

PREPARATION AND ELECTRONIC PROPERTIES OF MONOLAYER TUNGSTEN OXIDE ON SILICA PARTICLES

Jonathan K. LELAND¹ and Allen J. BARD²

Department of Chemistry, The University of Texas, Austin, TX 78712, USA

Received 22 May 1987; in final form 7 July 1987

Monolayer tungsten oxide on silica particles was prepared by a controlled hydrolysis technique. The material displays a bandgap which is 0.3 eV higher in energy than that for bulk WO_3 . The quasi-Fermi level for electrons, in this material, as determined by electrochemical measurements, is 170 mV more negative for SiO_2/WO_3 than that for particulate WO_3 .

1. Introduction

We report here a preparation and an examination of the electronic properties of a semiconductor (tungsten oxide) monolayer on silica particles (0.18 μm). This material is similar to the Q-state particles reported by Henglein and co-workers [1], Brus and co-workers [2], Nozik et al. [3], Watzke and Fendler [4] and others. Our particles differ from Q-state particles that are small ($\approx 20\text{--}100$ Å) in three dimensions while the layers here are small in only one dimension; thus, these layers are related to semiconductor superlattice structures [5]. The preparation of a monolayer is possible by a controlled hydrolysis technique, which is different from other methods of preparing a supported catalyst [6]. Controlled hydrolysis is analogous to the preparation of reverse-phase chromatographic packings [7] and modified electrode surface [8]. This technique is a general method which could be applicable to the preparation of monolayers of other oxides (e.g., iron oxide [9]) or multilayers of mixed oxides.

We used two techniques to characterize the electronic properties of these particles. The bandgap of the suspended particles was measured using UV/VIS absorption spectroscopy with a solution whose refractive index was closely matched to silica over the wavelength region of interest. In this way, light

scattering was minimized, thereby allowing the electronic transitions to be observed. The second method, an electrochemical charge collection technique by mediated electron transfer, was used to measure the quasi-Fermi level for electrons under illumination [9–11].

We are interested in this material for several reasons. The first is to examine and understand how the electronic properties of these materials (semiconductors) change as the dimensions become very small by analogy to the Q-state particles. Second is how to prepare a photocatalyst with larger efficiencies. Semiconductors with low charge carrier mobilities (e.g., oxides [12]) exhibit high recombination rates. Electron-hole pairs photogenerated in the bulk can recombine before diffusing to the surface. The efficiency for charge transfer (number of electrons or holes reacting at the surface per electron-hole pair generated) will be low. Eliminating the bulk semiconductor by layering the material only at the surface should eliminate bulk recombination losses [13].

2. Experimental

For the preparation of monolayer tungsten oxide on silica (SiO_2/WO_3) the controlled hydrolysis was carried out as follows. A WCl_6 solution in dry CH_2Cl_2 (prepared in a glove box) was allowed to hydrolyze on SiO_2 (Degussa powder dried at 140°C for 4 h)

¹ Present address: IGEN, Inc., Rockville, MD, USA.

² To whom correspondence should be addressed.

in dry toluene under high-purity N_2 . This mixture was stirred and refluxed for 24 h. The mixture was then filtered in air, washed with toluene, acetone, and methanol and air dried overnight ($140^\circ C$). During filtration, the material changed color from a dark blue to white, which represents the hydrolysis of the residual W-Cl bonds. The use of dry non-aqueous solvents prevents formation of larger clusters of WO_3 . The hydrodynamic diameter of the SiO_2 and SiO_2/WO_3 was measured by a photon correlation technique using the equipment described earlier [9].

The BET surface area of silica and SiO_2/WO_3 was measured using a Micrometrics surface area analyzer model 2200. X-ray powder patterns were measured using an IBM series 1 automated Phillips vertical scanning X-ray diffractometer fitted with a graphite beam monochromator and $Cu K\alpha$ radiation. Photoacoustic spectroscopy was performed using the same equipment described earlier [14]. Charge collection experiments were performed using a previously described technique [10,11]. The absorption spectrum of SiO_2/WO_3 with water in the reference compartment was measured using a Hewlett-Packard 8451 A diode array spectrometer. Suspensions of SiO_2 and SiO_2/WO_3 (0.1 mg/ml) for spectral study were prepared by first sonicating the particles in de-ionized water, followed by the addition of high-purity sucrose.

3. Results and discussion

The monolayer WO_3 on silica particles prepared by the controlled hydrolysis technique was characterized by the following measurements. The hydrodynamic diameter of SiO_2 was found to be unchanged by the formation of SiO_2/WO_3 and was $0.18 \mu m$ in both cases. The BET surface areas were similar: $340 m^2/g$ for SiO_2 and $290 m^2/g$ for SiO_2/WO_3 . The X-ray powder pattern for SiO_2/WO_3 showed no peaks for WO_3 and was identical to that of SiO_2 . Based on these findings, we conclude that our material probably very closely approaches that of a monolayer of tungsten oxide. Multiple layers could be formed by the introduction of moisture into the reaction vessel. Although it is impossible to completely eliminate all extraneous water, extreme precaution was used to minimize this. Another problem in the preparation

is aggregation of particles. To some extent this probably occurs as seen by the differences in the BET surface areas.

