

Underpotential Photocatalytic Deposition: A New Preparative Route to Composite Semiconductors

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We report results that show it is possible to use titania-based heterogeneous photocatalysis^{1–3} as a simple but versatile route to the preparation of composite semiconductors. Thus, we show that a titania surface, previously modified with a selenium layer (Se/TiO₂), can be used to subsequently prepare MSe/TiO₂ (M = Cd, Pb) composites. Composite or coupled semiconductor systems have recently received a good deal of attention in photochemistry, photoelectrochemistry, and energy conversion research communities.^{4–9} Such systems have been hitherto prepared, both in colloidal and thin film forms, by solution growth,^{4,5,7} spin-coating,⁶ thermal routes,⁸ or electrodeposition.⁹

The new finding that we now wish to report is that underpotential deposition or UPD, a tactic that initially emerged from the metal alloy plating field and was subsequently embraced by the electrocatalysis¹⁰ and semiconductor electrodeposition¹¹ communities, can be profitably coupled with the titania-based heterogeneous photocatalysis approach for the preparation of composite semiconductor materials. Thus, ultraviolet (UV) irradiation of titania particles in an aqueous solution of Se(IV) is shown below, to result in the facile deposition of a selenium layer on the TiO₂ surface. While such a Se/TiO₂ composite system itself may be of technological interest (because it combines a photoconductive semiconductor such as Se with a higher band gap material such as TiO₂), subsequent irradiation of such previously modified TiO₂ particles in an aqueous suspension containing M²⁺ ions results in the underpotential deposition of the latter to afford MSe/TiO₂ composites.

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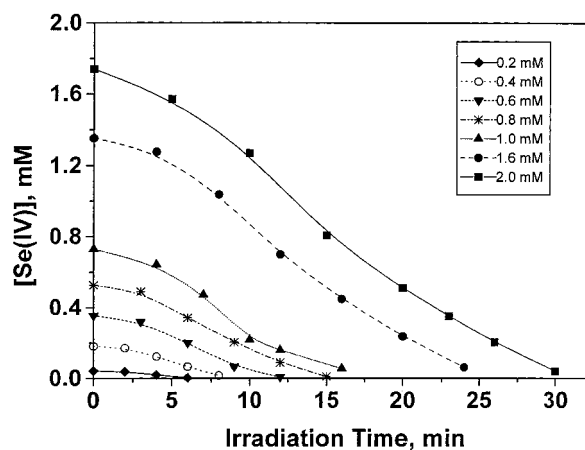


Figure 1. Photocatalytic reduction of Se(IV) in N₂-purged TiO₂ suspensions (2 g/L TiO₂ dose) under UV irradiation. The parameter is the initial Se(IV) concentration. Prior to irradiation, each suspension was equilibrated in the dark for ≈30 min. Thus, the difference between the initially added level of Se(IV) and the “time zero” values in Figure 1 represent the amount adsorbed on the TiO₂ surface (see Supporting Information). The lines in Figure 1 are simply drawn through the data points.

It is important to note that photocatalytic deposition of the metal candidates that we chose for this study (Cd and Pb) itself is either kinetically sluggish (Pb)^{12a} or thermodynamically unfavorable (Cd)^{12b,c} in the absence of the initial selenium layer on the TiO₂ surface. Thus, the deposition of M on the Se-modified TiO₂ surface is driven by the free energy of compound formation (−136.4 and −264.5 kJ/mol for CdSe and PbSe, respectively).¹³ We coin the term “underpotential photocatalytic deposition” for this process, which combines all of the elements of two rather well-established components, namely, the classic UPD and heterogeneous photocatalysis.

