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# A Practical Photoelectrochemical Cell Using Nonprecious Metal Electrodes

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# A practical photoelectrochemical cell using non precious metal electrodes

Patrick Enright · Anthony Betts · John Cassidy

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**Abstract** In this study a Photoelectrochemical Cell (PEC) constructed with inexpensive materials photodegraded selected organic compounds present in model waste waters, with the concomitant production of electrical current. Organic substrates dissolved in salt water included formic acid, 2-propanol, 1,2-dihydroxybenzene and ascorbic acid. Significant degradation of ascorbic acid was achieved when the cell was illuminated with a household 60 W tungsten light bulb, although better results were achieved with UV sources. Degradation of all the compounds was found to occur by zero order kinetics, and the PEC was shown not to work appreciably in dark conditions. Using a conventional light bulb, a formic acid PEC produced a power density of  $19.1 \pm 2 \text{ mW m}^{-2}$ . When exposed to natural daylight, a power density of  $31.5 \pm 2 \text{ mW m}^{-2}$  was achieved. There is considerable scope for scale up of this device for exterior use.

**Keywords** Photoelectrochemical cell ·  $\text{TiO}_2$  photocatalysis · Formic acid · Fuel cell · Water remediation · Alternative energy · Catechol · Ascorbic acid · Isopropanol

## 1 Introduction

Traditional waste water treatment methods include chemical treatments such as chlorination and ozonolysis, and physical methods such as adsorption and air stripping. However, the latter two methods, which are essentially non-destructive technologies, merely transfer contaminants from water on to the surfaces of adsorbents or alternatively volatilise them into the air. Following adsorption of contaminants, spent adsorbents such as activated granular carbon or synthetic resin often require further treatment, making this approach more complex than a simple single stage treatment. While air stripping is useful for the recovery of volatile organic compounds [1, 2], some toxic organic species are removed neither by adsorption nor by air stripping because of either their low adsorbabilities or their low volatilities. This considerably reduces the effectiveness of both of these physical processes.

Microbial Fuel Cells (MFC) have also been suggested as alternative systems for waste water remediation. MFCs typically use microbes such as *Geobacter metallireducens* [3] which can act as catalysts at platinum-loaded carbon anodes. This approach enables oxidation of a wide range of substances to take place and such systems have been used for treatment of a diverse range of waste waters including dairy manure [4], swine wastewater [5], and pure waste streams such as those containing cysteine [6]. In these cells oxygen acts as an electron acceptor at a Pt-based cathode. Not only does this process clean the water by removal of

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some organic pollutants, but also it generates a small amount of electricity, making such fuel cells potentially useful devices (although with low power densities) for waste water remediation.

In another approach the photocatalysed degradation of persistent organic pollutants in water can be achieved by using metal oxide semiconductor catalysts. Similar in concept to fuel cells, but requiring light to operate, Photoelectrochemical cells (PECs) consist of an electrode (anode) that oxidizes electron rich materials and a cathode (typically containing Pt) where  $O_2$  is normally the electron acceptor. PECs were developed in the early 1970s. Originally designed to undertake the photo-induced cleavage of water, these cells generate oxygen at a titanium dioxide electrode, in an aqueous solution with the concomitant production of hydrogen gas most often evolved at a platinum cathode [7]. All PECs rely on light for successful operation. Their use has since been extended for other applications, including the remediation of wastewater [8–10]. In this case nanoparticulate (Titania)  $TiO_2$  photocatalysts are employed for the mineralisation of numerous organic compounds. Recent reports have highlighted PEC cells that are capable of spontaneously degrading a wide variety of organic substrates ranging from biomass like polysaccharides, proteins, lignin, and cellulose to simple alcohols and sugars. Various other compounds were also successfully degraded with PECs including nitrogen-containing substances such as ammonia, urea, urine, and synthetic polymers like polyethylene glycol and poly(acrylamide). All these compounds were mineralised while also creating photocurrent [11–15].

Following their discovery, there has been sustained interest in both MFCs and PECs. Most of the recent research work has aimed at increasing their efficiency and making them much more cost-effective through catalyst development using nanoparticles and other approaches. In the original photocatalysis work of Fujishima and Honda [7] hydrogen production via water splitting took place at a  $TiO_2$ -coated anode in a twin cell [16], utilising a Pt cathode for the concomitant oxygen reduction reaction. A PEC employing aqueous formic acid as a substrate material was reported to produce electricity [17] along with the recovery of copper metal from solutions containing copper ions [18, 19]. However, because such work involved platinum electrodes these PECs cannot realistically be scaled up yet to apply them to field conditions.

The intention of this study was to investigate the fabrication and use of a relatively unsophisticated electrode and cell assembly using comparatively inexpensive materials to produce a novel PEC design. This design should be capable of being transferred from a laboratory sized apparatus by demonstrating the concept for the next step; a pilot plant scale device for exterior applications in the field. In this study, the photoelectrodegradation of selected

organic pollutants was investigated using various light sources and inexpensive materials. In a series of experiments a range of organic substrate species were deliberately chosen to represent different classes of compounds with widely varying photoreactivities. These species ranged from a simple carboxylic acid (formic acid containing no carbon–carbon bonds), to a multi-carbon alcohol (isopropanol or 2-propanol), to more complex compounds with unsaturated carbon-based rings (ascorbic acid and 1,2-dihydroxybenzene-also known as catechol). The process of employing a PEC to degrade organic compounds may be termed “underwater incineration” [20].

