Effect of surfactant-free addition and \( \gamma \)-irradiation on the synthesis of CdO quantum dots by thermal decomposition of \( \gamma \)-irradiated anhydrous cadmium acetate

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Effect of surfactant-free addition and γ-irradiation on the synthesis of CdO quantum dots by thermal decomposition of γ-irradiated anhydrous cadmium acetate

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Abstract: Pure phase of cubic (FCC) CdO quantum dots were successfully synthesized by thermal oxidation of γ-irradiated anhydrous cadmium acetate at 400°C for three hours in the presence and absence of benzyl alcohol as surfactant-free. Morphological and structural characteristic of the as-synthesized quantum dots were performed with X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). SEM image of CdO quantum dots synthesized using γ-irradiated anhydrous cadmium acetate with 102 kGy absorbed dose shows the formation of the mesoporous nanostructure. In the presence of benzyl alcohol surfactant, the calcination process afforded cauliflower-like structure. TEM image of CdO quantum dots synthesized using γ-irradiated anhydrous cadmium acetate in presence of benzyl alcohol surfactant shows formation of nanoribbon of CdO quantum dots.

1. Introduction
Cadmium oxide nanoparticles can potentially be applied to optoelectronics and other applications including solar cells, phototransistors, gas sensors, photodiodes, and transparent electrodes

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Refaat M. Mahfouz is now a professor of Materials Science and Nuclear Chemistry at the Faculty of Science, Assiut University, Egypt. He got his BSc, MSc, and PhD degrees from Assiut University, Egypt. He got more than one fellowship to work as guest scientist at a nuclear research centre, Juelich, Germany in the period from 1086 to 1990. He has more than 110 publications in ISI scientific journals in the field of radiochemistry and materials sciences and one patent.

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PUBLIC INTEREST STATEMENT
This paper describes the utilization of gamma rays to produce nanostructured materials of uniform morphology. Irradiating the precursor prior to the calcination process could lead to significant changes in the size, shape, and morphology of the metal oxide nanoparticles. The addition of surfactant-free has also another effect on the morphology of nanoparticles. We hope this study opens new approach in the synthesis of metal oxides nanoparticles with controlled size, shape, and morphology.
Different chemical methods have been reported for the synthesis of nanostructured CdO, like sol-gel (Dong & Zhu, 2003), spray pyrolysis (Manickathai, Viswanathan, & Alagar, 2008), pulsed laser deposition (Askarinejad & Morsali, 2009), hydrothermal (Ghosh & Rao, 2014), and solvothermal methods (Yang, Siu, Zhang, & Yang, 2004).

Radiation-induced synthesis of nanostructured materials plays an important role in the investigation and production of well-shaped and mono-dispersed nanoparticles. Methods based on the interaction of high energy-charged particles, and γ-ray is widely used in making ion-track membranes, polymeric nanocomposites, and metal oxide nanoparticles. Irradiation effects on the preparation of CdO nanoparticles were scanty reported (Veeraputhiran, Gomathinayagam, Udhaya, Francy, & Kathrunnisa, 2015).

In the present work, we describe the synthesis of CdO nanoparticles by thermal oxidation of anhydrous cadmium acetate. Factors including a surfactant-free addition and γ-irradiation of cadmium acetate precursor were thoroughly investigated in order to shed more light on the role of γ-irradiation and surfactant-free addition on the morphology, shape, and size of the as-synthesized nanoparticles.

2. Experimental

2.1. Synthesis of CdO nanoparticles

Anhydrous cadmium acetate (CdAc), 99.93% (metal basis), and anhydrous benzyl alcohol, 99.8% were purchased from Sigma-Aldrich and used without any further purification.

Two samples of anhydrous cadmium acetate were prepared for the experiment. The first sample contains 0.1 mole of γ-irradiated cadmium acetate, the second one contains 0.1 mole of γ-irradiated cadmium acetate and 2 mL of anhydrous benzyl alcohol. The two samples were encapsulated into two separate glass Pyrex cells and allowed to stand in a muffle furnace. The temperature was raised at a heating rate of 10°C min\(^{-1}\)–400°C and kept constant for three hours. The reaction took place under the autogenic pressure of the encapsulated materials. At the end of the reaction, the containers were gradually cooled (5 h) to room temperature, and after opening, the obtained nanoparticles were collected in clean and dry containers and subjected to characterization.

We will refer to the calcination using γ-irradiated precursor only as a method (a), and the calcination using γ-irradiated precursor in the presence of benzyl alcohol surfactant as a method (b). It should be mentioned that a trial to prepare CdO nanoparticles by thermal decomposition of un-irradiated cadmium acetate under the experimental conditions mentioned above afford microcrystalline plates of cadmium oxide. Further investigation of this product by TEM investigation indicated that the obtained material is not in nano-scale range.

