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Solid state synthesis of NiO nanoparticles from [(1,2-bis(2-formyl-3-methoxyphenyl)propane)nickel(II)] chloride

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Abstract

In this paper, nickel oxide (NiO) nanoparticles have been prepared by solid state thermal decomposition of an acyclic nickel(II) complex (1,2-bis(2-formyl-3-methoxyphenyl)propane)nickel(II) chloride, $[NiL]Cl_2$, in an electrical furnace at optimal temperature, 450 ºC for 3.5 h. The nickel(II) complex is obtained *via* solid state synthesis using nickel(II) chloride and tetradentate O_4 acyclic ligand 1,2-bis(2-formyl-3-methoxyphenyl)propane. The structure and morphology of NiO nanoparticles are characterized by Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD and TEM analysis show that NiO nanoparticles have pure and cubic phase with the average size of 5-10 nm.

Keywords: Nickel oxide; nanoparticles; solid state; nickel(II) complex.

Introduction

Recently, nickel oxide, which is one of the most important p-type oxide semiconductors, has received much attention for various applications *viz.* in lithium ion batteries [1], as supercapacitor [2], in electrochemical [3] and gas-sensing [4] processes. Several nanostructured transition metal oxide powders such as nanosphere [5,6], nanosheets [7], rambutan like [8], urchi and

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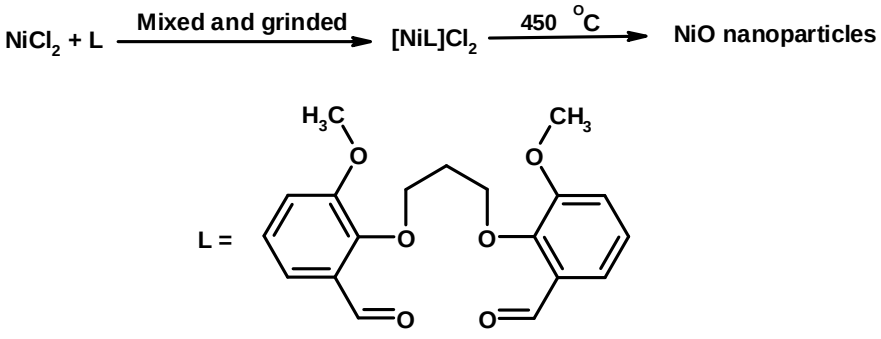
flowerlike [3], cubic [2] have been prepared by various methods such as sonochemical [9], sol-gel [10], electrochemical discharge [11], chemical precipitation [12], solvothermal [13] and thermal decomposition [14-18]. Alagiri and co-workers [19] have synthesized NiO nanoparticles by sol-gel method in the presence of agarose polysaccharide. Bhattacharjee and co-workers[5] have prepared spherical NiO nanoparticles with the average sizes of 5-15 nm by surfactant-assisted low-temperature thermal decomposition of new nickel-salicylate precursor. Farhadi and co-workers [15] have synthesized NiO nanoparticles of average size of 12 nm *via* thermal decomposition of $Ni(dmgH)_2$ complex. Recently, Salavati-Niasari and co-workers have prepared NiO [17] and ZnO [20] nanoparticles by thermal decomposition of Ni(salen) and Zn(salen) complexes prepared by solid state synthesis method.

Here in, we report the synthesis of cubic nano-sized NiO nanoparticles by solid-state thermal decomposition of a new precursor $[NiL]Cl_2$ at 450 ºC for 3.5 h in the absence of any template or surfactant. To our knowledge this is the first acyclic nickel(II) complex containing tetradentate O_4 ligand that is used for preparation of NiO nanoparticles by solid-state thermal decomposition. $[NiL]Cl_2$ complex (Scheme 1) is prepared by solid state reaction between 1,2-bis(2-formyl-3-methoxyphenyl)-propane and nickel(II) chloride (molar ratio, 1:1). The obtained cubic NiO nanoparticles are characterized by FT-IR, PXRD, SEM and TEM.



