



Semiconductor photoelectroanalysis and photobioelectroanalysis: A perspective



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ABSTRACT

Electrochemical sensor signal output, when recorded as a current, is primarily related to the target analyte concentration, but often also related to additional experimental or control parameters. When employing photo-active semiconductor electrodes, light intensity offers an additional control parameter for sensors and opportunities for new reaction/detection or signal amplification pathways. Light stimulation can (i) excite charge carriers to directly interact with analyte, (ii) excite charge carriers to interact with the analyte via a receptor, (iii) provide excited state solution intermediates to generate secondary analyte molecules, (iv) consume the target analyte to give a negative photoelectrochemical signal, or (v) be used to modify or amplify the sensor response. Light activated sensors have been reported for multiplexed arrays. In this perspective, recent developments in photoelectrochemical sensing methods based on semiconductor materials are summarised and new directions and opportunities are highlighted.

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1. Introduction to photoelectroanalytical methods

Light can trigger many important photochemical processes in biology and in chemistry. Solar energy harvesting technologies and photoelectrochemical processes involve photo-induced chemical phenomena such as charge separation and charge transport/transfer. These and similar mechanisms can be exploited in analytical detection. Even classic electroanalytical techniques such as electroanalytical stripping voltammetry can be enhanced by photoelectroanalytical strategies [1]. For example, in the generation of anodic photocurrent at an n-type semiconductor, the photo-induced holes at the electrode surface oxidise an electron donor in the solution (e.g. the analytical target), while the conduction band electrons are collected by a conductor into the external circuit as a signal (current response). This process could occur with high sensitivity as long as the analyte – surface interaction is strong and selective. Engineering the materials at the interface between sensor and solution is a critical task. There are opportunities for increased sensitivity or for amplified sensor signals depending on the interfacial design and the choice of mechanism. An essentially unlimited

plethora of mechanisms exists by which photoexcitation can be employed in sensing. Some typical or general options for photoelectroanalytical mechanisms are summarised in Fig. 1.

In Fig. 1A, a semiconductor electrode is photo-excited and consumption of analyte A occurs during reaction with holes. The remaining mobile electrons provide the sensor response. A receptor or modified surface (see Fig. 1B) can improve selectivity. Instead of the direct photocurrent photo-conductivity/resistivity can be monitored (Fig. 1C) as an amplified signal. In Fig. 1D, an external semiconductor particle (for example immobilized in a sensor film but not in direct electrical contact to the electrode surface) is excited and reacts with the analyte to give a reaction intermediate, which is then detected at the substrate electrode. In conjunction with a receptor the analyte could lead to substrate S being converted to P the detected species. This could also constitute an amplified detection mechanism. In fact, there are numerous further variations of mechanisms possible and there are additional reactions pathways benefiting from biological receptor systems in combination with photoactive semiconductor components. Based on such a photoelectroanalytical principle, strategies for application of photoelectrochemistry for analysis and bioanalysis have been developed aiming for ways to integrate signalisation with the selective recognition of a specific analyte. From the new field of photoelectroanalysis, the field of photobioelectroanalysis emerged by combining photoelectrochemical

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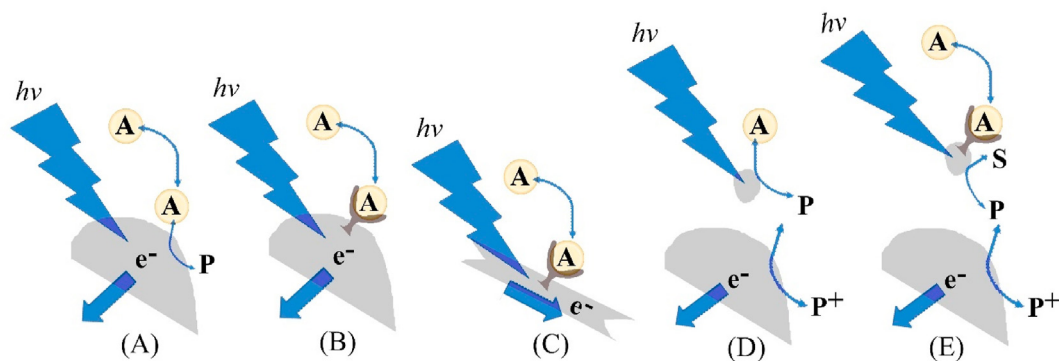


Fig. 1. Illustration of some photoelectroanalytical mechanisms based on (A) analyte A acting as a quencher to give photoanode signals after photoexcitation, (B) a receptor on the photoabsorber increasing selectivity, (C) photoexcitation monitored by conductivity or impedance, (D) an external photoabsorber producing an intermediate P that is detected, or (E) an external photoabsorber with receptor and photocatalytic conversion of a substrate.

processes with biological recognition/amplification elements. Photoelectrochemical enzymatic biosensors can integrate the intrinsic sensitivities from photoelectroanalysis with selectivity of enzymes [2,3]. So, photo-bioelectroanalysis is a rapidly emerging methodology. Also new opportunities arising from self-powered photoelectroanalytical sensors have recently been considered [4–6]. The light activation in bioelectroanalytical sensors can also be employed to multiplex. In this case parallel detection of several targets is achieved with a single device based on an array of sensors with light activation [7].

Important factors in the mechanism of photoelectroanalytical sensing, like charge carrier generation and separation at complex nano-bio interfaces, are not well predictable and can be developed and understood only with extensive experimentation. Some factors such as the effects of different electrode materials and architectures are relevant in charge transport/transfer and may strongly influence the analytical performance. Fujishima et al. [8] summarized some of the advances in photoelectroanalytical sensors in terms of the semiconductor materials employed, signal amplification approaches, and promising device architectures. Among the materials that can be useful for photoelectroanalysis are semiconductor oxides, in bulk state or as nanoparticles or quantum dots, but also carbon-based nanomaterials like fullerenes, carbon nanotubes and graphene, that show a better conductivity than semiconductor oxides and can be employed as an alternative to conventional photoactive materials [9,10]. Carbon nanomaterials also are beneficial for strategies with signal amplification, due to generally better electrical conductivity and enhanced surface area, leading in many cases to enhanced photocurrents and enhanced analytical sensitivity [11]. The photocurrent response can be physically amplified by materials with strong light scattering/absorption cross-section such as plasmonic nanoparticles [12], or by organic molecules that act as electron-relay units [13]. Also beneficial can be combining small and large band gap semiconductors at heterojunctions that lead to sensitised structures with stepwise band-edge levels enhancing charge separation, thereby achieving better utilisation of solar spectra and consequently enhancing the incident photon-to-current efficiency (IPCE) [14].

