Journal of Nano Research Vol. 10 (2010) pp 69-76
Online available since 2010/Apr/07 at www.scientific.net

doi:10.4028/www.scientific.net/JNanoR.10.69

Heavy Ion Irradiation Effects on Cadmium Oxide (CdO) Quantum Dots Prepared by Quenching Method

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Received: 4 October 2009, reviewed 20 December 2009, accepted: 20 January 2010

Keywords: Cadmium Oxide, Heavy Ions, Quantum Dots, Nanorods, XRD, SEM/TEM

Abstract

Cadmium oxide (CdO) quantum dots were synthesized in the laboratory by quenching method using CdO powder sintered at 900^0C and ethyl alcohol kept at ice cold temperature. X-ray diffraction investigations reveal the NaCl cubic structure of CdO quantum dots. Addition of ethylenediamine to a portion of reaction mixture containing quantum dots results in the conversion of nanoparticles to nanorods. Heavy ion irradiation using 90 MeV Carbon (C^{+6}) ion beam accelerated at 15 UD Pelletron, with fluence varying from 10^{11} to 10^{13} ions/cm^2 , produced enlargement in the size of quantum dots revealed by TEM investigations. Heavy ion irradiation effects need to be investigated further, in view of industrial applications of quantum dots.

Introduction

Fabrication of quantum dots has emerged as an important area of research in the field of nanotechnology during recent years [1-6]. Cadmium oxide (CdO) is a n-type semiconductor and finds applications in photodiodes, photovoltaics, liquid crystal displays, IR detectors, electrodes of storage batteries, phosphors, pigments and ceramic glazes [7]. A major use of CdO is as an ingredient for electroplating baths and in pigments [8]. A number of synthetic routes have been used to synthesize CdO nanoparticles and nanowires [9-11]. We employed a simple technique of sintering CdO powder and quenching it in ethyl alcohol to prepare quantum dots. The thin film of CdO quantum dots was prepared for irradiation using 90 MeV carbon ion beam (C^{+6}) available at Inter University Accelerator Centre (IUAC), New Delhi. Another part of CdO quantum dot solution was mixed with ethylenediamine, resulting in the formation of nanorods. This technique has already been tested for fabrication of nanorods of ZnO, but to our knowledge rarely for CdO, thus the diamine acting as a shape controlling agent [12, 13].

Materials and Methodology

In a typical synthesis, 4g of CdO powder (purity 99.5% CDH make) was sintered at 900^0C in a muffle furnace for 5 hrs. and then quenched into 7 wt. % aqueous ethyl alcohol kept at ice cold temperature followed by moderate stirring. The resulting solution contains CdO quantum dots. This solution is divided into two parts. One part was used in preparation of thin films of quantum dots on glass slides by placing a few drops of CdO quantum dot solution on a clean glass slide and stretching it over by another glass slide to cast a very fine film in the micron range. The glass slides were cut into pieces, 1x 1cm^2 each, for purpose of irradiation. One of the slides was kept intact as virgin sample for sake of comparison.

Irradiation experiment was carried out in the Material Sciences vacuum chamber under high vacuum (10^{-6} Torr) by mounting the cut glass slide specimens on a ladder having four rectangular faces. 90 MeV carbon ion beam (C^{+6}) available from 15 UD Tandem Pelletron at IUAC, New Delhi was used for irradiation of CdO quantum dots in the form of a thin film coated on glass slides. The ion beam fluence was varied from 10^{11} to 10^{13} ions/cm^2 in steps by rotating the ladder. In order to expose the whole target area, the beam is scanned in the x-y plane over the mounted sample. The ion beam energy and the thickness of the target film are chosen in such a way that the electronic energy loss of carbon beam plays the predominant role in creating modifications in the target. SRIM code calculations show that 90 MeV Carbon ion beam can easily traverse through the thin film of quantum dots solution [14, 15].