## 2 Experimental

The PEC consisted of a simple  $TiO_2$  nanoparticle-coated conducting ink anode and a manganese-containing air electrode which served as a cathode.

### 2.1 Anode preparation

Carbon ink (CI) electrodes were prepared by coating a projector acetate transparency with a graphite-based viscous polymer film ink (Electrodag 423 SS, Acheson). A cube applicator (75  $\mu m$ ) was used to spread the film on the sheet and it was then dried for 24 h at room temperature. Electrodes in the form of a flag of different areas were cut from the acetate sheet. Resistances of the CI electrodes were measured with a voltmeter (Mastech) and an average value of  $62 \pm 8 \Omega$  was obtained with a probe distance of 5 cm. After being dip coated with  $TiO_2$  from an organic suspension, conducting CI electrodes were found to yield an average value of  $75 \pm 10 \Omega$  at the same interprobe distance.

$TiO_2$  (Degussa P-25, BET specific surface area  $50 m^2 g^{-1}$ , 80% anatase, 20% rutile) suspensions ( $20 g dm^{-3}$ ) were prepared in 50:50 MeOH/THF, with 350 ppm of polyvinylchloride and the same quantity of poly(4-vinyl pyridine) added. Dried CI electrodes were dip coated in the organic suspension, with THF “softening” some of the ink thereby leaving nanoparticles of  $TiO_2$  embedded within the CI matrix. These exhibited good electrical conduction properties. Electrodes were left to dry overnight (16–20 h) at room temperature. The procedure was repeated three times resulting in the formation of three successive layers of embedded  $TiO_2$ . A blue color was observed on the surface of these coated electrodes. It is possible that this color may be due to the occurrence of photogenerated holes (arising from photoexcitation of the semiconductor). Migration into the underlying carbon could then take place leaving behind electrons on the  $TiO_2$  catalyst’s surface [21–23].

## 2.2 Air cathode manufacture

An air electrode (nominal area of 1.3 cm<sup>2</sup>) was used to catalyse the reduction of oxygen. This was fabricated from a sheet of MnO<sub>2</sub>/carbon paper/Ni mesh/Teflon dispersion (supplied by Electro-Chem-Technic) and was attached to the bottom of a 2-cm diameter × 10-cm long plastic tube to allow access of air. During the photodegradation experiments the air electrode was placed strategically at the solution/air interface. At this location an interaction of all three phases [24]—solid (MnO<sub>2</sub> on a Ni mesh), liquid (aqueous solution of 0.1 M KCl), and gas (atmospheric air) occurred. The air electrode assembly enabled a significant increase in the amount of oxygen available during the PEC reduction process. This represents a considerable enhancement in the oxygen supply level in comparison to dissolved oxygen levels.

## 2.3 Voltammetric characterisation experiments

Formic acid (FA) was used as a model pollutant since it is an intermediate found in the mineralization of many organic pollutants [25–27]. In addition its electrochemistry is well known [28–32]. For the investigation of the voltammetric response of FA in solution, TiO<sub>2</sub>-coated CI was used as the working electrode (1.0 cm<sup>2</sup> geometric surface area) in a three-electrode one-compartment cell configuration. The reference electrode was a saturated calomel electrode (SCE), with a platinum sheet serving as an auxiliary electrode (12 cm<sup>2</sup>). The potential was supplied by a computer-controlled potentiostat (CH Instruments, model 620A). For photoelectrochemical experiments the light source was a 150 W Xe arc lamp (Oriel model 6253 powered by an Oriel 69907 power supply). This source emitted strongly in the UV region and displayed sharp peaks at 467, 492, and 823 nm as determined by optical fiber spectroscopy (Ocean Optics software linked to CPU with P-100-2 UV/Vis 100 μm optical fiber linked to a USB2G15808 spectrometer).

## 2.4 PEC cell experiments

A single compartment cell containing an air electrode and a TiO<sub>2</sub>-coated CI anode (nominal surface area of 25 cm<sup>2</sup>) was utilised to make a PEC. A 1 kΩ resistor was connected between the anode and cathode and served as a load resistor through which currents were measured. Experiments were also conducted with an unconnected TiO<sub>2</sub>-coated CI anode exposed to the same light source. Finally control (blank) experiments were performed in which the solution alone was exposed to the incident light source.

A conventional tungsten incandescent standard household light bulb (60 W, emitting primarily in the visible and

infrared regions, λ-max of 633 nm) served as a light source for ascorbic acid (AA). A more powerful light source was used for 2-propanol (IPA) and 1,2-dihydroxybenzene (CAT) degradation. This was a 150 W Xe arc lamp (Oriel 6253). Low irradiance Dublin daylight (latitude 53°20' N) was used as the incident light source in a separate experiment to investigate the photodegradation of CAT. In that case, the PEC cell was placed on a window sill behind plate glass.

Photocurrent measurements were made using the one compartment cell with FA dissolved in aqueous 0.1 M KCl. A data acquisition system (Pico Technology) with an ADC 16 analog to digital converter was employed to measure the cell voltage and was measured for 500 s, with the data logger placed across the load resistance and converted to current using Ohm's law.

