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New trends on photoelectrocatalysis (PEC): nanomaterials, wastewater treatment and hydrogen generation

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The need for novel water treatment technologies has been recently recognised as concerning contaminants (organics and pathogens) are resilient to standard technologies. Advanced oxidation processes degrade organics and inactivate microorganisms via generated reactive oxygen species (ROS). Among them, heterogeneous photocatalysis may have reduced efficiency due to, fast electron-hole pair recombination in the photoexcited semiconductor and reduced effective surface area of immobilised photocatalysts. To overcome these, the process can be electrically assisted by using an external bias, an electrically conductive support for the photocatalyst connected to a counter electrode, this is known as photoelectrocatalysis (PEC). Compared to photocatalysis, PEC increases the efficiency of the generation of ROS due to the prevention of charge recombination between photogenerated electron-hole pairs thanks the electrical bias applied. This review presents recent trends, challenges, nanomaterials and different water applications of PEC (degradation of organic pollutants, disinfection and generation of hydrogen from wastewater).

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Introduction

Standard wastewater treatment technologies (typically bio-treatment) are effective to remove suspended matter, degrade most of the organic pollution and reduce partially the microbial contamination; nevertheless, they fail to remove some recalcitrant contaminants, to abate organic compounds concentration in the range between micrograms and nanograms per litre (micropollutants) which include pharmaceuticals and personal care products frequently found in urban wastewaters. These technologies also require the use of a post-treatment step for disinfection (tertiary) to reduce the presence of microbial contamination up to levels of acceptability for different restricted re-use, including aquifers recharge, environmental and recreational uses, agricultural irrigation and drinking water [1].

Advanced oxidation processes (AOPs) — known as those treatment technologies aimed at degrading and mineralizing recalcitrant organic matter from wastewater through reaction with hydroxyl radical ($^{\bullet}OH$) — face these challenges has attracted great interest in the last decades. Heterogeneous photocatalysis utilises UV and visible light (solar or lamps) and oxygen from the air to inactivate microorganisms and degrade organic pollutants in water. If solar energy is used, then it is a clean water technology. Its main limitation is the fast charge carriers recombination in the photocatalyst, after photo-activation, reducing its efficiency.

Photoelectrocatalysis (PEC) consists of the immobilization of a photocatalyst on an electrode that will act as a photoanode or photocathode. In the case of a photoanode, when the energy of the incident radiation is equal or higher than the band gap energy ($h\nu \geq E_{bg}$) an electron is promoted from the valence band to the conduction band of the semiconductor, giving rise to the generation of electron-hole pairs (e^{-}-h^{+}). An external anode potential or cell potential or a constant current density (j) is applied by using a power supply. This allows controlling the Fermi Level of a semiconductor, and therefore band bending, leading to an efficient separation of e^{-}-h^{+} pairs and reducing their recombination. While h^{+} migrate to the semiconductor surface to oxidize water and produce hydroxyl radicals or to directly oxidize the organic compound, photogenerated electrons are transferred to the counter electrode through an external circuit [2]. Compared to photocatalysis, PEC increases the efficiency of

the process and yields higher production rates of holes [3], and other ROS, due to the prevention of charge recombination. Furthermore, in comparison to slurry photocatalytic systems, in PEC processes the photocatalyst is immobilized on a substrate, so no separations units are necessary to recover the photocatalyst [4]. One last advantage, when inactivating bacteria, which are negatively charged, they shift towards the positively charged photoanode, so mass transfer rates of bacteria are enhanced by electromigration [5]. There are several important reactions that can take place during PEC and are stated in Table 1.

One of the research niches in this area includes the development and selection of adequate materials for photoelectrochemical cells. These materials must have key properties including high photo-activity in the UV and visible range, chemical and physical stability, and high electrical conductivity that permits the design of the cells for an optimal mass transfer and radiation absorption [7].

Using PEC as treatment for organics removal from water can be challenging in the case of complex matrices, where there are chemical and optical interferences between light, dissolved organic matter, inorganic ions, and target pollutants, which may affect-negatively and sometimes positively the PEC degradation efficiency [7]. Therefore, it is not surprising that many authors struggle to achieve ideal efficiencies (lab conditions) in real wastewater applications. This issue becomes even more challenging when targeting organic matter and microorganism simultaneously, as competition among them for the generated ROS may decrease the process efficiency. Moreover, key aspects of the design and scaling-up of PEC cells for water purification applications will be discussed. Lastly, the recent applications of PEC for the simultaneous treatment of wastewater and hydrogen production will be revised as one of the most appealing applications [8], as they are a great opportunity for energy harvesting from wastewater as well as water remediation, becoming an excellent sustainable technology.

