

The Photocatalytic Degradation of Orange G By using CdS / TiO₂ as an Available Configuration.

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Abstract

CdS/TiO₂ heterojunctions were prepared by direct mixture of both constituents and by precipitation of the sensitizer with commercial TiO₂ at different concentrations.

UV-Vis. Spectroscopy analysis showed that the junction – based 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 semiconductor is excited was observed when photo catalytic experiment was performed under uv-vis illumination . Orange G was used as a pollutant compound . photo activity of the junctions was found to be strongly dependent on the substrate . By using medium pressure mercury lamp (MPML) in 125 watt . Photocatalyst experiment was also done under uv-vis illumination to establish the behaviour of the junction in real solar irradiation conditions and to observe apart of electron – hole recombination that can take place under this conditions .

الخلاصة

تمت في هذه الدراسة تحضير التركيب الغير متجانس CdS / TiO₂ عن طريق التفاعل المباشر للمركب CdS مع مركب TiO₂ التجاري بتركيز مختلفة . تم استخدام اشعة Uv.-vis للمركب وتبين ان المركب قادراً على امتصاص الجزء الاكبر من الاشعة المرئية خصوصاً ما بين ٦٠٠-٨٠٠ نانوميتر وقد اكدت النتائج العملية صحة هذه الحقيقة باستخدام الاشعاع المرئي وقد تم استخدام مركب الصبغة Orange G كمركب ملوث للماء لهذا الغرض وقد تبين ان الفعالية الضوئية لهذا التركيب تعتمد كثيراً على المادة الملوثة باستخدام مصباح زئبقي متوسط الضغط بقدرة ١٢٥ واط . وكذلك اجرت التجارب تحت ظروف التشعيع بمنطقة UV-visible ملاحظة ظاهرة الاتحاد بين الالكترن- الثقوب التي تحصل تحت هذه الظروف .

1- Introduction

Photocatalytic reactions induced by illumination of semi conductors in suspension has proven to be a available technology for waste water treatment since they provide an interface with an aqueous medium and induce an advanced oxidation process (Mills, *et al.*, 1997; Bessekhoud *et al.*, 2003). Most semiconductor oxide used in this way, such as TiO₂ or SrTiO₃, 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 with out 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 (Nozik & Memming, 1996). This behavior appears to result from the constancy of the energy edges of O²⁻: 2p⁶ deep band which lies far below . The O₂ / H₂O level to be practical (>lev) (Scaif, 1980; Goodenough, 1982). Nowadays TiO₂ 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 (Ampo *et al.*, 1987; Xu *et al.*, 1991) or doping TiO₂ with transition metals ions in order to induce batho-chromic shift of the band gap (Wilke & Beruere, 1991). The doping process either changes the equilibrium concentration of electrons or holes, or increases the concentration of electrons or hole, or increases the concentration of charge carrier and improves their conductivity.

However, these doping processes modify other physied properties such as the lifetime of electron-hole pairs, adsorption characteristics (Goodenough, 1982) and photoelectronchemical stabilities, Also; it is possible to extend light absorption

spectral of smooth TiO₂ to the visible region by adsorption of organic dye mono-Layers at their surface. However semiconductor substrate resulted in poor harvesting efficiencies (Tributsch, 1972). 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 (Gerisher & Lubke, 1986). It is suggested that such semiconductors in junction offer the following advantages over dyes (Vogel *et al.*, 1990; Vogel *et al.*, 1994) the driving force for electron injection may be optimized through confinement effect; 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.

Serpone *et al.* (1984) are the first team to have discovered interparticle electron transfer (IPET) with subsequent enhancement of reductive processes on titania. This phenomenon can be also applied to photooxidative processes.

2. Experimental

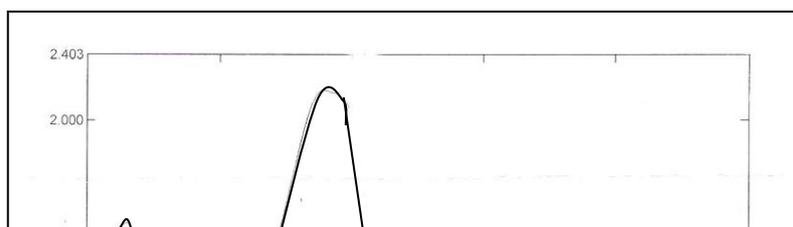
2.1. Materials

The following commercial reagents were used without any further purification: Cd (NO₃)₂ (Aldrich) (BDH), thiourea SC (NH₂)₂ (Aldrich), TiO₂-p25 (Degussa), orange G (Benzolaza-1-[2-naphthol-6,8-disulfonate] Dinatrium salt) (sigma), Aceton (BDH), Ammonia solution (BDH).