Figure 1 contains data showing the systematic decrease with time of the Se(IV) concentration in a series of UV-irradiated TiO₂ (P-25) suspensions. The initial Se(IV) concentration was a parameter in this set of experiments. After the runs in Figure 1 were completed, the initially milky white suspension turned visibly red, signaling the deposition of photocatalysis reaction products on the TiO₂ particle surface. Both X-ray powder diffraction (XRD) analyses and UV–visible reflectance spectroscopy (see Supporting Information) confirm that the reduction product is selenium. Thus, the photo-

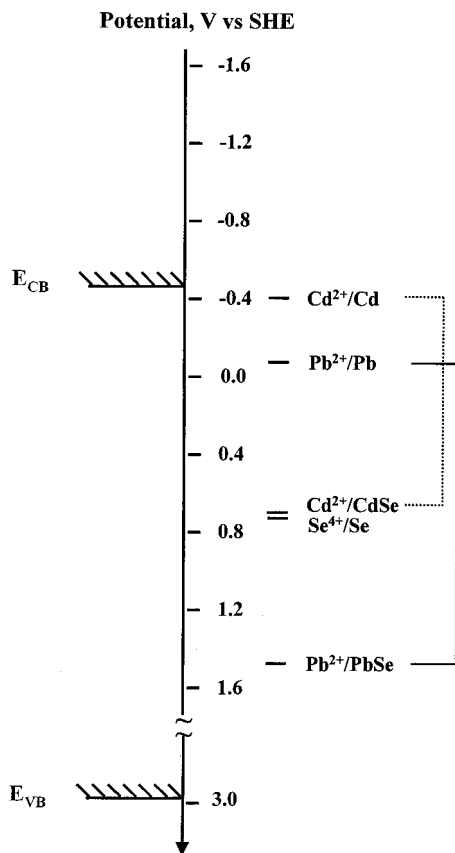
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Scheme 1. Relative Disposition of TiO₂ Conduction-Band Edges and Relevant Solution Redox Levels in an Aqueous Medium of pH 7 (Shifts in the Metal Ion Redox Potentials Because of MSe Formation (Leading to UPD, See Text) Are Also Shown)



generated electrons in the TiO₂ particles reduce Se(IV) to elemental Se, affording a Se/TiO₂ composite.

Unlike Se(IV), photocatalytic reduction of Cd(II) and Pb(II) on the TiO₂ particle surface suffers from both thermodynamic and kinetic limitations (Scheme 1).¹² On the other hand, as the data in Figure 2 illustrate, the Se/TiO₂ composite facilitates the subsequent reduction of these species. Figure 2 contains additional information on the effect that the initial extent of selenium coverage (of the TiO₂ surface) has on the subsequent reduction of Cd(II). Thus, experiments similar to those in Figure 1 were first performed on the UV irradiation of TiO₂ particles in Se(IV)-laden suspensions ranging in concentration from 0.2 to 2.0 mM. This initial irradiation was performed for 30 min; reference to Figure 1 shows that this period suffices for the complete removal of all the Se(IV) from the solution. Then, 200 μM of Cd(II) was injected into the photoreactor (as the sulfate salt) in each case, and the UV irradiation continued for the periods shown in Figure 2.

In the absence of selenium on the TiO₂ surface, there is no photocatalytic reduction of Cd(II) (Figure 2a).^{12b,c} On the other hand, too high or too low a loading of selenium (on the TiO₂ particle surface) is nonoptimal for subsequent Cd(II) reduction as exemplified by the 2.0 mM Se(IV) and 0.2 mM Se(IV) cases in Figure 2a, respectively. The 1.0 mM Se(IV) appears to reflect the best compromise, at least under the conditions extant in the data in Figure 2a.

