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The electrochemical behaviour of light-sensitive electrodes formed by coating a platinum mesh with a powdered semiconductor

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The formation of light-sensitive electrodes by coating a platinum mesh from an aqueous suspension of a semiconductor, is demonstrated. They behave as short-circuited semiconductor electrodes, and the short-circuiting can be reduced by incorporation of Teflon in the coating. The photochemistry of some little investigated or uninvestigated semiconductors (metallic oxides, sulphides and chromates) is described; all respond to visible light, all are unstable on irradiation, and only p-type Pb_3O_4 appears useful as a photocathode. Photoacoustic spectra of some of these materials are presented. The shortcomings, and possible improvements, of this photoelectrode preparation method are discussed.

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1. Introduction

Photoelectrochemical methods for harnessing solar energy is an area of active research [1–4]. An important part of the experimental systems is the light-sensitive electrode and its preparation. The semiconducting material can be a single crystal [5], a mineral specimen [6] or in a polycrystalline form obtained by chemical vapour deposition [7], chemical spray deposition [8], oxidation of a metal either thermally [9] or anodically [10], or by thermal decomposition of a precursor [11]. The powdered form of the semiconductor may be treated to produce an electrode by, for example, compression [12], sintering [13], arc-plasma spraying [14], or by being painted in the form of a slurry on to a conducting substrate [15]. The search for new electrode materials has led to electrode production by ceramic techniques [16]. We have employed a method of obtaining a light-sensitive electrode in which a platinum mesh is coated with powdered materials, and have studied the photoelectrochemistry of red mercury (II) sulphide electrodes prepared by such means [17–19]. In this paper we discuss this method of photoelectrode preparation.

2. Experimental procedure

Platinum mesh electrodes were obtained from Engelhardt Sales and are described as 'carriers for oxygen'. The mesh measures 3 cm × 1.5 cm and comprises interwoven platinum wires of 0.025 cm diameter. The mesh was mounted on a platinum wire (7.5 cm × 0.1 cm) mid-way along the longer side of the mesh, such that 6 cm of platinum wire was available for mounting the electrode in the cell. This wire also formed the electrical connection to the external circuit. Two grams of the semiconductor to be investigated were dispersed ultrasonically in 25 cm^3 of de-oxygenated, deionized water. The platinum electrode (previously boiled in 50:50 concentrated hydrochloric acid: water, then dried) was swirled in the suspension then dried in a hot air stream. The swirling–drying procedure was repeated until an even, complete coating covered the mesh. The loading of the electrode was controlled by the number of times the swirling–drying procedure was performed. Actual weights of coating are given in the Results and discussion section. The electrode was immersed for at least 15 h in the electrolyte in which it was to be investigated, and when it was

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under investigation care was taken to ensure that the electrolyte covered only the mesh, and not the uncoated stem of the electrode.

A 1.6 kW xenon arc lamp formed the light source, with either saturated copper (II) sulphate solutions or dilute copper (II) chloride acting as heat and UV filters. The light intensity reaching the semiconductor electrode was about 200 mW cm^{-2}. A one-compartment, three-electrode cell containing a working electrode, a reference electrode (saturated calomel electrode–SCE), and a counter electrode (a bare platinum mesh) were employed, with provision for nitrogen bubbling. Electrolytes were made up with de-ionized water and Analar potassium chloride or nitrate. The semiconductors were standard (or better) reagent grade chemicals from commercial sources. No pretreatment was performed. Potentials were measured with a Philips high impedance voltmeter (model PM 2434) and currents with a Heath polarography module (EUA-19-2) or Wenking potentiostat (LB 75 L). Photoacoustic spectra were obtained with an OAS 400 instrument (EDT Research Limited).

3. Results and discussion

3.1. Platinum mesh electrodes bearing semiconductors whose photoelectrochemical behaviour has been reported in the literature

TiO_2, ZnO, $SrTiO_3$, $BaTiO_3$, WO_3 and CdS are all known to be n-type materials and generate photocurrents upon irradiation with light of appropriate wavelength and a suitable electrochemical system [2]. Some powdered materials, supported by the platinum mesh electrodes are now described, and some data are presented in Table 1, along with photocurrent–applied potential plots in Fig. 1. It is evident that the semiconductors behave as expected, and the common increase in cathodic current for all except CdS, in Fig. 1, is due to oxygen reduction in the non-deoxygenated electrolyte. CdS is investigated in a solution containing KCl and Na_2S, which is nitrogen-purged, and the photocurrent onset potential is 0.2 V positive of the flat-band potential [20], which suggests CdS behaves as in other electrode forms, but a 'loss factor' is induced here. This can also be seen in the

