Photoelectrochemical Properties of Platinised TiO$_2$

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Metallization of semiconductors (Pt/TiO$_2$) has been shown to promote redox reactions which cannot be otherwise driven by the semiconductor alone under illumination. Redox reactions can be carried out in preferred unidirections by proper metallization of the semiconductor photoanode.

INTRODUCTION

Metallization by group VIII elements like Pt, Pd, Rh has been used to increase the photocatalytic efficiency of particulate semiconducting materials[1]. Depending upon the procedure adopted for metallization and the subsequent pretreatements employed, these systems behave either as Schottkey barrier junctions or as ohmic contact systems[2]. In such a particulate metallized semiconductor the reduction and oxidation reactions take place simultaneously on each particle[3]. This process is mainly favoured in the case of polycrystalline semiconductors (e.g. Pt/TiO$_2$) since the impurity levels and grain boundaries favour the transfer of electron from bulk semiconductor (TiO$_2$) to the metal (Pt)[4]. In spite of these developments, the electrochemical behaviour of metal/semiconductor (e.g. Pt/TiO$_2$) electrodes is little known. Augustynski *et al.*[5] studied the electrochemical behaviour of platinised polycrystalline TiO$_2$ and reported that adsorption of CO on the electrodes depended much on the method of platinum deposition and the reduction conditions. They attributed this difference to the strong metal support interaction (SMSI). In this communication we report the photoelectrochemical behaviour of polycrystalline TiO$_2$ platinised by photodeposition.

EXPERIMENTAL

Polycrystalline TiO$_2$ powder was compacted into pellets of 10 mm dia with a WC-lined die at 3 tons/cm^2 pressure and sintered at 1000°C for 12 h. The sintered pellets were found to be insulating with resistivities $\sim$10^{10} ohm-cm. In order to make them suitable for photoelectrochemical studies, they were reduced by hydrogen at 600°C for 2 hr. This treatment would produce Ti^{3+} ions which could act as shallow donor centres resulting in n-type behaviour.

Ohmic contacts were made on one face of the pellet with silver epoxy and silver paint. The samples were mounted on to a glass holder attached with a copper wire. Ordinary epoxy resin was used to insulate all the other surfaces of the electrode except the front surface to be exposed to light from an Oriel Corporation 900 W UV source.

Prior to metal deposition TiO_2 surface was etched with dil. HF. The TiO_2 electrode prepared as above was suspended in a solution of chloroplatinic acid and irradiated for different intervals of time upto 30 min. The pH of the solution was adjusted with 4N acetic acid. The electrode was removed at different time intervals and I/V characteristics were recorded with a sweep rate of 40 mV/sec. The potential range swept was from −2.0 to +1.0 V. It was found that the maximum current showed a progressive increase till about 20 min. of Pt deposition, thereafter showed a decrease indicating that photodeposition on TiO_2 had reached a saturation limit in this time interval. After washing the electrode many times with triple distilled water a brownish grey shiny deposit of platinum was observed on TiO_2 surface. Since the effective surface area of the pellet exposed for the deposition of platinum is less, the amount of metal deposited is small and could not be monitored analytically. Nakamatsu et al[6] have carried out a detailed electron microscopic study of Pt deposited on TiO_2 particles by this method and proposed that the radicals produced at the surface (in this case acetic acid radicals) furnishes the electron for the Pt reduction and thus controls the dispersion of Pt deposits. Using various sacrificial organic donors like methanol, ethanol, propanol, formic acid and acetic acid, they have shown that best dispersions were attained with acetic acid. The current potential (I-V) characteristics of the pelletised electrode was monitored using a Potentioscan (Wenking Model No. POS 73) in a standard three electrode configuration using calomel reference electrode as well as Pt foil counter electrode.

RESULTS AND DISCUSSION

The I–V characteristics obtained for pure TiO_2 and Pt/TiO_2 in 0.1 M KCl in the potential range −2.0 to +1.0 V are shown in Fig. 1. It is seen that the dark current is negligible for TiO_2 while under photoconditions, the current shows a drastic increase in the anodic region. In the case of Pt/TiO_2 the anodic current shows greater increase at lower potentials until around +0.3 V indicating that the photogenerated electrons are effectively utilized in the metallic sites for reduction reaction. It is also possible that platinization reduces the overpotential of hydrogen evolution reaction. At lower potential values, platinization increases the hydrogen evolution reaction catalytically.