Sensors require a signal output indicative of the presence and the concentration of the analyte. For electrochemical sensors usually the applied potential is the trigger for the signal with current as the output signal. Often interference signals are encountered as the applied potential (and electrode material) may not be sufficiently discriminative, or selective electrocatalysts are required. For example, in a typical application, Chauke et al. reported composites of gold nanoparticles with tantalum phthalocyanines (TaPc) complexes for bisphenol A detection based on

electrocatalytic oxidation of this molecule was demonstrated to be very sensitive. The presence of TaPc enhanced the charge transfer of the gold nanoparticles, allowing the sensor to reach a detection limit for bisphenol A of $2.76 \times 10^{-10} \text{ mol L}^{-1}$ [15]. Similarly, electrocatalysts can be applied in addition to light excitation in photoelectroanalytical methods, but under illumination the substrate electrode bias potential can be much more mild to suppress unwanted interference signals.

Instead of applying a potential externally, a local potential at the electrode surface can be generated by applying light. This locally induced potential (in the form of a local excess electrons or holes) triggers chemical reactions. In this way, a “light-on” response can be converted to a current response with analytical information. The opposite case of a “light-off” analytical signal can be observed when competition of the photochemical and electrochemical detection process occurs. At constant applied bias voltage, the current responses as function of turning light on/off can be compared and the difference signal demonstrated to provide selectivity for analytes. The light induced sensor mechanisms can occur via short-lived redox systems or photo-excited intermediates such as singlet oxygen producing analytical signals [16,17].

This report offers an up-to-date assessment of recent developments (without being comprehensive) and a combined overview on the topics photoelectroanalysis and photo-bioelectroanalysis. There has been considerable progress and the potential for applications in modern printed devices appears realistic. The broad range of opportunities in analytical point-of-care diagnostics is linked to the wide range of potential mechanisms. Fig. 2 summarises some of the main photoelectroanalytical sensor strategies that will be discussed in the present perspective: (i) the excitation of a semiconductor electrode for the detection of an analyte directly by a signal generated from a photoredox reaction; (ii) amplification of the signal by the combination with materials that enhance light harvesting and/or enhance charge separation; (iii) sensitisation of the semiconductor with material that can be photoexcited with lower energy radiation (longer wavelength) than that required for the semiconductor bandgap; and (iv) a combination with biological catalysts/receptors can improve the selectivity for detection. Herein, we review the state-of-art in photoelectroanalytical sensors and biosensors focusing on mechanisms, materials, architectures, signal amplification strategies, and approaches used for improving the sensing efficiency.

2. Semiconductor-based photoelectroanalytical detection

Photoelectroanalysis in liquids was pioneered initially by Compton and coworkers for solution phase photo-sensitised

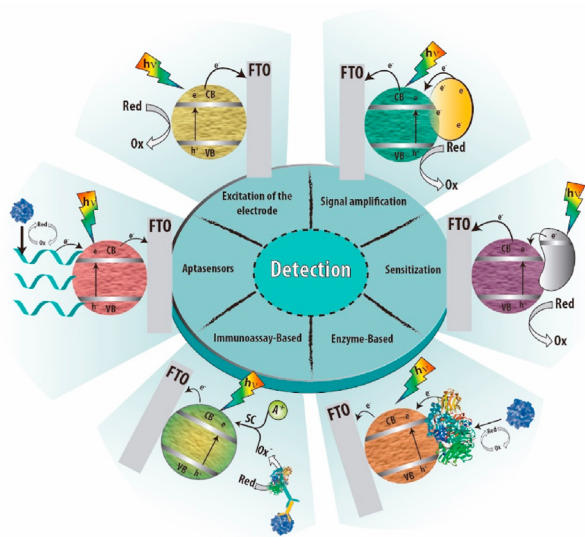


Fig. 2. Representation of the main photoelectroanalytical sensor approaches and mechanisms that will be covered in this review.

detection, for example of ascorbic acid [18]. Historically, the first solid state photoelectroanalytical system was suggested by Armstrong et al. [19] using a phthalocyanine thin film for detection of ammonia by detecting the photoconductivity response during illumination. Since then, many studies of novel sensor surface architectures and mechanisms have appeared, and the field of photoelectrochemical sensors has improved in terms of diversity of analytes, the selectivity, and the sensitivity. In contrast to these photoelectroanalytical processes, some new light-absorbing materials have been shown to also trigger purely thermal light-induced changes that lead to conductivity responses, for example in paper-based analytical device concepts [20]. Photoelectrochemical signals are obtained when the light-induced charge carriers react chemically.

Often n-type semiconductor materials are employed as photoanodes. Nanostructured WO_3 films synthesised using sol-gel method were applied as sensors to detect dopamine under visible light irradiation. Different solvents were employed in film production and high adhesion, good repeatability and reproducibility were obtained with poly-ethylene-glycol as solvents. WO_3 was applied as a photoelectrochemical sensor and when the electrode is illuminated and in the presence of dopamine the current density increased significantly. The dopamine oxidation process occurred at a more negative potential when WO_3 was illuminated, consistent with the photoelectrocatalytic properties. WO_3 electrodes were shown to be photosensitive to dopamine with a detection limit of $30 \mu\text{M}$ [21]. Dopamine detection via photoelectroanalysis was also reported on SnSe-modified gold surfaces [22]. SnSe nanosheet materials were employed and the visible light driven sensor gave a limit of detection of 3 nM. Plasmonic gold nanoparticles on tin-doped indium oxide were employed for the photoelectroanalytical detection of ciprofloxacin, a widely used antibiotic, with a limit of detection of 0.08 nM [23]. A photoanode architecture based on graphene laser-deposited onto tin-doped indium oxide was employed in conjunction with a nickel catalyst and CdS quantum dots for the photoelectroanalytical detection of glucose [24]. Titania nanomaterials were combined with silver nanoparticles [25] to give glucose photoelectrochemical sensors. But also pure TiO_2 nanotube structures have been employed for photoelectrochemical glucose detection [26]. Hydrogen peroxide

detection on hematite semiconductor photoanodes was reported [27].

