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Semiconductor Photocatalysis — Past, Present, and Future Outlook

The Past. In a 1972 review article, Steinbach¹ discussed, among other things, the direct observation of the interaction between photons and valence electrons of a semiconductor by means of photoelectron emission, photoannealing processes, photosorption and the occupation of electron levels in the solid, photosorption and related processes in ZnO, photosorption on TiO₂, photocatalytic reactions, photoenhancement by changes of rate constants, the influence of illumination on the activation energy, correlation between the activation energy of the catalytic reaction and conditions, the influence of wavelength and light irradiance, the decomposition of isopropanol on ZnO, and photocatalytic oxidations occurring on metals. An even earlier description of the photocatalytic properties of some metal oxides was given in 1955 by Markham² who dealt with ZnO, Sb₂O₃, and TiO₂ and the various types of photochemical changes that these oxides could undergo, including the catalyzed oxidation of organic compounds under UV light. Among the phenomena that follow when they are exposed to UV light, the author noted photoconductivity, phosphorescence or fluorescence, phototropy, and photolysis. A brief summary was given on the nature of these phenomena that provided the necessary background to interpret the initial effect(s) of the UV light and the manner in which external conditions might influence the subsequent observable changes.

The seminal short note published in *Nature* in 1972 by Fujishima and Honda³ demonstrated that water could be photolyzed electrochemically at an illuminated TiO₂ and dark Pt electrode combination to yield stoichiometric quantities of H₂ and O₂. What followed soon thereafter was a frenzied series of studies in search of the photocatalytic holy grail⁴ to produce H₂ fuel as part of the beginnings of the hydrogen economy, a result of the 1973 oil crisis. This note was responsible (in part) for initiating what could be labeled as modern heterogeneous photocatalysis with TiO₂ as the workhorse among other possible “photocatalysts”.

A strong push in that direction and in photoelectrochemistry was led by Bard and his colleagues at the University of Texas, Austin, among others, in the late 1970s (unpublished review 2011; see also ref 5). Of particular significance worth mentioning are the (i) photooxidation of CN[−] by O₂ in the presence of TiO₂ powder, (ii) the photodeposition of Pt, Cu, Pd, and other metals on TiO₂, WO₃, Al₂O₃, and SnO₂ to be used as cocatalysts, (iii) the photoinduced formation of CH₄ from CH₃COOH by the photo-Kolbe method, and (iv) the EPR identification of •OH radicals involved in photooxidations along with formation of HO₂• radicals from the reduction of O₂. In his 1980 article in *Science*, Bard described some of the principles and applications of semiconductor electrodes in photoelectrochemical (PEC) cells, together with the factors important in the design of practical systems and the extension of the principles of PEC cells to particulate systems for carrying out heterogeneous photocatalysis and photoelectrosynthesis.⁵ The photosynthetic production of amino acids (glycine, alanine, serine, aspartic acid, and glutamic acid) from a mixture of simple molecules such as CH₄, NH₃, and H₂O over Pt/TiO₂ particulates was also significant (unpublished review, 2011).

The 1980s saw the beginnings of an exponential growth of heterogeneous photocatalysis, with particular emphasis on the use of nanosized TiO₂ particles, which in 2010 alone saw several thousand related publications. From our experience, fundamental studies on what made semiconductor photocatalysts tick did not keep pace with this explosive growth that focused mostly on applications in the environmental arena, such as self-cleaning of TiO₂-containing substrates and photodegradations of a large number of pollutants.

First-generation metal oxide photocatalysts (e.g., pristine TiO₂) were greatly debated in the 1980–2000 period with regard to (i) the nature of the oxidative agent (•OH radicals versus h⁺), (ii) the site at which the reaction takes place (surface versus bulk solution), (iii) whether TiO₂ is indeed a photocatalyst because turnover numbers are difficult to determine (only a few years ago, we demonstrated two cases where so-called photocatalyzed reactions were catalytic, namely, photooxidation of H₂ and photoreduction of O₂ by assessing turnover numbers, whereas reactions involving NH₃ and CO₂ were shown not to be catalytic), and (iv) how to improve performance and assess process efficiencies; for the latter, a procedure was developed by us to assess quantum yields in a heterogeneous medium.

