SONOCHEMICAL SYNTHESIS OF SEMICONDUCTORS FOR PHOTOCATALYTIC APPLICATIONS

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ABSTRACT

Over the last few decades, photocatalysis with transition metal oxide nanoparticles has proven to be useful for the degradation of organic pollutants. It essentially converts organic pollutants into inorganic compounds such as CO_2, H_2O and inorganic acids. Semiconductor nanoparticles have attracted great attention due to their unique size-dependent optical properties. In addition, the disadvantages of individual components can be compensated by semiconductor composites, since they induce a synergistic effect, such as efficient charge separation and improvement of photostability. In the present work sonochemically synthesized nanoscale semiconductors TiO_2, CdS, CdS-TiO_2, ZnO-CdS were studied as solid phase catalysts during the degradation of Methylene Blue, via UV illumination. CdS has been observed to be a remarkable photocatalyst, while Zn and Ti, as transition metals, can have a beneficial effect on it. In conclusion several semiconductors were synthesized in the presence of ultrasounds in shorter reaction times compared to conventional techniques and acted as high performance photocatalysts.

INTRODUCTION

Titanium dioxide (TiO_2) is considered as one of the best semiconductor photocatalyst for pollutants degradation. UV exposition promotes redox reactions and charges separation that lead to oxidative processes. TiO_2 is often used in powder form as nano-sized particles with high surface area in order to enhance its photoactivity. Most often, literature reports the use of the nanometric TiO_2 materials for many applications, ranging from disinfection and air purification to decomposition of organic matter or heavy loads metals in waste waters. However, some recent papers have underlined the possible side effects on human health due to exposure to nanoparticles, as the ultra-small particles can penetrate inside human body from skin and nose especially when they are used in products like paints or simply cold-coated on materials surfaces for air purification [1-3,5].

Recent progress has shown that the coupling of TiO_2 with a narrow band gap semiconductor material, typically CdS, can extend the absorption to visible range and enhance the visible photocatalytic activity[1-3].

However, the wide band gap of TiO_2 limits the spectrum of solar light that can be utilized. CdS photocatalyst has attracted increasing attention because of its suitable Eg=2.3eV,and solar absorption spectrum extending from 400nm to 550nm (visible spectrum). The photocatalytic efficiency of CdS is highly dependent on various physicochemical properties such as crystallinity (e.g. cubic vs hexagonal) related to the annealing temperatures used and particle size affecting band gap energy (quantum size effect) and electron donors. Significant progress has been achieved in the production of CdS –based hybrid photocatalysts including binary CdS-TiO_2, CdS-ZnO [4,6].

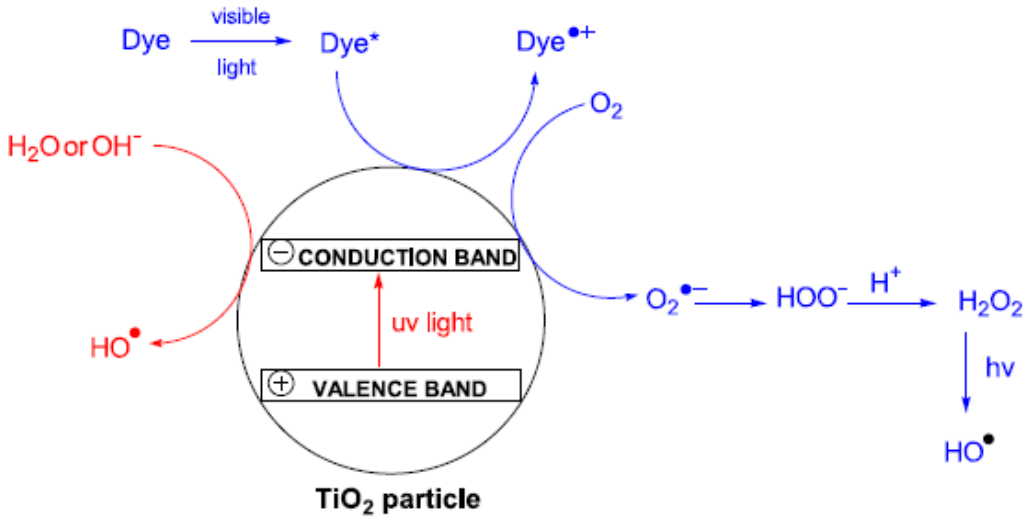

Figure 1. *Processes of TiO_2 in Photocatalysis.*

Noble metals (Pt,Ag,Au) are used as co-catalysts. The direct particle-to-particle contact of CdS and TiO_2 is required to achieve a potential gradient. Therefore, the Pt particles acting as a co-catalyst should be located on the TiO_2 particle surface for vectorial electron transfer (CdS-TiO_2-Pt).The spatial separation of Pt from CdS/TiO_2 is useful for the efficient electron-hole separation. The location of Au particles in the CdS-TiO_2-Au system builds up a transfer path for photogenerated electrons from the CdS to Au particles via a TiO_2 bridge[7,8].
Furthermore, noble metals co-catalysts (such as Au and Ag) act as sensitizers because of their strong surface plasmon resonance absorption, which is used to enhance the photocatalytic activity[4,7-10].