Table 1

Reduction and oxidation reactions and potentials [6]

Reaction	Potential/V versus NHE at pH 7	Application
$OH^- + h^+ \rightarrow {}^{\bullet}OH$	+2.29	ROS generation
$H_2O + 4h^+ \rightarrow O_2 + 2H^+$	+0.82	Oxygen evolution
$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$	+0.281	ROS generation
$O_2 + e^- + H^+ \rightarrow HO_2^{\bullet}$	−0.05	ROS generation
$O_2 + e^- \rightarrow O_2^{\bullet -}$	−0.33	ROS generation
$2H^+ + 2e^- \rightarrow H_2$	−0.41	Hydrogen evolution
$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$	−0.53	CO_2 reduction

Nanomaterials for photoelectrocatalysis

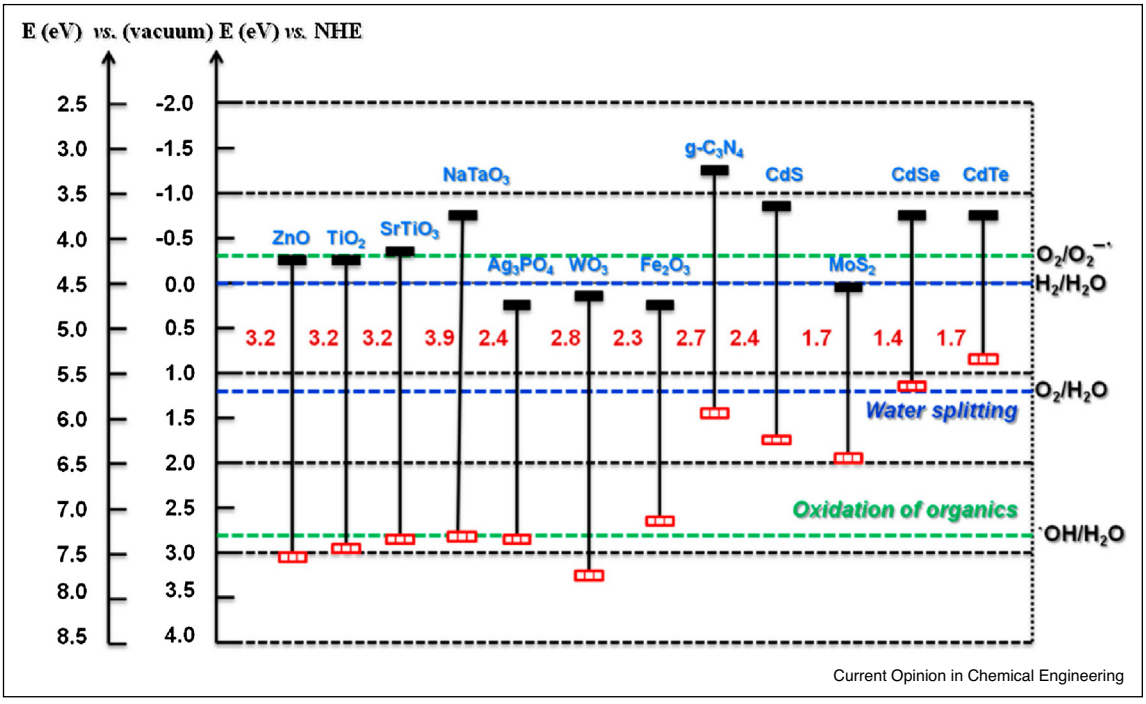
In photocatalysis, the nanomaterials' band edge potentials must facilitate the production of hydroxyl and superoxide ion radical, nevertheless when PEC is applied the generation of both is not so important as the counter electrode can assist one side of the redox reaction. Also, the generation of ROS via PEC reduction reaction can be facilitated by the applied bias, completing the redox cycle. In this sense, materials with a smaller E_{bg} can be used and the counter electrode can be used to enable the electron transfer to the solution. Band gap energies and edge potentials of different nanomaterials is shown in Figure 1 [9].

The majority of PEC studies utilise n-type materials as photoanode (Figure 2), due to the instability of p-type photocathode materials [9]. As such, significant research has focused on the enhancement of the photoanodes performance, using lower band gap materials, heterostructures and the addition of co-catalyst to improve the visible light absorption, charge transfer, stability and overpotential of the oxidation reaction. The improvement of photoelectrodes is of course important to enhance the overall performance. Lower band gap materials and/or heterostructures may offer improved solar performance by utilising more visible light, with extensive investigations primarily focused on solar energy harvesting rather than water treatment [11]. Moreover, not much consideration has been paid to the role of the counter electrode in PEC which can be used to generate additional ROS and impact the overall effectiveness of a system.

Many studies have focused on the development of semiconductor materials for use in PEC processes for various applications, such as pollutant degradation, microorganism inactivation [3,12,13••,14••,15] and hydrogen generation [16–19] (Table 2). For the purpose of PEC, semiconductor materials must exhibit, suitable band gap energies (E_{bg}), high charge carriers mobility and diffusion, optimal light absorption in the UV and visible range, stability, high catalytic activity, sustainability and low cost [7,20].

Several semiconductors photocatalysts have been applied as photoelectrodes for PEC processes including TiO_2, ZnO, WO_3, SnO_2, Fe_2O_3, $BiVO_4$, CdS, Cu_2O, Bi_2WO_6, $BiPO_4$, MoS_2, ZrO_2, MoO_3, and Bi_2MoO_6 [3,20–22]. These various semiconductors photocatalysts have been used as single, composite, and doped/metal-deposited Photoelectrode in PEC processes (Table 2).

Figure 1



Band gap and band edge potentials for different semiconductors (Reproduced with permission from Kumar *et al.* [10]).