Our fundamental studies over the last 30 years have attempted to answer many of the fundamental questions regarding the intricacies of semiconductor photocatalysis.⁶ For instance, with respect to (iv), in 1984, Serpone et al.⁷ showed for the first time that coupling the two semiconductors CdS and TiO₂ and others (Figure 1) led to significant increases in

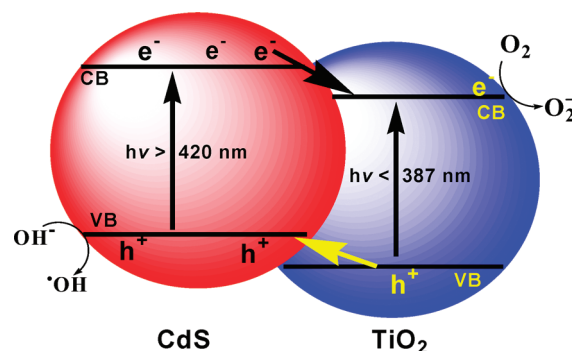


Figure 1. IPET process from the conduction band (CB) of photoexcited CdS to the CB of TiO₂. Hole transfer occurs from the valence band (VB) of TiO₂ to the VB of CdS. This leads to significant charge separation and to more efficient chemistry at the surface of the coupled particles.

process efficiencies as the charges formed upon light absorption by CdS were vectorially separated, e[−] on TiO₂ and h⁺ on CdS through a pathway that we referred to as interparticle electron

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transfer (IPET). Several combinations of semiconductor couples have since been examined extensively.

A significant breakthrough of the 1990s studies that caught our imagination was the 1991 seminal paper by O'Regan and Graetzel who showed that one could photosensitize TiO_2 with a dye in the presence of a redox couple to produce electrical power; this has since become known as the Graetzel solar cell⁸ (Figure 2). Hundreds if not thousands of papers have been published in this area ever since (see, e.g., ref 9).

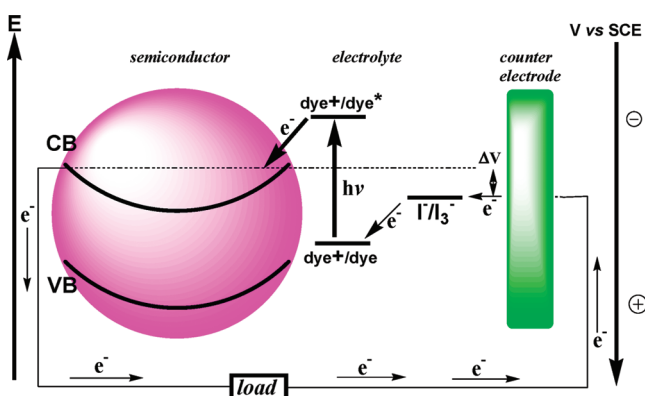


Figure 2. Cartoon illustrating the principle of the dye-sensitized (Graetzel) photovoltaic cell indicating the different phases. Adapted from ref 8. Copyright by the American Chemical Society.

The Present. With regard to improving photocatalytic process efficiencies, a strategy developed mostly in the past decade was to push the absorption onset of pristine TiO_2 toward longer wavelengths (anatase band gap, 3.2 eV; absorption onset, 387 nm) to dope TiO_2 with anions and/or cations (N, C, S, F, ..., and metal ions). The 2001 study of Asahi et al. in *Science* reported visible-light-active (VLA) N-doped TiO_2 's that triggered the nascent second-generation TiO_2 materials to be photoactive over the UV and much of the visible light region. This study and ensuing related publications by others have led to a lively debate on the root causes of the red shift of the absorption onset of TiO_2 to the visible region. One school proposed that corresponding increases in photoactivity of TiO_2 were due to a narrowing of its (intrinsic) band gap, while others contend that the band gap of TiO_2 is not narrowed but rather that the ensuing oxygen vacancies formed upon doping lead to formation of color centers that give rise to the absorption bands of doped TiO_2 's in the visible spectral region. Recent reviews have summarized arguments on the pros and cons of the nature of VLA TiO_2 materials.¹⁰

Curiously, the approach taken to produce second-generation photoactive materials to enhance performance has led to some unusual consequences, that is, extending the spectral sensitivity of TiO_2 to longer wavelengths by introduction of dopant(s) into the bulk causes the photoactivities of doped TiO_2 's and the chemical activity of surface active centers, formed under visible light, to decrease in comparison to those formed under UV light irradiation.¹¹

Future Outlook: Where to Next? In retrospect, despite the many studies carried out since the Fujishima/Honda report with TiO_2 as a photoelectrode for water electrolysis, no other metal oxide candidate has yet been found that might act as an efficient photoanode with conduction and valence band edges that straddle the redox potentials of water and where rapid charge-transfer events are more the rule than the exception. For

water splitting, TiO_2 's performance as a solar photoanode has proven deficient, owing to its relatively large band gap (3.2 eV) so that only UV radiation can activate it; its conduction band is somewhat positive in relation to the redox potential for H_2 evolution. Clearly, new semiconductor-based nanostructured materials are needed that would use lower-energy photons available in the visible spectral region. Addition of noble metal nanoparticles to TiO_2 have been used for some time to enhance its photocatalytic activity as they can scavenge photogenerated electrons and thus increase electron–hole pair separation. A theoretical framework to enhance the photoelectrochemical solar water splitting process has recently appeared.¹²

