



SYNTHESIS, CHARACTERIZATION AND PHOTO CATALYTIC ACTIVITY OF CADMIUM OXIDE AND METAL-DOPED CADMIUM OXIDE NANOPARTICLES

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ABSTRACT M-doped CdO nanoparticles (M = Cu, Ni) were prepared by the co-precipitation method. The X-ray diffraction (XRD), UV-VIS spectrometer techniques were used to characterize the synthesized products. XRD results confirm the formation of CdO, Cu-doped CdO, Ni-doped CdO nanoparticles with crystallite sizes in the range of 7.58-10.60 nm. The optical study shows that doping ions lead to an increase in the absorption edge wavelength and a decrease in the band gap energy of CdO. Photo catalytic activity of the synthesized nanoparticles was successfully tested for photo degradation of Methyl blue as model pollutant under UV light. The photo catalytic activity results confirm that the doped nanoparticles show higher activity than undoped CdO. The small grain size, high crystallinity, high specific surface area and decrease in the band gap energy of Cu-doped CdO may be responsible for the high photo catalytic activity.

KEYWORDS : Metal doping; CdO; Nanoparticle, UV-DRS; Photo degradation of methyl blue.

I. INTRODUCTION

Nanotechnology is an advanced technology which deals with the synthesis of nanoparticles. Nano is a prefix used to describe one billionth or 10⁻⁹ of something. [1] Nanotechnology is the technology of the 21st century. The work at nanometer scale has brought together many research and technological disciplines physics, chemistry, electronics and material science [2].

Engineered nanoparticles may be brought from commercial vendors or generated via experimental procedures by researchers in the laboratory. Engineered nanoparticles include metal or metal oxide, nanoparticles [e.g. gold, TiO₂, CuO, NiO, ZnO, CdO].

Nanoparticles or Nano crystals made of metals, semiconductors or oxides are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other properties.

Recent developments were achieved for the oxidative degradation of the organic compounds either dissolved or dispersed in aqueous media. Among these "advanced oxidation processes," heterogeneous photo catalysis has appeared as an emerging destructive technology. Leading to the total mineralization of most organic contaminants. [3-6] CdO is a degenerate, n-type semiconductor used in optoelectronic applications such as photovoltaic cells [12], and solar cells [13]. Phototransistors [14], IR reflectors [15], transparent electrodes [16], gas sensors [7-17, & 18] and a variety of other materials. There are some reports on the synthesis of CdO nanoparticle Co-precipitation or sonochemical methods [7, 19-21].

We report a simple method for the synthesis of nano-sized cadmium oxide and dopant metal [Cu, Ni] by Co-precipitation method.

To study the particle size oriented photo catalytic degradation of methylene blue using the cadmium oxide photo catalyst synthesized by the chemical Co-precipitation method. After identifying the crystal structure and phase formation, particle size was estimated to study its effect on photo degradation of methylene blue from the optical absorption studies.

II. METHODS AND MATERIAL

Experimental Chemicals

For the synthesis of pure CdO and Cu-doped CdO, Ni-doped CdO nanoparticles. Cadmium Sulphate, PEG (poly ethylene glycol) Ammonia, 0.5 M CuSO₄, 0.5 M NiSO₄, were used as the precursors for the CdO and Cu, Ni components respectively and deionized water was used as a solvent.

Synthesis of CdO nanoparticles

Pure CdO nanoparticles were synthesized by Co-precipitation method as follows. A 0.5 M cadmium sulphate solution stirs in 2 hrs. with

magnetic stirrer. The resultant mixture was slowly added 2 ml PEG (poly ethylene glycol). In ultrasonic the solution was added in ammonia (pH. ≈8) obtained to form a white precipitate. The system was refluxed in 2 hrs. The resultant precursor was then dried at 110° c for 12 hrs. And then finally calcined at 500°C for 2h in high temperature muffle furnace.

Synthesis of series of Cu and Ni-doped CdO

Doped CdO nanoparticles were also prepared using the same procedure by adding appropriate amounts of metal sulphate (Cu, Ni) to get 2 wt.% metal doped CdO.

The synthesized samples were abbreviated as undoped CdO, Cu-doped CdO, and Ni-doped CdO respectively.

Evaluation of photo catalytic activity of the samples

In this study, the photo catalytic activity was tested using methyl blue (MB) solution as a model pollutant under UV light radiation. The photo catalytic degradation was carried out with 100 ml aqueous methyl blue. Solution (100 ppm) containing 25 mg of catalyst nanoparticles. This mixture was stirred in dark for 30 min to reach adsorption equilibrium. Then the mixture was placed inside the photo reactor in which the vessel was 3.5-4 cm away from the UV-lamp. The quartz vessel and the light source were placed inside a black box to prevent UV leakage. The experiments were performed at room temperature and a pH. of about 6.3. Small portion of the mixture were taken at periodic intervals during the irradiation, and after filter, they were analyzed with the UV-Vis spectrophotometer. The % mineralization of dye was determined by COD measurement following the closed reflux volumetric method.