3.1. Electronic properties

Bandgap, E_g , measurements also provide evidence for the monolayer nature of SiO_2/WO_3 . By photoacoustic spectroscopy (PAS) the E_g of SiO_2/WO_3 was found to be blue-shifted from 2.7 eV for WO_3 to 3.0 eV [10,11]. The electronic absorbance spectrum of SiO_2/WO_3 was measured using UV/VIS absorption spectroscopy. Since the size of the silica particles is near that of the wavelength of UV/VIS light, scattering in aqueous solution prohibits obtaining the E_g from the optical excitation. To circumvent this problem, the SiO_2/WO_3 particles were suspended in a solution whose refractive index was matched over the wavelength range of interest as closely as possible to SiO_2 , so that light scattering was minimized. According to simple light scattering theory [15], as the difference in refractive index becomes very small, the scattering approaches zero.

A convenient solution was found to be highly concentrated aqueous sucrose solutions [16]. This solution is particularly attractive because the refractive index can be adjusted by changing the sucrose concentration. Due to the highly viscous nature, the particles stay suspended over a long period of time. Sucrose solutions also have been used recently in electrochemical studies [17]. To determine the proper concentration of sucrose, and hence, the optimum refractive index, silica particles were suspended at various concentrations of sucrose and the spectrum was recorded. The solution that showed the least scatter occurred with 67% sucrose with a refractive index (white light) of 1.458. The UV/VIS spectra of 67% sucrose with and without silica are shown in figs. 1a and 1b. Note that a small impurity peak with an onset at about 370 nm is observable in the sucrose solution and in the SiO_2 /sucrose suspension. Fig. 1c is a spectrum of SiO_2/WO_3 . Optical excitation from the tungsten oxide is distinguishable on the scattering background (as well as a shoulder for the impurity). The absorbance changed linearly with concentration of SiO_2/WO_3 . The E_g , taken as the absorbance onset, is about 400 nm or $\approx 3 \pm 0.1$ eV, which is about the same value measured by PAS [11].

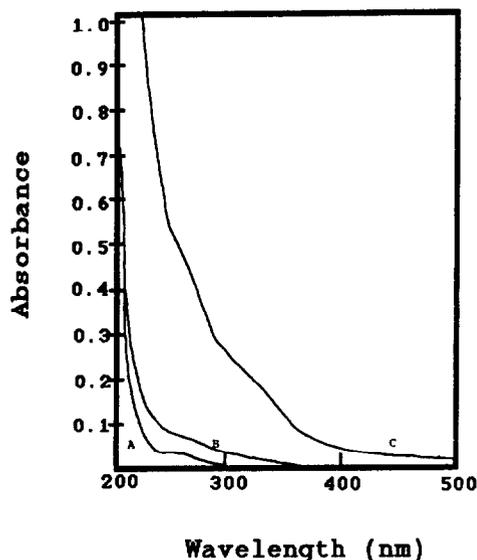


Fig. 1. UV/VIS spectrum of 68% sucrose solution (a) alone; (b) with SiO_2 suspension; (c) with SiO_2/WO_3 suspension.

Further evidence for the monolayer of tungsten oxide is provided by measurement of the quasi-Fermi level for electrons under illumination, nE_{F}^* . This parameter is a measure of the reducing power of photo-generated electrons in semiconductor materials [18]. As reported previously from our laboratory [11], by a mediated charge collection technique, SiO_2/WO_3 shows an nE_{F}^* that is 170 mV negative in potential to that of WO_3 particles.

The observed electronic properties (E_g and nE_{F}^*) of SiO_2/WO_3 are consistent with the properties expected for effective monolayer coverage of tungsten oxide. The expected change in bandgap, ΔE_g , for a layered semiconductor with large dimensions in a plane (XY) but a small lateral thickness (d_z) is given by [19]

$$\Delta E_g \approx (\hbar^2/2m_z)(\pi^2/d_z^2), \quad (1)$$

where m_z is the reduced effective masses of the electron-hole pairs perpendicular to the semiconductor plane ($m_z \approx am$, where m is the electronic mass). We do not know the value for m_z in our WO_3 phase, since m_z depends upon the structure and phase of the WO_3 . We can very roughly approximate it by the value for $\gamma\text{-WO}_3$, as $m_z \approx 1.25 m$ [20]. With this value, the ΔE_g of 0.3 eV corresponds to a $d_z \approx 10 \text{ \AA}$. Given the approximations in the derivation of eq. (1) and our

ignorance of the actual value of m_z , this thickness can probably be considered as only an order-of-magnitude estimation. However, it is also possible that the WO_3 does not form a continuous layer, but rather is a small particle distribution on the SiO_2 surface so that the small three-dimensional form of eq. (1) would be more appropriate. Experiments are under way with thin films prepared on different substrates to distinguish between these possibilities.

