

Platinum Group Metals and Their Oxides in Semiconductor Photosensitisation

BASIC PRINCIPLES, METAL PHOTODEPOSITION AND WATER PHOTOSPLITTING REACTIONS

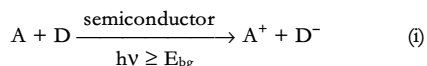
By A. Mills* and S.-K. Lee

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

*E-mail: a.mills@strath.ac.uk

The basic principles of semiconductor photochemistry, particularly using titania as a semiconductor photocatalyst, are discussed. When a platinum group metal or its oxide is deposited onto the surface of a sensitised semiconductor the overall efficiency of the reactions it takes part in are often improved, especially when the deposits are used as hydrogen and oxygen catalysts, respectively. Methods of depositing metal or metal oxide are examined, and a particular focus is given to a photodeposition process that uses a sacrificial electron donor. Platinum group metal and platinum group metal oxide coated semiconductor photocatalysts are prominent in heterogeneous systems that are capable of the photoreduction, oxidation and cleavage of water. There is a recent renaissance in work on water-splitting semiconductor-sensitised photosystems, but there are continued concerns over their irreproducibility, longevity and photosynthetic nature.

Photosensitisation of a semiconductor involves its electronic excitation by absorbed photons which promote its ability to mediate chemical reactions. At the end of such a reaction, the photosensitised semiconductor remains chemically (and usually physically) unchanged (1), as, generally speaking, does a conventional catalyst. A semiconductor has a manifold of electron energy levels filled with electrons – the valence band (VB) and also a manifold of higher energy levels that are largely vacant – the conduction band (CB). The energy difference between these two bands is called the bandgap energy (E_{bg}). A general semiconductor photosensitisation reaction can be summarised by:



where the change in the Gibbs free energy for this reaction may be negative (the usual reported case) when photocatalysis occurs, or positive when photosynthesis occurs (2–4). The usual form of a semiconductor photosensitiser in Reaction (i) is as particles of micrometre to nanometre diameter, which are aggregates of nanocrystals. These parti-

cles are used either as a powder dispersion or layered to form thin films (typically, 100–10,000 nm thick).

Each semiconductor particle can be considered to act as a micro-photoelectrochemical cell and the basic features of such cells for promoting a general chemical reaction, say Reaction (i), are shown in Figure 1 (2–4). The left hand side of the diagram shows a rough aggregated semiconductor particle comprised of one or more nanocrystals absorbing a photon of light of bandgap energy, $h\nu \geq E_{bg}$. This generates an electron-hole pair.

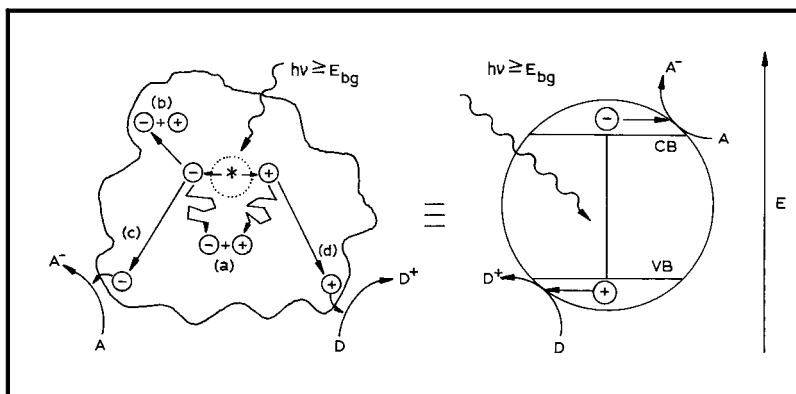
The fate of the components of the electron-hole pairs determines the overall photoactivity of a semiconductor. For instance, the photogenerated electron and hole can recombine in the bulk or at the surface, probably via trap states. Electron-hole recombination usually dominates semiconductor photosensitisation so the overall process is often not very efficient (typically < 1%) with respect to photons. If, however, the photogenerated electron and hole can make their separate ways to the surface of the semiconductor particle, they may react with species, such as A and D, adsorbed at the surface and drive Reaction (i) forward. The greater the

Fig. 1 The left hand side shows the major deactivation processes that can occur on a particle comprising many nanocrystals, after excitation with light of ultra-bandgap energy has created an electron-hole pair. The processes include:

- (a) electron-hole recombination – in the bulk,
- (b) electron-hole recombination – at the surface,

(c) reduction of an electron acceptor, A, – at the surface by a photogenerated electron, and
 (d) oxidation of an electron donor, D, – at the surface by a photogenerated hole.

The right hand side shows the electron energetics associated with Reaction (i), sensitised by a semiconductor particle



overall rate of this process, compared with the bulk and surface back reactions, the greater the photo-efficiency of the system.