## 2.5 Kinetic experiments

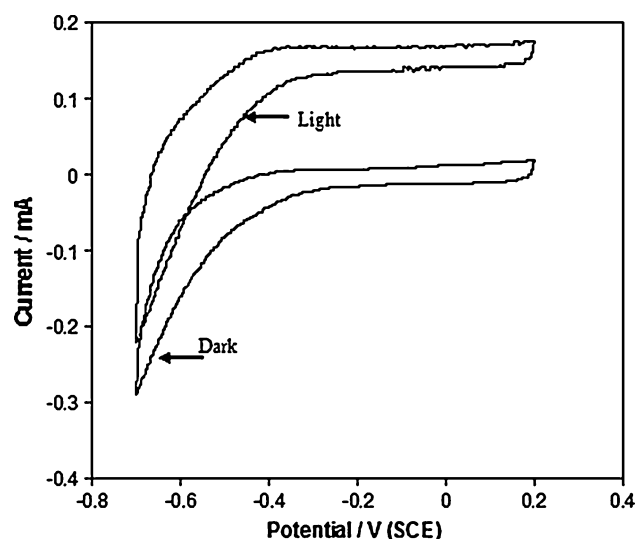
The rates of degradation of CAT and AA in PEC cells were determined by UV spectroscopy. Aliquots were removed with a Pasteur pipette at selected time intervals, then placed in a quartz cuvette and analysed with a Shimadzu UV-160 spectrometer within a wavelength range from 200 to 400 nm. The contents of each cuvette were returned to their respective cells after scanning thereby ensuring that the total solution volume remained constant throughout the period of the analysis. All PEC cells were stirred with a magnetic stirrer to ensure thorough mixing of solution components for the duration of each experiment.

Gas chromatography was performed using a Shimadzu GC-8A chromatograph linked to a Shimadzu Chromatopac C-R8A chart recorder. This technique was used to measure the change in concentration over time of IPA with 0.4 cm<sup>3</sup> aliquots taken from each cell. Each aliquot was added to 0.1 cm<sup>3</sup> of an internal standard (500 ppm 2-butanol) and 1 μL of the resulting solution was injected onto an OV-17 carbowax column in the chromatograph. All the compounds eluted in less than 7 min.

## 3 Results

### 3.1 Voltammetric characterisation of formic acid

The voltammogram obtained from FA at a TiO<sub>2</sub>-coated CI electrode in dark and light conditions is shown in Fig. 1. There is a clear difference between both. FA voltammetry in the dark yields little or no current, indicating that there is very little oxidation of FA at the underlying carbon-based electrode. This is in stark contrast to the distinctly higher current produced upon exposure to light. Upon



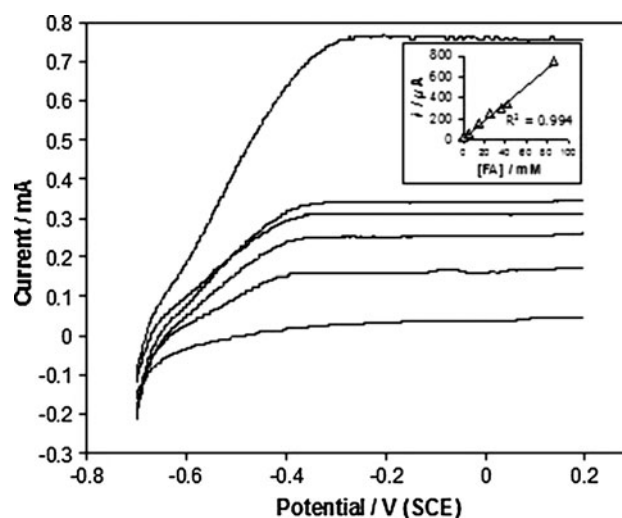
**Fig. 1** Cyclic voltammety of FA (16 mM in aqueous 0.1 M KCl) in dark and light (150 W Xe lamp) conditions cycled positively from  $-0.7$  to  $0.2$  V (SCE) at  $50$  mV/s. The working electrode is a  $\text{TiO}_2$ -coated CI electrode ( $25$  cm $^2$ )

exposure to light, current values reflect the rate at which photogenerated holes are captured by FA. Because of the large difference in current magnitudes between dark and light conditions, it is evident that FA oxidation depends on  $\text{TiO}_2$  photocatalysis. Thus on exposure to light, in the presence of  $\text{TiO}_2$ , FA is converted to a species that has a facile electrochemistry. For FA a steady state current is produced rather than a peaked output, because the oxidation is kinetically slow [33, 34]. The cathodic current at  $-0.7$  V (vs. SCE) is ascribed to  $\text{O}_2$  reduction.

There is a clear benefit in using such a simple method for production of anodes relative to other methods of catalyst deposition [35–42]. This system uses undoped  $\text{TiO}_2$  on an inexpensive carbon ink base with a cast solvent procedure and operates at room temperature. It does not involve thermal treatments such as calcination and yet still displays voltammetry similar to that found in the literature.

Figure 2 illustrates the dependence of the level photocurrent on FA concentration. It is evident from this that the steady state current increases together with FA concentration. Increased concentration of organic species (FA) leads to greater abstraction of photo-created holes from surface-bound  $\text{TiO}_2$ . Photocurrent increases with potential up to around  $-0.4$  V (vs. SCE), because at such low potentials the photocatalytic process is governed by electron transport within the  $\text{TiO}_2$  containing film [43].