The second portion of quantum dot solution was transferred into a stainless steel autoclave and heated slowly to 100^0C and maintained at this temperature for 24 hours. The resulting suspension was centrifuged to retrieve the end product, washed and then vacuum dried. Ethylenediamine was added to the reaction mixture obtained above, which resulted in the formation of nanorods.

Scanning Electron Microscope (Jeol, JSM-6100) at an accelerating voltage of 20 kV was used for recording the morphology of nasnorods prepared by adding ethylenediamine to a solution of quantum dots. X-ray Diffraction studies were carried out at Sophisticated Analytical Instruments Facility (SAIF) set up by Punjab University, Chandigarh using X' Pert PRO (PANanalytical, Netherlands) using Cu Kα radiation. High Resolution Transmission Electron Microscope (HRTEM, Hitachi H 7500) at SAIF was used for measurements of quantum dot diameters. The samples were prepared by dissolving irradiated thin film of quantum dots in ethanol and inserted in HRTEM after loading the drops of this solution on carbon coated gold grids. Measurements were carried out in imaging mode at 80 kV under ultra high vacuum conditions.

Results and Discussion

XRD spectrum of CdO nanoparticles, using a Cu-Kα radiation source of λ = 1.5406 Å, is shown in figure 1. The spectrum shows some prominent peaks at 2θ = 32.99^0, 38.29^0, 55.27^0, 65.94^0 and 69.26^0. The most prominent peak at 32.99^0 corresponds to hkl (111) with cell constant a = 0.4569 nm and d = 0.2714 nm. It clearly shows that CdO nanoparticles crystallize in rocksalt or NaCl cubic structure. Table 1 summarizes the XRD spectrum results calculated using the standard ICSD card #: 029291 [16].

Table1. Assignment of Miller indices to CdO nanocrystals

Sr. No.	2θ degree	d-spacing (nm)	hkl
1.	32.9996	0.2714	111
2.	38.2935	0.2350	200
3.	55.2720	0.1662	220
4.	65.9428	0.1416	311
5.	69.2593	0.1356	222

