Semiconductor Electrodes

V. The Application of Chemically Vapor Deposited Iron Oxide Films to Photosensitized Electrolysis

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ABSTRACT

The preparation of polycrystalline n-type Fe_2O_3 electrodes by the chemical vapor deposition (CVD) of iron oxide onto Ti and Pt substrates is reported. The behavior of these electrodes in aqueous solutions of different *p*H in the absence and presence of illumination is shown. Photoassisted electrolysis of water occurs at wavelengths longer than 400 nm and the current *vs.* wavelength curve for this process is compared to that of a CVD TiO_2 electrode.

Recently there has been much interest in the utilization of semiconductor electrodes for solar energy conversion by the photoassisted electrolysis of water (1-4). By illuminating an n-type electrode with light energy greater than the bandgap energy, holes are produced in the valence band which, under anodic polarization, migrate to the surface where they can react with a species in solution. Thus with a suitable semiconductor electrode it is possible to oxidize water to oxygen utilizing solar energy. However, only TiO_2 (1, 2, 4), SnO_2 (5, 6), and $SrTiO_3$ (7) have been shown to be capable of oxygen generation without decomposition of the electrode material. All of these materials have a large bandgap (greater than 3 eV) and thus require u.v. illumination for the reaction. Other semiconducting materials with smaller bandgaps (*e.g.*, GaAs, CdS, Si) decompose under anodic polarization and/or illumination. A nonreactive electrode which shows appreciable photocurrents at wavelengths longer than 415 nm (3.0 eV) has not been reported. Since the bulk of the solar radiation on the surface of the earth is found at longer wavelengths [only about 3% occurs in the 315-400 nm range (3, 8)], a practically useful material for solar energy conversion must be able to utilize this lower energy radiation.

We recently reported the preparation of n-type TiO_2 electrodes by chemical vapor deposition (CVD) (9). We report here the preparation of iron oxide (Fe_2O_3) electrodes by CVD and their use in the photoassisted oxidation of water at potentials less positive than those at platinum and at wavelengths longer than 400 nm. The unavailability of a single crystal of iron oxide prevented comparison of its characteristics with the CVD material, but based on our findings with CVD *vs.* single crystal TiO_2, we would expect generally similar behavior.

Experimental

The basic experimental setup for CVD has been described (9). The vapor source was iron acetylacetonate ($Fe(C_5H_7O_2)_3$) obtained from Alfa/Ventron. This was placed in a flask heated with a heating mantle. Prepurified nitrogen, the carrier gas, was passed over the heated compound, then through a glass tube situated approximately 1 cm above the substrate. A second line containing nitrogen which had been bubbled through heated water was attached to a side-arm on the inverted funnel over the substrate to provide a reactive atmosphere. Both Ti and Pt metal served as substrates. The Ti was cut into 1 × 1 cm squares after being polished to a mirror finish. The Pt was 0.002 in. thick foil cut into suitable squares. All substrates were cleaned in distilled water and ethanol prior to use. The substrate temperature was maintained at about 400°C, with a hot plate during CVD. The procedure used in depositing the iron oxide was as follows. A glass slide was placed on the hot plate and the nitrogen flow rate adjusted to give the desired film growth rate, determined by observing the change in interference colors. The rate of deposition did not appear to be critical and therefore no attempt was made to control this rate precisely. Typically a rate showing the formation of three sets of interference colors in 2 min was used. After the flow rate was adjusted, the desired substrate was positioned under the nozzle. When a suitable layer was deposited (usually in about 2 min), the substrate was placed in the flame of a Meeker burner for about 1 min. The substrate became almost white hot during this treatment and upon removal from the flame it was observed that the interference colors had disappeared. When cool the surface of the coated Pt had a reddish purple color, while with Ti the color was mostly gray, with some reddish patches. Several layers (between 3 and 7) were thus deposited on each substrate. With the Ti substrate some of the film flaked off of the electrode after the heat-treatment. In this case the affected portions were wiped off and deposition continued. Deposition on Pt produced no flaking problems. In fact, the best performing electrodes were made by continuing the deposition on Pt until no interference color change could be observed, indicating a fairly thick layer. The surface had a uniform steel-blue appearance. Heating produced a uniform red-purple coating. This was repeated 3-4 times. All films deposited on platinum exhibited a very low resistance, so that no vacuum treatment following CVD was used, as was necessary in the case of the TiO_2 electrodes. A copper wire was attached to the back of the substrate with silver epoxy (Epoxy Products Company, New Haven, Connecticut). The electrode was then mounted in a glass tube with Apiezon wax, exposing only the oxide-coated surface to the solution.

