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Research Article

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Synthesis and Characterization of Cdo Nanoparticles Prepared via Chemical Precipitation and Sol-Gel Techniques

Xinming Yu, Meng Zhao, Pingfang Han*, Xiaoping Lv

College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 210009, PR China

Abstract In this paper, two kinds of preparation methods were used to synthesize CdO nanoparticles. NaOH and citric acid were severally mixed with cadmium nitrate to produce the nanocatalyst via precipitation and sol-gel auto-combustion method respectively. The reactants were either ultrasonicated or mechanically shear-mixed for comparison. And the synthesised samples were characterized for their size and structure using X-Ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. And some molecular groups containing in the nanoparticle were detected by Fourier transformer Infra Red (FT-IR).The result revealed that the catalyst prepared by precipitation method under ultrasonic irradiation possesses the better surface characteristics and optical property, which means that theoretically it will shows great photocatalytic properties in the chemical reaction.

Keywords CdO, ultrasound, chemical precipitation, sol-gel, characterization

1. Introduction

Nanotechnology serves as an emerging science and technology with powerful market potentials which has received great interest for both industrial and academic applications [1-2]. This kind of material is different from those of conventional bulk materials [3-4] due to it could improve the overall performances of the polymeric materials [5]. These materials can be used for all sorts of application by tuning their properties through modifying the particle size and shape, suitable substitution and formation of different compositions [6]. The special properties such as small size, large specific area, strong interfacial interaction [7] could increase the surface of the active position making it possible to prepare nano-catalyst. Ultrasound is defined as a sound wave with a frequency above 20 kHz and it has advantage of good directivity, strong penetrating power and getting sound power intensively and easily which is widely applied to industrial, agricultural, military affairs and medical science [8-9]. For the ultrasonic-assisted technique, the ultrasound wave generates violent vibration and strike of the liquid particles which plays an important part in agitation and accelerating the chemical reaction with the cavitation phenomenon [10]. Cadmium oxide (CdO) is one of the promising semiconducting material with the electrical resistivity in the order of 10^{-2}-10^{-4}Ωcm [11-12]. In addition, it has a wide direct band gap of ~2.6 eV and a narrow indirect band gap of ~0.5 eV and exhibits an n-type conduction [13] along with the corresponding absorption wavelength is 500nm [14]. Based on these properties, CdO is often applied to sensors [15-17], solar cells [18-19], nonlinear optics [20], optoelectronic devices [21-22] and catalysts [23]. Nowadays, CdO nanocatalyst is prepared via various techniques such as sol-gel method [24], chemical coprecipitation method [25], thermal decomposition [26], hydrothermal method [27-28], thermal evaporation [29] and spray route [30].

In this paper, we have prepared CdO nanoparticles by precipitation and sol-gel auto-combustion techniques respectively with or without ultrasound for comparison. And then the structural and morphological properties were carried out by XRD, FT-IR and SEM.

2. Experimental

2.1. Sample preparation

Precipitation method (catalyst A): 0.1mol solution of Cd $(NO_3)_2 \cdot 4H_2O$ is dissolved using distilled water at 60^oC aiming to accelerate the dissolution of the cadmium salt. The aqueous solution of NaOH (0.5mol) is afterward added to the cadmium solution and then, the mixture is stirred with a magnetic stirrer or ultrasonic wave (H061 Ultrasonic processor, 20KHz, 150W) assisted respectively for some time. A cloud of suspended solids is immediately observed which indicates the formation of the Cd-hydroxide particles. The stirring is afterward stopped, and an increasing number of hydroxide particles are slowly to generate that is allowed to precipitate at the bottom of the beaker. The precipitate is filtered on a Buchner funnel and then washed with distilled water several times repeatedly. The obtained cadmium hydroxide is dried in an oven for 8 hours at 120 ^oC and finally, the hydroxide particles are converted to cadmium oxide in muffle furnace for 4hours at 500^oC.

