cm ⁻²	Rhodamine B	120	148
PbO ₂ /TiO ₂ NTAs	100W UV lamp	Methyl red	10	146
CdTe/TiO ₂ NTAs	Visible light 350 W xenon lamp	p-Nitrophenol	22	153
Cu ₂ O/TiO ₂ NRAs	Visible light 500 W tungsten halogen	Rhodamine B	12	154
BiOI/TiO ₂ NBAs	Visible light 150 mW cm ⁻²	Methyl orange	3.5	155
CQDs/ TiO ₂ NWAs	Solar light 1.5 mW cm ⁻²	Methyl blue	42	156
TiO ₂ nanopore arrays	4 W UV lamp	Tetracycline	0.8	157
Ti/TiO ₂ nanorods	UV lamp 6.9 mW cm ⁻²	Chlortetracycline (CTC)	74	11
Doubled-faced TiO ₂ nanotubes	UV lamp 5 mW cm ⁻²	Tetracycline hydrochloride	26	158
TiO ₂ /Ti	UV lamp	Landfill leachate	0.6	159

Fig. 15 Schematic of: (a) cylindrical PEC reactor [(1) lamp, (2) photoanode, (3) counter electrode and (4) outer glass tube], cross-sectional view of cylindrical PEC reactor with six plate-electrodes ⁵⁸; (b) cylindrical reactor with Teflon supporter ⁵⁹.

If the number of plate-electrodes grew and increased to infinity, the plate-electrodes will become a single cylindrical electrode, which minimizes the light scattering on the cracks of the surface showing the degradation efficiency of the reactor (Table 2). Zhao et al. ¹⁶⁰ designed a tubular photoelectrocatalytic reactor using an annular parallel TiO_2/Ti mesh anode for the destruction of Cu-EDTA complex and recovery of liberated Cu^{2+} ions in a continuous mode (Fig. 16). The cylindrical electrode design made adequate utilization of central illumination and achieved high Cu recovery efficiency and Cu-EDTA destruction (up to 85% and 80%, respectively).

Fig. 16 (a) The schematic view of the photoelectrocatalytic system; (b) full numerical scale and capacity of the photoelectrocatalytic reactor (1) outlet; (2) UV lamp; (3) TiO_2/Ti mesh anode; (4) inlet; (5) cathode; and (6) quartz tube ¹⁶⁰.

To enable practical application, Pablos et al.¹⁶¹ designed a vertical cylindrical reactor and applied it to degradation of methanol. The annular TiO_2/ITO and TiO_2/Ti electrodes were placed inside a cylindrical two-electrode photocatalytic reactor (Fig. 17). The total working volume of the annular reactor was 1 L, was 15 cm long, with a 3 cm inner-tube diameter and 5 cm external-tube diameter. From the PEC measurement, the normalized photocurrent densities of the up-sized cylindrical reactor and lab-scale conventional reactor were comparable. It indicated that the cylindrical PEC devices are much more adaptable to up-sizing in practice, especially for water purification.

Fig. 17 Schematic representation of a cylindrical photoelectrocatalytic reactor, which consists of an annular reactor 15 cm long, 3 cm inner-tube diameter and 5 cm external-tube diameter operating in a closed recirculating circuit driven by a centrifugal pump, with a stirred reservoir tank¹⁶¹.

Thin-layer PEC systems are widely adopted to maximize the efficiency of pollution degradation by (i) decreasing the energy loss in the pathway from lamp to electrode and (ii) enhancing the surface reaction by increasing the surface to volume ratio. Several attempts have been made using thin-layer cells for water purification (Table 3). Xu et al.⁵⁶ designed the slant-placed electrodes thin film PEC reactor for dye removal (Fig. 18a). The thickness of the solution film on the electrode is less than 1 mm so that the irradiation consumed by the absorption of

the solution is comparatively reduced. Moreover, the circulation of the solution could guarantee saturated dissolved oxygen and overcome the mass transfer barrier.

Table 2 Cylindrical PEC devices for pollution degradation

Design of Devices	Photoelectrod e	Illumination properties	Degradation compounds	Ref.
Electrode-packed bed PEC reactor	TiO ₂ /SiO ₂	500W high- pressure mercury lamp	Quinoline	162
Cylindrical PEC reactor with annular electrodes	TiO ₂ /Ti	UV light	Cu-EDTA	160
Cylindrical two- electrode PEC reactor	TiO ₂ /Ti TiO ₂ /ITO	UV lamp	Methanol	161
Cylindrical continuous flow reactor	TiO ₂ /Ti	UV lamp	Landfill leachate	159
Pyrex annular PEC reactor	Graphite- supported TiO ₂	Hg lamp	4-nitrophenol	59
Compound parabolic orparabolic trough reactor	TiO ₂	UV-light	2,4- Dichlorophen ol	163

