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The photoelectrochemistry of platinum phthalocyanine films in aqueous media

Abstract Platinum phthalocyanine (PtPc) films applied to glassy carbon (GC) and platinum surfaces have been shown to exhibit complex photoelectrochemistry in aqueous media, acting as an n-type semi-conducting material. Using chopped polychromatic radiation and a lock-in amplifier to detect the modulated photocurrent, photo-responses were measured for PtPc films on GC in a variety of background electrolytes. In all instances the photo-responses were anodic over the voltage ranges used. Two peaks were seen in each sweep direction for the experiments performed in sulfuric acid and sodium hydroxide solutions. The origin of the photocurrent has been ascribed to the photo-oxidation of water in the electrolyte by positive holes produced under illumination, which accumulate at the PtPc/electrolyte interface. Photocurrent transients were also recorded and indicated some recombination of excitons within the system.

Keywords Photoelectrochemistry · Voltammetry of microparticles · Platinum phthalocyanine

Introduction

Phthalocyanines (Pcs) show quite high photo-conductivities which has interested many researchers for several decades [1]. In particular Pcs have been used as charge generation materials in organic photoreceptors and as optical sensors [2], photovoltaic devices [3], in photocopying and gas sensing [4]. For these applications, in

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particular, knowledge of the rate of response is essential. It is for these reasons that the majority of attention in the literature has been to measuring the transient response of Pc particles and films to illumination.

Minami [5] has recorded photocurrent spectra for several thin film phthalocyanines in the visible and near infrared regions. Oekermann et al. [6] have investigated the role of surface states in the time resolved photocurrent spectroscopy of ZnPc and related materials and found that the number of surface states increased with exposure to air. Similar studies of thin phthalocyanine films have been made by Chau [7] and co-workers who have measured the absorption spectra and photocurrent spectra of group III phthalocyanine chlorides. These group III phthalocyanines were also investigated by Buttner et al. [8] who reported photocurrent against wavelength spectra and additionally measured photocurrent transient profiles. A study of the group III phthalocyanines in vacuo and in the presence of oxygen and nitrogen dioxide by Couves et al. [9] showed that the photocurrent rise and decay kinetics owed a strong dependence to the molecular ordering of the films. Additionally it was shown that the presence of nitrogen dioxide, and to a lesser extent oxygen, increased the conductivity and photoconductivity of the films. Bahra et al. [1] investigated the rise and decay kinetics of photoconductivity for copper, lead and chloro-aluminium phthalocyanine. Tanaka [10] and Twarowski [11] have used thin copper and zinc phthalocyanine films respectively sandwiched directly between two electrodes to investigate the effect of electric field on the photocurrent characteristics of the phthalocyanine films. Both investigations showed a minimum of modulated photocurrent at the equilibrium point of the photovoltage and the applied voltage.

Throughout the literature there has been almost no attention paid to the study of photocurrent intensity from phthalocyanines against applied potential in an electrochemical regime (rather that against electric field in a dry sandwich cell). However, Hamnett et al. [12] have investigated the photocurrent response from

200-nm PtPc films on 40-nm gold sputtered graphite surfaces. Their studies, conducted in de-oxygenated 1 mol/l NaOH solution, show, as expected for an n-type semiconductor, a basically anodic photo-response. In oxygen saturated and stirred oxygen saturated solution environments an almost completely cathodic photocurrent is observed. It is stated that the positive holes produced under illumination are insufficiently energetic to oxidise water and build up in the interfacial region until the electric field strength is reduced to the point at which no further exciton dissociation can occur.

The phthalocyanine films under study here bear better comparison to the photoelectrochemistry of dichalcogenides, on which there is much study in the literature. Dichalcogenides, the disulfides and diselenides of the transition metals, are well known in the literature for their photoelectrochemical and semi-conducting properties [13, 14]. These compounds usually possess band gaps between 1 and 2 eV. In most cases the transition metal is sandwiched between monolayers of sulphur (selenium or tellurium) and these (S-M-S) layers are arranged into stacks which are held together by van der Waals forces. Having created excited states the real interest lies in how they are discharged and dissipated. This depends on the material in question and the applied potential. The experimental fact that a photoelectrochemical reaction involving holes in an energy band derived from d-states, in contrast to p-bands, (Group VI and VIII n-type semiconductor dichalcogenides), permits charge transfer from OH- ions and water is a very interesting and promising result. However the dissipation of holes via water reduction to oxygen is only seen to a significant extent with PtS_2 [15] and normally the photo-anodic product is a sulfate or selenate and resulting photo-degradation. The production of a sulfate or selenate from these compounds is thermodynamically more favourable that the reduction of water and will occur unless kinetically inhibited. Indeed sufficient inhibition occurs in the case of PtS_2 since positive platinum ions cannot leave the surface and the dichalcogenide does not gradually dissolve. Additionally the completely different behaviour of PtS_2 to the crystallographically identical ZrS_2 leaves little doubt that the d-band character of PtS_2, as well as the ability of platinum to increase both oxidation state and co-ordination number at the electrode surface, is responsible for its ability to evolve oxygen during illumination.

Tributsch [14, 16] has thoroughly probed the photoelectrochemical behaviour of a range of transition metal dichalcogenides. For PtS_2, the closest analogue in structure and photoelectrochemical behaviour to PtPc, he observes that the photocurrents across a PtS_2 interface shift in the presence of redox systems and this shift appears to be approximately systematic with the change in redox potential [17]. For electrolytes lacking an additional redox couple in solution the photocurrent will show a peak at the redox potential for the O_2/H_2O couple with the photocurrent dropping off either side of the potential as charge exchange becomes less favourable as the energy gaps between the involved solid and solution states widen. It follows then that as the pH of the electrolyte is changed so the redox potential of the O_2/H_2O couple will shift and the photocurrent peak will occur at different potentials [18].

