

$\text{Bi}_2\text{S}_3/\text{TiO}_2$ and CdS/TiO_2 heterojunctions as an available configuration for photocatalytic degradation of organic pollutant

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Abstract

$\text{Bi}_2\text{S}_3/\text{TiO}_2$ and CdS/TiO_2 heterojunctions were prepared by direct mixture of both constituents and by precipitation of the sensitizer with commercial TiO_2 at different concentrations. UV-Vis spectroscopy analysis showed that the junctions-based Bi_2S_3 and CdS are able to absorb a large part of visible light (respectively up to 800 and 600 nm). This fact was confirmed by photocatalytic experiment performed under visible light. A part of charge recombination that can take place when both semiconductors are excited was observed when photocatalytic experiment was performed under UV-Vis illumination. Orange II, 4-hydroxybenzoïque acid (4-HBZ) and benzamide (BZ) were used as pollutants. Photoactivity of the junctions was found to be strongly dependent on the substrate. The different phenomena taking place in each case are discussed.

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Keywords: Titanium dioxide; Bi_2S_3 ; CdS ; Heterojunction; Photocatalysis

1. Introduction

Photocatalytic reactions induced by illumination of semiconductors in suspension has proven to be available technology for wastewater treatment since they provide an interface with an aqueous medium and induce an advanced oxidation process [1,2]. Most semiconductor oxide used in this way, such as TiO_2 or SrTiO_3 , are considered as wide band gap materials. Their specific advantages are high chemical stability and suitable flat band potential V_{fb} required for inducing the desired redox reactions without biased potential. However, such oxides absorb only a small fraction of solar light and are of little practical use, unless means to extend their light response in the visible spectrum are found [3]. This behavior appears to result from the constancy of the energy edges of O^{2-} : $2p^6$ deep band which lies far below the $\text{O}_2/\text{H}_2\text{O}$ level to be practical (>1 eV) [4,5].

Nowadays TiO_2 is the most popular semiconductors used in heterogeneous photocatalysis. To improve their photocatalytic efficiency, different strategies have been adopted such as: changing the electrical properties of titania by varying the crystallite size [6,7] or doping TiO_2 with transition metals ions in order to induce batho-chromic shift of the band gap [8]. The doping process either changes the

equilibrium concentration of electrons or holes, or increases the concentration of charge carrier and improves their conductivity. However, these doping processes modify other physical properties such as the lifetime of electron-hole pairs, adsorption characteristics [4] and photoelectrochemical stabilities. Also, it is possible to extend light absorption spectral of smooth TiO_2 to the visible region by adsorption of organic dye mono-layers at their surface. However, semiconductor substrate resulted in poor harvesting efficiencies [9]. Adsorption of additional dye layers further reduced injection efficiency, as a consequence of internal filtering. Other problems included poor overlapping of the sensitizer absorption with the solar emission spectrum, weak coupling of the electronically excited dye molecule with acceptor states of the semiconductor substrate, and sensitizer stability. A particular advantage is obtained by the substitution of organic dye with narrow band gap semiconductors as sensitizers [10]. It is suggested that such semiconductors in junction offer the following advantages over dyes [11,12]: the driving force for electron injection may be optimized through confinement effects; the ideal sensitizer having a gap of 1.5 eV is well approximated by narrow band gap semiconductor material; and highly stable electrodes may be produced by appropriate surface modification.

Sepone et al. [13] are the first team to have discovered interparticle electron transfer (IPET) with subsequent enhancement of reductive processes on titania. This phe-

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nomenon can be also applied to photooxidative processes. The aim of this work is to extend the absorption spectra of TiO₂ to the visible region by using junctions with CdS or Bi₂S₃. The interparticle electron transfer occurring in each case was studied. The efficiency of electron injection is defined as the ability to degrade three types of organic substrate under visible irradiation. Photocatalytic experiment was also done under UV-Vis illumination to establish the behaviour of the junction in real solar irradiation conditions and to observe a part of electron-hole recombination that can take place under this condition.

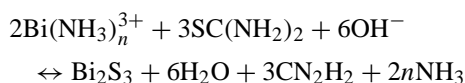
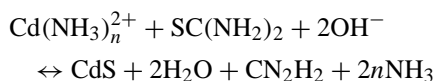
2. Experimental

2.1. Materials

The following commercial reagents were used without any further purification: Cd(NO₃)₂ (Aldrich), Bi(NO₃)₃ (Labosi), thiourea SC(NH₂)₂ (Aldrich), TiO₂-P25 (Degussa), Orange II (Sigma), benzamide (BZ) (Aldrich), 4-hydroxybenzoic acid (4-HBZ) (Aldrich).

2.2. Preparation of pure and mixed semiconductors

Pure CdS and Bi₂S₃ were prepared by direct reactions between their corresponding salt and thiourea in an ammonia bath (NH₄OH, 14.4 M) at 85 °C for 1 h. The reaction process can be described as follows:



We have also prepared semiconductors in contact by precipitating either CdS or Bi₂S₃ in a solution containing the appropriate amount of dispersed TiO₂-P25 as described below. The proportions of each sensitizer (CdS or Bi₂S₃) to the total weight of catalysts were 10, 30 and 50%. All products were subsequently washed with acetone, water and finally with absolute, ethanol and dried at 110 °C overnight. The samples containing Bi₂S₃ were heat treated at 240 °C for 1 h in an oven, and samples containing CdS were dried at 400 °C for 1 h. The rate of increasing temperature was 3 °C/min in each case.

2.3. X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns of pure CdS and Bi₂S₃ or CdS loaded with TiO₂ and Bi₂S₃ loaded with TiO₂ were obtained with a Philips diffractometer with monochromated high intensity Cu Kα in the scan range 2θ between 20 and 80°.

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. BaSO₄ was used as a reference to measure all samples. The spectra were recorded at room temperature in air in the range 200–1000 nm enabling to study the spectral properties of these materials.