Figure 2

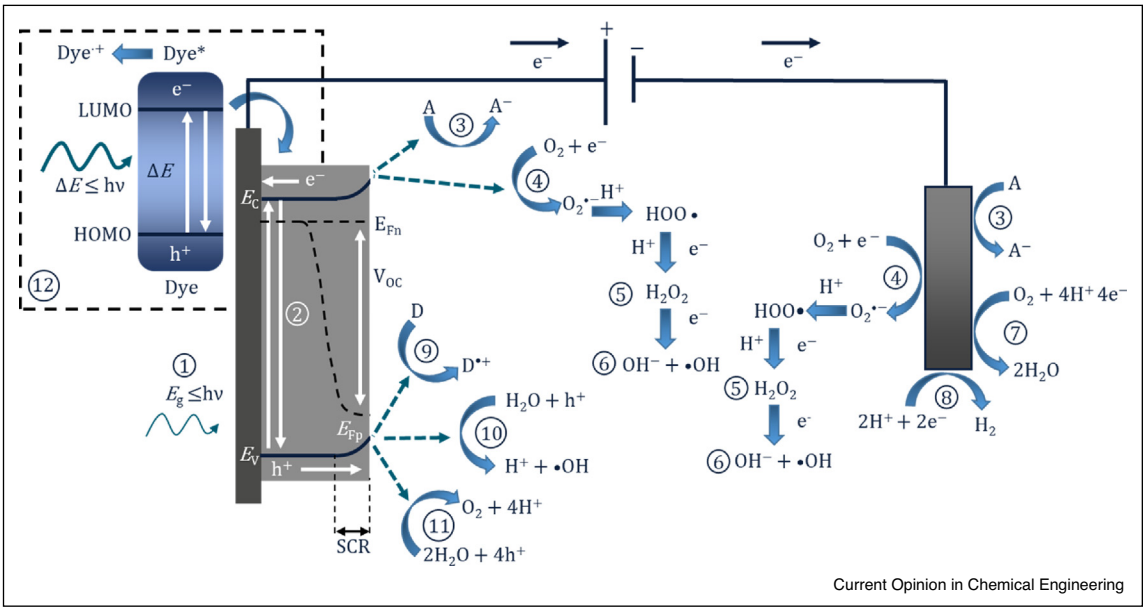


Diagram of the PEC process and pathways for radical production using a photoanode and a non-semiconducting counter electrode. (1) Photon absorption, (2) photo-excitation and recombination, (3) electron transfer to an electron acceptor, (4) oxygen reduction to superoxide, (5) formation of hydrogen peroxide, (6) formation of hydroxyl radical, (7) oxygen and proton reduction to water, (8) proton reduction to hydrogen, (9) donor electron transfer, (10) oxidation of water to form hydroxyl radical, (11) oxygen evolution reaction, (12) dye sensitisation (* excited state) and electron transfer to the conduction band (Reproduced with permission from McMichael *et al.* [12]).

Table 2

Revision of nanomaterials investigated for different applications of PEC for water treatment and hydrogen generation with summary of information on their performance, key advantages of the material and the reference of publication

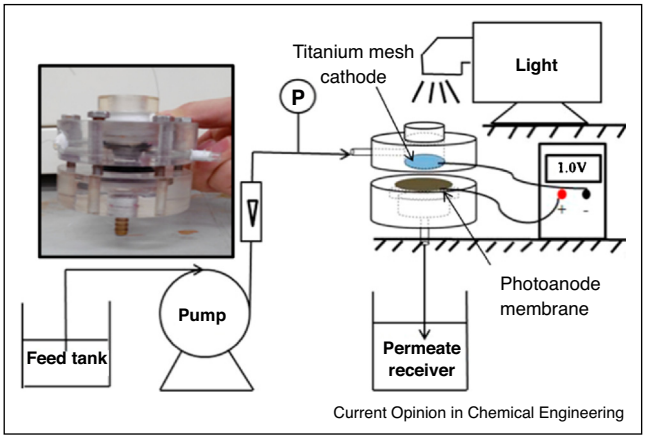
Main application	Nano-material	Experimental conditions	Performance	Key advantages	Reference
Pollutant degradation in water	BiVO4/FTO (F-SnO2)	10 mg/L Bisphenol A, Platinum cathode, 0.1 L 0.05 M NaClO4, 300 W Xe lamp ($\lambda \geq 420$ nm), 0.25 V	100% removal in 120 min	Low production cost and toxicity, high chemical and photostability, narrow band gap with VIS irradiation photoexcitation	[23]
	WO_3/W	20 mg/L Chlorfenvinphos, platinum cathode, pH = 1, 100 mW/cm^2 Xe lamp ($\lambda \geq 420$ nm), 1 V	95% removal in 360 min	Non-toxic, low-cost, stability in acidic condition, photocorrosion resistance, high conductivity, VIS irradiation photoexcitation, deep valence band and high-oxidation-power holes	[4]
	WO_3/FTO (F-SnO2)	30 mg/L Urea, Pd/Au/PM cathode, PH = 5, 0.05 M Na2SO4 and 0.05 M NaCl, 100 mW/cm^2 Xe lamp, 1.2 V	100% removal in 60 min		[4]
	WO3/W	20 mg/L Fenamiphos, platinum cathode, PH = 1, 100 mW/cm^2 Simulated solar light, 1 V	100% removal in 120 min		[24]
	WO3/ITO	10 mg/L Carbosulfan, platinum cathode, 0.1 M Na2SO4, Vis-light Irradiation, and 1 V	55% removal in 60 min		[24]
	WO3/FTO	10 mg/L Atenolol, Pt cathode, 0.1 M NaClO4, 15 mW/cm^2 Hg lamp ($\lambda > 360$ nm), 1.5 V	100 Removal in 300 min		[25]
	Fe2O3/ graphite and TiO_2 /glass	200 mg/L Berberine chloride, Stainless steel cathode, 0.6 L of 0.1 M Na2SO4, 0.078 mW/cm^2 UV lamp, 9.0 mA/cm^2	93% removal in 60 min	Low cost, non-toxic, and good chemical stability	[12]
	Fe2O3/FTO (F-SnO2)	10 mg/L Methylene blue, platinum cathode, pH = 2.5, 1.0 M NaHCO3l,100 mW/cm^2 simulated solar light, 0.2 mA	>90% in 60 min		[4]
	MoS2/ITO	20 mg/L Ammonia nitrogen (AN), 10 mg/L Bovine Serum Albumine (BSA), platinum cathode, pH = 10, 0.1 M Na2SO3,95.5 mW/cm2 Xe lamp (>420 nm), 0.6 V	80% removal of AN for 360 min 70% removal of BSA in 240 min	Earth-abundant elements, simple fabrication, VIS irradiation photoexcitation	[4]
	ZnO/EG	0.01 mM Eosin dye, platinum cathode, pH = 1.5, 0.1 M Na2SO4, 300 W halogen lamp, 1.5 V	95% removal in 120 min	Low-cost, lower recombination rate due its wide band-gab, excellent chemical, and photochemical stability, non-toxic	[4]
	MoO3/EG	0.1 mM Methyl red and 0.1 mM methylene blue dye, Pt cathode,0.1 M Na2SO4, 400 W simulated solar light, 1.5 V	92% MR, 89% MB removal 180 min	Easy preparation, high photoactivity and stability, large surface area, promising candidate for replacing TiO_2 due it is wide band gap, and wide absorption spectrum	[4]
	MoO3/ Mo	10 μM Methylene blue, Pt cathode, 0.2 M K2SO4, 150 W simulated solar light, 0.6 V	100% removal in 80 min		[4]
	Bi_2WO_6/CA	1 mg/L Nonylphenol, pH = 10, 500 mW/cm2 simulated solar light, 0.6 V and electrosorption	99% Removal 480 min	Good adsorption performance and conductivity, high-specific surface area, self-cleaning ability	[4]
	TiO_2 /Ti	25 mg/L Reactive Red 243, activated titanium cathode, 1.8 L of 635 μS/cmM KCl, 15 W UV ($\lambda = 254$ nm), 1.5 V	99% decolourisation in 60 min	High UV light absorption, high electrode stability, high photocurrent density, short diffusion path for photoinduced holes to the supporting electrode, and high disinfection performance	[12]
	TiO_2 /Ti	10 mg/L Acetaminophen, titanium cathode, 1 L of 0.02 M Na2SO4, 14 W UV ($\lambda = 275$ nm), 8 V	95% degradation in 300 min		[12]

