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Chapter

Introductory Chapter: Fundamentals of Semiconductor Photocatalysis

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1. Introduction

In semiconductor photo-catalysis, generally it is used to design, characterize, and potential photocatalytical applications with doped or undoped nanostructural materials especially considering their particle sizes as well as shapes. Nanostructured materials, for example, porous metal oxides, metal nanoparticles, porous carbons, and their composites are widely studied for their potential applications in energy conversion/storage devices, gas storage, photocatalysis as well as in electrocatalysis. Photocatalysis is the phenomena, which occurs in catalysis by influence of photons. An efficient photocatalyst is a conductive nanomaterial, which directly absorbs incident light to bring up to higher energy states, which provides such energy to a reacting substance to make a chemical reaction occur. The mechanism of *photocatalytic* water splitting over *semiconductor photocatalysts* is also discussed in this chapter. Thermodynamically, the reaction of complete water splitting under normal conditions is a highly endothermic process because the change in the standard Gibbs energy is very large.

2. Literature review

For photocatalytic applications, the location of the TiO_2 nanoparticle plays an important role in the photoactivity, since various nanoparticles should be accessible for both photons and reactive molecules. The advantages of using these materials as support for TiO_2 in relation to photocatalytic processes are addressed by comparing the photocatalytic activity of TiO_2 nanoparticles deposited by different routes with TiO_2 nanoparticles on mesoporous materials [1–3]. Three-dimensional nanostructures have interconnected networks of bulk materials and larger accessible surface areas with respect to their lower dimensional counterparts. The surface functionalities, controllable host-guest interactions, and size-selective sensing properties are enabled due to the spatial arrangement of particles within three-dimensional framework [4–15].

Here, catalysts based on Ti-containing mesoporous silica have been developed from different synthetic pathways for selective oxidation of bulky organic compounds and photoreduction of greenhouse gases [16–18]. To support particles of TiO_2 on mesoporous silica, maintaining or improving its photocatalytic activity is not an easy task as, in addition to be strongly attached to the substrate for avoiding leakage, nanoparticles' size, location, and agglomeration should be controlled to have accessibility for adsorbates and incident photons [19–22]. Nanostructure of

rare earth material is appropriate for these applications that can be synthesized with different methods, for example co-precipitation, hydrothermal, sol–gel, combustion, stearic acid route, pechini, cathode plasma, electrolysis, co-ions complexation, molten salt, and other approaches [13]. Rare-earth-based materials were used in different fields. In this section, we study a brief review of rare-earth-doped materials, rare-earth-based oxide–oxide composites, metal-modified semiconductors, and mixed-oxide materials in the fields of photocatalytic application as solar energy generation. When a photon is absorbed by rare-earth-based material using the energy gap of the materials, electron–hole pairs are generated in the photocatalysis mechanism [23–27]. Semiconductor photocatalysis can be of two types, homogenous photocatalysis and heterogeneous photocatalysis, depending on the phase differences of reactants and catalysts, which triggered the concept of advanced oxidation processes at the end of twentieth century. TiO_2 is the semiconductor, which can act as both the hetero- and homogenous photocatalyst photoreactions. There are numerous semiconductors, which can be coupled with other semiconductors and can be incorporated into heterostructures or composites. So, another example of inorganic heterostructure is the template-free simple synthesis of CdS-ZnO nanocomposites. This self-assembled flower-like structure resulted from coupling of two semiconductors, which increased the charge separation and demonstrated greater photocatalytic activity [28, 29].

Negheshi et al. attempted to improve the activity of mesoporous tungsten trioxide, and titanium dioxide (m-WO_3 and m-TiO_2) photocatalysts, which convert methane into methanol, by loading the ultrafine metal clusters as co-catalyst on the photocatalysts. They have succeeded in loading ultrafine metal-cluster co-catalysts onto m-WO_3 and m-TiO_2, and thereby improving their photocatalytic activity in presence of mesoporous nanomaterials. The photocatalytic activity measurements clearly demonstrated that the loading of such co-catalysts is effective in improving the activity for both types of photocatalysts. It is important to appropriately select the element of the co-catalyst according to the photocatalyst to improve the photocatalytic activity. In this approach, the particle diameter of the co-catalyst was reduced to approximately 1.0 nm to increase the reactive surface area [29–32]. Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that signify enhancing environmental pollution.

Contaminated water means undesirable substances; it adversely affects the quality and makes it inappropriate for use. Various sources such as residential, commercial, industrial practices, etc. contaminate the water and its sources as well. Wastewater parameters vary widely and depend on the source it is produced form. They are usually pathogenic, nonpathogenic microorganisms, organic, or inorganic [33, 34]. The toxic and carcinogenic nature of these dyes and their manufacturing precursors represent a danger to human beings and perturbation in aquatic life. The enlarged public concern about these environmental pollutants and the creation of international environmental standards have prompted the need for the development of novel treatment methods for converting organic pollutants (such as dye effluents) to harmless compounds. Reductive cleavage via anaerobic biological treatment generates potentially carcinogenic intermediates or end products, especially aromatic amines. Physical processes are like reverse osmosis, flocculation, absorption, air-stripping, combustion, and aerobic biological oxidation, which are nondestructive, and these processes only shift the pollutants from one medium to others, thus creating secondary pollution [35–38]. For the past two decades, a lot of research is going on for advanced oxidation processes, pointing out its potential vital role in the wastewater purification, in which the high oxidizing potential species like hydroxyl radicals are utilized as an alternative way of treating undesirable organic pollutants. Advanced oxidation processes shows great effort in solving the

bio-recalcitrant water-pollutant issues at near-ambient temperature and pressure [39–41]. Heterogeneous photocatalysis is a method wherein a blend of photochemistry and catalysis is operable and suggests that light and catalyst are necessary to bring out a chemical reaction. Lately, there has been a developing enthusiasm in usage of semiconductors as photosensitizers for the complete oxidative mineralization of pollutants by oxygen [42, 43]. Heterogeneously scattered semiconductor surfaces give both a fixed situation to impact the chemical reactivity of a wide scope of adsorbates and a means to initiate light-induced redox reactivity in these feebly related molecules.

When a semiconductor is intact with an aqueous solution, thermodynamic equilibration takes place at the interface. This may result in the development of a space-charge layer inside a slight surface area of the semiconductor, in which the electronic vitality bands are commonly twisted downward or upward, respectively, in the instances of p- and n-type semiconductors. The space-charge layer thickness is typically in the range of 1–10^3 nm, contingent upon the dielectric constant and carrier density of the semiconductor. If this semiconductor perceives photons with energies that are more noteworthy than that of the respective material's band gap energy, electron–hole pairs are produced and parted in the space-charge layer. The development of new and noble nanotechnology is urgently required for introducing the eco-friendly, safe, facile, non-toxic routes in synthesis-to-applications, which can be used by industrial sectors in broad scale.

Recently, the nanotechnology offers the control growth of semiconductor substances at the nanoscale, which exclusively facilitates the novel photocatalytic applications with transition doped semiconductor catalysts. Photocatalysis, reactions supported out in the presence of a low-dimensional semiconductor and light, is rapidly becoming one of the most dynamic areas of catalysis research, with potential applications in areas such as environmental, solar, renewable energy, medicine, and sensors [44–47]. Here, in this book, it presents an overview of current photocatalyst fundamental, substantial applications, and enactment of the research in worldwide. This investigated the techniques of photocatalyst preparation, various types of characterization, and possible industrial applications related to solar photocatalyst researches.

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