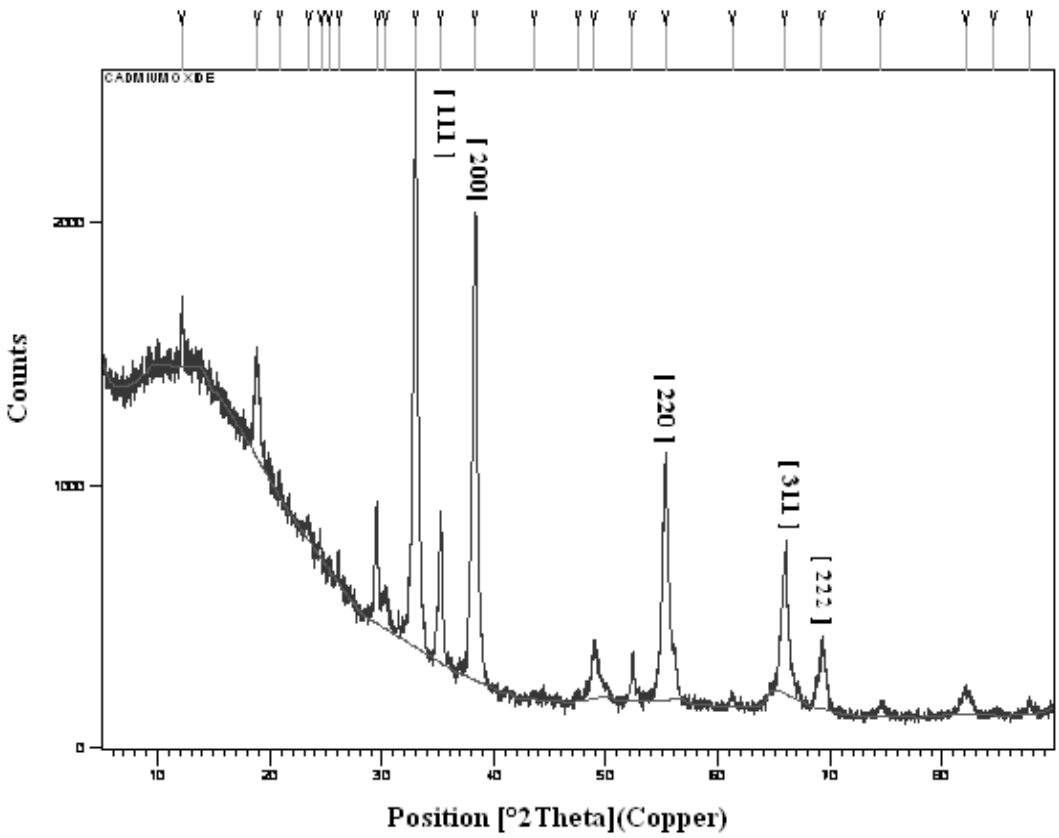

Figure 1. XRD spectrum of CdO nanoparticles showing some prominent peaks.

It has been established [10] that CdO nanowires prepared by electrodeposition also display NaCl cubic structure with Miller indices identical to the CdO nanocrystals (Table 1).

Figure 2 shows the SEM micrograph of CdO nanorods obtained by adding ethylenediamine to the reaction mixture containing CdO quantum dots. The nanorods display different lengths but almost a uniform diameter. It clearly shows the influence of ethylenediamine as a shape directing agent, inhibiting the radial enlargement of the nanorods [17].