Scheme 1. Synthetic protocol of NiO nanoparticles

Materials and physical measurements

All reagents and solvents have been used as received without further purifications. 1,2-bis(2-formyl-3-methoxyphenyl)propane was prepared by the reaction of 3-methoxysalicylaldehyde and 1,3-dibromopropane in the presence of K_2CO_3 at 80ºC described in the following literature procedure [21]. Elemental analyses have been performed on a Heraeus CHN-O-Rapid analyzer. Absorption spectra are recorded on a Cary 100 UV-Vis. spectrophotometer, VARIAN EL 12092335 in the wavelength range of 200 – 700 nm at room temperature. The sample for UV-Vis studies is well dispersed in distilled water by sonication for 10 min to form a homogeneous suspension. PXRD pattern of the complex is recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation with nickel beta filter in the range $2\theta = 30–80^{o}$. FTIR spectrum is recorded as a KBr pellet on a FT-IR spectrometer (Perkin–Elmer). The TEM image is obtained from a JEOL JEM 1400 transmission electron microscope with an accelerating voltage of 120 kV while the SEM image is collected by a Philips XL-30ESEM. The TGA is performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of 20ºC/min in the temperature span of 30–750ºC.

Complex synthesis

Methanol solution (20 mL) of $NiCl_2 \cdot 6H_2O$ (2 mmol) which is added to a methanol solution (20 mL) of L (2 mmol) with constant stirring to obtain a dark red precipitate is collected by filtration, then washed twice with ethanol. Finally, it was dried at room temperature for several days. Anal. calc. for $C_{19}H_{20}NiO_6Cl_2$: C, 48.15; H, 4.25%; Found C, 48.26; H, 4.19%. FTIR (KBr, cm^{-1}): 2960 (C-H), 1691 (C=N), 1481-1586 (C=C aromatic).

NiO nanparticles synthesis

The NiO nanoparticles are prepared by the following procedure: 2 mmol $NiCl_2 \cdot 6H_2O$ and 2 mmol L are mixed and pulverized well in a mortar then transferred to a beaker to heat at 75°C with continuous stirring for 3 h. Until the mixture become homogeneous. The mixture is loaded on a crucible and placed in the electrical furnace to be heated at a rate of 10ºC/min in the air, up to 450 ºC allowing organic contents to be removed. Thus, NiO nanoparticles are produced after 3.5 h, washed with ethanol and dried at room temperature. This as prepared NiO nanoparticles are characterized by FTIR and UV-Vis spectroscopy, PXRD, SEM

and TEM.FT-IR (KBr pellet, cm^{-1}): 3446, 1637 (H_2O), 418 (Ni-O) [24,25].

Results and discussion

The FTIR spectra confirms the formation of precursor, $[NiL]Cl_2$ complex (Figure 1) and NiO (Figure 2) nanoparticles. The peak observed at 1691 cm^{-1} indicates the presence of C=O in the complex. In the FTIR spectrum of the ~~as~~ prepared NiO, the two bands with less intensity *viz.* at 1637 and 3446 cm^{-1} have been attributed to the O-H stretching of adsorbed water on the NiO surface [24,25]. The spectrum also contains one strong peak at 418 cm^{-1} which confirms the stretching vibration of NiO band [22-25].

