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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.
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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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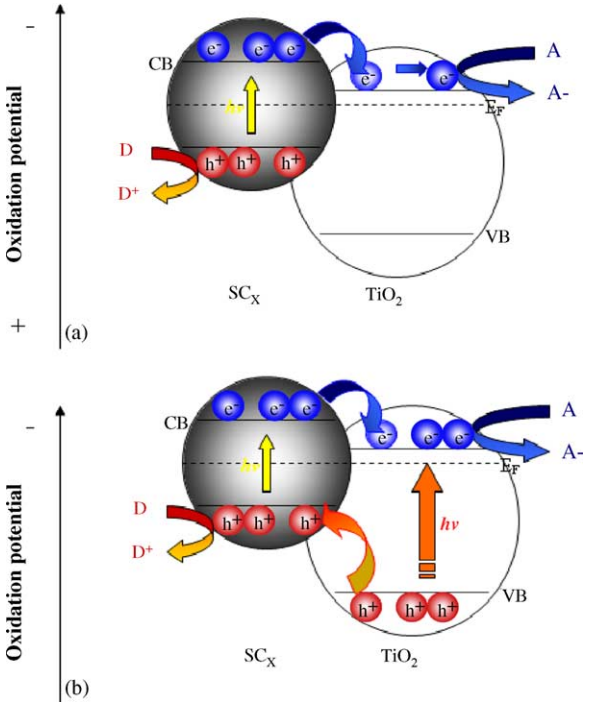

Fig. 1. (a) Energy diagram illustrating the coupling of two SC in which vectorial electron transfer occurs from the light-activated SC to the non-activated TiO_2. (b) Diagram depicting the coupling of SC in which vectorial movement of electrons and holes is possible.

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

equation using the full-width at half-maximum (FWHM) of the peak presenting the highest intensity and taking into account the instrument broading.

2.4. UV–vis diffuse reflectance spectroscopy

Absorption and reflectance spectra of pure and loaded semiconductors were recorded by a Bruins UV–vis–NIR spectrophotometer equipped with an integrated sphere. $BaSO_4$ was used as a reference to measure all samples. The spectra were recorded at room temperature in air in the range 200–1000 nm allowing the study of the spectral properties of these materials.

2.5. Measurement of photocatalytic activity

The efficiency of electron transfer from each sensitizer (Cu_2O, Bi_2O_3 and $ZnMn_2O_4$) to TiO_2 was taken as the ability to degrade: Orange II, 4-hydroxybenzoic acid and benzamide degradations under visible irradiation, and the effect of electron–hole recombination was examined when photocatalytic experiment was performed under UV–vis illumination. The solar box ATLAS Suntest *CPS+* simulating natural radiation and equipped with a vapour Xenon lamp was used in all experiments. A sheet of poly(methyl methacrylate) (PMMA) 12 mm thick was used as an optical filter to remove UV radiation. When Orange II was used as pollutant, typically 50 mg of TiO_2 and the appropriate amount of semiconductors (Cu_2O, Bi_2O_3 or $ZnMn_2O_4$) was dissolved in 100 ml of Orange II (10 mg/l) solutions. The mixture was sonicated before irradiation for 2 min to obtain highly dispersed catalysts. Before irradiation, solutions were maintained in the dark for 1 h. At given irradiation time intervals, the samples (5 ml) were taken out and then analyzed by UV–vis spectrophotometer: ''Shimadzu PC-1200''. The measure of maximum absorbance was taken at 485 nm.

4-Hydroxybenzoic acid and benzamide disappearance were followed by HPLC equipped by a C18 column to determine their concentrations. One hundred and twenty-five milligrams of TiO_2 and appropriate amounts of semiconductors (Cu_2O, Bi_2O_3 or $ZnMn_2O_4$) were dispersed in 250 ml of solution containing ether, 20 mg/l of benzamide or 30 mg/l of 4-hydroxybenzoic acid and sonicated for 2 min before their exposure to the light. During the irradiation process, 10 ml of each solution was sampled at regular time intervals, filtered (Whatmann 0.45 mm) and analyzed. C_i is the initial concentration and C_0 is the concentration at the equilibrium. The percentage of degradation is reported as C_i/C_0.

