275

PHOTOCATALYTIC BEHAVIOUR OF n-MoSe$_2$ SINGLE CRYSTALS IN CONTACT WITH THE I$^-$, I$_2$ REDOX COUPLE IN SOLAR PHOTO-ELECTROCHEMICAL CELLS

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Summary

The photocatalytic activity of the surface of n-MoSe$_2$ crystals for localized oxidation of iodide ions has been examined in a typical photoelectrochemical cell structure by direct microscopic observation and by output performance measurements under spot illumination.

The results demonstrate the presence on the semiconductor surface of 'active' and 'non active' areas. This drastic difference in the catalytic properties of superficial points in the same semiconductor sample may explain the unique role of the I$^-$, I$_2$ redox couple in the behaviour of layer-type semiconductor photoelectrochemical solar cells, as well as the different response to selective superficial chemical agents presented by layered semiconductor crystals of apparently comparable surface morphology.

Introduction

Of semiconductors for possible use in photoelectrochemical solar cells, molybdenum and tungsten dichalcogenides present very interesting characteristics, such as band gaps around 1.4 eV, high stability in aqueous solutions, as well as good output performance in terms of photovoltage, short-circuit current, and fill-factor.

Up to now research on these compounds, and particularly on MoSe$_2$, MoS$_2$ and WSe$_2$, has been carried out using n-type synthetic crystals grown by chemical transport reactions using either bromine or iodine as the transport agent. The basic work of Tributsch and Gerischer [1 - 8] and various subsequent investigations by other workers [9 - 17], have resulted in the acquisition of substantial data on the physico-chemical properties, as well as on the electrochemical behaviour of these layer-type semiconductor electrodes in contact with various redox couples in aqueous and non-aqueous solvents.

The best performance from electrochemical cells based on transition metal dichalcogenides is obtained using the I^-, I_2 redox couple. The unique role of this couple on the response of the layered photoanode/electrolyte interface has not yet been clarified: it has been tentatively attributed to a not-well-defined specific action of the iodide ions on the semiconductor surface [7].

In this work some preliminary results are presented which demonstrate the photocatalytic behaviour of n-MoSe$_2$ in contact with the I^-, I_2, Br^-, Br_2 and I^-, IO_3^- couples, recpectively. A correlation between the catalytic effect and the specific role of the halogen ions on the response of the transition metal photoanodes is also proposed.

Experimental

Semiconductor crystal samples were kindly provided by Dr. F. Lévy, of the Ecole Politechnique Fédérale de Lausanne, Switzerland.

The electrolyte solutions were prepared using high purity chemicals and distilled water, as described in detail in a previous paper [15].

A two-electrode, flat, sandwich-like cell was used. In this cell, MoSe$_2$ single crystal samples (of about 0.8 cm^2 surface area) first had contacts made to them by a copper wire welded with a conductive silver paste to a van der Waals surface*. The crystal was then assembled at the bottom of a flat Teflon container and kept in position by gluing with epoxy resin. A platinum wire counter electrode was spirally arranged above the semiconductor photoanode. The cell was then filled with the selected electrolyte and sealed with a glass window. Such an assembly allowed the cell to be adjusted in any desired orientation, always maintaining the contact between semiconductor and electrolyte. Therefore, with the help of a special support, the cell could be directly placed on the movable sample holder of an optical reflection microscope (Reichert MeF). The variable intensity microscope lamp (halogen, 100 W 12 V) was used as the light source.

The apparatus described allowed direct microscopic observations of the illuminated semiconductor sample either under open circuit conditions or under operation in conjunction with various redox couples, in a typical photoelectrochemical cell configuration.

Results and discussion

Microscopic observations of an illuminated MoSe$_2$ crystal in contact with an aqueous KI solution showed the formation of iodine at given points on the semiconductor surface, as revealed by intense localized coloration. Accordingly, the photopotential (under open circuit conditions) increased in

