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## Synthesis and Photocatalytic Studies of TiO<sub>2</sub>-CdS Nanocomposite

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### ABSTRACT

Considering the importance of photo catalytic oxidation of organic pollutants by semiconductors using sunlight, in the present study, we prepared and studied CdS-TiO<sub>2</sub> nanocomposite. The commonly used photocatalyst TiO<sub>2</sub> as such has the drawback that it uses only the UV portion of sunlight. The CdS-TiO<sub>2</sub> composite was prepared by a modified sol-gel method. The structure and optical properties were studied by means of XRD, TEM and UV-visible spectroscopy. The composite was tested for their photocatalytic efficiency by the time taken for the degradation of the dye methyl orange under illumination of by absorption spectroscopy of samples extracted at different time intervals. It is found that CdS-TiO<sub>2</sub> is more efficient as a photocatalyst than pure TiO<sub>2</sub>. This is due to better absorption of light in the visible range.

### 1. Introduction

The photocatalytic oxidation of organic pollutants TiO<sub>2</sub> is a highly promising solution for the water purification using sunlight and has been an intense area of research in the past decade. The band gap of TiO<sub>2</sub> is generally a range of 3.0–3.2 eV which means that UV light irradiation with a wavelength lower than 400 nm only initiate photo-reaction. Many composites have been tried to improve the efficiency of pure TiO<sub>2</sub> by improving the absorption in the visible region of the solar spectrum as well [1, 2]. This can be done either by Surface modifications achieved by anchoring colored inorganic semiconductors (for example, CdS and CdSe) or organic dyes on the TiO<sub>2</sub> surface, where they act as sensitizers [3, 4]. On the other hand, bulk modification is mainly effected by doping metals or non-metals into bulk TiO<sub>2</sub> [5,6]. Another method is the using composites of TiO<sub>2</sub> with carbonous materials like CNT and graphene [7,8]. In the present study, we prepared and studied CdS-TiO<sub>2</sub> nanocomposite and studied its photocatalytic efficiency.

### 2. Experimental Methods

For the synthesis of core TiO<sub>2</sub> nanoparticles, we followed a standard sol-gel procedure where 4.5 mL titanium tetra isopropoxide, Ti{OCH(CH<sub>3</sub>)<sub>2</sub>}<sub>4</sub>, (TTIP, Aldrich) was mixed with 30 mL 2-propanol (Merck) and stirred for 30 min for homogenous mixing. Then 4 drops of glacial acetic acid (Merck) was added. A gelatinous precipitate was formed after 4 hours of stirring during which ammonium hydroxide was added drop by drop. It was left overnight when dry gel was formed. This was powdered and calcined at 450 °C for 1 hour to obtain TiO<sub>2</sub>. The sample was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Pristine CdS was prepared using controlled precipitation using a complexing agent triethanol amine (TEA). Complexing agent or chelating agent is a substance capable of forming a complex compound with another material in solution. The formation of CdS nanoparticles requires the slow release of Cd<sup>2+</sup> ion in the aqueous medium, achieved by forming a complex of Cd. The Cd<sup>2+</sup> ion released from Cd-TEA complex and the S<sup>2-</sup> ion react to form CdS. Important parameters involved in the reaction are the concentrations of the reactants, temperature and pH of the solution. The pH can be controlled by adding ammonia solution. Changing the amount of the chelating agent from 5 mL to 7 mL was found to vary the size

(samples M1S1 and M2S2 respectively). The change in colour by direct observation itself showed the variation in size. To synthesize the composite, we took 0.1 M of cadmium chloride (CdCl<sub>2</sub>) in a beaker, 5 mL of TEA (Merck) was added with stirring. Ammonia was added drop by drop till the white precipitate formed was completely dissolved to give a clear solution. Then it was heated to 60 °C and 0.1 M 10 mL thiourea (Merck) is added drop by drop. When the solution turned cloudy, 2 mL of TTIP was added drop by drop while stirring. Formation of pale-yellow precipitate indicated the formation of CdS-TiO<sub>2</sub> nanoparticles. The sample was characterized by UV-Visible absorption spectroscopy.

The photocatalytic efficiency was performed with the study of time taken for the degradation of the Methyl orange dye solution. The CdS-TiO<sub>2</sub> powder was added to the dye solution which was magnetically stirred in the dark for 15 min, to establish an adsorption-desorption equilibrium. Then, the solution was irradiated by light from a 100W white LED lamp. Samples were then withdrawn and analyzed by JASCO V 670 UV-Vis spectrophotometer at 15 minutes interval. This was done for pure TiO<sub>2</sub> and CdS-TiO<sub>2</sub> composite.

### 3. Results and Discussion

Fig. 1 shows the XRD pattern of the TiO<sub>2</sub> powder derived from the stable colloid, which matches with the standard (JCPDS NO.21-1272). It has mainly anatase phase with a few peaks corresponding to rutile as well. Fig. 2 shows the TEM image of TiO<sub>2</sub> which shows the size to be about 9 nm.