Table 1. Photoeffects in an aqueous electrolyte (0.1 mol dm^{-3} KCl) of some semiconductors, whose properties are established, coated on platinum mesh electrode

Semiconductor	*Coating weight on the platinum mesh (g)*	*Relative photopotential (mV)*	*Relative photocurrent (μA) at zero bias (vs SCE)*	*Onset potential (V vs SCE)*	*Flatband potential pH 7 (V vs SCE)*	*Remarks*
TiO_2	0.005 308	−270	+ 17.5	∼ −0.1*	−0.65†	
ZnO	0.007 276	−286	+ 115.0	∼ −0.2*	−0.5‡	Electrode photochemically unstable
$SrTiO_3$	0.005 435	−110	+ 3.5	∼ −0.1*	−1.05†	
$BaTiO_3$	0.008 404	−135	0.0	∼ −0.1*	−0.4†	
WO_3	See remarks	−136	− 1.0	∼ 0.0*	+ 0.2†	WO_3 adheres feebly to the platinum mesh
CdS	0.008 400	−167	+ 105.0	−0.65	−0.88§	Electrode photochemically unstable

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* Influenced by oxygen reduction.

† See Rajeshwar *et al.* [2].

‡ Estimated from Maruska and Ghosh [3].

§ See Watanabe *et al.* [20].

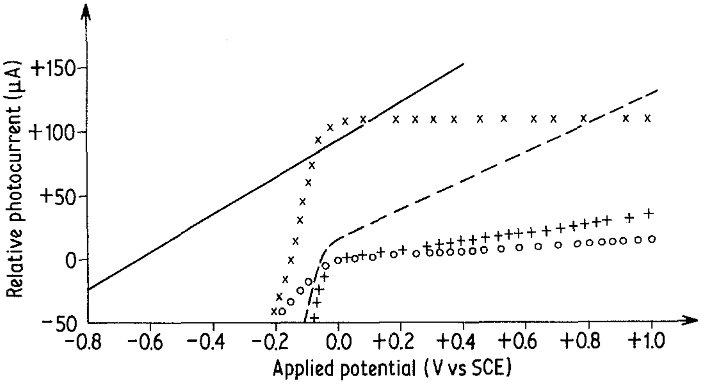


Fig. 1. Photocurrent–applied potential plots for platinum mesh electrodes bearing CdS (——), ZnO (XXX), reduced TiO_2 (– – –), WO_3 (000) and $SrTiO_3$ (+++) (the plot for $BaTiO_3$ is coincidental with that of $SrTiO_3$) in aerated 0.1 mol dm^{-3} KCl. For CdS, the electrolyte is N_2-purged 0.1 mol dm^{-3} KCl + 0.1 mol dm^{-3} Na_2S.

very low photocurrents for $SrTiO_3$ and $BaTiO_3$. These materials are known to cause hydrogen evolution at a platinum counter electrode when illuminated in aqueous electrolytes [21, 22]. If the mesh electrode has sites of uncovered platinum, these will act as a counter electrode and induce a short-circuit. Thus, lower photocurrents will be seen for these materials, and the short-circuit is probably responsible for the 'loss factor' in CdS electrodes. WO_3 exhibits poor photocurrents, either because of the rather positive flat-band potential [13], or because of the poor photosensitivity of this particular sample. The method of preparation of WO_3 is known to affect its response to light [23].

It is possible, therefore, to construct light-sensitive electrodes by this method, and obtain photoelectrochemical effects which can be correlated to those observed with electrodes of the same material fabricated by other means. The main problems with this method are likely to be (i) short-circuiting due to incomplete mesh coverage, (ii) a high internal resistance of the semiconductor, since materials are not pretreated, and (iii) a non-reproducible surface exposed to the electrolyte with different electrodes. Grain boundaries will encourage electron-hole recombination and add to the resistance. These boundaries cannot be controlled in the preparation method, as they might, for example, in the growth of a film where the growth rate can be varied.

