

## Electrochemically-deposited Thiophenolatocopper(I) Coating for Cadmium Sulphide

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A thiophenolatocopper(I) (CuSPh) coating has been deposited on Pt, Mo, and CdS by electrochemical oxidation of the bithiophenolatocopper(I)-anion  $[\text{Cu}(\text{SPh})_2^-]$  in solution.

While photoelectrochemical cells (PEC) incorporating p-type semiconductors have been shown to provide reasonable energy conversion efficiencies and stabilities,<sup>1</sup> a continuing problem in the use of non-oxide n-type semiconductors has been their inherent lack of stability at the liquid junction owing to oxidation of the crystal.<sup>2,3</sup> To solve this problem research has proceeded along two paths: incorporation of suitable redox couples in the liquid phase;<sup>3-5</sup> and modification of the semiconductor surface.<sup>6-10</sup>

In this communication we report an approach to surface modification that involves the anodic electrodeposition of thiophenolatocopper(I) (CuSPh) on polycrystalline cadmium sulphide. One advantage of the anodic electrodeposition technique is that the depth of the coating can be controlled from a few monolayers up to thicknesses that permit mechanical removal of the coating for analysis.

Thiophenolatocopper(I) was deposited by electrolysis of a solution of the 0.004 M bithiophenolatocopper(I) complex,

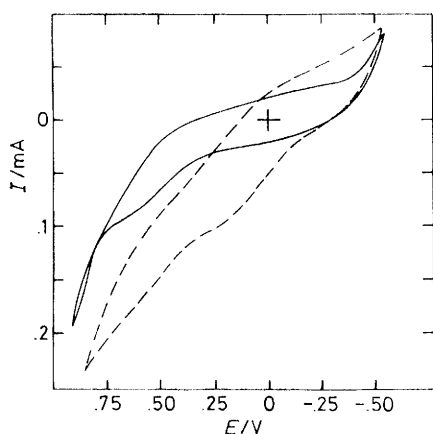
$\text{Cu}(\text{SPh})_2^-$ , and 0.2 M sodium trifluoromethanesulphonate dissolved in nitrogen-bubbled triglyme as solvent at 90–100 °C in a three-electrode cell at constant potential of 0.5 V (relative to Ag/AgCl/satd. KCl). This potential corresponds to the first wave in the cyclic voltammogram of  $\text{Cu}(\text{SPh})_2^-$  at the CdS anode. The irreversible oxidation of  $\text{Cu}(\text{SPh})_2^-$  results in the formation of CuSPh and apparently PhSSPh.† The semiconductor electrodes consisted of a 5000–7000 Å polycrystalline cadmium sulphide film deposited electrochemically on H<sub>2</sub>O<sub>2</sub>-etched molybdenum foil.<sup>11</sup> Physical properties of the film have been characterized.<sup>12</sup> Thiophenolato copper(I) was also deposited on platinum and molybdenum foils, and it seems likely that a wide variety of other metal and semiconducting materials are suitable substrates. Dark

† The study of the electrochemistry of the deposition will be described in a subsequent paper. PhSSh is soluble in triglyme.

**Table 1.** Output-power characteristics for the coated and uncoated CdS<sup>a</sup>/[Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> photoelectrochemical cell.

Electrode	Maximum power/ $\mu$ W			Fill factor <sup>f</sup>	$V_{oc}$ <sup>f</sup> /V
	Initial	5 min	15 min		
CdS, <sup>b</sup> uncoated unetched	82 $\pm$ 16	43 $\pm$ 21	26 $\pm$ 7	0.35 $\pm$ 0.03	0.76 $\pm$ 0.08
CdS, <sup>c</sup> uncoated etched	14	17	15	0.22	0.27
CdS, <sup>d</sup> coated	76 $\pm$ 26	81 $\pm$ 4	71 $\pm$ 5	0.29 $\pm$ 0.03	0.82 $\pm$ 0.01
CdS, <sup>e</sup> coated	171	152	142	0.53	0.84

<sup>a</sup> Platinum counter electrode. Power determined after operating cell for periods indicated, see text. Approximate area of the electrode is 0.5 cm<sup>2</sup>. <sup>b</sup> Average for three CdS electrodes. <sup>c</sup> 10 s nitric acid etch. <sup>d</sup> Average for two coated electrodes. CuSPh was deposited on etched CdS (HNO<sub>3</sub>, 10 s) for 20 s while stirring. <sup>e</sup> CuSPh was deposited on etched CdS (HNO<sub>3</sub>, 10 s) for 20 s under stationary conditions. Hence deposition occurred at a slower rate. <sup>f</sup> Maximum value.  $V_{oc}$  is the open circuit voltage.