Table 2 (*Continued*)

Main application	Nano-material	Experimental conditions	Performance	Key advantages	Reference
Disinfection	TiO_2 /Ti	10^6 CFU/mL *E. coli*, Pt cathode, 0.19 L surface water 697 μS/cm, 5 mW/cm^2 black light UV (λ = 365 nm), 1 V	2.0-log reduction in 120 min		[14••]
	TiO_2 /Ti	≥10^6 CFU/mL *E. coli and P. aeruginosa*, carbon felt cathode, 0.3 L of rainwater 70 μS/cm, real solar radiation, 1 V	5.5 log reduction of *E. coli*. 5.8-log reduction of *P. aeruginosa* in 240min		[13••]
	TiO_2/ ITO	10^3 CFU/mL *E. coli*, nickel mesh cathode, 1 L of 0.1 M Na2SO4, 0.047 mW/cm^2 clack light UV (λ = 362 nm), 1 V	*E. coli* conc. <1 CFU/mL in 200 min		[12]
Pollutant degradation and disinfection	TiO_2 /Ti	10 mg/L Benzophenone (BP), 10^6 CFU/mL *Candida parapsilosis*, DSA cathode, 1 L of 0.1 M Na2SO4, 36 W UVB lamp irradiation, 2 V	100% removal in 90 min for BP by PEC, 6-log reduction of *C. parapsilosis* by (PEC + O3) in 60 min		[26]
H_2 production and pollutant degradation	TiO_2/SS	Ni/SS cathode, 0.0768 g/L NaCl, 0.0082 g/L KCl, 0.0024 g/L $MgCl2{\cdot}6H_2O$, 0.0191 g/L $CaCl_2{\cdot}2H_2O$, 0.05 g/L Phenol and 29.21 Na_2SO_4 g/L (simulated wastewater) or oilfield-produced wastewater. 150 W metal-halide lamp with UV filter	H2 production rate 12.36 μmol/hour and phenol degradation 80% (simulated wastewater). Hydrogen production rate 9.11 μmol/hour (oildfield-produced wastewater)	Low cost and toxicity, high stability. Filter-press reactor.	[27]
	TiO_2/Pt /FTO (F-SnO2)	Pt cathode. 0.1 mM methyl orange dye, 2 M methanol and 0.01 M Na2SO4, UV light	Hydrogen production rate of 11.4 mmol/hour. Quantum yield of 3.70%.	Improved charge separation.	[28]
	TiNT/WO3/ Ti	Pt cathode, 5×10^{-5} M, RB5 dye in 0.1 M-Na2SO4. H-type reactor; Nafion membrane	H2 generation efficiency (46%), dye removal (100% discoloration and 85% reduction in TOC)	Improved charge separation.	[29]
	C-N-TiNTs/ Ti	Pt cathode. 40 mg/L of perfluorooctanoic acid. H-type reactor	After 180 min, removal of 56.1% of perfluorooctanoic acid and production of 8.3 mmol H2.	Improved charge transport and carrier lifetime.	[30]
	$Bi/BiVO_4$/ ITO	Pt cathode, 0.2 M Na2SO4, 20 mg/L phenol	H2 production rate 27.8 μmol/cm^2 hour	Narrow bandgap and reduced recombination rate.	[31]
	g-C_3N_4/Ni foam	Pt cathode, 20 mL NaOH(0.5 M) and 10 mg/L Rhodamine B, Methyl Orange or Phenol. Visible light (λ > 420 nm)	H2 evolution rate 5.8 μmol/cm^2 hour and 21.6% PhB pollutant removal.	Strong visible light absorption.	[32]
	TiO_2-1 wt% Au@TiO_2/ Al_2O_3/Cu_2O	Pt anode. 30 mg/L humic acid, H-type reactor. Solar with AM 1.5 irradiation.	Solar-to-hydrogen conversion 0.5%. Humid acid degradation efficiency of 87% in 2 hour.	Wide-range photon absorption and efficenct charge separation. Self-biased PEC.	[33]
	Ti-Fe2O3/ FTO (F-SnO2)	Pt dispersed in carbon as cathode. 1 M NaOH and 1 g/L glucose. H-type reactor. 100 mW/cm^2 Xenon lamp	H2 production 2.3 μmol/min in presence of glucose.	Narrow bandgap.	[34]
H_2 production, pollutant degradation and disinfection	g-C_3N_4/Ag/ AgCl/BiVO4	Pt or MoS_2 as cathode. Sewage with 2 ppm of benzophenone. H-type cell. Nafion-117 membrane. 1.5 A.M solar simulator 150 W	Benzophenone degradation efficiency of 11.15%/cm^2 hour, disinfection of ≤1000 CFU/100 mL/cm^2	Efficient charge transfer ability. H2 production coupled to EP's degradation and *E. coli* desinfection.	[35••]