In Fig. 2 the cyclic voltammograms obtained for the system with redox couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ are given. The experiments were

carried out using 10^{-4} M $K_3[Fe(CN)_6]$ solution. On pure TiO_2 this reaction is not favoured, while on Pt/TiO_2 this reaction does occur as revealed by the large anodic current. Compared to the redox levels of H^+/H_2 the
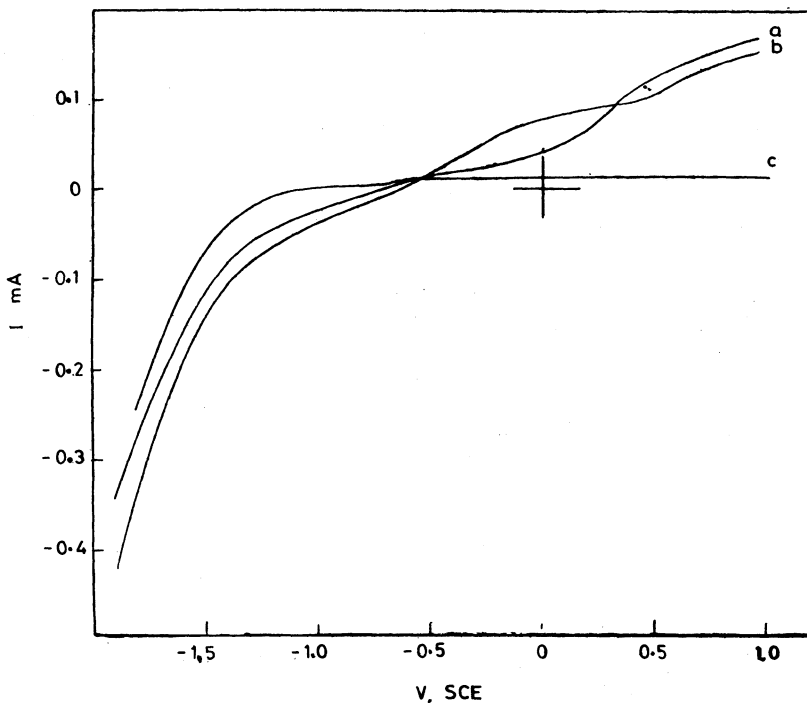

Fig. 1 I-V curves for TiO_2 electrode in 0.1 M KCl: (a) before platinisation; (b) after platinisation under illumination; and (c) in dark.

$[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ level is more negative and hence it is expected that this process is favourable both on TiO_2 and on Pt/TiO_2. Since there are many impurity levels and interface states in polycrystalline semiconductors, the electronic equilibrium between the polycrystalline TiO_2 and deposited Pt is easily attained even under anodic polarization conditions, the oxidation reaction occurs on Pt on TiO_2 around the same voltage as on Pt itself. The onset potential for the anodic process is different from that observed in KCl solution at different pH values. This indicates that the preferential redox reaction at lower potentials in the anodic region is the oxidation of $[Fe(CN)_6]^{4-}$.

From the redox potential values one can presume that on TiO_2 water oxidation reaction is favoured over the glucose oxidation. Normally glucose oxidation will not occur on TiO_2. However, the presence of Pt has made this reaction feasible at a particular pH range namely 7 to 10

(Fig. 3). At this pH range proper matching of the redox level of the substrate and that of the photoanode takes place. Glucose oxidation thus becomes favourable photoanodic reaction over the water oxidation reaction.
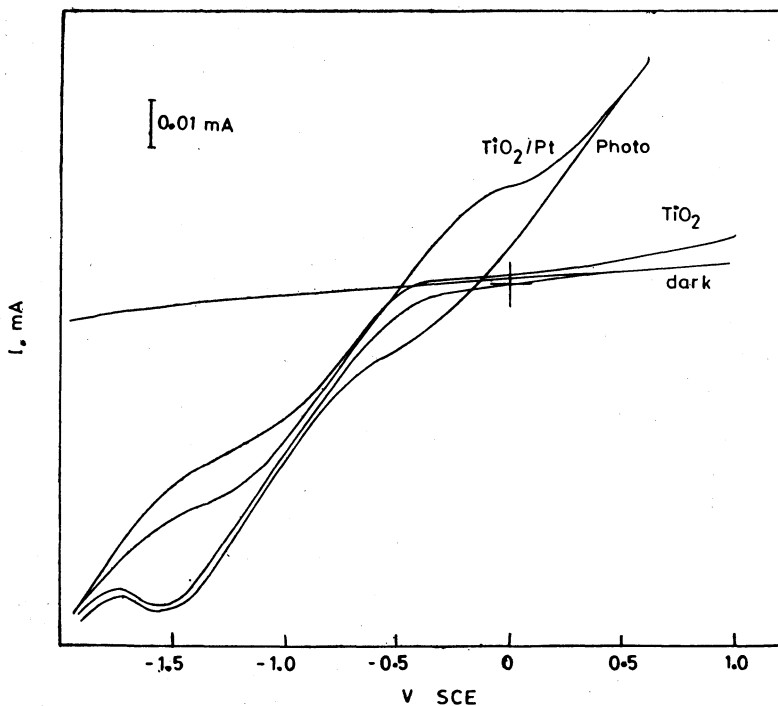

Fig. 2 Cyclic voltammograms with [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] for Pt/TiO₂ in dark and photocondions.

The preferential performance of this reaction in a particular pH range namely 7–10 can be either due to (i) the alteration of the reduction strength of the semiconductor, or (ii) the adsorption of OH⁻ species on the semiconductor results in surface Ti(OH)ⁿ⁺ species which on illumination generates excitations in a different photochemical pathway.