Bai et al.¹⁵⁸ indicated that the efficiency of organic degradation by thin-layer PEC reactors was much higher than conventional batch PEC reactors especially in high concentration levels of the organic compounds. The removal rate of tetracycline in different pollution concentrations could reach 54.8-96.4% for the thin layer cell in 1 hour, while only 14.6-80.4% for the batch PEC cells. Gan et al.⁵¹⁻⁵² designed a thin-layer PEC system for PEC degradation of organic compounds using mesoporous TiO₂ film electrodes (Fig. 18b) and a UV-LEDs array as the illumination source. The UV-LED provides high intensity UV light (365 nm) without producing much heat as well as good stability and flexibility for different PEC device shapes, and long lifetimes as illumination sources. Microfluidic PEC reactors for water purification have been recently developed and reported by Wang et al.¹⁶⁴ (Fig. 18c). The reactor had a planar reaction

chamber ($10 \times 10 \times 0.1 \text{ mm}^3$) and the degradation rate of methylene blue reached $5.2 \% \text{ s}^{-1}$. The device was tested more than 200 times and showed little degradation in performance. With the small volumes of fluids used, this microfluidic PEC reactor exhibits numerous advantages, including large surface area to volume ratio, short diffusion length, uniform irradiation, self-refreshing effect and short reaction time for PEC water purification.

Table 3 The thin-layer PEC devices for pollution degradation

Design of Devices	Photoelectrode	Illumination properties	Compounds for degradation	Ref.
Parallel thin-layer reactor	TiO ₂	Black-light-blue lamps	MS-2 bacteriophage	165
Thin-layer PEC reactor with double-faced electrode	doubled-faced TiO ₂ NTAs	UV light	Tetracycline	158
Slant-placed electrode PEC reactor	TiO ₂ /Ti film	UV lamp	Rhodamine B	166
Dual slant-placed electrodes thin-film PEC reactor	TiO ₂ /Ti film	UV light	Carmin	56
Serial thin-layer PEC system	Mesoporous TiO ₂	UV-LED array	Succinic acid/glucose	51
Rotating disk PEC reactor:	TiO ₂ /Ti film	UV lamp	Rhodamine B	167
Vortex PEC reactor	TiO ₂ sol-gel films	Hg lamp	Phenol, catechol and quinol	168

Jia et al.^{167, 169} developed a rotating thin aqueous film PEC reactor with a rotating TiO₂/Ti disk electrode. The system could combine the thin-film photocatalysis on the upper half of the disk and conventional bulk-phase photocatalysis on the lower half of the disk (Fig. 18d and e). Hence, the loss of the irradiation light

absorbed by the aqueous solution becomes negligible and correspondingly, the photocatalytic activity would be enhanced. In the meantime, due to the significant enhancement of the mass transport at 90 rpm, continuously refreshing reactor interfaces are generated. The rotating disk PEC cells could remove total Rhodamine B and TOC by 57% and 41%, respectively, in 1 h which is much higher than conventional PEC cells.

Fig. 18 Schematic diagram of (a) dual electrodes slant-placed PC reactor. (1) TiO_2/Ti anode, (2) cathode, (3) UV lamp, (4) reaction chamber, (5) reservoir bracket, (6) pump, (7) wastewater flowing direct and (8) reservoir ⁵⁶; (b) PEC reactor incorporated with UV-LED array and a PeCOD detector ⁵²; (c) microfluidic thin-layer PEC system ¹⁷⁰; (d) side view of the $\text{Cu-TiO}_2/\text{Ti}$ dual rotating disks PC reactor. (1) speed controller, (2) motor, (3) axis, composed with two Cu tubes connected by a glass rod, (4) Cu disk, (5) TiO_2/Ti disk, (6) carbon brush, (7) reaction cell, (8) wastewater, (9) UV lamp, (10) aluminum foil; (e) the front view of the reaction cell and disk electrodes ⁵⁴⁻⁵⁵.

4.1.2 Large-scale PEC degradation devices

The ultimate goal of PEC processes is to utilize sustainable solar light for large-scale wastewater treatment to reduce the energy usage. Practical outdoor water purification by the PEC method based on TiO_2 photoelectrodes has been

attempted in the last decade ^{58-59, 149, 161}. In the case of outdoor field utilization, a solar light concentrator is an effective way to further improve the processing ability of the PEC devices. In 1999, Fernandez-Ibañez et al. ¹⁷¹ set up a pilot-scale reactor and performed outdoor field tests (Global solar light), with a compound parabolic concentrator (CPC) and a Helioman collector configuration (see Fig. 19). The TiO₂ was immobilized on a Ti substrate as the anode and Pt/SnO₂ was the counter electrode in the reactors. In the outdoor experimental results, the CPC design performed better than the Helioman model in terms of photocurrent harvesting and the degradation of 4-chlorophenol. The CPC collected 70% of photocurrent in a 0.095 m² electrode area while the Helioman model needed 0.22 m². Seventeen per cent 4 chlorophenol (4Cl-phenol) could be degraded in 6 h of solar light illumination.