BiVO_4 photoanodes have been employed for the detection of nitrite in aqueous media [28]. Nitrite anions act as efficient hole scavenger at low externally applied potential. The photoexcited BiVO_4 produces photocurrent responses that increase linearly with nitrite concentration in the solution, as illustrated in Fig. 3. Yu et al. employed a hydrothermal method for synthesis of BiVO_4 micro-rods, and this material was further developed into a photoelectrochemical sensor for H_2O_2 [29]. Under visible light irradiation, the photogenerated holes capture electrons from the hydrogen peroxide, leading a photocurrent response that increases linearly with the H_2O_2 concentration in the range from $50 \mu\text{mol L}^{-1}$ to 1.5 mmol L^{-1} , and with a limit of detection of $8.5 \mu\text{mol L}^{-1}$. This photoanode material works at 0.0 V (vs Ag/AgCl), and the photocurrent can be measured with simple instrumentation such as digital multimeters. This approach offers a promising candidate for the development of an inexpensive sensing method.

Due to the superior photoelectrochemical performance, combined with low toxicity, low-cost, and high stability properties, BiVO_4 has become a popular n-type semiconducting photoanode material [30]. The BiVO_4 performance can be further improved by the combination with other photoactive materials aiming at a better charge separation and/or better charge transfer. Nanocomposites of BiVO_4 with different polyoxometalates (POMs) were studied for photoelectrochemical gas sensing for NO_2 gas detection [31]. The photocurrent response of the BiVO_4/POM was directly proportional to the gas concentration, and the highest gas sensing performance at room temperature was exhibited by $\text{BiVO}_4/\text{PW}_{12}$ (a nanocomposite with $\text{H}_3\text{PW}_{12}\text{O}_{40}$). The response exhibited by $\text{BiVO}_4/\text{PW}_{12}$ was of 32.8% for 50 ppm NO_2 , which was three times higher than pristine BiVO_4 . The incorporation of POMs could facilitate charge separation and charge transfer in the semiconductor to give improved responses.

The strategy of semiconductor heterojunctions is commonly exploited in the literature for enhanced photoelectrochemical devices. A recent mini-review offers a comprehensive overview with examples of sensor applications [32]. Particularly applications in phenolic waste streams have been reviewed by Lei Shi et al. [33]. An example to highlight is the BiPO_4 nanocrystal/ BiOCl nanosheet heterojunction that as photoelectrochemical sensor effectively quantified 4-chlorophenol, a toxic chlorinated organic pollutant that can result in many harmful effects in the environment [34]. The $\text{BiPO}_4/\text{BiOCl}$ heterojunction was synthesized via an *in situ* hydrothermal method assisted employing an ionic liquids, and the photocurrent in the presence of 4-chlorophenol was 3.5 and 10 times higher than those reported for pure BiOCl and for BiPO_4 , respectively. The effective separation of photoinduced electron-hole pairs due the heterojunction can explain the enhanced photoelectrochemical activity of $\text{BiPO}_4/\text{BiOCl}$.

The use of other photoabsorbers such as semiconductor quantum dots is increasingly frequently reported. The use of semiconductors as quantum dots is ideal for the development of optical or optoelectronic sensors due to the uniquely tuneable quantum dot photophysical properties. In the work of Wang and coworkers, a photoelectrochemical sensor for 4-aminophenol was prepared using an FTO (fluorine-doped tin oxide) electrode modified with CdS quantum dots, graphene, and molecularly imprinted polypyrrole [35]. The presence of graphene enhanced the electron transfer process, as well the photoelectrochemical behaviour of the CdS modified electrode. The molecularly imprinted polymer was selective for 4-aminophenol. The sensor gave a linear photocurrent response for 4-aminophenol from $5.0 \times 10^{-8} \text{ mol L}^{-1}$ to $3.5 \times 10^{-6} \text{ mol L}^{-1}$, with a detection limit of $2.3 \times 10^{-8} \text{ mol L}^{-1}$. This observed selectivity and sensitivity is likely due to the specific

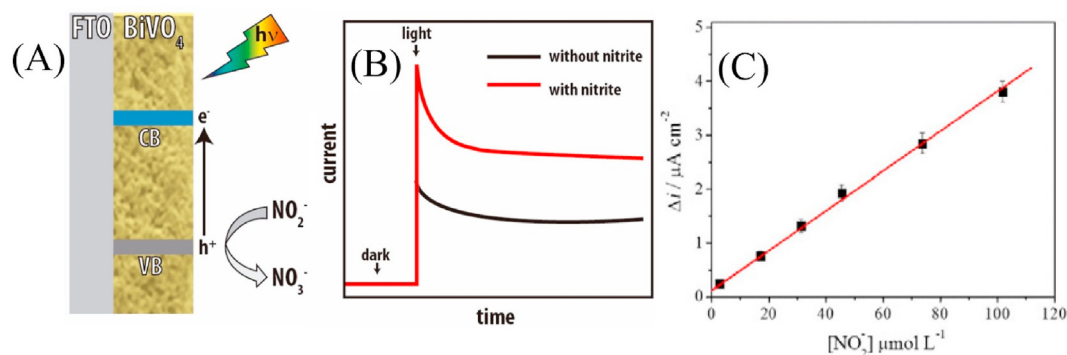


Fig. 3. (A) Schematic representation of a nitrite photoelectrochemical sensor. (B) Effect of nitrite on the photocurrent response. (C) Plot of nitrite photocurrent versus nitrite concentration (reproduced with permission [28]).

binding of the 4-aminophenol with the template sites in the molecularly imprinted polymer on the modified electrode.

