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Synthesis of cadmium(II) hydroxide, cadmium(II) carbonate and cadmium(II) oxide nanoparticles; investigation of intermediate products

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ABSTRACT

Sonochemical and hydrothermal routes have been used in different conditions for preparation of $CdCO_3$ and $Cd(OH)_2$ nanoparticles at air and inert atmospheres, respectively. The CdO nanoparticles were obtained by heating of $CdCO_3$ and $Cd(OH)_2$ nanoparticles at 400 °C. Powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) microscopy have been used to characterize the nanoparticles. The XRD results of intermediate products showed that the origin of $CdCO_3$ is CO_2 from air atmosphere.

1. Introduction

CdO is one of the most important transparent conducting oxides (TCO) used to fabricate photovoltaic (PV) solar cells [1]. CdO is an n type semiconductor, with a well-established direct band gap at approximately 2.5 eV, and has found various applications such as its use in solar cells, as transparent electrodes, as photodiodes, and in sensors [2–4]. The nanoparticles of CdO if used for such applications are expected to play a major role in further improving the optical and electrical properties.

There have been some efforts for preparation of CdO nanoparticles with different methods such as, solvothermal synthesis [5,6], sol–gel [7], microemulsion method [8], precipitation method [9] etc. [10–12]. Recently, sonochemical synthesis, an alternative means to the general synthetic methods, has been used in the preparation of many materials. Ultrasound induces chemical changes due to cavitations phenomena involving the formation, growth, and instantaneously implosive collapse of bubbles in liquid, which can generate local hot spots having a temperature of roughly 5000 °C, pressures of about 500 atm, and a lifetime of a few microseconds [10]. These extreme conditions can drive chemical reactions such as oxidation, reduction, dissolution, and decomposition, which have been developed to fabricate a variety of metal, oxide, sulfide, and carbide nanoparticles [13–18].

In our previous work [19], we have reported the synthesis of $CdCO_3$ nanoparticles *via* sonochemical route in the air atmosphere. In a recent published paper by Tang and coworkers [20], the synthesis of $CdCO_3$ by a hydrothermal process has been reported and claimed that $CdCO_3$ may be directly converted from a cadmium carboxylate precursor through a self-catalytic process. In this paper it has been suggested that carbonate ion is formed from the reaction of acetate and hydroxide ions.

In this paper, we report the synthesis of cadmium(II) hydroxide, cadmium(II) carbonate and cadmium(II) oxide nanoparticles and investigate the intermediate products by means of XRD and SEM. Our results prove that the origin of ${CO_3}^{2-}$ may not be acetate ion and CO_2 from air can be responsible for forming $CdCO_3$.

2. Experimental

In the sonochemical route 50 ml $Cd(CH_3COO)_2$ (0.1 M) was titrated with 100 ml TMAH or NaOH (0.1 M) in an ultrasonic bath. Some of the reactions were performed in air atmosphere and in other ones the reaction vessels were purged with CO_2 or argon. The obtained nanopowders were calcinated to 400 °C to recrystallize to CdO nanoparticles.

In the hydrothermal procedure, 50 ml $Cd(CH_3COO)_2$ (0.1 M) and 100 ml NaOH (0.1 M) were dissolved in a mixture of H_2O and EtOH. The solution was charged into a Teflon-lined stainless steel autoclave and heated at 150 °C for 24 h. Then the autoclave has been cooled to room temperature, the product has been filtered, dried, and characterized. The obtained nanopowders were calcinated to 400 °C to recrystallize to CdO nanoparticles.

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Table 1
Different conditions of reactions for preparation of CdO nanostructures.

Reaction number	Initial materials	Atmosphere	Solvent	Product before calcination	Method
1	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml TMAH (0.1 M)	Air	EtOH	$CdCO_3$	Sonochemical
2	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml TMAH (0.1 M)	Argon	EtOH	$Cd(OH)_2$	Sonochemical
3	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Argon	EtOH	$Cd(OH)_2$	Sonochemical
4	50 ml $Cd(NO_3)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Air	EtOH	$Cd(OH)_2 + CdCO_3$	Sonochemical
5	50 ml $Cd(CH_3COO)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Argon	EtOH + H_2O	$Cd(OH)_2 + Cd_3(OH)_5(NO_3)$	Hydrothermal
6	50 ml $Cd(NO_3)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	CO_2	EtOH	$CdCO_3$	Sonochemical
7	50 ml $Cd(CH_3COO)_2$ or $Cd(NO_3)_2$ (0.1 M) + 100 ml NaOH (0.1 M)	Air	EtOH + H_2O	$CdCO_3$	Simple titration