All electrochemical measurements were performed with a PAR Model 173 potentiostat (Princeton Applied Research Corporation, Princeton, New Jersey) controlled by a PAR Model 175 universal programmer. Current-potential curves were recorded on a Model 2000 X-Y recorder (Houston Instruments, Austin, Texas). A simple H-cell with a glass frit separating working and auxiliary compartments was used. A Pyrex window allowed illumination of the working electrode. Platinum wire served as the counterelectrode and a saturated calomel electrode (SCE) was the reference electrode. All potentials are reported *vs.* SCE.

The illumination system consisted of a 450 Watt Xenon lamp (Oriel Corporation, Stamford, Connecti-

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cut) in an Oriel Model 6140 housing with an Oriel Model 6242 power supply. For current-wavelength curves, an Oriel Model 7242 grating monochromator with 12 nm band pass slits was used. The intensity of the incident light from the monochromator (in microwatts/square centimeter) was measured with a Model 550 radiometer (EG & G, Salem, Massachusetts). The intensity was normalized to the intensity at 470 nm and then used to correct the photocurrent *vs.* wavelength curves for variations in intensity with wavelength.

Results and Discussion

Current-potential curves for Fe_2O_3 films on Ti and Pt substrates in neutral unbuffered media (0.5*M* KCl for Ti and 0.5*M* Na_2SO_4 for Pt) are shown in Fig. 1. Qualitatively the two curves are similar. The dark current is slightly larger with the Ti substrate electrode, possibly because of some reaction at bare Ti, since the surface had a very patchy appearance. The cathodic currents in the dark can be attributed to the reduction of dissolved oxygen and of the Fe_2O_3. When nitrogen was bubbled through the solution, the current at potentials more positive than −0.4V markedly decreased; however the currents at more negative potentials were not affected appreciably. Continued scans to potentials negative of −0.4V gradually reduced the photoresponse of the electrode. The surface became lighter in color until the coating was virtually gone.

Under illumination there is a large rise in anodic current commencing at about +0.2V *vs.* SCE, with both Pt and Ti substrates. Gas evolution appears promptly with the anodic current and is quite noticeable on the electrode surface, implying that the reaction is the photoassisted oxidation of water to produce oxygen. Prolonged illumination in an unbuffered solution at $E = +0.800$V results in a decrease in *p*H. The current rise continues with increasing positive potentials to at least +1.5V without showing the current plateau characteristic of TiO_2 electrodes. However, even in the dark at *ca.* +1.2V (shifting to more negative potentials with increasing *p*H), the Fe_2O_3-coated substrates exhibit a large current rise with simultaneous gas evolution. This probably represents the direct oxidation of water at these potentials as a result of tunneling through the film. A similar gas evolution and current rise is observed in the dark on CVD TiO_2 electrodes, but at more positive potentials (*ca.* +2V). Thus at Fe_2O_3 the nonphotoassisted oxidation current at large positive potentials adds to the photoassisted current and thus masks the appearance of the photocurrent plateau.

There appears to be a small photocurrent beginning at about −0.4V *vs.* SCE under white light illumination with the Ti substrate. The current continues to rise gradually until the onset of the large photocurrent at +0.2V. This small photocurrent is probably due to the presence of some TiO_2 formed during the heat-treatment. Evidence of this is the gray color of the surface and the flaking problems encountered during preparation. This photocurrent appears at about the same potentials as those observed with CVD TiO_2 electrodes. On scan reversal from positive potentials with a Pt substrate electrode, a cathodic peak appears at about +0.20V (the shape and location of this peak vary somewhat with different electrodes). The peak shifts to negative potentials with increasing *p*H and does not appear on Ti substrates. This peak probably represents the reduction of adsorbed oxygen produced during the anodic scan under illumination. It does not appear in dark scans to potentials less positive than +1.2V, but is seen if an anodic scan is made to more positive potentials. It is also observed when the anodic scan is made under illumination and the light turned off during the cathodic scan. The cathodic current negative of 0.0V is also increased after anodic scans with light, representing an increase in the concentration of dissolved oxygen.

The potential for the onset of the photocurrent (E_L) shifts to more negative values with increasing *p*H. The current-potential curves for an Fe_2O_3-coated Pt electrode in solutions of several different *p*H values are shown in Fig. 2. The value of E_L varied somewhat (about 200 mV) for different electrodes.

