

## Photocurrent Stability of CdS Sensitized TiO<sub>2</sub> Electrodes

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In recent years, there has been significant progress using metal complexes coated on a nanocrystalline TiO<sub>2</sub> film which is prepared to maximize its surface area.<sup>1-3</sup> Grätzel and co-workers reported that TiO<sub>2</sub>-electrodes coated with cis-di(thiocyanato)-bis(2,2'-bipyridyl)-4,4'-dicarboxylate ruthenium(II) was found to be the most efficient amongst a series of ruthenium-containing dyes.<sup>1</sup> Solar energy conversion efficiencies as high as 10 % have been achieved. Together with the efforts to synthesize new efficient dyes, the use of semiconductor particles of nanometer size has recently received increasing attention as sensitizers.<sup>4-7</sup> Those particles having a small bandgap and an energetically high-lying conduction band possess some advantages as compared to organic dyes:<sup>8-10</sup> the absorption ranges are adjustable by controlling the size of the particles, and the surface properties of the particles can be modified in order to increase the photostability of the electrodes. In contrast to organic dyes, however, the photophysics and photochemistry of nanoparticles are still only poorly understood, and most of the knowledge is empirically based.

In this study, to understand the photocurrent stability of nanocrystalline TiO<sub>2</sub> electrodes sensitized by CdS particles we have examined the current-voltage characteristics of the electrodes in aqueous solution containing S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> electrolytes. Nanocrystalline TiO<sub>2</sub> electrodes were prepared by sintering spin-coated TiO<sub>2</sub> films,<sup>2</sup> and CdS particles were coated on the TiO<sub>2</sub> by a chemical bath deposition as described below.<sup>11</sup> The photoelectrochemical measurements were complemented by electrochemical quartz crystal microbalance (EQCM) gravimetry.

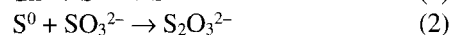
### Experimental Section

The CdS films on nanocrystalline TiO<sub>2</sub> films were deposited for 5 min at 85 °C from 50 mL solution of 2 mM of Cd<sup>2+</sup>, 5 mM of NH<sub>4</sub>Cl, 4 % NH<sub>4</sub>OH and 0.02 M thiourea. The CdS-coated TiO<sub>2</sub> (hereafter CdS/TiO<sub>2</sub>) was washed with 1.0 M HCl and distilled water. The area of a CdS/TiO<sub>2</sub> electrode in contact with electrolytic solution was typically about 0.1 cm<sup>2</sup>. The electrode was illuminated with a 250W tungsten-halogen lamp. Current density-voltage curves were obtained with an EG&G Princeton Applied Research model 273 potentiostat/galvanostat or a Keithley 236 source measure unit using a Pt counter electrode. A Seiko EG&G quartz crystal analyzer QCA917 was used to measure mass changes in ng during the photoelectrochemical process by use of the equation  $\Delta m = -1.099\Delta f$ , with  $f$  in Hz. For characterizing the surfaces, a Philips XPERT-MPD X-ray diffractometer, a

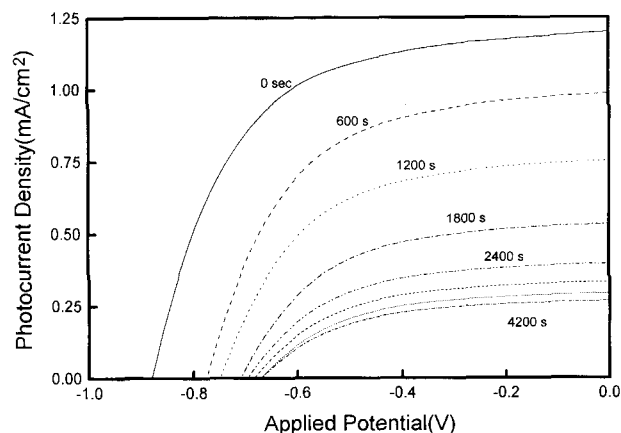
Physical Electronics PHI-680 Auger nanoprobe, and a Hitachi S-4200 SEM were utilized. A Perkin-Elmer OPIMA 3000XL ICP-AES analyzer was used to measure the amount of Cd in the electrolyte solution.

