Fabrication of EDA passivated CdO nanostructures with morphological investigation

K. ANANDHAN, R. THILAK KUMAR[a,*]
Department of Physics, Periyar University, Salem-636 011, Tamilnadu, India
[a]*Department of Physics, Periyar Arts College,Cuddalore-607 001, Tamilandu, India*

Cadmium Oxide nanostructures with curious morphologies from nanospheres to nanorods were fabricated by a wet chemical approach. Ethylenediamine (EDA) was used as morphology directing organic ligand and function of its concentration was investigated. In the absence of EDA, irregular nanospheres were obtained. Addition of Ethylenediamine in various concentrations had an attentive consequence of morphology. The fabricated samples were characterized by XRD, FESEM, TEM, UV-Vis and FTIR methods. The structural studies exposed the formation of cubic CdO, field emission scanning and transmission electron microscopy were performed to characterize nanostructures. UV-visible absorption and Fourier transform infrared (FT-IR) spectroscopy analysis confirmed the formation of EDA passivated nanostructures.

(Received February 03, 2015; accepted September 29, 2016)

Keywords: CdO, EDA, XRD, FESEM, UV-Vis, FTIR

---

1. Introduction

Nanostructure materials reveal unusual physical and chemical properties significantly which were different from these conventional bulk material, due to its extremely small size or large specific surface area. So its synthesis and characterization have attracted increasing attention in the past decade [1-2]. Cadmium oxide (CdO) is a III-IV semiconductor with a direct band gap 2.5eV and indirect band gap of 1.98eV, promising applications in catalysis, sensors, solar cells, and optoelectronic devices [3-4]. Also number of methods have been used to synthesize the various CdO nanostructures. The methods have been employed to prepare the cadmium oxide nanostructures such as microemulsion [5], sonochemical/ hydro thermal technique [6], mechanochemical process [7-9] and wet chemical method etc. [10].

Among these methods wet chemical method is the simplest and most cost effective method for synthesizing nanoparticles. Reproducibility is one of the most important factors in the preparation of nanostructures. The wet chemical methods have high reprodutivity when compared to all other methods [11]. As the particle size decreases, there is an increase in surface area and the presence of dangling bond lead to high stability. This brings about the need to passivate the surface with strong ligand which prevents agglomeration among the particles. In recent years various reports are available for synthesis of CdO nanostructures using surfactants like polymers, thiols, amine, amino acid and other reducing agents [12-16]. Among them the amines have been enormously used as solvents and capping ligand for creation of cadmium oxide nanostructures. In this paper ethylenediamine capped CdO nanoparticles are synthesized and characterized.

2. Materials and methods

All the chemicals were of analytical grade, and used without further purification. Wet chemical synthesis carried out with $CdNO_{3.4}H_2O$ (99%.Merck) and sodium hydroxide NaOH(99% Merck) as precursors with EDA was used as capping ligand. In distinctive experiment 0.1 mol/L of $CdNO_{3.4}H_2O$ was dissolved in 50ml of deionised water and it was labeled as solution A). Then by adding 0.1 mol/L of NaOH was dissolved in 100ml of deionised water and it was labeled as solution B. The solution B was stirred before the one hour with the addition of solution A. After that the mixture was allowed to stir vigorously by 15 hours and a milky white precipitate was obtained. The obtained milky white precipitate creation was separated by centrifugation, washed with deionised water and ethanol for several times. The creation was allowed to dry at 80°C for one hour. For the preparation of nanostructures the obtained CdO precursors were further annealed at 400°C for 2 hours in Muffle furnace. Finally brown color CdO nanoparticles were obtained and the resulting sample was labeled as UC.

For the synthesis of EDA passivated nanostructures, the same procedure was repeated with small changes;

various amount of EDA were added drop-wise to $CdNO_3$. 4H2O solution before adding of NaOH and remaining procedure is the same as mentioned above. The samples were labeled as EC.1(1ml), EC.2(2ml) respectively.