We present in this paper a novel, important, unusual and extremely interesting new addition to the study of photoelectrochemistry of semiconductor thin films. This work is of particular relevance to the application of phthalocyanine materials to photoelectrochemical cells.
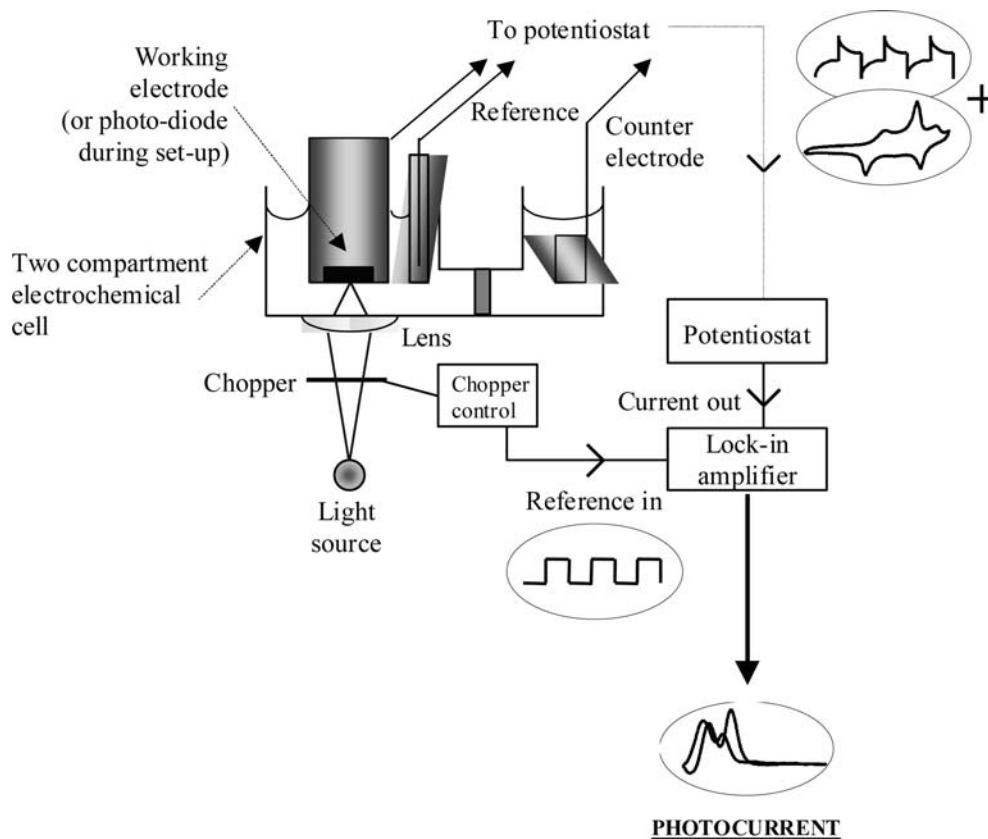
Experimental

Electrochemical experiments were performed using an EcoChemie AUTOLAB PGSTAT30 potentiostat. A standard three electrode arrangement was employed using glassy carbon (GC) or platinum working electrode (0.2 cm^2), a large area platinum flag counter electrode and a saturated calomel electrode (SCE) as a reference, in a two-compartment cell with a glass sinter separating working and counter electrode compartments. PtPc was prepared as described previously [19] and applied to the electrodes using the well-established mechanical abrasion technique [20] (a review of the techniques is available [21]). All solutions were saturated either with argon (>99.9%) or oxygen (>99.9%) by bubbling the appropriate gas though the solution for 30 min prior to each experiment and keeping a positive pressure above the solution during experiments. A schematic representation of the experimental set-up is shown in Fig. 1.

The current output of the potentiostat was fed into a Stanford SR460 lock-in amplifier along with the reference channel from the chopper. A broad-band polychromatic light source was employed and this radiation was symmetrically modulated usually at a frequency of 222 Hz (however other frequencies were employed) during experiments but it was determined that the frequency of chopping had no discernible effect on the dynamic photocurrent response. It is desirable to have as high a chopping speed as possible in order to minimise noise, obtain a more stable signal and extract maximum detail from the photocurrent against potential response. After slight focusing of the light the power density incident upon the PtPc-GC surface was approximately 60 mW/cm^2 although there was some variation of this figure between experiments. The lock-in amplifier was pre-adjusted to the correct phase by replacing the working electrode with a photodiode and feeding the photodiode signal directly to the lock-in amplifier where the phase of the response was determined prior to the commencement of experiments. The output of the lock-in amplifier thus represented the modulated photocurrent. The time constant employed on the lock-in amplifier was usually 1 s for experiments. This time constant represented the best compromise between rapid response to changes in photocurrent and minimisation of noise on the signal. Other time constants were used occasionally. Furthermore, with these considerations in

Fig. 1 Schematic representation of the experimental set-up used for photo-electrochemical experiments

mind, the sweep rate used for the experiments was mostly 10 mV/s. This relatively low sweep rate allowed a longer time constant to be used on the lock-in amplifier (1 s) in order to achieve the optimum signal to noise ratio. This sweep rate was also about the lowest that could be employed consistent with achieving quasi-reversible electrochemistry characteristic of the system under study. The modulated photocurrent signal was fed back into the PGSTAT20 via the analogue to digital converter module so both the electrochemical and photoelectrochemical responses could be displayed concurrently against potential. Photocurrent transients were measured using the same electrochemical cell and light source but employing a battery powered potentiostat and sweep generator (to reduce noise), both of in-house

construction, and capturing the responses on a Tektronix TDS 220 digital oscilloscope and compiling the data using Wavestar software. Lower chopping speeds were employed for these transients measurements so there was enough time for the system to establish a steady state photocurrent response before illumination was interrupted.