Charge Transport

In these nanocrystalline semiconductor photo-systems the semiconductor is not deliberately doped and the combination of low or negligible doping and small size prevents the formation of any appreciable space charge layer at the surface of the semiconductor particles (5–7). This situation is different from that found in macro-photoelectrochemical cells where the semiconductors are usually deliberately doped to improve function, and as a consequence, possess a fully-formed space-charge layer that allows for the efficient separation of the photogenerated electron-hole pairs in the layer via migration (6, 7). Most nanocrystalline photosensitiser systems lack a space-charge region and the photogenerated electrons and holes move from the bulk to the surface mainly via diffusion.

Despite this apparent drawback, in nanocrystalline materials at least, transport of the charge carriers (electrons and holes) appears much faster (10 ps) than bulk recombination (100 ns) and these materials can thus act as efficient photosensitisers of reactions at their surface. Obviously, diffusion is only possible if a concentration gradient is set up for both holes and electrons and this is thought to be achieved by trapping states at the surface. For

most oxide semiconductor photosensitisers, such as titania and zinc oxide, it is generally believed that the photogenerated holes are readily trapped by surface-adsorbed water to form adsorbed hydroxyl radicals, which can diffuse, or ‘spill over’, across the photocatalyst surface (2–4). Recent work indicates such species can desorb from the surface and then diffuse into the reaction medium over distances exceeding tens of microns (8). Due to the apparent facile hole trapping action exhibited by many semiconductor photosensitisers, the photogenerated electrons tend to accumulate at the surface of the semiconductor. For titania these trap sites are Ti(IV) surface species, becoming Ti(III) on trapping the electrons.

Illuminating this system can thus cause a build-up of negative charge on the surface of the semiconductor particles if an easily reducible species, such as oxygen, is absent. Electrophoretic mobility measurements show that on illumination titania particles are negatively charged (9). Illuminating titania under anaerobic conditions in the presence of an easily oxidised species, such as EDTA, causes the photosensitiser to turn blue, indicating the presence of Ti(III) (10). The blue colour quickly disappears when oxygen is admitted as Ti(III) is converted to Ti(IV).

One way to prevent the accumulation of photogenerated electrons on semiconductor particles is to add easily reducible species, such as ceric (Ce^{4+}), ferric (Fe^{3+}) and PtCl_6^{2-} ions; for example

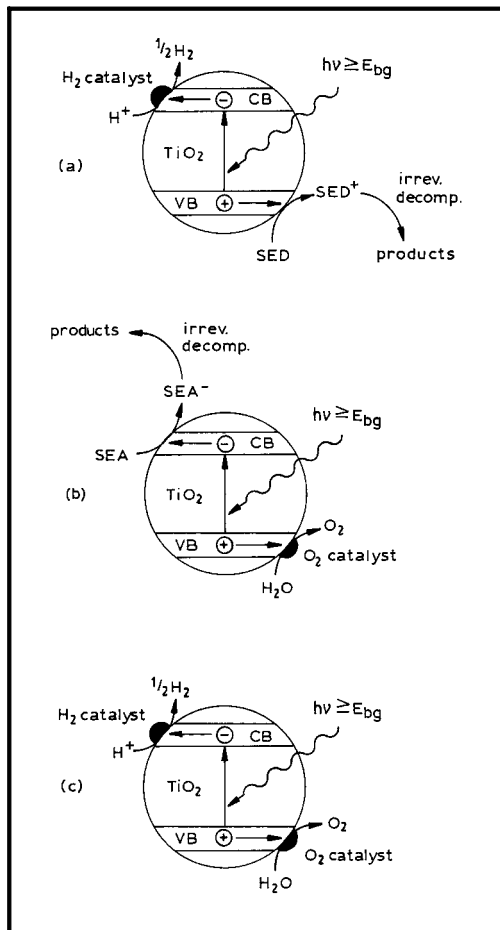


Fig. 2 Schematic illustrations of the electron energetics associated with:
 (a) the photoreduction of water by a sacrificial electron donor (SED), sensitised by semiconductor particles which have surface deposits of a hydrogen catalyst, such as Pt. Products are formed by irreversible decomposition.
 (b) the photooxidation of water by a sacrificial electron acceptor (SEA), sensitised by semiconductor particles with surface deposits of an oxygen catalyst, such as RuO₂. Products are formed by irreversible decomposition, and
 (c) the photocleavage of water, sensitised by semiconductor particles with surface deposits of a hydrogen catalyst and an oxygen catalyst

PtCl₆²⁻ is readily reduced to Pt metal. Thus, if a solution containing titania and H₂PtCl₆ is illuminated, Pt is usually photodeposited onto the titania surface (11). This is a common way to deposit a metal on semiconductors.