The synthesized nanoparticles were characterized using an X'Pert PRO(PANalytical) advanced X-ray diffractometer with CuKa radiation (1.5406A) with 2ϴ° value ranging between 20° and 80°, morphology and particle size of the creation were observed by HITACHI, Japan model no. SU660 field emission microscope at an accelerating voltage of 15KV. TEM analysis made with JEOLJEM 2100F. EDX with HORIBA, Japan. UV-VIS spectrum was measured by Shimadzu spectrophotometer. Functional group was analyzed by FTIR 6300 TypeA, Serial No. A021161024.

3. Results and discussion

3.1. XRD analysis

Fig. 1 represented the XRD patterns of samples UC to EC.2 indicated the formation of crystal structure of CdO. All the peaks were reflections of samples indexed to Cubic phase of CdO. It was matched well with the standard data of JCPDS 05-0640. XRD diffraction peaks corresponding to EDA capped CdO were of higher intensity than the diffraction peaks with uncapped CdO nanoparticles. This was due to re-orientation of CdO nanoparticles in the presence of EDA. The XRD results confirmed the formation of pure CdO nanoparticles. Crystal size of the CdO was calculated from the XRD data using Scherer formula.

$$D = K\lambda / \beta \cos\theta$$

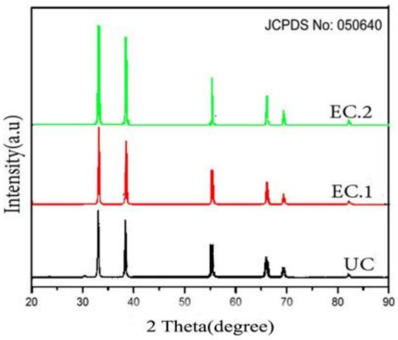

Fig. 1. XRD pattern of CdO Nanostructures

Where λ was the wave length of X-ray diffraction (1.5418A°), K was the Scherrer constant (0.9), ϴ was the characteristic peak angle. β was the full width of half maximum. The calculated average particle size of samples UC-EC.2 for (111) peak were 42, 44 and 49 nm respectively. The formation of CdO nanostructures are presented in Fig. 2.

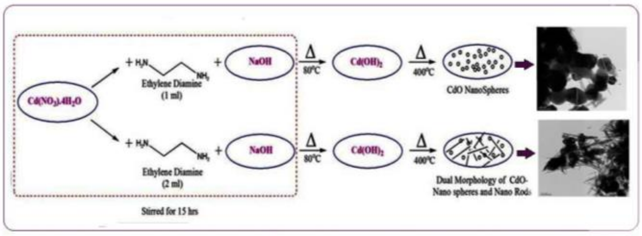

Fig. 2. Formation of CdO nanostructures

3.2. FESEM and TEM analysis

Morphology and size were observed by FESEM and TEM. FESEM image of the sample UC [Fig. 3(a)] corresponding TEM image [Fig. 3 (b and c)] indicate without any defined morphology with size of 75-163 nm. These nanoparticles seem to be aggregated. FESEM sample of EC.1 [Fig. 3 (d)] indicated the formation of well-defined shape of nanosphere with size of 62-167nm.Clearly seen, this changes in morphology occurred in the presence of EDA as observed in TEM images [Fig. 3 (e and h)]. The agglomeration was effectively constrained by surface passivation of amine molecule.