Results and discussion

Firstly it is important to establish that no photoelectrochemical responses above the noise from the lock-in amplifier were observed from bare GC under illumination or, as shown in Fig. 2, from PtPc on GC in the

Fig. 2 Photoelectrochemical (*continuous lines*) and current response (*dashed lines*) against potential for a PtPc film on GC in 0.2 mol/l sulfuric acid in the dark. Scan rate, 10 mV/s
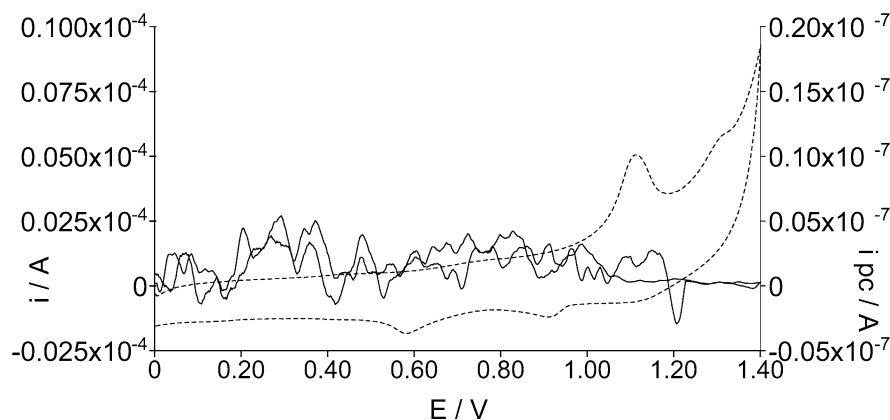
dark. This unequivocally shows that the photoelectrochemical response is due to the illumination of the PtPc film. It is important that this point is established since bare, highly oriented pyrolytic graphite (HOPG) and GC surfaces have been shown to exhibit small electrochemically generated photocurrent responses [22, 23, 24].

The electrochemistry of platinum phthalocyanine films in aqueous media has been described previously [20]. The photoelectrochemical response of the PtPc films with potential was unexpected and showed substantial development with repetitive scanning, similar to the electrochemical response. An example of the photoelectrochemical response and its development is shown in Fig. 3.

There are several important features to note from Fig. 3. First, the response is totally anodic suggesting strongly that the PtPc film is acting as an n-type semiconductor. This hypothesis is strongly supported by the observation of the coincidence of the absorption spectrum of identical PtPc films [19] with the observed PtPc photocurrent spectrum. The only point at which the photocurrent dips into a cathodic regime is briefly, just after 0 V on the anodic sweep. The cathodic current response is not significant but the crossover point from cathodic to anodic photocurrent behaviour is thought to occur near the flat-band potential (see later). Second, there is a first scan discrepancy in the photoelectrochemical behaviour analogously to that seen with the electrochemical behaviour. Interestingly, a large photoelectrochemical response is seen on the first scan before any electrochemical behaviour has occurred and the film has not become irreversible intercalated with electrolyte, i.e. before the threshold potential has been reached on the first scan. In this way it is possible that the development of the photoelectrochemical response is governed by the structural changes occurring within the film during redox cycling. On the first scan just one anodic peak is seen on the positive scan whilst on the reverse scan almost no photoelectrochemical activity is seen. The second scan then shows a large anodic photocurrent

with a small second peak and two clear peaks on the reverse scan. The third and subsequent scans show two peaks on the positive and reverse scans. The fully developed photoelectrochemical response is shown in Fig. 4.

It is necessary to point out at this stage that once again the presence of oxygen in the electrolyte solution had no discernible effect on the photoelectrochemical response. This may be a result of the PtPc's exposure to air for long periods before use and hence was oxygen saturated regardless of the composition of the electrolyte solution. Hamnett et al. [12] have observed that oxygen saturated electrolyte did have an effect on the photoelectrochemical response observed from their PtPc films, superimposing a second cathodic response on the anodic photocurrent by capturing an exciton in the following manner:

$$(e_{cb}^-, p_{vb}^+) + O_2(aq) = O_2^-(aq) + p_{vb}^+$$
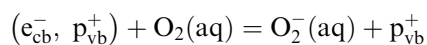
where e^-_{cb}, p^+_{vb} represent the conduction band electron and valence band positive hole, respectively, produced as the result of exciton formation within the material under illumination.

Figure 4 shows there is no photoelectrochemical activity from the film in its oxidised state. Clearly the photocurrent drops to zero at about 0.65 V just as the first oxidation peak occurs. Similarly and more significantly the photocurrent does not exhibit a non-zero response again until after the final reduction peak has been passed at about 0.5 V on the reverse scan. It seems that the oxidation of the film suppresses the photocurrent completely and exciton formation is not possible in a positively charged film. Such behaviour suggests that the removal of electron density from the film, although probably initially centred at individual phthalocyanine moieties, can be considered as a universally, film-wide delocalised process. This is a good explanation for the observed behaviour although the observed response may have more to do with the external redox process mediating the photocurrent and the dissipation of positive holes at the electrode/electrolyte interface. Once the