In semiconductor photochemistry, platinum group metal (pgm) deposits on the surface of semiconductor particles are often used to act as traps or

wells for any photogenerated electrons that may accumulate. The pgm deposits are assumed to reduce the overall probability of electron-hole recombination and so increase the overall efficiency of the photosystem. Such electron wells must be continuously 'drained' during illumination if they are to function efficiently.

In the absence of oxygen but in the presence of water, most pgms, if made sufficiently reducing by accumulated negative charge, will readily reduce water to H₂. In this process, most pgms stabilise the intermediate hydrogen atoms and catalyse their combination to form H₂. For increased efficiency a sacrificial electron donor (SED), such as EDTA or methanol, must be added to remove irreversibly any photogenerated holes or oxidising species, such as hydroxyl radicals, from the semiconductor surface. Many systems that overall photoreduce water to H₂ have been reported, but most utilise an SED and a UV-absorbing semiconductor photocatalyst.

In water photooxidation by semiconductor photocatalysis, a sacrificial electron acceptor (SEA), such as Fe³⁺ or silver (Ag⁺) ions, is usually added to the system to prevent accumulation of any photogenerated electrons. Oxides of the pgms, such as RuO₂ or IrO₂, which are recognised O₂ evolution catalysts (12), are often deposited on the surface of the semiconductor photocatalyst to improve the efficiency of water oxidation.

Finally, in studies of water photodissociation by semiconductor photosynthesis ($\Delta G^\circ > 0$), a H₂ and an O₂ catalyst, both pgm-based, are usually deposited on the surface of the semiconductor particles to help effect the overall process.

The general electronic features of semiconductor-sensitised photosystems for the reduction, oxidation and cleavage of water are illustrated in Figure 2.

Semiconductor Photosensitisers

There are many semiconductor materials but few that are sufficiently robust photochemically and chemically to be described as a 'photocatalyst' or 'photosensitiser'. Most semiconductors, such as CdS, ZnO or tungsten oxide (WO₃), are either photochemically or chemically unstable. For

Table I			
Electronic Properties of Rutile and Anatase			
Phase	E_{bg} , eV	E_{CB}^* (vs. NHE), V at pH 0	E_{VB}^* (vs. NHE), V at pH 0
Anatase	3.23	-0.32	2.91
Rutile	3.02	-0.11	2.91

* Both E_{CB} and E_{VB} vary with pH;

$$E_{CB} = E_{CB}(pH = 0) - 0.059 \times pH;$$

$$E_{VB} = E_{VB}(pH = 0) - 0.059 \times pH$$

instance, CdS can be photoanodically corroded to form an inert layer of surface sulfur and dissolves in acid, i.e. it is both photochemically and chemically unstable. ZnO is soluble in alkali and in complexing agents, such as EDTA. WO₃ is soluble in alkali and is mechanically 'soft', making production of robust film difficult. Of the very few photochemically and chemically stable semiconductor photosensitisers, one compound dominates: titania (titanium dioxide), that is TiO₂.

Titania exists as anatase, rutile and brookite crystalline forms. The latter is not common, does not possess good photocatalytic properties and is rarely used as a photocatalyst. Anatase is generated by the usual low temperature production methods, such as alkaline hydrolysis of titanium(IV) compounds followed by calcination at moderate temperatures (400–500°C). Anatase readily converts to rutile at elevated temperatures (> 700°C) although this phase change is often accompanied by extensive sintering (13). As a consequence, rutile usually has a much lower specific surface area (by a factor of 10 or more) than the anatase from which it was derived.

Titania is chemically and biologically inert, photostable, photoactive and cheap (2–4). In Table I are key electronic features of anatase and rutile. Their high bandgap energies show that the major drawback in using them as photosensitisers is that they only strongly absorb UV light (rather than visible light). Titania only absorbs 2–3% of the solar spectrum so is of limited use as a photosensitiser in any solar-driven system. Despite this, much research has been carried out on titania-based systems for water reduction, oxidation and splitting, as the photogenerated electrons and holes on titania have favourable redox potentials

($E_{CB} < E^\circ(H^+/H_2)$ and $E_{VB} \gg E^\circ(O_2/H_2O)$). Thus, the photogenerated electrons on both rutile and anatase are sufficiently reducing to be able to reduce water to H₂ ($E^\circ(H^+/H_2) = 0$ V). The photogenerated holes are more oxidising than fluorine ($E^\circ(F_2/F^-) = 2.85$ V) and can oxidise water to form hydroxyl radicals ($E^\circ(^{\bullet}OH/H_2O) = 2.31$ V) or oxygen ($E^\circ(O_2/H_2O) = 1.23$ V). Titania is the most used semiconductor in photosystems for water reduction, oxidation or cleavage.

