Novel Materials and Cathodic Processes in Heterogeneous Photocatalysis

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ABSTRACT

While heterogeneous photocatalysis is a relatively mature topic now, there are still many aspects related to photocatalyst materials synthesis and reaction mechanisms that are worthy of further exploration. In this spirit, this talk focuses on three such aspects. Cathodic photoprocesses are the focus of study in all the cases and the heterogeneous photocatalytic reduction of toxic metals (e.g., $Cd^{2+}$and Cr^{6+}) will be used as models to illustrate our new approaches. First, the underpotential photoassisted deposition (UPAD) of metal ions such as Cd^{2+} on Se-modified TiO_2 surfaces, will be described. The mechanistic aspects of UPAD will be discussed. The use of $CdSe/TiO_2$ composite structures to drive the photocatalytic reduction of Cr(VI) will be illustrated as an environmental application example.

In the second part of the talk, the photocatalytic reactivity of 12 metal or metalloid species on the UV-irradiated TiO_2 surface will be discussed in a comparative sense. It is shown that Cu(II) species constitute a conceptual bridging link between two groups of these species, one reactive and the other inert, with respect to photoinduced electron transfer between the solution and the TiO_2 surface. A novel “synergistic photocatalysis” mechanism involving Cu^{2+} ions and Cr(VI) species in N_2-purged UV-irradiated aqueous TiO_2 suspensions, will be described.

In the last part of the talk, the indirect photocatalytic reduction of metal ions using formate radical anions in UV-irradiated TiO_2 suspensions, will be presented. Using Tl^+ as a model metal ion, a simple kinetics scheme is presented for this indirect route, and the predictions from this model are shown to be in excellent agreement with experimental data.

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