**Figure 1.** Cyclic voltammograms of etched CdS in the dark (—) and under illumination (---) in Cu(SPh)<sub>2</sub><sup>-</sup> solution at 20 mV s<sup>-1</sup> scan rate with Ag/AgCl/satd. KCl reference; electrode areas are each approximately 1 cm<sup>2</sup>. Since CuSPh coats CdS, fresh electrodes were used to obtain each cyclic voltammogram.

current densities for Cu(SPh)<sub>2</sub><sup>-</sup> on etched (0.1 M HNO<sub>3</sub>, 10 s) cadmium sulphide are comparable with those found on Pt, a surprising result since dark charge transfer processes involving minority carriers are not expected to be efficient.<sup>13</sup> Such processes do sometimes occur. Wrighton *et al.*<sup>14</sup> observed the dark reduction of ferrocene at p-type single crystal silicon in methanol, and Bard *et al.*<sup>15</sup> observed the dark oxidation of thianthrene at dark n-type single crystal WSe<sub>2</sub>. Whether or not this dark process is promoted by surface states<sup>14,15</sup> will become clearer after the flat-band potential has been measured for our CdS film in polyether. The uncoated film exhibits behaviour found for other p- and n-type semiconductors under illumination.<sup>8,14,15</sup> Thus, Figure 1 illustrates a cathodic shift of 400–500 mV in the position of the first wave<sup>‡</sup> in the cyclic voltammogram of illuminated *vs.* dark CdS. Based on preliminary photocurrent–photovoltage characteristics (reported below) and Rutherford backscattering data (to be reported), corrosion of the CdS film to form elemental sulphur does not appear to occur during electrodeposition of CuSPh.

Preliminary results (Table 1) from a study of the photocurrent–photovoltage characteristics of uncoated and CuSPh-coated CdS films indicate that the coating stabilizes the film to some extent. Thus after running the photoelectrochemical cell at approximately maximum power for 15 min (Table 1), there is a marked decrease in the maximum power output for

the uncoated, unetched CdS film but not for the coated CdS films. Furthermore there is an indication that CuSPh deposition under stationary conditions improves the power output of the CdS film. However more tests are needed to verify this result. Nevertheless, it should be noted that the CuSPh coatings are deposited on *etched* CdS films (HNO<sub>3</sub>, 10 s). Comparison of the results for the etched, uncoated CdS film with those of the coated films indicates that a CuSPh coating causes a significant improvement in the photocurrent–photovoltage characteristics of the etched CdS film. For this study, an aqueous [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> solution at pH 7.0 (sodium phosphate) was used<sup>16</sup> in a two electrode cell (platinum counter electrode) that was connected to a variable resistor, and the CdS film was illuminated with a 150 W xenon lamp.