Deposition of PGMs and PGM Oxides onto Titania

In many semiconductor-sensitised water reduction, oxidation or cleavage photosystems a hydrogen catalyst, usually a pgm, and/or an oxygen catalyst, usually a pgm oxide, is/are required, or used (not quite the same thing), see Figure 2. The H₂ catalysts and O₂ catalysts described will be limited to platinum (Pt) and ruthenium dioxide (RuO₂), respectively, the most popular used. Titania is generally the semiconductor photosensitiser.

An early, now classic, approach to depositing Pt onto a titania surface is to impregnate the semiconductor powder particles with a pgm salt (for example H₂PtCl₆) followed by reduction in a stream of H₂, at ~ 480°C for 15 hours (14).

Another popular method requires the initial preparation of a citrate colloid of the pgm, followed by destabilisation in the presence of the semiconductor. Destabilisation of a pgm sol is achieved by stripping the colloid particles of their electrostatically protective citrate outer layer (15) or by coagulating the colloid by addition of an excess of salt, such as NaCl (16). Both approaches produce effective photocatalysts for reducing

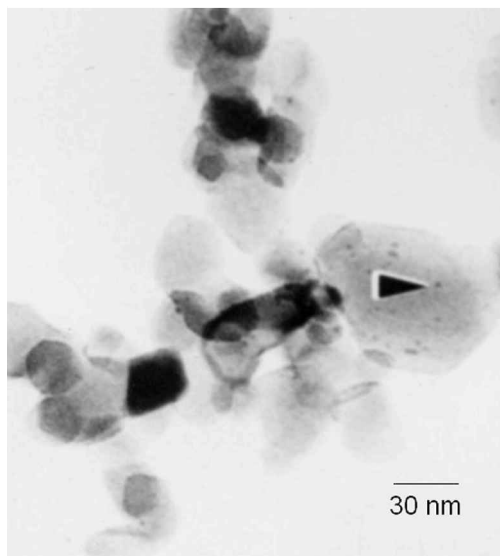
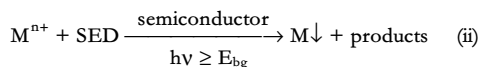


Fig. 3 Typical transmission electron micrograph of a Degussa P25 titania photocatalyst having Pt island deposits on its surface, generated by a Pt colloid coagulation method (16). The black arrowhead points to one of the Pt islands, typically ~ 4 nm in diameter

water. A typical titania photocatalyst (Degussa P25) with a polka-dot coating of ~ 4 nm Pt particles, created by the colloid coagulation method is shown in Figure 3.

Another deposition method involves the room temperature chemical reduction of a pgm salt in the presence of the semiconductor in aqueous solution. The reducing agent is usually sodium borohydride but, more recently, zinc powder has been used (17).

However, the most common method of depositing metals, especially pgms, onto titania and other semiconductor photocatalysts, is by photodeposition:



where M^{n+} is the pgm salt and the SED is methanol or ethanol, but can be almost any easily oxidised organic solvent, or dissolved species (such as EDTA or cysteine), or even water. Before irradiation the photosystem must be rendered anaerobic (usually by sparging the reaction solution with nitrogen or argon) since O_2 interferes with pgm reduction. The first example of Reaction (ii)

was reported in 1978 by Kraeutler and Bard, with titania as the semiconductor and water as the SED (18). To ensure complete reduction of the photodeposited pgm salt to metal, the system was irradiated under anaerobic conditions for 4 hours; further, the solution was neutralised, had an excess of hydroquinone added to it and then maintained at 50°C for 12 hours under nitrogen. Acetic acid was soon substituted as the SED, for Reaction (ii) (19). Since then many different SEDs have been used, although for Pt photodeposition, methanol or ethanol is preferred.

The key processes behind pgm photodeposition onto the semiconductor particle surface (Reaction (ii)) are shown in Figure 4. Ultra-bandgap irradiation generates an electron-hole pair that can migrate to the surface, where the photo-generated electron is sufficiently reducing (see Table I) to reduce most pgm salts to their zero-valence metal form. In titania, the photogenerated hole is sufficiently oxidising to oxidise water and most organics.

The organic chosen to remove the photogenerated hole is an SED (easily and irreversibly oxidised). If methanol or ethanol is the SED, the initial product of their oxidation via the photogenerated hole or the hydroxyl radical is an α -radical that can reduce most pgm salts. Using TiO_2 photoelectrodes in a study of this system, pgms can be deposited onto the titania surface by the oxidative route alone, without involving pgm reduction by photogenerated conductance band electrons (20). Obviously, when both pgm reduction routes (oxidative and reductive) operate (Reaction (ii) with methanol or ethanol as the SED) for each photon absorbed two reducing equivalents are produced. This is often referred to as a 'current-doubling' effect, as it was first observed as a doubling in reduction current in macro-photoelectrochemical cells (20).