3. Result and discussion

3.1. Structure analysis

It has been reported that Bi_2O_3 has four polymorphic forms, several non-stoichiometric compounds and impurity phases [18]. The α-Bi_2O_3 is a stable low temperature polymorph, which is reported to be monoclinic [19,20]. The tetragonal form is a metastable two-dimensional superstructure of β-Bi_2O_3 [18]. The cubic γ shape is the high temperature phase, which is to be observed between 730 and 820 °C and appears to be impurity-stabilized at room temperature [18]. In all cases, the temperature of each transition strongly depends on the synthesis method. In our case, the shape diffraction lines of Bi_2O_3 patterns indicate that the powder has a high degree of crystallinity. All peaks were assigned to Bismite crystallized in monoclinic form according to JCPDS files no. 41-1449. The average crystallite size of the powders thus synthesized, estimated from the full-width at half-maximum intensity of (1 2 0) X-ray line diffraction, was found to be approximately of 62.42 nm. Also, XRD patterns of commercial Cu_2O showed that the compound is well crystallized, and the peaks were attributed to cuprite crystallized in cubic shapes according to JCPDS files no. 5-667. The crystallite size was estimated by taking into account (1 1 1) X-ray line diffraction and was found to be of the order of 35.48 nm. The X-ray powder pattern of $ZnMn_2O_4$ revealed that the sample was a single phase with good crystallinity and all peaks were assigned to spinel oxide in tetragonal system according to JCPDS files no. 45-505. Their crystallite size was estimated as 93.56 nm by using (2 1 1) X-ray line diffraction.

3.2. UV–vis diffuse reflectance spectroscopy

Fig. 2 shows the evolution of absorbance towards the incident wavelength of pure Cu_2O, TiO_2 and Cu_2O mixed with TiO_2 prepared by the direct mixture of both semiconductors. At first sight, it is clear that the junctions absorb the light in the VIS region, up to a wavelength of 650 nm. The presence of two peaks in spectral absorption of each junction corresponding, respectively, to both semiconductors indicates that the junctions can be excited using light having the appropriate wavelength. We also observed that increasing Cu_2O concentration produces an increase of the junction absorptions. The same results were obtained for the junctions Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$, where the absorptions in the visible region start, respectively, at 460 and 1000 nm. The results obtained signify that the junctions can be excited by visible light, but do not prove that electron exchange can occur between both semiconductors. It is only the photoactivity, which can be observed under VIS light that demonstrates the phenomenon of interparticle electron injection.

3.3. Photocatalytic activity

3.3.1. Cu_2O/TiO_2 heterojunction

Cu_2O/TiO_2 heterojunction was studied for its potential application as a photoelectrochemical diode-inducing oxidation process of organic compounds. Almost 20% of initial Orange II concentration (C_i) is adsorbed on pure Cu_2O

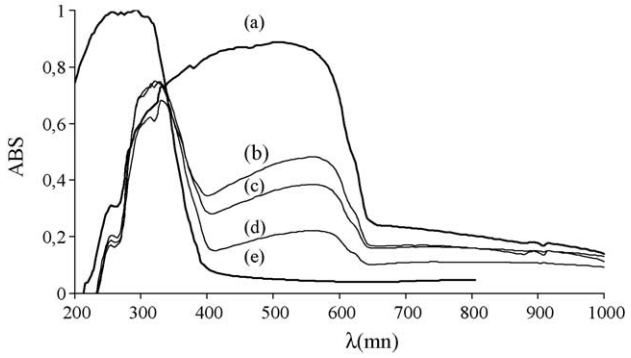

Fig. 2. Normalized UV–vis spectra of: (a) Cu_2O, (b) Cu_2O (50%)/TiO_2, (c) Cu_2O (30%)/TiO_2, (d) Cu_2O (10%)/TiO_2, (e) TiO_2–P25.

in conditions of darkness. Fig. 3 shows the variation of Orange II concentration versus irradiation times at different amounts of Cu_2O when the system is subjected to visible light. At this stage, it is important to note that during photocatalytic experimentation performed with pure Cu_2O, a shifting of the solution to red was observed without variation of the pH. In addition, the wavelengths corresponding to the maximum absorption did not change. This observation indicates that a redox process is induced by illuminated Cu_2O. In this regard, Orange II degradations cannot be confirmed. When Cu_2O was mixed with TiO_2, degradation of Orange II occurred under visible light in less than 30 min. In fact, the initial solutions became colorless during this period. In addition, the amount of Cu_2O in the heterojunction plays an important role since it was observed that photocatalytic efficiency increases with increases of the Cu_2O amount. However, when the Cu_2O amount is more than 30% of the catalyst's total weight, the degradation rate reached saturation. Photocatalytic activities of the junction, when observed under visible light, demonstrate that the electrons generated from Cu_2O can be injected into the conduction band of inactivated TiO_2. These electrons react at the surface with dissolved oxygen molecules and induce a formation of oxygen peroxide radicals, $O_2^{\bullet -}$. From the results, we can conclude that Cu_2O is an effective sensitizer.