Fig. 19 PEC reactors in operation: (a) Helioman model and (b) Compound Parabolic Concentrator (CPC) model ¹⁷¹.

4.2 PEC Fuel Generation

PEC solar fuel generation is a sustainable energy technology for converting and storing solar energy into chemical energy, which can be obtained by two main processes; PC and PEC. Considering the desired energy efficiency from these renewable energy sources, product yield obtained through photocatalysis is still very low compared to that of PEC devices ¹⁷². PEC fuel generation has been widely studied as a solution to the global energy shortage due to it being cost-effective, simple and convenient, with huge potential for further development

and practical applications. The practical application of PEC generation of fuel is dependent on STF efficiency. The STF is defined as solar-to-fuel conversion efficiency, which can be expressed as:

$$\text{STF (\%)} = \frac{\text{Output energy of fuel evolved}}{\text{Energy of incident solar light} + \text{Energy of eletrical power input}} = \frac{\text{Productivity}(\text{mol s}^{-1}) \times \Delta H_{\text{comb}}^0 (\text{J mol}^{-1})}{[P_{\text{solar}} + P_{\text{bias}}](\text{W m}^{-2}) \times \text{Area}(\text{m}^2)} \times 100 \quad (37)$$

In which P_{solar} is the energy of incident solar light, which can be the power generated by the solar light simulator that irradiates the PEC cell for lab research, P_{bias} is the electrical bias applied by the potentiostat in the absence of any sacrificial electron donors or acceptors. ΔH_{comb}^0 is the molar heat of combustion of the reactant. For instance, the solar-to-hydrogen (STH) efficiency is used to illustrate the performance of PEC water splitting efficiency. In terms of fuel generation, PEC devices are used for photocatalytic splitting of water into H_2 and O_2 , and the photocatalytic reduction of CO_2 into hydrocarbon fuels.

a. PEC water splitting.

Production of hydrogen in a PEC system involves a series of electron transfers from a semiconductor photoanode to a metal photocathode enabled by an external bias. The transferred electrons reduce protons to generate hydrogen at the cathode leaving behind holes at the photoanode which oxidize water molecules into oxygen and protons. These protons then migrate to the cathode and the process is continuous. This principle is the same in all PEC devices¹⁷³. In a PEC device, H_2 and O_2 are either co-generated or generated separately in different cathode and anode chambers. Practically, during the production of solar H_2 separation of products is paramount to avoid gas crossover and generation of explosive mixtures. Separators or ion-conducting membranes are used for product separation. To date, little has been done in this area of solar PEC hydrogen production, however, it is important for the design and development of efficient PEC devices.

b. PEC CO_2 reduction

Conversion of CO_2 to hydrocarbon fuel C1 - C3 products has been a well-known area of research for many years. CO_2 can be converted into useful hydrocarbon products such as methanol, formic acid, acetic acid, methyl formate and formaldehyde¹⁷⁴. CO_2 reduction/conversion involves two reactions regardless of

the system used: oxidation and reduction ¹⁷⁵⁻¹⁷⁶. In the PEC system approach the oxidation and reduction processes are separated into two half-cell reactions but this is not so for a photocatalytic system ⁶².

As discussed earlier, one of the most important components of a PEC device is the electrode, particularly the semiconductor photoanode, as this dictates the performance and efficiency of the system for optimal fuel generation. Although the TiO₂ is the first successful demonstration for PEC water splitting, its large band gap still finite the solar conversion efficiency. Unfortunately, most band-engineering strategies are able to narrow the band-gap of TiO₂ but could reduce its durability. Therefore, the ideal photocatalyst for solar fuel generation should have suitable band-gap energy and band to fulfil the solar absorption and drive the catalytic reactions ¹⁷⁷. For now, a series narrow band semiconductors have been explored and studied, including Fe₂O₃, CeO₂, BiVO₄, Bi₅O₇Br, Ta₃N₅, Cu₂O, GaAs CdS, CdTe, SnNb₂O₆, BaTaO₂N, TaON, LaTiO₂N, etc.¹⁷⁷⁻¹⁸³ The STF of TiO₂ photoelectrode is not enough for practical application, but there are successful designs based on TiO₂ PEC system as guides to further develop whole device and address many technical issues. In this section, the various studies and designs of PEC devices for water splitting and CO₂ reduction are discussed and compared to define challenges and current limits to research and development.