2.5. Measurement of photocatalytic activity

The efficiency of electron transfer from each sensitizer (CdS and Bi₂S₃) to TiO₂ was taken as ability to degrade: Orange II, 4-hydroxybenzoic acid and benzamide degradations under visible irradiation, and the effect of electron-hole recombination was observed 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 glass of poly (methyl methacrylate) (PMMA) with a thickness of 12 mm was used as an optical filter to remove UV radiation. When Orange II was used as pollutant,

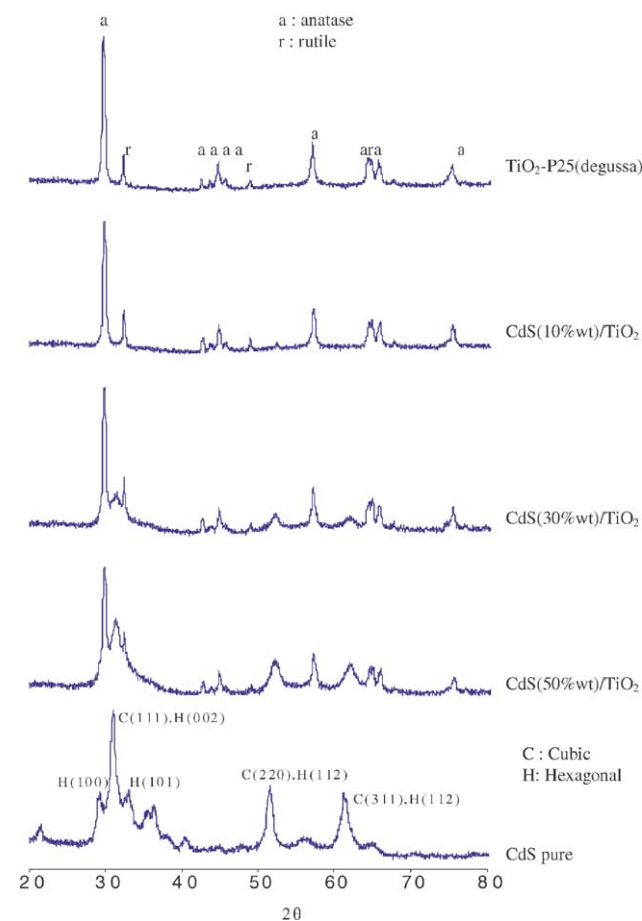


Fig. 1. XRD patterns of CdS/TiO₂ heterojunction prepared by precipitation of CdS on TiO₂ at different concentration.

typically 50 mg of TiO_2 and the appropriate amount of semiconductors (CdS or Bi_2S_3) were 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 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 for to determine their concentrations. One hundred and twenty-five milligrams of TiO_2 and appropriate amount of semiconductors (CdS or Bi_2S_3) 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 exposition to the light. During the irradiation procedure, 10 ml of solutions were sampled in regular time interval, filtered (Whatmann, 0.45 mm) and analyzed. C_i is the starting concentration and C_0 is the concentration at the

equilibrium. The percentage of degradation is reported as C/C_0 .

3. Result and discussion

3.1. Structure analysis

Fig. 1 shows the XRD pattern of CdS/TiO_2 heterojunction prepared by precipitation of CdS in the presence of TiO_2 at different concentrations and heat treated at 400°C for 1 h. We observe that the crystalline structure of TiO_2 -P25 is unchanged and consists of anatase and rutile phase mixture. At low concentration of CdS (10 wt.%), the presence of CdS was not detected significantly by XRD analysis. Only a very small peak located at 52.22° and assigned to CdS can be observed. At higher concentrations, different peaks attributed to CdS are observed, some of them inducing shoulders with anatase and rutile peaks of TiO_2 . XRD patterns of pure CdS showed the presence of mixture crystallized

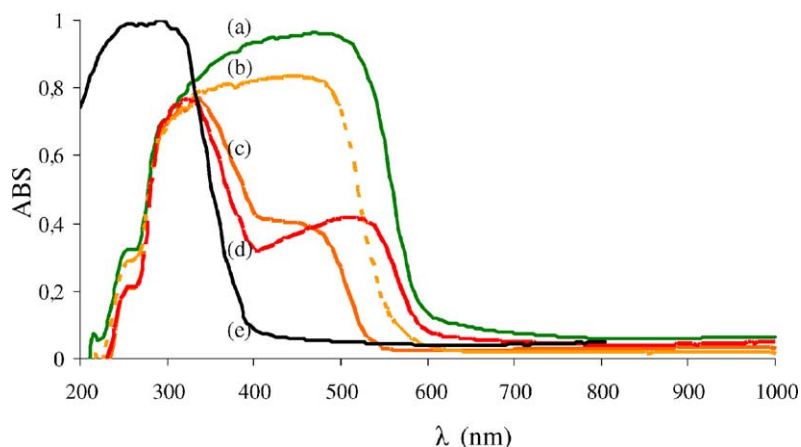


Fig. 2. Normalized UV-Vis spectra of: CdS (a), CdS (50 wt.%) / TiO_2 (b) and CdS (10 wt.%) / TiO_2 (c) prepared by precipitation, and CdS (50 wt.%) / TiO_2 (d) prepared by mixture, TiO_2 -P25 (e).

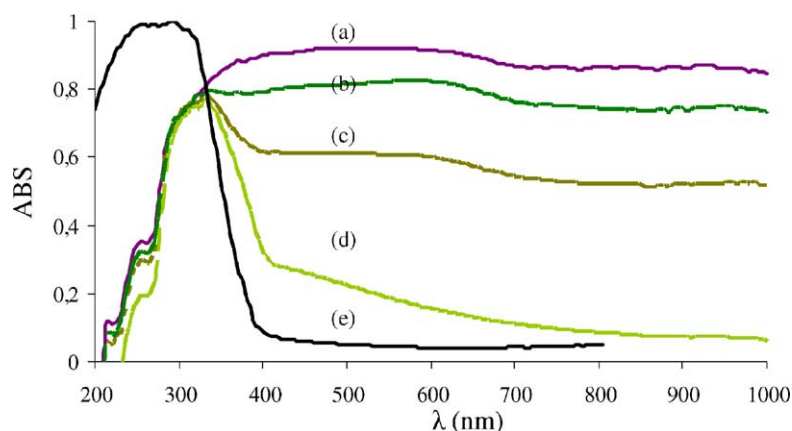


Fig. 3. Normalized UV-Vis spectra of: Bi_2S_3 (a), Bi_2S_3 (10%) / TiO_2 (b), Bi_2S_3 (30%) / TiO_2 (c), Bi_2S_3 (50%) / TiO_2 prepared by precipitation, TiO_2 -P25 (e).

phases. The peaks were attributed to CdS crystallized in cubic and hexagonal structure according to JCPDS files nos. 10-454 and 41-1049. It is well known that cubic CdS is a metastable phase [14]. The crystal transformation from cubic phase to hexagonal phase may be induced by heat treatment or by X-ray irradiation, since it was reported that CdS is very sensitive to X-ray irradiation [15].

