

# Semiconductor Electrodes. 44. Photoelectrochemistry at Polycrystalline p-Type WSe<sub>2</sub> Films

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Photoelectrochemical (PEC) cells (1) based on layered semiconductors (e.g., WSe<sub>2</sub>, MoSe<sub>2</sub>) are particularly attractive for solar energy conversion for a number of reasons. The excitation process involves d-d transitions and this may provide good stability for the photoelectrode. The band gaps of these materials are well-matched with the solar spectrum so that high efficiencies, in principle, can be realized. Finally, they are made of relatively abundant and inexpensive materials (e.g., W, Mo, S, Se). The pioneering work of Tributsch and co-workers (2) on the use of these materials for regenerative photoelectrochemical cells has stimulated research in this area (3) and cells using small, selected single crystals have shown high efficiencies (e.g., 14% in red light (4) and 10.2% under solar irradiation). (5)

One of the major drawbacks of these systems, however, is that crystal imperfections and exposed edges on the surface perpendicular to the C axis ( $\perp$  C) act as recombination centers for the photogenerated carriers or as sites for back-reaction of photogenerated products, thus decreasing efficiencies dramatically. (3b,h) As a result the observed efficiencies are strongly dependent on the nature of the surface of the individual crystals and large area electrodes (0.1 cm<sup>2</sup>) which show good efficiencies have not been produced. Our research group (6) and others have attempted to produce materials as electrodes by vapor deposition or sintering, but these generally showed no or very small photocurrents under conditions (e.g., with I<sup>-</sup>/I<sub>2</sub> electrolytes) where single crystals work well, presumably because of the abundance of surface imperfections and exposed edges. We report here the preparation of polycrystalline p-WSe<sub>2</sub> electrodes which show better than 1% red light efficiencies in photovoltaic (regenerative) PEC cells.

Films of p-WSe<sub>2</sub> on quartz were prepared as follows. Tungsten selenide (WSe<sub>2</sub>) powder (Gallard Schlesinger 99.8%) was introduced into a quartz tube (15 cm long and 18 mm diameter) which had been cleaned successively

with HF(48%), 1:1 HNO<sub>3</sub>:HCl by volume, HF(48%), then thoroughly rinsed with distilled water and dried. After evacuating for about 45 min to 1 x 10<sup>-5</sup> torr, the tubes were sealed under vacuum and placed inside a Jelrus dental furnace at 850<sup>o</sup> C for a period of 67 h. The furnace was then turned off and the tube was allowed to come to ambient temperature. At this stage, part of the material had deposited on the walls of the tube, giving it a mirror-like appearance; the underside of the film had a black matte appearance. The tube was opened and pieces of the quartz with deposited WSe<sub>2</sub> were mounted as electrodes. This was done by contacting the front surface of the deposited material with conductive silver paint (Acme Industries, New Haven, Conn.) to a copper lead which was inserted into 6 mm bore glass tubing. The electrode was masked with 5-min epoxy cement except for the surface to be investigated; the areas investigated were typically 0.04 to 0.20 cm<sup>2</sup>. In some cases it was possible to dislodge thin films of WSe<sub>2</sub> from the quartz tubes. These were mounted in the same fashion, except that back surface contacts were made. Electrochemical equipment and techniques were as previously reported. (7) Irradiation of the photoelectrodes was performed with an Oriel (Stamford, Conn.) 450 Watt Xe lamp with a water filter and a 590 nm cut-on filter. The focused power was ~ 88 mW/cm<sup>2</sup>.

PEC Cells. The PEC behavior of these electrodes was investigated in cells containing a number of redox couples: Co(bpy)<sub>3</sub><sup>3+</sup> (bpy = 2,2'-bipyridine), MV<sup>2+</sup> (4,4'-dimethylbipyridinium or methyl viologen) FeY<sup>-</sup> (Y<sup>-</sup> = ethylenediaminetetraacetate), Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Fe(L)<sup>3+</sup> (where L is the macrocyclic ligand shown in Figure 1 prepared by condensation of diacetylpyridine and triethylenetetraamine as described by Curry and Busch. (8a) Table I is a compilation of the results obtained with these different redox couples. The highest output power was obtained with the Fe(L)<sup>3+</sup> complex. The electrochemical response of a polycrystalline Fe(L)<sup>3+</sup> and 0.5 M p-WSe<sub>2</sub> electrode in aqueous 0.3 M Na<sub>2</sub>SO<sub>4</sub> under chopped illumination is