4.2.1 Lab scaled PEC fuel generation devices

PEC fuel generation is mainly investigated in lab-scale devices due to low PEC efficiency. To model the practical operation level, Lopes et al. ⁶⁰ developed a lab PEC cell for water splitting, which was suitable for continuous operation and permitted easy collection of the evolved gases (Fig. 20). The illuminated sample surface area could be up to 100 cm². The H₂ and O₂ evolution zones were separated (exclusivity of the O₂/H₂ mixture) by a membrane, which added extra resistance compared to the original cell (Fig. 20). In this design, a cheap and adaptable membrane (Teflon diaphragm) was used between the two photoelectrodes to separate H₂ and O₂ evolution zones with ca. 47% photocurrent density enhancement. These properties enabled detailed characterization of wired, non-monolithic PEC configurations under outdoor conditions.

Fig. 20 The design of a typical photoelectrochemical cell for research: (a) disassembled, (b) under operating conditions, and (c) details of the innovative feeding system. 1: transparent acrylic cap (gas collection chamber), 2: Teflon membrane, 3: transparent acrylic cap (electrode contacts), 4: photoelectrode, 5: diaphragm to separate electrodes, 6: Pt-counter electrode, 7: black acrylic for light blocking, 8: transparent window, 9: transparent PEC cell body, 10: removable metallic window, 11: electrolyte inlet, 12: electrolyte outlet ⁶⁰.

In addition to water splitting, several research groups are working on the use of TiO_2 and other photoactive materials to develop artificial leaves. The concept is to make solar fuel by photo-electrolysis of water photo-reforming at the photoanode, and the gas phase conversion of CO_2 to isopropanol at the cathode. A modular design of an artificial leaf was demonstrated by Perathoner et al. as shown in Figure 21a and b ¹⁸⁴. The PEC reactor, made of Plexiglas and equipped with a quartz window, has a two-electrode configuration with two compartments for separated evolution of H_2 (or CO_2) and O_2 . This PEC solar cell consists of three layers: a nanostructured TiO_2 thin film supported on Ti prepared by anodization, a Nafion® membrane for electrical insulation and proton transport, and an electrocatalyst (Fig. 21b). In the H_2 photoproduction configuration, the electrocatalyst is a carbon cloth (E-tek®) with a high platinum dispersion (20%). In CO_2 reduction, the electrocatalyst is the electrode prepared by the deposition of Fe/ or Pt/CNT on carbon cloth. A prototype flow cell has been developed by Audreu et al. as illustrated in Fig. 21c-e ⁶¹. As seen in Fig. 21c, the cell had three inputs (catholyte, anolyte and CO_2) and two outputs (anolyte and catholyte). The anolyte and catholyte were kept in two separated tanks and recirculated continuously to the cell by a dual peristaltic pump to accumulate liquid products. A mass flow controller was used to control CO_2 flow rate entering the system,

measured downstream by a volumetric digital flowmeter. The flow of CO₂ gas and electrolytes was kept at 10 mL min⁻¹ (gas-to-liquid ratio of 1), as shown in Fig. 21e. The experiments were carried out under potentiostatic conditions in two-electrode configuration, applying a voltage between photoanode and cathode. Higher Faradaic efficiencies of about 40% were obtained at applied potentials as low as 0.95 V, and after optimization the achieved STF efficiency was 0.24%. These PEC reactor designs are successful attempts in the direction of practical implementation of solar fuels, even if their applicability is still a long way off.

Fig. 21 (a) Image of the photo/electro-catalytic disc. (b) Scheme of the PEC device for CO₂ reduction to fuel and H₂ production¹⁸⁴. (c) Schematic PEC flow cell. (d) Assembling scheme of PEC flow and (e) photograph of the PEC cell setup⁶¹.

In the solar fuel generation *via* PEC devices process, the applied external bias could facilitate the charge separation and result in increased energy cost. Without the biased external potential, the self-driven PEC cells can reduce the energy and operating costs by discarding electric input. There are two models in self-driven PEC devices. One is applying n- and p-type semiconductors as photoanode and photocathode, respectively, into a tandem cell. In this case, the external electric bias can be completely removed by using two appropriate photoanodes and photocathodes with matched band gaps leading to a Z-scheme heterojunction. Another model is delivered with a tandem PEC system consisting of a photovoltaic/photoelectrode (PV/PEC) device. In such a device, the photoelectrodes or PV cells with different absorption ranges can effectively absorb solar irradiation¹⁸⁵. In many cases, the solar cell can be replaced by other

power sources, e.g. wind-driven generator¹⁸⁶ and thermoelectric, to fully utilize the sustainable energy.

