Part 3

New Materials

CHAPTER 10

New Materials: Outline

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Photocatalysis has shown great potential as a green technology to help solve the energy shortage and environmental pollution issues. In particular, TiO_2 has attracted a great deal of attention as a representative photocatalytic material due to its chemical inertness, strong oxidizing activity, long-term stability against photocorrosion and chemical corrosion, cost-effectiveness, and non-toxicity.[1,2] However, TiO_2 possesses a wide band gap (3.0–3.2 eV) that limits its photo-absorption to the UV region, which accounts for only about 4% of the total irradiated sunlight. From the perspective of practical applications, it is highly desirable to develop new photocatalytic materials that harvest photons over a wide range of visible wavelengths or even into the infrared region.

In general, a photocatalytic reaction consists of three steps: firstly, light illumination generates photo-excited electrons (e^-) and holes (h^+) in the conduction band (CB) and valence band (VB), respectively; secondly, the excited electrons and holes become separated from each other and migrate to the surface; finally, the electrons and holes, which possess certain reductive and oxidative potentials, react with adsorbed electron acceptors and donors, respectively, as the photocatalytic reaction takes place. This basic mechanism is common to the degradation of organic species, water splitting, and CO_2 reduction, which represent three important photocatalytic reactions.

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However, these three reactions differ both in the details of their mechanisms and in their redox potential requirements. Thermodynamically, the overall water splitting reaction and especially the photocatalytic reduction of CO_2 with H_2O to form hydrocarbon fuels are uphill reactions with highly positive changes in the Gibbs free energy, whereas the photodegradation of organics is a downhill reaction accompanied by a negative change in the Gibbs free energy. Therefore, CO_2 reduction is the most challenging of these three reactions to accomplish. Moreover, special attention should be paid to the design of catalytic materials for CO_2 reduction since it involves a kinetically difficult multiple e^-/H^+ transfer process, and the adsorption and activation of thermodynamically stable CO_2 molecules is also a key issue in this reaction.

From the viewpoint of basic reaction mechanisms, research activities on the possibilities of new photocatalytic materials have been focused on how to improve their light harvesting, charge separation, and surface reactivity properties.[3]

Energy band engineering is a fundamental aspect of the design and fabrication of new photocatalytic materials, since the energy band configuration of a semiconductor plays a significant role in the absorption of light and in determining its redox potentials. It is desirable to modulate the energy band configuration of a material to extend its light absorption range while also meeting the redox potential requirement of the specific photocatalytic reaction to which the catalyst will be applied. A photocatalytic reaction can be accomplished by using a single catalytic material or by a combination of materials such as composites, p–n or n–n heterojunctions, and Z-scheme systems. In systems consisting of more than one catalyst, the redox potential requirements can be simultaneously fulfilled by the different materials, while allowing a wider range of visible light to be harvested. Precise modulation of the band gap and band-edge positions has been achieved both by doping with different elements and by solid-solution strategies.[4–11] Furthermore, it has been found that the loading of photosensitizers such as plasmon-active metals,[12,13] sulfide/selenide/telluride quantum dots,[14,15] and other materials[16] is effective to further improve the light harvesting properties of a photocatalytic material.

In recent decades, tremendous effort has been devoted to the development of "new-generation" TiO_2-based materials, including energy band modulation by doping with elements such as N, C, and S,[4,5] the construction of hetero-junctions by combining TiO_2 with metals such as Pt and Pd or with other semiconductors such as NiO, RuO_2, WO_3, and CdS,[17–19] the addition of quantum dots or dyes to the TiO_2 surface for better light sensitization,[20–23] and surface-disorder engineering by hydrogenation to sensitize TiO_2 to the visible and near-infrared regions.[24] The diversity of complex metal oxides has also been exploited to develop a large number of new photocatalysts including Ti, V, Nb, Ta, Mo, and W-based materials, which contain cations with d^0 electronic configurations, and Cu, Ag, Zn, Cd, Ga, and Ge-based materials, which contain cations with d^{10} electronic configurations.[3,25–27] Several sulfides, nitrides, and oxynitrides have also been investigated.[25] In addition to inorganic semiconductors, polymeric C_3N_4 and metal–organic framework (MOF)-based materials have received considerable attention in recent years.[28–30] As shown in Tables 11.1–11.4, a total of more than 130 new materials have thus far been developed for different photocatalytic reactions.

Another key issue influencing the photocatalytic activity of a material is the nature of its surface/interface chemistry. The surface energy and chemisorption properties play crucial roles in the transfer of electrons and energy between substances at the interface. These properties also govern the selectivity, rate, and overpotential of redox reactions on the photocatalyst surface, and determine how susceptible the material is to photocorrosion. The rapid development of both nanotechnology and advanced characterization techniques such as TEM, EELS, and XPS provide great opportunities for the design and fabrication of new photocatalytic materials with superior performance. In recent years, notable progress has been made in the shape-controlled synthesis of photocatalytic materials and in understanding the relationships between morphological or structural characteristics and the photocatalytic properties.[31–33] Furthermore, particular emphasis has been placed on developing co-catalysts that do not contain noble metals,[34] and on constructing complex or hierarchical hetero-nanostructures to facilitate the separation of photogenerated electron–hole pairs to further improve the photocatalytic activity.[35,36] For example, photon coupling in semiconductor photonic crystals has been found to further improve the utilization efficiency of incident photons.[37] Approaches that involve engineering the interactions between nanocrystalline building blocks or designing assemblies of such building blocks have shown great potential to produce extraordinary properties beyond those exhibited by the individual components.[38,39]

Overall, significant progress has been made in the development of novel photocatalytic materials over the last few decades.[3,25,40,41] Nevertheless, the efficiencies of the new materials, especially for solar fuel production, are still far from adequate from the viewpoint of engineering requirements. Furthermore, the stability and cost of these materials should also be carefully considered. It is thus a challenge of great importance to design and fabricate new semiconductor materials that are efficient, stable, and yet abundant.

The following chapters give a detailed overview of the state-of-the-art research activities being carried out to design new materials for the three major photocatalytic reactions, *i.e.*, the degradation of various organic species in the gaseous and liquid phases, pure water-splitting or hydrogen evolution/oxygen evolution from aqueous solution containing a sacrificial reagent, and CO_2 reduction for the production of hydrocarbon fuels.

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