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Preparation of Nanostructured Zinc Oxide from Single Source Precursors

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Nanostructured ZnO was prepared by pyrolysis of single source precursors, $ZnCl_2(benzsczH)_2$ and $ZnCl_2(cinnamsczH)_2$ (where, benzsczH = benzaldehyde semicarbazone and cinnamsczH = cinnamaldehyde semicarbazone). Powder X-ray diffraction pattern (PXRD) shows formation of hexagonal ZnO. The peak broadening in PXRD and absorption towards blue region in absorption spectra confirms the formation of nanoscale ZnO. The transmission electron microscopy images reveal formation of nanocrystals along with nanorods. The optical band gaps of both the materials were determined by using Tauc's plots. They are found to be higher than the band gap of bulk ZnO. Infrared spectra also showed formation of ZnO.

Keywords nanostructures, semicarbazone complexes, zinc oxide

INTRODUCTION

ZnO is a wide band gap (3.4 eV) semiconductor with wurtzite structure.^[1] It has applications in short wavelength light emitting devices, field emission devices and surface acoustic wave devices as well as transparent conducting electrodes.^[1] It has useful physical properties suitable for optical and electronic applications.^[2] ZnO thin films can be used in organic light emitting diodes and efficient UV lasers.^[2,3] Its strong piezo-electric and pyroelectric properties make it useful material in actuators, nanogenerators and piezoelectric sensors.^[3] It is biosafe and biocompatible material; hence it can be directly used in biomedical applications without coating.^[4]

Nanostructured materials can play important role in electronics, optics and photonics as their properties such as electrical, mechanical, chemical and optical can be tuned by preparing desired nanostructured materials.^[3] A variety of ZnO nanostructures such as nanowires,^[5] nanobelts,^[6] nanosprings,^[7] nanorings,^[8] nanobows,^[9] and nanohelices^[10] have been reported. Also nanorods,^[11] nanosheets,^[12] hollow spheres,^[13] tetrapods,^[14] ellipsoids,^[15] hexagonal pyramids,^[16] cylinders,^[17] and radial nanowire arrays^[18] have been prepared by the various researchers.

Many preparation methods for ZnO have been reported. Methods such as thermal evaporation, pyrolysis, hydrothermal and capping agent assisted wet chemical methods, chemical vapor deposition (CVD) have been used.^[4] ZnO thin films have been prepared by chemical bath deposition (CBD), spray pyrolysis, pulse laser deposition (PLD), electrodeposition, atomic layer deposition (ALD), molecular beam epitaxy (MBE), and metal organic chemical vapour deposition (MOCVD) techniques.^[2] Though plenty of methods for the preparation of ZnO have been described, there are only few reports on the preparation using single source precursors (SSPs).^[19] Considering the advantages of SSPs such as low toxicity, limited pre-reactions, clean decomposition, etc., we thought it worthwhile to use them for the preparation of ZnO. In the present investigation, we have used zinc semicarbazone complexes, ZnCl₂(benzsczH)₂ and $ZnCl_2(cinnamsczH)_2(where, benzsczH = benzaldehyde semi$ carbazone and cinnamsczH = cinnamaldehyde semicarbazone) as SSPs, which on pyrolysis gave ZnO nanoparticles with some nanorods.

EXPERIMENTAL

Preparation of ZnCl₂(benzsczH)₂

To a round bottom flask containing 1.202 g (7.366 mmols) of benzaldehydesemicarbazone dissolved in a \sim 20 mL THF, 0.502 g (3.683 mmols) of ZnCl₂dissolved in 10 mL THF was added with continuous stirring and stirring was continued for 36 h. Then the solvent was evaporated in vacuo, when a yellow solid was obtained. It was repeatedly washed with n-hexane and cyclohexane (3 \times 5 mL) to remove any impurities present and then dried under vacuum to get free solid. (Yield, 0.892 g, 89.03 %) M.P.: 164°C.

Elemental analysis, found (calcd): Zn: 14.00 (14.13), C: 41.35 (41.53), H: 3.45 (3.92), N: 17.92 (18.16), Cl: 15.12 (15.32). I.R.: 3460 cm⁻¹, 3277 cm⁻¹ (v_{NH2} asym and sym), 3161cm⁻¹ (v_{NH}), 1599 cm⁻¹ ($v_{C=N}$), 1650 cm⁻¹($v_{C=O}$). N.M.R. (δ in ppm): 6.52 (s, NH₂), 7.34–8.22 (m, C₆H₅-CH=), 10.27 (s, NH). ¹³C (δ in ppm): 157.26 (<u>C</u>=O), 139.85 (<u>C</u>=N), 135.18, 129.48, 129.02, 126.98 (aromatic carbons).