Shintaro et al.¹⁸⁷ prepared a tandem PEC cell for water splitting with a p-type CaFe_2O_4 film as the photocathode and n-type TiO_2 as the photoanode (see Fig. 22a). Under light illumination, the amount of hydrogen and oxygen gases produced by the tandem PEC cell after two days of the reaction was about 70 μmol and 4 μmol without bias potential, respectively (see Fig. 22b). Combining the PEC cell with a perovskite solar cell could further improve the tandem cell STH efficiencies, as evidenced by Zhang et al.⁴⁰ as shown in Fig. 22c. In this design the perovskite solar cell supplied the bias potential between the $\text{TiO}_2/\text{BiVO}_4$ photoelectrode and Pt electrode through harvesting the transmitted photons above 500 nm; leading to improvement of STH efficiency ($\sim 1.24\%$ based on data in Fig. 22d). Recently, a wind-driven triboelectric nanogenerator was connected to a PEC cell to supply electricity¹⁸⁶. When this system is used for PEC water splitting, the hydrogen evolution at the TiO_2 nanowire photoelectrode is significantly increased under assistance from the wind-driven nanogenerator. Such systems could be remotely and autonomously operated, which further reinforces the versatility and usefulness of PEC water splitting devices.

Fig. 22 (a) Reaction and band model in photovoltaic cells using p-type and n-type semiconductor electrodes. (b) Hydrogen and oxygen gases generated from the photocell short-circuited by connecting the CaFe_2O_4 and TiO_2 electrodes as a function of illumination time in 0.1 M NaOH (aq) under illumination (500 W Xe lamp). (c) Schematic tandem cell for solar water splitting without external bias. (d) Amount of hydrogen gas measured by gas chromatography during the experiment^{40, 187}.

4.2.2 Scale-up solar fuel generation devices

There are numerous technical challenges and cost-related issues associated with large-scale PEC devices for fuel generation. From a practical application or probable scale-up to industrial usage perspective, technical challenges and cost-related issues are equally important when considering the construction of a new reactor design to further improve water splitting efficiency. Even though there remain low efficiency and stability issues for many PEC devices, researchers have attempted relatively large-scale applications of PEC water splitting. One of the principles of the design of a practical PEC system should facilitate effectively absorbing incident light with minimal photonic losses¹⁸⁸. Aroutiounian et al.⁴¹ proposed a photocell configuration containing two photoactive electrodes, i.e. photoanode and photocathode (Fig. 23). The two photoelectrodes were placed side-by-side in two separate chambers, connected by an ion-exchange membrane. With a concentrator in the form of a parabolic mirror with an area of 0.2 m², the PEC devices (with reduced and doped TiO_2 as photoelectrodes) produced 0.04 L/h hydrogen. Bicer et al.¹⁸⁹ reported a photovoltaic cell coupled PEC system using a Fresnel lens as a solar light concentrator (Fig. 23b). In this scheme, the light is split to illuminate PEC and PV cells using dielectric mirrors after Fresnel lenses. The concentration ratio of solar light using Fresnel lenses was increased more than 10x, resulting in the energy conversion efficiency of the PEC system increasing to 49.3%¹⁸⁹.

Fig. 23 (a) PEC setup with compound cylindrical concentrator: 1 - body of photoelectrochemical cell, 2 - quartz windows, 3 - semiconductor matrix, 4 – electrolyte, 5 - ion-exchanging membrane, 6 - cylindrical concentrator ⁴¹. (b) Scheme and set up of PEC system including the PEC reactor, photovoltaic cell and concentrated solar light ¹⁸⁹.

When industrialize the PEC water splitting system, the risk assessment of explosive product (2:1 H₂:O₂ mixtures) need to be considered on system design, especially for single compartment reactor. Therefore, all parts of system, including reactors, gas pipes, gas separator and pump should be specially designed to avoid the combustion. Fortunately, Domen et al. tested oxyhydrogen risk within the whole system with or without the ignition, after estimated the maximization production rate under the Sunday lunch time (15.5mL s⁻¹ per 1 m²). The results are very exciting that probability and hazard of combustion are negligible ¹⁹⁰. These founding are able to inspire “bold” design for PEC system.

4.3 PEC Sensing

With advantages such as low cost, simple instrumentation and high sensitivity, the PEC method has been considered for many analytical applications. The light irradiation allows potentially higher sensitivity (reduced background) and superior detection properties (lower detection limits) in the PEC method compared with conventional electrochemical analysis. PEC analysis has attracted enormous research effort and as a result, the popularity of new PEC analytical

methods has grown tremendously. To date, the PEC method has been developed into various analytical devices, including the commercialization of onsite and online chemical oxygen demand (COD) analysers (Aqua Diagnostics Pty Ltd, Australia), and functional transducers for DNA sensors and specific biomolecular sensors. The working principle that the PEC sensor is based on is monitoring the interaction between photogenerated species and target molecules *via* photoelectrodes. In the PEC process, the target chemical information (e.g. concentration of analyte) is converted into electric signals under illumination.

4.3.1 PEC COD sensor

The importance of water quality control and monitoring is widely acknowledged. The first PEC cell was proposed, designed and developed based on TiO₂ photoanodes for PEC determination of COD, namely PeCOD technology in 2004 [25, 28, 191].