When pgms are photodeposited via Reaction (ii), the oxidation state of the deposited metal is assumed to be zero. (The white titania starting material is certainly grey at the end of the process!) However, if the SED is acetic acid or water, Pt is photodeposited on titania in the Pt (0) and (II), or Pt (II) and (IV) oxidation states, respectively, and

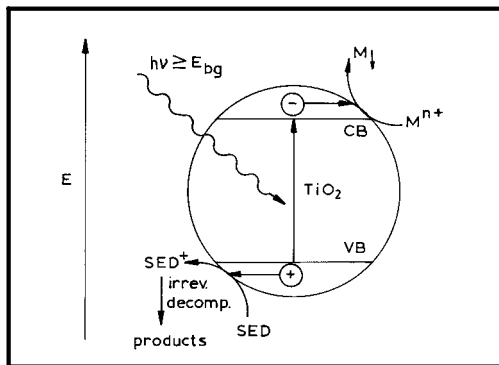


Fig. 4 Schematic illustration showing, under anaerobic conditions, the electron energetics associated with the photoreduction of a metal salt (M^{n+}) to form metal deposits (M). The sacrificial electron donor (SED), is sensitised by a particle of semiconductor photocatalyst

not Pt(0) as expected and often presumed (21). If the pgm/semiconductor photocatalyst produced is used to promote a reduction reaction, such as water reduction, any pgm deposit not in the (0) oxidation state will quickly become so upon illumination, due to the reducing nature of the environment. The need to reduce the pgm deposit to the (0) oxidation state may be the cause of the initial 'induction' period sometimes observed in such systems when hydrogen photogeneration is monitored.

Physical and Chemical Properties

Any semiconductor with a pgm (usually Pt) deposited on its surface has very different physical and chemical properties to the original uncoated semiconductor material. For example, platinumised titania samples form poorer dispersions than unplatinised titania and do not adhere as well to borosilicate glass (22, 23). The pzc (point of zero charge) and pzzp (point of zero zeta potential) of a platinumised titania photocatalyst decrease with increasing Pt loading. Thus, at a 5% Pt loading, the pzc and pzzp for Pt/TiO₂ are 5.6 and 5.1, respectively, whereas for naked TiO₂ (Degussa P25 TiO₂) they are 7.6 and 6.3, respectively (24). The amount of oxygen photoadsorbed by a titania photocatalyst decreased with increasing Pt loading (25). As factors which determine the overall rate of the process, all these characteristic differences may be as important (if not more so) as the assumed

electron-trapping and catalytic actions of the pgm, especially when taken in combination.

Photodeposition of a pgm oxide (RuO₂) onto the surface of semiconductor particles is usually achieved by either alkaline aerobic hydrolysis of a pgm salt, such as RuCl₃ to RuO₂ (26), or thermal decomposition of the pgm in a high oxidation state, such as RuO₄ to RuO₂ (27). When an aqueous dispersion of the semiconductor powder is stirred at room temperature with the pgm chloride or high oxidation state pgm oxide, the product is likely to be a highly hydrated form of the oxide: RuO₂·xH₂O or 'RuO₂', which is not a good oxygen catalyst as it is prone to oxidative corrosion (12). RuO₂·xH₂O is converted into a more stable and active oxygen catalyst, such as RuO₂ by heat treatment. This 'thermal activation' step rarely seems to be applied and its omission may explain the often less-than-beneficial effects of 'RuO₂' deposits on sacrificial semiconductor photocatalytic systems for water oxidation. Indeed, today, most O₂-evolving semiconductor-sensitised photosystems do not use a pgm oxygen catalyst, as it appears superfluous.

Photoreduction and Oxidation of Water

In the late 1970s and early 1980s research into artificial photosynthetic systems, such as water splitting, reached a peak. Work on macro-photoelectrochemical cells incorporating single-crystal semiconductor photoanodes had advanced to micro-photoelectrochemical cells based on semiconductor particles (28). Water photocleavage using such cells was problematic, but the use of semiconductor particles as micro-photoelectrochemical cells to mediate water reduction (and concomitant oxidation of an SED, such as EDTA or methanol), or water oxidation (and concomitant reduction of an SEA, such as Fe³⁺ ions) proved easy to achieve and highly reproducible.

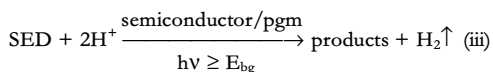
Most photocatalysts were able to mediate water reduction to H₂ by SEDs only if a suitable H₂ catalyst, such as a pgm, was present. The pgm was usually deposited onto the semiconductor by one of the techniques described earlier. The system also worked well if the pgm was simply mixed in with the semiconductor in a finely divided form,