Fig. 3 Photocurrent response with potential for a PtPc layer applied by mechanical abrasion to a glassy carbon substrate in 0.2 mol/l sulfuric acid. Scan 1 to 10, 10 mV/s
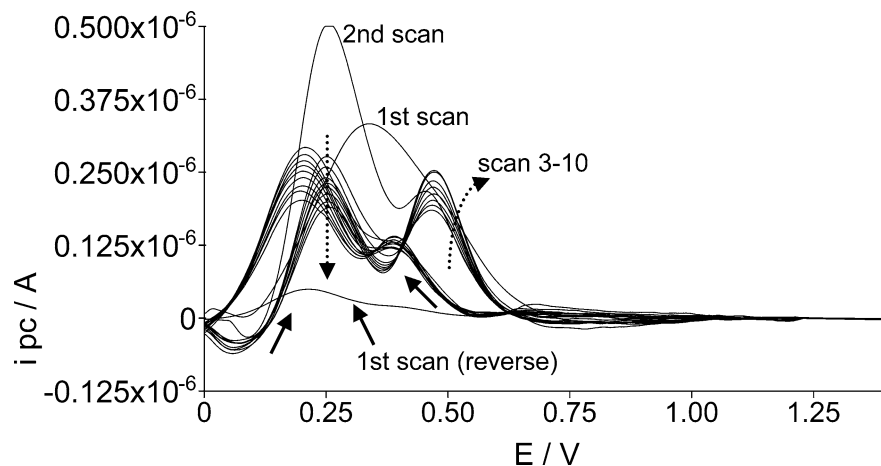
Fig. 4 Photocurrent (*continuous lines*) with peak assignments and current response (*dashed lines*) against potential for a PtPc layer deposited by mechanical abrasion on GC in 0.2 mol/l sulfuric acid. 10th scan, 10 mV/s
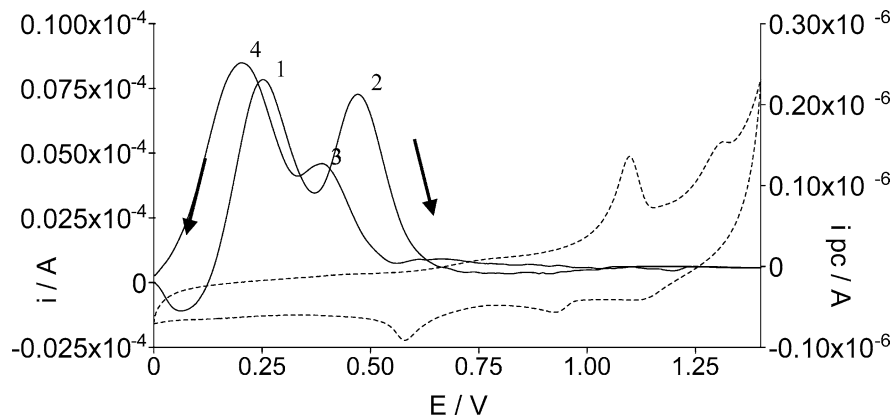
developed photoelectrochemical response has been obtained there is still some movement in the peak heights. Peak 1 shows a steady decrease in intensity whilst peak 2 shows an increase with repetitive scanning. On the reverse scan peak 3 shows a steady increase with cycling whilst peak 4 shows a steady decrease.

An explanation of the processes occurring to produce the observed photoelectrochemical response is proffered. The excitation occurring is assumed to be a HOMO-LUMO, π-π^* transition equivalent to the Q-band transition in a UV-VIS spectrum at around 700 nm. Evidence for this is derived from the observation of no photocurrent if a blue glass filter is placed in front of the light source since only light between about 500 nm and the glass cut-off frequency at 350 nm will be allowed to illuminate the electrode. Since the experiments are all conducted will a glass cell bottom between the light source and the electrode the opaqueness of glass below 350 nm eliminates the possibility of Soret band absorption within the phthalocyanine film, thus the effect of this transition on the photoelectrochemistry of the system is unknown. The PtPc is behaving as an n-type semiconductor and on formation of the exciton electrons move towards the GC substrate whilst the minority carrier, the positive hole, will move to and accumulate at the PtPc-electrolyte interface. The nature of the application of the PtPc film results in a disordered, porous film where many different PtPc-electrolyte interfaces in different environments throughout the film, not just at the uppermost surface, may be considered. What happens next is of some dispute in the literature. Hamnett et al. [12] proposed that for their PtPc films holes at the interface but were not sufficiently energetic to oxidise water and thus built up at the surface to the point where the electric field was reduced to extent that no further dissociation could occur. The anodic photo-current response was thus thought to be highly transient. The photocurrent transient (see later) suggests that there is some recombination occurring within the system but the photocurrent response is not as short lived as might be expected if holes were not dissipated in some manner.

It is proposed that in this system holes are lost in the photo-oxidation of either water or another species present in solution. This has been previously suggested in the literature [17, 25, 26, 27]. It is also noted that whilst some dichalcogenides undergo photo-corrosion (FeS_2) others oxidise water with no corrosion (RuS_2, PtS_2) although their physical and electronic structures are directly comparable [28]. Thus the results presented here are not inconsistent with a photoelectrochemical mechanism involving the oxidation of electrolyte.

Explaining the shape of the dynamic photocurrent responses is not an easy task and one that is only attempted qualitatively from this study. The onset and broad shape of the response is thought to be governed by redox species or, more specifically here, electron donors in solution. The onset of the photocurrent will occur when the edge of the PtPc valence band reaches the electronic distribution curve of the electron donor in solution. It is then that electron transfer may occur and thus a photo-response may be observed. This assumes, of course, that the PtPc is not oxidised. This is unlikely since Pt is not readily liberated as a cation [17] and it would be difficult to imagine a reduced phthalocyanine ring under such circumstances. The photocurrent will increase until the Fermi level of the PtPc and the redox solution species are equal after which time the photo-current response will decrease. The model discussed here relies on no band bending occurring in the potential range under consideration. This is probably not the case but is a workable simplification in understanding the behaviour of the system.