When the experiment is performed under UV–vis irradiation, the efficiency of Cu_2O/TiO_2 junction increases as the Cu_2O amounts increase (Fig. 3b). Unfortunately, at high concentration, their efficiency remains close to that observed for pure TiO_2, and at a low concentration of Cu_2O, a real deactivation of TiO_2 is observed. This fact can be attributed to the increase of charge trapping mechanism contributions when both semiconductors are excited. Their effects certainly depend on the sensitizer concentration. The best-performing junction (Cu_2O (50 wt.%)/TiO_2) was selected for investigation of its photoefficiency with other models.

Experiments performed with benzamide showed that pure Cu_2O is able to adsorb benzamide, not only in the dark, but also under illumination. In fact, more than 16% of benzamide was adsorbed under light-activation. In the case of selected junction, 20% of benzamide disappeared after 1 h of visible light irradiation. However, in this case the disappearance of benzamide is not attributed to adsorption phenomena, but to photocatalytic degradation of benzamide since some intermediate products were observed by chromatography analysis. When the junction was irradiated by UV–vis light, degradation of benzamide was not observed until 40 min of irradiation time had elapsed. After this point, degradation of benzamide occurs and the generation of intermediate products was observed. However, the efficiency of the junction remained less than that obtained using pure TiO_2 when close to 98% of benzamide was removed in a 1 h period of irradiation. At the end of the experiment with the junction, we observed that the color of Cu_2O had changed from red to black. However, no copper ion was detected by chemical analysis. It is possible that generated charges on both semiconductors then induced photocorrosion of Cu_2O. Black particles are probably CuO, which is generated by valence evolving from Cu^+ to Cu^{2+} due to holes scavenging by Cu^+ [21]. From all the results, we assume that this junction is not useful for degradation of benzamide though interparticle electron transfer was demonstrated in the case of Orange II degradation. A large part of the generated charges are lost by the trapping process and/or by photocorrosion of Cu_2O.

Less than 3% of 4-hydroxybenzoic acid is adsorbed on pure Cu_2O in conditions of darkness. Cu_2O (50 wt.%)/TiO_2 junction was found to be inefficient in relation to degradation of 4-hydroxybenzoic acid under VIS light.

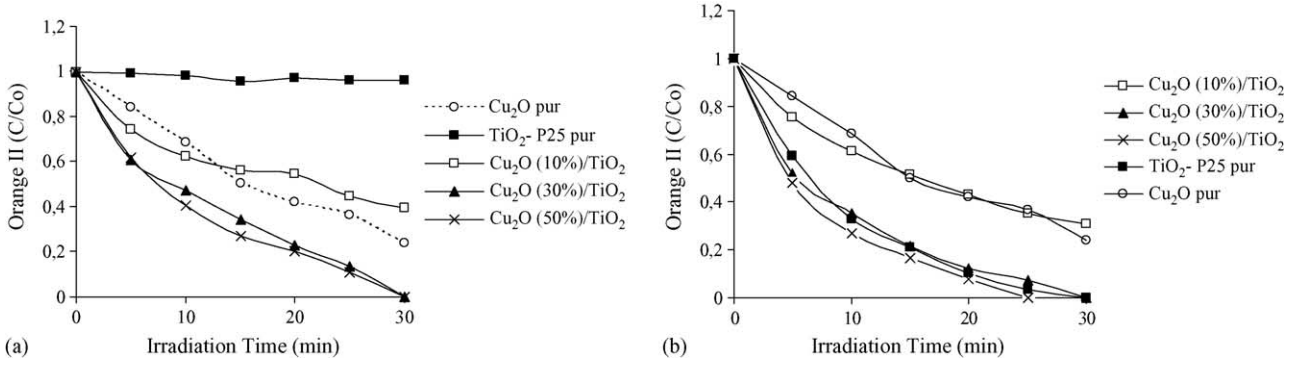

Fig. 3. Photocatalytic degradation of Orange II using Cu_2O sensitized TiO_2: (a) under visible irradiation and (b) under UV–vis irradiation.