Within the present context, a possible approach to improve the performance of a wide band gap metal oxide such as TiO_2 (and others) and use of low-energy visible-light photons for photoexcitation could involve a step-by-step multiphoton (herein, a two-photon case) excitation of nanocomposite semiconductor (insulator) photoactive materials to achieve the excited state formed under the fundamental light absorption stage. Such an approach requires the existence of proper electronic states whose energy positions lie within the band gap. These states could be the localized electronic states (LS) of either dopants or intrinsic defects, Figure 3a (see, e.g., ref 13). In

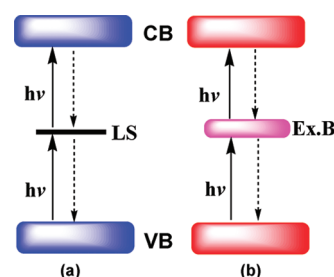
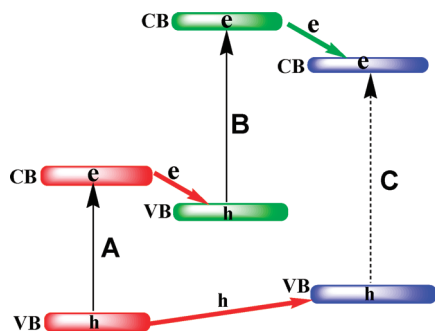


Figure 3. Mechanism of the step-by-step two-photon photoexcitation of a photoactive material (a) through localized dopant states (LS) and (b) through delocalized dopant states forming the extrinsic band (Ex.B).

turn, such states should conform to a specific behavior. For instance, the lifetime of the LS with the localized electron formed by the photoinduced electron transition $\text{VB} \rightarrow \text{LS}$ should be sufficiently long so as to permit the second photoinduced transition step $\text{LS} \rightarrow \text{CB}$, which in turn requires that such states possess very low probability for back electronic decay. At the same time, such states should have negligible activity as centers of charge carrier recombination.

Multiphoton excitation might also be achieved through formation of the band of delocalized states in the middle of the band gap by doping of source material at a sufficiently high level to provide the required conditions for delocalization of dopant electronic states (see Figure 3b and ref 14),

Another approach for multiphoton excitation might be based on heterojunctions involving two low band gap photoactive materials and TiO_2 with appropriate positioning of their corresponding CB and VB bands through the quantum size effect to yield what, in effect, may be considered as third-generation materials that could serve as photocatalysts and as photoelectrodes in photoelectrochemical cells (Scheme 1). Visible light activation would achieve the same stored energy in the excited state of TiO_2 as that obtained under UV irradiation. However, to the extent that low band gap materials tend to be photochemically unstable, they would, of necessity, need to be

Scheme 1. Steps in a Three-Component Nanostructure^a

^aThe first step in such a three-component nanostructure would involve a VB \rightarrow CB electronic transition in solid A to generate free electrons and holes, and since the VB position of solid A is lower than the VB band of solid C, hole transfer would then occur from A to C, resulting in charge separation in the A–C junction. Photoexcitation of solid B also generates e and h in solid B, and as the CB position of solid B is higher in energy than the CB of solid C, electron transfer will occur from B to C, thereby causing charge separation at the B–C junction. Positioning the CB of solid A higher in energy than the VB of solid B causes e transfer from A to B and recombination of e in A with h generated in B, thus completing the photoexcitation cycle in which the excited state of solid C has been achieved via a lower-energy two-photon process. As such, the photoactivity of the wide band gap material would be similar to the higher-energy one-photon process. Photoexcitation of components A and B would be very efficient because the two solids are activated through their fundamental absorption band.

encapsulated to form a heterojunction with a wider band gap but stable photoactive materials so as to enhance charge separation in the nanostructure.

A similar three-component nanostructure involving a dye, CdS, and TiO₂ was reported by Kamat and co-workers for liquid junction solar cells.⁹

Yet, an alternative strategy to improve performance is to use the surface-localized plasmon resonance (SLPR) energy of irradiated noble metals (e.g., Au, Ag, Pt) deposited on metal oxide particles in nanocomposite materials (e.g., ZnO/M and TiO₂/M) to activate, selectively, various electron states localized at the surface and subsurface of the photoactive metal oxide. Spectrally selective photoexcitation of such states might lead to alteration of the reaction pathways, that is, to the effect of spectral selectivity.¹⁵