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Preparation of ZnCl₂(cinnamsczH)₂

1.027 g (5.428 mmols) of cinnamaldehydesemicarbazone was dissolved in ~ 20 mL THF in a round bottom flask. To this 0.373 g (2.714 mmols) of ZnCl₂ dissolved in 10 mL THF was added with continuous stirring and stirring was continued for 36 h. Then the solvent was removed using vacuum to get a pale yellow solid. It was repeatedly washed with n-hexane and cyclohexane (3 \times 5 mL) to remove impurities present and dried under vacuum to get free solid. (Yield, 1.200 g, 85.89 %) M.P.:182°C.

Elemental analysis, found (calcd): Zn: 12.73 (12.70), C: 45.99 (46.66), H: 4.18 (4.30), N: 16.43 (16.32), Cl: 13.42 (13.77). I.R.: 3454 cm^{-1} , 3279 cm^{-1} (υ_{NH2} asym and sym), 3152 cm^{-1} (υ_{NH}), 1610 cm⁻¹ ($\upsilon_{\text{C=N}}$), 1650 cm⁻¹, ($\upsilon_{\text{C=O}}$). N.M.R. (δ in ppm): 6.45 (s, NH₂), 6.87–8.19 (m, C₆H₅-CH=CH-CH-), 10.23 (s NH). ¹³C (δ in ppm): 157.07 (C=O), 142.60, 136.84, 136.56 (CH=CH-CH=N), 129.26, 128.88, 127.13, 126.01 (aromatic carbons).

Preparation of Nanostrucutred ZnO

Nanostructured ZnO was prepared by pyrolysis of above precursors in furnace under nitrogen atmosphere. The precursor was taken in quartz boat. The boat was kept at the center of a horizontal wall furnace. The furnace was then heated at a rate of 25° C / min to 515° C and held at this temperature for one hour. After that the furnace was naturally cooled to room temperature. The residue obtained in the boat was removed and then characterized by microanalysis, XRD, TEM, SAED, UV-VIS and IR spectroscopy.

INSTRUMENTATION

The absorption spectra were recorded on a UV-2401 PC Shimadzu UV-vis spectrophotometer. XRD studies were carried out using Cu K_{α} radiation on a X'pert PRO PANalytical X-ray diffractometer (Philips). TEM were recorded on a PHILIPS, Model no-CM 200 with operating voltages 20–200 kV. IR spectra were taken on a Perkin Elmer FT-IR spectrometer in 4000–400 cm⁻¹ range. Microanalysis was carried out on Thermo Finnigan, Italy Model FLASH EA 1112 Series elemental analyzer.

RESULTS AND DISCUSSION

In the present investigation, $ZnCl_2(benzsczH)_2(1)$ and $ZnCl_2(cinnamsczH)_2$ (2) were used as single source precursors for the synthesis of ZnO nanocrystallites. The precursors were prepared by simple addition reactions of $ZnCl_2$ to corresponding ligand (Eq. 1). Chemical structures of (1) and (2) are given in Figure 1.

$$\operatorname{ZnCl}_2 + 2 \operatorname{LH} \xrightarrow{\operatorname{THF}} \operatorname{ZnCl}_2(\operatorname{LH})_2$$
 [1]

LH = semicarbazones of benzaldehyde and cinnamaldehyde The complexes obtained were characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopic techniques. Ele-



Where, $R^1 = H$, $R^2 = C_g H_5$ (1), $R^1 = H$, $R^2 = CH = CH - C_g H_5$ (2)

FIG. 1. Chemical structures of $ZnCl_2(benzsczH)_2$ (1) and $ZnCl_2$ (cinnamsczH)₂ (2).

mental analysis was found to match with 1:2 metal to ligand stoichiometries. In the IR spectra of complexes the bands due to asymmetric and symmetric stretchings of NH_2 group as well as N-H and C=O stretchings are observed. In the ¹H NMR spectra peak due to -NH proton is observed at about 10.2 ppm. These observations are consistent with the ligand coordination through oxygen and azomethine nitrogen atoms.^[20,21]

Thermal decomposition of these complexes was carried out at 515°C in furnace under nitrogen atmosphere. The black residue obtained was characterized by microanalysis, powder XRD, TEM, SAED, UV-VIS and IR spectroscopy. The black colors of the materials obtained are due to carbon contamination coming from the organic ligands. Thus, for ZnO obtained from pyrolysis of precursor (1) microanalysis showed presence of 12.37% carbon whereas, for the material obtained by pyrolysis of precursor (2) carbon present is found to be 13.52%.