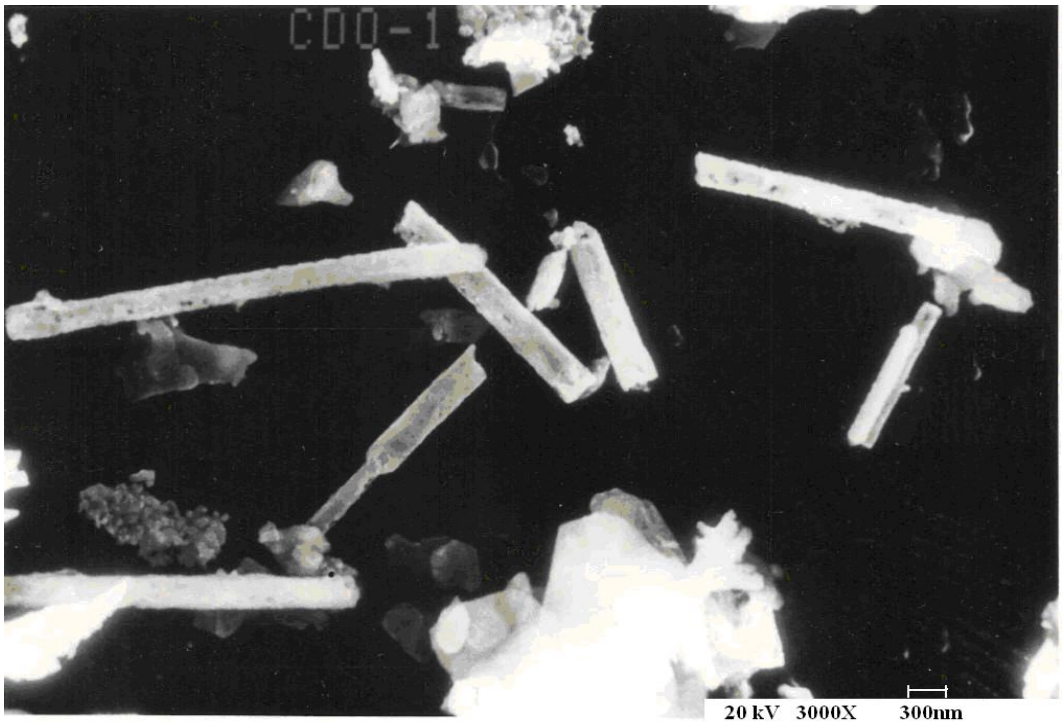

Figure 2. SEM micrograph of CdO nanorods prepared by addition of ethylenediamine

The most interesting results are obtained on irradiation of CdO quantum dots using 90 MeV carbon ion beam. The mean diameter of CdO quantum dots shown in TEM micrograph (figure 3) of virgin (unirradiated) sample is 9.33 nm. The irradiation effect produces agglomeration of quantum dots due to intense heating by carbon ion beam, resulting in the enhancement of quantum dot size. There is no linear relationship between the mean diameter and the fluence of carbon ion beam used in this experiment. The CdO sample irradiated by using minimum fluence of 10^{11} ions/cm^2 displays a mean diameter of 25.6 nm (figure 4), an enhancement of nearly three times of the mean diameter of its virgin sample. The mean diameter for the CdO irradiated with a fluence of 10^{12} ions/cm^2 is determined to be 32.5 nm; whereas the one irradiated at a maximum dose (10^{13} ions/cm^2) has a mean diameter of 32 nm (figure 5). It shows that the diameter attains a plateau value after irradiation using 10^{12} ions/cm^2. Mean diameter is determined by counting on the average 20-25 quantum dots in several grids. There is a random distribution in the size and shape of quantum dots in virgin and irradiated samples. The statistical counting error (1σ) in diameter measurement is on the order of 20%.

Heavy ion irradiation effects have been studied on ZnO quantum dots [11] and ZnS nanoparticles [18] using 100 MeV Cl^{+9} ion beam, with fluence varying from 10^{11} to 10^{13} ions/cm^2 , as in our experiment. The enhancement in the size of quantum dots with ion beam fluence has been reported in both these experiments. The novel result of these experiments is a claim that heavy ion irradiated ZnO quantum dots can act as nano LED of high quantum efficiency in green region [11] and sensitivity of the optical sensors supposed to be made of ion irradiated and doped semi-conductors like ZnS, can be tuned by proper choice of ion dose [18]. We are also planning to investigate the behaviour of irradiated CdO quantum dots from a study of their photoluminescence spectra for use in opto-electronics.