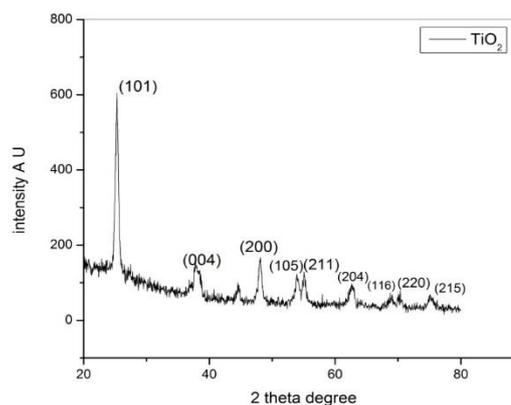


Fig. 1 XRD pattern of synthesized TiO<sub>2</sub>

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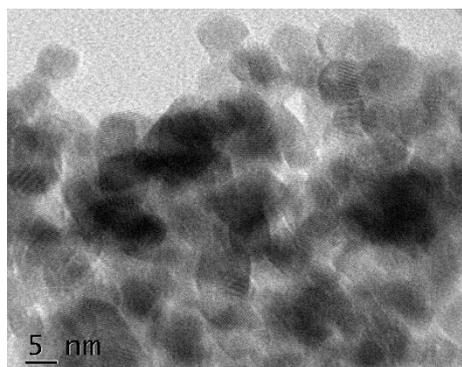


Fig. 2 TEM image of TiO<sub>2</sub>

It is known that in the case of semiconductor nanocrystals, size is calculated from the shift of the band edge compared to that of bulk, by theories based on effective mass approximation (EMA) [9-11]. However, this method has the disadvantage of overestimating the size in the small size region. Hence, we have used the new empirical formula suggested by Ranjani Viswanatha et al. [12],

$$E_g = 100(18.1d^2 + 41.4d - 0.8)^{-1} \quad (1)$$

where  $E_g$  is the shift in the energy band gap and  $d$  is the diameter of the particle. The particle size of CdS thus calculated was 2 nm (Table 1).

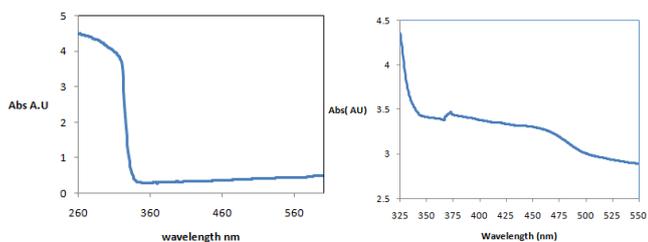


Fig. 3 a) Absorption spectrum of sol-gel TiO<sub>2</sub> and b) CdS-TiO<sub>2</sub> composite

Table 1 Size calculation of CdS quantum dots with different amounts of chelating agents

Sample	Cut off $\lambda$ (nm)	Bandgap $E_g$ (ev)	Particle size (nm)
CdS M1S1	427.73	2.89	2.23
CdS M2S2	414.81	2.99	2.05

In Fig. 3a, one can see the typical UV absorption of synthesized TiO<sub>2</sub>. Fig. 3b shows the absorption spectrum of TiO<sub>2</sub>-CdS composite which clearly shows that while the main absorption peak is still that of TiO<sub>2</sub>, the addition of CdS extends the absorption all through the visible region.

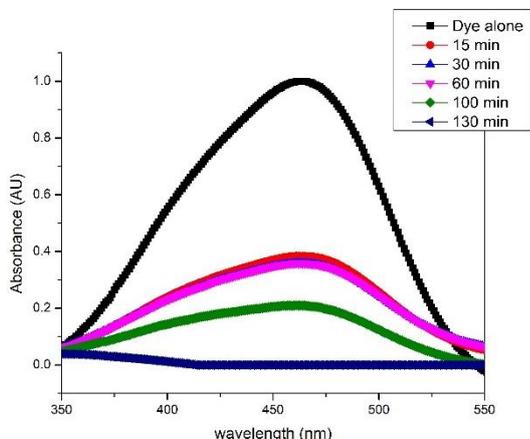


Fig. 4 Photodegradation of dye at different irradiation time

The kinetics of MO photodegradation can be used to quantify the photocatalytic activity. The photocatalytic degradation reaction approximately obeys the first-order kinetics, which is expressed as follows:

$$\ln C_0/C = kt \quad (2)$$

where  $C$  and  $C_0$  are the concentration at a specific time  $t$  and initial concentration of MO,  $t$  is the irradiation time and  $k$  denote the overall degradation rate constant. By plotting  $\ln(C/C_0)$  as a function of time, we can compare performance of different samples.

Fig. 4 shows the absorption spectrum of CdS-TiO<sub>2</sub> composite powder at different time intervals. One can clearly see the emission from the dye getting quenched over the time. Fig. 5 shows the ratio of concentration of dye at a particular time to the initial concentration at different time periods. One can see that the composite reduced the dye much faster than pure TiO<sub>2</sub>. The improvement in time is because of extended absorption in the visible region due to CdS.

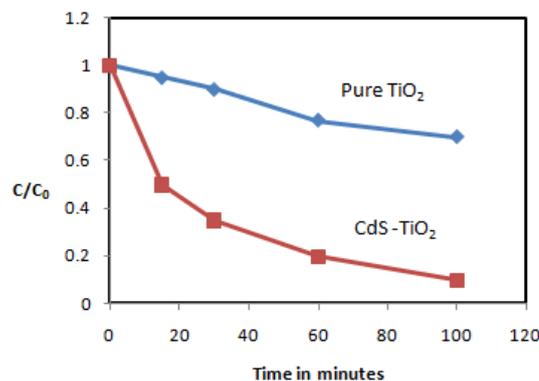


Fig. 5 Comparison of photocatalytic performance of pure TiO<sub>2</sub> and TiO<sub>2</sub>-CdS composite

#### 4. Conclusion

In the present work, we have successfully synthesized TiO<sub>2</sub>-CdS nanocomposite by a modified sol-gel process. Its efficiency as a photo catalyst was studied by the time taken for the degradation of the dye Methyl Orange. The composite is found to be better compared to TiO<sub>2</sub> alone. The reason for this is the extended absorption of light in the visible region.

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