Figure 2 shows powder XRD patterns of the nanostructured ZnO obtained by pyrolysis of $ZnCl_2(benzsczH)_2$ and $ZnCl_2(cinnamsczH)_2$ complexes. All the diffraction peaks could be clearly indexed to hexagonal ZnO (JCPDS: 79-0205). In both



FIG. 2. XRD patterns of hexagonal ZnO (JCPDS: 79-0205) obtained by pyrolysis of (a) $ZnCl_2(benzsczH)_2$ and (b) $ZnCl_2(cinnamsczH)_2$ at 515°C.





FIG. 3. (a) TEM image and SAED pattern (inset) of ZnO nanoparticles obtained by pyrolysis of $ZnCl_2(benzsczH)_2$ at 515°C.

(b) TEM image of ZnO nanorods obtained by pyrolysis of $ZnCl_2(benzsczH)_2at 515^{\circ}C$.

the cases ZnO particles are found to have preferred growth along (101) plane. The peak broadening in XRD patterns suggest presence of nanosize ZnO. The average grain size (D) was calculated using Scherrer's formula.^[22] For the material obtained from precursor (1), average particle size calculated was found to be 32.51 nm whereas for material obtained from precursor (2) it is found to be 14.64 nm. It can be seen that the peaks for ZnO obtained from precursor (1). This suggests smaller particle size for ZnO obtained from precursor (2) compared with the material obtained from precursor (1). This is also evident from the particle sizes calculated using Scherrer's formula.

Figure 3a and 3b show representative TEM images and SAED pattern of the nanostructured ZnO. Plate-like morphol-



FIG. 4. Absorption spectra of nanostructured ZnO obtained by pyrolysis of (a) ZnCl₂(benzsczH)₂ and (b) ZnCl₂(cinnamsczH)₂at 515°C.

ogy along with few nanorods is observed. The average grain size of nanoparticles is 27 nm for material obtained from precursor (1) whereas for precursor (2) it is about 10 nm. These values are consistent with those calculated from XRD. The width of nanorods obtained from precursor (1) is between 100 to 130 nm (Figure 3b). For nanorods obtained from precursor (2) width is about 80 nm. SAED patterns of ZnO obtained from precursor (1) and (2) show the presence of well defined rings indicating that the materials obtained are crystalline in nature. It also confirms the formation of hexagonal ZnO.

The absorption spectra of nanostructured ZnO were recorded by dispersing particles in methanol. In spectra of materials obtained from both the precursors a blue shift is observed compared to bulk ZnO (305 nm). The absorption bands are observed at 280 nm and 272 nm for materials obtained from precursor (1) and (2), respectively (Figure 4). The optical band



FIG. 5. A plot of $(\alpha h\nu)^2$ versus $h\nu$ of nanosructured ZnO obtained by pyrolysis of (a) ZnCl₂(benzsczH)₂ and (b) ZnCl₂(cinnamsczH)₂ at 515°C.

FIG. 6. IR spectra of nanostructured ZnO obtained by pyrolysis of (a) $ZnCl_2(benzsczH)_2$ and (b) $ZnCl_2(cinnamsczH)_2$ at $515^{\circ}C$.

gaps were calculated using graphical plot of $(\alpha h v)^2 versus h v$ using Tauc's relation.^[1] Here α is calculated using relation, $\alpha = 4\pi A/\lambda$, where A is the absorbance and λ is wavelength.^[23] The extrapolation of the curves to the energy axis gave band gaps of 3.83 eV and 3.92 eV for ZnO nanocrystals obtained from ZnCl₂(benzsczH)₂, and ZnCl₂(cinnamsczH)₂, respectively (Figure 5). These band gaps are found to be higher than the band gap of bulk ZnO (3.4 eV).

Figure 6 shows infrared spectra of the nanostructured ZnO. The bands due to Zn-O stretching are observed at 509 cm⁻¹, 444 cm⁻¹ and 506 cm⁻¹, 440 cm⁻¹ for materials obtained from precursor (1) and (2), respectively. Along with these peaks, additional broad peaks are observed at 3438 cm⁻¹ (for 1) and 3429 cm⁻¹ (for 2) due to -OH stretching vibrations. Also additional bands at 1584 cm⁻¹ (1) and 1560 cm⁻¹ (2) are attributed to the bending O-H vibrations. All these additional bands are due to absorbed water molecules.^[4]

CONCLUSION

Nanostructured ZnO was successfully obtained by pyrolysis of single source precursors, ZnCl₂(benzsczH)₂ and ZnCl₂(cinnamsczH)₂. The PXRD showed formation of hexagonal ZnO. The morphology of the materials was found to be mainly nanoparticles with presence of some nanorods. This suggests that the single source precursors could be promising molecules for convenient synthesis of nanostructured materials as they have inherent advantages over conventional dual source precursors.

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