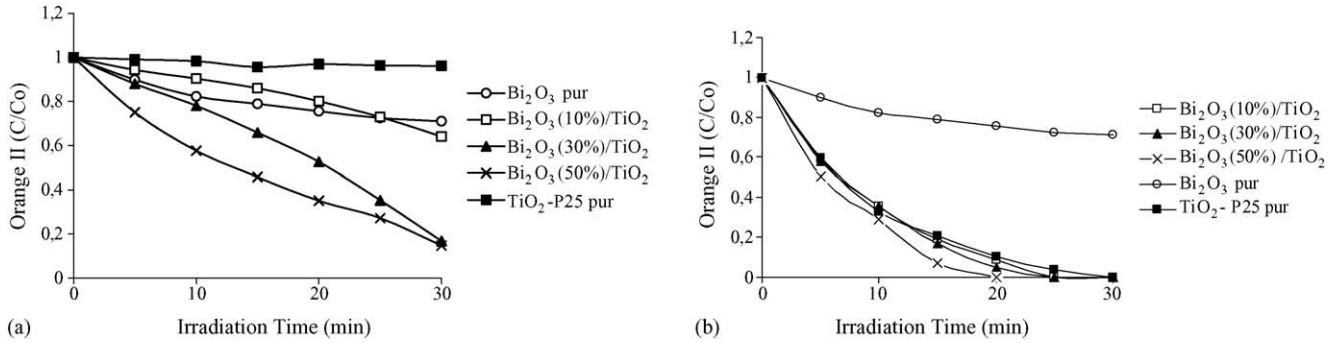

Fig. 4. Photocatalytic degradation of Orange II using Bi_2O_3 sensitized TiO_2: (a) under visible irradiation and (b) under UV–vis irradiation.

Indeed, only 15% of 4-hydroxybenzoic acid was removed after 120 min of irradiation. Using UV–vis light, an activation of the junction was obtained. Unfortunately, it was also observed that TiO_2, when applied alone, showed the best-photoactivity (close to 100% of degradation after 120 min of irradiation).

3.3.2. Bi_2O_3/TiO_2 heterojunction

Orange II is adsorbed on Bi_2O_3 in conditions of darkness (∼8% C_i). Photocatalytic experiment performed with pure Bi_2O_3 showed that this material is able to degrade Orange II under VIS light (Fig. 4a). The junctions based on this material mixed with TiO_2 proved to be efficient under VIS irradiation. Indeed, we observed that efficiency of the junctions increases when Bi_2O_3 increases. This demonstrates that interparticle electron transfer occurs between both semiconductors. The increase of photoactivity is attributed to the increasing of sensitizer concentrations, which under VIS light, perform like an electron pump. A great increase in efficiency was obtained when the junctions were submitted to the UV–vis light (Fig. 4b). Indeed, the efficiency of all junctions was increased, whatever the concentration of sensitizer. The most interesting results are obtained with Bi_2O_3 (50 wt.%)/TiO_2, where more than 33% of irradiation time is saved in comparison to the use of pure TiO_2. This last junction was selected to investigate its efficiency in relation to degradation of benzamide and 4-hydroxybenzoic acid.

When benzamide was used as model and the system was illuminated with VIS light, less than 10% of benzamide was removed by pure Bi_2O_3 during 1 h of irradiation. In the case of the junction, 20% of benzamide was removed during the same period of time. In all cases, adsorption of benzamide on Bi_2O_3 or TiO_2 was never observed. It should be noted that at the end of the photocatalytic tests performed with benzamide, the color of Bi_2O_3 changed from yellow to grey. This phenomenon is believed to be a consequence of photocorrosion.[1] Photocatalytic experimentation performed under UV–vis light showed that the junction efficiency is highly improved in comparison with its performance under VIS light. However, the rate of benzamide degradation remained low in comparison to degradation achieved with pure TiO_2.

Adsorption of 4-hydroxybenzoic acid on Bi_2O_3 was observed in conditions of darkness. However, under irradiation, a strong desorption was observed. Photocatalytic experimentation performed under visible light showed that Bi_2O_3 alone is not able to remove 4-hydroxybenzoic acid. Nevertheless, the junction was found to be able to degrade 4-hydroxybenzoic acid and more than 33% of the initial concentration of pollutant was removed after 120 min of irradiation. Under UV–vis light, 62% of 4-hydroxybenzoic acid was degraded by Bi_2O_3 (50 wt.%)/TiO_2 in 120 min of irradiation. However, this rate of degradation remains low in comparison to that obtained using pure TiO_2. From these results, we assume that interparticle electron transfer occurs between Bi_2O_3 and TiO_2, and that Bi_2O_3 acts as a sensitizer.