2.2. Characterization

X-ray powder diffraction patterns (XRD) were recorded on Siemens D 5,000 X-ray diffractometer with CuK\(\alpha\) radiation (\(\lambda = 1.54\) Å). TG measurements were recorded on Perkin-Elmer TG A7 thermogravimetric analyzer in the temperature range of 30–1,000°C. The sample weight was 10.0 ± 0.1 mg with a heating rate of 10°C min\(^{-1}\). FT-IR measurements were recorded as KBr pellets in the range of 200–4,000 cm\(^{-1}\) on Perkin-Elmer FT-IR spectrophotometer (spectrum 1,000). SEM and TEM images were captured using the models (SEM, JSM-6360 ASEM, JEOL, Japan) and (TEM, JEM-2100F, JEOL, Japan) electron microscopes.
For irradiation, samples were encapsulated under vacuum in glass vials and exposed to successively increasing doses of radiation at a constant intensity. A Co-60 $\gamma$-ray source model gamma cell 220 from MDS (Nordion, Canada) was used for irradiation of the samples. The source was calibrated against a Fricke ferrous sulfate dosimeter and the absorbed doses in the irradiated samples were calculated by applying appropriate corrections on the basis of photon mass attenuation and the energy absorption coefficients for the sample and the dosimeter solutions (Spinks & Woods, 1990). The transient dose was estimated to be 12.07 Gy and the dose rate was 9.83 kGy h$^{-1}$. All of the irradiations were conducted at 25°C. After irradiation, the samples were stored at room temperature for 24 h before analysis.

3. Results and discussion

Figures 1 and 2 show XRD patterns of CdO nanoparticles synthesized by methods (a) and (b), respectively. The sharp and well-defined peaks indicate the crystalline nature of the as-synthesized CdO. The $2\theta$ values of 32.90°, 38.20°, 55.20°, 65.30°, and 69.30° are indexed, respectively, as the (111), (200), (311), (220), and (222) crystal planes and correspond to the (FCC) cubic structure of CdO with a lattice parameter $a = 4.693$ Å (JCPDS-05-0640). No foreign lines from impurities were detected indicating that the obtained CdO was pure phase. The (1 1 1) plane was also selected to calculate size of the obtained CdO nanoparticles using the following Debye–Sherrer’s formula

$$D = \frac{0.89 \lambda}{\beta \cos \theta_B}$$

where $D$ is the average size of the crystallite, assuming that the grains are spherical, $\lambda$ is the wavelength (in Å), $\beta$ is the broadening of the diffraction peak (in radians) of full width at the half maximum (FWHM), and $\theta_B$ is the Bragg diffraction angle. The calculated average particle size of CdO nanoparticles was found in the range of 2–3 nm indicating quantum dots morphology of the as-synthesized CdO product.
Figure 2. XRD patterns of as-synthesized CdO nanoparticles obtained by calcination of \(\gamma\)-irradiated cadmium acetate for three hours at 400\(^\circ\)C in presence of benzyl alcohol as surfactant-free.

Figure 3. SEM images of CdO nanoparticles synthesized by method (a). The image displays the formation of the mesoporous structure of CdO nanoparticles.

For the method (b) The SEM image, Figure 4 displays the formation of cauliflower-like mesoporous structure of CdO.

The TEM image, Figure 5 shows the formation of dark spots of tiny nanostructured grains of CdO quantum dots obtained by method (a). The nanocrystalline grains were single crystalline in nature with an average size in the range of 2.5 nm.

The TEM image, Figure 6 shows the formation of nanoribbon of CdO quantum dots of average size 2–3 nm synthesized by method (b).
FT-IR spectrum of CdO quantum dots synthesized by method (a) is shown in Figure 7. The spectrum exhibits stretching broad band around 3,422 cm$^{-1}$ attributed to adsorbed water ($\nu_{OH}$). The formation of CdO phase was characterized by a very broad IR band in the range of 400–1,000 cm$^{-1}$. This result gave further evidence for the formation of CdO quantum dots (Askarinejad & Morsali 2008). No
significant change in the IR spectra of the as-synthesized CdO nanoparticles was obtained as a result of the surfactant-free addition. Therefore, only one FT-IR spectrum is displayed for representation.

4. Role of irradiation
In solid sample the radiation effect is dominated by direct ionization of the material, where's for aqueous solutions the reaction with radical species, such as OH• or solvated electrons is dominate mechanism for damage to a solute.

Upon irradiation with Co-60 γ-ray source, Compton scattering is the main mode of interaction of the γ-ray with Cd and O atoms and multiple indirect ionization occurs. These events create electron–hole pairs, lattice imperfection, and extended defects. These defects lead to the creation of specific damage in the host lattice of CdO crystal and may be responsible for the formation of CdO quantum dots.

In the presence of benzyl alcohol, the trapped electrons in the host lattice of cadmium acetate may react with surfactant molecule to create another source of point and line defects in cadmium acetate crystal due to the damage of benzyl alcohol on the surface of new phase formed by CdO nanoparticles as a result of λ-irradiation. This damage may increase the rate of nucleation of the nanoparticles to give another impact on the morphologies and shapes of the as-synthesized quantum dots (West, 1999).

5. Conclusion
This study reports the synthesis of CdO quantum dots of high purity by thermal decomposition of γ-irradiated anhydrous cadmium acetate precursor. Calcination of precursor irradiated with 10^2 kGy absorbed dose at 400°C for three hours led to the formation of the mesoporous structure of CdO quantum dots. In the presence of surfactant-free as benzyl alcohol, the calcination afforded nanoribbon of CdO quantum dots and cauliflower-like structure. The interaction of γ-ray with matter lead to the formation of the lattice imperfections (ion pairs, ion defects, and extended defects) responsible for the formation of CdO quantum dots as result of the radiation damage induced by these defects in host lattice of cadmium acetate precursor.
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