

Platinisation of Semiconductor Particles

Andrew Mills

Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS, U.K.

Precipitation of a platinum sol, using an inert electrolyte, in the presence of a semiconductor powder leads to an efficient photocatalyst for the reduction of water.

In recent years numerous studies¹ have been made on the use of semiconductor powders, suspended in liquid solution, in photosynthetic and photocatalytic reactions, especially the photo-reduction of H₂O to H₂. In the latter case, the presence of Pt is often essential for efficient H₂ production²⁻⁴ (for reasons of overpotential). There are two major methods used to deposit Pt on to semiconductor powders. Developed by Grätzel *et al.*,³⁻⁵ the first method involves the preparation of a Pt-citrate sol, followed by removal of the protective citrate (using an ion-exchange resin), addition of the semiconductor powder, and sonication of the resulting mixture. However, using this procedure, we have encountered problems, including Pt adhering to the resin and incomplete precipitation of the non-protected Pt sol on to the semiconductor powder. Preferred over the citrate reduction method⁴ (because it is easier to perform and gives results of excellent reproducibility) is the second method of platinisation, *i.e.* photoplatinisation. Although there are several variations of this method, they all involve the u.v. irradiation of a semiconductor powder suspended in a solution containing a Pt salt and, usually, an electron donor (*e.g.* acetic acid,⁶ formaldehyde,^{3,4} and ethanol^{1(c)}). In general, this procedure is suited only for photo-stable semiconductors because long, high intensity, irradiations are involved. With this in mind, we instigated an investigation to determine a facile, routine method for depositing Pt on to a variety of different supports, so that reproducible batches of catalyst could be produced without elaborate techniques.

The methods of platinisation used were as follows.

Method A involved the preparation of a N₂-purged suspension of the semiconductor powder (1 g) in a solution containing 15 mg of chloroplatinic acid [H₂PtCl₆, (B.D.H.)] and 10 ml of a 40% formaldehyde solution stabilised by methanol (B.D.H.). This suspension was stirred continuously on irradiation, for 8 h, in a quartz vessel, with a 250 W Hg medium pressure lamp (this method is analogous to that reported by Grätzel *et al.*).^{3,4} The photocatalysts produced using this photoplatinisation technique were compared in activity to those produced by the alternative methods (B-E).

Method B involved the preparation of a Pt-citrate sol by refluxing, for 4 h, a solution containing 30 mg of H₂PtCl₆,

30 ml of a 1% sodium citrate solution, and 120 ml of H₂O. A third (50 ml) of the resultant Pt sol was stirred with 1 g of the semiconductor powder and 5.8 g of NaCl were added. The destabilisation of the sol, followed by Pt precipitation, appeared to be complete within seconds of the addition.

Method C involved the preparation of the Pt colloid described in method B, in the presence of 1 g of the semiconductor powder.

Method D involved rotatory-evaporation of the solvent from a suspension of the semiconductor powder (1 g) with 50 ml of the Pt sol in method B.

Method E involved the preparation of a suspension of the semiconductor powder (1 g) in an acetic acid solution (10 ml, 1M) containing 15 mg of H₂PtCl₆. Saturation of this suspension with H₂ brought about the reduction of the Pt salt to the metal.

For all the methods described above, the final platinised powder suspensions were filtered and repeatedly washed with distilled water before being dried in air. Oxide powders platinised by the above methods include B.D.H. and Aldrich Chemicals forms of titanium dioxide (TiO₂), as well as strontium titanate (SrTiO₃, Alpha Chemicals), aluminium oxide (Banner Scientific), and a TiO₂-RuO₂ catalyst (the preparation of which has been previously described).⁷

A test system was devised to compare the activities of the different photocatalysts towards water reduction. Such a system requires an electron donor [such as ethylenediamine-tetra-acetic acid (EDTA)] to scavenge efficiently, and irreversibly, the 'hole' of the 'electron-hole pair', produced on irradiation of the semiconductor with band-gap light. The remaining conductance-band electron should then be able to migrate to a platinum site where water reduction can occur.