3.3.3. $ZnMn_2O_4/TiO_2$ heterojuncion

Orange II is adsorbed on $ZnMn_2O_4$ in conditions of darkness. However, it was observed that a strong desorption is observed under illumination. When $ZnMn_2O_4/TiO_2$ junctions were placed under VIS light, degradation of Orange II was not observed, whatever the amount of $ZnMn_2O_4$. These results suggest that electrons generated in $ZnMn_2O_4$ are not injected onto the TiO_2 conduction band.

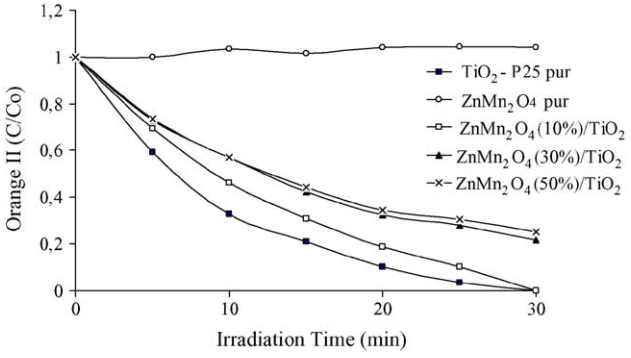

Fig. 5. Photocatalytic degradation of Orange II using $ZnMn_2O_4/TiO_2$ under UV–vis irradiation.

[1] The presence of Bi^{3+} into the solution was not observed by chemical analysis. However, it is possible that some secondary phases are produced at the surface of Bi_2O_3 and induce the color variation of catalyst. For this purpose, a study of Bi_2O_3 photocorrosion by XPS and EDS analysis will be investigation.

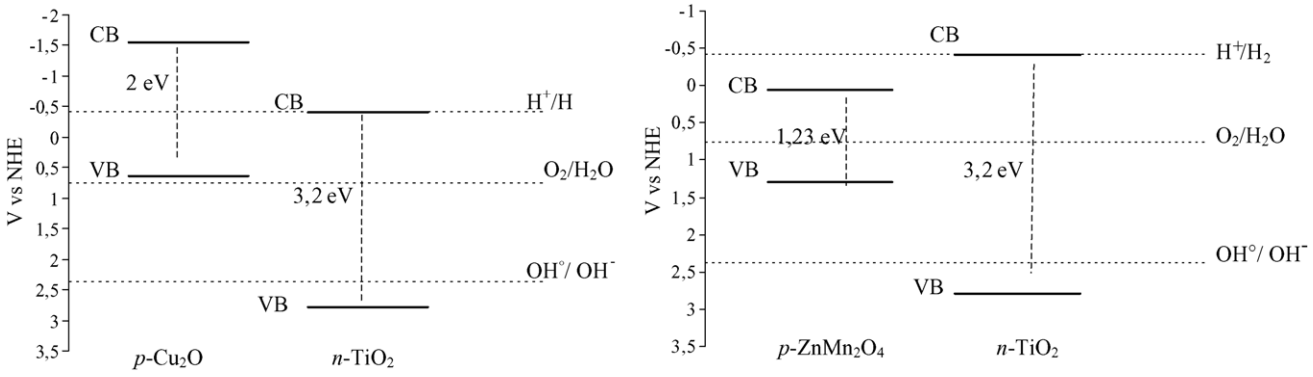

Fig. 6. Energetic diagrams of Cu_2O/TiO_2 and $ZnMn_2O_4/TiO_2$ heterojunction [1,13,15].

As a consequence, radicals cannot be generated. The submission of the junctions to the UV–vis light showed an Orange II degradation (Fig. 5). Unfortunately, it was also observed that the rate of Orange II degradation decreases with an increasing quantity of $ZnMn_2O_4$, and in all cases, the junctions present a lower efficiency than that of pure TiO_2. The experiment performed with benzamide and 4-hydroxybenzoic acid leads to the same observations, i.e. no photoactivity of the junctions was observed under VIS light, and an increasing in the quantity of $ZnMn_2O_4$ induces a decrease of TiO_2 photoactivity when submitted to UV–vis light. It is clear from the results that the phenomena are governed by physical laws rather than by chemical laws due to the fact that the type of pollutant used in this work has no influence on the photoactivity of the junctions.