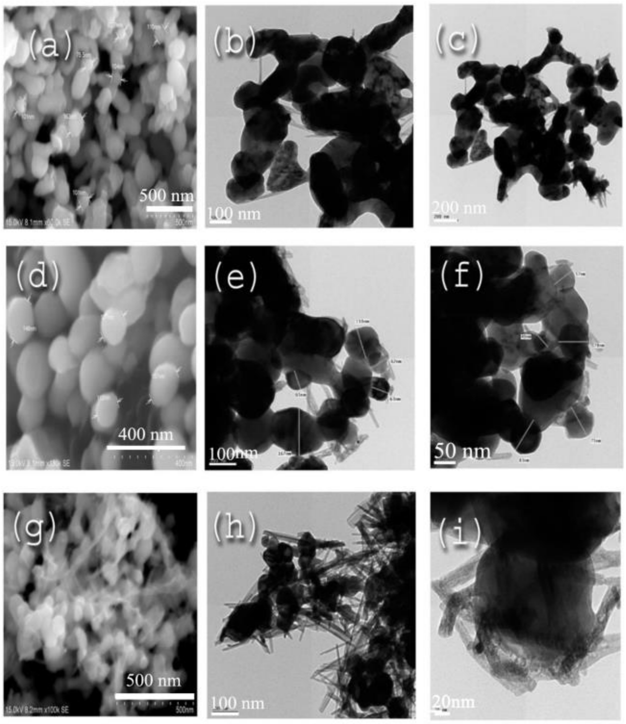

Fig. 3. FESEM and TEM images of (a, b & c) UC, (d, e & f) EC.1, (g, h & i) EC.2

Fig. 3 (g) shows the FESEM image of sample Ec.2 formation of mixture of aggregated nanospheres and nanorods. The pareticle sizes were 50 to 150 nm.

Concentration of EDA influences the dual morphology. Morphology and dimension of the products were found to be strongly depends on concentration of EDA. An increase in the Oleyleamine amount in the surfactant not only led to the formation of small CdO nanocrystals but also changed the nanocrystal shape from octahedral to spherical. The change of result from the different binding abilities on the nano crystals between oleic acid and Oleyamine [17]. Fig. 4(a) shows the selective area electron diffraction (SAED) clearly spotted with the bright spots of the CdO plane orientation reveals good conformity to the obtained XRD spectra. Fig. 4(b) shows the EDAX pattern with the presence of Cadmium and Oxygen peaks, as it confirms the absence of other impurities among the prepared CdO sample. The presence of Cd and O ions present in CdO and atomic percentages are found to be at 49.86% and 50.14% respectively.

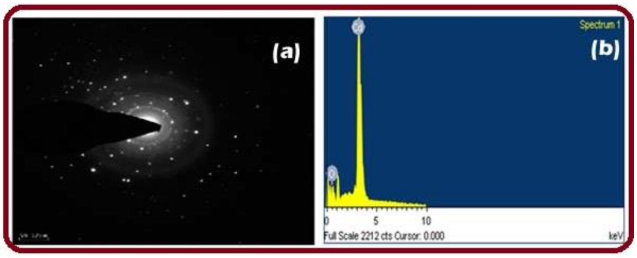

Fig. 4. (a) SAED pattern and (b) EDAX spectrum of CdO nanostructures

3.3. UV-Vis analysis

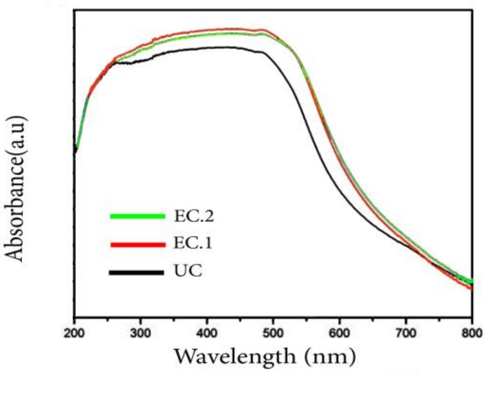

Fig. 5. UV-Vis spectrum of CdO nanostructures

UV-Vis spectrum of the CdO samples synthesized with different concentrations of EDA were presented in Fig. 5. The absorption ability of capped EDA became stronger than uncapped CdO nanomaterial and also the absorption edge shifted towards the red region. This shift may be predictable to the quantum confinement compared with bulk CdO [18].