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Table I: Photoelectrochemical Behavior of p-WSe<sub>2</sub> Electrodes in the Presence of Different Redox Couples

Redox Couple	Supp. Elect.	E <sup>0'</sup> vs. SCE (V)	V <sub>oc</sub> <sup>(a)</sup> (MV)	i <sub>ph</sub> <sup>(b)</sup> <sub>@</sub> mA/cm <sup>2</sup>	E <sub>appl.</sub> (V)
1) Ru(NH <sub>3</sub> ) <sub>3</sub> <sup>3+/2+</sup>	0.67 M KCl	-0.18	137	3.8	0.25
				5	0.0
2) Fe(CN) <sub>6</sub> <sup>3-/4-</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	+0.45	130	2.8	+0.4
3) MV <sup>2+/+</sup>	0.6 M KCl	-0.69	---	0.5	-0.4
4) Fe(EDTA) <sup>1-/2-</sup>	0.2 M Na <sub>2</sub> SO <sub>4</sub>	-0.085	---	2	+0.2
5) Co(bpy) <sub>3</sub> <sup>3+/2+</sup>	0.15 M Na <sub>2</sub> SO <sub>4</sub>	0.05	322	1.5	0.2
6) Fe(Macro) <sup>3+/2+</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	-0.10	480	i <sub>ph</sub> <sup>(c)</sup> <sub>sc</sub> = 6-7	

(a) V<sub>oc</sub> = open circuit photovoltage under 88 mW/cm<sup>2</sup> illumination.

(b) i<sub>ph</sub><sub>@</sub> E<sub>appl.</sub> = photocurrent under 88 mW/cm<sup>2</sup> illumination and under potentiostatic control at the stipulated value.

(c) Short circuit photocurrent under 88 mW/cm<sup>2</sup> illumination.

shown in Figure 2. The potential for onset of photocurrent is about 0.40 V, which represents an underpotential of ~0.5V; E<sup>0</sup> for the Fe(L)<sup>3+/2+</sup> couple is -0.10V at pH 4.0. (8b) There was little dark current over this potential range and the photocurrent density approached a limiting value of 10 mA/cm<sup>2</sup> at 0.0 V vs. SSCE. A two-electrode PEC cell containing 0.3 M Fe(L)<sup>3+</sup> and 5 mM Fe(L)<sup>2+</sup> in aqueous 0.5 M Na<sub>2</sub>SO<sub>4</sub> with a large area Pt counter electrode<sup>2</sup> showed short circuit photocurrent densities of 6 mA/cm<sup>2</sup> (geometric area) and open-circuit photovoltages of 480 mV. The fill factor for the cell was only 0.28. This represents a solar energy conversion efficiency of about 1% in terms of the light incident on the cell wall (88 mW/cm<sup>2</sup>). A somewhat larger value would be obtained if corrections for reflectivity and solution absorbance were made.

Characterization of Polycrystalline p-WSe<sub>2</sub> Electrodes. Characterization of the films<sup>2</sup> involved the measurement of the flat band potential (V<sub>fb</sub>), the apparent doping density in terms of the geometric area of the electrode, and film resistivity, as well as investigation of film appearance by scanning electron microscopy (SEM).

A Mott-Schottky plot (1/C<sup>2</sup> vs. V) for a polycrystalline p-WSe<sub>2</sub> electrode in aqueous 0.2 M Na<sub>2</sub>SO<sub>4</sub> at a frequency of 1 kHz was linear (Fig. 3). The intercept yields a value of +0.78V vs. SCE for V<sub>fb</sub>. This is in good