2.2. Preparation of and mixed semiconductors : pure CdS was prepared by direct reactions between its corresponding salt and thiourea in an ammonia bath (NH₄OH. 14M) at 85°C for 1hr. The reaction process can be described as follows equ. (1)

$$\text{Cd}(\text{NH}_3)_n^{2+} \text{SC}(\text{NH}_2)_2 + 2\text{OH}^- \rightleftharpoons \text{CdS} + 2\text{H}_2\text{O} + \text{CN}_2\text{H}_2 + 2n\text{NH}_3 \dots (1)$$

The semiconductor was prepared in contact by precipitating either CdS in a solution containing the appropriate amount of dispersed TiO₂ – P25 as described below. The proportions of sensitizer (CdS) 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 CdS were dried at 400°C for 1hr.



Abs.

Wavelength (nm)

Fig.1: shows the uv-visible absorption of orange G in aqueous solution.

3. Result and Discussion :-

Fig. 1 shows the uv-visible absorption of orange G in aqueous solution.

Fig.2 shows the evolution of Absorption spectra of pure and loaded semiconductors were recorded by shemadza uv-vis spectrophotometer BaSO₄ was used as a reference to measure all samples.

The spectra were recorded at room temperature in air in the range 190-nm enaling to study the spectral properties of these materials.

From Fig.2 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 TiO₂ is not observed. This fact can be attributed to the total coating TiO₂ 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 the semiconductors , two peaks are observed.

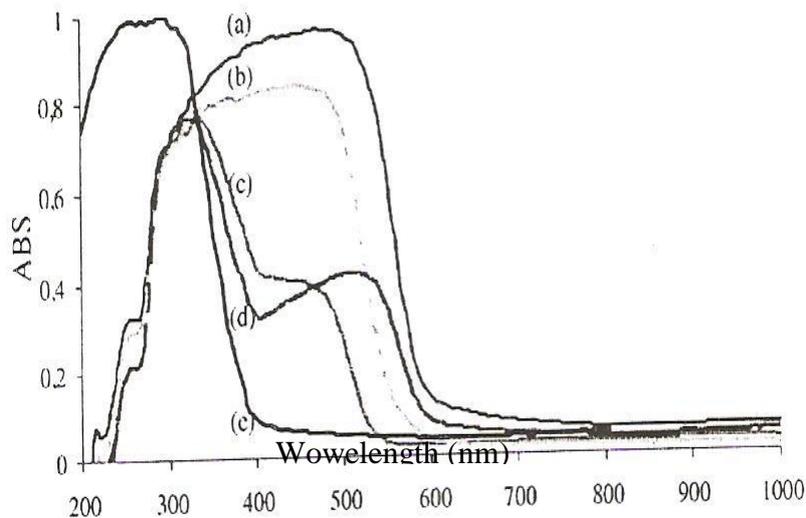


Fig.2: Normalized UV-Vis spectra of : CdS (a) , CdS (50 wt. %) / TiO₂ (b) and CdS (10 wt. %) / TiO₂ (c) prepared by precipitation and CdS (50 wt. %) / TiO₂ (d)

(d) prepared by mixture TiO₂ – P25 (e).

The first , attributed to CdS absorption is located between 600 and 4000 nm, and the second, attributed to TiO₂ harvesting, starts at a wavelength shorter than 400nm. From the last result concluding that when the junction is prepared by direct mixture of the semiconductor. An extension of TiO₂ light harvesting occurs. In this case it starts at 600nm. As to the junction containing the lowest contraction (10_{wt} %) , the same spectral bearing as the junction described above is observed Al though the amount of CdS is very low. However , this junction absorbs the light at wavelengths short than 550nm. From these results . the junctions based on CdS are able to be excited by visible light.

3.2 Cds TiO₂ hetero junction

CdS is an important semiconductor owing to its unique electronic and optical properties, and its potential applications in solar energy conversing, non-linear optical, photo electrochemical cells, and heterogeneous photo catalysis orange G is slightly adsorbed by pure CdS (Fig.3) shows degradation efficiencies of pure CdS and CdS/ TiO₂ heterojunction versus orange G under visible irradiate 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 rats of orange G 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 used CdS (50 wt%) TiO₂. When the junctions are obtained by precipitation of CdS in presence of TiO₂ very low efficiency versus orange G degradations was observed. In this case, pure CdS was found to be more efficient than the junctions. TiO₂ surface is certainty recovered by a film of CdS .