Sol-gel method (catalyst B): CdO nanocrystals are synthesized by the similar method as reported in these papers [5-6]. $Cd(NO_3)_2 \cdot 4H_2O$ and $C_6H_8O_7 \cdot H_2O$ are mixed together according to special molar ratio(about 2:1) in a minimum amount of distilled water to get a clear solution. Then the ammonia solution is slowly added to adjust the pH at about 8.5. The mixed solution is stirred with a magnetic stirrer or ultrasound (Same as the above ultrasonic treatment conditions) assisted continuously at 80^oC. As the brine dries, the sol becomes viscous gradually and finally converts into gel. The obtained gel is aged for 18h at 70^oC and after that it is calcined at 500^oC for 4h to obtain CdO nanoparticles.

2.2. Characterization

The brown colored nano CdO is characterized for its phase purity, lattice parameter and average grain size by X-ray Diffraction (XRD) which is performed by a Bruker-ACS, D8 Advance model using Cu K_α radiation in the 2theta ranging from 20^o to 80^o.The crystallite size is calculated from FWHM（full width at half maximum）using the Scherrer equation [31]. Fourier transformer Infra Red (FT-IR) spectra (ranging from 4000 cm^{-1} to 400 cm^{-1}) is used to identify structure, purity and chemical groups and analyze chemical group quantitatively. The morphology and size of the particles are characterized by scanning electron microscope (SEM) under the acceleration voltage of 10 kV.

3. Results and Discussion

The structural, morphological and surface characteristics of catalysts prepared by two different methods are discussed throughout this section. The contrast between ultrasonic wave aided method and mechanical stirring method are also illustrated.

3.1. X-ray diffraction (XRD) analysis

The structural characterization of synthesized CdO nanoparticles from the X-ray diffraction data XRD are shown in Figure 1a-d. The peaks at 2θ values of 33.1^o, 38.3^o, 55.3^o, 65.9^o, and 69.3^o for catalyst A and 33.0^o, 38.5^o, 55.3^o, 65.9^o and 69.2^o for catalyst B are matching with the (110), (200), (220), (311), and (222) plans, respectively (Joint Committee for Powder Diffraction Studies (JCPDS) File No. 05-0640).The sharp peaks can be clearly seen from the figures which indicates that the prepared samples show excellent crystallinity and high purity and there being no secondary phase. The crystallite size (D) of the CdO nanoparticles are determined by using the well-known Scherer's formula, $D = 0.89\lambda / (B \cdot Cos\theta)$, where B is the FWHM, θ is the bragg angle for the most intense peak(111) and ƛ is constant. The surface characteristics of catalyst A and B are listed in Table 1. It shows that these prepared catalysts are almost classed as mesoporous materials which have advantages in adsorption, separation and catalytic reaction. The partical size of catalyst B is approximately43% higher than that of catalyst A which means

that the surface area of catalyst B is lower than that of catalyst A. The result proves that the precipitation method can control the particle diameter size and distribution to a high degree of effect, but by contrast, the catalyst prepared by sol-gel possess large volume shrinkage in desiccation and calcination stages, which usually results in agglomeration phenomenon between the nanoparticles. On the other hand, the surface area of catalysts without the assist of ultrasound is lower than that of with the assist of ultrasound. In general, the catalysts with the higher surface area could provide better catalytic activity and play more important role in absorbing radiation.