3.4. Discussion of interparticle electron transfer

Fig. 6a depicts the flat band potentials [1,15] of the valence and conducting bands at pH 7 (versus the normal hydrogen electrode (NHE)) for Cu_2O and TiO_2 with their band gap energy. As we can see, the conduction band of Cu_2O is located at -1.54 eV. This value is more negative than the conduction band potential of TiO_2 (-0.41 eV). In this case, thermodynamic conditions favor the electron transfer from Cu_2O to TiO_2. This fact is confirmed in the case of Orange II degradation. However, the thermodynamic conditions are not sufficient for an efficient use of the junctions. Other conditions such as the kinetics of reactions occurring at each surface are also an important parameter. The holes generated in Cu_2O are thought to react faster in order to induce an efficient charge separation. If the holes cannot induce an oxidation process, photocorrosion of the sensitizer is thought highly likely to occur [5,6]. We believe that this situation occurs when benzamide and 4-hydroxybenzoic acid are used as pollutants.

Concerning the junction Bi_2O_3/TiO_2, it is clear that interparticle electron transfer is effective between both semiconductors, as we have demonstrated by the photoactivity observed under visible light. To our knowledge, this junction has never been studied before. However, the same observations concerning the adsorption of pollutant on a sensitizer such as Cu_2O/TiO_2 and its influence on the activity of the junction can be made.

The results obtained from the study of the junction $ZnMn_2O_4/TiO_2$ seem to be interesting though the interparticle electron transfer from $ZnMn_2O_4$ to TiO_2 was not observed under VIS light. The results of photocatalytic activity performed under UV–vis light lead to the belief that $ZnMn_2O_4$ induces the dissipation of the created charge on TiO_2 by trapping electrons and holes and as a consequence decreasing the amount of radicals produced. Fig. 6b depicts the flat band potentials [1,17] of the valence and conducting bands at pH 7 (versus the normal hydrogen electrode) for $ZnMn_2O_4$ and TiO_2 with their band gap energy. The conduction band of $ZnMn_2O_4$ is located at +0.062 eV. This value is greater than the conduction band energy of TiO_2. In this condition, the electrons generated on the conduction band of $ZnMn_2O_4$ cannot be transferred to the corresponding band of TiO_2. However, electrons created on the conduction band of TiO_2 can be injected in the conduction band of $ZnMn_2O_4$. This fact can be considered as a valid explanation of TiO_2 decreasing efficiency when both semiconductors are excited. From the position of the $ZnMn_2O_4$ valence band, we can assume that holes generated on the TiO_2 valence band can be transferred to $ZnMn_2O_4$. The directions that involve the migration of charges (electron and hole) induce the loss of TiO_2 created charges, and as a consequence a decrease in the production of radicals occurs. The phenomenon as described favors the increase of charges on $ZnMn_2O_4$, but not on TiO_2. This fact explains the deactivation of TiO_2 in presence of $ZnMn_2O_4$ when both semiconductors are excited. From this analysis, we concluded that this configuration of the junction is not adequate for photocatalytic degradation of organic pollutants in aqueous media, particularly because $ZnMn_2O_4$ is not able to produce radicals.

4. Conclusion

This work is a study started with CdS and Bi_2S_3 in junction with TiO_2 [5]. The aims of both works were: (i) to

study the feasibility of extending the light-absorption property of TiO_2 to the visible light by the formation of heterojunction with narrowband gap semiconductors; (ii) to demonstrate the interparticle electron transfer from the sensitizer to TiO_2 when it exists; (iii) to take advantage of interparticle electron transfer phenomena to induce an advanced oxidation process of organic pollutant in aqueous media; (iv) to study so far as is possible the limitations of the use of such process. The results obtained demonstrate that the extension of the light-absorption property of TiO_2 to the visible light can be easily obtained according to the UV–vis spectroscopy analysis. However, the most important issue is to demonstrate the existence of interparticle electron transfer between both semiconductors following the procedure described in the experimental section. This phenomenon is believed to occur only if the relevant thermodynamic conditions are respected. If we compare the activities of the studied junctions, it is clear that the ideal junctions must have the energy of the conduction band of the sensitizer well matched to the lower bound of the TiO_2 conduction band to minimize energy losses during the electron transfer reaction.

The photocatalytic activities of the junctions studied, in combination with different model pollutants, lead to the observation that the efficiency of each one strongly depends on the substrate, and is also a consequence of the kinetic reactions at the surface of each semiconductor. From a mechanistic point of view, we assume that for efficient interparticle electron injection to occur, each hole must be reacting at the surface at a sufficiently high rate to improve the charge separation process.

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