3.2. Short-circuiting in the electrodes and attempts to eliminate it

Applying a thicker semiconductor coating to the platinum mesh should increase the chance of covering all the platinum substrate. This has been done for red mercury (II) sulphide, and the results are shown in Table 2. The lowering of photoeffects as the sulphide weight increases shows that the higher internal resistance of the thicker coatings is the dominant effect. When the sulphide has been blackened to give a more sensitive electrode [17, 19] rather different results are noted. There is an optimum electrode loading which gives optimum photocurrents, but at applied potentials positive of + 0.2–+ 0.3 V (vs SCE), photocurrents fall, see Fig. 2. It is seen that the best photocurrents obtained with a loading of about 0.03 g

Table 2. Photoeffects obtained for platinum electrodes bearing different weights of red HgS in nitrogen-purged, 0.1 mol dm^{-3} $NaNO_3$ (pH 11.5)

Weight of red HgS coating the mesh (g)	*Relative photovoltage (mV)*	*Relative photocurrent (μA) at a given bias (V vs SCE)*	
		0.0	+ 0.4
0.008 054	− 215	+ 5.0	+ 7.5
0.032 152	− 235	+ 2.8	+ 6.0
0.044 308	− 100	+ 1.0	+ 2.3
0.069 186	− 45	+ 0.4	+ 2.7

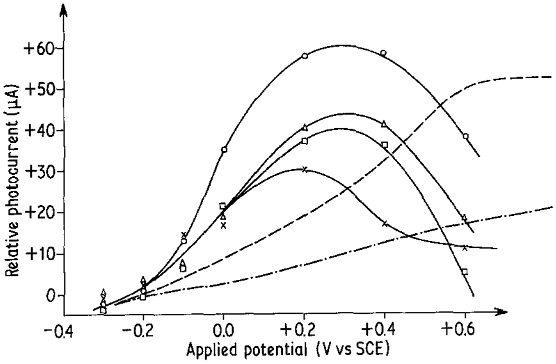


Fig. 2. Photocurrent–applied potential plots for platinum mesh electrodes bearing blackened red HgS of weight 0.007 464 g (X), 0.030 218 g (0), 0.042 760 g (Δ) and 0.068 324 g (□). Plots are shown for Teflon-bonded blackened HgS on platinum. Weights of HgS/PTFE are 0.065 36 g (– – –) and 0.021 54 g (–·–·–). The electrolyte is pH 11.5, 0.1 mol dm^{-3} NaNO$_3$ (N_2-purged).

of blackened sulphide. For all the electrodes, gas evolution (hydrogen) is observed at the counter electrode for applied potentials greater than + 0.2 V, and we attribute the drop in photocurrents at voltages anodic of this value to oxygen evolution at the HgS electrode. This oxygen is either reduced at uncovered platinum surfaces or adsorbed on to the sulphide [24] and then reduced. The photocurrent–potential curve for the electrode bearing the heaviest HgS coating shows the largest 'falling-off' effect, either because of the extensive influence of oxygen (at either HgS or Pt), or because the higher resistance of the thicker electrode prevents generation of larger photocurrents. The two dashed plots in Fig. 2 help to explain which process is dominant. These plots are for Teflon-bonded blackened HgS electrodes. Fluon powder (commercial PTFE) (0.2 g) are included in the HgS suspension used to coat the platinum electrode (methanol is used to make up the suspension, not water). The shape of the plots for Teflon-bonded electrodes indicates that no 'fall-off' occurs for photocurrents with increasing applied voltages, suggesting short-circuiting has been overcome. The upper (dashed) curve is for an electrode bearing 0.06 g HgS/PTFE, and the lower one (dash-dotted) is for an electrode with a 0.02 g HgS/PTFE covering. The generation of larger photocurrents with a thicker electrode implies internal resistance is not a significant factor at loadings of this order and the influence of oxygen causes the 'fall-off'. Teflon in the electrode reduces short-circuiting by covering bare platinum sites, but it also lowers photocurrents by hindering reactions of electrolyte species with positive holes in HgS, since PTFE is hydrophobic. We have found the HgS/PTFE ratio, and the total electrode loading, to be very critical in this work, and prevention of short-circuiting is offset by lowering of photocurrents due to the hydrophobic nature introduced into the electrodes [25].

Internal resistance is the controlling factor when little or no oxygen is produced at the HgS electrode on illumination (Table 2), and so the faults which are manifested in these kinds of electrodes are dependent on the reaction which is taking place.

