

## n-MoSe<sub>2</sub> GRAFTED WITH POLYCARBAZOLE FOR AN EXTENDED LIFE OF THE PHOTOANODE

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### Summary

A n-MoSe<sub>2</sub> photoanode has been stabilised in an acid chloride solution by grafting it with polycarbazole. The mechanism of stabilisation has been investigated and it appears to be a process of regeneration of the n-MoSe<sub>2</sub> on the anode by reaction between Se and polycarbazole. The grafted electrode is potentially useful for applications in photovoltaic power sources.

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The stability of synthetic n-MoSe<sub>2</sub> in electrochemical solar cells is solely dependent on the microscopic smoothness of the van der Waals planes [1 - 5] in the crystal. This microscopic smoothness means that there are fewer imperfections, and surfaces with higher fill factors are generated. As a result several attempts have been made to produce more perfect crystals. Gobrecht *et al.* [6] synthesised an n-MoSe<sub>2</sub> by the bromine gas transport technique and obtained a fill factor of 0.67 as compared to the previously reported values of 0.20 - 0.25 [7, 8]. The higher fill factor is also indicated by a more rectangular photovoltage-photocurrent output characteristic. This semiconductor has a direct bandgap of 1.4 eV and an indirect bandgap of 1.7 eV (estimated from the optical measurements) [9]. Further, the semiconductor lattice oxidation reaction competes with the redox reaction in solution during photoelectrochemical experiments. Because of these factors the best way of stabilising the semiconductor has been through competing kinetics. This kinetic stability is dependent on the medium and the choice of the redox couple. The kinetic stabilisation against photocorrosion was discovered [10] in CH<sub>3</sub>CN electrolyte solutions containing halogen/halide of the type X<sub>n</sub>/X<sup>-</sup> (X = Cl, Br or I) redox couples. The extent to which MoSe<sub>2</sub> can be stabilised was less in aqueous medium except when I<sub>2</sub>/I<sup>-</sup> was used as the redox couple. The reactions which stabilise the anode are represented below.

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With  $\text{Cl}^-$  or  $\text{Br}^-$ , the oxidation occurs at potentials more positive than the photoanodic decomposition



as  $E_{\text{Cl}_2/\text{Cl}^-}^\circ = 1.10 \text{ V}$  and  $E_{\text{Br}_2/\text{Br}^-}^\circ = 0.63 \text{ V}$  [11]. The photoanodic reaction of n-MoSe<sub>2</sub> starts in aqueous medium at 0.55 V *versus* SCE and in CH<sub>3</sub>CN containing 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub> at +1.40 V *versus* SCE.

One of the challenging problems of n-MoSe<sub>2</sub> photoelectrochemistry has been in its stabilisation in acid chloride solutions; this problem was partly solved by using high concentrations of chloride in the medium [12a]. Thus, by using 15 M LiCl and reducing the activity of water at high ionic strengths [12b], stabilisation of n-MoSe<sub>2</sub> against photocorrosion has been achieved. The photocorrosion cannot be reduced using 1 M LiCl as the activity of water is high and that of chloride ions is low.

In this paper we report a different approach to the stabilisation of n-MoSe<sub>2</sub>, *i.e.*, by grafting it with polycarbazole. The n-MoSe<sub>2</sub> gives a more stable photocurrent in 1 M HCl than the ungrafted electrode. The results we obtained open up the possibility of using liquid junction solar cells based on transition metal chalcogenides using the chloride electrolyte.

## Experimental

n-MoSe<sub>2</sub> was 'grown' as described earlier [13]. The electrode was encapsulated using Dow Corning 3145 RTV adhesive/sealant [1].

### Procedure

The supporting electrolyte solutions were prepared from reagent grade chemicals and distilled water. Tetra-n-butyl ammonium perchlorate (TBAP), procured from South-Western Analytical Chemicals, was vacuum dried at 100 °C before use. Carbazole was obtained from Sojuzchim export, Moscow. *N,N*-Dimethyl formamide (DMF) (Merck) was purified by distillation. The current-voltage curves were recorded using a potentiostat/galvanostat and an X-Y recorder. The illumination was carried out using a 500 W tungsten-halogen lamp.

n-MoSe<sub>2</sub> was grafted with polycarbazole by holding the potential of the anode at 1.60 V *versus* a quasi Ag reference in the dark in a 60 mM carbazole solution containing 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub> until a total charge of 1 coulomb had been passed. With a potential sweep from 0 to +0.8 V, under illumination in the above medium, the photocurrent first increased followed by the appearance of a red deposit throughout the surface except in the middle region. When the potential limit was increased from +0.8 to 1.5 V, the red deposit increased initially but a black deposit soon appeared on the surface

of the crystal when the current decreased. These features may be explained as due to lattice oxidation occurring under illumination. It is ideal, therefore, to carry out the grafting of the polymer at potentials below 0.80 V under illumination for preserving the microscopic smoothness of the film.

