

PD-DOPED CdS NANOPARTICLES: SYNTHESIS AND PHOTOCATALYTIC DECOMPOSITION OF AR183 DYE

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Abstract: Pd doped CdS nanoparticles were successfully synthesized by the cost effective chemical co-precipitation method at room temperature. The structural, morphological, compositional and Raman studies were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET techniques respectively. Broadened XRD peaks show the formation of Pd doped CdS nanoparticles with wurtzite structure. SEM show surface morphology of prepared nanoparticles. SEM images depict the presence of spherical nanoparticles and pores in the sample. From the optical absorption measurement, it is supposed that the blue shift in the absorption peak of 480 nm from that of bulk is at 512 nm may be due to the quantum confinement effect. The effect of the simultaneous photodegradation of the azo dye was also investigated and we observed that the degradation rates increased with dopant content. The repeatability of photocatalytic activity of the photocatalyst was also tested. After five cycles of CdS reuse the rate of colour lost was still up to 92% of the initial rate. The degradation was followed monitoring the change of azo dye concentration by UV-Vis spectroscopy. Results show that the use of an efficient photocatalyst and the adequate selection of optimal operational parameters may easily lead to a complete decolorization of the aqueous solutions of azo dye in short time.

Keywords: Photocatalytic degradation; Pd doped CdS Nanoparticles; photocatalysis; AR183 dyes;

INTRODUCTION

Dye pollutants from textile, papers and other industries are important sources of environmental contamination. It is estimated that fifteen percent of the total World dye production is lost during dyeing process and it is released in textile effluents [1]. During the dyeing process, the colours produced by minute amounts of dyes accidentally released in water are considered to pose serious problems, because they have considerable environmental effects on the water and make them visually unpleasant [2]. Moreover, environmental pollution by organic dyes also sets a severe ecological problem, which is increased by the fact that most of them are often toxic to microorganisms and take a long degradation times in the environment [3].

Azo dyes are a large class of very effective synthetic organic dyes used for colouring a variety of consumer goods such as foods, cosmetics, carpets, clothes, leather and textiles. Today, azo dyes are produced for the most part in China and India, followed by Korea, Chinese Taipei and Argentina [4]. The azo dyes with -N=N group in their molecular structure constitute the makes up to 60–70% of all textile dyestuffs produced [5]. However, some azo dyes break down during use and release chemicals known as aromatic amines, some of which can cause cancer [6].

In recent years Advanced Oxidation Processes (AOPs) using inorganic semiconductors have been effectively used to detoxify recalcitrant pollutants present in industrial wastewater. On exposure to the light, organic molecules on a semiconductor surface can be photochemically oxidized or reduced in high chemical yields. Since organic compounds have finite oxidation and reduction potential energies, variable electronic band energy of a semiconductor, which can be simply controlled by decreasing nanoparticle diameter, can modify the photocatalytic efficiency. Cadmium sulphide is an important semiconductor possessing interesting optical and electronic properties and is being increasingly used as catalysts for various photocatalytic reactions [7-8]. The method of synthesis is found to have a pronounced effect on the catalytic activity of CdS. In this study, we report the synthesis of CdS nanoparticles and its photocatalytic activities for degradation of acid red 183 (AR183) dyes.

MATERIALS & METHODS

pd-doped CdS (Pd content 0-2% mole fraction) 100 ml of 0.2 M 1-thioglycerol, 0.1 M (NH₄)₂S solution and 50 ml of 0.1 M NaOH was added slowly to 150 ml of 0.09M (Cd(NO₃)₂) solution and vigorous stirring was continued for 1 hour. To this solution, calculated amount of palladium nitrate was added and the mixture was further stirred for 2 hours. Then the mixture was kept in furnace at 180°C for 10 hours and then allowed to cool at room temperature. The light yellow precipitates were centrifuged and washed several times using water and ethanol. The final products were dried at room temperature for 4 hours.

The structural and morphological properties of prepared samples have been studied using XRD, SEM and TEM techniques. The photocatalytic activity of samples was tested for the degradation of AR 183 dye under the condition: 0.5-3 g/L catalyst/dye solution ratio, 0.0004M concentration of AR 183, and 2 h reaction time. The photocatalytic experiments were conducted under ambient atmospheric conditions in a reactor using 150W tungsten halogen lamp as the light source. In order to ensure adsorption equilibrium, the solution was stirred for about 45 min in dark, prior to irradiation. The apparent kinetics of dye degradation was determined by monitoring the concentration of the substrate using spectrophotometer. The photodegradation efficiency of the dye by CdS samples was calculated using the Eq. (1) :

$$\% \text{ Degradation} = \frac{C - C_0}{C_0} \times 100 \quad (1)$$

where, C₀ and C are the concentration of the AB before and after UV irradiation, respectively.