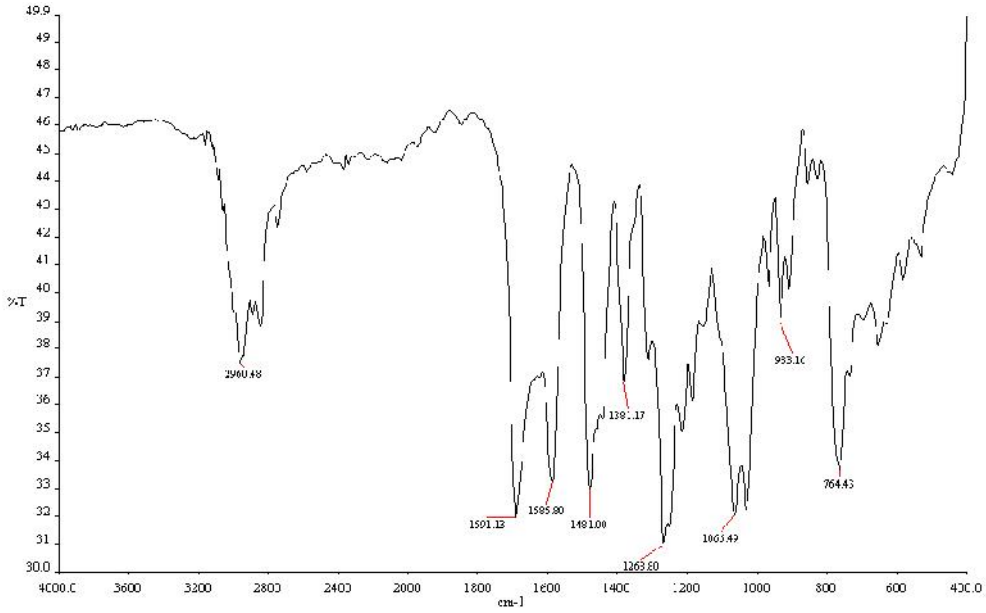


Figure 1. FT-IR spectrum of $[NiL]Cl_2$ as new precursor

Figure 3 shows the PXRD pattern of the well synthesized NiO nanoparticles. The peaks at about the 2θ values of 37.26º, 43.29º, 62.86º, 75.38º and 77.42º are assigned to the (111), (200), (220), (311) and (222) crystal planes, respectively. The line broadening of the peak of the main plane (200) is related to the size of the *fcc* crystal structure of the pure nickel oxide nanoparticles [13,24,25]. No obvious peaks of impurities are observed in this pattern. The average crystalline diameter of the as-prepared NiO, *D*c, is calculated from the major diffraction peak of (200) using the Scherrer equation, $Dc = K\lambda / \beta\cos\theta$, is 10-20 nm. This result conforms to the TEM.