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*This contact was found to behave as an ohmic contact.
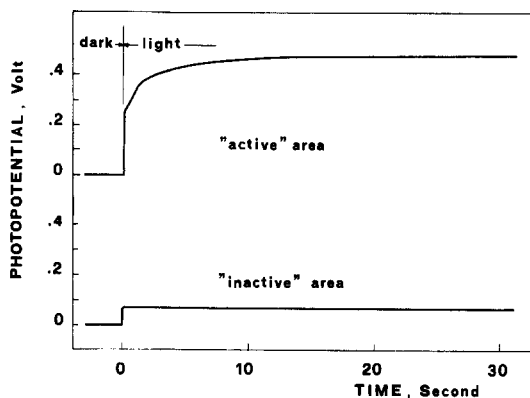
Fig. 1. Photopotential–time behaviour of an MoSe$_2$/I$^-$, I$_2$ (1M, 0.01M)/Pt cell measured under open circuit conditions on an 'active' and a 'non active' area of the same crystal sample.

relation to the light intensity to finally reach a steady value. If the intensity of the light is then reduced, the locally formed iodine disappears and the photopotential declines: the phenomenon is therefore totally reversible.

However, such a phenomenon is not typical of the entire crystal; there are, in fact, points on the surface which have little or no photocatalytic activity, as revealed by the reduced formation or absence of iodine as well as by the low photopotential value, under comparable intensity of illumination.

As an indication of this difference, in Fig. 1 the time trends of photo-potentials obtained separately on 'active' and 'non active' points on the surface of the same crystal are compared. Such a dramatic difference presented by points on the same crystal surface could be demonstrated just by shifting the light beam a few micrometers.

Moreover, if the light spot is shifted from an 'active' to a 'non active' area, the photopotential shifts too, assuming intermediate values between those of the 'active' and 'non active' areas.

A behaviour similar to that described above is observed when the KI electrolyte is replaced by the I$^-$, I$_2$ redox couple. Figure 2 shows the output current–voltage characteristics of the MoSe$_2$/I$^-$, I$_2$ cell, as measured under steady state conditions by illuminating an 'active' and 'non active' area of the semiconductor electrode. The results of both Figs. 1 and 2 refer to the same conditions of illumination.

It must be pointed out that the MoSe$_2$ samples used for the experiments described above were of the 'smooth' type [17], i.e., having the van der Waals surface exposed to the electrolyte without macroscopic structural defects such as crack-like steps or ruptures. In fact, when observed under the microscope, the two areas to which Fig. 2 refers, appeared as smooth portions of the crystal sample.

This indicates that a layer-type semiconductor photoanode, which has an apparently defect-free, smooth surface, does not necessarily give high output characteristics, as is often assumed [9, 18].
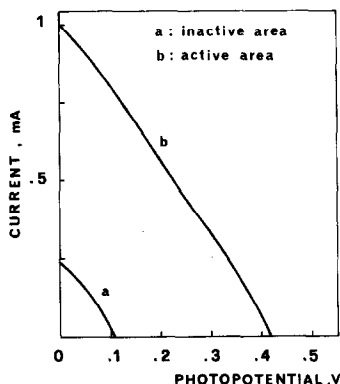
Fig. 2. Current–voltage characteristics of an MoSe$_2$/I$^-$, I$_2$ (1M, 0.01M)/Pt cell, obtained on a 'non active' area (curve a) and an 'active' area (curve b) of the same crystal sample.

The different behaviours presented by the various regions of the same crystal surface may be attributed either to a non-homogeneous distribution of impurities on the crystal surface or to a different defect concentration (density of dislocations, atomic vacancies), both undetectable with the optical microscope but both influencing the photocatalytic properties of the semiconductor.

The catalytic activities of transition metal dichalcogenides (and in particular of MoSe$_2$ and of WS$_2$) are well known [19, 20]. Therefore, the photocatalytic behaviour of MoSe$_2$ observed here is not surprising. However, this behaviour may furnish the explanation for the unique action exerted by the I$^-$, I$_2$ couple on the photoresponse of layer-type semiconductors.

The dependence of the photopotentials of various redox couples on the intensity of the light, measured under open circuit conditions in correspondence with the same 'active' and 'non active' areas, respectively, of an MoSe$_2$ crystal sample, is compared in Fig. 3.

A linear relationship between photopotential and the logarithm of the light intensity (as measured with a photopile), is expected on the basis of the equation

$$U_p = \cos t + KT/e \, (\ln I_L) \tag{1}$$

where U_p is the photopotential, I_L is the intensity of the light and the other symbols have their usual meanings.

However, when illuminating an 'active' area in conjunction with the I$^-$, I$_2$ couple, the photopotential of MoSe$_2$ does not follow this relationship (curve (a) 1), as is the case for other redox couples (curves (a) 3 and (a) 4).