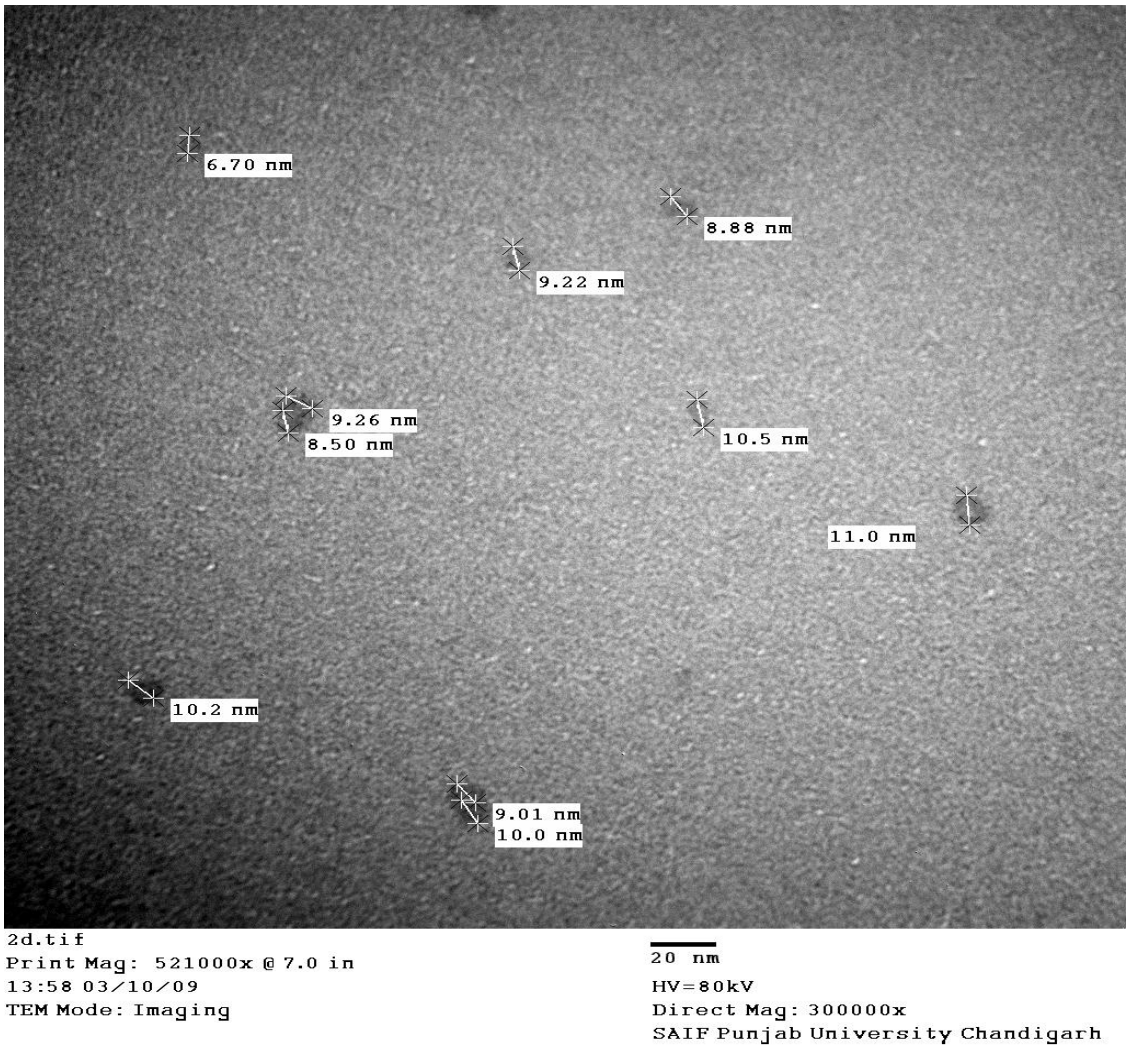

Figure 3. TEM micrograph showing variable size of CdO quantum dots in virgin sample.

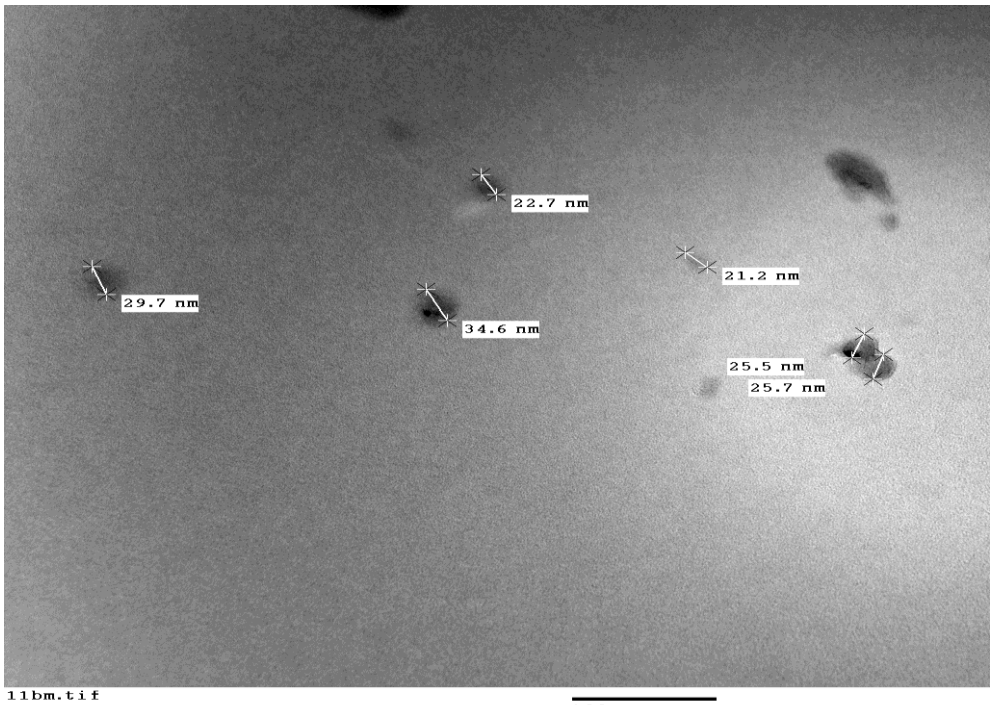

Figure 4. TEM micrograph of CdO quantum dots irradiated at a fluence of $1* 10^{11}$ ions/cm^2