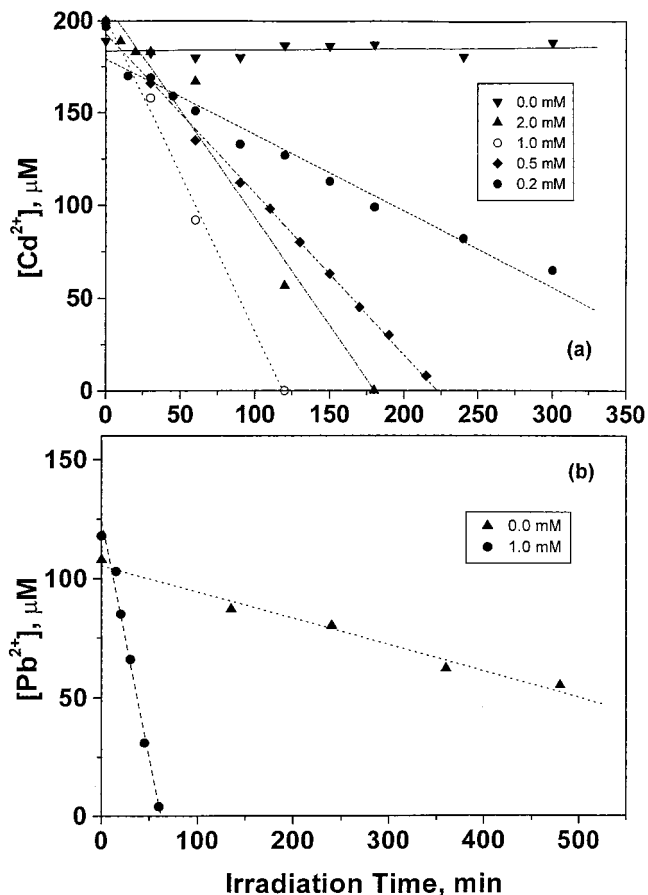
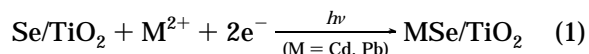


Figure 2. (a) Photocatalytic reduction of 200 μM Cd(II) under conditions as in Figure 1, except that the TiO₂ suspensions were preirradiated for 30 min in Se(IV)-containing suspensions (as shown). Of course, the control run ("0 mM") did not require this preirradiation step. Then, Cd(II) was added and irradiation continued as shown in Figure 2a. The lines are least-squares fits. (b) As in Figure 2a but for Pb(II). Note that, as in the Se(IV) case, a significant concentration of Pb(II) is initially adsorbed on the TiO₂ surface in the dark.

Figure 2b contains corresponding data for the Pb(II) reduction case; the selenium-modified TiO₂ case is for the 1.0 mM "optimized" condition. The lead ion was introduced as the nitrate salt. As also discussed by us elsewhere,^{12a} the process $\text{Pb}^{2+} \rightarrow \text{Pb}^0$ is kinetically sluggish as seen in the control experiment in Figure 2b. On the other hand, Pb²⁺ reduction on the Se/TiO₂ surface is completed well within ≈100 min (Figure 2b). Concomitantly, the suspension changes in hue from red to brownish-gray.

We envision that the UPD of the metal ions on the selenium-modified TiO₂ surface



leads to the composite or coupled semiconductor, MSe/TiO₂. In all the cases above, we also presume (based on what is already known about TiO₂-based photocatalysis) that the photogenerated holes are consumed in the oxidation of surface hydroxyl groups on TiO₂ or water molecules.¹⁻³

Confirmation that reaction (1) on the Se-modified TiO₂ surface does indeed lead to MSe/TiO₂ formation comes from UV-visible reflectance spectroscopy, XRD,

and X-ray photoelectron spectroscopy (XPS). These data are contained in the Supporting Information.

In conclusion, we have demonstrated a simple photocatalytic underpotential deposition approach for the preparation of composite semiconductors. Although we have demonstrated this approach here for particulate suspensions, the strategy ought to be straightforwardly applicable to thin films (layered structures) as well. Similarly, the UPD element in this proof-of-concept study was selenium and the underlying semiconductor was TiO_2 . Other UPD-inducing layer/semiconductor combinations can be envisioned as precursors to a wide array of composite materials systems.

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Supporting Information Available: Experimental details on the photocatalytic reactor, procedures, and chemical analyses; UV–visible reflectance spectra of TiO_2 , Se/TiO_2 , and CdSe/TiO_2 films; Langmuir isotherm plot for the adsorption of Se(IV) on the TiO_2 surface; X-ray diffraction patterns of an authentic sample of TiO_2 (Degussa P-25), a composite film of Se/TiO_2 , an authentic sample of PbSe , and a composite film of PbSe/TiO_2 ; and a summary of the UV–visible reflectance spectroscopy, X-ray photoelectron spectroscopy, and energy-dispersive X-ray emission data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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