XRD analysis of Bi_2S_3 - TiO_2 heterojunction revealed also that at low concentration of Bi_2S_3 , TiO_2 patterns was not affected by the presence of Bi_2S_3 . At more than 10 wt.% of Bi_2S_3 , some additional peaks were observed. The pattern of pure Bi_2S_3 revealed that a large part of crystalline structure was amorphous, though some peaks were attributed to the presence of bismuthinite crystallized in orthorhombic structure according to JCPDS files no. 17-320.

3.2. UV-Vis diffuse reflectance spectroscopy

Fig. 2 shows the evolution of absorbance versus the incident wavelength of pure CdS and CdS loaded TiO_2 prepared by direct mixture and precipitation. We observe that the junction containing high concentration of CdS (50 wt.%) and prepared by precipitation method has the same spectral profile as pure CdS. The effect of the presence of TiO_2 is not observed. This fact can be attributed to the total coating

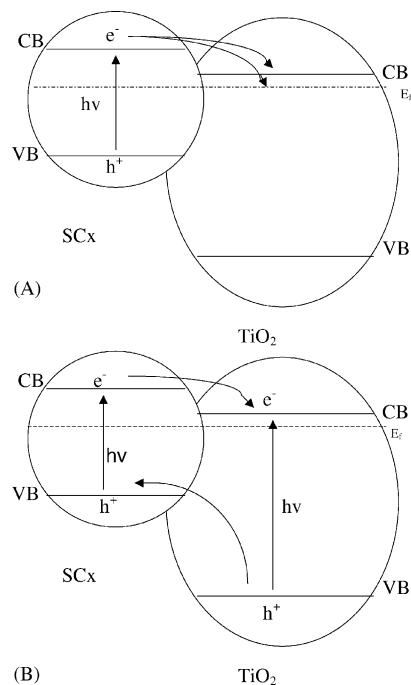


Fig. 4. (A) Energy diagram illustrating the coupling of SC in which vectorial electron transfer occurs from the light activated SC to the non-activated TiO_2 . (B) Diagram depicting the coupling of SC in which vectorial movement of electrons and holes is possible.

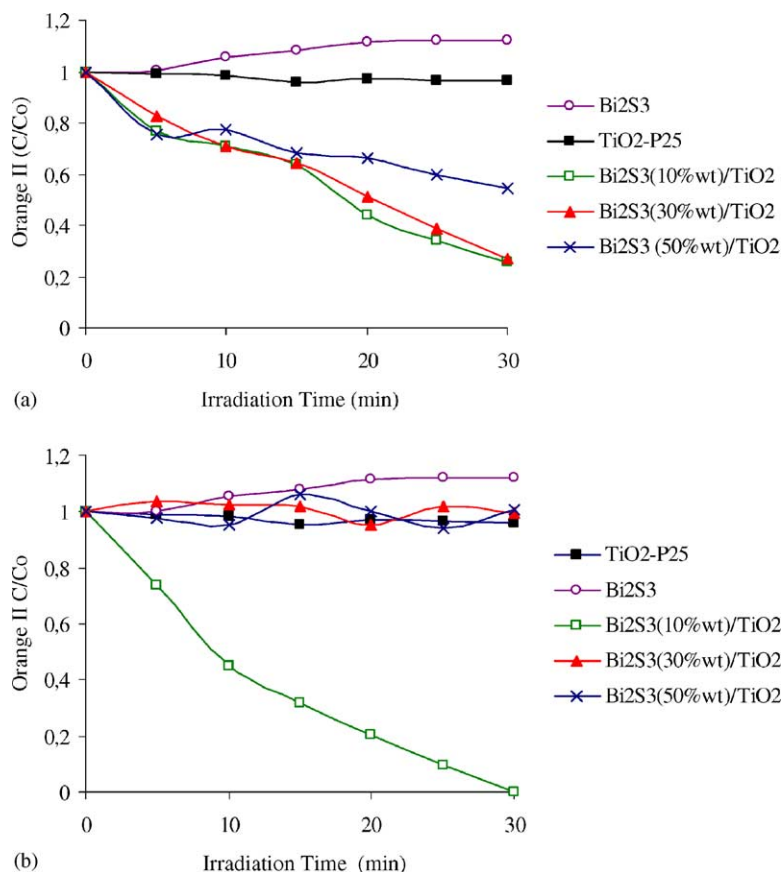


Fig. 5. Photocatalytic degradation of Orange II using Bi_2S_3 sensitized TiO_2 under visible irradiation: (a) direct mixture of semiconductors; (b) Bi_2S_3 precipitated on TiO_2 .

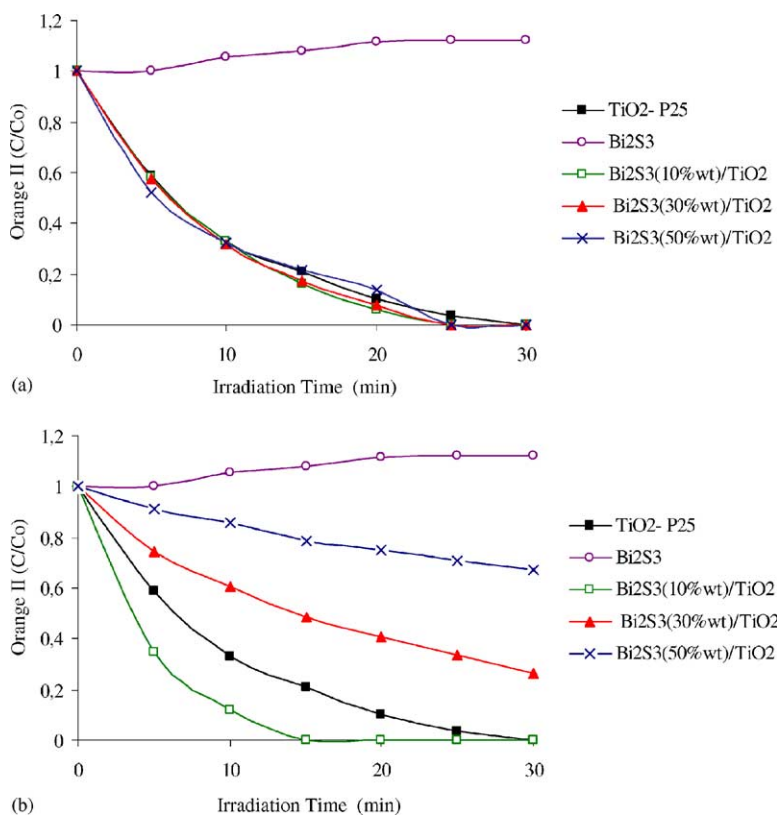


Fig. 6. Photocatalytic degradation of Orange II using Bi₂S₃ sensitized TiO₂ under UV-Vis irradiation: (a) direct mixture of semiconductor; (b) Bi₂S₃ precipitated on TiO₂.