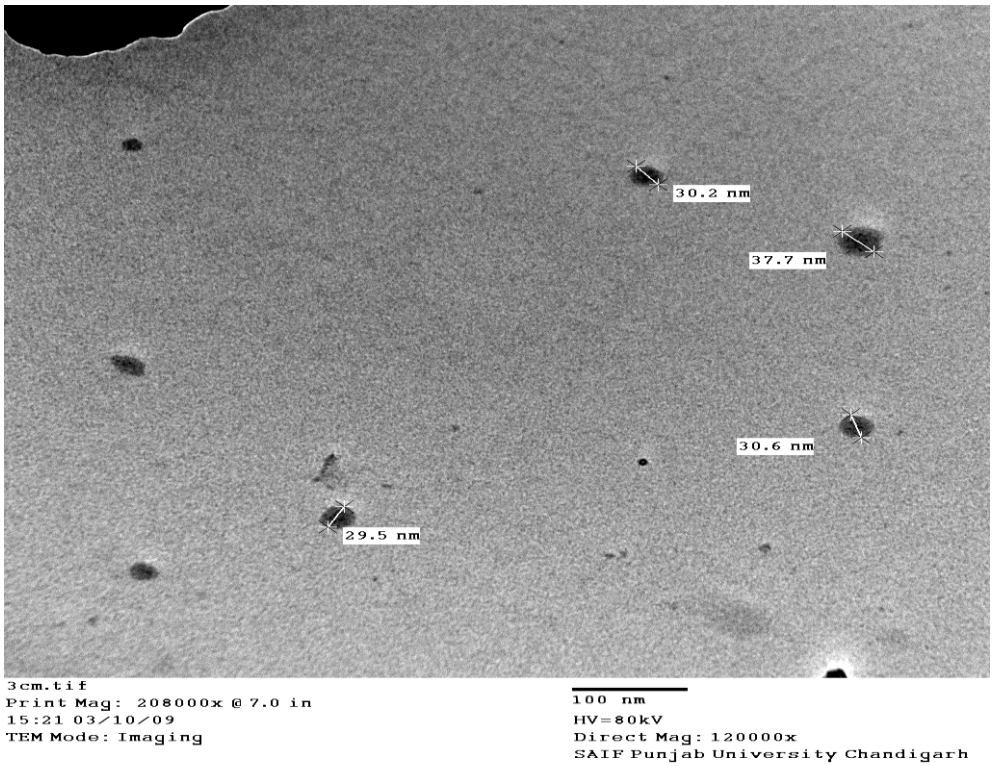

Figure 5. TEM micrograph of CdO quantum dots irradiated with a fluence of $1* 10^{13}$ ions/cm^2

Conclusion

Cadmium oxide (CdO) quantum dots/nanoparticles prepared by quenching method exihibit NaCl cubic structure. The addition of ethylenediamine converts nanoparticles into nanorods. The carbon ion beam irraditation results in the intense local heating and agglomeration of quantum dots; resulting in the enhancement of mean diameter of CdO nanoparticles. This property of CdO quantum dots/nanoparticles needs to be exploited in its industrial applications.

Acknowledgements

The authors wish to express their gratitude to the Principal DAV Institute of Engineering & Technology, Jalandhar and DAV College Managing Committee, New Delhi for providing research grants for setting up Research Centre and Nanotechnology Laboratory in Jalandhar. They are thankful to Dr Navjeet Sharma and Dr. Rajeev Sharma of DAV College, Jalandhar for his help in irradiation experiment at IUAC, New Delhi.

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