

Charge carrier kinetics in MoSe₂ and MoS₂ powders

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The dynamics of laser-induced excess charge carriers is investigated in MoSe₂ and MoS₂ powders by contactless time-resolved photoconductivity measurements. Remarkably long lifetimes of excess charge carriers are found. It is shown that platinization of the MoSe₂ and halogen treatment of the MoS₂ powder dramatically shorten the lifetimes of excess charge carriers. The experimental results are discussed with respect to photocatalysis.

1. Introduction

Molybdenum disulfide and diselenide are semiconducting layer-type compounds [1]. Their bandgaps are about 1.4 and 1.6 eV. Therefore they match the bandgap for optimum solar-energy conversion (1.3–1.5 eV) better than, for example, titanium dioxide and cadmium sulfide, which have much larger bandgaps [2]. Consequently, photoelectrochemical solar cells with high energy conversion efficiencies could be developed with group 16 (former group VIB) dichalcogenides [3]. They also show good stability against photocorrosion, which is due to the fact that the valence band and conduction band are composed of d-orbitals of the metals [4]. In addition, they are well-known catalysts for dehydrogenation and hydrosulfurization of organic compounds [5]. This aspect should favour these materials for photocatalytic reactions.

However, there are only a few examples where group 16 dichalcogenide powders are used in heterogeneous photocatalytic reactions [5,6]. The photocatalytic activity is usually small compared to other materials. The question is whether the reason for the small activity of the powders is fast recombination of the light-induced excess charge carriers or some kind of activation barrier for the transfer of excess charge carriers across the surface to substrates.

A convenient method to grow single crystals of group 16 dichalcogenides is the chemical vapour transport (CVT) by halogens [7]. Doping of the

crystals strongly depends on transport conditions, especially the choice of the halogens [8]. Therefore, it is interesting to investigate whether halogens also influence the dynamics of excess charge carriers.

In this work a contactless microwave technique was used to examine the dynamics of excess charge carriers. This technique was successfully used to probe the transient photoconductivity of a number of semiconducting powders [9].

2. Experimental

The time-resolved microwave-conductivity (TRMC) method is based on the measurement of the relative change $\Delta P(t)/P$ of the microwave power reflected from a sample caused by a change $\Delta\sigma$ of the conductivity of the sample which is induced by a laser flash. In a small perturbation ($\Delta P(t) \ll P(0)$) approximation, a proportionality between $\Delta P(t)/P$ and $\Delta\sigma$ was derived [10]:

$$\frac{P(t) - P(0)}{P(0)} = \frac{\Delta P(t)}{P} = A \Delta\sigma(t), \quad (1)$$

where A is a time-independent proportionality factor. The contribution of the photogenerated species to the photoconductivity is weighted by their mobility. In MoS₂ and MoSe₂, species other than electrons in the conduction band and holes in the valence band can be neglected due to their much lower mobility. Trapped charge carriers may cause a change

$\Delta\epsilon''$ of the imaginary part of the dielectric constant which also contributes to the signal $\Delta P(t)/P$. However, it was shown that even in materials with a high number of trapped excess charge carriers, their contribution can be neglected [11].

The electron mobility μ_e and the hole mobility μ_h in MoS_2 and MoSe_2 are comparable [1]. In this case, the contribution of electrons and holes to the signal is determined by the density relative to each other. Bandgap excitation creates equal numbers of electrons and holes. Recombination processes decrease the density of electrons and holes in the same way. Only trapping processes can change the relative contribution of electrons and holes to the signal.

In doped semiconductors, especially in systems with a high density of states in the bandgap as powders, it is reasonable to attribute the change $\Delta\sigma(t)$ of the conductivity mainly to excess majority charge carriers because fast trapping processes are relatively improbable for majority carriers and, on the contrary, very probable for the minority charge carriers:

$$\Delta\sigma(t) \approx \Delta n(t) e \mu_m, \quad (2)$$

where $\Delta n(t)$ is the number of the excess majority charge carriers and μ_m their mobility.

Excess charge carriers were produced by illumination with 12 ns (full width at half maximum) pulses of a doubled Nd:YAG laser (JK-Lasers System 2000) at 532 nm. The laser intensity was varied by neutral filters (Schott). The photon energy (2.4 eV) at the excitation wavelength is sufficiently high to induce a band-to-band transition leading to the creation of mobile electrons and holes in the conduction band and the valence band, respectively.