Deviation from current/potential linearity at low concentrations of FA (e.g., at  $15$  mM) is probably due to competitive adsorption and subsequent photooxidation of water on the surface of the  $\text{TiO}_2$  nanoparticles. FA adsorbs onto  $\text{TiO}_2$  reasonably well because there is a saturated



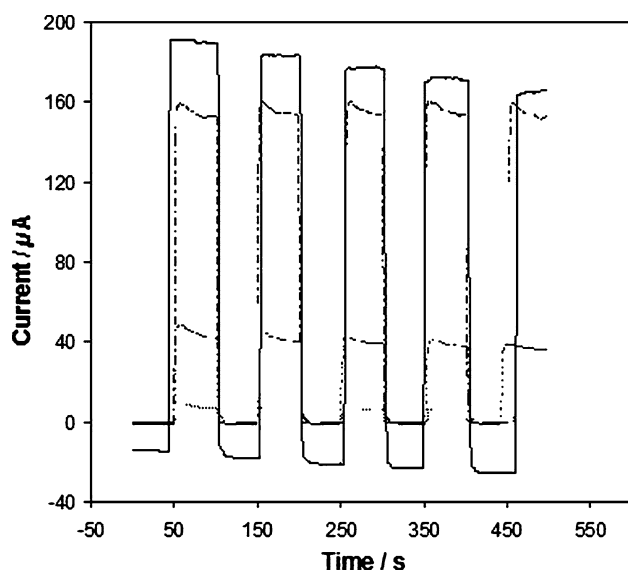
**Fig. 2** Linear sweep voltammety at a  $\text{TiO}_2$ -coated CI electrode (area =  $25$  cm $^2$ , swept at  $50$  mV/s) of aqueous  $0.1$  M KCl with incremental amounts of FA added with exposure to a  $150$  W Xe lamp. Photocurrent increases with FA concentrations of  $0$ ,  $15$ ,  $25$ ,  $36$ ,  $42$ , and  $85$  mM

photocurrent observed from photooxidation at a relatively low FA concentration.

The graph in the inset of Fig. 2 shows the resulting photocurrent plotted against FA concentration. Because the increase in photocurrent is linear at such low concentrations, it is clear that the presence and availability of FA at the  $\text{TiO}_2$  surface/electrolyte interface controls photooxidation rate. In contrast at concentrations larger than about  $0.1$  M, the current appears to reach a plateau, possibly due to mass transport or kinetic effects. Deviation from linearity at higher concentrations can also possibly occur as a result of products generated from FA photooxidation that may adsorb to the  $\text{TiO}_2$  surface.

The effect of concentration (dependence of photocurrent on substrate concentration) is further highlighted in Fig. 3, where photocurrent transients in a PEC cell are shown. In this case the  $\text{TiO}_2$ -coated CI electrode and the air cathode were both linked through a  $1$  k $\Omega$  load resistor. An instantaneous current response was found both in the presence and absence of light. At relatively high concentrations of FA ( $100$  mM), a negative dark current of around  $-15$   $\mu\text{A}$  was recorded while the current was found to be negligible for lower FA concentrations (generally only about  $-1$  or  $-2$   $\mu\text{A}$ ). As this current was recorded before the light was switched on, this indicates the existence of a dark reaction. In addition because its polarity is negative, it is believed to be due to FA consumption at the air electrode.

Upon exposure to light FA oxidation is limited at the  $\text{TiO}_2$ -coated anode at low concentrations. It can be seen in Fig. 3 that at high FA concentrations ( $100$  mM), the magnitude of photocurrent has levelled off. This may be due to the large anode/cathode ratio as the anode area is



**Fig. 3** In situ transient photocurrent-time profile in order of increasing concentrations (— = 0 mM, --- = 1 mM, - - = 10 mM, — = 100 mM) of aqueous FA in 0.1 M KCl on intermittent exposures to a 60 W tungsten lamp. 25 cm<sup>2</sup> TiO<sub>2</sub>/CI anode and 1.3 cm<sup>2</sup> air cathode were used. Current was collected for 500 s with a Pico technology ADC-16 data logger across a 1 kΩ resistor

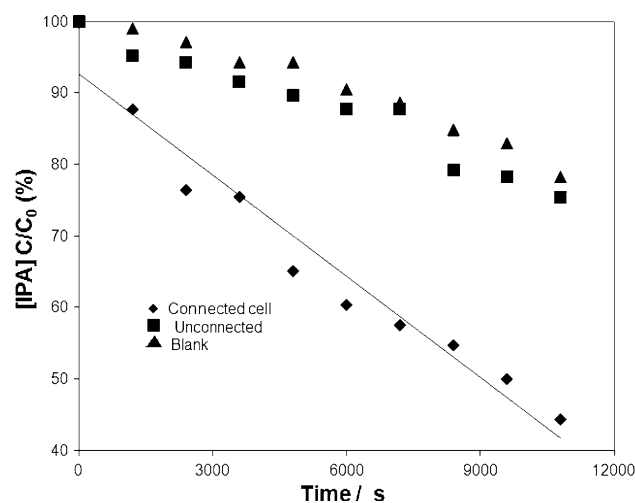
around 19 times bigger than that of the air electrode. There is simply not enough of the cathodic reaction occurring to drive the overall process.