### Results and Discussion

SEM images were obtained to compare the top and cross-sectional views of the CdS/TiO<sub>2</sub> surface with those of the TiO<sub>2</sub> surface. No size difference was apparent, indicating that the CdS particles on CdS/TiO<sub>2</sub> are smaller than a few nm in diameter. One of the drawbacks of a CdS/TiO<sub>2</sub> electrode is poor stabilities of photocurrent and photovoltage, which can be demonstrated with photocurrent-voltage curves. Figure 1 shows typically those curves of a CdS/TiO<sub>2</sub> electrode with the time of illumination at an intensity of 100 mW/cm<sup>2</sup> in 0.4 M S<sup>2-</sup> and 0.1 M SO<sub>3</sub><sup>2-</sup> aqueous solution. The curves were obtained at a scan rate of 100 mV/s in a two electrode arrangement. With an increase in the time, the current density decreases. For the period of 1 hr, the current density decreases by 75%. The poor stability was considered to stem most likely from the reactions of photogenerated holes. Photogenerated holes in CdS are known to react with the electrolyte to result in the formation of a small amount of sulfur or polysulfide which are converted into S<sub>2</sub>O<sub>3</sub><sup>2-</sup> by reacting with SO<sub>3</sub><sup>2-</sup> as follows:



The holes can also oxidize CdS on the surface. The latter



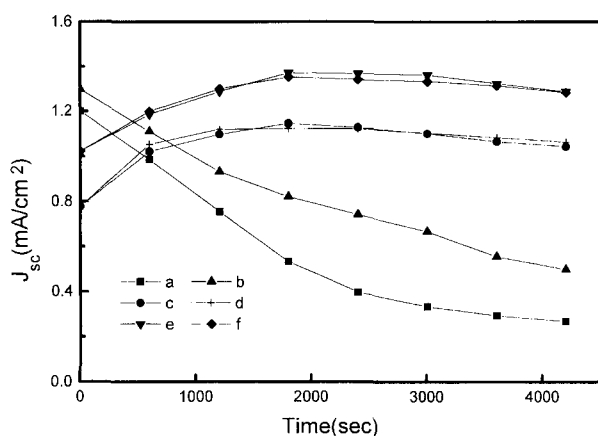
**Figure 1.** Typical photocurrent density-voltage curves of an untreated CdS/TiO<sub>2</sub> electrode with the time of illumination in 0.4 M S<sup>2-</sup>/0.1 M SO<sub>3</sub><sup>2-</sup> aqueous solution. Light intensity was 100 mW/cm<sup>2</sup> and the potential scanned at 100 mV/sec.

reaction leads to a photocorrosion. By scavenging the holes, one would expect increases in photocurrent as well as its stability. When a film of pyridine as a hole scavenger is coated on the CdS/TiO<sub>2</sub> electrode, the photocurrent stability indeed enhances as summarized in Figure 2, where the short-circuit current densities,  $J_{sc}$ , are plotted vs. the illumination time. The  $J_{sc}$  decreases with the time, however, the rate of decrease is slower than that of the untreated CdS/TiO<sub>2</sub> electrode.

Colloidal semiconductor particles contain a high density of surface states, usually present at the semiconductor surface, and the nature of these defect sites depends strongly on the preparation method of the electrodes. One of key issues to improve the efficiencies of a sensitized TiO<sub>2</sub> solar cell is to block the surface states whose energy levels lie below the conduction band. It has been shown<sup>2</sup> that treatment with 4-tert-butylpyridine on a TiO<sub>2</sub> surface increases the photocurrent due to the reduction of an interfacial back electron transfer mediated by Ti<sup>3+</sup> surface states. Large increases in the  $J_{sc}$  with all the pyridine coated electrodes in Figure 2 can thus be partially attributed to the blocking of the surface states at CdS/TiO<sub>2</sub> electrode in the present of a film of pyridine on the electrode surface.

A preliminary result by Auger spectroscopy indicated that annealing of a CdS/TiO<sub>2</sub> electrode at 300 °C yielded a loss of sulfur, suggesting that some sulfur containing compounds are volatilized during the annealing in the air. Annealing is expected to remove some surface states derived from surface defects. Figure 2 reveals that annealing at 300 °C for 1 hr indeed increases the photocurrent by approximately 25% in comparison with that of untreated, non-annealed one. Annealing, however, above 400 °C showed an adverse effect on the photocurrent, although annealing of a CdS/TiO<sub>2</sub> electrode up to 400 °C revealed no changes in the crystal structures of the semiconductors as confirmed by XRD (not shown).

To obtain a constant charge flow in the outer circuit,



**Figure 2.** Comparative time-curves of  $J_{sc}$  with various CdS/TiO<sub>2</sub> electrodes in 0.4 M S<sup>2-</sup>/0.1 M SO<sub>3</sub><sup>2-</sup> aqueous solution. Electrodes: (a) untreated; (b) annealed at 300 °C for 1 hr; (c) pyridine coated, non-annealed; (d) same as (c), but 3 mM S<sub>2</sub>O<sub>3</sub><sup>2-</sup> added in the solution; (e) pyridine coated after annealing at 300 °C for 1 hr; (f) same as (e), but 3 mM S<sub>2</sub>O<sub>3</sub><sup>2-</sup> added in the solution.