Among potential photocatalytic materials, TiO_2, ZnO, and WO_3 are the most common used photocatalysts in PEC processes. TiO_2 as an n-type semiconductor is the most widely used and investigated owing to its well-recognised properties such as photocatalytic activity compared to other semiconductor materials, non-toxicity, improved chemical stability, reusability, and adequate E_{bg} values ranging between 3.0–3.2 eV ensures its

Figure 3



PEC membrane reactor set-up, insert photo of the reactor (Adapted with permission from Wang *et al.* [20]).

effectiveness under UV irradiation, accounting for 4–5% of the solar spectrum [3,20].

ZnO has been widely studied for use in PEC processes as its properties are similar to TiO_2 as an n-type semiconductor. ZnO photocatalysts are considered cost-effective and environmentally friendly. However, the major limitation with ZnO is the chemical instability when placed in an aqueous medium. A limited pH range is established where ZnO remains chemically stable. WO_3 with E_{bg} values of 2.5–2.7 eV exhibit high stability in acidic solutions as well as photocorrosion resistance, photoexcitation by sunlight irradiation, and high conductivity [4,24]. WO_3 performance improves under visible light irradiation, resulting in easier generation of charge carriers due it is relatively low E_{bg}; moreover, it has been widely applied for pollutant degradation [25]. The primary limitations of WO_3 are its irritant and toxicity properties [3].

Another type of thermally and chemically stable photocatalyst is SnO_2 with a higher E_{bg} than TiO_2, ranging between 3.5–3.8 eV. However, in SnO_2 the conduction band position limits its ability to reduce oxygen in PEC processes [20,24]. Therefore, this photocatalyst has not been used as photoelectrode material in PEC for water treatment. However, its coupling with other photocatalytic materials has been widely studied for use in PEC processes [24]. Fe_2O_3 is a cost-effective, chemically stable, and non-toxic semiconductor with a low E_{bg} between 2.1–2.2 eV. However, it has a high recombination rate and low conductivity, limits its application as a photoelectrode [3,4]. Another semiconductor with low E_{bg} (2.4–2.5 eV) is $BiVO_4$ which can be photoexcited under sunlight. $BiVO_4$ is nontoxic and stable under neutral pH conditions [23].

Semiconductor photoelectrodes including CdS, Cu_2O, Bi_2WO_6, MoS_2, Bi_2MoO_6, MoO_3, $BiPO_4$, and ZrO_2 have been applied primarily for the PEC degradation of pollutants. Their band gaps are lower than 3 eV excluding MoO_3 (3.2 eV), $BiPO_4$ (3.8 eV), and ZrO_2 (5.0 eV). All materials were mostly applied for organic pollutant degradation in water, including dyes and pharmaceuticals [4]. Thus, the development of semiconductor materials for PEC process should be further researched for the various PEC process application and should be directed to the utilization of sunlight irradiation and the increase in their PEC activity in order to increase the process efficiency and decrease the costs of the treatment. Moreover, the PEC should facilitate simultaneous energy generation to make the processes sufficient and enable their practical application.