RESULTS AND DISCUSSION

The XRD patterns also confirmed the formation of CdS. The XRD pattern exhibited diffraction peaks at 26.4° , 43.7° , and 51.6° corresponds to (111), (220), (311) planes of cubic phase CdS nanoparticles. The calculated lattice parameter value for undoped CdS comes out to be 5.870 \AA where as for Pd doped CdS shows slightly decrease in lattice parameter with increase of Pd concentration (Table 1). Figure 1 shows the XRD pattern of Pd-CdS (Pd content 1% mole fraction) nanoparticles. All the diffracted peaks of CdS nanoparticles are indexed to cubic structure. The broadening of the XRD pattern is larger indicating that the sample is nano-crystalline in nature. The mean crystallite size of Pd-CdS (1 mol% Pd), calculated from the FWHM of the peak 26.4° (111) was $\sim 9 \text{ nm}$.

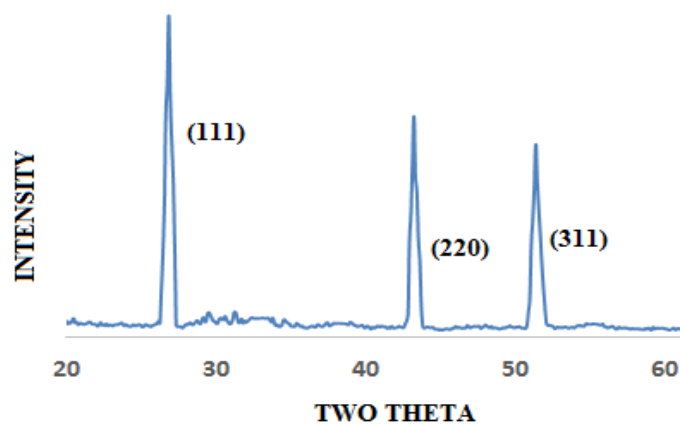


Figure 1. XRD of Pd-CdS (Pd content 1% mole fraction).

To study the morphology of the samples, SEM analysis was performed. The SEM micrograph of the Pd-CdS (Pd content 1% mole fraction) is shown in Figure 2. It can be seen that the particles adopt irregular morphology with different sized particles. The CdS particles appear highly agglomerated in nature. This might be due to the fact that the crystal growth itself because of the small size regime which is evident from the XRD analysis.

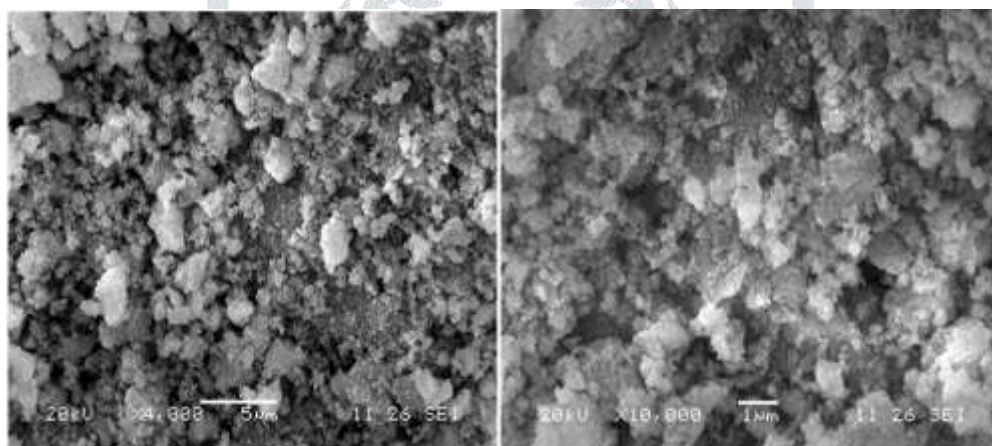


Figure 2 SEM of CDSA1 (1% mol Pd).

Table 1. Structural parameters of undoped and Ag doped CdS.

Sample	Sample code	Phase	Specific Surface Area (m^2/g)	a (\AA)	Band gap (eV)	Particle size (nm)
CdS	CDS	Cubic	64.56	5.870	2.40	14.4
Pd -CdS (1 mol% Pd)	CDSA1	Cubic	77.22	5.814	2.49	9.4
Pd -CdS (2 mol% Pd)	CDSA2	Cubic	71.01	5.805	2.54	12.6

The specific surface area (SSA_{BET}) of CdS samples were measured by nitrogen adsorption as shown in Figure 3 and the results clearly showed that SSA_{BET} increased with increasing Pd concentration up to 1 mol% and tends to fall with 2 mol%. It was presumed that, when in excess, the existence of dopant on the CdS surface lessens the specific surface area of catalyst. This prevents the adsorption of reactant and thus, inhibits the photocatalytic activity [9].