An approach to improve the photoelectroanalytical performance is the sensitisation of wide band gap semiconductors with an energy gap in the UV range. This strategy allows excitation of the sensitizer dye with charge injection into the semiconductor in the visible range, leading to a better utilisation of sunlight. Since the UV light represents only 4–5% of total energy in solar irradiation [36], in contrast, the visible light accounts for about 43–46% [37]. A sensitised photoelectrochemical method for L-dopa detection at low applied bias potential was developed based on TiO₂ sensitised with iron phthalocyanine (FePc/TiO₂) [38]. The resulting composite was suggested to give synergistic efficiency, where photoexcitation of the composite occurs through the iron phthalocyanine, followed by charge transfer. The hetero-architecture could then hinder charge recombination. The coordination of L-dopa onto TiO₂ was exploited to give detection with a linear response range between 20 up to 190 μmol L⁻¹. Metal nanoparticles may be used as sensitizers with additional benefits in combination with semiconductors. Five important functions can be suggested based on the use of metal nanoparticles in photoelectroanalysis: (i) roughening of the conductive high-surface sensing interface; (ii) added catalytic properties allowing amplification of electrochemical signals; (iii) light absorption into plasmon bands followed by charge separation; (iv) improved charge separation due to metal-semiconductor interaction; and (v) improved conductivity properties that allow better electrical contact to redox centers, for example into proteins and from the substrate electrode surfaces in architectures for biosensing [39].

Graphitic carbon nitride (g-C₃N₄) with photo-attached platinum nanoparticles (Pt@g-C₃N₄), can photo-generate hydrogen in aqueous media, especially in the presence of hole quenchers such as sugars. In a study by Zhao et al. [40], photocurrents from photo-hydrogen production were achieved on a platinum electrode substrate, driven by glucose as hole quencher, and enhanced by a polymer of intrinsic microporosity (PIM-1) coating deposited over the Pt@g-C₃N₄ deposit (see Fig. 4). PIM-1 can be used to control surface conditions. The polymer can hold the photocatalysts close to the electrode surface and capture hydrogen in its pores to yield an enhanced photocurrent response even in the presence of dissolved oxygen. In the case of glucose detection, a concentration-dependent (super-Langmuirian) photo-response was observed.

In a similar strategy, an indirect photo-electrochemical sensor for the measurement of a mixture of analytes, such as reducing and non-reducing sugars was developed [41]. In this work, a palladium film separated a cell, creating a two-compartment system, one for

electrochemical reactions and the other for the photocatalytic process (see Fig. 4). This approach allows the electrochemical detection to occur separately from the complex analyte matrix, which may contain colloids, salts, additives, among other elements that make it a difficult environment for electrochemistry. As Pt@g-C₃N₄ coated with PIM-1 is deposited onto a thin palladium membrane, the hydrogen photogenerated in the photocatalytic compartment quickly diffuses through the palladium membrane, which is then monitored by chronopotentiometry response in the electrochemical compartment. Soft drink sugar content sensing was demonstrated without the need for deaeration. The sensor has been shown to give total sugar readings even for non-reducing sugars in the analytical sample.

By combining PIM-1 with a titanate nanosheet photocatalyst (Pt@titanate), it was possible to obtain a microporous film that allows the permeation of oxygen. In the absence of light, a typical oxygen reduction signal was recorded (Fig. 5). But when a blue LED (λ = 385 nm) is pulsed into this material, the reduction signals from oxygen are effectively decreased (an effect proportional to light intensity), with a similar oxygen concentration dependence observed in different aqueous media (Na₂HPO₄, NaCl, or NaOH). This reduction current decrease response can be explained with an oxygen depletion process caused by illumination of Pt@titanate in the membrane on the electrode surface. Oxygen reduction occurs with/without the photocatalyst illuminated and a linear response in the photocurrent difference to aqueous oxygen concentration was demonstrated [42].

As can be seen from these examples, the integration between the different materials and sensing techniques provides a key factor for development of photoelectroanalytical sensors with enhanced performance. However, future photoelectroanalytical methods will be beneficial only if the additional complexity of introducing/controlling a light source can be justified. Sensitivity and selectivity gains are important as well as reproducibility in order to overcome potential commercial barriers to complexity and power requirements in point-of-care devices.

Many devices such as electrochemical impedimetric and amperometric sensors, electrochemical luminescence sensors as well as photoelectrochemical sensors, offer wider potential for sensing both chemical and biological analytes. The recent advances in nanomaterial-based electrochemical signal amplification are valuable for improving selectivity and sensitivity of electrochemical sensors and biosensors [43]. Introducing biorecognition elements into the sensor architecture to give photobioelectroanalytical sensors opens up an even wider range of analytical applications and highly selective targeting of specific analytes.

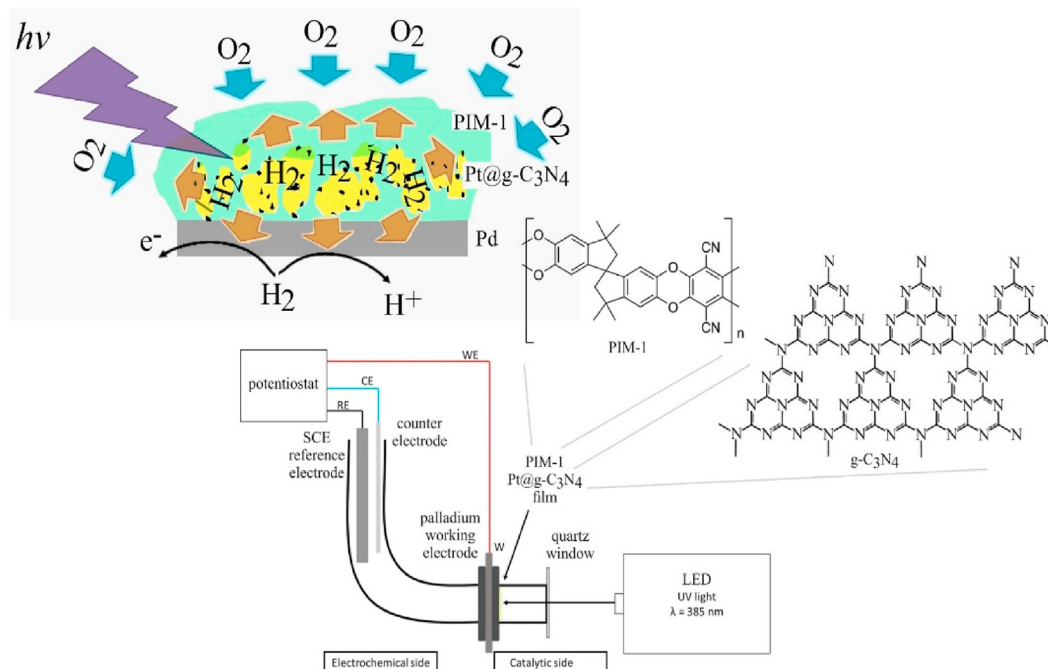


Fig. 4. Experimental system for Pt@g-C₃N₄ immobilised in PIM-1 polymer at a palladium film electrode. On the catalysis side hydrogen generation occurs followed by hydrogen diffusion through the palladium membrane. Light pulses in the presence of glucose quencher lead to locally produced hydrogen which then results in oxidation current responses (reproduced with permission [41]).