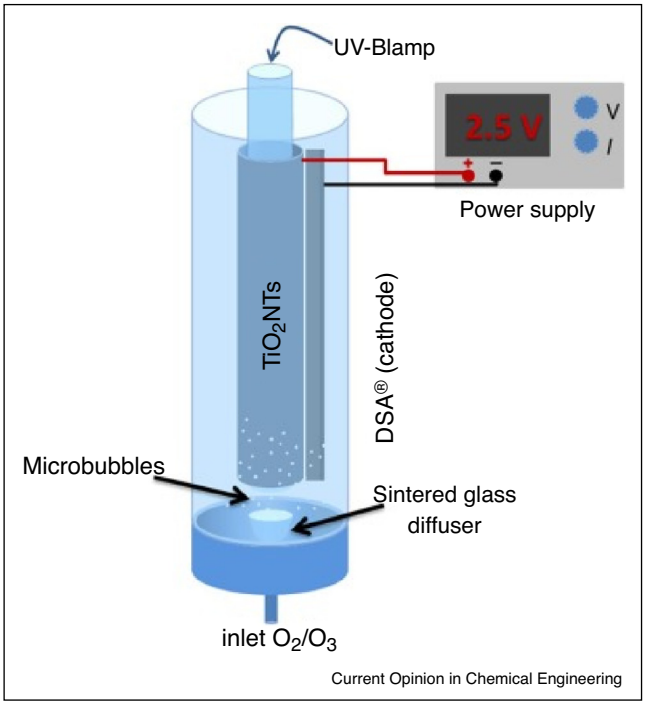
PEC reactors for removal of organic pollutants and pathogens in water

The degradation of organic compounds and inactivation of microorganisms in water using photoelectrocatalysis (PEC) is achieved by direct oxidation/reduction of the contaminate or indirectly by the generation of ROS [36]. There are serval reactor configurations reported in literature; however, a commonality with them highlights the need for a high surface to volume ratio with minimal distance between electrodes, mass transport can impact/improve the degradation rates, an adequate supply of oxygen is important for the reductive pathways to produce ROS, and depending on the contaminate and electrolyte used there is an optimal bias [26,37]. Given the number of variables, the generation of a computer-simulated model may identify optimal designs.

Ideally, a scaled-up reactor design should enable a continuous flow, in which the effluent is treated to a required standard and enables a suitable quantity of potable water in a reasonable time. One such design is the growing area of PEC membrane reactors, the design Wang *et al.* [38] (Figure 3), demonstrated that the reactor could degrade phenol by 94% with a bias of +1.5 V; while the membrane alone could only remove 7% via absorption. The PEC reactor also displayed anti-foiling capabilities; therefore, increasing the lifetime of the membrane and in theory decrease the cost per unit treated. Sheydaei *et al.* [39] examined degradation of diazinon with a continuous flow PEC/reverse osmose hybrid set-up, in which non-degraded diazinon returned to the PEC reactor for further degradation.

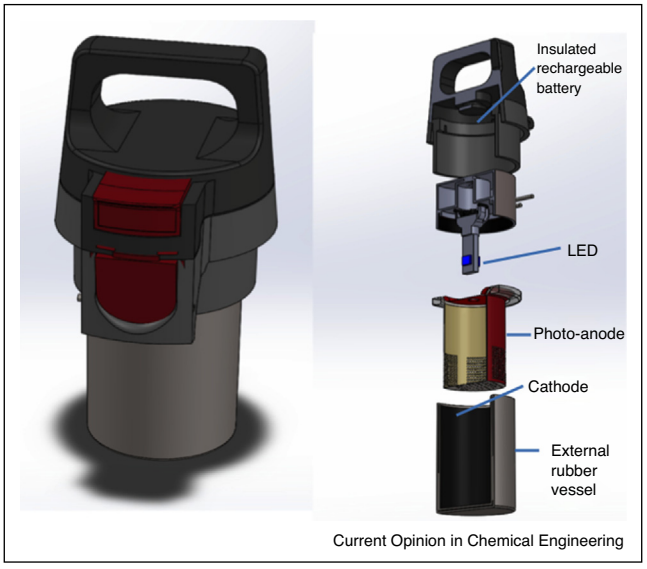
The inclusion of aeration into a reactor has dual purposes, ensuring oxygen for the reductive pathway to from an ROS and improving mass transport. Kim *et al.* [26] (Figure 4) examined purging with both O_2 and O_3 for the degradation of benzophenone-3 and *Candida parapsilosis*. The economics of the reactor was examined by using figures-of-merit as proposed by Bolton *et al.* [40].

Figure 4



Annular bubble column reactor (Reproduced with permission from Kim *et al.* [26]).

Figure 5



Left — diagram of the point-of-use 'e-DRINK' device (Reproduced with permission from Montenegro-Ayo *et al.* [42]).

The results demonstrated that the use of O_3 resulted in a lower figures-of-merit than O_2. Though this method only considers the electrical usage per order of reduction (i.e. the running cost) and not the capital cost.