### 3.2 Power of the cell

The power density of the cell with results presented in Fig. 3 for a 10 mM solution of aqueous FA in 0.1 M KCl electrolyte solution was measured with a voltmeter (Mastech). The photovoltage of the cell obtained upon exposure to a 60 W tungsten lamp was measured to be 0.337 V. This photovoltage was measured across a fixed load resistance of 1 kΩ. This allowed the current to be calculated via Ohm's law. With both current and potential known, the cell power was calculated to be  $19.1 \pm 2 \text{ mW m}^{-2}$ . In a similar experiment, the maximum power of the cell was calculated to be  $31.5 \pm 2 \text{ mW m}^{-2}$  using natural daylight at Dublin latitude of 53°20' north. These power values compare well to the values reported by Min et al. [3] whose Pt-containing MFC produced a power density of up to  $40 \text{ mW m}^{-2}$ .

#### 3.2.1 Degradation of IPA using a PEC cell

The range of photodegradable organics was extended from a simple carboxylic acid to a small alcohol molecule (IPA), and a kinetic study was carried out. Results from this are presented in Fig. 4. Three different situations were



**Fig. 4** Photodegradation of IPA (13.9 mM) in aqueous 0.1 M KCl over 3 h in a one compartment cell. The advantages of the PEC cell compared to the unconnected TiO<sub>2</sub>/CI electrode are evident. 25 cm<sup>2</sup> TiO<sub>2</sub>/CI anode and air cathode connected through a 1 kΩ resistor. Unconnected cell and blank are also included. Irradiated by a 150 W Xe lamp

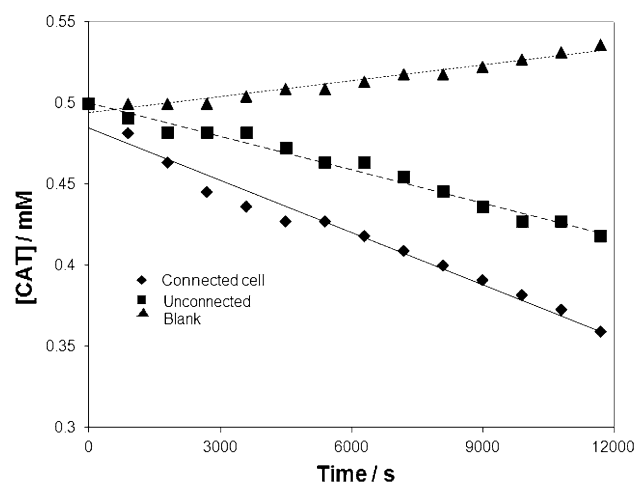
employed for IPA photodegradation and each was exposed to a 150 W Xe lamp. These were:

1. Connected: 25 cm<sup>2</sup> TiO<sub>2</sub>/CI anode and air cathode in an aqueous IPA solution linked through a 1 kΩ load resistor.
2. Unconnected: aqueous solution of IPA containing a single 25 cm<sup>2</sup> TiO<sub>2</sub>/CI electrode.
3. Blank: aqueous solution of IPA only. No electrodes were present in this case.

These three configurations were utilised for each organic compound photodegraded, with the exception of ascorbic acid. In this case an unconnected cell (no. 2 above) was not used. IPA degradation was successfully conducted via an irradiated surface confined TiO<sub>2</sub> coated on an electrode as part of a PEC cell. The kinetics appear to conform to a zero order reaction as can be seen in Fig. 4. A clear benefit in having the connected cell (i.e., a PEC with both connected anode and air cathode) also can be seen. Once the cell is connected the concentration of IPA dropped much more rapidly than if not connected. For both the unconnected cell and the blank sample, the decomposition is far less pronounced.

### 3.3 Degradation of CAT using a PEC cell

Some derivatized aromatics were degraded using semiconductor photocatalysis, made possible by strong binding of aromatic pollutants to TiO<sub>2</sub> (such as 1,2-dihydroxybenzene or catechol, CAT, shown in Fig. 5). Unlike the IPA photodegradation reaction presented in Fig. 4, where



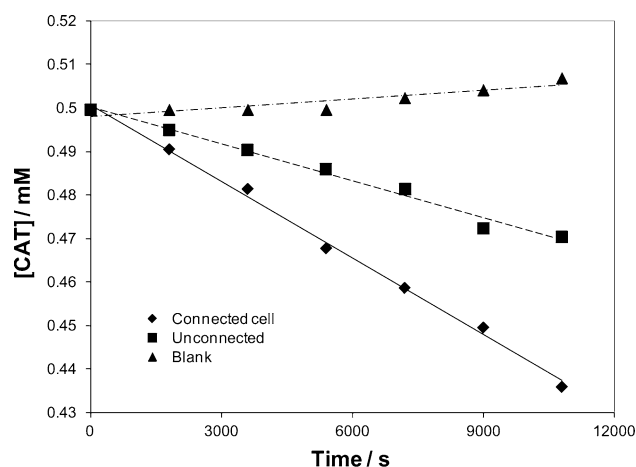
**Fig. 5** Photodegradation of CAT (0.5 mM) in aqueous 0.1 M KCl over 3.5 h. Irradiated by a 150 W Xe arc lamp in a PEC cell as in Fig. 4

the presence of irradiated  $\text{TiO}_2$  alone resulted in degradation of IPA, this is not the case for CAT. It is believed that CAT is much more stable to UV light and more resistant to simple open air oxidation. The absorbance at 275 nm decreases when the conjugation in the ring is broken. Absorbance for the control sample actually increased over time period, due to partial evaporation of the aqueous solution, thereby slightly increasing the concentration of CAT present in solution with time.