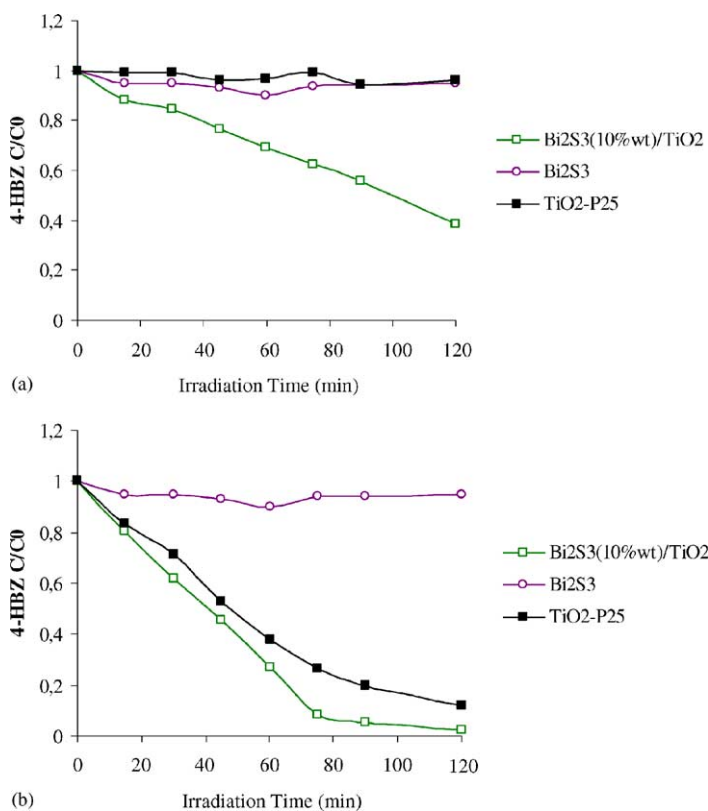


Fig. 7. Photocatalytic degradation of 4-hydroxybenzoic using Bi₂S₃ sensitized TiO₂: (a) under visible irradiation; (b) under UV-Vis irradiation.

of TiO_2 surface by CdS that acts as an optical filter. Under this condition, only CdS can be activated. On the contrary, when the junction was obtained by direct mixture of both semiconductors in the same weight ratio, two peaks are observed. The first, attributed to CdS absorption, is located between 600 and 400 nm, and the second, attributed to TiO_2 harvesting, starts at a wavelength shorter than 400 nm. We can conclude from the last result that when the junction is prepared by direct mixture of both semiconductors, an extension of TiO_2 light harvesting occurs. In our case it starts at 600 nm. As to the junction containing the lowest concentration (10 wt.%), the same spectral bearing as the junction described above is observed, although the amount of CdS is very low. However, this junction absorbs the light at wavelengths shorter than 550 nm. From these results, we can conclude that the junctions based on CdS are able to be excited by visible light.

As in the case of CdS/ TiO_2 junctions, we have studied $\text{Bi}_2\text{S}_3/\text{TiO}_2$ junctions prepared by precipitation of Bi_2S_3 on TiO_2 at different concentrations. As can be observed in Fig. 3, Bi_2S_3 absorb a large part of visible light. This fact induces an extension of the light absorption spectrum of the junction even at low Bi_2S_3 concentrations. In fact, when the junction contains (10 wt.%) of Bi_2S_3 the absorbance start at 800 nm. At greater concentrations, the junctions absorb in

all visible region. Nevertheless, it seems to be clear that at these concentrations Bi_2S_3 act as an optical filter.

3.3. Photocatalytic activity

Using two semiconductors in contact having different redox energy levels of their corresponding conduction and valence bands can actually be considered as one of the most promising methods to improve charge separations, to increase the lifetime of charge carriers, and to enhance the efficiency of the interfacial charge transfer to adsorbed substrate. For 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 electrons generated to their conduction band are injected into inactivated TiO_2 conduction band. If the valance band of the sensitizer is more cathodic than the valance band of TiO_2 , hole generated in the semiconductor remains there and cannot migrate to TiO_2 . These thermodynamic conditions favor the phenomenon of electron injections. Fig. 4A. is an illustration of interparticle electron transfer behavior.

When the system is under UV-Vis irradiation, both semiconductors are excited; electrons are injected from the