Zinc oxide (ZnO) is also an important semiconductor for photocatalytic degradation of environmental pollutants due to its photodegradation mechanism, which has been proven to be similar to that of TiO_2. Since the photocatalytic process is based on generation of electron/hole pairs by means of band – gap radiation, the coupling of different semiconductor oxides seems useful in order to achieve a more efficient electron/hole air separation under irradiation and consequently a higher photocatalytic activity. To enhance the photodegradation efficiency of TiO_2 catalyst, a coupled semiconductor photocatalyst of TiO_2/ZnO has been investigated by a number of researchers[11].

EXPERIMENTAL SECTION

All chemicals ($(Cd(NO_3)_2 \cdot 4H_2O$ (≥99.9%), ethylene-diamine (99%), CS_2(95%), Titanium(IV) isoproxide (TTIP) (≥97%), Zinc oxide (ZnO) (≥99%) ethanol (≥98%),Methylene Blue(MB)), were used as received without further purification.

Synthesis of CdS

Two precursor solutions are needed for the synthesis of CdS. The first precursor solution was prepared by dissolving 0.21 g $Cd(NO_3)_2 \cdot 4H_2O$ in 10 ml distilled water. The second precursor solution is a mixture of ethylene-diamine (0.6 mL), distilled water (40 mL) at 15°C. In this second solution 0.2ml CS_2 was added under ultrasound irradiation for 10 min (the sonicator used was a Vibra Cell VCX 750 W (20 KHz) at a power output of 65 %). This white suspension is mixed with the first precursor solution and it is irradiated for 30 min. At this moment the temperature has reached 70 °C due to irradiation. The color of the suspension changes within the first five minutes

from white to yellow. After letting the vessel cool down to room temperature, the solid was recovered by centrifugation and washed twice with distilled water, and then with ethanol.

Synthesis of CdS-TiO_2

The above procedure is followed until the synthesis of CdS and then 0.4ml TTIP is added under ultrasonic irradiation for 90 min.

The received nanoparticles (CdS and CdS-TiO_2) were dried overnight at room temperature.

Preparation of ZnO-CdS

For the preparation of 5% w/w ZnO/CdS, 1.44g of CdS and 0.07g ZnO were mixed with 20 mL distilled water and the solution was stirred for 30 min. Finally, ZnO-CdS is received and nanoparticles were dried for 2 hours at 100°C.

Photocatalysis

2mg catalyst was added in 50ml Methylene Blue solution $2x10^{-5}$ M. The 100 mL glass vessel was placed into a custom made photocatalytic chamber with dimensions of 60cm×70cm×30cm (H, W, D), containing six UV lamps (UV-A) (Philips PL-S 11W/10/2P) emitting in the 315-400nm wavelength range .

RESULTS AND DISCUSSION

Photocatalytic tests have shown good results during the degradation of MB. The characteristic absorption peak of MB is at 663-665 nm, but this peak dropped with UV illumination time. Nano-sized decorated powder shows the best result achieving degradation in 120 minutes.

