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Photocatalytic activity of Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ heterojunctions

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Abstract

Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ heterojunctions were studied for potential applications in water decontamination technology and their capacity to induce an oxidation process under VIS light. UV–vis spectroscopy analysis showed that the junctions-based Cu_2O, Bi_2O_3 and $ZnMn_2O_4$ are able to absorb a large part of visible light (respectively, up to 650, 460 and 1000 nm). This fact was confirmed in the case of Cu_2O/TiO_2 and Bi_2O_3/TiO_2 by photocatalytic experiments performed under visible light. A part of the charge recombination that can take place when both semiconductors are excited was observed when a photocatalytic experiment was performed under UV–vis illumination. Orange II, 4-hydroxybenzoic and benzamide were used as pollutants in the experiment. Photoactivity of the junctions was found to be strongly dependent on the substrate. The different phenomena that were observed in each case are discussed.

Keywords: Titanium dioxide; Cu_2O; Bi_2O_3; $ZnMn_2O_4$; Heterojunction; Photocatalysis

1. Introduction

Currently, TiO_2 is the most popular semiconductor used in heterogeneous photocatalysis [1]. However, TiO_2 absorbs only a small fraction of solar light. This behavior appears to result from the constancy of the energy edges of the O^{2-}: $2p^6$ deep band, which lies far below the O_2/H_2O level to be practical (>1 eV) [2,3]. Moreover, the rapid recombination that occurs in relation to photoproduced electrons and holes in TiO_2 significantly diminishes the efficiency of the photocatalytic reaction [4].

One of the most promising ideas to extend the light-absorbing property of TiO_2 and to enhance its photocatalytic efficiency is to couple TiO_2 with narrow band gap semiconductors. In these circumstances, both semiconductors must have different energy levels from their corresponding conduction and valence bands. In this configuration, several advantages can be obtained: (1) an improvement of charge separation; (2) an increase in the lifetime of the charge carrier and (3) an enhancement of the interfacial charge transfer efficiency to adsorbed substrate [5,6].

For an efficient interparticle electron transfer between the semiconductor that is considered as sensitizer and TiO_2, the conduction band of TiO_2 must be more anodic than the corresponding band of the sensitizer. Under visible irradiation, only the sensitizer is excited and the electrons generated to their conduction band are injected into the inactivated TiO_2 conduction band. If the valence band of the sensitizer is more cathodic than the valence band of TiO_2, the hole generated in the semiconductor remains there and is not able to migrate to TiO_2. These thermodynamic conditions favor the phenomenon of electron injections. Fig. 1a provides an illustration of interparticle electron transfer behavior. CdS and ZnO fall within the category of photoexcited semiconductors, which are typically coupled with non-photoexcited semiconductors of TiO_2 and SnO_2 to promote permanent charge separation. In the literature, heterojunctions are described as providing attractive approaches to achieve better efficiency of photodegradation of refractory organics. For example, Serpone et al. [6] examined the kinetics of phenol disappearance in relation to various combinations of heterojunctions (CdS/TiO_2, TiO_2/Fe_2O_3, ZnO/TiO_2, SnO_2/TiO_2 and TiO_2/WO_3) [20]. More recently, Lo et al. [4] showed the efficiency of the coupled $CdSe/TiO_2$ combination, compared with TiO_2 alone, for the photodecomposition of 4-chlorophenol.

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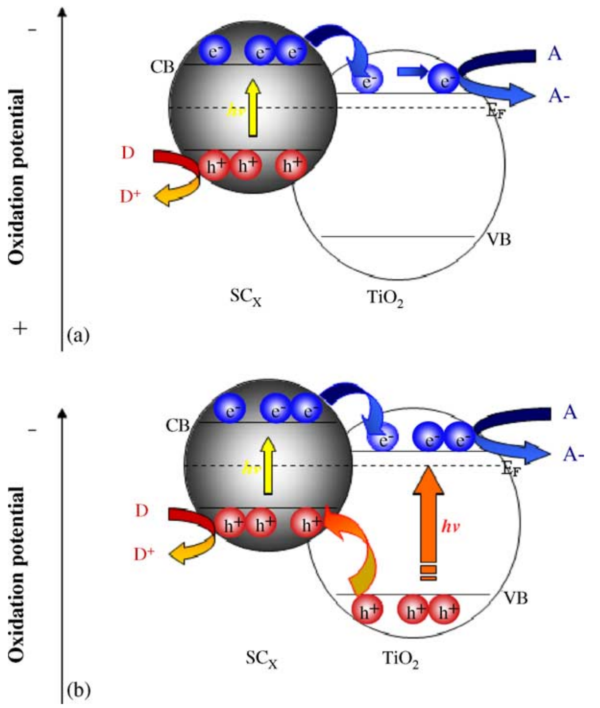

Fig. 1. (a) Energy diagram illustrating the coupling of two SC in which vectorial electron transfer occurs from the light-activated SC to the non-activated TiO_2. (b) Diagram depicting the coupling of SC in which vectorial movement of electrons and holes is possible.