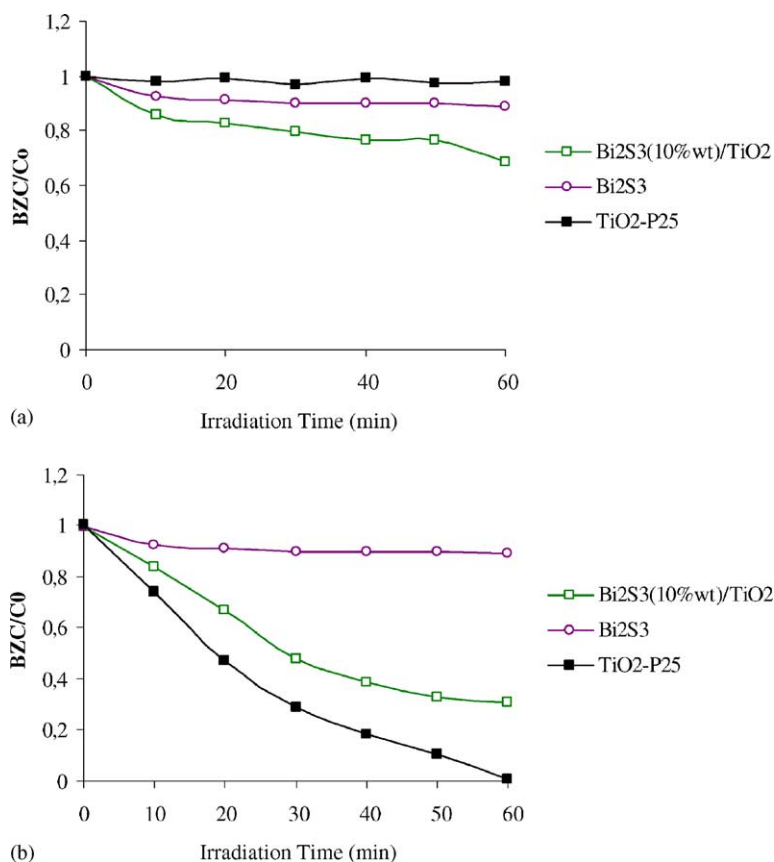


Fig. 8. Photocatalytic degradation of benzamide using Bi_2S_3 sensitized TiO_2 : (a) under visible irradiation; (b) under UV-Vis irradiation.

sensitizer to TiO_2 as in the case of visible illumination with an additional presence of electrons from activated TiO_2 . In this case, high concentration of electrons is obtained in conduction band of TiO_2 . Holes generated on 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. 4B). All the phenomena described are ideal, as in reality different mechanisms of electrons and holes trapping can occur.

3.3.1. $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterojunction

Bi_2S_3 is a direct band gap materials ($E_g \sim 1.3 \text{ eV}$) with a lamellar structure and is useful for photodiode arrays and photovoltaics [16,17]. It also belongs to a family of solid-state materials in use in thermoelectric cooling technology based on the Peltier effect [18]. Bi_2S_3 is a material with physico-chemical properties strongly dependent on the method used for their preparation [19]. In our study, we have prepared this material as reported in the experimental section without trying to obtain semiconductor with specific characteristics.

Orange II is not adsorbed at the surface of pure TiO_2 in our experimental conditions and no photoactivity is observed under visible irradiation. However, less than 15% Ci

of Orange II adsorptions occur at the surface of pure Bi_2S_3 in the dark. When catalytic experiment was made under illumination, a strong photodesorption was observed and photocatalytic degradation of pollutant was not observed.

Fig. 5 showed photocatalytic efficiency of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterojunction versus degradation of Orange II at different conditions. When $\text{Bi}_2\text{S}_3/\text{TiO}_2$ heterojunction is made from direct mixture of both semiconductors into the contaminated solution and the system is illuminated by visible light, photodegradation of Orange II occurs. We observe that the junction efficiencies decrease when the amount of Bi_2S_3 increases. Interparticle electron transfer occurs when both semiconductors are in contact. Increasing the amount of Bi_2S_3 in solution can entail two effects: an increase of the amount of generated electrons, and an increase of the probability of interparticle collisions. These two effects are benefic for the improvement of the efficiency of degradation. However, a reverse phenomenon is observed. This fact is believed to be a consequence of charge carrier dissipations by trapping when the amount of Bi_2S_3 reaches a critical concentration.

When the junction is obtained by precipitation of Bi_2S_3 at the surface of TiO_2 , no degradation of Orange II is observed under visible light, except for Bi_2S_3 (10 wt.%)/ TiO_2 . We

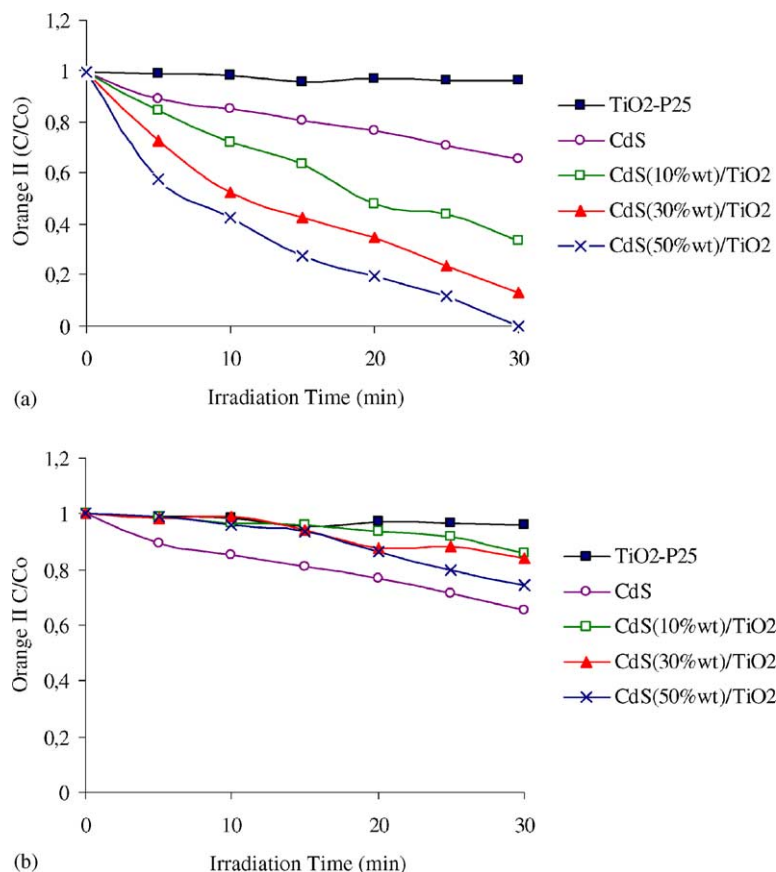


Fig. 9. Photocatalytic degradation of Orange II using CdS sensitized TiO_2 under visible irradiation: (a) direct mixture of semiconductor; (b) CdS precipitated on TiO_2 .

believe that increasing the amount of Bi_2S_3 induces a formation of films that cover TiO_2 particles. As a result, the electrons present in the conduction band of TiO_2 and made from Bi_2S_3 cannot react to create radicals, and as a consequence Orange II is not degraded. This result is in good agreement with the results obtained with UV-Vis spectroscopy. In the case of low amount of Bi_2S_3 (Bi_2S_3 (10 wt.%) / TiO_2), a high rate of Orange II degradations is observed by visible light. Bi_2S_3 is present at TiO_2 surface but a part of surface particles are uncovered. Electrons are injected with high efficiency due to a good surface contact between Bi_2S_3 and TiO_2 .