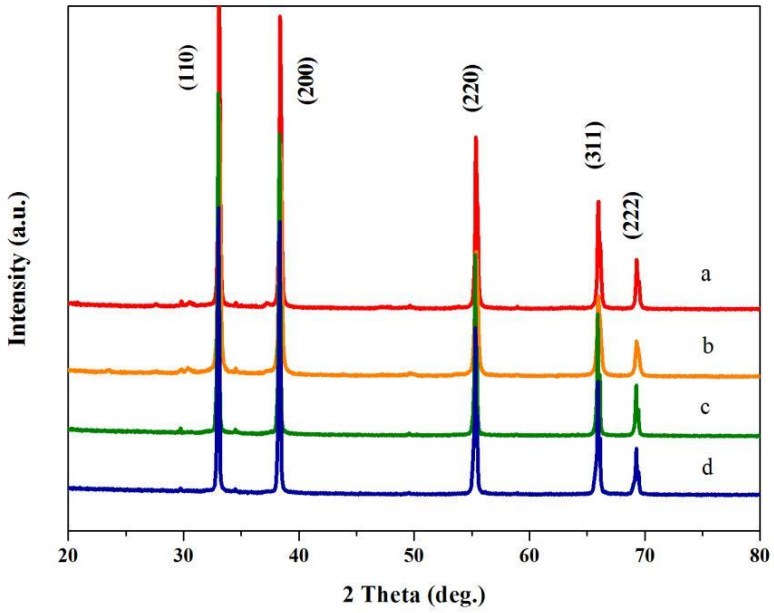


Figure 1: XRD patterns of CdO: (a) catalyst A with ultrasound; (b) catalyst A without ultrasound;(c) catalyst B with ultrasound; (d) catalyst B without ultrasound

Table 1: Particle size (D) of CdO

Sample	Type	D (nm)
CdO	Catalyst A with ultrasonic	33.6
	Catalyst A without ultrasonic	40.2
	Catalyst B with ultrasonic	50.2
	Catalyst B without ultrasonic	55.3

3.2. FT-IR spectroscopy analysis

The FT-IR spectra of the nanophase materials in Figure 2a and Figure 2b have been recorded at wave numbers ranging from 4000–400 cm^{-1}. There are strong and sharp peaks of stretching vibrations of structural OH groups in the wavenumber of 3587 cm^{-1}, 3245 cm^{-1} and 3460 cm^{-1}, respectively [32-33]. The weak peak at 2920 cm^{-1} can be associated with C-H. In fact, the small band at 1637 is attributed to free H_2O molecules resulting from tableting process. The absorption peaks at 1381 cm^{-1}, 698 cm^{-1} according to Figure 2a and 1400 cm^{-1}, 1047 cm^{-1} on the basis of Figure 2b are assigned to C-O [34]. The peaks observed around 450 cm^{-1} in Figure 2a and about 480 cm^{-1} in Figure 2b are related to CdO [35] which confirms the formation of the pure catalyst. The products are all discovered from these chromatograms and the peaks of sample prepared under ultrasonic wave are significantly sharper stronger.