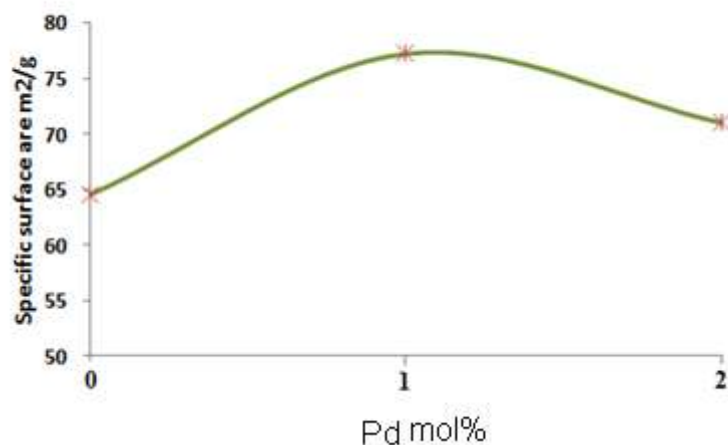


Figure 3. The specific surface area (SSABET) of Pd doped CdS (Pd content 0-2% mol fraction) nanoparticles.

Figure 4 shows the relative change in the concentration (C/C_0) of AR-183 in the presence and absence of prepared CdS samples as a function of time. A maximum photocatalytic activity is found for CDSA1 which almost completely decolorized the solution in a period of only 90 minutes. Such an increase in photocatalytic activity of CdS could be due to three reasons: one, a decrease in energy to exit electron from conduction band to valence band, two, Ag deposited on the CdS particles can form a space charge layer, which can separate the photo induced electron-hole pairs and three, the defects produced due to lattice deformation (Table 1) caused by Pd doping can inhibit the recombination of electron-hole pairs and, eventually, enhance the photocatalytic activity. In present study, CDSA1 has the best photoactivity, since it has a band gap of 2.45 eV, the lowest particle size and the largest surface area.

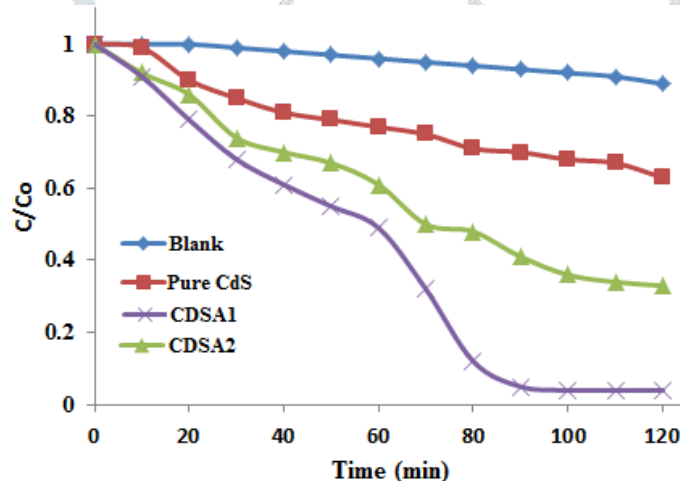


Figure 4. Change in the concentration of AR-183 dye with time in presence and absence of CdS samples.

A series of experiments has been carried out to study the effect of pH on AR183 removal efficiency of the optimized catalyst amounts of sample CDSA1 (i.e. 1.5 g/L) and UV-irradiation times (up to 120 min). pH variation can in fact influence the adsorption of dye molecules onto the catalyst surfaces [10]. The findings are summarized in Table 2. The results indicate that increasing the pH of AR 183 solution from 2 to 8 leads to an increase in dye removal efficiency from 54 to 96.0%, but at pH more than 7, the AR183 removal efficiency almost remains unchanged. The possible reason for this behavior is that alkaline pH range favours the formation of more OH radicals due to the presence of large quantity of OH⁻ ions in the alkaline medium, which enhances the photocatalytic degradation of AR183 significantly [11]. The optimum condition for pH is 7 at which photodegradation percentage of AR183 reach to 96%.