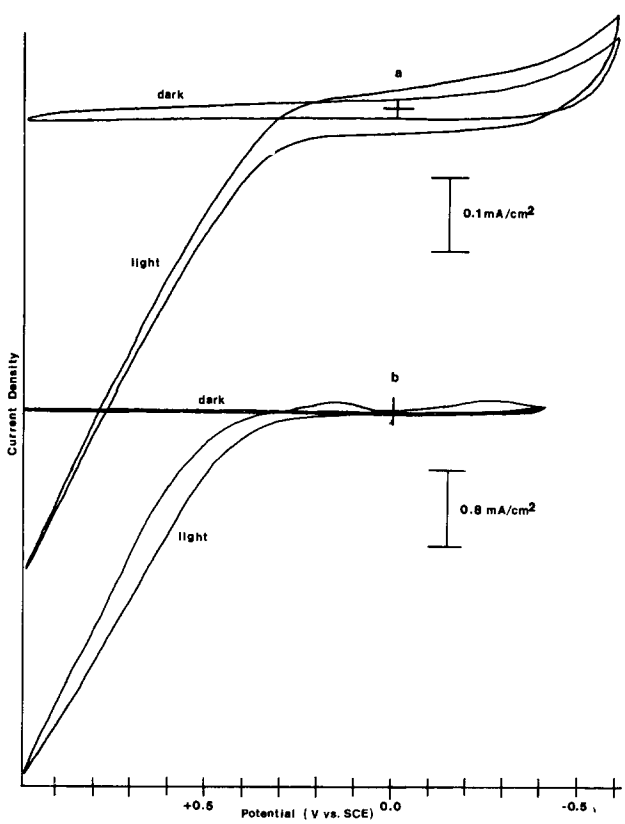

Fig. 1. Current density *vs.* potential for Fe_2O_3 films on (a) Ti, in 0.5*M* KCl, and (b) Pt, 0.5*M* Na_2SO_4.

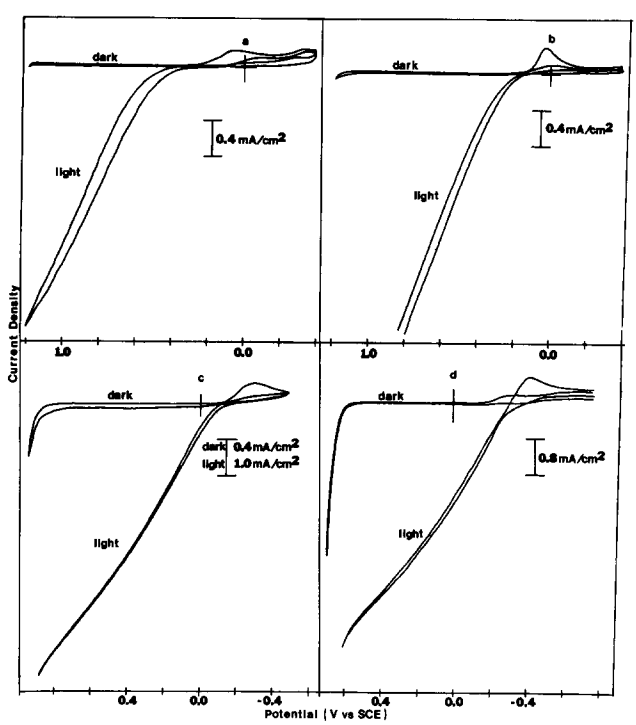

Fig. 2. Current density *vs.* potential for Fe_2O_3-coated Pt electrodes in 0.25*M* Na_2SO_4 solutions buffered to *p*H (a) 4.50, acetate, (b) 6.70, acetate, and (c) 10.36, ammonia. Curve (d) is for 1*M* NaOH.

The iron oxide electrodes appeared stable at open circuit in alkaline solutions up to 1*M* NaOH. Acid solutions (pH less than 4) slowly dissolved the oxide coating. Continuous potential scans between +1.0 and −0.6V in alkaline solutions produced no noticeable changes in surface appearance or *i-E* characteristics, although holding the electrode at potentials negative of −0.6V could possibly damage the electrode. There was no detectable change in behavior after holding the electrode at +0.600V at a pH of 10.4 (NH_4Cl-NH_3 buffer containing 0.25*M* Na_2SO_4) for 1 hr (current density, 4.7 mA/cm²); under these conditions the electrode was covered with gas bubbles. In pH 4.5 acetate buffer the Fe_2O_3 film gradually dissolved during a series of scans between +1.2 and −0.6V. However if the electrode was held at +0.600V in this buffer under illumination no decrease in photocurrent was observed.