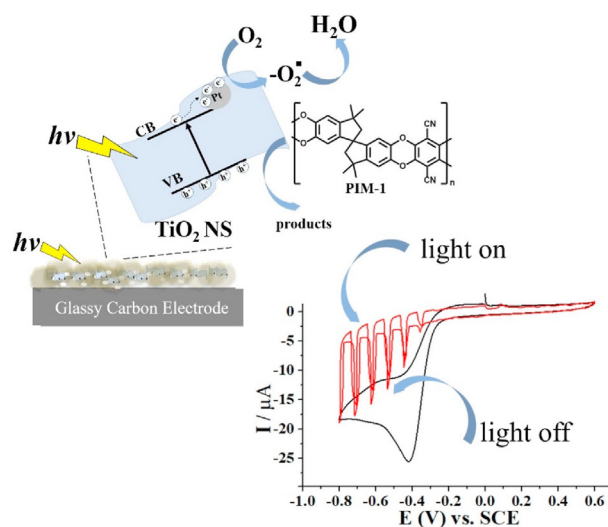


Fig. 5. Schematic representation of oxygen photoelectroanalysis with a film of titanate nanosheets in PIM-1 immobilised on a glassy carbon electrode. The photoresponse is “negative” due to light consuming oxygen before it can react at the electrode (reproduced with permission [42]).

3. Semiconductor-based photobioelectroanalytical detection

(Photo)electrochemical sensors have attracted interest because of their rapid response and potential for simple on-site measurement in cases where an embedded light source is tolerable. They can be employed directly to detect biological molecules such as alkaline phosphatase [44], but they can also be designed with integrated enzymes and bio-molecules to enhance their function. In a recent review del Barrio et al. [45] have summarised many of the benefits of adding a light stimulus to biosensing devices. A good

example is the photobioelectroanalytical glucose sensor [46]. The combination of TiO₂ and SnS₂ with glucose oxidase was reported [47]. Photoactive TiO₂/gold/poly-dopamine nano-architectures were employed for glucose sensing with a combination of glucose oxidase and horseradish peroxidase [48]. Jing Tang and coworkers have reviewed the use of TiO₂ nanowires in photobioelectrochemical sensing [49]. A TiO₂ nano-brush electrode was employed for β-amyloid photoelectroanalytical detection [50]. TiO₂ nanocrystal arrays were also combined with glucose oxidase in a triphasic surface tension dependent sensor concept [51,52]. Photobioelectrochemical device architectures more generally were reviewed by Devadoss et al. [53]. Porous silicon nanostructures have been suggested as semiconductor material for photo-enhanced biosensing [54]. Also, ZnO with graphene oxide (and glucose oxidase) have been shown to give enzymatic photoelectrochemical responses for glucose [55]. Both glucose (with glucose oxidase) and lactose (with β-galactosidase) detection were demonstrated on a g-C₃N₄/MnO₂ modified TiO₂ photo-active material [56].

Semiconducting polymer-graphene network structures with enzymes have been employed for sarcosine (with sarcosine oxidase) sensing [57]. This study shows how the photo-current response can be “negative” in the sense of lowering an oxygen reduction signal under light illumination. The consumption of oxygen in the photo process correlates with the presence of sarcosine. A novel synthetic porous carbon material (poly-(1,3,5-triethynylbenzene)) was utilized combined with glucose oxidase to give an interesting new device architecture able to link glucose content to the photocurrent for oxygen reduction [58]. More complex architectures based on innovative nanomaterials have been suggested [59].

Enzymes or oligonucleotides may introduce intrinsic chemical instabilities depending on the system conditions. The challenge to maintain enzyme activity is in the architecture of photobioelectroanalytical devices. Biosensors for detection of

compounds such as nucleic acids usually comprise an oligonucleotide as sensing agent and a charge-transporting mediator between the sensing agent and the transducer. This transducer is needed to convert the chemical signal into the electrical signal. Many different materials can be used as transducers. Photoelectroactive materials are suitable for this function, mainly due to combining advantages of both electrochemical and optical methods. The light is used to excite a photo-active species and a photocurrent response is obtained as the detection signal. Due to separating the source for excitation and for detection, photoelectroanalytical methods are potentially more sensitive compared to traditional sensors [60].

Sensitive detection of drug molecules and antibiotics was highlighted in recent work exploiting singlet oxygen intermediates. This work does not use bio-recognition elements but does have a biomimetic approach. De Wael and coworkers integrated aerobic photocatalysis and electrochemical sensing [61] by employing a perfluorinated Zn phthalocyanine as photosensitizer that under visible irradiation generates singlet-oxygen from oxygen in air. The singlet-oxygen oxidises analytes leading to electrochemically detectable products, as can be observed for amoxicillin (detected in nanomolar scale). De Wael and co-workers also reported a sensor based on a type II photosensitiser, where under red-light, singlet oxygen is produced by the sensitiser which then oxidises phenolic compounds. The oxidised phenolic compounds are reduced at the electrode surface, leading to a quantifiable photocurrent [16,17]. The same group reported optimisation of this system for the photoelectrochemical detection of 4-aminophenol (4-AP), cefadroxil (CFD) and doxycycline (DXC) in terms of pH and applied potential. After optimisation, detection limits of $0.2 \mu\text{mol L}^{-1}$, 20 nmol L^{-1} and 7 nmol L^{-1} have been achieved for DXC, CFD and 4-AP, respectively [62].

The development of high-performance biosensors can be inspired by biological transformations. Redox polymers for example, can mimic biological processes acting as electrical interfaces between redox centers and an enzymatic environment. The immobilisation of the enzyme nitrate reductase was reported in an acrylamide-*N*-methyl-*N'*-acrylamido-4,4'-bipyridinium copolymer, that allows the electrical communication with photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ [63]. By associating this immobilised enzyme with a TiO_2 substrate, it was possible to achieve the photoelectrochemical biocatalysed reduction of nitrate to nitrite. In this process, the redox polymer acts as electron trap of photogenerated electrons while it electrically communicates a semiconductor (TiO_2) with biological component (nitrate reductase).