The TRMC experiments were performed in a X-band (8–12.5 GHz) home-made equipment similar to one described previously [8]. An increase in sensitivity is obtained by insertion of the sample into a microwave cavity. Further stability was obtained by preparing pellets with 100 mg KBr (Merck, p.A.) and 10 mg of the MoX_2 powder as described previously [12]. The signal $\Delta P(t)/P$ obtained by this technique will be called photoconductivity.

The transient photoconductivity data is displayed on double-logarithmic plots in most cases. Although this way of representation can obscure details of the decay processes, it is convenient because of the large

signal and time range covered by the photoconductivity decay in the powders.

MoS_2 was prepared by heating stoichiometric amounts of the elements in an evaporated and sealed quartz ampulla at 873 K for four days. The resulting powder was treated with the halogens chlorine, bromine and iodine at 773 K for two days in an initially evaporated and sealed quartz ampulla.

MoSe_2 powder was obtained by CVT of MoSe_2 as starting material and n-doped. Platinization was achieved by mixing appropriate amounts of a suspension of the powder and a colloidal platinum solution [13], and subsequent evaporation at room temperature and under vacuum of ≈ 30 hPa.

Powder diffractograms were recorded with a Siemens D500 Diffractometer, operating a copper anode ($\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$) at 45 kV and 30 mA.

3. Results and discussion

3.1. Photoconductivity (TRMC) of molybdenum diselenide (MoSe_2)

3.1.1. Molybdenum diselenide

Fig. 1 shows the transient photoconductivity of molybdenum diselenide (MoSe_2) after excitation with a 532 nm laser flash at three intensities. As mentioned above, the photoconductivity can be attributed to excess majority charge carriers, in this case (n-doped material) to excess electrons in the conduction band.

The decay of the photoconductivity does not obey simple homogeneous first- or second-order kinetics as was also found with other powders [9]. The initial signal amplitude depends sublinearly on the laser intensity. This and the initial shape of the decay at the highest intensity quite clearly indicate higher-order decay processes faster than the time resolution of the setup, which are measured as the convolution with the time profile of the laser flash. These processes are apparently quenched after the excitation because after about 20 ns, the decay behaviour does not depend any longer on the excitation density.

Under realistic assumptions, recombination or simple trapping processes lead to much shorter lifetimes of charge carriers than observed with this powder (lower curve: 10% of the initial signal amplitude