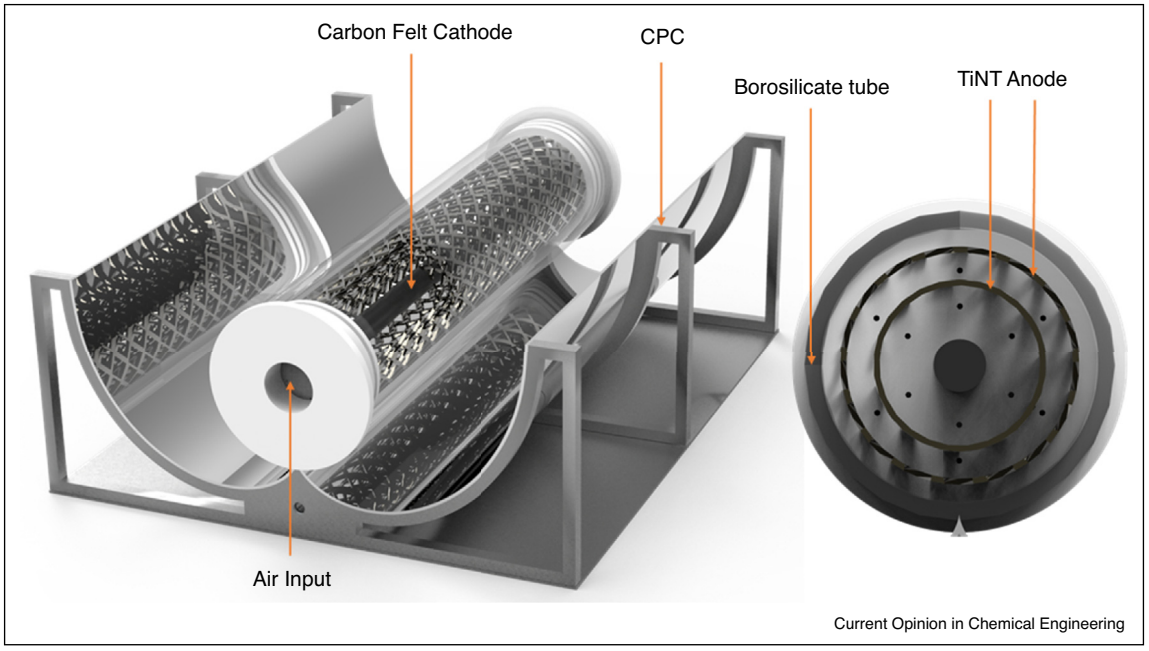
As these systems require an irradiance source there are only two options, solar or artificial. The use of energy-efficient LED's enables an PEC reactor to be operated at any time but there is an additional capital and running cost associated [41]. The reactor design of Montenegro-Ayo *et al.* (Figure 5) [42] reported a small-scale (350 mL) point-of-use device, which consisted of a TiO_2 nanotube photoanode, a titanium cathode and a UVA-LED (365 nm) for inactivation of *E. coli* in natural water within 6 min, showing promising application of UV-LEDs for PEC.

The use of real solar irradiation eliminates the need for an artificial irradiation source, which should reduce the cost of a system. Though this introduces additional problems, such as adequate reactor designs and variance in solar irradiation, which in turn will change the treatment time. The reactor design of McMichael *et al.* [13••] (Figure 6) reported testing under real solar irradiation, for the inactivation of *E. coli* and *P. aeruginosa*, more importantly it demonstrated that photocurrent correlates linearly with changing UV intensity (for a titanium nanotube photoanode), which could potentially be developed into a quality assurance method when using real solar irradiation.

PEC for wastewater treatment and scale-up

The ultimate goal is to use PEC systems for real-world applications; however, currently most studies are based on lab-scale experiments with volumes less than 3 L [43]. The absences of scaled up systems may be due to the lack of predictive models that can be used to design and develop of PEC systems [44]. Only a few manuscripts have been published in which they report an empirical model to remove organic pollutants [45]. However, several models have been reported for the design and optimisation of photoelectrochemical reactors for water splitting into hydrogen and oxygen [46]. The models were developed using Multiphysics software since it allows coupling and solving the different physics that govern the process, such as radiation absorption, electrochemistry or fluid flow. The existing models [44] can be adapted for wastewater treatment by developing intrinsic kinetic models, estimating the intrinsic kinetic parameters and the chemical reactions taking place at the electrode-electrolyte interface, akin to models reported for photocatalytic simulation [47]. The water splitting model of Hankin *et al.* [46] (Figure 7) could potentially be adapted to simulate the assessment of different electrode geometries, electrode configurations and the resulting performance by evaluating the spatial distributions of potential, photon flux and current densities.

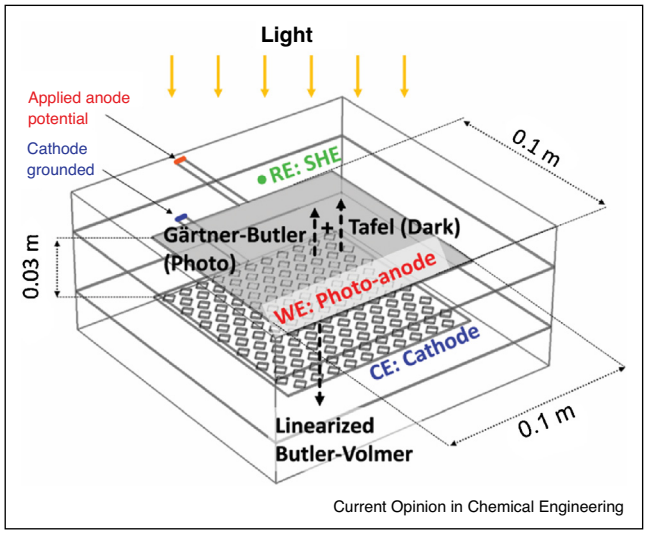
Figure 6



Solar PEC reactor configuration (Reproduced with permission from McMichael *et al.* [13••]).