The electrical communication between a semiconductor and the electrode can be mediated by a biological structure such as a nucleic acid or an enzyme. Freeman and co-workers obtained CdS nanoparticles linked to an Au electrode through a thiol-functionalized duplex DNA [64]. When doxorubicin was intercalated into the duplex DNA, doxorubicin trapped photoexcited electrons from CdS, and presented a photocurrent associated with a hopping mechanism, that makes the electron transport to the electrode easier (illustrated in the Fig. 6). The obtained photoanode works under mild pH condition and, by oxidising triethanolamine (TEOA) under mild conditions it was possible to observe the formation of a steady state photocurrent, that is proportional to the amount of doxorubicin intercalated in the duplex DNA, allowing the effective detection of this chemotherapy drug.

The combination between different methods and architectures may lead to exceptionally low detection limits, in some cases reaching the level of pM. An example of an extremely sensitive material was developed for detect N^6 -methyladenosine (m^6A). The design of this photoelectroanalytical biosensor consists of a $\text{TiO}_2/\text{BiVO}_4$ heterojunction and gold nanoparticles decorated with

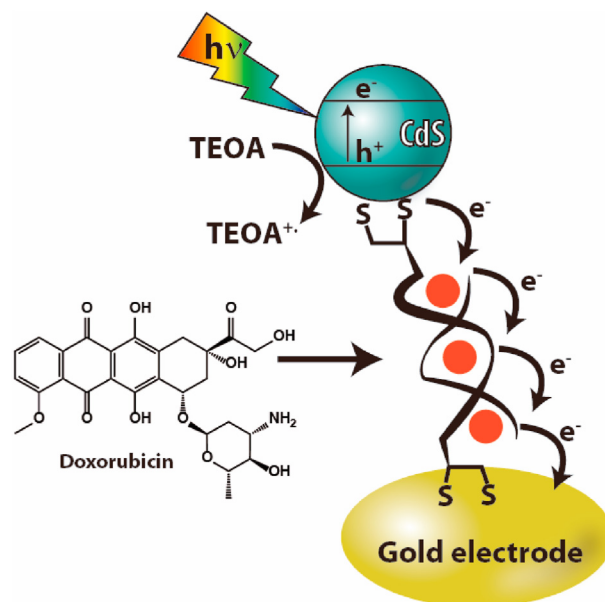


Fig. 6. Illustration of doxorubicin detection by its intercalation on thiol functionalised duplex DNA, where the photo-generated electrons from CdS nanoparticles are conducted to a gold electrode by a hopping mechanism (reproduced with permission [64]).

MoS_2 as photoactive materials, Ag^+ -mediated cytosine pairs for the signal amplification and anti- m^6A antibody as the recognition unit. The gold nanoparticles have three main functions on this sensor: (i) as visible light absorbers, injecting hot electrons into the conduction band of MoS_2 ; (ii) as carriers to immobilise m^6A antibodies by Au-S bond and; (iii) as site for the Ag^+ adsorption and consequent reduction that increases the photocurrent response [65].

The main advantages resulting from the use of biological components in photoelectroanalysis is the significant gain in the selectivity and sensitivity. It is possible to combine bio-inspired photoelectrochemical sensors with immunoassay approaches. A photoelectrochemical immunoassay (for serum cystatin C with a page display nanobody library) based on TiO_2 nanotube structures was reported [66]. A further good example of the combination of photoelectrochemistry with immunoassay methodology was explored in the work of Barroso et al. [67]. As illustrated in the Fig. 7,

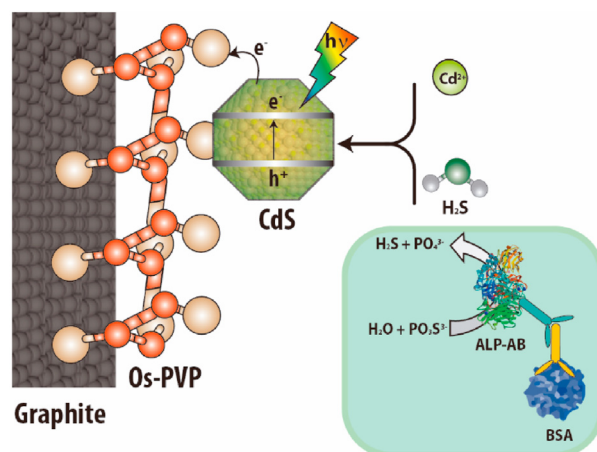


Fig. 7. Representation of CdS quantum dot generation followed by PEC immunoassay method for BSA detection (reproduced with permission [67]).

the system operational mechanism was based on the *in situ* generation of CdS quantum dots after reaction of Cd^{2+} with an enzymatic product. A polyvinylpyridine osmium complex (Os–PVP) was employed as signal transducer. Alkaline phosphatase (ALP) catalyses the hydrolysis of sodium thiophosphate, and the product (hydrogen sulfide) in the presence Cd^{2+} ions generates CdS quantum dots. Thus, UV irradiation (365 nm) of the CdS quantum dots results in photooxidation of 1-thioglycerol, mediated by the Os–PVP complex. Combining this photobioelectroanalytical methodology with an immunoassay based on specific enzyme linked immunosorbent assay (ELISA), the authors achieved a photo-enhanced immunoassay method for bovine serum albumin antibody (BSA) detection with a detection limit of 2 ng mL^{-1} .

Metabolites such as H_2S being produced in the sensor system are often not desired, because sulphide is quite aggressive to most materials used as sensors compromising its performance. However, it is possible to take advantage of this reactivity for *in situ* generation of sulphide based semiconductors, as the CdS quantum dots. In recent work of Yang et al. [68] were by taking advantage of the H_2S produced by sulfate-reducing bacteria (SRB), the metabolite was bio-etched onto a BiOCl to yield $\text{Bi}_2\text{S}_3/\text{BiOCl}$ p-n heterojunction (Fig. 8) for the detection of the own SRB. The sensor presented a good linearity and specificity for SRB with a detection limit of 29 cfu/mL and the advantage to do not be damaged during the measurements, overcoming one of the main challenges for detection of microorganisms that produce corrosive metabolites.