It must be noted that photo-effects at n-type semi-conductors are not expected to be observed for redox couples which are positioned at potentials negative of the flat-band potential. Under these circumstances the bands would be bend down and the majority charge carrier (here the electron) would accumulate at the surface and the behaviour moves from that of semi-conductor to inert metal. In the absence of any other suitable redox couple in reasonable concentration the reaction occurring to liberate holes at the PtPc-electrolyte interface will be the oxidation of water to oxygen. The O_2/H_2O couple will change its redox potential depending on the pH of the electrolyte and this would explain the change in the peak potentials of the photo-responses in acid and alkali media encountered with various electrolytes. The peak potentials are in good

agreement with those seen in acid and alkali media for platinum disulfide [17]. However what was not observed in Tributsch's study [17] was a total absence of photocurrent at potentials significantly more positive than the equilibrium potential for the redox probe under consideration. It is proposed here that the other factor to be considered is the oxidation state of the PtPc. After about 0.7 V and the onset of the first PtPc oxidation wave the PtPc$^+$ moiety is now not amenable to exciton formation at these potentials and the photocurrent drops rapidly to zero. It is also suggested here that the absence of a photocurrent below 0 V but positive of the sulfate desorption peak is probably because the potential is now well below the flat-band potential of the PtPc (which has been determined roughly from Mott-Schottky plots to be −0.05 V).

The characteristics of the photoelectrochemical response off platinum are similar to those described above for PtPc layers on GC. The most interesting feature of the behaviour of PtPc on platinum under illumination is the development of the electrochemical response and the evidence it provides in proving that the build up of positive holes in surface states is energetic enough to oxidise water. The electrochemical and photoelectrochemical response of a PtPc layer on Pt is shown below (Fig. 5).

The photoelectrochemical response shows a very sharp peak on the forward scan and almost no response on the reverse scan similar to the behaviour of a gold substrate. The electrochemical response of the platinum at potentials positive of 0.5 V for the five consecutive scans is almost concurrent whilst the current response below 0.5 V shows a drop with continuous scanning. This was observed even though the experiment was performed in rigorously deoxygenated solution with an argon positive pressure maintained over the electrolyte surface. The appearance of the platinum electrochemistry is not as well defined as one might expect for three reasons. First, the presence of the PtPc layer is known to block the surface processes on platinum to some extent. Second, the current due to surface process is always underestimated on Autolab units not possessing a current integration unit since the Autolab uses a staircase voltammetry method to vary potential [29]. The result of this is that current is lost in the hydride terminated platinum region and the peak detail is also lost [30]. Finally at low scan rates such as those used for the photoelectrochemical studies it is known that even very low levels of organic impurities ($< 10^{-7}$ mol/l) in solution can have profound effects on the appearance of the platinum cyclic voltammetry especially in the hydride adsorption region [31].

It was hypothesised that the decrease in current on the platinum CV was due to oxygen reduction occurring at the platinum as a result of oxygen produced from water oxidation facilitated by capture of positive holes formed during illumination. In order to test this theory the experiment was re-run again in deoxygenated solution with an argon positive pressure but in the absence of illumination. The current at −0.22 V on the positive scan was measured and plotted against scan number. The results are shown in Fig. 6.

Clearly there is a slight drop in the current when no illumination is present. This is probably because it is impossible to exclude all oxygen from the electrolyte either before or during the experiment plus the PtPc itself is already known to be oxygen saturated. However the decrease in current is far more dramatic under chopped illumination conditions. It is suggested that this provides very strong evidence that the positive holes accumulating in surface states during illumination do have enough energy to oxidise water to oxygen which is then reduced at the platinum substrate. This is contrary to Hamnett's conclusions [12]. Further proof would be provided by a rotating ring disk study of the system. Unfortunately the porous nature of the PtPc layer would mean that the system would behave non-ideally in terms of RRDE kinetics and mass transport and such an investigation would not be possible.

The photocurrent responses were exceptionally reproducible and only the magnitude of the response and occasionally the number of scans required to fully develop a layer changed from run to run. This is thought to be an effect of the thickness of the PtPc layer which is