agreement with measurements in aqueous media (3g) on single crystal p-WSe<sub>2</sub> electrodes (V<sub>fb</sub> = 0.72V vs. SCE). From the slope of the plot, an apparent value of N<sub>A</sub> of 2.8 x 10<sup>20</sup> cm<sup>-3</sup> can be calculated. The black matte surface of the film is quite rough, however, so that the actual acceptor density is probably of the order of 10<sup>18</sup>-10<sup>19</sup> cm<sup>-3</sup>. There was some frequency dispersion in the Mott-Schottky plots over frequencies of 100 Hz to 1 KHz, but the calculated values of V<sub>fb</sub> and N<sub>A</sub> were not affected significantly. The surface topography of these materials was investigated by SEM (Fig. 4). The surfaces appear to be composed of randomly oriented thin plates and in some cases scattered islands of small crystals (~200 μm) were observed. The presence of these small crystalline islands were not necessary for the observation of a photoeffect, however, and some of the best results were obtained on samples that showed no such islands. The average film thickness, estimated from the weight of the deposit and the density of WSe<sub>2</sub> (9.35 g/cm<sup>3</sup>) was 35 μm. The resistance of the films across two front surface contacts 0.5 cm apart yielded values of 250 to 3000 ohms for different samples.

It is difficult for us to account for the success of these polycrystalline films as photoelectrodes compared to earlier preparations. The method of surface pretreatment of the substrate appears to be important. Similar photoeffects have been

found with over 60 electrodes prepared in four independent batches, so that accidental special conditions of preparation or experimental artifacts appear unlikely. We have been informed that 99.999% WSe<sub>2</sub> will not transport under the conditions of this work and that minor impurities, including residual water in the tube, may play an important role in the deposition of our material.<sup>(10)</sup> The manufacturer reports the following levels of impurities (in %): Al, 0.01; Cr, 0.01; Cu, 0.01; Fe, 0.05; Ni, Mn, Si, < 0.01; no halogens were detected. We have also detected Fe on the transported material by electron microprobe analysis. Perhaps the very large surface (I/C) to edge ratio or fortuitous passivation of the edge planes in the preparation leads to the reasonable efficiencies observed. While the efficiency of these materials is still too small to be of practical interest, modifications of the method of preparation, the film pretreatment, and solution conditions should lead to significant improvements. For example the 0.3 M Fe(L)<sup>3+</sup> solution is highly colored and absorbs substantial amounts of light. Several methods have also been suggested for passivating the edges of n-type layer compounds which have resulted in improved performance.<sup>(5,9)</sup> Finally, the tubular method of preparation may allow a simple direct fabrication of a PEC cell, where the photoelectrode is deposited on one side of the tube, which itself is the cell body, with a concentric internal counter electrode.

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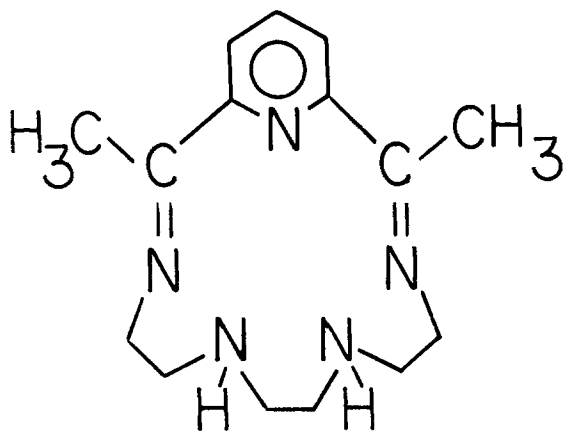


Figure 1: Structure of macrocyclic ligand used.

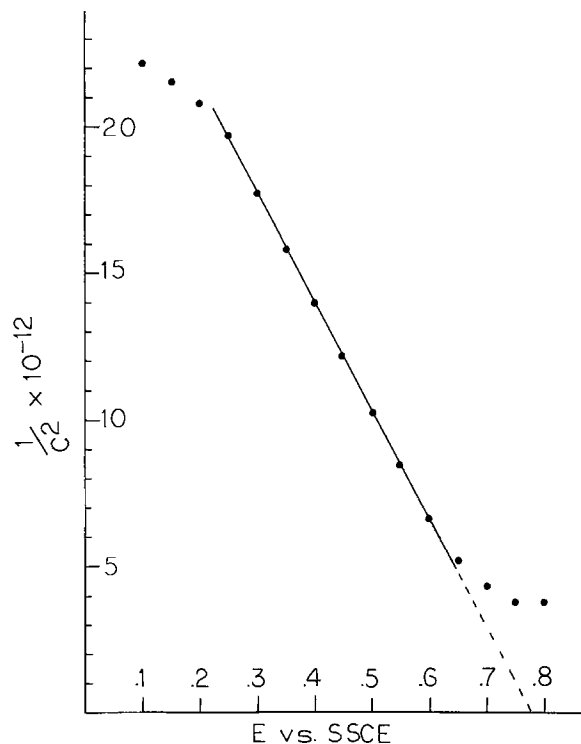


Figure 3: Mott-Schottky plot ( $1/c^2$  vs.  $E$ ) for polycrystalline p-WSe<sub>2</sub> in aqueous 0.2 M Na<sub>2</sub>SO<sub>4</sub> in the dark at 1 KHz.