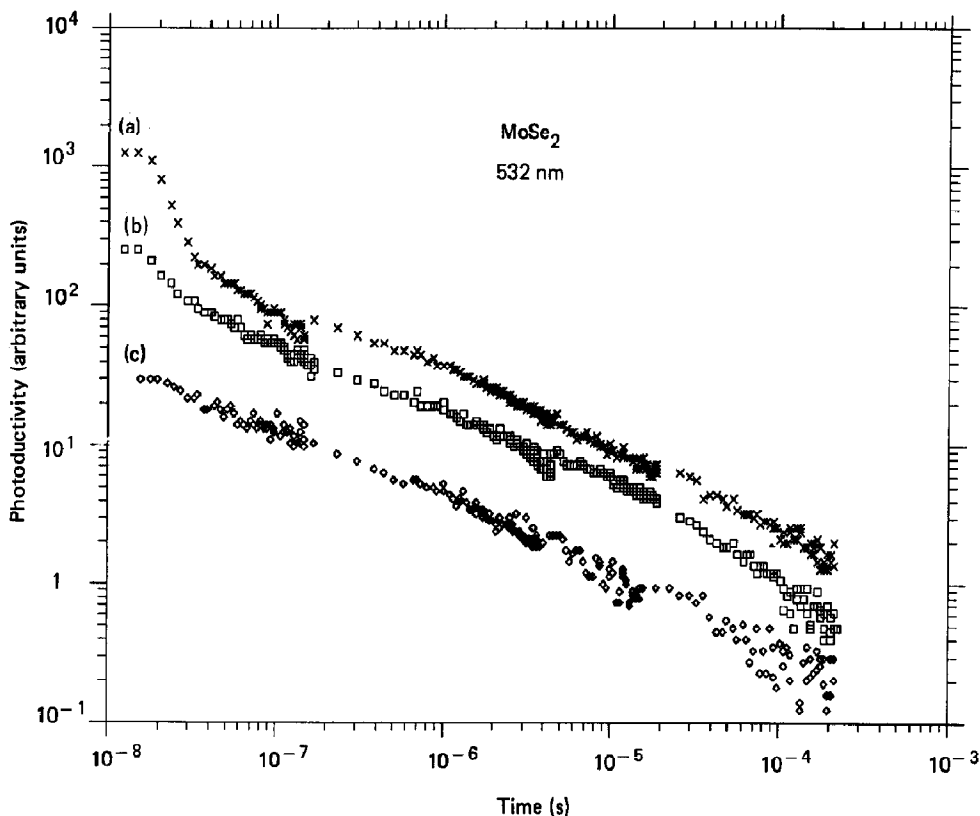


Fig. 1. Photoconductivity of MoSe_2 powder after excitation with a 532 nm 12 ns (fwhm) laser pulse. Laser intensity: (a) $5 \mu\text{J}/\text{cm}^2$; (b) $1 \mu\text{J}/\text{cm}^2$; (c) $0.25 \mu\text{J}/\text{cm}^2$.

left at $\approx 1.5 \mu\text{s}$), especially in view of the large and defect-rich surface, and the grain size of the powder. Only complex trap-related mechanisms lead to long lifetimes. A simple model would be initial fast trapping of minority charge carriers in deep traps with a small cross section for majority charge carriers. The decay of the photoconductivity could be due to trapping of the electrons in a distribution of electron traps close to the conduction band or to recombination with holes. In the latter case, the release of the holes from traps may be the rate-determining step. The higher-order process at higher excitation intensities might be second-order recombination of free charge carriers.

3.1.2. Platinized molybdenum diselenide

A commonly used method to enhance the activity of a photocatalytic powder is the deposition of a catalyst for subsequent chemical reactions on the sur-

face. The best-known example is the deposition of platinum islands on titanium dioxide or cadmium sulfide to enhance the evolution of hydrogen. In this context, an interesting question is the nature of the junction between the semiconductor and the metal island and whether there is an influence of this junction on the charge-carrier dynamics in the semiconductor. The ideal case would be that the catalyst not only catalyses the subsequent reaction but also improves the separation of the created excess charge carriers.

Fig. 2 shows the decay of the photoconductivity of platinized MoSe_2 powder after excitation with a 532 nm laser flash for four intensities. In this case, the decay is much faster than with the untreated sample in fig. 1. After $\approx 35 \text{ ns}$, the photoconductivity decays to 10% of its initial signal amplitude. In addition, much higher laser intensities are necessary to obtain comparable signals, which indicates further decay