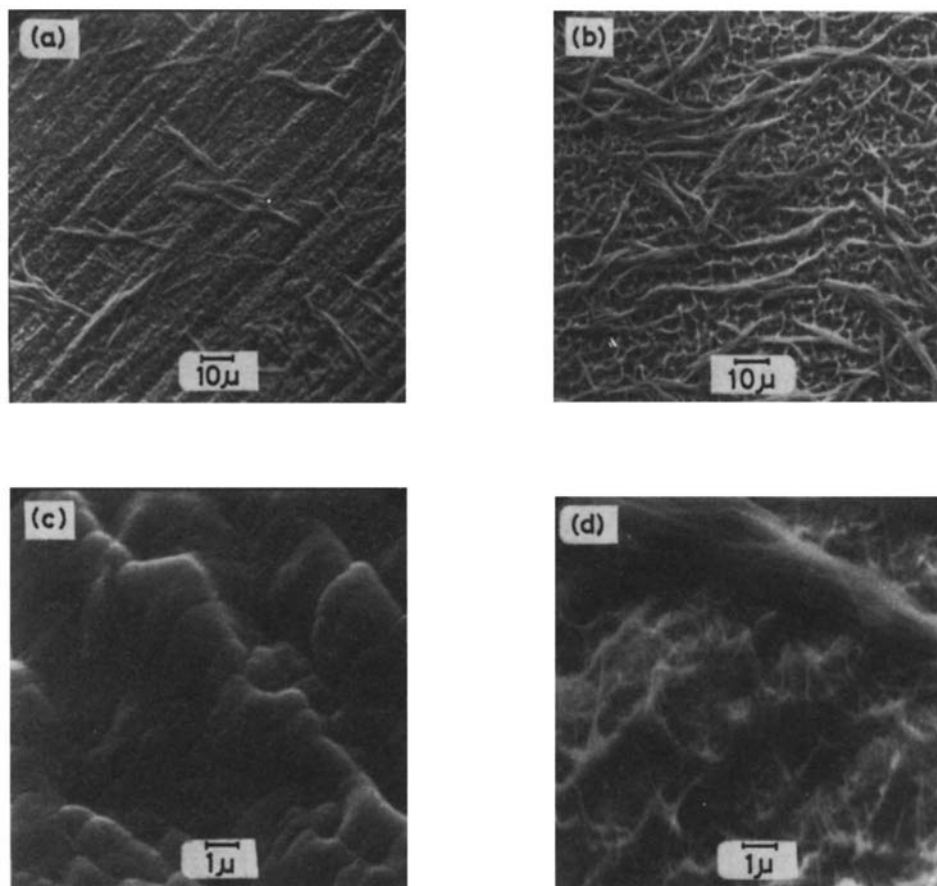
A major aspect of this study has been the identification of the deposit. A variety of techniques have been employed to confirm that the material is indeed CuSPh. Thus, coatings scraped from the surface of platinum electrodes give a mass spectrum identical with that of authentic thiophenolato-copper(I). Principal peaks found at masses of 186 and 218 are assigned to diphenyl sulphide and diphenyl disulphide, respectively. No peaks were found at molecular weights consistent with copper-containing fragments, indicating that pyrolysis of the samples occurs in preference to vaporization. Consequently, it appears unlikely that this material could be deposited using vapour deposition techniques.

Rutherford backscattering spectroscopy<sup>17</sup> of coatings on CdS confirmed the presence of copper and sulphur in significant amounts on the surface of the semiconductor. Thus, bombardment of the sample with 1.60 MeV alpha particles produced sharp plateaus at backscattering energies predicted for copper (1.25 MeV) and sulphur (0.977 MeV) on the surface.<sup>18</sup> The surface energy approximation<sup>18</sup> shows the copper-to-sulphur ratio to be 1:1 as expected for CuSPh. Probing various sections of the surface revealed that the thickness of the coating varies slightly. However, there appear to be no pinholes in the 200 s deposit since scattering due to Cd or Mo was not detected.

An indication of the purity of the CuSPh coating is given by atomic absorption, which showed a copper content of 35.1  $\pm$  0.9% compared with 37.8  $\pm$  0.8% for an authentic sample of thiophenolato-copper(I) (theoretical value: 36.6%).

Scanning electron microscopy reveals needle-like crystals on the surface of CdS [Figure 2 (a,d)]. A sample grown for a longer period shows the thicker deposit to possess the same needle-like structure [Figure 2(b)]. These are in sharp contrast to the morphology of etched cadmium sulphide [Figure 2(c)]. In conclusion, it seems likely that a wide variety of organometallic compounds are potential candidates for this deposition process. In addition, both growth rate and thickness are electrochemically controlled.

<sup>‡</sup> Measurements in the absence of copper complex do not exhibit these waves.



**Figure 2.** Scanning micrographs of CuSph coatings [deposited at +0.5 V relative to Ag/AgCl/satd. KCl reference on etched (HNO<sub>3</sub>, 10 s) CdS films]: (a) 50 s deposit, 700× magnification; (b) 200 s deposit, 700× magnification; (c) etched CdS, no deposit, 7000× magnification; (d) 50 s deposit, 7000× magnification.

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