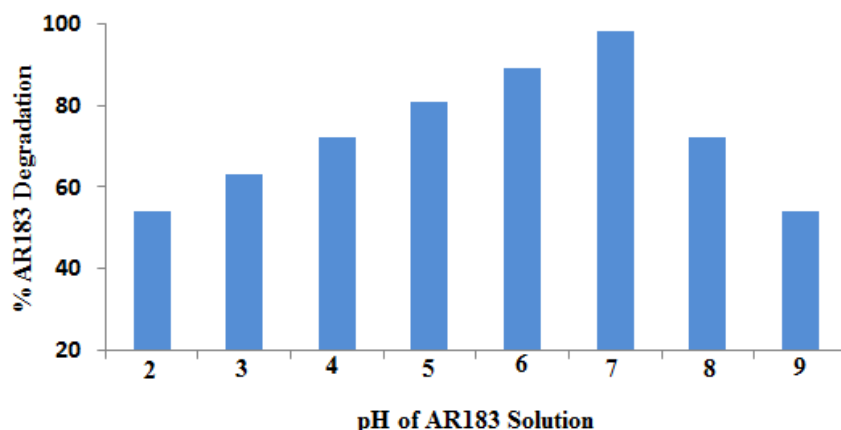


Figure 5. CDSA1 (1.5 g/L) photodegradation efficiency of AR183 dye at different pH.

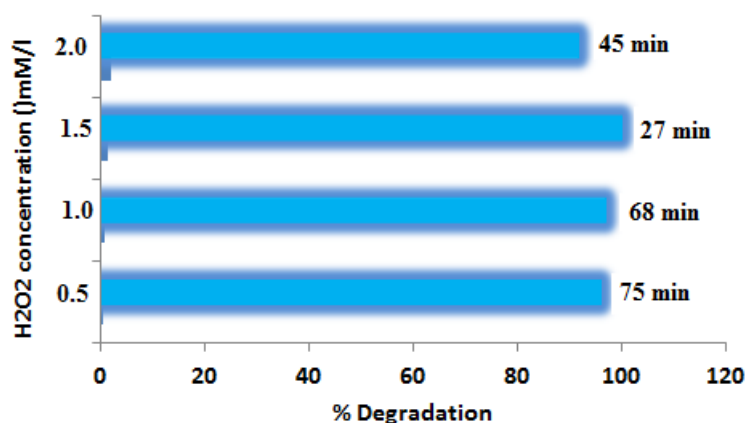
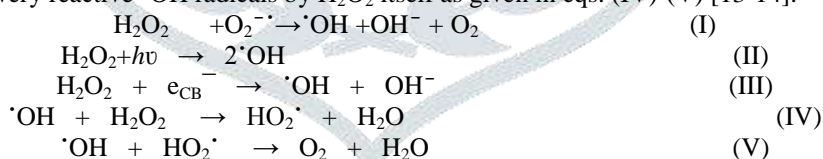


Figure 6. Effect of H₂O₂ concentration on degradation efficiency of AR183 (pH=7) over CDSA1. Catalyst (1.5 g/L)

Reports show that, oxidizing agents (H₂O₂, KBrO₃, (NH₄)₂S₂O₈ etc.) have a great deal of influence on the photocatalytic degradation of dyes. In the present study, the effect of adding H₂O₂ on the degradation of AR183 (pH=7) using CDSA1 is reported. The experiment was conducted at the concentration range 0.5-2 mM/H₂O₂. From Figure 6, it can be seen that the degradation rate increases with increase in H₂O₂ concentration. The results indicated that 1.5 mM/l was an optimal dosage of H₂O₂, at which the degradation efficiency of the AR183 on the CDSA1 attained the height. The H₂O₂ acts as a source of [•]OH radicals by reaction with photogenerated electrons and plays a dual role: as strong oxidants themselves and as electron scavengers (according to equations I-III), thus inhibiting the electron-hole recombination at the catalyst surface [12]. At higher dosage of H₂O₂ beyond the optimum, the degradation efficiency of AR183 decreased. This may be due to consumption of very reactive [•]OH radicals by H₂O₂ itself as given in eqs. (IV)-(V) [13-14].



Stability of the catalyst was tested by carrying out the degradation with the used catalyst. The results for four cycles of the catalyst are shown in Figure 7. The CDSA1 sample exhibited 100, 97.2, 96.3 and 95.4% degradation in first, second, third and fourth cycles, respectively. These results indicate that CDSA1 catalyst remains effective and reusable under UV light.