Fig. 5 The photoelectrochemical (*dashed lines*) and current response (*continuous lines*) against potential for a PtPc layer on platinum in deoxygenated 0.2 mol/l sulfuric acid, 10 mV/s. Five consecutive scans
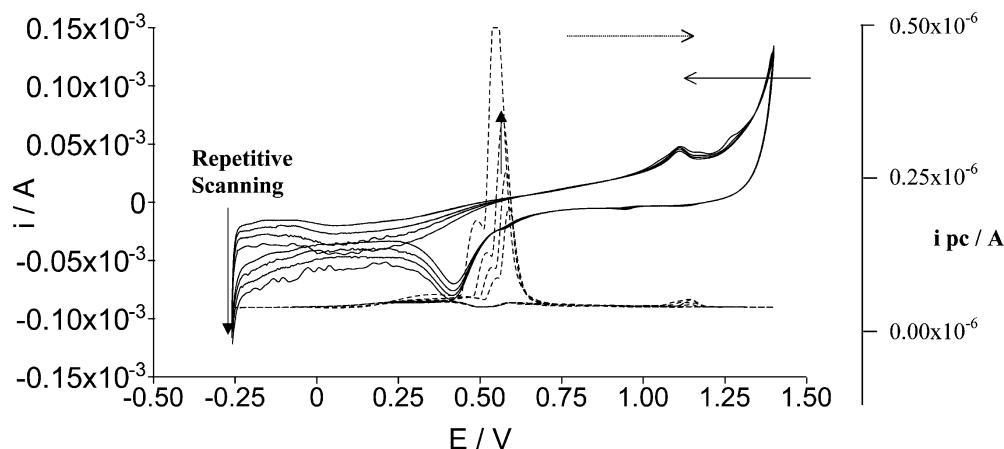
Fig. 6 Plot of the current at −0.22 V on the forward scan of the cyclic voltammetry of a PtPc layer on Pt in deoxygenated 0.2 mol/l sulphuric acid against scan number when exposed to chopped illumination (*filled squares*) and in the dark (*open squares*)
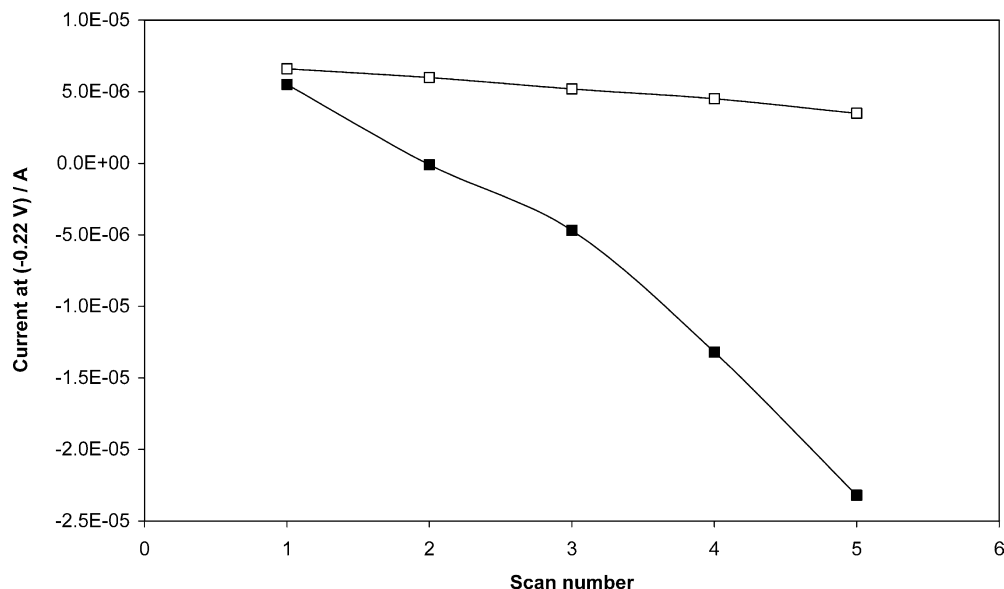

essential to photocurrent work but very difficult to measure and reproduce accurately with the deposition method used here. Clearly the thickness of a layer is a balance between having a film thin enough for light to penetrate into the PtPc and produce an exciton near the GC substrate where recombination is least likely and yet thick enough to create a sufficient absorption cross section for excitons to be produced.

An example of a typical photo-transient for the system under study is shown in Fig. 7. The shape of the photo-transient shows clearly that some recombination of excitons is occurring within the phthalocyanine film [32] and indicates the mechanisms of excitation, intermediate formation and product formation [26]. If the response was symmetrical about the zero of photocurrent this would indicate total recombination and equally if the photocurrent did not dip into the cathodic regime

on the cessation of illumination this would indicate no recombination. Clearly the situation here is between these two limiting cases. The decay of the transient photocurrent response after illumination is dependent upon the rate at which minority carriers trapped at surface states capture majority carriers. The photocurrent can been seen to tend towards a steady state value, after longer periods, which depends on the relative rates of recombination and charge transfer to redox species. After the interruption of light the carriers trapped at surface states continue to recombine. This overshoot current is of different sign since it is now only dependent on majority charge carriers flowing to surface states.

Because the photoelectrochemical response is independent of the phthalocyanine electrochemistry one would not expect the upper scan range limit to have much effect on the photoelectrochemistry of the

Fig. 7 Photo-response transient for a PtPc film on GC in 0.2 mol/l sulfuric acid at 0.48 V. Chopping speed 20 Hz
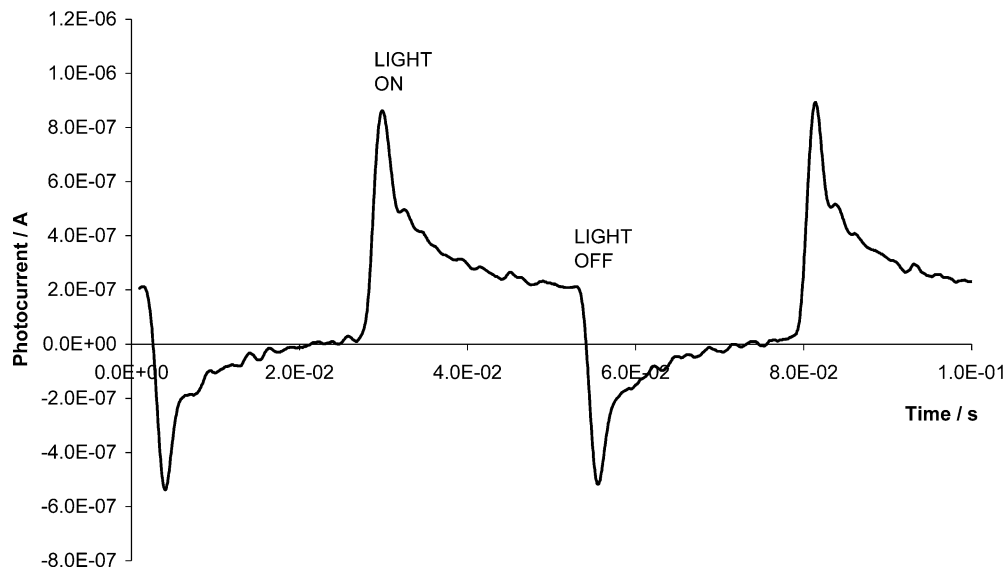
Table 1 Listing of the peak potentials for the four identified photocurrent peaks for a new PtPc layer on GC in 0.2 mol/l sulfuric acid developed between different scan limits. (sh) indicates a shoulder rather than a peak and the potential quoted is an estimate

Scan limits	Photoelectrochemical peak potentials			
	Forward scan		Reverse scan	
	Peak 1	Peak 2	Peak 3	Peak 4
$0 \rightarrow 1.40$ V	0.253	0.472	0.388	0.201
$0 \rightarrow 1.17$ V	0.282	0.456	0.384 (sh)	0.228
$0 \rightarrow 0.75$ V	0.354	0.555	0.461	0.281

electrochemically developed layer. Indeed this is seen to be the case. The plots appear to follow each other very closely regardless of scan range. However the situation is somewhat different for variation of the scan limit in an *electrochemically undeveloped* PtPc layer, i.e. one which has been freshly applied. Now the photoelectrochemical response observed appears to be very dependent on scan limit. The effects of this are summarised in Table 1.