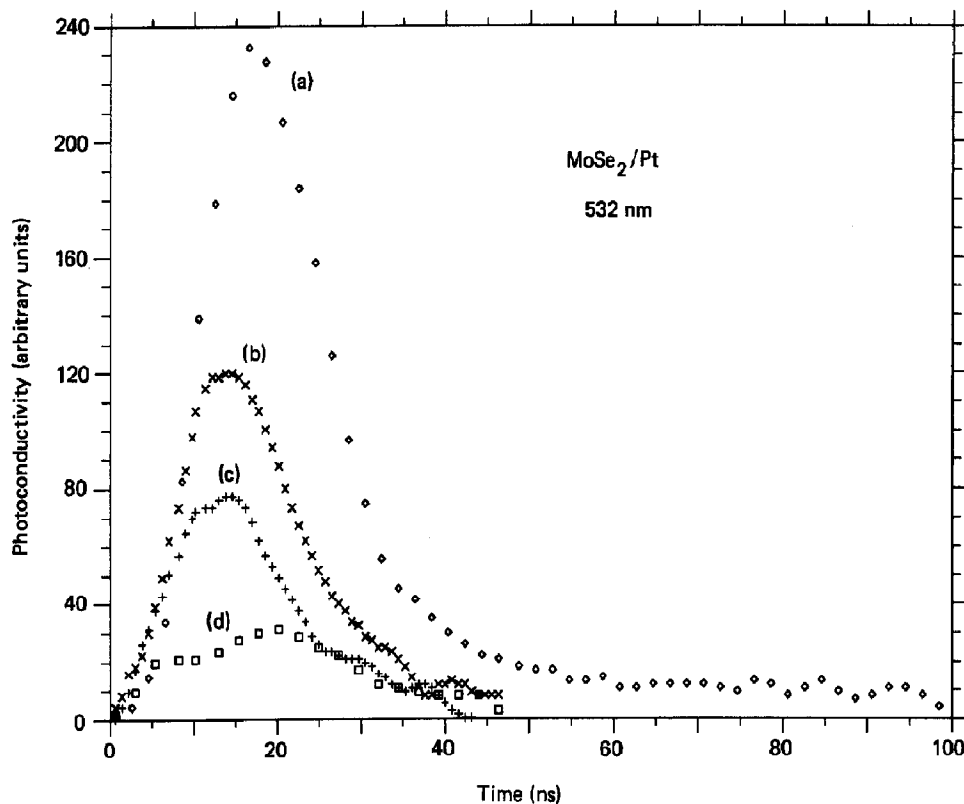


Fig. 2. Photoconductivity of platinized MoSe_2 powder after excitation with a 532 nm 12 ns (fwhm) laser pulse. Laser intensity: (a) 1 mJ/cm^2 ; (b) 0.5 mJ/cm^2 ; (c) 0.25 mJ/cm^2 ; (d) 0.1 mJ/cm^2 .

processes faster than the time resolution of the setup.

There are two possibilities: recombination or trapping. In the first case, the excess charge carriers would recombine via the metal or new states at the semiconductor/metal interface. The chance for any photocatalytic reaction would be even smaller than with the untreated powder.

The second possible mechanism is the fast trapping of both charge carriers in different trap states without recombination. A reasonable assumption for this case is fast trapping of the holes in the semiconductor and transfer of the electrons to the platinum. This would mean better separation of the charge carriers. If the hole traps are located on the surface of the semiconductor, subsequent photocatalytic reactions still would be possible.

3.2. Molybdenum disulfide (MoS_2)

3.2.1. X-ray diffractograms

MoS_2 exists in two hexagonal polytypes $\text{MoS}_2\text{-2H}$ and $\text{MoS}_2\text{-3R}$. Both show trigonal prismatic coordination of the Mo by the S atoms. Their main difference is the stacking sequence of the layers, i.e. ABAB or ABCABC.

Diffractograms of MoS_2 powders were taken for 2θ angles from 12° to 70° . All four powders show the same patterns of either sharp or significantly broadened reflections. The sharp reflections correspond to the common reflections of the two hexagonal polytypes $\text{MoS}_2\text{-2H}$ and $\text{MoS}_2\text{-3R}$ with Miller indices $002''$ and $003''$, respectively, and 110 [14]. The corresponding planes are vertical or parallel to the c -axis. The other reflections with Miller indices $10''$ or $01''$ are significantly broadened. They correspond to planes which are tilted relative to the c -

axis. The sharp reflections indicate good long-range order within and perpendicular to the layers. However, the broadening of the other reflections cannot be explained by just superpositioning of the reflections of two polytypes. It rather indicates a mixture of the two polytypes in single crystallites of the powder due to poor long-range order of the stacking sequence.

Diffraction patterns of all powders were identical and showed no additional reflections except the iodine-treated sample. These additional reflections coincide well with MoO_2 (Tugaronovite, Powder Diffraction File No. 32-671). In contrast to bromine and chlorine, the treatment with iodine seems to lead to the presence of MoO_2 .

3.2.2. Photoconductivity (TRMC)

(1) *Untreated molybdenum disulfide.* Fig. 3 shows the transient photoconductivity of the untreated mo-

lybdenum disulfide powder after excitation with a 532 nm laser flash for five different laser intensities. The lifetime of the excess charge carriers is even longer than with MoSe_2 . The decay extends over a wide range in time from nanoseconds to milliseconds (the photoconductivity decays to about 10% of the initial signal amplitude in 1–2 ms). Again, the decay does not obey simple homogeneous first- or second-order kinetics and the initial signal amplitude depends sublinearly on the laser intensity. In addition the decay becomes somewhat faster at higher laser intensities. This leads to the same kind of model for carrier kinetics as above: At short times and at high-excitation density, excess charge carriers recombine rapidly; at longer time and at lower excitation density, this recombination is quenched. Consequently, the same conclusion regarding the kinetics of the excess charge carriers may apply in this case: Fast trapping of the minority charge carriers in deep