The observations can be rationalised in terms of a more generalised band picture of the semiconductors[7]. For a facile photocatalytic reaction on a semiconductor the band gap of the semiconductor should be greater than the sum of the theoretical decomposition voltage of both the anodic and cathodic processes and these redox values should be within the band gap. Normally the light induced positive holes in the valence band of the semiconductor promote the oxidation of the substrate when they have potentials more positive than the redox potential of the substrate plus the overvoltage for the oxidation reaction while the hydrogen evolution

reaction is preferred when the photogenerated electrons have potentials more negative than the hydrogen electrode potential plus the overvoltage for hydrogen evolution. In the case of metallized semiconductors, the unfavourable situations resulting from the positions of the valence and conduction bands with respect to the redox levels of the substrates could
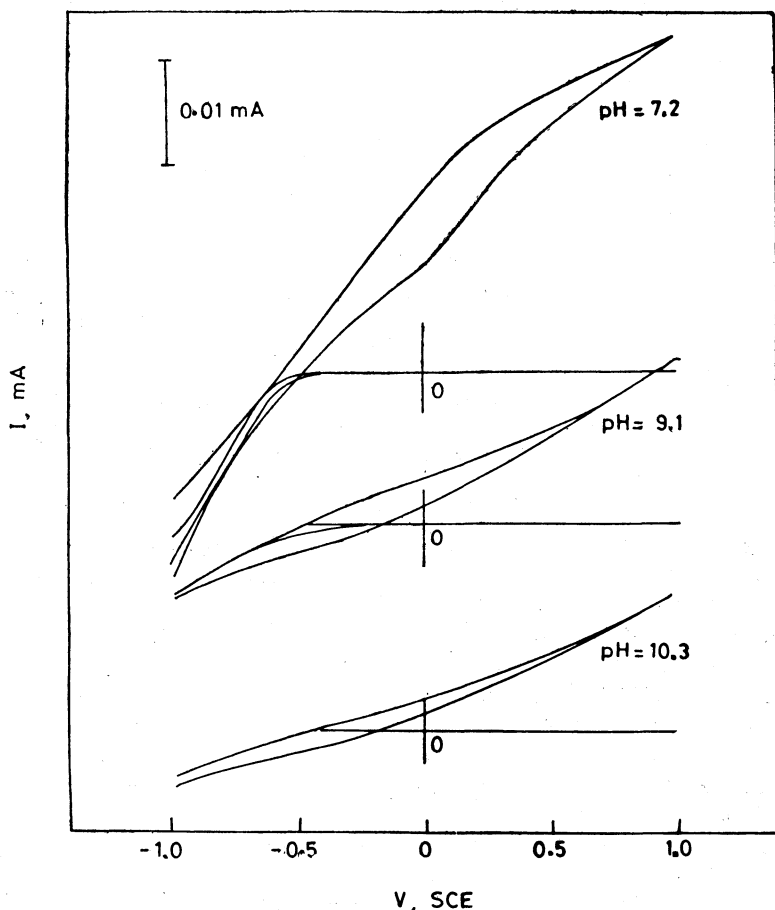

Fig. 3   Cyclic voltammograms for Pt/TiO$_2$ in 0.1 M glucose solution at different pH values under illumination.

be altered so as to be favourable for the reaction. This could result from (1) the Fermi level alignment in the metallized condition depresses the position of the valence band so as to be more positive than the redox potential of the substrates. (2) The photogenerated electron is easily made available through the metal for the H$^+$ reduction or the position of the conduction band is so adjusted as to be more negative to the redox

potential of the reduction reaction. These situations are shown schematically in Fig. 4.

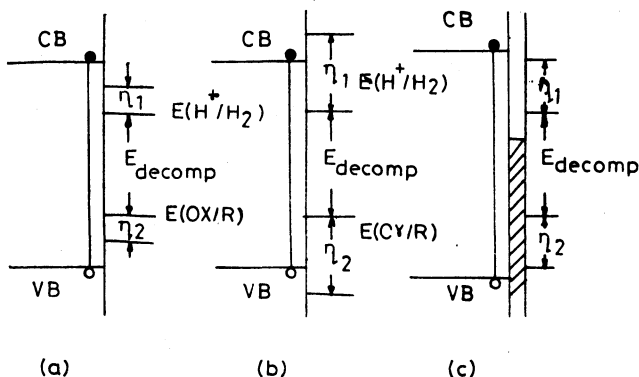(a)   (b)   (c)

Fig. 4   Diagrammatic representation of energy correlations for the photocatalytic decomposition of a substrate on a semiconductor with hydrogen evolution: (a) conditions favourable for oxidation of the substrate and hydrogen evolution; (b) conditions unfavourable either for oxidation of the substrate or of hydrogen evolution; (c) conditions made favourable by metallization of the semiconductor by the alteration of the position of the conduction and valence bands: η_1 and η_2 are the overvoltages for reduction and oxidation reactions respectively.

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