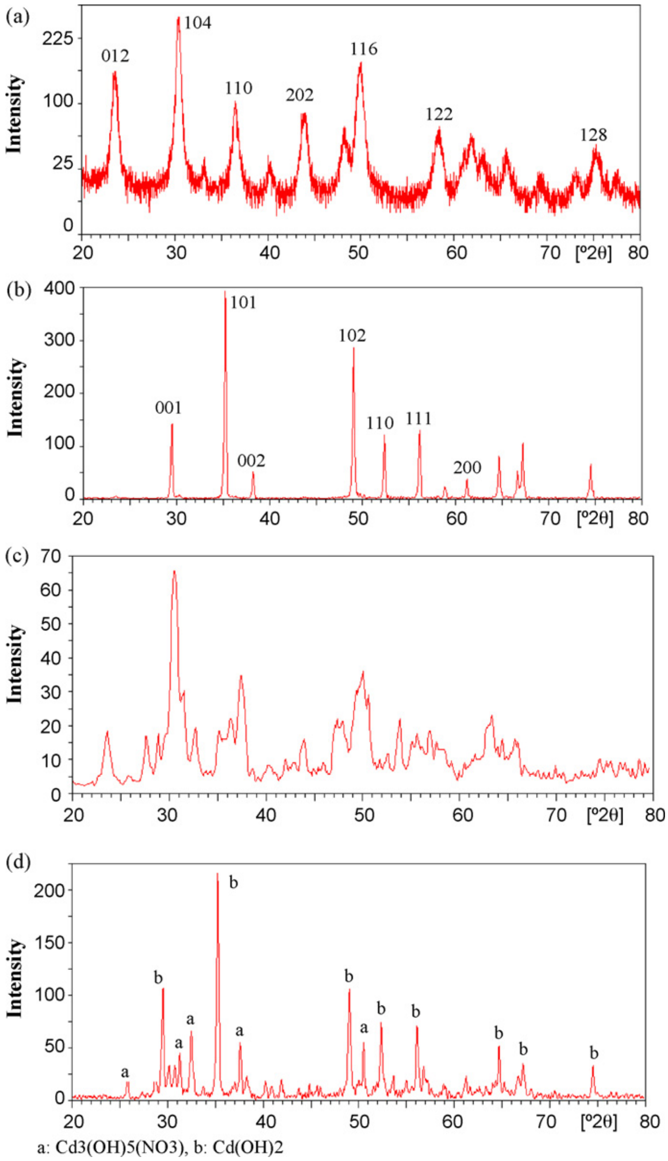


Fig. 1. The XRD pattern of (a) $CdCO_3$ nanoparticles of sample no. 1, (b) $Cd(OH)_2$ nanoparticles of sample no. 2, (c) a mix of $CdCO_3$ and $Cd(OH)_2$ nanoparticles of sample no. 4 and (d) a mix of $Cd(OH)_2$ and $Cd_3(OH)_5(NO_3)$ nanoparticles of sample no. 5.

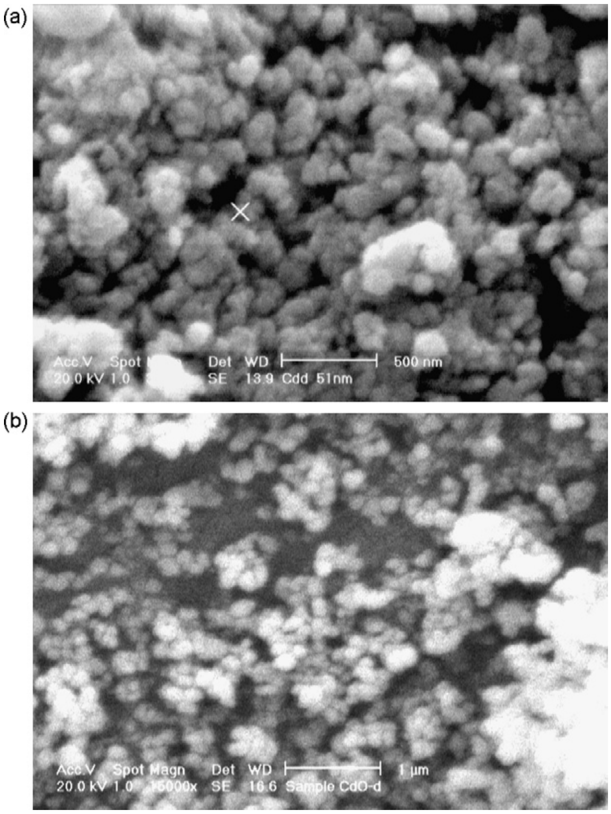


Fig. 2. The SEM image of (a) the intermediate product ($Cd(OH)_2 + CdCO_3$ nanoparticles) and (b) CdO nanoparticles obtained by calcination of the intermediate product (reaction no. 4).

$$Cd^{2+} + 4\,NH_3 \rightleftharpoons [\,Cd\,(NH_3)_4\,]^{2+} \qquad (1)$$

$$CH_3COO^- + OH^- \longrightarrow CH_4\uparrow + CO_3^{2-} \qquad (2)$$

$$Cd^{2+} + CO_3^{2-} \rightleftharpoons CdCO_3\downarrow \qquad (3)$$

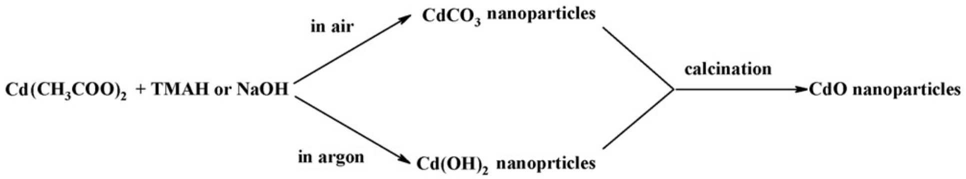
Scheme 1.

$$Cd(CH_3COO)_2 \xrightleftharpoons{\text{Solvent}} Cd^{2+} + 2\,CH_3COO^- \qquad (1)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (2)$$

$$Cd^{2+} + CO_3^{2-} \longrightarrow CdCO_3 \qquad (3)$$

Scheme 2.