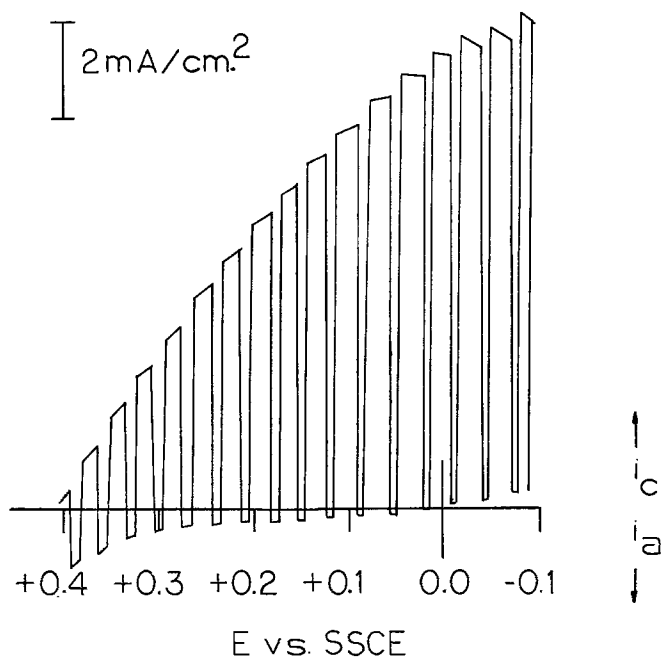


Figure 2: Electrochemistry under chopped illumination for a polycrystalline p-WSe<sub>2</sub> electrode in aqueous .5 M Na<sub>2</sub>SO<sub>4</sub> containing .3 M Fe<sup>III</sup>(Macro), .005 M Fe<sup>II</sup>(Macro). Incident light  $\sim 88$  mW/cm<sup>2</sup>.

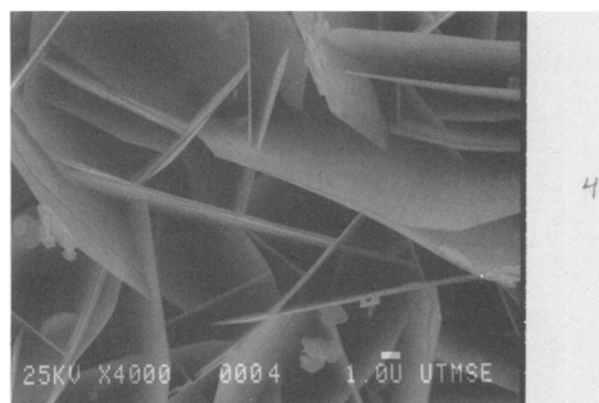
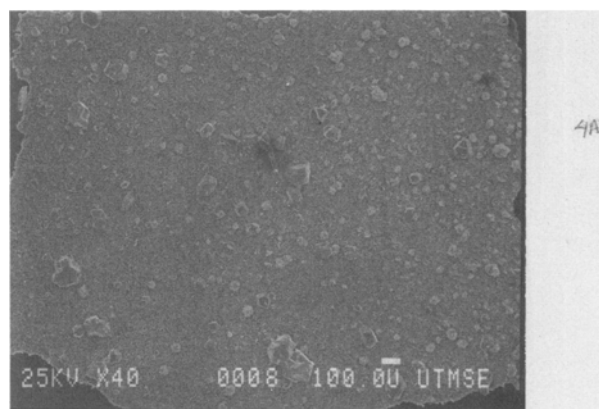


Figure 4: Scanning electron micrographs of polycrystalline p-WSe<sub>2</sub>. (a) Low magnification (40X). Note small crystalline islands. (b) High magnification (4,000X).