3.3. Investigation of other light-sensitive materials

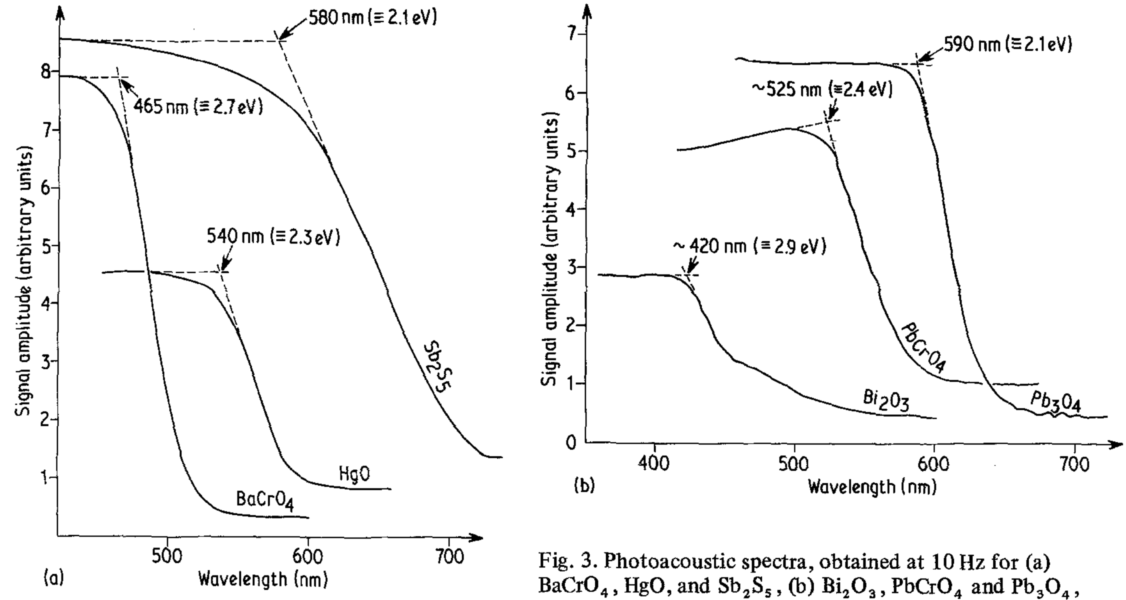
Reasonable success with semiconductors of known properties (Table 1 and Fig. 2), with HgS [17–19] and TiO_2 [26–29], coated on platinum meshes, encourages us to probe materials with little or no reported photoelectrochemistry, by this method. Experiments were conducted to determine the sign and magnitude of photovoltages, the ability to promote photocurrents and the photostability of the light-sensitive materials. Table 3 shows some pertinent data for metallic oxides, chromates and sulphides [30]. Compounds which give a positive photovoltage are taken to be p-type, namely Bi_2O_3, Cu_2O, CuO, HgO, Pb_3O_4, Sb_2S_5 and TiS_2. All these materials are unstable on illumination, and only Pb_3O_4 has a sufficiently positive photocurrent potential (which gives a guide to the value of the flatband potential) to make it worthy of consideration as a viable photocathode, if it can be stabilized. Pb_3O_4 has been investigated for usage in a Schottky barrier solar cell [31]. Photoelectrochemical reactions have been reported for Cu_2O [32], Bi_2O_3 and CuO [33]. Materials which show a negative photovoltage are taken to be n-type, namely, Sm_2O_3, Tl_2O_3, $BaCrO_4$,

Table 3. Photoeffects in 0.1 mol dm^{-3} KCl for powdered semiconductors coating a platinum mesh

Material	*Band gap (eV)*	*Weight coating platinum mesh (g)*	*Relative photovoltage (mV)*	*Relative photocurrent (μA) at zero bias (vs SCE)*	*Onset potential (V vs SCE)*	*Remarks*
Bi_2O_3	2.9*	~ 0.007	+ 61	− 9.0	+ 0.25	Unstable, adheres poorly to platinum
Cu_2O	2.1*	0.009523	+ 35	− 11.0	+ 0.20	Unstable
CuO	1.95†	0.006868	+ 50	− 5.0	+ 0.25	Unstable
HgO (yellow)	2.3*	0.008128	+ 20	~ − 70	+ 0.15	Very unstable
Pb_3O_4	2.1*	0.003354	+ 90	− 4.0	+ 0.70	Unstable, orange electrode turns brown, counter electrode is deposited with lead
Sm_2O_3	2.3†	0.008096	− 135	− 10.0	+ 0.25	Unstable. Adheres poorly to platinum
Tl_2O_3	2.2†	0.007126	− 25	~ − 300	+ 0.30	Very unstable, counter electrode and electrolyte become brown in illumination
$BaCrO_4$	2.7*	0.006155	− 30	0.0	~ + 0.3	Unstable, adheres poorly to platinum, electrolyte becomes yellow
$PbCrO_4$	2.3*	0.007025	− 60	− 2.0	+ 0.15	Unstable
FeS	?	0.004862	− 40	− 3.0	+ 0.10	Unstable, electrolyte smells of H_2S
Sb_2S_5	2.1*	0.005700	+ 150	− 1.8	+ 0.05	Unstable, orange electrode becomes brown and electrolyte turns green
TiS_2	1.2†	0.004934	+ 20	+ 0.5	~ 0	Unstable, solution becomes blue and smells of H_2S

* Determined by photoacoustic spectroscopy (see text).