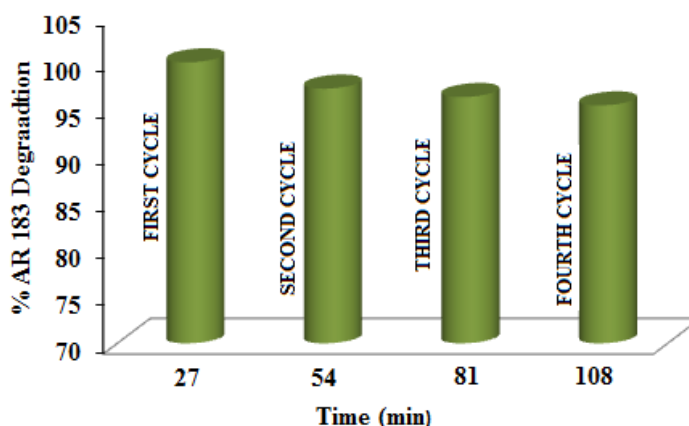


Figure 7. Reusability of CDSA1 catalyst: [AR183] = 0.0004 M, pH=7, CDSA1 dosage = 1.5 g/L, H₂O₂ concentration = 1.5 mM/l.

REFERENCES

- [1] Vautier, M.,Guillard, C.,and Herrmann, J., (2001). Photocatalytic Degradation of Dyes in Water: Case Studyof Indigo and of Indigo Carmine. *Journal of Catalysis*,**201**, 46-59.
- [2] Wang, C., Lee, C.,Lyu, M., andJuang, L., (2008) Photocatalytic degradation of C.I. Basic Violet 10 usingTiO₂ catalysts supported by Y zeolite: An investigation of the effects of operational parameters.*Dyes and Pigments*.**76**, 817-824.
- [3]Zainal, Z.,Hui, L.K., Hussein, M.Z.,Taufiq-Yap, Y.H., Abdullah, A.H., andRamli, I., (2005). Removal of dyes using immobilized titanium dioxide illuminated by fluorescent lamps. *Journal of Hazardous Materials*.**125**, 113-120.
- [4] Organisation for economic cooperation and development (2005). Environmental Requirements and Market Access. Chapter 2: Limits on Aromatic Amines in Textiles Coloured with Azo Dyes. OECD Publishing. ISBN-92-64-01373-3.
- [5] Habibi, M.H.,Hassanzadeh, A., andMahdavi, S.,(2005). The effect of operational parameters on thephotocatalytic degradation of three textile azo dyes in aqueous TiO₂ suspensions.*Journal of Photochemistry and Photobiology: A Chem.* **172**, 89-96.
- [6] Dom, N., Knapen, D., Benoot, D., Nobels, I.,andBlust, R., (2010). Aquatic multi-species acute toxicity of (chlorinated) anilines: Experimental versus predicted data. *Chemosphere*,**81(2)** 177-186.
- [7] Kothari, S., Kumar, A., Vyas, R., Ameta, R., and Punjabi, P. P.,(2009).*Journal of Brazilian Chemical Society*, **20(10)**,1821-1826.
- [8] Giribabu, K., Suresh, R., Manigandan, R., Vijayraj, A., Prabu, R., and Narayanan, V., (2012). *Bulletin of Korean Chemical Society*, **33(9)**, 2910-2916.
- [9] Liu, G., Zhang,X.,Xu,Y.,Niu,X.,Zheng,L., and Ding, X., (2005). The preparation of Zn²⁺-dopedTiO₂ nanoparticles by sol-gel and solid phase reaction methods respectivelyand their photocatalytic activities, *Chemosphere* **59**, 1367-1371.
- [10] Wang, N., Li, J., Zhu, L., Dong, Y., and Tang, H., (2008). Highly photocatalytic activity of metalhydroxide/titanium dioxide nanoparticles prepared via a modified wet precipitation process. *Journal of Photochemistry and Photobiology A Chemistry*,**198**, 282-287.
- [11] Concalves,M.S.T., Oliveira-Campos,A.M.F., Pinto,M.M.S.,Plasencia,P.M.S., andQueiroz,M.J.R.P., (1991).Photochemical treatment of solutions of azo dyes containingTiO₂, *Chemosphere*,**39**, 781-790.
- [12] Carp, O.,Huisman,C.L.,and Reller, A.,(2004). Photoinduced reactivity of titanium oxide photoinducedreactivity of titanium oxide, *Solid State Chemistry*,**32**, 33-177.
- [13] Coleman,H.M.,Vimonses, V., Leslie, G., andAmal, R., (2007) Degradation of 1,4-dioxanein water using TiO₂ based photocatalytic and H₂O₂/UV processes, *Journal of Hazardous Materials*,**146(3)**, 496-501.
- [14] Mahmoodi,N.M.,Arami,M., Limaee,N.Y., andTabrizi,N.S., (2006) Kinetics of heterogeneousphotocatalytic degradation of reactive dyes in an immobilized TiO₂photocatalytic reactor, *Journal of Colloid Interface Science*,**295(1)**, 159-164.