## Results and discussion

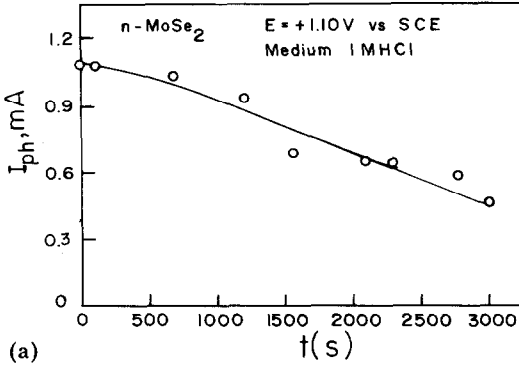
A positive test for determining the stability of n-MoSe<sub>2</sub> in the chosen medium would be to monitor the photocurrent with time; during this measurement any change in the dark current should be corrected for the final analysis. As photodecomposition of n-MoSe<sub>2</sub> occurs at 0.50 V *versus* SCE in 1 M HCl, for a suitable comparison (see below) it is necessary to bias the potential of the photoanode to limit the chloride ion discharge. This ensures that the interfacial energy requirements are satisfied during illumination. Figure 1 shows the photocurrent decay curve corrected for the background current in 1 M HCl medium. The background current was obtained by light interruption. The photocurrent decay in all three samples of n-MoSe<sub>2</sub> examined showed a similar behaviour; when the crystal surface was cleaned after the first illumination, the second photocurrent-time curve was markedly different. With these samples the magnitude of photocurrent was reduced by a factor of almost twenty. The photocurrent-time curve of the polycarbazole-grafted n-MoSe<sub>2</sub> obtained by passing 1.0 C/cm<sup>2</sup> charge, is shown in Fig. 2. The photocurrent onset starts at about +0.70 V *versus* SCE and starts to level off at about 1.10 V *versus* SCE (Fig. 3). This feature is comparable to the onset photocurrent shift observed in the two media discussed earlier [10]. Previous studies of n-MoSe<sub>2</sub> indicated that the shift in the onset potential with reference to the electrochemical oxidation against platinum can be divided into five types.

(a) The first type of redox couple where the electrochemical oxidation occurs at the same potential as with platinum, *i.e.*, the peak potential with n-MoSe<sub>2</sub> is identical to that with platinum — the peaks are reversible in the dark with n-MoSe<sub>2</sub> and upon illumination there is no effect. These couples have  $E^\circ$  more negative than -0.1 V *versus* SCE.

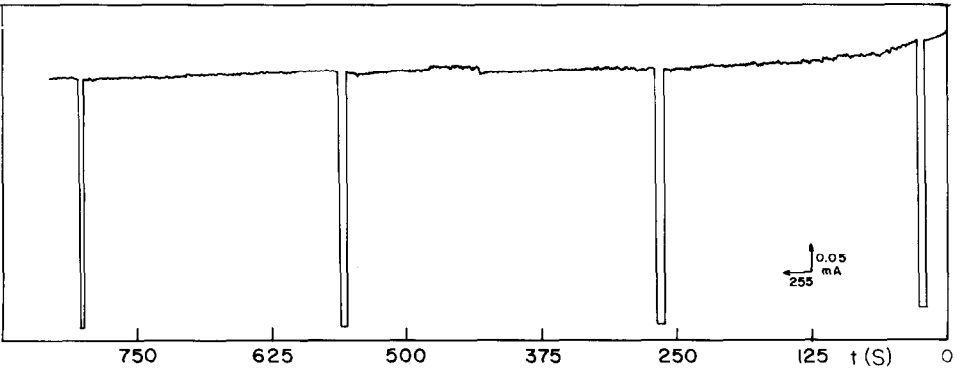
(b) With redox couples having an  $E^\circ$  of about +0.10 V, the behaviour of the photoeffect is significant. While oxidation can be effected in the dark with these redox couples using n-MoSe<sub>2</sub>, a negative shift of both the anodic current onset and the anodic peak current as compared with platinum has been observed.

(c) When the  $E^\circ$  of the redox couples is more positive than +0.2 V, the oxidation of these couples can be effected upon illumination; the oxidation is not effective in the dark with MoSe<sub>2</sub>. Under illumination the oxidation of the reduced form of the couple occurs at a more negative potential than platinum.

(d) By using redox couples having  $E^\circ$  more positive than +0.7 V, a photoanodic peak occurs at more negative potentials than the anodic peak



(a)



(b)

Fig. 1. (a) The photocurrent-time curve obtained using  $n\text{-MoSe}_2$  ( $A \approx 0.18 \text{ cm}^2$ ) in 1 M HCl when the potential of the photoanode was maintained at +1.10 V vs. SCE. The counter electrode was platinum gauze. (b) A segment of the photocurrent-time curve to indicate the dark current values. Experimental conditions are identical to those given in Fig. 2.