Scheme 3.

X-ray powder diffraction (XRD) measurements have been performed using a Philips diffractometer of X'pert Company with mono chromatized CuK$_\alpha$ radiation. The samples have been characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating.

3. Results and discussion

In our new report [19], we have reported the synthesis of $CdCO_3$ and CdO nanoparticles from reaction of $Cd(CH_3COO)_2$ and tetramethylammonium hydroxide (TMAH) or NaOH by a sonochemical method under different conditions. In this work, we have done further experiments by using sonochemical and hydrothermal routes to investigate the mechanism of $CdCO_3$ preparation. Table 1 shows the reactions and their conditions which were performed. In the reaction no. 1, cadmium acetate and TMAH have been used as precursors and the reaction was performed in air atmosphere. As it can be observed from the XRD pattern (Fig. 1a), the obtained product is cadmium carbonate. In the reaction no. 2, the conditions are the same as reaction no. 1 and the only difference is the atmosphere in which the reaction is performed. In this case the reaction was performed under argon atmosphere and the obtained product is cadmium hydroxide (Fig. 1b) with a hexagonal crystal structure and lattice parameters of $a = 3.4947$, $c = 4.7106$, $z = 1$ and space group = $P3m1$ (JCPDS card number 31-0228). In the reaction no. 3, NaOH has been used instead of TMAH and the result is the same as the reaction no. 2. In the reaction no. 4 $Cd(NO_3)_2$ was used as precursor and the reaction was performed in air atmosphere and the XRD pattern of the obtained product shows a mixture of $Cd(OH)_2$ and $CdCO_3$ (Fig. 1c). Sample no. 5 is obtained by a hydrothermal method and characterized as a mixture of $Cd(OH)_2$ and $Cd_3(OH)_5(NO_3)$ (Fig. 1d). In the reaction no. 6, CO_2 is purged to the reaction of $Cd(NO_3)_2$ and NaOH in an ultrasonic bath, the product obtained by this procedure is $CdCO_3$.

In all the reactions, the CdO nanoparticles are the result of calcinations at 400 °C. Fig. 2a shows the SEM image of the intermediate product and Fig. 2b shows the SEM image of CdO nanoparticles of the reaction no. 4.

In the recent article [20], the authors have reported the synthesis of $CdCO_3$ by a hydrothermal process and claimed that $CdCO_3$ may be directly converted from a cadmium carboxylate precursor through a self-catalytic process, and they suggested that this reaction is performed *via* the following mechanism (Scheme 1).

In a recent report by Han and coworkers [21], a simple top-down method by purging carbon dioxide to the reaction of cadmium foil and formamide has been used to produce cadmium(II) carbonate microcrystals, which is requisite for fabricating porous cadmium oxide nanoarchitectures. In this work, cadmium nitrate aqueous solution has been used as precursor and is aerated with carbon dioxide to form cadmium carbonate nanocrystals. The mechanism of $CdCO_3$ formation is similar to our work.

Our proposed mechanism for producing $CdCO_3$ nanoparticles can be seen in Scheme 2.

The result obtaining from the performing reactions has been summarized in Scheme 3.

As it can be seen in Scheme 3, the intermediate product of the reaction of cadmium acetate and TMAH or NaOH is cadmium carbonate nanoparticles in air atmosphere and in the existence of carbon dioxide [19], and cadmium hydroxide nanoparticles in inert atmosphere.

4. Conclusion

In summary, a simple sonochemical route and a hydrothermal route by modifying the different parameters have been used to successful synthesis of CdO nanoparticles. Different intermediates have been obtained by using different precursors, different methods and different atmospheres. The obtained products have been analyzed by means of SEM and XRD. The XRD results showed that $CdCO_3$ and $Cd(OH)_2$ nanoparticles were obtained in air and inert atmospheres, respectively. Based on our results in this work and reactions with different conditions at both air and inert atmospheres, it is proved that actually the $CO_3{}^{2-}$ anions may not be originated from decomposition of acetate anions. If this mechanism was correct, it must be formed at argon atmosphere with same conditions. In addition, $CdCO_3$ has been formed when the reaction has been done without using any acetate anion (reaction no. 4). Meanwhile $CdCO_3$ has been produced *via* a simple titration by the reaction of cadmium acetate or nitrate with sodium hydroxide (reaction no. 7). Therefore, it is suggested that the origin of $CO_3{}^{2-}$ is not acetate and it is actually from CO_2 of air atmosphere.

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