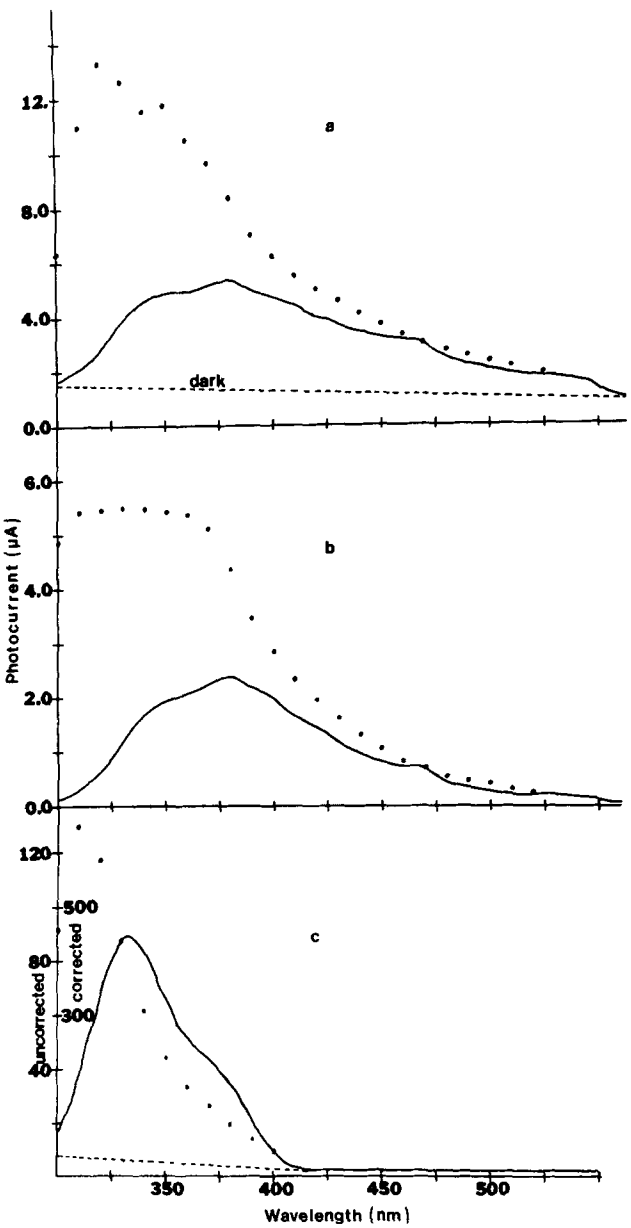

Fig. 3. Photocurrent *vs.* wavelength at a potential of E = +0.800V (*vs.* SCE) for Fe_2O_3 films on (a) Ti, in 0.5M KCl, (b) Pt, in 0.5M Na_2SO_4, and (c) CVD TiO_2 electrode in 0.5M KCl. Solid line is uncorrected for intensity variations; circles are the corrected curve.

On the other hand, holding it at −0.5V under the same conditions caused a rapid dissolution of the coating.

The spectral response of the Fe_2O_3 electrodes at E = +0.800V is shown in Fig. 3a (Ti substrate) and 3b (Pt substrate). Figure 3c is a spectral curve of CVD TiO_2 on Ti shown for comparison. Curves are given with and without corrections for lamp/monochromator output variations. The dark current for the Ti substrate decayed slowly during measurement resulting in a sloping base line. The spectral response curves for all of the Fe_2O_3-coated substrates were virtually identical in shape, indicating that the photoeffect is due to the Fe_2O_3 itself. A significant portion of the total photocurrent under the curve shown (approximately 20% of corrected curve) is at wavelengths longer than 400 nm, compared to virtually zero for TiO_2. Thus the Fe_2O_3 electrode could be operated at +0.400V in 1*M* NaOH with a yellow filter having <0.1% transmittance below 450 nm, yielding a current density of 700 μA/cm² with gas bubbles being observed on the surface.

The photocurrent for the iron oxide begins at about 550 nm which would correspond to the reported bandgap of Fe_2O_3, *i.e.*, 2.2 eV (10). A coating of the iron oxide was deposited on a quartz slide and heated in flame. Although the coating was quite adherent, it showed a high resistance. An absorbance *vs.* wavelength curve (taken with a Cary 14 spectrophotometer) of the Fe_2O_3 on quartz sample showed a steep rise in absorbance beginning at about 580 nm, with absorbance above 1.0 at 550 nm, again agreeing with the bandgap energy of Fe_2O_3.

The spectral response and reasonable stability of the iron oxide film electrode makes it suitable for use in photoelectrochemical experiments at longer wavelengths, as well as a possible electrode for the photo-assisted electrolysis of water and in photoelectrochemical solar cells (3, 11).

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