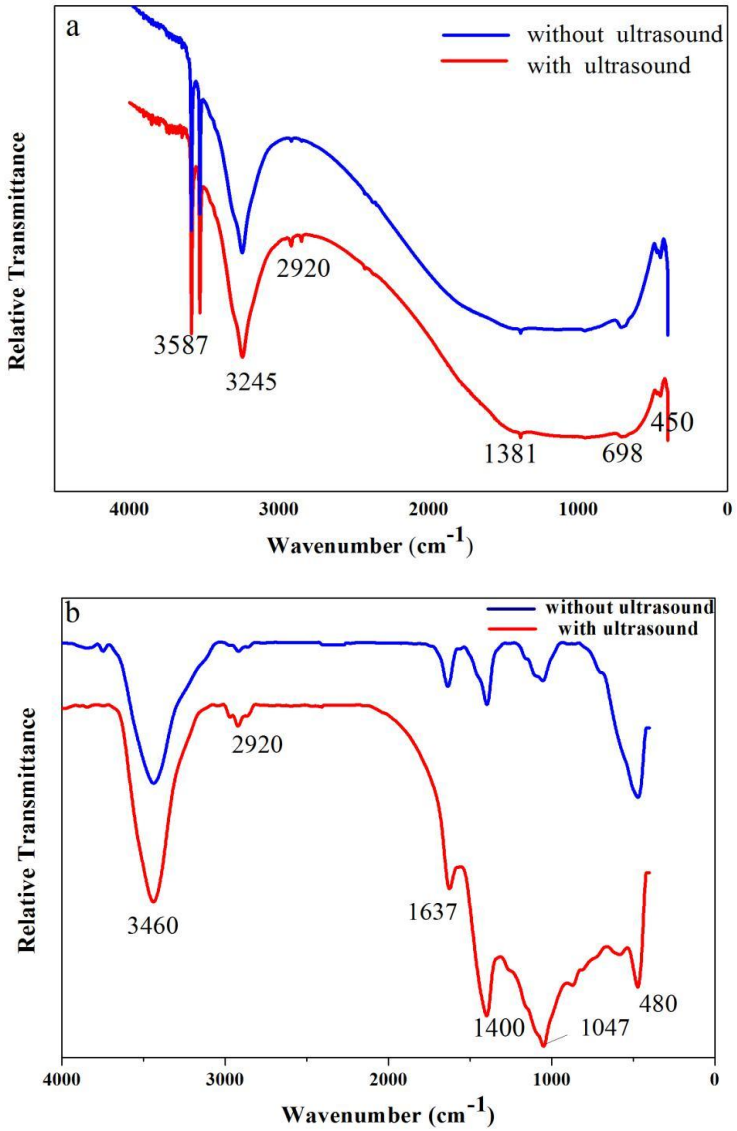
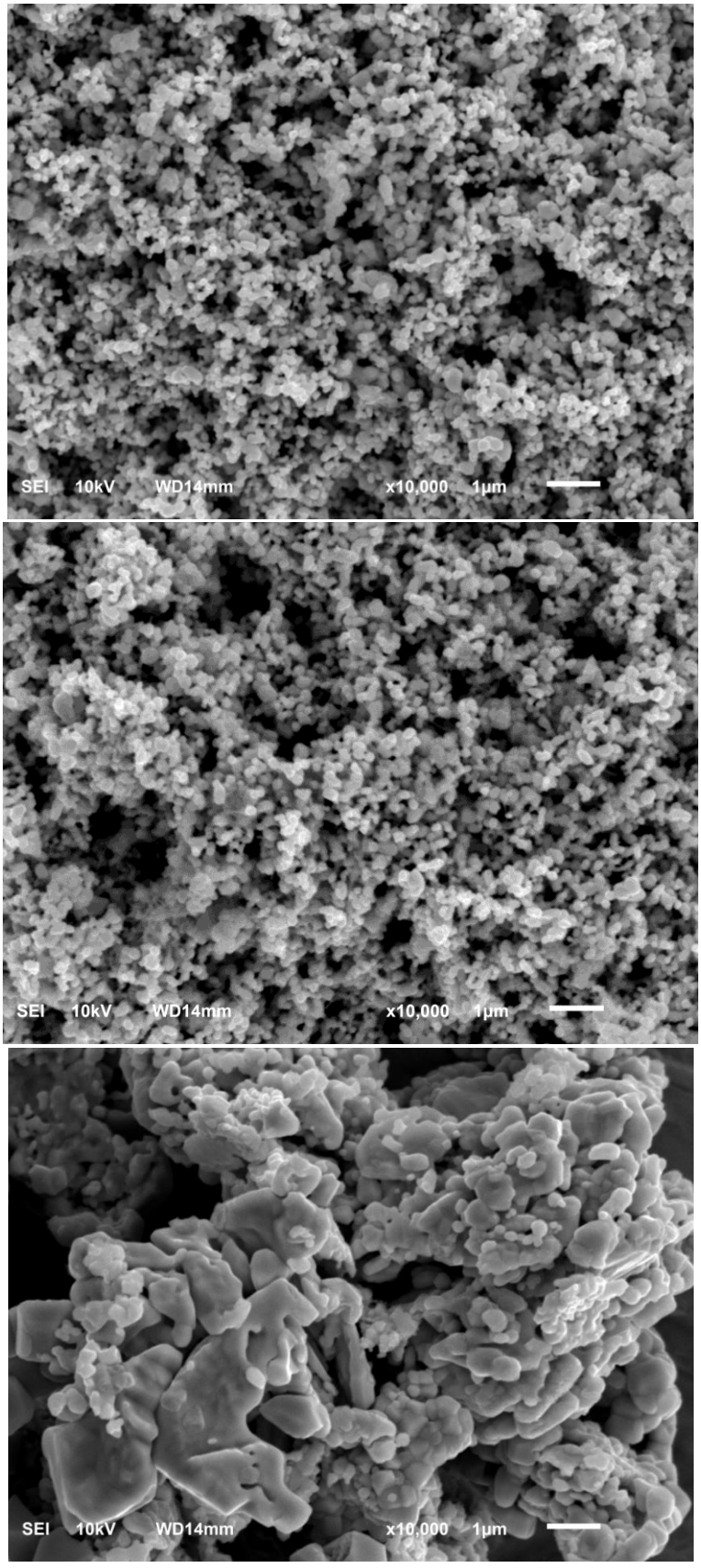