This PEC cell can be used in two modes, stopping the flow for exhaustive oxidation mode and continuous flow for partial oxidation mode¹⁶. In PEC sensors, a constant photocurrent (i_{blank}) is observed for the blank solution (see Fig. 24), when the TiO₂ photoanode is under constant UV illumination. The i_{blank} results from the photoelectrocatalytic oxidation of water. When the sample containing organic compounds is injected and flows through the thin layer cell, a typical chromatographic peak is observed (see Fig. 24). The current (i_{sample}) consists of two parts, the PEC oxidation of water (i_{blank}), and the PEC oxidation of organic compounds (i_{net}). Because the concentration of water is constant, i_{blank} can be considered constant. i_{net} is therefore calculated by subtracting i_{blank} from i_{sample} (Eq. 20):

$$i_{\text{net}} = i_{\text{sample}} - i_{\text{blank}} \quad (38)$$

By integrating the photocurrents i_{blank} and i_{total} with time, the blank charge, Q_{blank} , and the total charge, Q_{total} , can be obtained, respectively (Eq. 21):

$$Q = \int i dt = nFVC \quad (39)$$

Where the i is the photocurrent generated from the PEC oxidation reaction, n , F , V , and C are the oxidation number, Faraday constant, reactor cell volume and molar concentration of the injected sample, respectively. Subsequently, the net

charge Q_{net} (the shaded area in Fig. 24), generated from the oxidation of organics, can be obtained by subtracting Q_{blank} from Q_{total} (Eq. 40):

$$Q_{\text{net}} = Q_{\text{total}} - Q_{\text{blank}} \quad (40)$$

Q is a direct measure of the total number of electrons transferred after the complete degradation of all compounds in the sample. Since one oxygen molecule is equivalent to four transferred electrons, the measured Q value can be easily converted into an equivalent O_2 concentration (or oxygen demand). The equivalent COD value can therefore be represented as (Eq. 41):

$$\text{COD} (\text{mg L}^{-1} \text{ O}_2) = \frac{Q}{4FV} \times 32,000 \quad (41)$$

For a given TiO_2 photoanode, the net charge value should increase linearly with organic concentration according to Eq. (41), which has been experimentally demonstrated in the literature ²⁵. The linear relationship of Q vs. concentration enables the TiO_2 photoanode at a thin-layer cell to be a sensor for organic compounds.

Fig. 24. Photocurrent responses of a blank solution (solid line) and a sample containing organic compounds (dashed line) in a photoelectrochemical thin-layer cell ²⁸.

The evaluation of water quality, using the COD index, involves determining the oxygen needed to oxidize certain types of organic matter in water. The COD of water must be closely monitored by different levels of government and many industries to safeguard water quality and environmental protection. The standard COD index can be obtained by using a strong oxidizing agent (such as Ag_2SO_4 ,

H₂SO₄ and Hg(II)) to fully oxidize all organic compounds under acidic conditions ²⁰.

As a chemical sensor, the TiO₂ electrode can detect organic compounds indiscriminately. This enables the PEC electrode to detect aggregative organic compounds in water bodies, i.e. the COD value. The principle of the PEC COD sensor is that all organic matter (including organic compounds, microbial pollutants, and whole cells of microorganisms) can be fully mineralized due to the strong photocatalytic oxidation capability of TiO₂ under illumination. The PEC COD sensor based on TiO₂ photoelectrodes is superior to other methods because it is rapid, non-toxic, low cost and environmentally friendly.

Based on the analytical principles of PEC COD, the PeCOD is a direct and absolute method that requires no calibration. Using TiO₂ photoelectrodes, an analytical linear range of 0-360 ppm COD with a practical detection limit of 0.2 ppm COD was achieved ¹⁹². These results demonstrated that the COD values measured using the PeCOD sensor and standard methods were significantly correlated. Using the exhaustive oxidation model, the PEC sensor reactor is designed as a prototype bulk cell in which a three-electrode system is well immersed in electrolyte solution. An external light source passes through the aqueous solution and ultimately reaches the photocatalysts to stimulate a series of photocatalytic reactions. The flexibility of the configuration makes it possible for a bulk cell to easily change different characteristics, such as potential bias, substrate concentration, light intensity, pH and irradiated photocatalyst area, to determine the optimized parameters for COD sensing ¹⁹³. The bulk cell is promising in this field despite several drawbacks, such as the massive light loss during passing through the solution and low mass transfer rate, which cause comparatively low oxidation efficiency and directly impact the accuracy of this method.