Table II

Systems for the Semiconductor-Sensitised Photoreduction of Water to Hydrogen

Semiconductor	Electron donor	Hydrogen catalyst	$\Phi(\text{H}_2)$	References
TiO ₂	biomass (including grass, wood, algae, seaweed, cockroach and urine)	Pt (4%)	0.02–0.04	29
TiO ₂	glucose	Pt (12–4%)	0.085	29, 30
TiO ₂	MeOH, <i>i</i> -PrOH	Pt (10–0.05%)	–	31
TiO ₂	<i>i</i> -PrOH	Pt, Pd, Rh, Au (0.5%)	–	32
TiO ₂ & TiO ₂ /SiO ₂	MeOH- <i>t</i> -BuOH	Pt (0.6%)	–	33
TiO ₂	EDTA	Pt (2–0.1%)	0.03	34
TiO ₂	MeOH	Rh(bpy) ₃ ³⁺	–	35
TiO ₂	EtOH	Pt	–	36

for example Pt black. The basic overall process can be summarised as follows:



The semiconductor is invariably anatase. Figure 2(a) shows the electron transfer processes associated with Reaction (iii).

Table II contains some of the (now hundreds) of TiO₂/p gm sacrificial systems for water reduction (29–36). The most intriguing is the first entry, where the SED is various types of biomass (29). Such micro-photoelectrochemical systems were

then being promoted as potential solar-driven biomass conversion systems to deal with unwanted biological waste material, such as sugar cane/maize waste from alcohol production. Nothing came of this idea, probably due to difficulties of scale-up and the low conversion efficiencies of such systems. Certainly the quantum yields for hydrogen evolution, $\Phi(\text{H}_2)$, are very low (typically 2–4%), and as noted earlier, sunlight contains little UV.

An example of Reaction (iii) is given in a study of the photoreduction of an ethanol:water mix (50:50 v/v) by titania with various levels of deposited Pt (36), see Figure 5. The rate of hydrogen

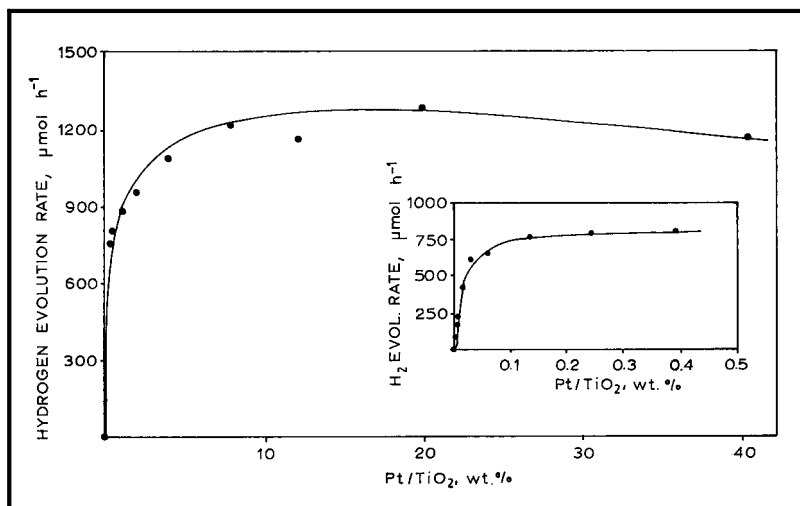


Fig. 5 The measured variation of the rate of hydrogen evolution as a function of wt.% Pt on a Pt/TiO₂ photocatalyst when illuminated. The SED is ethanol (50:50 v/v with water), [Pt/TiO₂] = (10 g dm⁻³). The light source was a 500 W Xe lamp. The insert diagram is an enlargement of data in the main diagram over the range 0–0.4 wt.% Pt

Table III

Systems for the Semiconductor-Sensitised Oxidation of Water to Oxygen

Semiconductor	Electron acceptor	Oxygen catalyst	$\Phi(O_2)$	References
TiO ₂	Fe ³⁺	Rh, Ru, Ir, Au, Co or none	–	37
TiO ₂	[PtCl ₆] ²⁻	–	–	11
WO ₃	Fe ³⁺ or none	Pt, Rh, Ru, RuO ₂ or none	0.0031	38
WO ₃	Ag ⁺	RuO ₂ ·xH ₂ O	–	39
WO ₃ and CeO ₂	Fe ³⁺ and Ce ⁴⁺	none	–	40
TiO ₂	Fe ³⁺	Ru	–	41
TiO ₂ -WO ₃	Fe ³⁺	none	–	42

photoevolution is shown as a function of the percentage of Pt (w/w) deposited onto the titania powder. The Pt is essential for the overall process to occur, but high (> 20 wt.%) Pt levels seem to have a detrimental effect on the overall kinetics of the process, probably due to surface screening by the Pt particles as well as an increased likelihood of electron-hole recombination. This feature is common and often more clearly seen in this area of semiconductor photocatalysis.