In a typical experiment, a platinised semiconductor powder (37 mg) was added to a EDTA solution (37 ml; 10⁻³ M) and the mixture sonicated for *ca.* 30 s. The resulting suspension was then placed into the Pyrex irradiation cell of a hydrogen membrane polarographic detector (H₂MPD, see ref. 8). The suspension was N₂ purged and then irradiated with an Applied Photophysics quantum yield reactor, using a 900 W Xe lamp and a cold water i.r. filter. The initial rate of H₂ evolution was determined from the concentration of H₂ (measured using the

Table 1. A comparison of the activities of the different photocatalysts towards water reduction.

Type of semiconductor support	Method of platinisation	Relative initial rate of H ₂ production/% ^a
SrTiO ₃	A	5
"	B	3
"	E	4
"	none	0
TiO ₂ (B.D.H.)	A	28
"	B	46
"	C	11
"	D	22
"	E	14
"	none	0
TiO ₂ (Aldrich)	A	96
"	B	100
"	E	13
"	A (Rh, from RhCl ₃)	63
"	none	0
TiO ₂ (B.D.H.)-RuO ₂	A	40
"	B	24
"	none	4
Al ₂ O ₃	B	0

^a A relative initial rate of 100% corresponds to 1.2×10^{-5} M H₂/min.

H₂ MPD) evolved over the first 4 min of irradiation. The results of this work are shown in Table 1.

From Table 1, it appears that only method B produces photocatalysts of similar (if not greater) activity to those produced by photoplatinisation (*i.e.* method A). Using method A, other metals (Rh, Ru, Ir, Co) were deposited on TiO₂ (Aldrich) but only Rh¹⁸ showed any appreciable photocatalytic activity (see Table 1). Action spectra for both platinised (using method B) Aldrich and B.D.H. forms of TiO₂ corresponded well with the characteristic absorption spectra of direct band-gap semiconductors. Work with Al₂O₃ ($E_{bg} > 7\text{eV}$)^{1c} indicated that the oxide powder support must be light absorbing for H₂ evolution to occur. In the absence of EDTA, H₂ evolution [although greatly reduced (*ca.* 10 ×)] was still observed for

most of the powders. Indeed, the initial rates of H₂ evolution appeared to parallel those for the EDTA system.

In conclusion, method B represents a quick, easy, and efficient method of platinisation of powders. It should be possible to extend its use to depositing many other materials (*e.g.* metals, other semiconductors) provided they can be obtained in colloidal form (as most colloids are destabilised by the addition of electrolytes).⁹ Method B also allows platinisation of powders that are not photostable to u.v. light (*e.g.* CdS, CdSe, and dye-coated semiconductors) or do not absorb light (*e.g.* Al₂O₃).

We thank the members of the Davy Faraday Research Laboratory for their help and advice, particularly Professor Sir George Porter and Dr. A. Harriman. This work was supported by the S.R.C.

Received, 19th January 1982; Com. 056

References

- (a) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 2239, 5985; 1977, **99**, 7729; (b) S. N. Frank and A. J. Bard, *J. Phys. Chem.*, 1977, **81**, 1484; (c) A. J. Bard, W. W. Dunn, and B. Kraeutler, U.S. P., 1981, No. 4 264 421; (d) S. Sato and J. M. White, *Chem. Phys. Lett.*, 1980, **72**, 83; 1980, **70**, 131; (e) T. Sakata and T. Kawai, *Nouv. J. Chim.*, 1981, **5**, 279; (f) T. Sakata and T. Kawai, *Nature (London)*, 1980, **286**, 474; (g) J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, 1980, **4**, 623; (h) J. R. Darwent, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1703; (i) J. R. Darwent and G. Porter, *J. Chem. Soc., Chem. Commun.*, 1981, 145.
- C. D. Jaeger and A. J. Bard, *J. Phys. Chem.*, 1979, **83**, 3146.
- D. Duonghong, E. Borgarello, and M. Grätzel, *J. Am. Chem. Soc.*, 1981, **103**, 4685.
- E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, and M. Grätzel, *J. Am. Chem. Soc.*, 1981, **103**, 6324.
- P. A. Brugger, P. Cuendet, and M. Grätzel, *J. Am. Chem. Soc.*, 1981, **103**, 2923.
- B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 4317.
- A. Mills and M. L. Zeeman, *J. Chem. Soc., Chem. Commun.*, 1981, 948.
- A. Mills, A. Harriman, and G. Porter, *Anal. Chem.*, 1981, **53**, 1254.
- W. J. Popiel, 'Introduction to Colloidal Science,' Exposition Press, New York, 1978, p. 158.