Figure 2: FT-IR patterns of CdO: (a) catalyst A; (b) catalyst B

3.3. Morphological structure studies

The surface morphology of the prepared catalyst carried out using SEM was shown in Figure 3a-d. From Fig.3, it can be seen that the particle size of catalyst B is larger than that of catalyst A, which because of the serious agglomeration phenomenon of the crystallites. On the contrary, the grain size of catalyst A is relatively small and the grains are uniformly and smoothly distributed and it turns out that this material is much easier to contact the reactants uniformly. And the size of the particles can be read roughly through the scale, which means that this characterization can be intuitively verified the XRD data obtained by Scherer' s equation. Moreover, the partical size of catalyst A ultrasonically assisted is smaller than that without ultrasonic which possibly because that the ultrasonic dispersion effect can prevent nanoparticles aggregation effectively through weakening nanoaction. Therefore, this sample has large contact area with reactant and exhibits more excellent catalytic properties, according to general catalyst mass transfer and reaction theory.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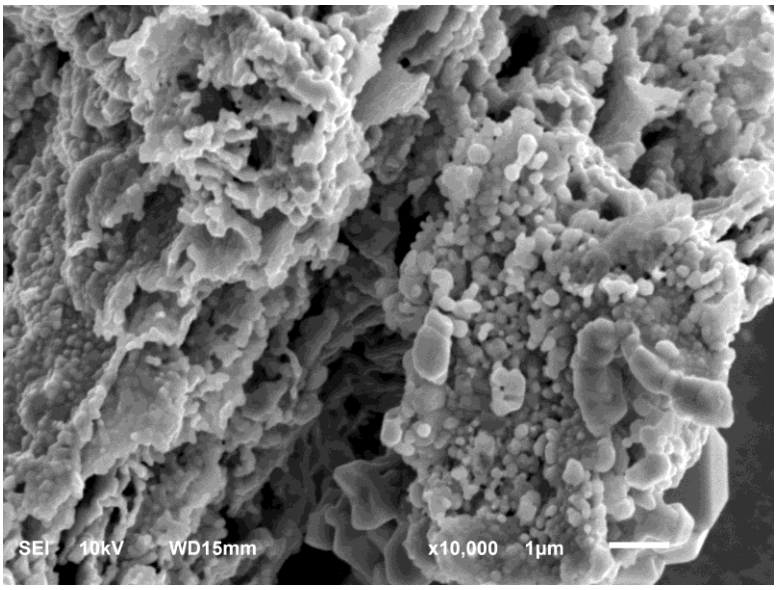

Figure 3: SEM patterns of CdO: (a) catalyst A with ultrasound; (b) catalyst A without ultrasound; (c) catalyst B with ultrasound; (d) catalyst B without ultrasound

4. Conclusion

In this paper, CdO nanocrystals are synthesized successfully by chemical precipitation and sol-gel techniques with the assist of mechanical agitation and ultrasonic wave severally. The results of the FT-IR and XRD analyses prove that all the samples obtained by precipitation method and sol-gel method are pure and of good crystallinity and the size of the catalysts can be in the range of 33–56nm. Besides, the SEM micrographs illustrate that the resulting catalysts are granular nano-scale particles which in turn verifies the characterization results above. Overall, the catalyst prepared by chemical precipitation method with the assistance of ultrasound shows the best morphological structure than others under the same conditions. The particle size of this sample is about 33.6nm that is smaller than three other samples (40.2-55.3nm) and the particles are arranged neatly and distributed evenly. Moreover, this sample possesses better light absorption efficiency due to the position of its absorption wavelength. It predicates that this kind of catalyst can be contacted to the reactants adequately and be full use of light in the photocatalytic reaction which will promote the progress of a reaction.

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