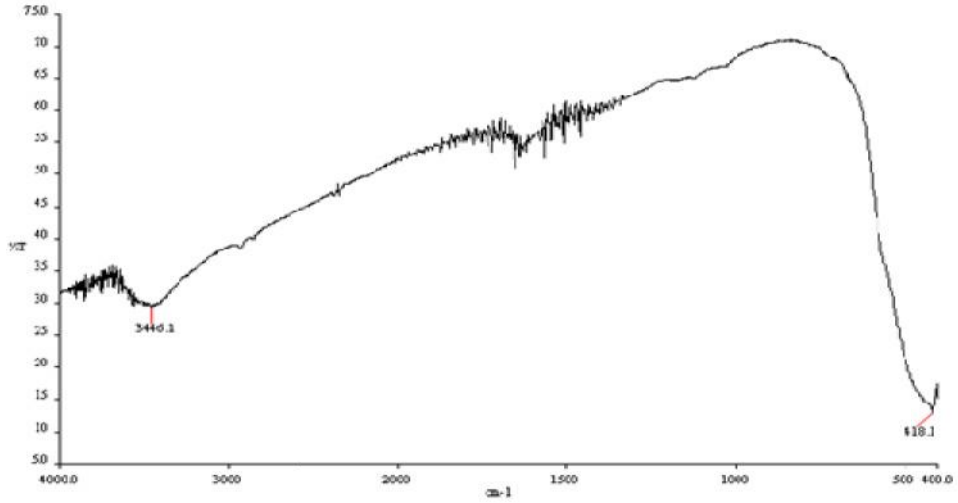


Figure 2. FT-IR spectrum of NiO prepared from $[NiL]Cl_2$

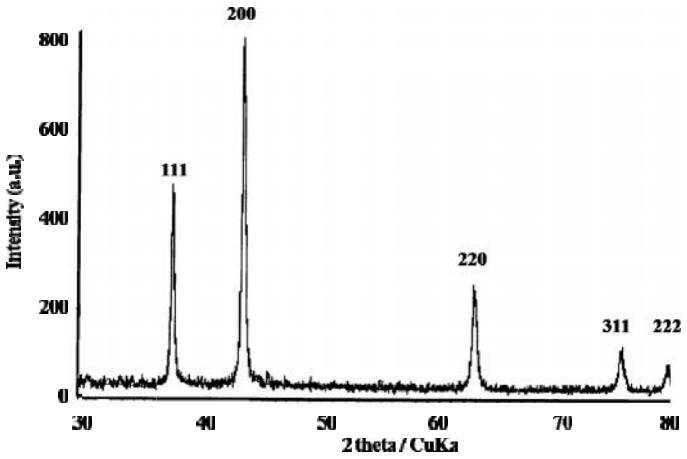


Figure 3. PXRD pattern of NiO nanoparticles as prepared

The morphology of the NiO nanoparticles is investigated by SEM and TEM. The SEM and TEM images are shown in Figs. 4 and 5, respectively. The sample for TEM is prepared by dispersing the powder in ethanol *via* ultrasonic vibration. Typical SEM and TEM micrographs clearly show that the NiO nanoparticles are of uniform sizes but these particles do agglomerates. The NiO nanoparticles with particle size about 10-20 nm are seen in TEM image.

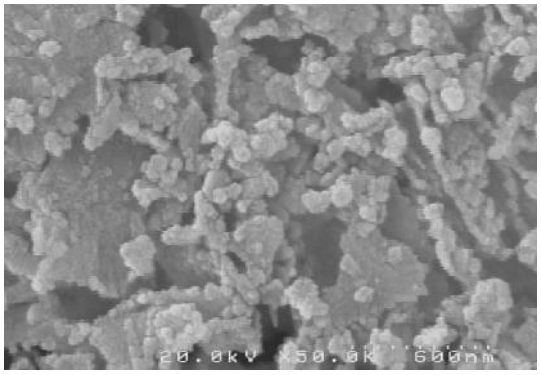


Figure 4. SEM image of NiO nanoparticles as prepared

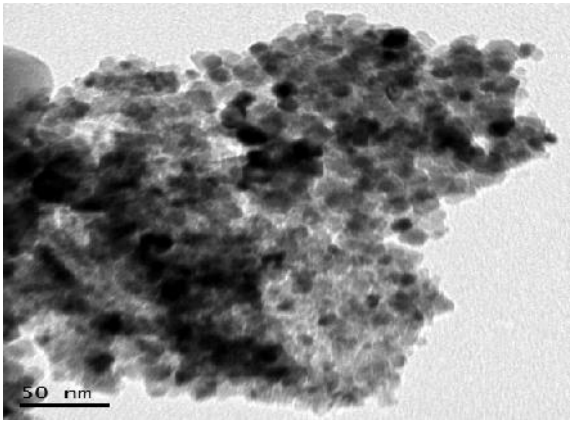


Figure 5. TEM image of NiO nanoparticles as prepared

The choice of nickel(II) complexes as new precursors for preparation of NiO nanoparticles by solid state thermal decomposition is a key step [26-30]. Until now, many different nickel(II) complexes have been used for preparation of NiO nanoparticles [36-30]. In Table 1 some of the nickel(II) complexes used in solid state thermal decomposition are compared with present work. According to these results, NiO nanoparticles were successfully synthesized with the small size from the nickel(II) acyclic complex $[NiL]Cl_2$.

Table 1. Comparision of particle size of NiO by solid state thermal decomposition method in several woks

Precursor	**T (°C) / Time (h)**	**Size (nm)**	**Ref**
Ni(salen)	500 / 5	15-30	26
Ni(Brsalph)(NO_3)	550 / 3.5	55	27
Ni(Me-salophen)	550 / 3.5	35-70	28
Ni(salophen)	550 / 3.5	35-70	28
$[Ni(Phen)_2]^{2+}$	500 / 2	56	29
Ni(caph)(N_3)(NO_3)	450 / 3	30-70	30
$[NiL]Cl_2$	450 / 3.5	< 20	This work

Conclusion

In brief, NiO nanoparticles having average size 10-20 nm have been successfully prepared by solid-state thermal decomposition method. At first, we have prepared acyclic nickel(II) complex as a new precursor *via* solid state reaction of nickel(II) chloride with tetradentate O_4 ligand 1,2-bis(2-formyl-3-methoxyphenyl)propane. The crystalline structure and morphology of the synthesized NiO nanoparticles have been studied by FT-IR, XRD, SEM and TEM. The absence of any residual complex traces or other phases indicate the as-prepared NiO nanoparticles which are of high purity. FT-IR and XRD studies confirm the nanocrystalline particles. The present method is nontoxic, simple and low-cost which may boost for the production of other metal oxide nanoparticles.

Acknowledgments

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