Research Article

Characterisation of Zinc Oxide and Cadmium Oxide Nanostructures Obtained from the Low Temperature Thermal Decomposition of Inorganic Precursors

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Low temperature syntheses of zinc oxide and cadmium oxide nanoparticles are reported in this paper. The inorganic precursor complexes were prepared and characterised by hydrazine and metal analyses, infrared spectral analysis, and thermal analysis. Using appropriate annealing conditions, zinc oxide and cadmium oxide nanoparticles of average particle sizes around 13 nm and 30 nm were synthesised from the precursors by a simple thermal decomposition route. The synthesised nanoparticles were characterised for their size and structure using X-Ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and scanning electron microscopy (SEM) techniques.

1. Introduction

This century has witnessed a tremendous escalation in the field of science and technology, for which the contribution of nanotechnology is much substantial. In the past decade, nanoscale research has opened revolutionary opportunities for a wide number of technological applications. Due to their special optical, magnetic, electrical, and catalytic properties and improved physical properties like mechanical hardness, thermal stability, or chemical passivity [1], metal oxide nanostructures are extensively used as paint pigments, cosmetics, pharmaceuticals, medical diagnostics, catalysts and supports, membranes and filters, batteries and fuel cells, electronics, magnetic and optical devices, flat panel displays, biomaterials, structured materials, and protective coatings [2].

Nanostructures based on zinc oxide and cadmium oxide are particularly interesting because of their n-type conductivity with a wide band gap (3.3 eV and 2.2 eV, resp.) which makes these materials more suitable for modern technologies. ZnO and CdO have promising applications in catalysts [3, 4], gas sensors [5, 6], solar cells [7, 8], paint pigments, and so on.

There are several accepted techniques for the preparation of ZnO and CdO nanoparticles such as sol-gel method

[9, 10], microemulsion method [11, 12], precipitation method, thermal decomposition [13], hydrothermal method [14, 15], chemical coprecipitation method [16], and thermal evaporation [17]. One of the simplest methods to obtain ZnO and CdO nanoparticles is the thermal decomposition of a suitable precursor. In this context, we have attempted to synthesise ZnO and CdO nanoparticles by the thermal decomposition route from the corresponding inorganic precursor $M(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ ($M = \text{Zn}/\text{Cd}$, cin = cinnamic acid) which involves low temperature, low cost, and low time consumption.

2. Experimental

2.1. Preparation of the Precursor $M(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ ($M = \text{Zn}/\text{Cd}$, cin = Cinnamic Acid). The precursor complex was prepared by the addition of an aqueous solution (50 mL) of hydrazine hydrate (1 mL, 0.01 mol) and cinnamic acid (0.74 g and 0.055 mol) to the corresponding aqueous solution (50 mL) of metal nitrate hexahydrate (0.7437 g and 0.002 mol of zinc nitrate hexahydrate and 0.77 g, 0.002 mol of cadmium nitrate hexahydrate). The complex formed immediately was kept aside for an hour for digestion, then filtered and washed with water and alcohol followed by diethylether, and air-dried.

FIGURE 1: (a) TG-DTA curve of $\text{Zn}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$, (b) TG-DTA curve of $\text{Cd}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$.

2.2. Preparation of Metal Oxide Nanoparticles. Zinc oxide and cadmium oxide nanoparticles were obtained from the autocatalytic decomposition of their respective precursors. In this method, the dried precursor was transferred to a silica crucible and heated to red hot condition in an ordinary atmosphere for about 45 minutes. The precursor started decomposing violently. The total decomposition of the precursor complex led to the formation of the corresponding oxide nanoparticles, which are quenched to room temperature, ground well, and stored.

2.3. Quantitative Methods. The hydrazine content in the precursor was determined by titration using KIO_3 as the titrant [18]. The percentage of the metal (zinc or cadmium) in the precursor was estimated by the standard methods given in the Vogel's textbook [18] and that in the corresponding oxide was known from SEM-EDAX.