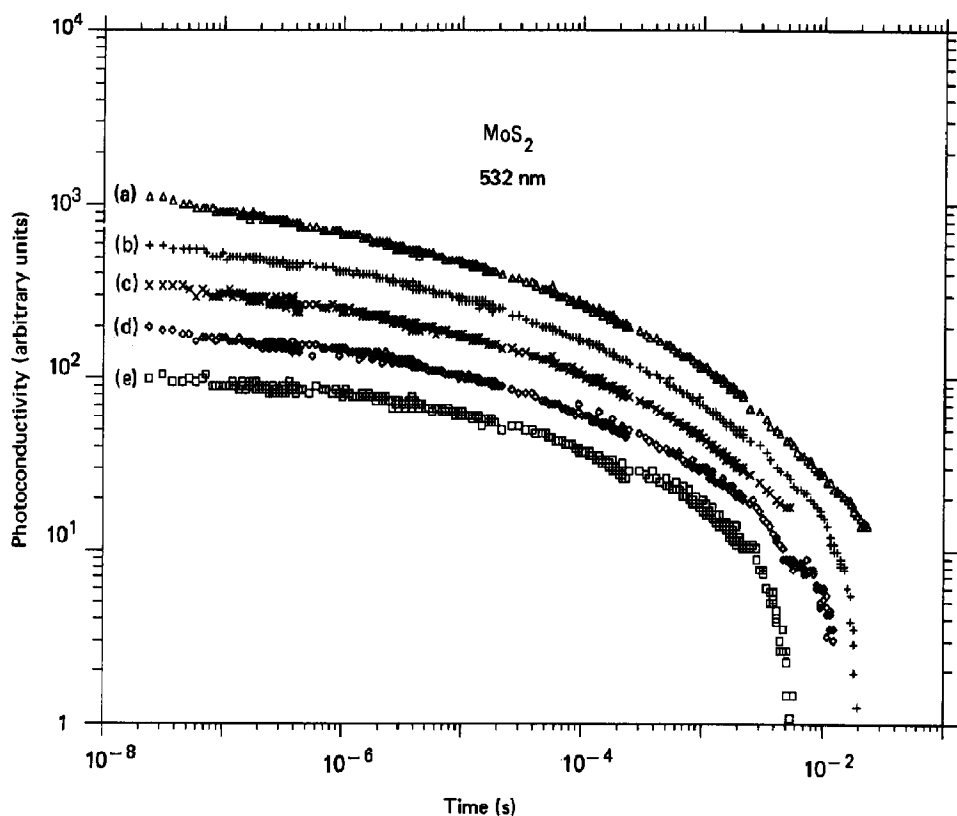


Fig. 3. Photoconductivity of MoS_2 powder after excitation with a 532 nm 12 ns (fwhm) laser pulse. Laser intensity: (a) $0.1 \mu\text{J}/\text{cm}^2$; (b) $0.25 \mu\text{J}/\text{cm}^2$; (c) $0.5 \mu\text{J}/\text{cm}^2$; (d) $1 \mu\text{J}/\text{cm}^2$; (e) $2.5 \mu\text{J}/\text{cm}^2$.

traps delays and/or quenches recombination of the majority carriers. Further, the decay of the photoconductivity is due to trapping of the majority charge carriers in a distribution of trap states or to recombination with minority charge carriers, and the release of the minority charge carriers from their traps may be the rate-determining step.

(2) *Halogen-treated molybdenum disulfide*. In fig. 4 the transient photoconductivity of the bromine-, chlorine-, iodine-treated and untreated molybdenum disulfide powders are compared at the same laser intensity. The absolute initial signal amplitude has a considerable error. (The dependence of the initial signal amplitude on the geometrical arrangement of the sample is one reason.) Therefore, it is justified for the sake of clarity of the plot, to shift some of the decay curves by multiplying the amplitudes of all points with a constant factor. Consequently, the or-

dering of the different curves according to their initial signal amplitude is not significant.

It was found that the dependence of the decays on the laser intensity with all three halogen-treated samples was very similar to that of the untreated powder. The overall decay behaviour of the photoconductivity remains the same compared to the untreated sample. However, there are considerable differences in the life times. In all three treated samples, the life times are shorter than in the untreated sample. After treatment with bromine, the photoconductivity decays to 10% in 0.5–1 ms, with chlorine in 0.05–0.1 ms, and with iodine in 0.1–0.6 ms. This leads to the following order regarding the effective lifetime, which holds for all measured laser intensities:

chlorine-treated < iodine-treated

< bromine-treated < untreated.