The results reveal that there is no breakdown for the blank, so it is evident that light from a 150 W Xe lamp cannot degrade CAT. This experiment was repeated using low irradiance daylight as the source (results are shown in Fig. 6).

It seems that the PEC cell/CAT system works both in low intensity daylight and when it is exposed to powerful UV sources. This is another indication of possible scale up and successful exterior use. When irradiated by daylight, for a 2.5 h exposure time, there is a modest 11% decrease in CAT concentration for the connected cell, while a 7% concentration decrease was observed for the unconnected cell within the same time frame. Using a UV light source (Fig. 5), over a period of 2.5 h, a CAT concentration decrease of 22% was found. In the same time period when using daylight (Fig. 6) a decrease in CAT concentration occurred from 55 to 49 ppm (11%).

The experiment featured in Fig. 6 was left run and sampled for a further week. Interestingly, there was no further breakdown after 4 days, possibly because all of the sites on the  $\text{TiO}_2$  electrode were used up at that stage. A brown colored product emanating from CAT photoelectrodegradation was adsorbed onto the  $\text{TiO}_2$  electrode surface. In a scaled up system, the current produced could be stored and subsequently used to clean the fouled electrodes



**Fig. 6** Degradation of CAT (0.5 mM) in aqueous 0.1 M KCl.  $\text{TiO}_2$ -coated CI electrode is the anode ( $25 \text{ cm}^2$ ) while an air cathode was used. Irradiated by daylight for 3 h. It is shown that the PEC cell can work competently with low irradiance

possibly through a capacitive discharge process. This presents a possible use for current produced during photo-degradation of organic species in aqueous solutions.

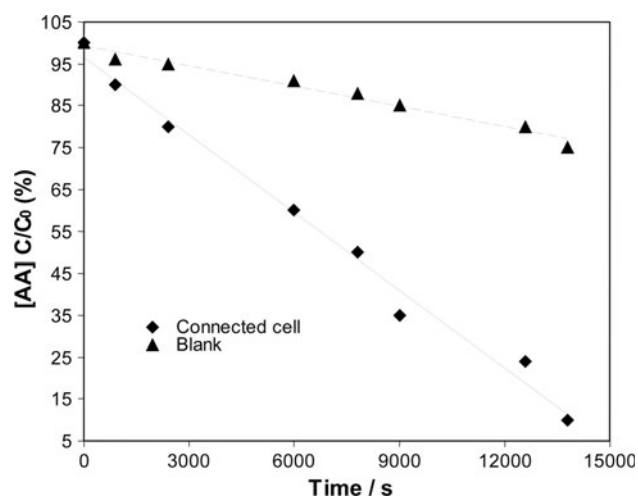
Incomplete mineralisation or partial degradation of CAT could lead to the formation of several other organic species, such as 1,2-benzenedione. Oxidation reactions of a similar molecule, phenol were found to yield ring opening products like maleic, formic, acetic, oxalic, malonic, succinic, and fumaric acids. These occurred not only on the electrode, but also in the liquid or solution phase [44].

### 3.4 Degradation of AA using a PEC cell

Ascorbic acid absorbs UV light (like CAT) enabling its degradation to be monitored using UV absorption. This was advantageous, allowing fast accurate readings to be taken with little preparation time.

Over a 4-h period ascorbic acid concentration was found to steadily decrease as a function of time when in a connected PEC cell exposed to a light source (Fig. 7). A blank aqueous ascorbic acid solution (also 10 ppm) was also used to assess the degradation taking place under ambient conditions. The linear decrease in concentration with respect to time indicates zero order degradation in agreement with the other results obtained in this study. This is also in good agreement with literature reports involving surface confined  $\text{TiO}_2$  [45]. Results presented in Fig. 7 indicate that while AA is known to be quite prone to open air oxidation [46], the PEC cell greatly accelerates this process. The zero order slopes of Figs. 4, 5, 6, and 7 were calculated over a 3-h period, and the results are presented in Table 1.

Light sources used in this work included a UV intense 150 W Xe arc light, natural daylight and an incandescent tungsten 60 W lamp. IPA photodegrades in a connected



**Fig. 7** Degradation of AA (60 μM) in aqueous 0.1 M KCl. 60 W tungsten household lightbulb was the light source. PEC cell as in Fig. 3. For the PEC cell there is almost complete photodegradation of organic within 4 h

cell at a rate of 80 nM/s when irradiated by a 150 W Xe lamp; but CAT degrades at around 12 nM/s under identical conditions.