2.4. Physicochemical Techniques

2.4.1. Infrared Spectrum. The infrared spectrum of the solid precursor sample was recorded by the KBr disc technique using a Perkin Elmer 597/1650 spectrophotometer.

2.4.2. Thermal Analysis. The simultaneous TG-DTA experiment was carried out in Shimadzu DT40, Stanton 781, and STA 1500 thermal analyzers. Thermal analysis was carried out in air at the heating rate of 10°C per minute using 5–10 mg of the sample. Platinum cups were used as sample holders and alumina as reference. The temperature range was ambient to 700°C .

2.5. Characterization of Nanoparticles

2.5.1. HRTEM. The particle size of the synthesised nanoparticles was determined by high resolution transmission electron microscopy (HRTEM) operating on Hitachi Model H-800 using an accelerating voltage of 200 kV.

2.5.2. SEM. Scanning electron microscopy (SEM) was performed with a Hitachi Model S-3000H by focusing on nanoparticles to study the morphology.

2.5.3. XRD. To check phase formation and purity, XRD pattern was recorded using an X-ray diffractometer (X'per PRO model) using $\text{CuK}\alpha$ radiation, at 40 keV in the 2 θ range of 10 – 80° .

3. Results and Discussion

3.1. Chemical Formula Determination of the Precursor. The chemical formula $\text{M}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ ($\text{M} = \text{Zn}/\text{Cd}$) has been assigned to the precursor complex, based on the observed and calculated percentage values of hydrazine and the metal. The observed percentages of hydrazine (14.50) and zinc (15.00) are found to match closely with the calculated values (15.12 and 15.44) of hydrazine and zinc, respectively, proving the correctness of the determined chemical formula.

The observed percentages of hydrazine (13.70) and cadmium (23.60) are also found to match strongly with the calculated values (13.61 and 23.90) of hydrazine and cadmium, respectively, which confirms the fixed chemical formula for the corresponding precursor.

3.2. FT-IR Analysis of the Precursor. From the IR spectrum of the precursor complexes, the following are observed. The bidentate bridging nature of the hydrazine ligand in $\text{Zn}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ and $\text{Cd}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ is shown by the N–N stretching frequencies at 968 cm^{-1} and 962 cm^{-1} , respectively [19]. The $\Delta\nu$ ($\nu_{\text{asymm}} - \nu_{\text{sym}}$) separation of carboxylate groups at 194 cm^{-1} and 196 cm^{-1} indicate their monodentate linkage in both the complexes. The N–H stretching bands of N_2H_4 molecule appeared as a triplet in the region 3300 cm^{-1} in both the complexes.

3.3. Thermal Analysis of the Precursor. As can be observed from Figure 1(a), the precursor $\text{Zn}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ loses weight in three particular steps. The first step is the loss of one of the hydrazine molecules between 142 and 201°C . The corresponding peak in DTA is observed as an endotherm at 173°C . In the second step, zinc cinnamate is formed by the loss of another hydrazine molecule, which is also endothermic and observed at 219°C in DTA. The major weight loss of 80%

FIGURE 2: (a) X-ray diffraction pattern of ZnO nanoparticles, (b) X-ray diffraction pattern of CdO nanoparticles.

FIGURE 3: (a) TEM micrograph of ZnO nanoparticle, (b) TEM micrograph of CdO nanoparticles.

on the TG curve from 231 to 525°C is attributed to the third step involving the decarboxylation of the dehydrazinated precursor, which gives zinc oxide as the final residue.

From the simultaneous TG-DTA curves in Figure 1(b), the precursor $\text{Cd}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ loses weight in three particular steps. The first step is the endothermic dehydrazination of the two hydrazine molecules between 166 and 297°C. In the second step, the unstable cadmium cinnamate gives cadmium acetate as the intermediate exothermically in the temperature range, 297–395°C. Our attempt to separate the cadmium acetate intermediate was unsuccessful since the decomposition is continuous and is proposed from the percentage weight loss which best fits with the TG curve. In the third step, the proposed intermediate undergoes exothermic decomposition to give CdO as the end product.