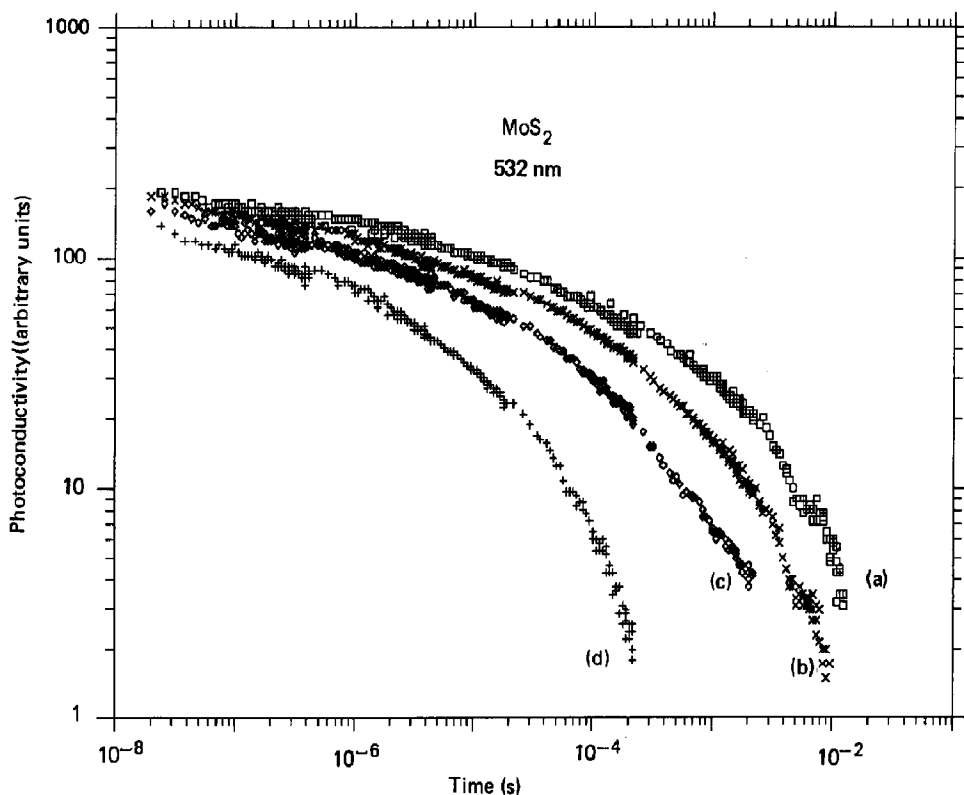


Fig. 4. Photoconductivity of MoS_2 powders after excitation with a 532 nm 12 ns (fwhm) laser pulse. Laser intensity: $1 \mu\text{J}/\text{cm}^2$; (a) untreated powder, (b) bromine-treated powder, (c) iodine-treated powder, (d) chlorine-treated powder.

It is known from examinations of the surface of layer-type compounds that MoS_2 reacts at the stepped surfaces with air under the formation of species similar to MoO_3 , whereas the van der Waals surfaces remain oxygen-free [15]. The reason for the long life time of the excess charge carriers might be due to inhomogeneous fields, separation of the charge carriers and trapping of the minority charge carriers. It is reasonable to assume that the treatment with the halogens rather changes the surface properties than the bulk properties of the powder. Under this assumption, the change of the life time indicates that the trap states for the charge carriers are located at the surface and relate to the oxidic surface species. It is known that MoO_3 reacts with chlorine and bromine under the formation of oxihalogenides and/or halogenides [16]. The faster decay of the photoconductivity after the halogen treatment indicates a change in the nature of the traps, i.e. oxides and perhaps the formation of new traps or recombination centers at the surface, i.e. halogenides. The greater reactivity of chlorine compared to bromine is reflected in the greater effect in life time after chlorine treatment. This may indicate that the reaction with chlorine is faster and more complete than with bromine.