When the combination is under UV–vis irradiation, both semiconductors are excited. Electrons are injected from the sensitizer to TiO_2, as is the case, where use is made of visible illumination with an additional presence of electrons from activated TiO_2. In this case, a high concentration of electrons is obtained in the conduction band of TiO_2. Holes generated on the TiO_2 valence band are transferred to the valence band of the sensitizer, and consequently create a high concentration of holes in the sensitizer/electrolyte interface (Fig. 1b). All the phenomena described are ideal, as in reality different mechanisms of electrons and holes trapping can occur.

In this study, we have selected three semiconductors for use as in potential application as the sensitizer with TiO_2 in order to induce the oxidation process under VIS light. Cuprous oxide has attracted much current research interest since Cu_2O is an important metal-oxide p-type semiconductor [7–9] and has a direct band gap 2.2 eV, which makes it a promising material for the conversion of solar energy into electrical or chemical energy [10,11]. Recently, Cu_2O was reported to act as a stable catalyst for water splitting under conditions of visible light irradiation ($\leq$600 nm) although its exact role is unclear [12–14]. Cu_2O/TiO_2 heterojunction as a potential thin film photocathode for hydrogen production has been studied by Siripala et al. [15]. It was observed that at -1 V bias, high photoactivity was obtained with additional limitation of Cu_2O corrosion. The existence of Bi_2O_3 in thin films makes it an interesting material due to its different gap energy, which depends on crystallographic structure, its high value of refractive index and dielectric permitivity as well as its remarkable photoconductivity and photoluminescence [16]. $ZnMn_2O_4$ is a spinel p-type semiconductor and has recently been proved to be efficient as a photocatalyst for hydrogen production and removal of hydrogen sulfide under visible light [17].

Many researchers have gone through great efforts to prepare real heterojunctions (for example, references [4,6]). In the other works [5], we have prepared CdS/TiO_2 and Bi_2S_3/TiO_2 heterojunctions by direct mixture and by precipitation of the sensitizer (CdS or Bi_2S_3) with TiO_2. Interparticle electron transfers occurring on CdS/TiO_2 and Bi_2S_3/TiO_2 junctions were demonstrated by performing photocatalytic tests under visible light. However, the preparation of heterojunctions by precipitation of the sensitizer with TiO_2 is more attractive than direct mixture of both components. For this reason, we have prepared Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ heterojunctions by direct mixture of two semiconductors. In this case, we assume that Brownian motion suffices to permit charge transfers between the particles of the two solids.

2. Experimental

2.1. Materials

All reagents used in this work were of analytical grade and were used without any further purification: $Bi(NO_3)_3$ (Labosi), $Zn(NO_3)_2$ (Prolabo), $MnCl_2$ (Prolabo), hydroxypropyl-cellulose (HPC, MW: 100,000) (Aldrich), Cu_2O powder <5 μm (Aldrich), TiO_2–P25 (Degussa).

2.2. Preparation of catalyst

Bi_2O_3 was prepared by dissolving $Bi(NO_3)_3$ in 1 M NaOH solutions containing HPC (10^{-2} g/l). The precipitate thus obtained was filtrated and washed with water. The samples were dried at 110 °C overnight and then heat-treated at 500 °C for 1 h in an oven. $ZnMn_2O_4$ spinel powder was prepared by dissolving appropriate amounts of $Zn(NO_3)_2$ and $MnCl_2$ in a solution of 14.4 M NH_4OH. The precipitate was recovered by filtration and dried at 110 °C overnight. The powder obtained was homogenized by grinding in mortar and then heat treated at 400 °C for 10 h. After cooling, the powder was ground in mortar, and finally heated at 850 °C for 72 h. Cu_2O was used without any additional treatment.

2.3. X-ray diffraction (XRD)

Powder XRD patterns of prepared and commercial catalyst were obtained using a Philips diffractometer with monochromated high intensity Cu Kα in the scan range 2θ between 20° and 80°. The average crystalline sizes of the catalyst used were determined according to Scherrer's