This difference could be attributed to the photoxidation of the I$^-$ ion, catalyzed by the semiconductor crystal surface, which progressively alters the semiconductor/electrolyte interface, up to a steady value (see Fig. 1). In fact, if only the 'non active' area is illuminated, the curve of the MoSe$_2$/I$^-$,
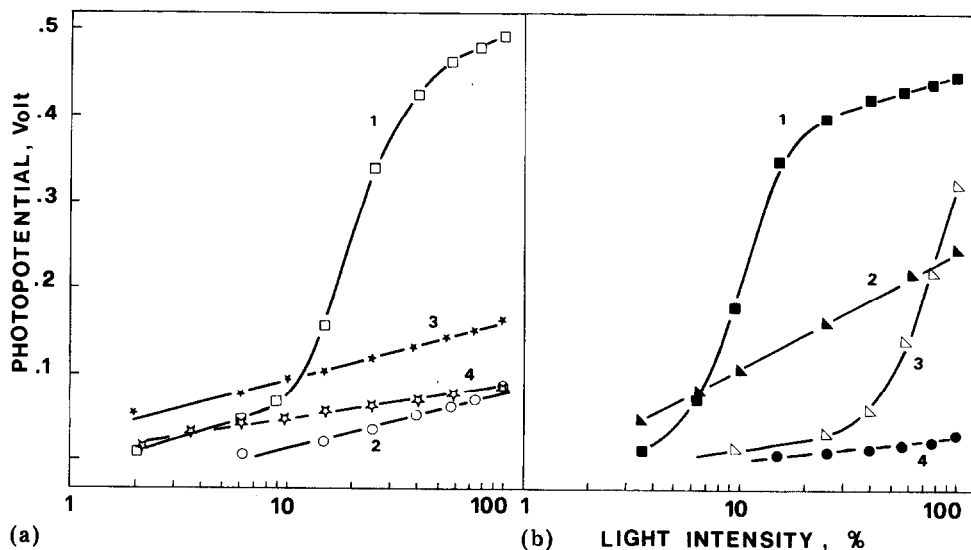
Fig. 3. Photopotential–light intensity dependence of n-$MoSe_2$ in conjunction with various redox couples. (a) I^-, I_2 (1M, 0.01M), active area (curve 1); non active area (curve 2); Fe^{2+}, Fe^{3+} (1M, 0.01M, pH: 1.5), active area (curve 3); $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ (1M, 0.01M), active area (curve 4). (b) Br^-, Br_2 (1M, 0.01M), active area (curve 1), non active area (curve 2); I^-, IO_3^- (1M, 0.01M), active area (curve 3), non active area (curve 4).

I_2 system becomes linear, with a slope of about 59 mV/decade (curve (a) 2), *i.e.*, showing a trend similar to that for other redox couples.

It is then possible to infer that the van der Waals surfaces of $MoSe_2$, and presumably of transition metal dichalcogenides in general, present areas of different catalytic activity. Photopotentials measured in conjunction with redox couples containing I^-, and halogen ions generally, are higher than expected because of the photochemical reactions catalyzed by the semi-conductor surfaces. Indeed, anomalous photopotential–light intensity behaviour has also been observed with I^-, IO_3^- and Br^-, Br_2 couples, respectively, as shown in Fig. 3 (b), which shows the drastic difference between the response of 'active' areas (curves (b) 1 and (b) 3) and of 'non active' areas (curves (b) 2 and (b) 4).

It is, then, reasonable to conclude that the overall performances (photo-potential, short circuit current, fill-factor) of layer-type transition metal photoanodes are the average of the characteristics of 'active' and 'non active' areas. Therefore, these performances depend not only on the macroscopic structural defects, but also, and particularly, on the intrinsic catalytic prop-erties of the surface of the semiconductor. It follows that the chemical treat-ments so far proposed for the selective blocking of recombination centers on the crystal surface [13, 14, 16, 17], being unable to improve the catalytic activity of the semiconductor in the 'non active' areas, cannot indiscri-nately improve the performance of the treated photoanode. Indeed, various authors [13, 17] have observed completely different responses to these

selective chemical agents from semiconductor crystal samples apparently having a comparable surface morphology.

Acknowledgements

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