4. Conclusions

The preparation of thin films of semiconductors on inert substrates, such as SiO_2 and clays, which show different electronic properties than larger particles of the semiconductor, appears promising. The material should show higher stability towards aggregation than the colloidal dispersion and does not require the addition of stabilizing agents. A related approach recently has been reported in the precipitation of semiconductors within the cages of zeolites [21]. The WO_3 reported here is blue-shifted by 0.3 eV and the quasi-Fermi level for electrons is 170 mV negative of that for bulk WO_3 .

Acknowledgement

Support of this research by the National Science Foundation (CHE 8304666) is gratefully acknowledged.

References

- [1] H. Weller, U. Koch, M. Gutierrez and A. Henglein, Ber. Bunsenges. Physik. Chem. 88 (1984) 649; A. Fojtik, H. Weller, U. Koch and A. Henglein, Ber. Bunsenges. Physik. Chem. 88 (1984) 969; A. Henglein, Pure Appl. Chem. 56 (1984) 1215; H. Weller, A. Fojtik and A. Henglein, Chem. Phys. Letters 117 (1985) 485; A. Fojtik, H. Weller and A. Henglein, Chem. Phys. Letters 120 (1985) 552; U. Koch, A. Fojtik, H. Weller and A. Henglein, Chem. Phys. Letters 122 (1985) 507.
- [2] R. Rossetti, S. Nakahara and L.E. Brus, J. Chem. Phys. 79 (1983) 1086; L.E. Brus, J. Chem. Phys. 79 (1983) 5566; 80 (1984) 4403.

- [3] A.J. Nozik, F. Williams, M.T. Nenadovic, T. Rajh and O.J. Micic, *J. Phys. Chem.* 89 (1985) 397.
- [4] H.J. Watzke and J.H. Fendler, *J. Phys. Chem.* 91 (1987) 854.
- [5] V. Narayanamurti, *Science* 235 (1987) 1023.
- [6] D.G. Rethwischg and J.A. Dumesic, *J. Phys. Chem.* 90 (1986) 1863;
R. Deen, P.I.Th. Scheltus and G. de Vries, *J. Catal.* 41 (1976) 218;
K.S. Seshadri and L. Petrakis, *J. Catal.* 30 (1973) 195;
K.T. Ng and D.M. Hercules, *J. Phys. Chem.* 80 (1976) 2094;
A.W. Miller, M. Atkinson, M. Barber and P. Swift, *J. Catal.* 22 (1971) 140;
R.J. Farrauto, *J. Catal.* 41 (1976) 482.
- [7] H. Colin, N. Ward and G. Guiochon, *J. Chromatography* (1978) 169;
H. Colin and G. Guiochon, *J. Chromatography* 141 (1977) 289.
- [8] R.W. Murray, in: *Electroanalytical chemistry*, ed. A.J. Bard (Dekker, New York, 1984) p. 191.
- [9] J.K. Leland and A.J. Bard, *J. Phys. Chem.*, to be published.
- [10] J.R. White and A.J. Bard, *J. Phys. Chem.* 89 (1985) 1947;
M.D. Ward, J.R. White and A.J. Bard, *J. Am. Chem. Soc.* 105 (1983) 27.
- [11] J.K. Leland and A.J. Bard, *J. Phys. Chem.*, to be published.
- [12] D.E. Scaife, *Solar Energy* 25 (1980) 41.
- [13] A. Ueno, N. Kakuta, K.H. Park, M.F. Finlayson, A.J. Bard, A. Campion, M.A. Fox, S.E. Webber and J.M. White, *J. Phys. Chem.* 89 (1985) 3828.
- [14] R.C. Gray, V.A. Fishman and A.J. Bard, *J. Anal. Chem.* 49 (1977) 697.
- [15] B.J. Berne and R. Pecora, *Dynamic light scattering with applications to chemistry, biology, and physics* (Wiley-Interscience, New York, 1976).
- [16] R.C. Weast, ed., *CRC handbook of chemistry and physics* (CRC, Cleveland, 1984-1985).
- [17] J. Leddy, X. Zhang and A.J. Bard, *J. Am. Chem. Soc.* 107 (1985) 3719;
X. Zhang, H. Yang and A.J. Bard, *J. Am. Chem. Soc.* 109 (1987) 1916.
- [18] G. Hodes and M. Grätzel, *Nouv. J. Chim.* 8 (1984) 509;
D. Duonghoug, J. Ramsden and M. Grätzel, *J. Am. Chem. Soc.* 104 (1982) 2977;
M.T. Nenadovic, T. Rajh, O.I. Micic and A.J. Nozik, *J. Phys. Chem.* 88 (1984) 5827.
- [19] C.J. Sandroff, S.P. Kelty and D.M. Hwang, *J. Chem. Phys.* 85 (1986) 5337.
- [20] B.L. Crowder and M.J. Sienko, *J. Chem. Phys.* 38 (1963) 1576.
- [21] Y. Wang and N. Herron, *J. Phys. Chem.* 91 (1987) 257.