A notable characteristic of the SLP resonance absorption is the dependence of the spectral position of the corresponding absorption bands on the size and shape of the noble metal nanoparticles and on the distance between them.¹⁶ The existence of such dependencies allows “tuning” of the composition of metal nanoparticles on the manifestation of resonance absorption within the desired spectral region by synthesis of metal nanoparticles of the prescribed size and shape. Thus, utilization of such metal nanoparticles as “antennae” in nanocomposite photoactive materials should enhance the excitation of photoactive materials within a given spectral region and thus enhance the desired selectivity in heterogeneous photoprocesses (see Figure 4). In turn, the effect of spectral selectivity manifested in the spectral region of extrinsic light absorption enhanced with the SLPR can be utilized for the creation of photochemical sensors whose photoresponse depends on the ability to interact with a given

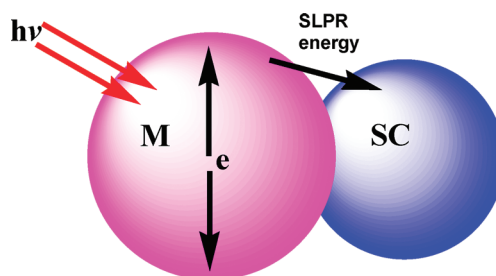


Figure 4. Mechanism of photoexcitation of the heterostructure formed by a noble metal nanoparticle and a photoactive material. Excitation of the SLP resonance in the noble metal nanoparticle induces a resonance excitation of appropriate localized states in the photoactive material.

sort of molecule dictated by the selected wavelength of the actinic light.

The Perspectives in this issue of *J. Phys. Chem. Lett.* are particularly attractive with regard to the nanoarchitectures that are somewhat related to the novel strategies just outlined.

Unlike the features of Figure 4, Kamat's Perspective¹⁷ focuses on photoinduced electron transfer from a (UV) light-harvesting semiconductor to the metal deposits and electron transfers between one semiconductor and another, reminiscent of the coupled semiconductor nanostructures of Figure 1. Factors that influence the rate of electron transfer at the interface are described in which storage and discharge properties of the metal nanoparticles play an important role in dictating the photocatalytic performance of semiconductor–metal constructs in photocatalyzed reactions.

Both electron and hole transfers across the interface with comparable rates are emphasized as being most important to maintain high photocatalytic efficiency and stability of the semiconductor assemblies, and we agree that the beautiful physical constructs such as nanorods, nanotubes, nanoforests, nanoflowers, nanoleaves, and the like do not per se inspire increased performance. Furthermore, we wish to emphasize as well that what is most important in building the nanoconstructs are the electronic structures and the thermodynamic properties (redox potentials) of the components and the ensuing electronic properties of the assembly. Semiconductor and metal nanoparticles assembled on reduced graphene oxide sheets offer novel designs of multifunctional catalyst materials. Fundamental underpinnings of charge-transfer processes are emphasized in future designs of light-harvesting nanoconstructs.

On the contrary, the Perspective by Zhou and O'Brien¹⁸ examines an interesting class of constructs, so-called mesocrystals composed of individual nanocrystallites stuck together by linkers (bridges). The paper describes a bottom-up view in which the properties of the construct reflect those of the individual crystallites forming it, with the performance of the mesocrystal depending very much on the shape, structure, and compositions of the nanocrystallites. The top-down view describes the construct as a bulk single crystal some components of which could be replaced by inorganic/organic species to produce a network structure within which the linkers (bridges) would influence electron transfer, hole transfer, and the like. Unlike nanoconstructs, however, mesocrystals tend to be relatively larger in size. Relationships between performance and structural features of mesocrystals need further examination for a fuller appreciation of their properties and ultimate applications in photocatalysis and in photoelectrochemistry.

The Perspective by Amal and co-workers¹⁹ focuses almost exclusively on heterogeneous photoinduced conversions (organic oxidations, hydrogen evolution, and water splitting) and emphasizes that the most significant advancement in the field of photocatalysis is currently driven by its association with materials science and nanotechnology. The review also examines four essential requirements in the design of a “functional” photocatalytic system that follows a multiscale integrated approach: (1) charge transport needs to be better understood, (2) reaction mechanisms need to be unraveled, (3) design of efficient photocatalysts demands innovation in syntheses and in nanoarchitectures, and, finally, (4) photon delivery must be so engineered as to reach the photoactive sites. In addition, the paper notes the significant increase in research output by Chinese researchers in the field of photocatalysis; in the decade of 2000–2009, there were nearly 5200 publications from China versus less than 200 the previous decade (1990–1999); in the last 2 years alone, research output nears almost 3500 publications.

One final comment regards water splitting. Too often, too many researchers claim to have achieved water splitting. A close scrutiny, however, often reveals the presence of sacrificial electron donors and/or acceptors, for instance, reactions carried out in a water/alcohol media. Producing hydrogen from the reduction of water is not the issue; the issue in water splitting is the oxidation of water to O₂, which requires simultaneously four oxidizing equivalents per molecule; a one-electron sequence would be too costly in energy as emphasized by Balzani's group (University of Bologna, Italy) way back in the mid-1970s.

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