The semiconductor-sensitised photocatalytic oxidation of water by an SEA can be expressed by:

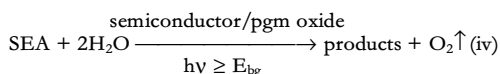


Figure 2(b) shows the electron transfer processes associated with Reaction (iv). Curiously, there are far fewer studies of Reaction (iv) than of Reaction (iii). This may be because the H₂-evolving system, nominally providing a route to generate a useful fuel, would have attracted funding via the 'alternative energy' initiatives available then. Oxygen photogeneration from water appears to be a less 'useful' process to study!

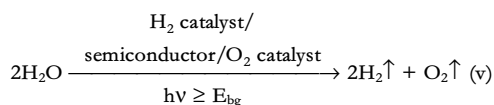
Table III contains examples of Reaction (iv) (37–42). These show the dominance of titania as the semiconductor photocatalyst. Many of the early examples illustrate the assumption made in the 1980s, that for efficient water oxidation, an oxygen catalyst, such as RuO₂, should be added to the system, usually as fine particles on the semiconductor photocatalyst. In fact, the photo-

generated hole on titania and WO₃ (the two most commonly used semiconductor sensitiser) is so oxidising that an oxygen catalyst seems not to be needed. Work has also shown that water photooxidation is possible without a pgm oxide oxygen catalyst, if WO₃ is the photosensitiser and Fe³⁺ ions are the SEA (38). Research shows that the addition of an oxygen catalyst, such as RuO₂, has little or no effect on the ability of TiO₂ or WO₃ to oxidise water to O₂ (37, 38).

The variation in concentration of the photo-generated oxygen (measured using a Clark cell) in a WO₃/Fe³⁺ photosystem was monitored as a function of irradiation time for a series of repeat irradiations, see Figure 6. The rate of photogenerated oxygen decreases with repeated use. This is due to inhibition by ferrous ions (Fe²⁺) photogenerated during the process (38). Thus, not surprisingly, Fe³⁺ ions are not a particularly good example of an SEA material, since the product of electron scavenging, Fe²⁺, interferes with the hole scavenging process – water oxidation to oxygen.

The Photocleavage of Water

The semiconductor-sensitised photocleavage of water into hydrogen and oxygen can be summarised as follows:



where the H₂ catalyst is usually Pt, and the O₂ catalyst is RuO₂ (or more usually RuO₂·xH₂O) or

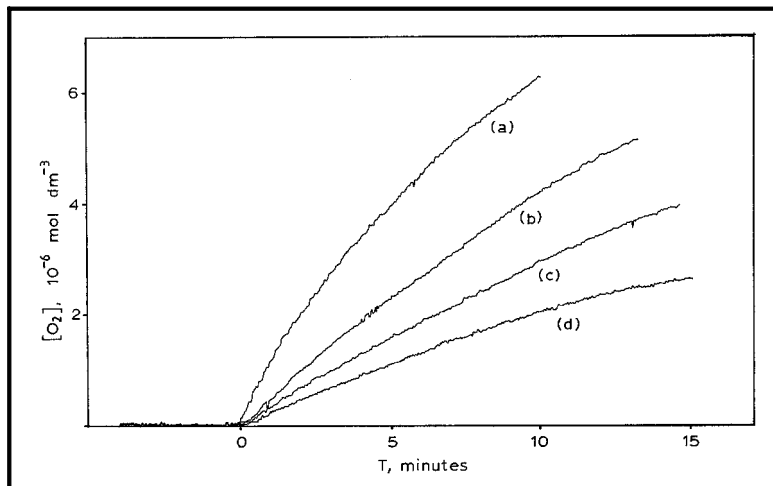


Fig. 6 Profiles of the observed dissolved $[O_2]$ versus illumination time for a WO_3 dispersion (6.5 g dm^{-3}) in $0.005 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ containing 0.01 mol dm^{-3} ferric chloride. Profiles (a)–(d) were recorded consecutively and show that the rate of water oxidation decreases with repeated irradiation. This is due to inhibition by ferrous ions formed during the overall light driven process. The light source was a 900 W lamp fitted with a heat and UV filter

nothing. The semiconductor photosensitiser is invariably titania or SrTiO_3 . Reaction (v) has been and is the subject of controversy. The early claims of 'bifunctional' photosynthetic systems, based on titania, capable of splitting water with high quantum efficiencies (up to 30%) under ambient conditions appear irreproducible, and now, with hindsight, unjustified (2, 27). However, interest in water splitting has recently increased and those involved suggest that forcing conditions, such as reduced pressures and elevated temperatures, are likely to be needed, to help strip out the photo-generated O_2 and H_2 from the system before they have time to back react (2, 43).

Table IV (44–62) lists most of the reported titania- and SrTiO_3 -based water splitting photo-systems. The new interest stems from work by Sayama and Arakawa in the early 1990s showing that while Reaction (v) is difficult or impossible in water at any pH, it can be readily achieved in concentrated ($> 2 \text{ M}$) sodium carbonate solution, using platinised titania (50). The role of the carbonate is not as a pH effect, instead, it is proposed that peroxycarbonates form in solution and these somehow enhance oxygen evolution (43).