3.4. Characterization of Zinc Oxide and Cadmium Oxide Nanoparticles. The X-ray diffraction spectrum (Figure 2(a)) of ZnO nanocrystals has three similar characteristic peaks, 36.28, 31.82, and 34.40, which can, respectively, be indexed to the (1 0 1), (1 0 0), and (0 0 2) planes of a hexagonal pattern of ZnO (JCPDS card no. 89-0510) [20] with lattice constants $a = 3.2488 \text{ \AA}$ and $c = 5.2054 \text{ \AA}$. The measured c/a value of 1.60 was

found to match closely with the value 1.633 for an ideally close packed hexagonal structure (hcp) [21]. The strong diffraction peaks in the XRD spectrum of CdO (Figure 2(b)) at 2θ values of 33.04, 38.33, and 55.33 corresponding to the (1 1 1), (2 0 0), and (2 2 0) planes can be indexed to a cubic pattern of CdO (JCPDS card no. 65-2908). The average particle size was calculated using Debye-Scherrer formula, $D = K\lambda/\beta \cos \theta$, where θ is Bragg diffraction angle, K is Blank's constant, λ is the source wavelength (1.54), and β is the width of the XRD peak at half maximum height. The calculated average particle sizes of zinc oxide and cadmium oxide nanoparticles were found to be around 13 nm and 30 nm, respectively. No characteristic peaks for other impurities were detected, confirming that the products obtained are phase pure.

The TEM micrograph of ZnO and CdO powders synthesised by the thermal decomposition of the precursors are pictured in Figures 3(a) and 3(b). The presence of some bigger particles should be attributed to the aggregation or overlapping of some small particles. The average particle sizes of ZnO and CdO nanoparticles observed from the micrograph are about 12–15 nm and 30–31 nm, respectively, which are in agreement with the calculations using Scherrer's equation. Figures 4(a) and 4(b) show the selected area

FIGURE 4: (a) SAED pattern of ZnO nanoparticles, (b) SAED pattern of CdO nanoparticles.

FIGURE 5: (a) SEM micrograph of ZnO nanoparticles ($\times 10000$), (b) SEM micrograph of ZnO nanoparticles ($\times 60000$), (c) SEM micrograph of CdO nanoparticles ($\times 10000$), (d) SEM micrograph of CdO nanoparticles ($\times 20000$).

electron diffraction (SAED) patterns indicating sharp rings, which reveal the polycrystalline nature of the nanoparticles.

The morphologies of the as-synthesised zinc oxide and cadmium oxide nanoparticles were characterised by Scanning electron microscope (SEM). The SEM images of ZnO and CdO nanoparticles synthesised through decomposition route are shown in Figures 5(a) and 5(b). The SEM pictures clearly show randomly distributed ZnO grains with smaller size and rock candy like CdO structures with agglomeration

of particles. EDX spectra of ZnO and CdO nanoparticles are presented in Figures 6(a) and 6(b), which furnish the chemical compositional analysis of the nanoscale ZnO and CdO.

4. Conclusion

ZnO and CdO nanoparticles were successfully synthesised through a simple and novel thermal decomposition method from the corresponding inorganic precursors,

FIGURE 6: (a) EDX spectrum of ZnO nanoparticles, (b) EDX spectrum of CdO nanoparticles.

$Z(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$ and $\text{Cd}(\text{cin})_2 \cdot (\text{N}_2\text{H}_4)_2$, and characterised by XRD, TEM, SAED, and SEM techniques. The average particle sizes of ZnO and CdO particles determined from XRD and TEM are about 13 nm and 30 nm, respectively. The present method is very simple, effective, and economically viable. It does not require the constraint of sophisticated equipment and pricey chemicals. Therefore, this method can be employed at large scale for the industrial production of metal oxide nanoparticles.

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