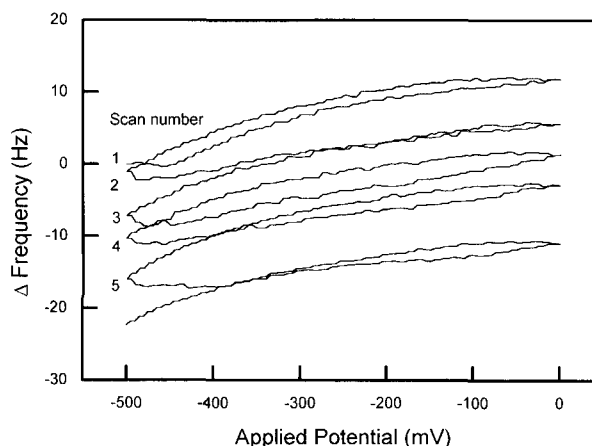
S<sub>2</sub>O<sub>3</sub><sup>2-</sup> should be reduced at the counter electrode. Upon the addition of 3 mM S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, the  $J_{sc}$  was found to increase by as much as 40%. Figure 2 shows, however, the addition of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> into the electrolyte solution essentially affects little on the  $J_{sc}$ , which implies that the effect of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> on the  $J_{sc}$  is obscured by pyridine when the electrode surface has been already coated with pyridine. The amount of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> produced by the photogenerated holes (Eq. (2)) is apparently sufficient for the charge flow with a pyridine-coated CdS/TiO<sub>2</sub> electrode. It is interesting to note in Figure 2 that all of the pyridine-coated electrodes show monotonic increases in  $J_{sc}$  in the early period and then stabilizes. The cause of the gradual increase is not certain. A possible explanation is that some time is required to reach an equilibrium caused by the retarded indiffusion of electrolytes through a hydrophobic film of pyridine toward the electrode surface.

Table 1 summarizes the data on the atomic concentration of a CdS/TiO<sub>2</sub> electrode obtained by Auger spectroscopy and reveals that the atomic ratio of sulfur to cadmium (S/Cd) increases after 1 hr of the illumination under 0 V. This result possibly suggests that sulfur accumulates on the electrode surface during the photoelectrochemical process. The accumulation can be explained by assuming that the reactions with S<sup>2-</sup> and/or SO<sub>3</sub><sup>2-</sup> do not effectively remove the oxidized elemental sulfur from the CdS surface. In addition, the deposition of sulfur appears to be predominant over the competing reaction, *i.e.*, the dissolution of CdS. If the latter reaction dominates, a decrease in the ratio of S/Cd would be expected. An EQCM measurement was performed to obtain a supporting evidence for the explanation. Figure 3, a plot of frequency change vs. applied potential under illumination,

**Table 1.** Atomic concentration (%)<sup>a</sup> and the ratio of a CdS/TiO<sub>2</sub> electrode surface

electrode	Cd	S	S/Cd
untreated	43.9(±0.7) <sup>b</sup>	47.3(±0.2)	1.08(±0.01)
exposed to light <sup>c</sup>	35.7(±0.9)	50.8(±0.5)	1.42(±0.03)

<sup>a</sup>average of three measurements. <sup>b</sup>one standard deviation, <sup>c</sup>at 0 V for 1 hr



**Figure 3.** Frequency change of a CdS/TiO<sub>2</sub> electrode in 0.4 M S<sup>2-</sup>/0.1 M SO<sub>3</sub><sup>2-</sup> aqueous solution with the time of illumination against applied potential scanned at 100 mV/sec.

shows that a CdS/TiO<sub>2</sub> electrode gains in mass as the potential scan increases and that the electrode becomes heavier with the time of illumination at a given potential, e.g., near the short-circuit region. For the period of 50 sec in Figure 3, the mass gain is calculated to be about 20 ng. Nevertheless, the result supports the sulfur accumulation on the CdS/TiO<sub>2</sub> electrode.

It may be concluded based on the experimental data described above that the electrode surface is primarily deteriorated by the accumulation of elemental sulfur formed according to Eq. (1). The electrode deterioration appears to result in the lowering of the photocurrent with the time of illumination. A competing reaction with CdS also occurs, judging from an ICP analysis that a ppb level of Cd<sup>2+</sup> above the background level in the illuminated solution was detected. Under the present condition, although the competing photocorrosion reaction appears to play a minor role, it would certainly cause the photocurrent instability to some extent. Further studies on the removal of accumulated sulfur from CdS, e.g., by cathodic stripping would be worthwhile.

### Conclusion

The CdS nanoparticles were coated on TiO<sub>2</sub> by a chemical bath deposition and the photocurrent stability of the CdS/TiO<sub>2</sub> electrodes has been investigated in S<sup>2-</sup>/SO<sub>3</sub><sup>2-</sup> aqueous solution. The photocurrent stability is found to be closely related to the sulfur accumulation on the electrodes caused by the photogenerated holes in CdS, and by the insufficient removal of the sulfur from the CdS surface by the reacting

with S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup>. The photocurrent increases and the stability improves upon adding of pyridine as a hole scavenger and annealing the electrodes at 300 °C for 1 hr.

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