The scan range from 0 to 1.4 V encompasses all the observed electrochemical peaks. The 0 to 1.17 V range does not include the highest potential redox pair, whilst the range from 0 to 0.75 V encompasses neither the highest potential nor second highest potential redox couples. The general trends are for all the observed photoelectrochemical peaks to shift up in potential as the scan range is decreased. It is suggested that this is strong evidence that the photoelectrochemical response of the system is strongly dependent on the structure and state of the PtPc film as defined by the various electrochemical redox process occurring. It is particularly interesting that strong photoelectrochemical responses are shown for the 0 to 0.75 V range when then film never undergoes the irreversible intercalation oxidation seen on the first full electrochemical scan. This may indicate that the conductivity between microcrystals is good even before the oxidations accompanying phase transformations and deeper intra-domainal intercalation. The photoelectrochemical behaviour between 0 and 0.75 V

show significant development with repetitive scanning. This behaviour is shown in Fig. 8.

Initially the photoelectrochemistry shows just one peak in each direction but with repetitive scanning this develops into two in each direction. This suggests that some structural changes are occurring within the film either induced by the photoelectrochemical process or by the repetitive inter-domainal ingress and egress of electrolyte during oxidation process at about 0.75 V. The photoelectrochemistry shown when the scan limits are restricted to being between 0 and 1.17 V develops less with repetitive scanning and starts to resemble the response seen over the full range scan. The main difference is that the photoelectrochemical peaks at higher potential in each scan direction are not as large and sometimes just appear as a shoulder

Photoelectrochemical responses have been recorded in different electrolytes in an attempt to better understand the processes occurring during the photoelectrochemical process. Changes in the supporting electrolyte have little effect on the shape of the photoelectrochemical response unless the electrolyte contains an oxidisable species apart from water, for example Cl^- or $[K_3(CN)_6]^{3-}$ (see later). However changes in the electrolyte have caused changes in the potential range of the observed photoelectrochemical response. This has been qualitatively ascribed to changes in the pH of the electrolytes causing net changes in the potential of the O_2/H_2O couple. Heindl et al. [25] speculate that changes in position of photocurrent peaks with concentration are very complicated because of strong electrolyte-surface interaction and the added problem that the oxygen and hydrogen evolution potentials from the electrodes may not vary linearly with pH. However for very large shifts in pH and/or a change of the majority species in solution the shift in dynamic photocurrent is very obvious. An example of the photocurrent behaviour in acid and base is shown in Fig. 9.

Such behaviour is consistent with the theory proposed by Tributsch and Gorochov [17] that the photocurrent shift with change of redox system is a typical

Fig. 8 Photocurrent against potential for a PtPc layer deposited by mechanical abrasion on GC in 0.2 mol/l sulfuric acid at 10 mV/s over a reduced scan range (0 to 0.75 V). Scan 1–10
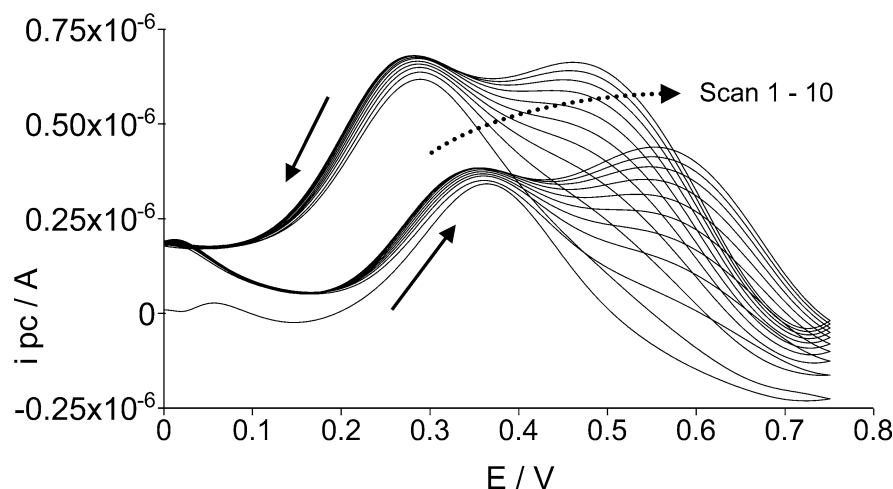
Fig. 9 Dynamic photoelectrochemical response for a PtPc layer on GC in 0.2 mol/l sodium hydroxide solution (*continuous lines*) and 0.2 mol/l sulfuric acid (*dashed lines*). Scan rate, 10 mV/s
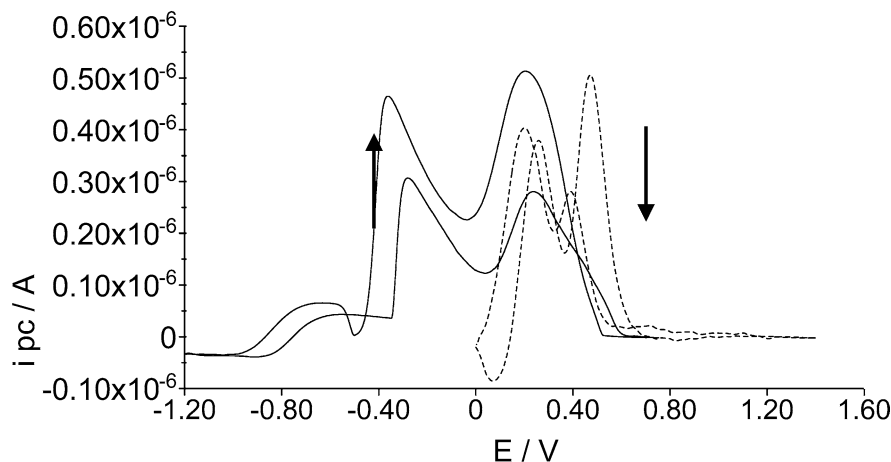
property for d-band semiconductors and is caused by a specific interaction of the redox system with holes on the d-states. The charge on the produced surface states depends on the redox properties of the electrolyte. This effect is shown very clearly when a better defined redox couple at a lower concentration is used in solution. The effects of a ferro/ferricyanide couple in solution are shown in Fig. 10.