Fig. 6 shows degradation of Orange II under UV-Vis irradiation. The same photoactivity as pure TiO_2 is obtained by the junctions obtained from direct mixture of semiconductors and that regardless of the amount of Bi_2S_3 . In this case, both semiconductors are excited by the light. However, a large part of created charges are recombined. The efficiency of $\text{Bi}_2\text{S}_3/\text{TiO}_2$ junctions obtained by precipitation of Bi_2S_3 versus degradation of Orange II was found to be dependent on the amount of Bi_2S_3 . The rate of degradation decreases as well as the concentration of sensitizer increases. The degradation rate of Bi_2S_3 (10 wt.%) / TiO_2 is twice greater than pure TiO_2 -P25. Under such conditions,

electrons are injected with high efficiency from conduction band of Bi_2S_3 to conduction band of TiO_2 due to the constancy of contact between particles (Bi_2S_3 and TiO_2). Accumulation of electrons also results from natural excitation of TiO_2 , which induces an increasing of Orange II degradations by radicals. A part of electron and hole recombination seems to be very low for this junction.

This last junction (Bi_2S_3 (10 wt.%) / TiO_2) was used to investigate their efficiency with other types of pollutants. 4-Hydroxybenzoic acid is slightly adsorbed by Bi_2S_3 but is not a subject of degradation. It was observed that under visible light, 4-HBZ is efficiently removed by Bi_2S_3 (10 wt.%) / TiO_2 (Fig. 7). This fact indicates a high ability of electron injection. Under UV-Vis light, 4-HBZ degradation is achieved in less than 80 min by using Bi_2S_3 (10 wt.%) / TiO_2 , contrary to pure TiO_2 -P25 where more than 120 min are needed.

Benzamide is not adsorbed by both Bi_2S_3 and TiO_2 . Fig. 8 showed efficiency of Bi_2S_3 (10 wt.%) / TiO_2 under visible light. The selected junction showed low abilities to BZ degradations. Indeed, less than 30% of BZ is degraded after 60 min of irradiation. Nevertheless, the efficiency of the junction was increased by using UV-Vis light, but it remains poorer than pure TiO_2 -P25.

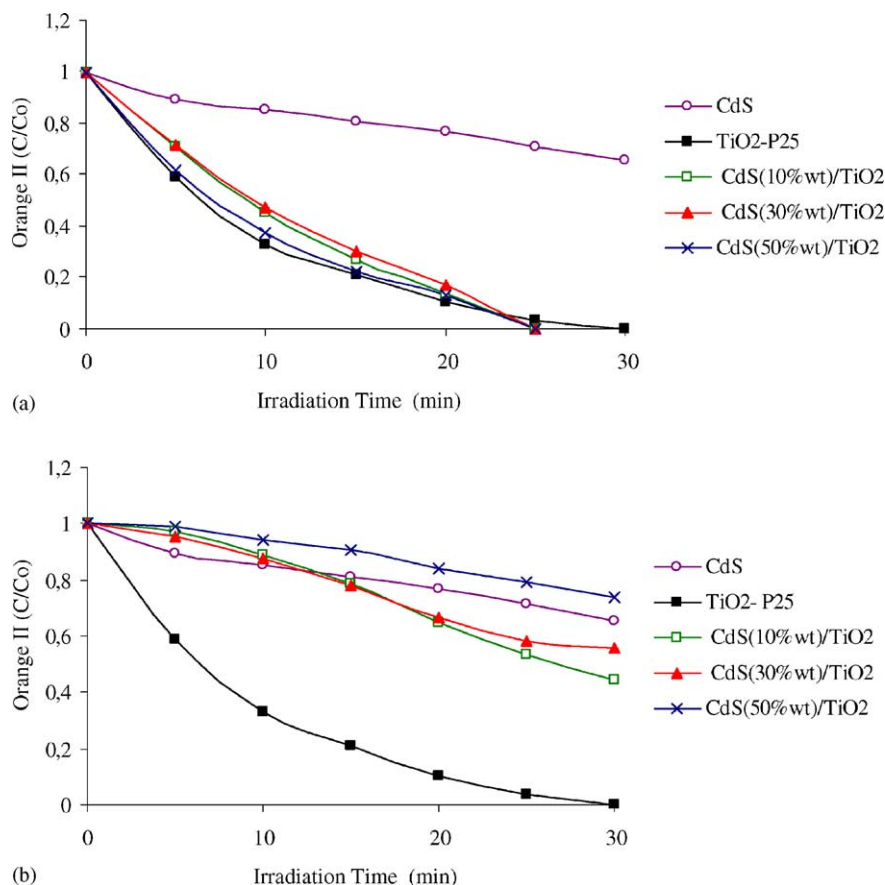


Fig. 10. Photocatalytic degradation of Orange II using CdS sensitized TiO_2 under UV-Vis irradiation: (a) direct mixture of semiconductor; (b) CdS precipitated on TiO_2 .

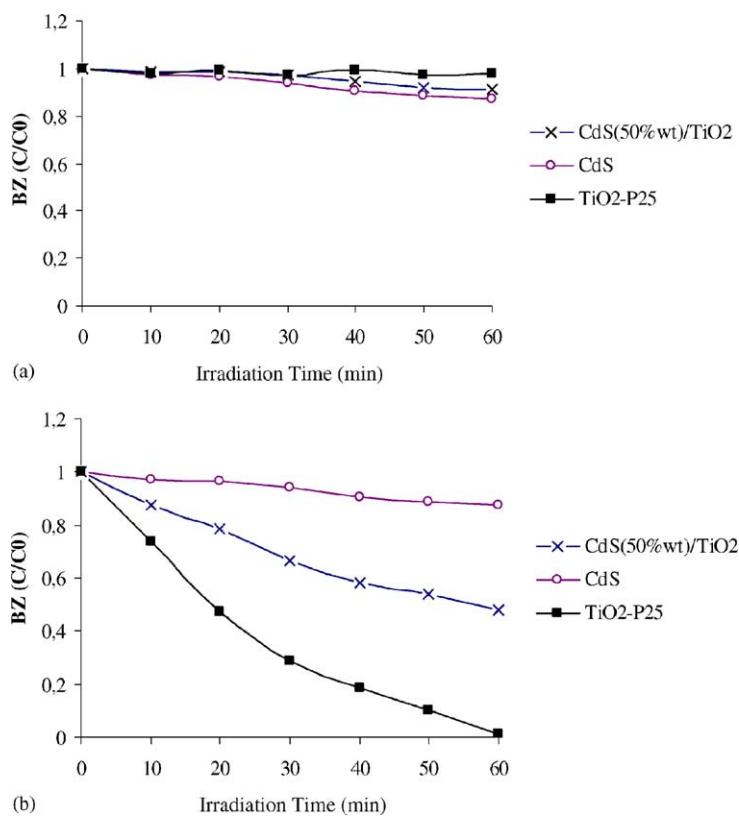


Fig. 11. Photocatalytic degradation of benzamide using CdS sensitized TiO₂: (a) under visible irradiation; (b) under UV-Vis irradiation.