While it is now accepted that a pgm oxide is not needed to act as an oxygen catalyst for Reaction (v), it might be thought that Pt or another pgm will always be needed in any system where water is reduced to H_2 . This may not be the case. Recent work has successfully achieved Reaction (v) using

a layered perovskite, such as $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, with ~ 3 wt.% deposit of nickel (Ni) as a photosensitiser material but without a pgm H_2 catalyst. The Ni may be acting as a H_2 catalyst (61).

Visible Light Splitting

All these water-splitting systems require UV-light to drive them forward, and although the visible light photocleavage of water via Reaction (v) has been claimed, notably using CdS as the photocatalyst, these findings are even more controversial and irreproducible than those based on titania (2). Reaction (v) has recently been driven by visible light alone, using delafossite (CuFeO_2) as the photosensitiser, without a separate H_2 or O_2 catalyst, pgm-based or otherwise (43). Others have reported that $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$ ($x = 0-0.2$) coated with NiO, or ' RuO_2 ', is a visible-light activated water-splitting photocatalyst (62). However, all claims of water splitting are still controversial and require reproduction by other groups.

Even if the systems in Table IV can be reproduced, albeit inefficiently, questions of longevity and their photosynthetic nature remain unanswered. The long search for the 'Holy Grail' of photochemistry: a semiconductor-sensitised system for water splitting that is efficient, long-lasting, reproducible and driven by visible light, is still far away. If such a system is discovered it is hard not to believe that at least one component will be a pgm, and most probably Pt. Although there is

Table IV

Systems for the Semiconductor-Sensitised Photocleavage of Water into Hydrogen and Oxygen

Semiconductor	Hydrogen catalyst	Oxygen catalyst	$\Phi(\text{H}_2)$	References
TiO ₂	Pt	none	–	44–50
TiO ₂	Pt	'RuO ₂ '	0.3	26, 51, 52
TiO ₂ doped with Cr	Pt	'RuO ₂ '	–	53
SrTiO ₃	Pt, Ir, Pd, Os, Ru, Re or Co	none	–	54
SrTiO ₃	Pt	none	–	55, 56
TiO ₂ and B/TiO ₂	Pt	none	–	57
NiO-TiO ₂	none	none	–	58
ZrO ₂	none	none	–	59
BaTi ₄ O ₉	none	'RuO ₂ '	–	60
K ₂ La ₂ Ti ₃ O ₁₀	Ni	none	–	61
In _{1-x} Ni _x TaO ₄	none	'RuO ₂ ' or NiO	0.0066	62
CuFeO ₂	none	none	–	43

much that still needs to be achieved in developing semiconductor-sensitised systems for water splitting, another area of research that involves semiconductor photochemistry and pgms appears to offer great commercial promise; namely, water and air purification by semiconductor photocatalysis. This will be discussed in a later issue of this Journal, and the role of pgms, most notably Pt and Pd, will be described.

Conclusions

Semiconductors can photosensitise several different reactions, usually with titania as the semiconductor because of its excellent photochemical and chemical stability and high activity as a sensitizer. In many cases the presence of a pgm, or pgm oxide, can improve the overall efficiency of the photochemical reaction. Of the many methods of depositing a pgm onto a semiconductor surface, the most popular involves photodeposition, with ethanol or methanol as an SED. Depositing a pgm oxide, such as RuO₂, can be achieved by oxidation of a pgm chloride or reduction of a volatile pgm oxide. The physical characteristics of a pgm-coated semiconductor are

quite different from those of the original semiconductor material. Semiconductor photochemistry has focused on systems capable of the photoreduction, oxidation and cleavage of water.

In water photoreduction systems, a pgm as a H₂ catalyst is essential, either deposited on the semiconductor surface or intimately mixed with it. Many systems have been reported and may be precursors of a water-splitting system. The semiconductor-sensitised photooxidation of water has been less well studied and using a pgm oxide as an O₂ catalyst does not appear essential, especially if a stable oxide semiconductor is used as the sensitizer. The latest systems resulting from the renewed interest in heterogeneous water-splitting photosystems appear to work under visible light illumination without a pgm-based H₂ and/or O₂ catalyst. However, all reported water-splitting systems are controversial and require confirmation. Further work is certainly required to create a reproducible, stable, efficient photosystem for water splitting probably requiring one or more pgms.

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The Authors

Andrew Mills is a Professor of Physical Chemistry at the University of Strathclyde. His interests include dye and semiconductor photochemistry, electrochemical sensor development for gases, sensors for use in clinical analysis and catalysis of redox reactions.

Soo-Keun Lee is a Postdoctoral Research Fellow at the University of Strathclyde. His research interests include semiconductor photochemistry, optical sensors and laser photochemistry.