Characterization

The synthesized materials were characterized by various sophisticated techniques. X-ray diffraction (XRD) patterns were carried out by using Philips X-ray diffractometer with diffraction angle 2θ in between 200 and 800 using Cu-Kα radiation of wavelength 1.540 Å. The light absorption by sample was carried out using Varian Carry 5000 (UV-VIS-DRS) spectroscopy in the range 800-200nm.

RESULTS AND DISCUSSION

X-Ray diffraction of doped and pure CdO

Figure 1 shows XRD patterns of the pure CdO and Cu-doped CdO, Ni-doped CdO with calcined at 500°C. Also, the undoped CdO sharp, intense peak at 2θ = 28.524 correspond to (321) phase, Cu-doped CdO sharp, intense peak at 2θ = 30.879 correspond to (840) phase, Ni-doped CdO sharp, intense peak at 2θ = 27.784 correspond to (221) phase, representing that the synthesized nanomaterials were well crystallized. All the diffraction peaks obtained from XRD agreed with the reported JCPDS card no. 39-1221, 24-0191, 28-0191 respectively. The crystallite sizes were estimated by the Scherrer's equation, using the most intense reflection (2θ = 28.524, 30.879, 27.784) The particle sizes samples were in the range of 7.54, 10.03, 10.60 nm when calcined at 500°C.

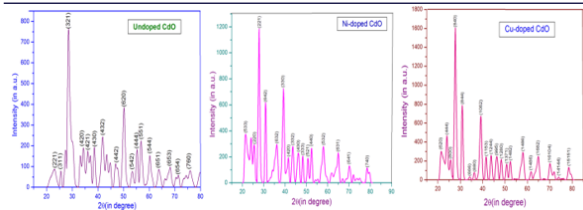


Fig.1 XRD Pattern for (a) Undoped CdO, (b) Cu-doped CdO, (c) Ni-doped CdO nanoparticles calcined at 500°C

UV-visible diffusion reflectance spectroscopy (UV-DRS)

The band gap energies (E_{bg}) of the synthesized nanomaterial's were calculated by using UV-visible diffusion reflectance spectroscopy (DRS). To determine band gap energy of the synthesized materials, the diffusion reflectance spectra were recorded and cut off wave length at which absorption sharp edge rises were determined by drawing a tangent on this curves (fig). The band gap energies were calculated using cut-off wavelength and are represented in the following table. The band gap energy is calculated using the following equation (Bhatkhande et al. 2002):

$E_{bg} = \frac{1240}{\lambda}$ where λ is the wavelength in nanometer and E_{bg} is the band gap energy. From the results of band gap energy data (Table 2), we can conclude that pure CdO had weak visible light response M- doped CdO (M= Cu, Ni) i.e. due doping ability of light absorption of CdO is slightly enhanced.

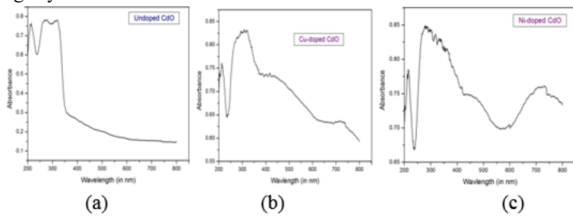


Fig.2 UV-DRS image of (a) undoped CdO, (b) Cu-doped CdO, (c) Ni-doped CdO

Table 1 Band gap energies of the synthesized photocatalyst

| Photocatalyst | Undoped CdO | Cu-doped CdO | Ni-doped CdO |
|------------------|-------------|--------------|--------------|
| Band gap (in eV) | 3.54 | 3.30 | 2.61 |

Photo catalytic activity result

Photo catalytic activity of the synthesized nanomaterial's were tested using methyl blue as a wide spread dye in textile industry, was chosen as the organic contaminant.

The photo catalytic activity study of synthesized nanomaterials was carried out under UV light irradiation and the results of photo catalytic performance are shown in the in the Figs. 3 (a,b,c,d) we can conclude that removal of dye reaches an approximately value after 90 min of photo catalytic treatment for all the tested photo catalyst and also methyl blue removal achieves values between 73.43 and 80.46 % after 90 min of irradiation time presenting the Cu-doped CdO and Ni-doped CdO. The almost photo degradation under UV light (74.95% removal of methyl blue after 90 min of irradiation time Cu-doped CdO. The almost photo degradation under UV light (80.06%) remove of methyl blue after 90 min of irradiation time. Among the studied photo catalyst. Table 2 shows % methyl blue photo catalytic removal after 2 h under both UV light irradiation. The higher photo catalytic activity of Cu-doped CdO.