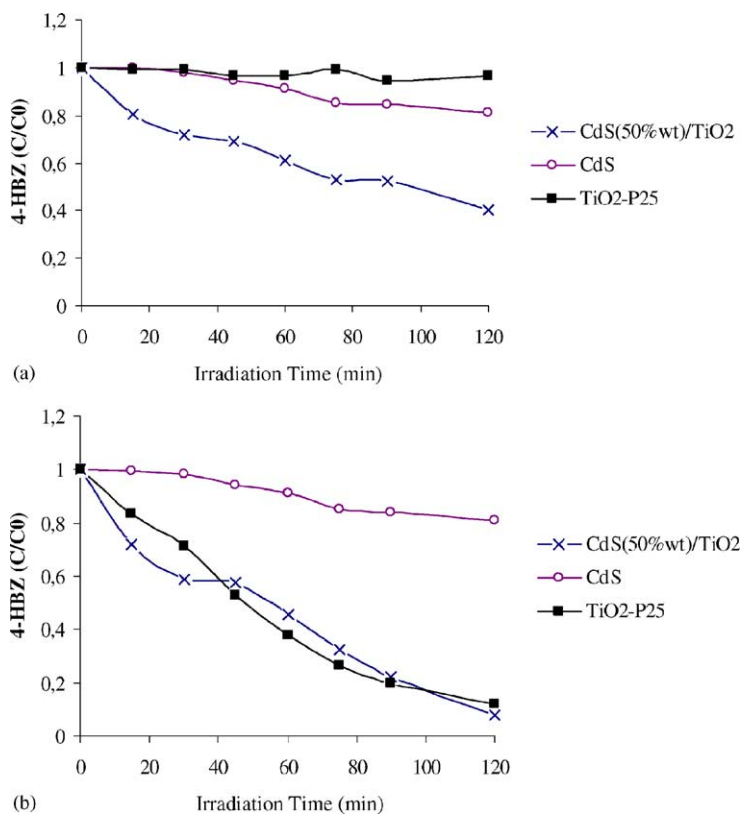


Fig. 12. Photocatalytic degradation of 4-hydroxybenzoic using CdS sensitized TiO₂: (a) under visible irradiation; (b) under UV-Vis irradiation.

3.3.2. CdS/TiO₂ heterojunction

CdS is an important semiconductor owing to its unique electronic and optical properties, and its potential applications in solar energy conversion, non-linear optical, photoelectrochemical cells, and heterogeneous photocatalysis [20,21].

Orange II is slightly adsorbed by pure CdS (11% Ci). Fig. 9 shows degradation efficiencies of pure CdS and CdS/TiO₂ heterojunction versus Orange II under visible irradiation. When the junction is obtained by direct mixture of CdS with TiO₂, the efficiency of degradation was found to be strongly dependent on CdS amount. Indeed, the rates of Orange II degradations increase as the amount of CdS increases. CdS absorb visible light and generate electrons and holes. Electrons are injected in conduction band of TiO₂ and radicals are produced. The best photoactivity is obtained using CdS (50 wt.)/TiO₂. When the junctions are obtained by precipitation of CdS in presence of TiO₂, very low efficiency versus Orange II degradations was observed. In this case, pure CdS was found to be more efficient than

the junctions. TiO₂ surface is certainly recovered by a film of CdS and surface contact between TiO₂ and solution is not sufficient for the creation of active radicals.

Illumination of CdS/TiO₂ junctions obtained by direct mixture of both semiconductors by UV-Vis light showed a slight improvement of TiO₂ efficiency (Fig. 10). The amount of CdS has not significant influence under this condition. Indeed, the rate of degradations does not change when the CdS concentration increases. The same phenomenon was observed in the case of Bi₂S₃/TiO₂ junctions. For the junction prepared by precipitation, we observe that the efficiency of junction increases under UV-Vis illumination. However, in comparison with the efficiency of pure TiO₂-P25, it remains very low. CdS (50 wt.)/TiO₂ was selected to study efficiency of BZ and 4-HBZ degradations under visible and UV-Vis light. BZ is not adsorbed by CdS in the dark. The rate of BZ degradation using pure CdS or CdS (50 wt.)/TiO₂ is very low under visible light (Fig. 11). Under UV-Vis light, the performance of the junction increased. Nevertheless, their efficiency is lower than

