

Controlling Photoelectrochemical and Photocatalytic Properties through Semiconductor Support Interaction

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A few methods are available to alter the band edge positions of a given semiconductor in a controlled fashion. One is to decrease the particle size down to a few nanometers resulting in an increase of the bandgap energy according to the quantum size effect. However, whereas the corresponding nanoparticles are excellent materials for various physical devices, they are in general too unstable to be used as photocatalysts in chemical reactions. Another method, doping with a transition metal, results only in a very few cases in a shift of the bandgap but rather in formation of surface states.

Figure 1. CdS (A, $v_{\text{rel}} = 1$), CdS-50/SiO₂(B), CdS-30/SiO₂(C), and CdS-12/SiO₂(D).

Recently we found that the electronic semiconductor support interaction (SEMSI effect) induced by the covalent attachment of CdS to high surface silica ($308 \text{ m}^2\text{g}^{-1}$) increases the bandgap energy from 2.40 to 2.59 eV and improves the photocatalytic activity by a factor of ten (Figure 1). [1]

To find out whether this novel effect is of more general relevance, we investigated if a bandgap widening can be also induced for titania, and how the nature of the support influences photoelectrochemical and photocatalytic properties of cadmium sulfide.

Silica supported titania powders with 50, 36, 13 and 4 wt% of TiO_2 ($\text{TiO}_2\text{-50/SiO}_2$, $\text{TiO}_2\text{-36/SiO}_2$, $\text{TiO}_2\text{-13/SiO}_2$ and $\text{TiO}_2\text{-4/SiO}_2$) were prepared by hydrolysis of TiCl_4 in the presence of silica, followed by calcination at $500 \text{ }^\circ\text{C}$. The formation of Ti-O-Si linkages was confirmed by diffuse reflectance infrared Fourier transform spectroscopy. Atomic Force Microscopy indicated the presence of titania crystals larger than 15 nm. All supported materials exhibited a blue shift of the TiO_2 absorption edge, originating from a high anodic shift of both the valence and the conduction band which was attributed to an electronic semiconductor-support interaction. [2]

Alumina supported cadmium sulfide powders were prepared similarly as reported for silica as support. Although a bandgap widening was observable, it was smaller than in the case of the silica supported semiconductor.

References

[1]. H. Weiß, A. Fernandez, H. Kisch, *Angew. Chem.* 113(2001)3942-3945. *Int. Ed.* 40 (2001)3825-3827.

[2] M. Gärtner, S. Dremov, P. Müller, H. Kisch, *ChemPhysChem* 6(2005)714 and references cited therein.