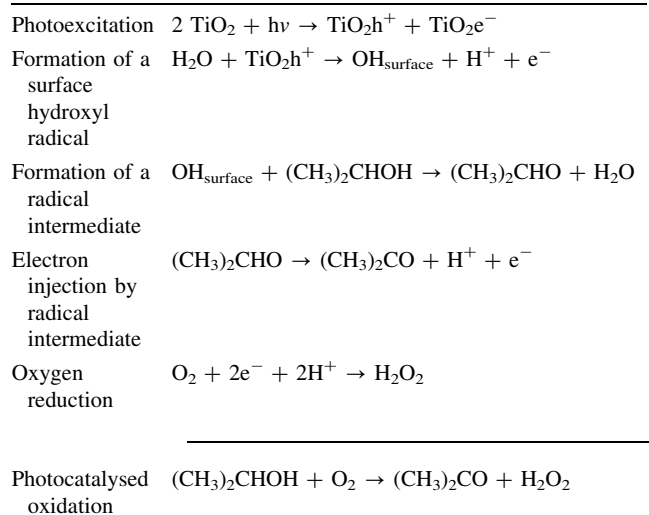
#### 4 Discussion

While it is unusual to see photodegradation of organic compounds using pure semiconductors, absorbing solely visible light, the result achieved in Fig. 7 can be explained. TiO<sub>2</sub> has three main crystal forms including brookite, but the most common two are anatase and rutile. Anatase is the most photoactive form. The band gap (or potential difference between the two band edges) for anatase is 3.2 eV, corresponding to a cut off of 388 nm. Rutile has a band gap of 3.0 eV corresponding to 412 nm, and therefore is partially visible light active. But for the most part, TiO<sub>2</sub> needs to absorb UV light to be an efficient photocatalyst. For optimum results, a mixture of the two crystal forms is desirable, as this can help trap photogenerated electrons and allow the majority carriers (holes) to attack electron

rich compounds. The anatase to rutile morphology ratio of 4:1 makes Degussa P-25 a very useful photocatalyst which is widely used in photocatalytic research.

Photogenerated charge carriers (electrons and holes) must either be injected into or be captured by the organic substrate to keep the photodegradation reaction in full flow and to avoid competition from the recombination reaction. When dealing with aqueous solutions, it is possible that organic species (pollutant) degradation happens as a result of attack by hydroxyl radicals, provided that water binds well to TiO<sub>2</sub> nanoparticles. As long as there is sufficient charge separation, the concentration of hydroxyl radicals on the TiO<sub>2</sub> surface is directly proportional to the intensity of the incident light source. This explains the superior degradation of the organic compounds (including pollutants) used in this study when TiO<sub>2</sub> was irradiated by a 150 W Xe lamp (Table 1) relative to other sources (which contain significantly less UV light).

Li et al. [47] proposed a mechanism for IPA oxidation and subsequent acetone production.



Currents in Fig. 3 were ascribed to a normal Faradaic PEC response resulting from the photoelimination of FA adsorbed onto TiO<sub>2</sub>, as the time scale was significantly

**Table 1** Zero order rate constants in nM/s

Substrates	Initial concentration/mM	Light source	Rate PEC A	Rate B	Rate C	$t_{1/2}/\text{s}$	$\sim t_{1/2}/\text{h}$
IPA	1.76	150 W Xe	80.2	39.8	35.2	$1.1 \times 10^4$	3
CAT	0.50	150 W Xe	12.0	6.8	-3.4	$2.1 \times 10^4$	6
CAT	0.50	Daylight	5.6	2.8	-0.9	$4.5 \times 10^4$	12
AA	0.06	W 60 W	3.7	N/A	1.0	$0.8 \times 10^4$	2

PEC A was a connected PEC cell, B was an unconnected TiO<sub>2</sub>-coated CI electrode while C was a control. Half lives in seconds ( $t_{1/2}$ ) are listed for PEC A, and these are then approximated to hours



larger than that expected from double layer charging. The degradation achieved in Fig. 7 can be due to the very small percentage of UV light present in a standard household light bulb (as measured by fiber optic spectroscopy), with TiO<sub>2</sub> absorbing these wavelengths. This small amount of UV present (perhaps less than 5%) is significant, as it is sufficient to activate a photocatalytic process on a TiO<sub>2</sub> surface. In addition, TiO<sub>2</sub> in contact with carbon ink may change its band edge potentials, and therefore alter its bandgap slightly. Support for this was provided by the appearance of a blue tinge scattered across the TiO<sub>2</sub>-coated electrode surface, possibly indicating the presence of excess electrons [21–23].

## 5 Conclusion

The occurrence of photocatalysed decomposition of a range of organic species in PEC cells using a variety of light sources and non precious metal-based electrodes was demonstrated in this communication. Organic species ranging from a simple one carbon carboxylic acid, to a compound such as ascorbic acid, an aliphatic alcohol and a benzene ring compound were examined and displayed a wide range of photoreactivities. This has allowed for the application of PEC technique to study the effects of cell configuration on photocatalytic decomposition of organic compounds. Zero order kinetics was found to occur for the photodegradation of all substrates (organic species) examined in this communication. For optimum pollutant degradation, there was a clear advantage in having a connected cell (TiO<sub>2</sub>-bearing CI anode a Mn-containing air electrode) over results achieved via an unconnected TiO<sub>2</sub>-coated CI electrode. We have demonstrated that power levels similar to those obtained by a MFC are possible, with daylight as the light source. This has obvious potential for use of the PEC system outdoors in the form of a scaled up system, using daylight as the incident light source. Because of an inherent resistance in both electrodes, it would be realistic to envisage many cells being connected together if scaling up the PEC for outdoor applications were to occur.