Semiconductors can be employed as template for label-free sensors in order to reduce the costs of the analysis. By immobilising a specific antibody on a semiconductor, the photoresponse increase proportionally to the antigen concentration. As observed in the paper of Monteiro and co-workers, titanium dioxide nanoparticles ($\text{TiO}_2(\text{a-r})$) sensitised by Bi_2S_3 and modified with the antibodies of the prostate-specific antigen (PSA), presented linear relationship for PSA from 1 pg mL^{-1} to 100 ng mL^{-1} , but the most impressive, was the recovery percentage of 94.6 and 98.6% when employed for the determination of PSA in artificial blood plasma samples, with recoveries between 94.6 and 98.6% [69].

The measurement of an analytical target assisted by enzymes can be made directly or indirectly via mediators, by enzymes reacting with the analyte of interest and giving a signal as a response. For example, ZnO nanoparticles and acetylcholinesterase (AChE) immobilised onto a Pt electrode by chitosan (CHI) allowed the detection the pesticide malathion [70,71]. Alternatively, quantifying the analyte indirectly by the metabolite after an enzymatic

reaction, as the hydrogen peroxide from the enzyme-catalyzed (glucose oxidase) oxidation of glucose, changing the transient photocurrent allowing the glucose measurement. By the glucose oxidase immobilisation on the inner wall and surface of ZnO inverse opal photonic crystals (IOPCs) and due to large surface area and porous structure of ZnO IOPCs, Xia et al. obtained a sensitivity about 18 times higher in comparison to a biosensor containing glucose oxidase immobilised on a ZnO thin film [72]. The changes the transient photocurrent response on an electrode due to the presence of glucose can be easily measured by intensity modulated photocurrent spectroscopy (IMPS), where the frequency of intensity modulation of the light source is varied, and then determined the maximum frequency of photocurrent out-of-phase component. Based on this principle, Tantra et al. developed a glucose biosensor using a n-type silicon photoelectrode and employing IMPS to determine the hydrogen peroxide generated by the glucose oxidase (see Fig. 9) [73].

Quantum dots are employed to improve photoelectrochemical sensing processes, or in chemiluminescence resonance energy transfer (CRET), in fluorescence resonance energy transfer (FRET), in electron transfer, and photoelectrochemical processes [74] (see Fig. 10). In a typical application, a CdS quantum dot-based photoelectrochemical aptasensor was used for tetracycline (TET) detection [75]. CdS quantum dots were grafted in graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) enhancing the absorption of $\text{g-C}_3\text{N}_4$, when tetracycline (TET)-binding aptamer was immobilised in the nanocomposite ($\text{g-C}_3\text{N}_4\text{-CdS}$), it acts as PEC aptasensing platform for TET determination, with $\text{g-C}_3\text{N}_4\text{-CdS}$ working as transducer. The linear response range of the sensor was between 10 and 250 nM with a detection limit of 5.3 nM.

A photobioelectroanalytical aptasensor developed by Golub and co-workers was based on the anticocaine aptamer subunit. The aptamer subunit is labeled with CdS nanoparticles, then in contact with cocaine, occurs the formation of supramolecular complexes with the NP-labeled aptamer subunits. With the addition of a hole scavenger (TEOA), the quantitative photoelectrochemical detection of cocaine is possible, due to the modulation of the photocurrent by the supramolecular complex [76].

CdS quantum dot sensitisers were employed with three-dimensional (3D) nanoporous NiO (3D NiO/CdS) and glucose oxidase for glucose sensing. Due to the enzyme selectivity, commonly encountered interferents such as H_2O_2 , ascorbic acid, cysteine, dopamine, among others, showed negligible effect for the cathodic photocurrent. This sensor gave satisfactory results in real samples

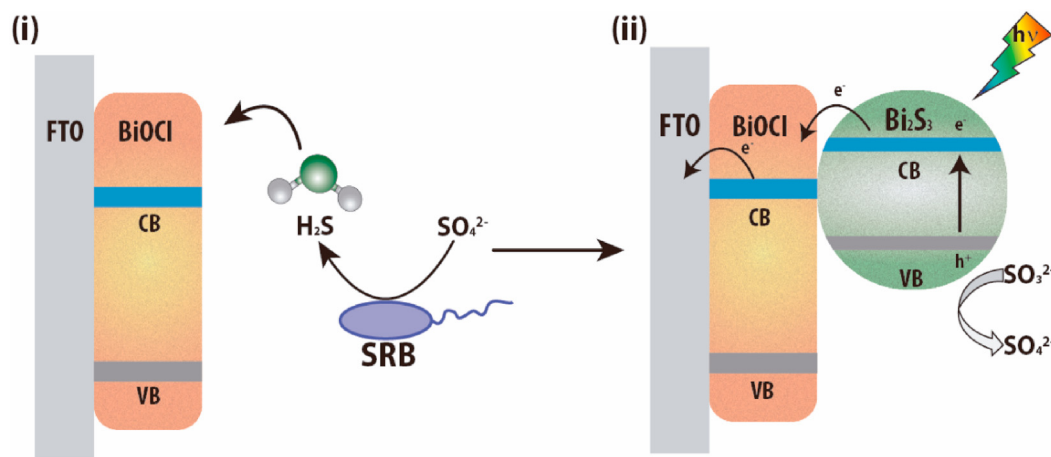


Fig. 8. Representation of the mechanism for SRB sensing: (i) The sulphate is biological reduced to H_2S that reacts with the BiOCl electrode leading to (ii) $\text{Bi}_2\text{S}_3/\text{BiOCl}$ p-n heterojunction that shows better charge separation and photoresponse (reproduced with permission [68]).