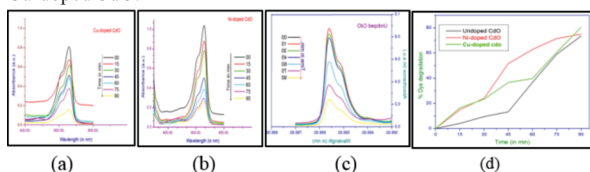


Fig. 3 Photodegradation graphs of methyl blue with a undoped CdO, b Cu-doped CdO, c Ni-doped CdO, d Temporal evolution of MB removal during photocatalytic experiments under UV light irradiation.

CONCLUSION

Here in, we report very simple route for synthesis of Nano crystalline

CdO, Cu-doped CdO and Ni-doped CdO nanoparticles via Co-precipitation method by using PEG as capping agent. The XRD pattern of all synthesized sample calcined at 500°C. The XRD and UV-VIS results it was confirmed that the doping of Cu, Ni in CdO decreases the grain size and shifts the absorption to higher wavelengths.

The results of photo catalytic study confirm the highest photo degradation of methyl blue under UV irradiation for Cu-doped CdO compared to Ni-doped CdO and Undoped CdO synthesized catalyst

REFERENCES

- [1] <https://en.m.wikipedia.org/wiki/Nanoparticle>
- [2] <https://www.understandingnano.com/nanoparticles.html>
- [3] P.Y.Chan, M.G.El-Din, J.R. Bolton, Water Res.46 (2012) 5672-5682.
- [4] I.Oller, S. Malato, J.A. Sanchez-Perez, Sci. Total Environ. 409 (2011) 4141-4166.
- [5] V.K. Sharma, T.M. Triantis, M.G. Antoniou, X. He, M. Pelaez, C.Han, W. Song, K.E. O'Shea, A.A. de la Cruz, T. Kaloudis, A. Hiskia, D.D. Dionysiou, Sep. Purif, Technol. 91(2012) 3-17.
- [6] S.Cortez, P. Teixeira, R. Oliveira, M. Mota, J. Environ. Manage. 92 (2011) 749-755.
- [7] R.B. Waghulade P. P. Patil, Renu Pasricha, Talanta, 72, 594 (2007).
- [8] G. N. Chaudhari, A. M. Bende, A. B. Bodade, S. S. Patil, V. S. Sapkal, Sens. Actuators B, 115 297 (2006).
- [9] A. Srivastava, Lakshmi Kumar, Mater. Chem. Phys. 97,85 (2006).
- [10] G. N. Chaudhari, A. M. Bende, A. B. Bodade, S.S. Patil, S.V. Manorama, Talanta, 69, 187, (2006).
- [11] C. Aifan, H. Xiaodong, T. Zhangfa, B. Shouli, L. Ruixian, L. C. Chiun, Sens. Actuators B, 115, 316 (2006).
- [12] C. H. Champness, K. Ghoneim, J. K. Chen, Can. J. Phys., 63, 767 (1985).
- [13] L. M. Su, N. Grote, F. Schmitt, Electron. Lett., 20, 716 (1984).
- [14] L. M. Su, N. Grote, F. Schmitt, Electron Lett., 20, 717 (1984).
- [15] I. M. Ocampo, A. M. Fernandez, P. J. Sebastian, Semicond. Sci. Technol., 8, 750 (1993).
- [16] F. A. Benko, F. P. Koffyberg, Solid State Comm., 57, 901 (1986).
- [17] K. Gurusugan, D. Mangalaraj, S.A. K. Narayandass, K. Sekar, C. P. Girija Vallabham, Semicond. Sci. Tech., 9, 1827 (1994).
- [18] C.Xiangfeng, L. Xingfeng, L. Xingqin, M. Guangyao, Sens. Actuators B, 65, 64 (2000).
- [19] A. Askarinejad, A. Morsali, Mater. Lett., 62, 478 (2008).
- [20] R. R. Salunkhe, V. R. Shinde, C. D. Lokhande, Sens. Actuators B, 133, 296 (2008).
- [21] Y. W. Wang, C. H. Liang, G. Z. Wang, T. Gao, S. X. Wang, J. C. Fan, L. D. Zhang, J. Mater. Sci. Lett., 20, 1687 (2001).