Zhang et al. ⁵³ shortened the distance between the light source and photocatalysts to 5 mm using a Ø14 mm quartz lens-fitted tube. A stirrer was used to improve mass transfer. This modified bulk cell successfully characterized TiO₂ thin films fabricated with different colloids in organic oxidation for COD sensing. Due to its rapidity, the thin-layer reactor has been used to achieve better performance for on-line COD monitoring. Zhang et al. ¹⁹ developed a thin-layer COD sensor with an aqueous solution thickness of 200 µm which was optimized from experimental

results (see Fig. 25). The configuration of the thin-layer cell successfully achieved a relatively large (electrode area)/(solution volume) ratio that ensured rapid sample oxidation. Reliable and reproducible hydrodynamic conditions were also achieved to improve the accuracy, reproducibility, and reliability of the COD monitoring process. The improvement in light utilization efficiency was attributed to the thin liquid layer because less UV radiation was absorbed in the aqueous media.

Fig. 25. Schematic (a) assembly view and (b) cross view of a thin-layer PEC cell for continuous flow analysis ¹⁹.

A PEC portable probe was developed using a nanostructured anatase-rutile mixed phase TiO₂ photoelectrode to rapidly detect COD levels in waterbodies (Fig. 26a) ²¹. A UV-LED light source and a USB microelectrochemical station (Fig. 26b) can be powered and controlled by a laptop computer. This makes the probe portable for onsite COD analyses. When the PEC degradation is conducted on a nanoparticulate TiO₂ photoanode in a bulk cell, typical photocurrent profiles can be collected. Fig. 31 displays a set of photocurrent-time profiles obtained in the presence and absence of organic compounds at the TiO₂ photoanode in the bulk cell under UV illumination.

Fig. 26 (a) Schematic diagram of the photoelectrochemical setup and PeCOD probe, (b) typical photocurrent response of a 0.1 M NaNO₃ blank solution (i_{blank} , dash line) and a 0.1 M NaNO₃ solution containing organic compounds (i_{total} , solid line); i_{net} is the difference between the two steady state currents. The inset shows the dimensions of the UV-LED (left) and the ECS microelectrochemical system (right) ²¹.

A very small applied potential (+0.2 or +0.3 V) is sufficient to draw all the electrons into the external circuit. The current was around zero when the UV light was switched off. Under illumination, the current increased rapidly and then decreased to a steady value. Similar to the thin-layer PEC cell, the net steady state photocurrent i_{net} (generated from the oxidation of organics) can be obtained by subtracting the blank photocurrent i_{blank} from the total photocurrent i_{total} (see Eq. 20). i_{net} is directly proportional to COD concentration (Eq. 42).

$$i_{\text{net}} \propto [\text{COD}] \quad (42)$$

The photoelectrochemical measurement of COD was optimized in terms of light intensity, applied bias, and pH. Under optimized conditions, the net steady state photocurrents originating from the oxidation of organic compounds were directly proportional to COD concentrations. A practical detection limit of 0.2 mg L⁻¹ of O₂ and a linear range of 0-120 mg L⁻¹ of O₂ were achieved. The analytical method, using the portable PeCOD probe, was successfully used to determine the COD values of synthetic samples and real samples from various industries. Strong correlations were found between the proposed method and the standard dichromate method.

4.3.2 PEC biosensor

Biosensors are designed to convert a biological response into a readable or quantitative electric signal *via* a transducer to analyse analytical parameters in a variety of samples, such as glucose concentration and cholesterol in body fluids, food and cell cultures and phenolic compound environmental samples ¹⁹⁴⁻¹⁹⁵. To date, various methods have been reported as new technology for bioanalysis, including a large spectrum of optical, acoustic, gravimetric, electrical, and electrochemical techniques ¹⁹⁶. Compared with established biosensors, such as electrochemiluminescence, the PEC biosensor has various advantages including

simple instrumentation, low cost, easy to miniaturize and high sensitivity¹⁹⁷. PEC biosensors also have superior detection limits for identical analytes due to the superior oxidation power of TiO₂ under light illumination and “light-switching” reaction properties¹⁹⁸. In PEC biosensors, the photo-energy is employed by signal excitation and detection leading to a rapid response, wide concentration range, low applied potential, reduced background and potentially higher sensitivity²⁶.

For PEC biosensor, the photoelectrode is commonly modified by the biological recognition elements, such as enzymes, antibodies, nucleic acids and DNA, to endow their selectivity to targets. For instance, Tu et al.¹⁹⁹ used a porphyrin-functionalized TiO₂ photoelectrode as a glutathione (GSH) sensor prepared through the dentate binding of TiO₂ nanoparticles with sulfonic groups of [meso-tetrakis(4-sulfonatophenyl)porphyrin] iron(III) monochloride(FeTPPS) (Fig. 27a). The proposed PEC biosensor showed a rapid response, wide concentration range, low bias potential and good selectivity in monitoring GSH under UV light. The photocurrent density signal was inversely correlated with GSH concentration. Under optimal conditions, the response displayed a linear increase as the GSH concentration increased from 0.05 to 2.4 mmol L⁻¹ with a detection limit of 0.03 mmol L⁻¹. A similar design was demonstrated by Shi et al.²⁰⁰ with polypyrrole-based molecularly imprinted polymer modified TiO₂ nanotubes used as a PEC biosensor for selective detection of 2, 4-dichlorophenoxyacetic acid (2, 4-D) (Fig. 27b). Under UV illumination, the detection limit was 10 nM (2.2 ng/mL) (S/N = 3) in 0.1 M phosphate buffer solution (pH = 7).