The short life time after iodine treatment is contrary to the reactivity of iodine with molybdenum oxides. It is known from the photoelectrochemistry of MoS_2 , that iodine has a specific stabilising chemistry different from other halogens [17]. The reason for this specific behaviour has to be a different reaction which is also indicated by the powder diffractogram. Obviously several per cent of the MoS_2 were converted into MoO_2 by a reaction with air after the formerly evacuated ampulla was opened. By this reaction, minority charge carrier traps were removed or recombination centers were created causing the short life time of excess majority charge carriers.

4. Summary

From the pronounced effect of platinization of MoSe_2 , it became evident that in general the influence of the catalyst on the dynamics of the excess charge carriers cannot be neglected. However, it depends on the specific system whether the separation

of the excess charge carriers is improved or the recombination via states in the catalyst or at the interface is enhanced.

The shape of the decay measured with the MoS_2 powder seems to be a common feature of most powders [9]. It can be characterized by an effective rate constant decreasing with increasing time. The long life time of excess charge carriers with the MoS_2 powder suggests that the material should in principle be suited for photocatalysis. The low efficiencies found may be due to the fact that the bandgap of these materials is smaller than the bandgap of commonly used CdS or TiO_2 and that there are less usable reactions. In addition, the charge transfer at the interface may be hindered by an activation barrier.

It was shown that halogen treatment sensitively affects the decay of the photoconductivity in MoS_2 powder. The influence of halogen treatment on the charge-carrier dynamics in MoS_2 reflects the order in reactivity of molybdenum compounds with chlorine and bromine. However, iodine seems to have a different reaction behaviour than the other ones.

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References

- [1] O. Madelung, ed., *Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaft und Technik, Neue Serie, Gruppe III, Vol. 17g* (Springer, Berlin, 1984).
- [2] H. Gerischer, in: *Topics in applied physics*, Vol. 31, ed. B.O. Seraphin (Springer, Berlin, 1979) p. 115.
- [3] R. Tenne and A. Wold, *Appl. Phys. Letters* 47 (1985) 707.
- [4] H. Tributsch, *Ber. Bunsenges. Physik. Chem.* 81 (1973) 3719.
- [5] A. Sobczynski, A. Yildiz, A.J. Bard, A. Campion, M.A. Fox, T. Mallouk, S.E. Webber and J.M. White, *J. Phys. Chem.* 92 (1988) 2311.
- [6] W.B. Hoyer, Y. Mao and K.-D. Asmus, manuscript in preparation.
- [7] J.A. Wilson and A.D. Yoffe, *Advan. Phys.* 18 (1969) 193.

- [8] R. Späh, U. Elrod, M. Lux-Steiner, E. Bucher and S. Wagner, *Appl. Phys. Letters* 43 (1983) 79;
M.K. Agarwal, V.V. Rao and V.M. Pathak, *J. Cryst. Growth* 97 (1989) 675;
L.H. Brixner, *J. Inorg. Nucl. Chem.* 24 (1962) 257.
- [9] J.M. Warman, M.P. de Haas, M. Grätzel and P.P. Infelta, *Nature* 310 (1984) 306;
R.W. Fessenden and P.V. Kamat, *Chem. Phys. Letters* 123 (1986) 233;
C.J. Dobbin, A.R. McIntosh, J.R. Bolton, Z.D. Popovic and J.R. Harbour, *J. Chem. Soc. Faraday Trans. I* 82 (1986) 3625.
- [10] M. Kunst and G. Beck, *J. Appl. Phys.* 60 (1986) 3558.
- [11] M. Kunst and A. Werner, *J. Appl. Phys.* 58 (1985) 2236.
- [12] K.-M. Schindler and M. Kunst, *Z. Naturforsch.* 43a (1988) 189.
- [13] D. Bahnemann, A. Henglein, J. Lilic and L. Spanhel, *J. Phys. Chem.* 88 (1984) 709.
- [14] Joint committee on powder diffraction standards, JCPDS, Powder diffraction file No. 37-1492.
- [15] W. Jaegermann and D. Schmeißer, *Surface Sci.* 165 (1986) 143.
- [16] *Gmelin Handbuch der anorganischen Chemie*, 8. Auflage, System Nr. 53 Molybdän, *Ergänzungsband Teil B1 Verbindungen* (Springer, Berlin, 1975).
- [17] H. Tributsch, T. Sakata and T. Kawai, *Electrochim. Acta* 26 (1981) 21.