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## References

- Sheng Lin H, Chuen Wang S (2004) *J Hazard Mater* 106B:161
- Harrison DP, Valsaraj KT, Wetzal DM (1993) *Waste Manag* 13:417
- Min B, Cheng S, Logan BE (2005) *Water Res* 39:1675
- Oh SE, Logan BE (2005) *Water Res* 39:4673
- Min B, Kim JR, Oh SE, Regan JM, Logan BE (2005) *Water Res* 39:4961
- Logan BE, Murano C, Scott K, Gray ND, Head IM (2005) *Water Res* 39:942
- Fujishima A, Honda K (1972) *Nature* 238:37
- Frank SN, Bard AJ (1977) *J Am Chem Soc* 99:4667
- Frank SN, Bard AJ (1977) *J Am Chem Soc* 99:303
- Frank SN, Bard AJ (1977) *J Phys Chem* 81:1484
- Kaneko M, Nemoto J, Ueno H, Gokan N, Ohnuki K, Horikawa M, Saito R, Shibata T (2006) *Electrochem Commun* 8:336
- Kaneko M, Ueno H, Ohnuki K, Horikawa M, Saito R, Nemoto J (2007) *Biosens Bioelectron* 23:140
- Hirano K, Suzuki E, Ishikawa A, Moroi T, Shiroishi H, Kaneko M (2000) *J Photochem Photobiol A Chem* 136:157
- Kaneko M, Hoshi T, Kaburagi Y, Ueno H (2004) *J Electroanal Chem* 572:21
- Nemoto J, Sakata M, Hoshi T, Ueno H, Kaneko M (2007) *J Electroanal Chem* 599:23
- Dholam R, Patel N, Adami M, Miotello A (2008) *Int J Hydrogen Energy* 33:6896
- Canterino M, Di Somma I, Marotta R, Andreatti R, Caprio V (2009) *Water Res* 43:2710
- Byrne JA, Eggins BR, Byers W, Brown NMD (1999) *Appl Catal B Environ* 20:L85
- Byrne JA, Davidson A, Dunlop PSM, Eggins BR (2002) *J Photochem Photobiol A Chem* 148:365
- Enright P (2009) PhD thesis, Dublin Institute of Technology
- Serpone N, Texier I, Emeline AV, Pichat P, Hidaka H, Zhao J (2000) *J Photochem Photobiol A Chem* 136:145
- Rothenberger G, Fitzmaurice D, Grätzel M (1992) *J Phys Chem* 96:5983
- Hagfeldt A, Grätzel M (1995) *Chem Rev* 95:49
- Verma A, Basu S (2005) *J Power Sources* 145:282
- Dinsdale RM, Hawkes FR, Hawkes DL (2000) *Water Res* 34:2433
- Chou S, Huang YH, Lee SN, Huang GH, Huang C (1998) *Water Res* 33:751
- Davis AP, Green DL (1999) *Environ Sci Technol* 33:609
- Ferrer JE, Victori LI (1993) *Electrochim Acta* 38:1631
- Lović JD, Tripković AV, Gojković SLj, Popović KDj, Tripković DV, Olszewski P, Kowal A (2005) *J Electroanal Chem* 581:294
- Jovanović VM, Tripković D, Tripković A, Kowal A, Stoch J (2005) *Electrochem Commun* 7:1039
- Xuguang Li, Hsing I-Ming (2006) *Electrochim Acta* 51:3477
- Wang Xin, Ji-Ming Hu, Hsing I-Ming (2004) *J Electroanal Chem* 562:73
- Macia MD, Herrero E, Feliu JM (2003) *J Electroanal Chem* 554:25
- Tian M, Conway BE (2005) *J Electroanal Chem* 581:176
- Seery MK, George R, Floris P, Pillai SC (2007) *J Photochem Photobiol A Chem* 189:258
- Koelsch M, Cassaignon S, Ta Thanh Minh C, Guillemoles JF, Jolivet JP (2004) *Thin Solid Films* 451:86
- Chung-Chieh C, Chung-Kwei L, Chih-Chieh C, Chao-Sheng H, Chin-Yi C (2006) *Thin Solid Films* 494:274
- Tryba B, Morawski AW, Inagaki M, Toyoda M (2006) *Appl Catal B Environ* 63:215
- Balasubramanian G, Dionysiou D, Suidan MT, Baudin I, Laine J-M (2004) *Appl Catal B Environ* 47:73
- Joon-Chui L, Moon-Sun K, Byung-Woo K (2002) *Water Res* 36:1776
- Vinodgopal K, Hotchandani S, Kamat PV (1993) *J Phys Chem* 97:9040

42. Byrne JA, Eiggins BR, Brown NMD, McKinney B, Rouse M (1998) *Appl Catal B Environ* 17:25
43. Plieth W (2008) Oxides and semiconductors. In: *Electrochemistry for materials science*, 1st edn. Elsevier, Amsterdam, p268
44. Santos A, Yustos P, Quintanilla A, Rodriguez S, Garcia-Ochoa F (2002) *Appl Catal B Environ* 39:97
45. Duffy EF, Al Touati F, Kehoe SC, McLoughlin OA, Gill LW, Gernjak W, Oller I, Maldonado MI, Malato S, Cassidy J, Reed RH, McGuigan KG (2004) *Sol Energy* 77:649
46. O'Connell PJ, Gormally C, Pravda M, Guilbault G (2001) *Anal Chim Acta* 431:239
47. Li J, Peter LM, Potter R (1983) *J Appl Electrochem* 14:495