Moreover, many studies use unrealistic water solutions that is, ultrapure water with an inorganic salt for example, Na_2SO_4. To scale up PEC systems more research is required with synthetic or real wastewater. Real water matrixes will contain a mixture of organic and inorganic compounds that will compete for the ROS and would be expected to result in slower reaction rates [43]. Though the presence of chlorine can be beneficial as it results in reactive chlorine species, which can inactivate bacteria and react with organic compounds [48]. Commonly, only one contaminant is tested at a time, though it is of interest to examine the effect of having a combination of pollutants that is, organic microcontaminants and microorganisms as performed by Salmeron *et al.* [14••]. Their work used a TiO_2 nanotube photoanode and a carbon-felt cathode to remove a mixture of *E. coli* and three organic microcontaminants (terbutryn, clorfenvinphos and diclofenac) dissolved in surface water. They successfully proved both the inactivation of bacteria and degradation of the pollutants, without adding any supporting electrolytes was possible. Though more research is required to move from lab-scale systems to scaled-up pilot systems treating real wastewater, the use of simulation may help facilitate in the design process or to optimise existing designs.

Figure 7



Isometric view of the reactor showing relative positions of the working (Ti|SnIV–Fe2O3 photo-anode), counter (Ti|Pt) and reference (SHE) electrodes as well as the kinetic models applied at each electrode| solution interface (Reproduced with permission from Hnakin *et al.* [46]).

PEC generation of H_2 from wastewater

The PEC-based generation of hydrogen can be coupled to pollutant removal from wastewater. In this configuration, the benefit of energy recovery as hydrogen fuel is combined to the reduction of environmental pollution in the water ecosystem. In this photoelectrochemical system, the holes oxidate the wastewater compounds in the photoanode, while the electrons are drawn to the photocathode through the external circuit, where the reduction occurs, producing hydrogen.

Very diverse photoanodes have been used in the degradation of wastewater pollutants coupled to hydrogen production including TiO_2 [27], TiO_2/WO_3 [29], TiO_2/Pt [28], C-N-TiO_2 nanotubes (TiNTs) [30], Bi/$BiVO_4$ [31], g-C_3N_4 [32], Ti-Fe_2O_3 [34] and g-C_3N_4/Ag/AgCl/$BiVO_4$ [35••]. Platinum is the most used cathode material, as it has generally shown the best performance as a hydrogen evolution catalyst, with low overpotential and high reaction rates in acidic environments. However, due to the high cost and scarcity of Pt, the development of this technology should involve the utilisation of alternative inexpensive and abundant materials. Alternatively, a recent study reported de use of a z-scheme photocathode formed by TiO_2-1wt% Au@TiO_2/Al_2O_3/Cu_2O, resulting in a self-biased PEC with good charge separation [33].

Most of the research does not study the effect of different reactor configurations in this process. Commonly, studies are performed using small volume (i.e. <100 mL) one compartment reactors; alternatively, other studies use a H-type reactor where the anolyte and catholyte compartments are usually separated by a membrane [29,34]. It has also been proven the possibility of using a filter-press reactor operated in batch recirculation mode [27].

Wastewater composition varies greatly depending on its origin, it usually consists of a complex mixture containing organic and inorganic compounds, microorganisms, and metals. Nevertheless, the majority of the research is centred on the study of hydrogen production from the degradation of just one pollutant. Studies have mainly focused on the following compounds: ammonia, urea, formamide, glucose, phenol, ethanol and glycerol [49]. Only limited works have proven the feasibility of hydrogen production using real wastewater samples as sewage from a wastewater treatment plant [35••] or wastewater produced from oil fields [27]. Moreover, it has been shown the possibility of coupling as well water disinfection to pollutant degradation and hydrogen production [35••].

Techno-economic reports on PEC for hydrogen (with a STH 10%) and PV-electrolysis have been done [50•]. With PEC projected to be more expensive than their competitors, therefore the dual treatment of water and hydrogen production may improve cost effectiveness and become an economically sustainable technology.

Conclusions

For the optimisation of the effectiveness of the PEC processes, the most important step is the proper selection of the electrode materials, the optimisation of the photoelectrode (including TiO_2, ZnO, SnO_2, WO_3, Fe_2O_3, $BiVO_4$, CdS, Cu_2O, Bi_2WO_6, $BiPO_4$, MoS_2, ZrO_2, MoO_3, and Bi_2MoO_6) and the reactor design is required, while the counter electrode is not usually analysed (stainless steel, carbon paper/felt, platinum, titanium). The reactor design will require the surface to volume ratio to be maximised, reduce the separation between electrodes and non-limiting mass transfer and dissolved oxygen levels.

Most of the published articles report lab and very controlled conditions of water matrix and pollution, therefore research using synthetic and real wastewater is required to assess the applicability of these systems in real case scenarios. This will bring additional insights into the possible side reactions and the interactions between different pollutants and inorganic compounds in the photoelectrochemical cell.

PEC reactors for wastewater remediation and hydrogen production need to be considered as dual solution for water remediation and energy solution, as this reduces the cost of the technology, including the capital cost, effective cost per unit treated and it is potential for real-world adoption against existing technologies.

Conflict of interest statement

Nothing declared.

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This article shows a techno-economic comparison of photoelectrochemical (PEC) systems and its major competitor, a photovoltaic system connected to a conventional water electrolyzer (PV-E system), extrapolated to future commercial scale with proven designs and materials. This paper is key because this approach is rarely considered and is key to promote the development of PEC applications. The main results show that the levelized cost of hydrogen (LCOH) for the off-grid PV-E system was found to be 6.22$/kgH2, with a solar to hydrogen efficiency of 10.9%. For the PEC system, with a similar efficiency of 10%, the LCOH was calculated to be much higher, namely 8.43$/kgH2. A sensitivity analysis reveals a great uncertainty in the LCOH of the prospective PEC system. This implies that much effort would be needed for this technology to become competitive on the market.