Fig. 27 Schematic illustration of biosensing: (a) photoelectrochemical process for the oxidation of GSH at a FeTPPS-TiO₂-modified ITO electrode¹⁹⁹; (b) (A) fabrication and (B) detection mechanism of the photoelectrochemical sensor²⁰⁰.

However, pristine TiO_2 photoelectrodes can only work under UV illumination and cause severe damage to biorecognition components, which is a critical issue. This issue can be addressed by using visible light rather than UV light. TiO_2 photoelectrodes have been modified *via* various methods, such as doping²⁰¹ and heterostructure coupling²⁰² to achieve this. For instance, Han et al.²⁰¹ developed a N-doped TiO_2 PEC biosensor for the detection of Hg^{2+} under visible light illumination (Fig. 28a). The linear response was maintained in the region 2-6 μM concentration of Hg^{2+} with a 0.40 μM detection limit in 10 mM Tris- HNO_3 (pH = 7.4) electrolyte (Fig. 28b). In contrast, heterostructured TiO_2 (TiO_2 -Au) photoelectrodes as biosensors use a different mechanism in which the decorated components absorb light instead of the TiO_2 . PEC sensing measurement using an Au nanoparticle-decorated TiO_2 (TiO_2 -Au) photoelectrode was introduced by Da et al.²⁰³ for real-time detection of cholera toxin subunit-B (CTB) by employing the SPR effect of Au. Au nanoparticle surfaces are functionalized with a surface receptor (GM1), which can selectively capture the presence of CTB. The addition of different concentrations (final concentration increase of ~ 16.7 nM) of CTB into the PEC cell leads to an increase in photocurrent density of TiO_2 -Au NWs, which reaches equilibrium within 10-30 s. Compared to the non-Au-decorated TiO_2 nanowire electrode, TiO_2 -Au@GM1 NW sensors achieved much-improved sensitivity with a detection limit of 0.167 nM.

Fig. 28(a) Schematic illustration of the transformation of QT1 (left) and the mechanism of the electron transfer routes (right) before and after the binding of

Hg²⁺. (b) Photoelectrochemical responses of the DNA/N-doped TiO₂ electrode before and after incubating with concentrations of Hg²⁺ ranging from 1-7 μ M for 30 min. The arrow shows the increasing Hg²⁺ concentrations. (c) The calibration curve of the photocurrent responses for various concentrations of Hg²⁺ 201.

5. Conclusions

PEC devices have been widely developed into technologies for resolving global environmental and energy shortage issues. However, its poor performance hinders practical application despite considerable industrial interest. Although most developed PEC devices remain at the lab-scale stage, many strategies have been tried to drive PEC technology to industrial-scale levels. PEC cell design, electrochemical bias potential, interfacial manipulation and band gap engineering on TiO₂ photoelectrodes have efficiently enhanced PEC performance.

As the core of PEC devices, TiO₂-based photoelectrodes have been continuously improved to address barriers. Recent advances in TiO₂ modification for various applications can be achieved *via* two strategies. Firstly, interfacial manipulation could directly improve the charge separation of photogenerated electron-hole pairs and provide active sites to enhance photochemical reaction efficiency and reduce energy loss. Secondly, electronic structure modification *via* doping and heterostructure design could extend light absorption range and charge-carrier separation *via* interface carrier transfer. Most modification methods can effectively improve the performance of TiO₂ photocatalysts, however, the instability and cost of photoelectrodes are also increased. Further research on new materials for visible-light-active and high-efficiency photocatalysts as well as on novel PEC electrodes is expected to significantly advance the development of PEC technologies.

PEC technologies have been widely applied in PEC fuel generation, PEC sensors and PEC pollution degradation based on the superior performance of the TiO₂ photoelectrodes. Due to the different requirements of PEC reactors for different PEC applications, the design of PEC devices plays a crucial role in applications. However, both types of PEC systems encounter several obstacles that currently limit overall performance. The energy demand for PEC systems is immense due to the need for simultaneous irradiation and the large potentials applied. This

leads to efficiencies that are often orders of magnitude lower than purely electrochemical systems operating under similar temperatures and pressures. Therefore, to obtain practical PEC devices, the performance of TiO₂-based photoelectrodes and PEC reactors must be further improved.

Overall, the proposed strategies for improving mechanical, morphological and electronic properties of TiO₂ photoelectrodes and the designs of PEC devices can be used as a guide for practical application and commercialization of TiO₂ nanomaterials and its devices.

Conflicts of interest

There are no conflicts of interest to declare.

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