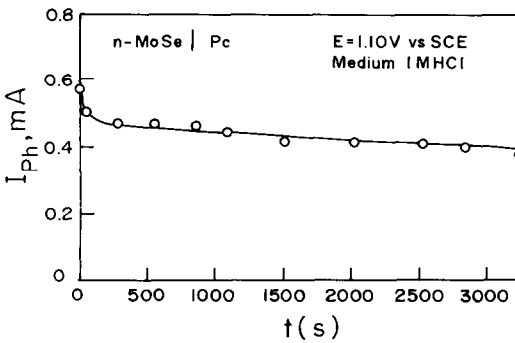


Fig. 2. The photocurrent-time curve obtained using  $n\text{-MoSe}_2$  ( $A \approx 0.18 \text{ cm}^2$ ) grafted with polycarbazole by passing  $1 \text{ C/cm}^2$  charge. The potential of the photoanode was maintained at +1.10 V vs. SCE in 1 M HCl.

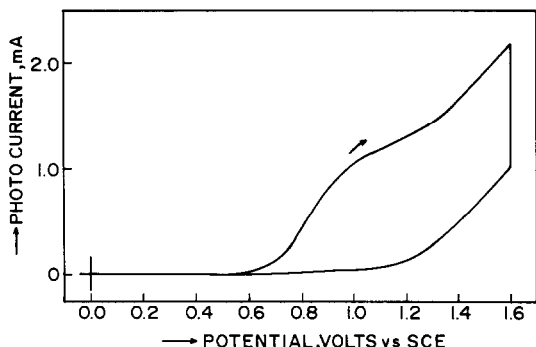


Fig. 3. The current-voltage characteristics of n-MoSe<sub>2</sub> grafted with polycarbazole by passing 1 C/cm<sup>2</sup> charge under constant illumination using tungsten-halogen lamp (500 W).

with platinum. The output voltage is independent of  $E^\circ$  with these redox couples. This behaviour is quite inconsistent with the accepted band model [14].

(e) With  $E^\circ$  of the redox couples more positive than 1.6 V, the electrochemistry is obscured by photoanodic decomposition of the photoanodes.

Of these five types of behaviour observed with n-MoSe<sub>2</sub>, the independence of the output voltage with varying  $E^\circ$  conclusively supports 'Fermi Level pinning' or hot carrier injection [15]; this behaviour is observed with redox couples more positive than  $E_{VB}$  of n-type semiconductors. The polycarbazole grafted n-MoSe<sub>2</sub> shows a positive shift of the onset photocurrent suggesting the 'Fermi Level pinning' is occurring at the polymer-coated electrode; this 'pinning' may be caused by the surface states present on the crystal during illumination. The oxidation



occurs at the MoSe<sub>2</sub> surface at +1.10 V and the evolution of chlorine gas was identified by smell and colour.

With the redox potential of polycarbazole (PC) situated at -0.20 V, the following stabilisation scheme may be proposed; reaction (3) may be followed by



and



would result in redeposition of MoSe<sub>2</sub> on the surface. This reaction is thermodynamically feasible as  $\text{Se} + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{Se}(\text{aq})$  has an  $E^\circ = -0.115$  V [11]. The regeneration of PC will be occurring through the redox couple in the solution. This grafting stabilisation method differs from the solution redox stabilisation using the polyselenide medium [16]. The attenuation of the incident radiation by the medium which occurs in a polyselenide medium is reduced or eliminated at the polycarbazole surface. The

polycarbazole film is transparent to the exciting radiation. The semiconductor regeneration scheme is localised to the semiconductor surface. By the grafting of n-MoSe<sub>2</sub>, the rapid surface photocorrosion is reduced in the aqueous medium. The stabilisation of n-MoSe<sub>2</sub> in aqueous medium with the production of Cl<sub>2</sub> is proving to be a most difficult process.

Bucher *et al.* [17, 18] have discussed the need for developing inexpensive and high efficiency thin-film solar cells as an alternative solution for Si III-V or II-IV compounds. Several oxide semiconductors have been investigated [17] for this application. The stabilisation of n-MoSe<sub>2</sub> by grafting it with polycarbazole suggests the suitability of using it as a photoanode in PEC devices; these devices will be quite analogous to Schottky barrier solar cells with the metal layer being substituted by aqueous conducting electrolyte [19]. With an acid electrolyte the output voltage  $V_{oc} = 1.10$  V and  $I_{ph} = 3.33$  mA/cm<sup>2</sup> (illumination = 14 mW cm<sup>-2</sup>) can be reached at the grafted electrode. Previous reports [20, 21] have stabilised the n-MoSe<sub>2</sub> using solution redox couples such as I/I<sub>2</sub> or Fe<sup>2+</sup>/Fe<sup>3+</sup> generating  $V_{oc}$  in the range 0.09 - 0.55 V. The higher power output obtained at the grafted electrode supports its potential for practical utilisation in PEC devices.

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