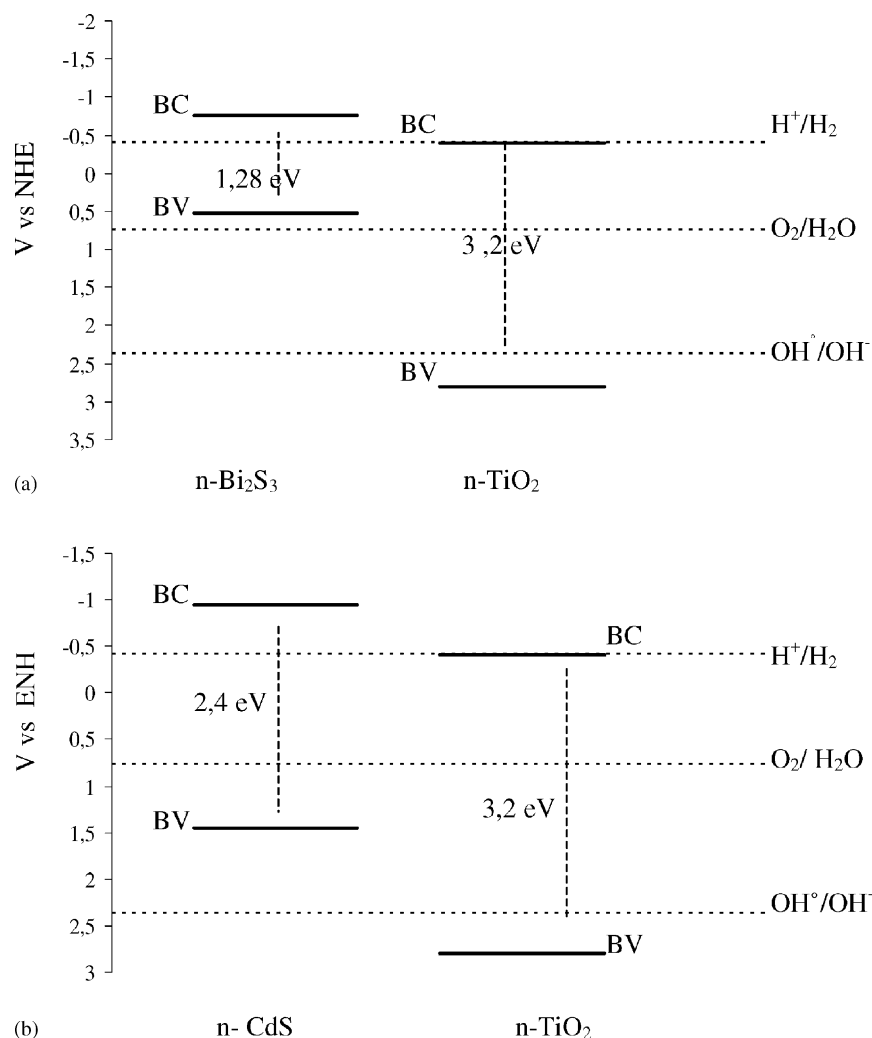


Fig. 13. Energetic diagrams of Bi₂S₃/TiO₂ (a) and CdS/TiO₂ (b) heterojunction.

that observed for pure TiO₂-P25. Degradation of 4-HBZ under visible light was observed using CdS (50 wt.%) / TiO₂. This fact proves that electrons are injected to TiO₂. The same junction under UV-Vis irradiation showed improvement of their activity. However, the same rate of 4-HBZ degradations was obtained as pure TiO₂-P25 (Fig. 12). From these results, it can be concluded that CdS/TiO₂ heterojunction is very attractive for photocatalytic removal of organic compound under visible light. However, under UV-Vis light their efficiency remains close to TiO₂-P25 efficiencies.

Fig. 13 depicts the flat band potentials [22,23] of the valence and conducting bands at pH 7 (versus the normal hydrogen electrode (NHE)) for Bi₂S₃, CdS and TiO₂ with their band gap energy. Thermodynamic conditions for efficient electron injection from Bi₂S₃ to TiO₂ and from CdS to TiO₂ are respected. Indeed, the conduction band of Bi₂S₃ located at -0.76 eV is more cathodic than the conduction band of TiO₂ (-0.5 eV). Also, the conduction band of CdS which is located at -0.95 eV is more cathodic than the conduction band of TiO₂. In general, the higher the difference between conduction bands of two semiconductors, the higher the driving forces of electron injection are. However, we observe that Bi₂S₃/TiO₂ is more efficient than CdS/TiO₂. This fact can be attributed first to the efficient light spectral absorption of Bi₂S₃ which absorbs the totality of visible light, and second to the proximity of their conduction band to conduction band of TiO₂. The later property favors the kinetic of electron transfer [3]. It should be noted that suitable redox levels are only one factor affecting interparticle electron transfer and thus photocatalysis. It should be kept in mind that the coupling aspect between acceptor and donor states of both semiconductors, the geometry of the particles, the surface texture and the mode of contact between particles also play a significant role.

Photocatalytic experiment revealed that when the pollutants are not adsorbed by the sensitizer, the junctions are not efficient. This fact is observed in the case of benzamide degradation. A possible explanation is that under illumination, holes remain in activated sensitizer and if holes do not find an opportunity to induce oxidation process, a large part of generated charges are lost by recombination or by inducing photocorrosion of the sensitizer.¹ Both phenomena cause a low photoactivity of the junctions. Serpone et al. [24] also observed the photoactivity decrease of some junctions in the case of degradation of non adsorbed molecules in the sensitizer. From all these results, we concluded that for efficient interparticle electron injection, holes must react at the surface at sufficiently high rate to improve charge separations and limit the probability of photocorrosion.

¹ Chemical analysis of metals in solution was not performed in our study.

4. Conclusion

CdS/TiO₂ and Bi₂S₃/TiO₂ heterojunctions were prepared by direct mixture and by precipitation of the sensitizer (CdS or Bi₂S₃) with TiO₂. XRD junction analyses revealed that at low concentration (10 wt.%) CdS and Bi₂S₃ are not detected. However, when the product is more concentrated, peaks corresponding to each constituent are observed and induce in some case the apparition of shoulders. Pure CdS was found to be a mixture of cubic and hexagonal phases. Bi₂S₃ was found to be partially amorphous, although some peaks were attributed to bismuthinite crystallized in orthorhombic structure. UV-Vis spectroscopy analysis showed that the junctions CdS/TiO₂ and Bi₂S₃/TiO₂ are able to absorb the light up to 600 and 800 nm, respectively. Interparticle electron transfers occurring on CdS/TiO₂ and Bi₂S₃/TiO₂ junctions were demonstrated by performing photocatalytic test under visible light. Bi₂S₃ (10 wt.%) / TiO₂ prepared by precipitation of Bi₂S₃ with TiO₂ demonstrate high ability to Orange II and 4-hydroxybenzoic degradation in both visible light and UV-Vis light. Indeed, the later junction exhibits a rate of Orange II degradation twice greater than pure TiO₂-P25 and more than 40 min are saved when 4-HBZ is used as pollutant. In those cases, electrons are injected with high efficiency due to a good surface contact between Bi₂S₃ and TiO₂, and spectral light absorption property of Bi₂S₃. CdS/TiO₂ heterojunction also showed an efficient use under visible light, in particular the junctions prepared by direct mixture of both semiconductors. However, under UV-Vis irradiation, their performances remain close to TiO₂-P25 efficiencies and that whatever the amount of CdS. From the results, it is clear that the preparation of heterojunctions by precipitation of the sensitizer with TiO₂ is more attractive than direct mixture of both components. However, it is very important to maintain sufficiently available surface of TiO₂ to obtain a good interaction with the species present in the solution. From a mechanistic point of view, we assume that for efficient interparticle electron injection, hole must be reacting at the surface at a sufficiently high rate to improve charge separations.

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