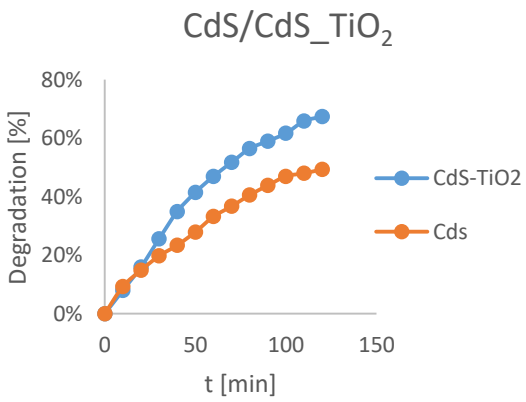

Figure 2. *Photocatalysis of Methylene Blue performed with CdS and CdS-TiO_2 .*

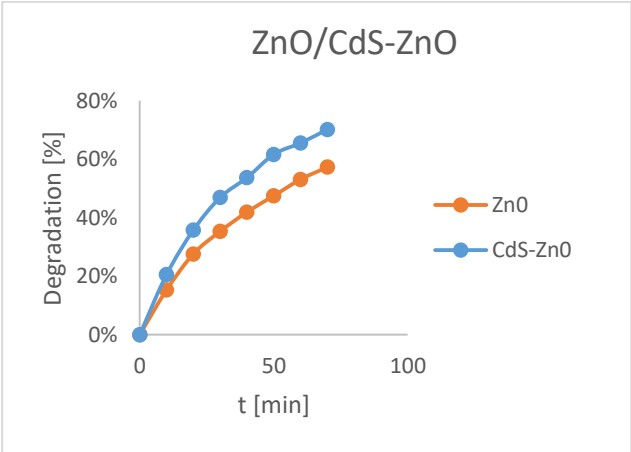

Figure 3. *Photocatalysis of Methylene Blue performed with ZnO and ZnO-CdS.*

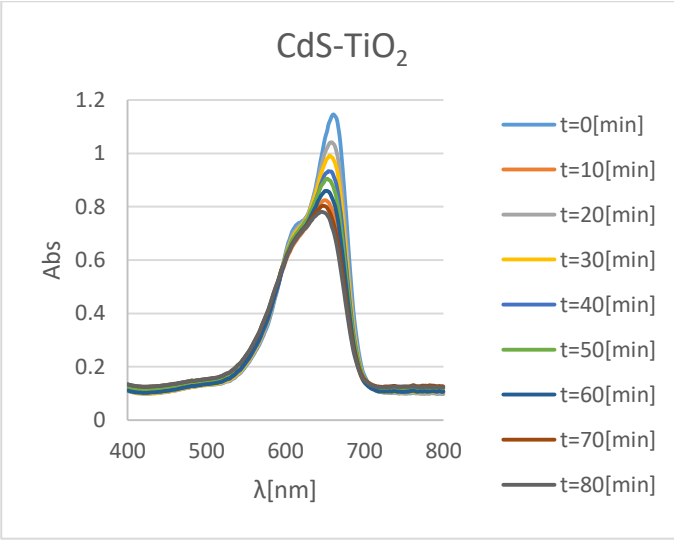

Figure 4. *Absorption of Methylene Blue solution with CdS-TiO_2 .*

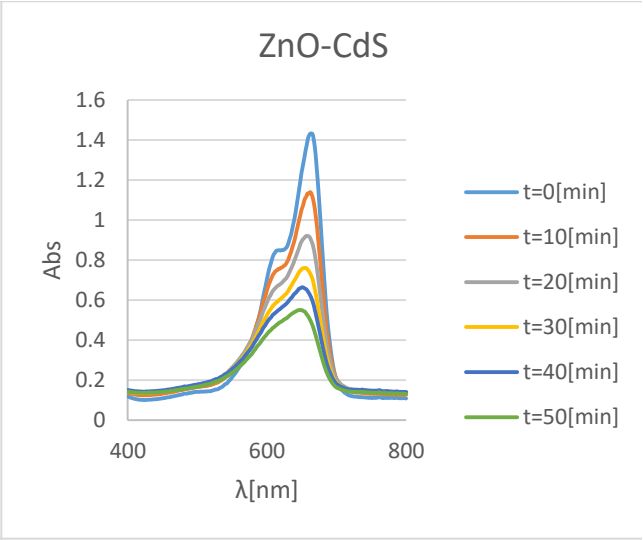

Figure 5. *Absorption of Methylene Blue solution with ZnO-CdS.*

The ZnO favors the degradation comparing to TiO_2 when it decorates the surface of CdS since its decoration is 70% at 70 min and the corresponding CdS-TiO_2 is 120 min (Fig.2,3).The absorption of MB with CdS-ZnO is greater than the absorption of MB with CdS-TiO_2(Fig.4,5).
Metal oxides such as ZnO or TiO_2, have a positive effect on CdS nanoparticles and the decoration can enhance their photocatalytic properties. The ZnO with respect to TiO_2 when decorating the CdS has achieved a higher percentage in less time. The above results with the use of metal oxide can be explained by taking to the consideration of the active centers of $OH^{\bullet}$ radicals which can take part in the discoloration of the pollutant (the active surface).

CONCLUSIONS

Finally, the use of sonochemical procedures for the synthesis of nanoparticles appears to have very good results. Nanoparticles prepared this way have desirable dimensions and photocatalytic properties. CdS nanoparticles decorated with metal oxides such as ZnO and TiO_2 have better results, while the degradation rate during the photocatalysis of methylene blue is greater. In other words they have a positive effect when they are present on the nanoparticles since they enhance their photocatalytic properties.

Various ceramic or polymeric materials can be modified on their surface with transition metals and with varying ratios in order to be able to better and more efficiently approach the increase in photocatalytic activity. The study on photocatalytic oxidation of aqueous organic pollutants is considered necessary. Particularly useful is the study of semiconductor catalysts fabricated via various synthesis techniques (Sol gel, Spray pyrolysis, DC/RF Sputtering, PLD, etc.), either in the form of powders or other structures (fine films, nanotubes, etc.).

The effect of the nature of the pollutants, and the various amounts of catalyst are factors that influence the photocatalytic process that have not yet been fully elucidated. The photocatalytic arrangement plays a very important role, where special attention should be paid to its design and construction so that it meets the requirements and the needs of photocatalytic study.

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