† See Strehlow and Cook [30].



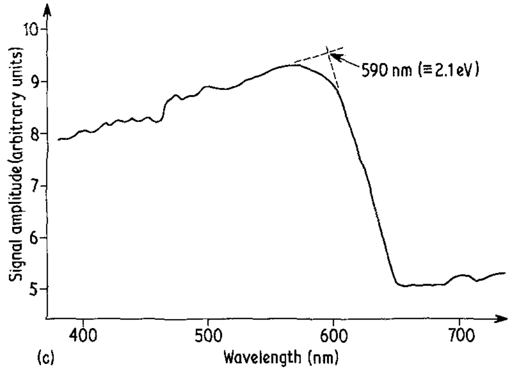


Fig. 3. Photoacoustic spectra, obtained at 10 Hz for (a) $BaCrO_4$, HgO, and Sb_2S_5, (b) Bi_2O_3, $PbCrO_4$ and Pb_3O_4, and (c) Cu_2O. Extrapolation is shown to indicate the absorption edge, given in nanometres and electron-volts.

$PbCrO_4$ and FeS. None has an onset potential sufficiently negative to afford a suitable anode, and all are unstable.

Figure 3 shows photoacoustic spectra of some of the materials mentioned above. The spectra show the optical absorption edge, and we infer from this that the compounds exhibit semiconducting properties. (The other materials are classified as semiconductors [30], although the status of FeS is uncertain.) This absorption edge will control photoeffects, and the band gap can be deduced, see Fig. 3. The value of this gap correlates quite well with tabulated ones obtained by other means, where known [30]. The energies of the band gaps indicate that the materials are responsive towards visible light. We could not obtain an absorption edge for CuO by photoacoustic spectroscopy, although a band gap of 2.05 eV has been reported using this method [34]. Cu_2O gives a photoacoustic spectrum (see Fig. 3c) and the band edge agrees with that obtained similarly [34].

By a very simple method of photoelectrode preparation, we have illustrated how materials can be quickly checked for possible usage in photoelectrochemical systems. Of course the method is useless if the powder fails to adhere to the mesh, or if a rectifying semiconductor–platinum junction is formed. Furthermore, the materials employed here may be intrinsically photosensitive, but the lack of pretreatment means they show only feeble photoeffects. Improvements can be made as follows: (i) the semiconductor can be treated to render it in its most photosensitive form before application to the platinum mesh; (ii) the semiconductor can be similarly pretreated to lower its internal resistance; (iii) application to the mesh can be in such a manner that a more uniform coating is obtained, e.g. by vapour deposition, which may give more control over the contact with platinum, the grain size and hence improve the 'physical' performance of the electrode (short-circuiting etc). We note that the electrodes as used here are probably at their worst since short-circuiting occurs the non-irradiated face of the electrode is not insulated from the electrolyte and the semiconductor is of ordinary reagent grade, i.e. it is not specially prepared or purifed.

No photoeffects were obtained with red HgS coated on a nickel mesh. Nickel is reported to form an ohmic contact with HgS [35], and it is suggested that a bad physical contact means that formation of a suitable junction does not occur. This presents another problem with these electrodes in their present form; the lack of control in the formation of the semiconductor–metal junction means it is purely by chance that the contact is ohmic, even if the materials' work functions are correctly matched. The semiconductor remains lodged in the platinum mesh by some force of adhesion between the metal and powder, and this situation is unlikely to offer the lowest resistance to the semiconductor–platinum interface.

4. Conclusions

A crude, simple semiconductor electrode can be made by coating a platinum mesh from an aqueous suspension of the powdered material. The electrode suffers from short-circuiting, which can be reduced by incorporating Teflon in the coating. Photoeffects obtained with the electrodes in an electrochemical cell show that known materials behave as expected, and the method permits easy investigation of new materials. Our investigation shows that Pb_3O_4 has possibilities as a photocathode, if it can be stabilized.

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