An anodic spike appears very clearly in the in the forward sweep at the E^0 of the ferro/ferricyanide couple as positive holes accumulating at the surface are dissipated by the oxidation of Fe^{2+} to Fe^{3+}. The current response is observably noisy as the chopped photocurrent response is superimposed upon the Faradaic current response. Because of the electrochemical oxidation of the Fe^{2+} at potentials positive of the E^0 on the reverse sweep there will be little Fe^{2+} present adjacent to the electrode to be oxidised by the photo-generated positive holes and hence almost no photoelectrochemical response is seen at the ferro/ferricyanide E^0 on the reverse sweep.

Conclusion

It has been shown that both platinum and palladium phthalocyanine produce reproducible photoelectro-

chemical responses off glassy carbon, gold and platinum substrates. The slight differences between the responses off the different substrates has indicated that the photoelectrochemical activity may well be centred about phthalocyanine molecules residing on, or close to, the substrate/Pc interface. This is certainly the part of the system where exciton formation is most likely to produce complete charge separation and not recombination.

The photoelectrochemical response has been attributed to exciton formation via a π-π*, HOMO-LUMO transition from the Q-band absorption region of the film. The PtPc is acting as an n-type semiconductor and after exciton formation the minority charge carrier, the positive hole, moves through the space charge region and accumulates at the Pc/electrolyte interface. The phototransient studies have shown that some recombination occurs, but the majority of the positive holes are dissipated by reaction with the electrolyte or species within the electrolyte. It is thought that the holes are energetic enough to oxidise water to produce oxygen. This has been proved by the observation of an increased oxygen reduction current on a PtPc layer on platinum under illumination. As the potential is scanned anodically it passes the flatband potential of the material (determined to be about −0.05 V) and photoactivity in an n-type semiconductor is then possible. The dynamic

Fig. 10 Photocurrent (*dashed lines*) and current response (*continuous lines*) against potential for a PtPc layer on GC in 1 mmol/l / 1 mmol/l potassium ferro/ferricyanide in 0.1 mol/l KCl. Scan rate, 10 mV/s
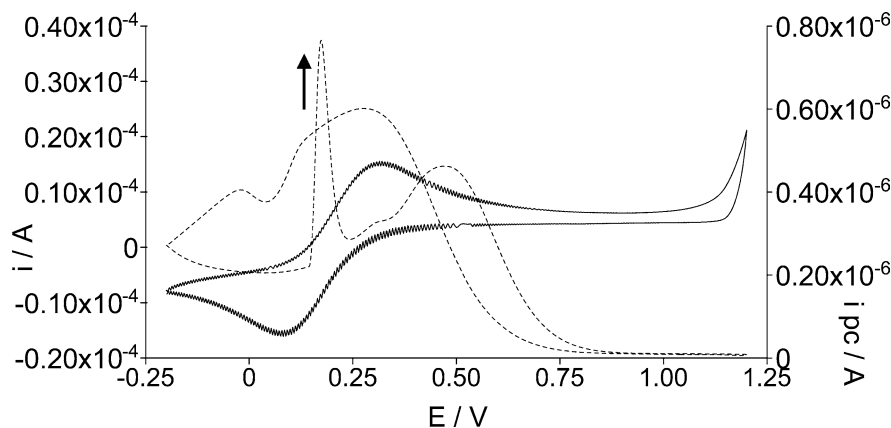
photocurrent response increases and is at a maximum when the applied potential is equal to that of the E^0 of the redox couple in solution with which the positive holes are reacting. It is clearly at this potential that charge transfer is most facile. It has also been shown, as expected, that the potential at which the photoelectro-chemistry occurs shifts with the pH of the solution (and the E^0 of the O_2/H_2O couple). The double peaked nature of the photocurrent response has been attributed to two different kinetics regimes governing the photoelectro-chemical behaviour, as shown in the phototransient response at different potentials.

The nature of the electrolyte has been shown to have a marked effect on the appearance of the photocurrent response. Both the anion and the cation are important in defining the shape, position and behaviour of the response. This has been qualitatively attributed to the structural changes in the film brought about by inter-calation using different electrolytes. Differences in the film's structural properties have also been invoked to explain the variation in photocurrent response with changes in the scan range over which the film is developed. The overall behaviour of the films is very similar to that exhibited by transition metal dichalcogenides.

Palladium phthalocyanine has shown very similar behaviour to the PtPc and any slight discrepancies observed have been attributed to the minor differences in crystal structure between the two materials.

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