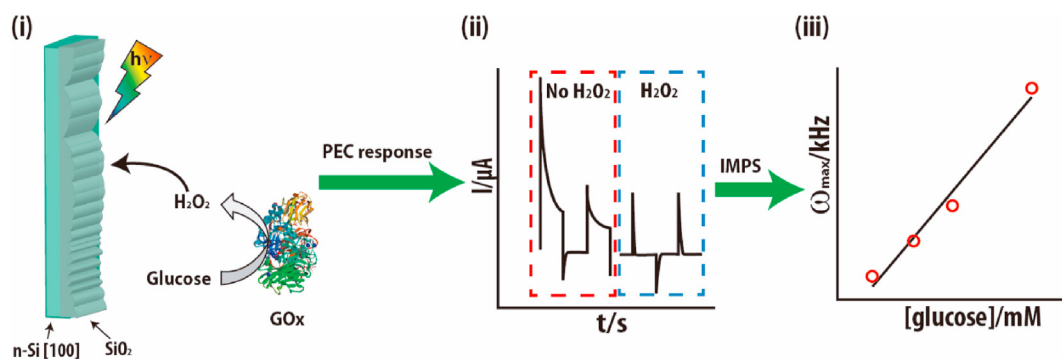


Fig. 9. Representation of IMPS silicon biosensor for glucose: (i) The product H_2O_2 from glucose oxidation is adsorbed on the SiO_2 film and quenches the charge carrier photo-generated leading to (ii) a decrease in the photocurrent response due to the high thickness of the SiO_2 film; (iii) Applying IMPS the max frequency (ω_{max}) is linearly related to the glucose concentration added to the system (reproduced with permission [73]).

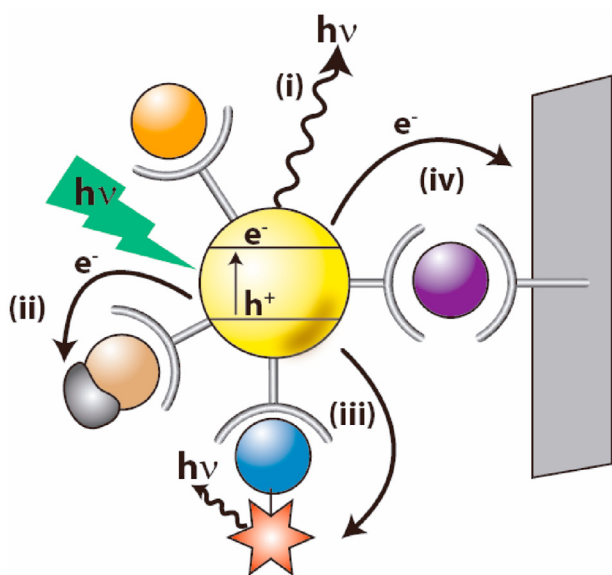


Fig. 10. Representation of semiconductor quantum dot process suitable for sensing applications: (i) CRET; (ii) Electron transfer for an adsorbed substrate; (iii) FRET and (iv) Photocurrent response (reproduced with permission [74]).

like serum with glucose injections [77]. Similarly, the nanocomposite $\text{TiO}_2/\text{CdSe}@\text{CdS}$ was used for glucose photoelectrochemical sensing. $\text{TiO}_2/\text{CdSe}@\text{CdS}$ was obtained by depositing water-soluble $\text{CdSe}@\text{CdS}$ and a mixture of $[\text{cobalt}(\text{o-phen})_3]^{2+/3+}$ and poly(ethyleneimine) over mesoscopic TiO_2 films [78]. The modified electrode showed stable and higher photocurrent intensity when coated with glucose oxidase. The photocurrent intensity was further enhanced through the addition of glucose and presented a linear relationship with the glucose concentration proving to be able for quantitative detection of this molecule. Zhao et al. observed by attaching the enzyme ALP to TiO_2 nanoparticles that during the enzymatic hydrolysis of ascorbic acid 2-phosphate, the biocatalysis product containing enediol can self-coordinates onto the surface defect sites to form a ligand-to-metal charge transfer complex. This gives strong absorption bands in the visible region of the semiconductor absorbance, thus leading to another unusual photobioelectroanalytical approach [79].

As can be seen from the broad range of examples given here, the combination of materials and with biomaterials not only allows a synergistic improvement in the electronic properties, but also provides higher surface area, electrochemical signals, and

analytical signals for direct or indirect detection of targets with high sensitivity and good specificity. Most examples for photo-bioelectroanalytical mechanisms to date are exploratory in nature and focused on proof-of-concept rather than providing commercially attractive sensor solutions. Nevertheless, the development of new sensor materials and mechanisms is rapid, and it offers a test bed for new ideas and potential start points for future sensor concepts.

4. Conclusions and outlook

In summary, the development of efficient photoelectroanalytical sensors and biosensors in terms of high sensitivity, reproducibility requires strategies to control the charge transport, separation and recombination in the semiconductor by a smart optimisation of architectures and the precise combination with materials capable of improving the intrinsic properties of the photoelectrode. A diverse range of strategies (and mechanisms) have been developed for improving the photo-electroanalytical activity and, consequently the sensing efficacy. Heterojunctions and sensitisation have been exploited to improve charge separation and light harvesting, and also signal amplification as can be seen for metal nanoparticles as carriers or tracers. Quantum dots are a typical example of a transducer material, but also have been introduced aiming at production of hybrid materials with better conductivity, catalytic activity, and biocompatibility.

Generally, the introduction of a light source into the sensor is an obstacle to commercialisation and genuine benefits from the photo-response are required to justify this development. Self-powered photoelectroanalytical devices offer an interesting alternative, but also chemical selectivity based on the interaction of the photoexcited electrode and the analyte can be beneficial. Although very interesting from an academic perspective, it remains to be seen how significant the real application benefits of photoelectroanalytical tools are.

In photobioelectroanalysis, the synergic effects of the multifunctional materials together with biological materials such as enzymes lead to enhanced selectivity, sensibility, and reproducibility. Enzymatic reactions are more specific (in contrast to many bare photo-active films). The use of biological components for biorecognition (aptasensors and DNA sensors) combined with photoelectrochemistry offers a way to take advantage of natural selectivity potentially with good performance combined with low cost.

The area of photocatalytic materials suitable for photo(bio) electroanalysis is in constant development. New nano-materials often trigger new concepts for sensor architectures and for

example the recent development of permeable and processable polymers of intrinsic microporosity [80] will help realising further new photoelectroanalytical sensor designs. Commercialisation of these kinds of sensors is challenging in part due to requirements in long-term stability and the need to combine a light source within the sensor. More detailed studies about the assembly of nano-bio interfaces in such sensors are required in order to achieve simpler biomolecule immobilisation routes, new biomolecule encapsulation and stabilisation approaches, and thus to enable a large-scale production of simple semiconductor-based sensors with complex surface architectures.

Declaration of competing interest

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

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