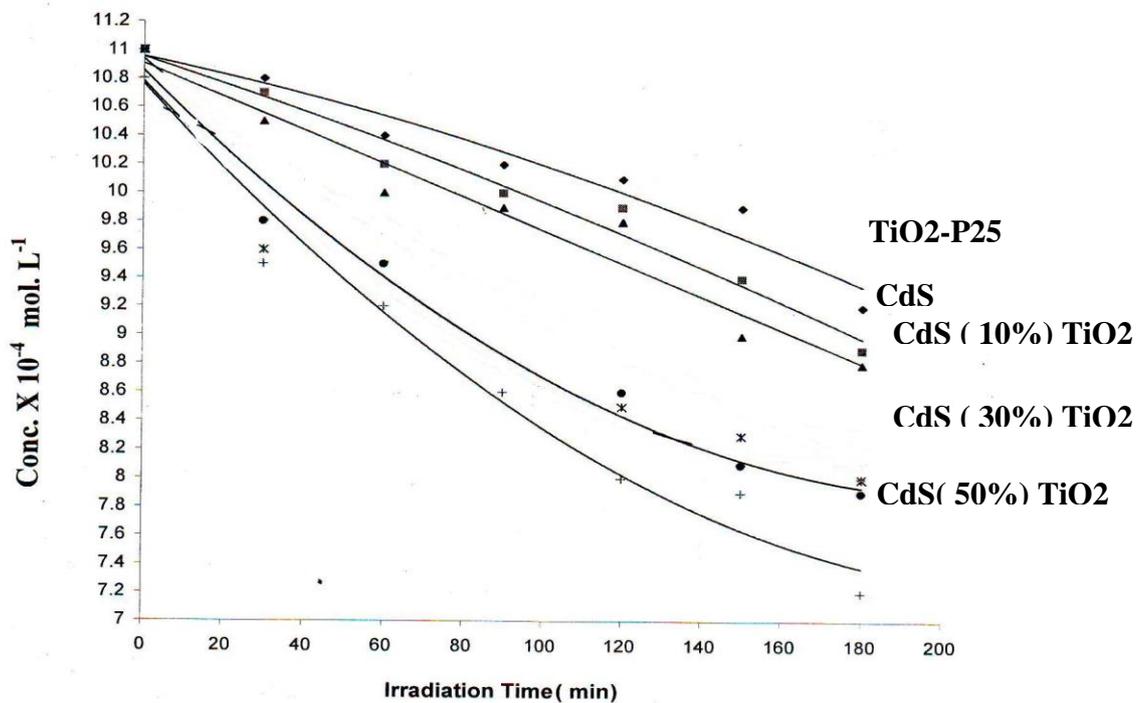


Fig 3 versus orange G under visible irradiate n

Fig. (4) show the illumination of CdS/ TiO₂ junction obtained by direct mixture of the semiconductor by uv-vis light showed as light improvement of TiO₂ efficiency. The amount of CdS has not significant influence under this condition, the rate of degradation does not change when the CdS concentration increases. The efficiency of junction increases under uv-vis illumination, in comparison with the efficiency of pure TiO₂ –p25, it remains very low CdS. (50 wt.%) / TiO₂ was selected to study efficiency of orange G degrading under visible and uv-vis light

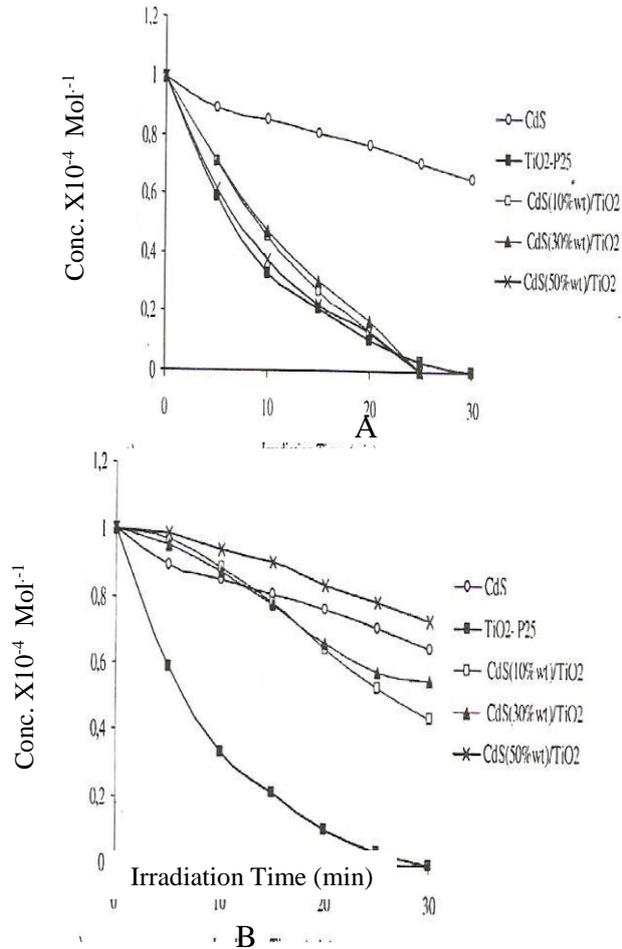


Fig.4: Photocatalytic degradation of orange G using CdS sensitized TiO₂ under uv-visible irradiation : (a) a direct mixture of semiconductor (b) CdS precipitated on TiO₂

4- Conclusion

CdS TiO₂ heterjunction was prepared by direct mixture and by precipitation of the sensitizer CdS with TiO₂.

Uv-vis spectroscopy analysis showed that the junction CdS TiO₂ is able to absorb the light up to 600 and 800 nm the CdS / TiO₂ junction exhibit a rate of orange G degradation twice greater than pure TiO₂ –p25. From the results, It is clear that the preparation of heterojunction 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 is used as pollutant.

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