3.4. FTIR analysis

FTIR spectrum for the synthesized nanoparticle was presented in Fig. 6. The IR absorption band at 3457 cm^{-1} was assigned to stretching vibrations of hydroxyl group (O-H). The bands observed at 3248, 3254 cm^{-1} were assigned to N-H stretching vibrations. The bands identified at 2970 and 2947 cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of C-H group. A strong absorption band at 1379 cm^{-1} was wagging vibrations of C-H group. The above peaks confirm the presence of EDA. In the synthesized product, the metallic bonds near the 856 cm^{-1} due to Cd-OH and the formation of Cd-O phase was characterized with band at 712 cm^{-1}.

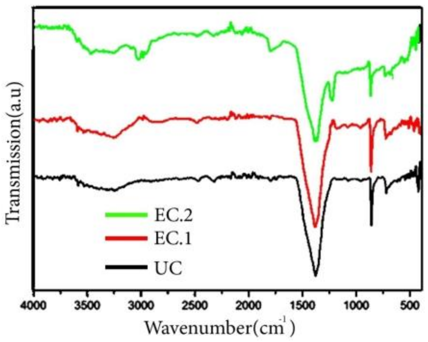

Fig. 6. FTIR spectrum of CdO nanostructures

4. Conclusion

A simple wet chemical technique was used to synthesis CdO nanostructures with different morphologies. The effect of ethylenediamine molecule concentration on morphology, structural, elemental, optical, and functional group properties were studied, without capping agent. The synthesized CdO irregular nanospheres were aggregated and regular nanospheres were formed when the concentration of EDA 1ml. As the EDA concentration was increased to 2 ml nanospheres were changed in to nanorods.

Acknowledgements

The authors are thankful to the UGC, SERO, Hyderabad for its financial support under Minor Research Project.

References

[1] H. Gleiter Prog. Mater. Sci. **33,** 223 (1989).
[2] H. J. Fendler, Chem. Rev. **87,** 877 (1987).
[3] R. M. Navarro, F. D. Valle, J. L. G. Fierro. Int J Hydrogen Energy **33,** 4265 (2008).
[4] X. Q. Liu, Z. L. Xu, Y. F. Liu, Y. S. Shen. Actuators B: Chem. **52,** 270 (1998).
[5] W. Dong, C. Zhu, Opt. Mater. **22,** 227 (2003).

[6] A. Askarinejad, A. Morsali, Chem. Eng. J. **150,** 569 (2009).
[7] H. Yang, G. Qiu, X. Zhang, A. Tang, W. Yang, J. Nanopart. Res. **6,** 539 (2004).
[8] A. Tadjarodi, M Imani, Mater. Lett. **65,** 1025 (2011).
[9] A. Tadjarodi, M. Imani, Mater. Res. Bull. **46**, 1949 (2011).
[10] K. Manickathai, S. K. Viswanathan, M. Alagar, Indian J. Pure Appl. Phys. **46,** 561 (2008).
[11] T. Prakash, Materials research Bulletin **48,** 1541 (2013).
[12] J. Archana, M. Navaneethan, Y. Hayakawa, S. Ponnusamy, C. Muthamizhchelvan. Mater. Res. Bull. **47,** 1892 (2012).
[13] M. Navaneethan, J. Archana, Y. Hayakaw, Cryst. Eng. Comm. **15,** 8246 (2013).
[14] M. Navaneetham, J. Archana, K. D. Nisha, Y. Hayakawa, S. Ponnusamy, C. Muthamizhchelvan, Material Letts. **68,** 78 (2012).
[15] M. Navaneethan, K. D. Nisha, S. Ponnusamy, C. Muthamizhchelvan, Mater Chem. Phys. **117,** 443 (2009).
[16] K. Anandhan, R. Thilak Kumar, Spectrochim. Acta A **149**, 476 (2015).
[17] W. S. Seo, H. H. Jo, K. Lee, B. Kim, S. J. Oh, J. T. Park Angew. Chem. Int. Ed. **43**, 111 (2004).
[18] Y. B. Xie, C. W. Yuan, Appl. Catal. B; Environ. **46**, 251 (2003).

---

[*] Corresponding author: manojthilak@yahoo.com