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Cubic NiO Nanoparticles: Synthesis and Characterization

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ABSTRACT

In this paper, cubic nickel oxide nanoparticles were successfully prepared by solid-state thermal decomposition of nickel(II) macrocyclic Schiff-base complex at 450°C for 3 h without employing toxic solvent or surfactant and complicated equipment. nickel(II) macrocyclic Schiff-base complex was synthesized by the reaction of 1,2-bis(2-formyl-3-methoxyphenyl)propane, $NiCl_2 \bullet 6H_2O$ and 1,3-phenylenediamine in methanol at room temperature and characterized by elemental analyses and FT-IR spectroscopy. The as prepared NiO nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD pattern result shows that the synthesized NiO nanoparticles are pure and single phase. The SEM and TEM results show the morphology of the as prepared NiO nanoparticles is almost cubic shape with the average size between 20-150 nm. On the basis of the above results, other transition metal macrocyclic Schiff base complexes are therefore potentially capable of forming metal oxide nanoparticles.

Keywords: NiO Nanoparticles; Nickel(II) macrocyclic; Characterized; Schiff base; Thermal decomposition.

1. INTRODUCTION

The synthesis of macrocyclic Schiff base compounds containing nitrogen and oxygen donor atoms have received much attention in recent years because their potential applications in fundamental and applied sciences [1-3] and in the area of transition metal coordination chemistry [4-7]. The formation of nickel(II) macrocyclic complexes depends significantly on the nature of ligand, such as the dimension of internal cavity, the rigidity and its donor atoms [4, 8-10]. Nickel oxide is considered a p-type semiconductor with wide band gap energy of about 3.6-4 eV and is candidate for supercapacitor [11-13], lithium ion batteries [14, 15], photocalatysis [16], electrochromic [17] and magnetic properties [18]. Until now, many different methods such as

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sol-gel [11], calcinations [12, 14], chemical bath deposition [13], spray pyrolysis [15], solvothermal [19] and solid-state thermal decomposition [20-25] used for the preparation of nickel oxide nanoparticles. But, solid-state thermal decomposition method is one of the simplest, lowest cost (low energy consumption) and environment-friendly method (no need for solvent) for preparing pure nickel oxides nanoparticles [20-24]. Recently, Farhadi et al. prepared nickel oxide nanoparticles by solid-state thermal decomposition of octahedral nickel(II) complexes as new precursors at various temperature [23, 24].

In this work, and as a part of the ongoing study on preparation of nickel oxide nanoparticles by solid-state thermal decomposition of Schiff base complexes [21,22], we wish to report the preparation of nickel oxide nanoparticles from nickel(II) macrocyclic Schiff base complex (Figure 1). To the best of our knowledge, this is the first report on the synthesis of nickel oxide nanoparticles with nickel(II) macrocyclic Schiff base complexes.

2. EXPERIMENTAL

2.1. Material and characterization

All reagents and solvents for synthesis and analysis were commercially available and 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 according to the literature [25]. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values.

X-ray powder diffraction (XRD) pattern was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation with nickel beta filter in the range 2θ = 10°-80°. Fourier Transform Infrared spectra were recorded as a KBr disk on a FT-IR Perkin. Elmer spectrophotometer. The transmission electron microscopy (TEM) images were obtained from a JEOL TEM 1400 transmission electron microscope with an accelerating voltage of 120 kV while the scanning electron microscopy (SEM) images were obtained from a Philips XL-30E SEM.

2.2. Preparation of nickel(II) macrocyclic Schiff base complex

To a stirred solution of 1,2-bis(2-formyl-3-methoxyphenyl)propane (2 mmol) and $NiCl_2•6H_2O$ (2 mmol) in methanol (50 mL) was added dropwise 1,3-phenylenediamine (2mmol) in methanol (10 mL). After the addition was completed, the stirring was continued for 2 h. The microcrystalline powder of the complex was filtered and washed with cold methanol and then dried in air for 2 days. *Anal.* calcd for $C_{25}H_{24}N_2NiO_2C_{l2}•2H_2O$: C, 54.58; H, 5.13; N, 5.09%; Found C, 54.49; H, 5.15; N, 5.01%. FT-IR (KBr, cm-1): 3375 (H_2O), 1624(C=N), 1578, 1476 (C=C aromatic).

2.3. Preparation of NiO nanoparticles

Microcrystalline powder of the mononuclear nickel(II) macrocyclic Schiff base complex (about 0.5 g) is loaded into a platinum crucible and then placed in the electrical furnace and heated, at a rate of 10ºC/min in air, up to 450ºC. After 3.5 hours, the resulting nanoparticles of NiO are washed with ethanol - at least three times - to remove eventual impurities, and then dried in air for 2 days. FT-IR (KBr pellet, cm^{-1}): 3412, 1627(H_2O), 459 (Ni-O).

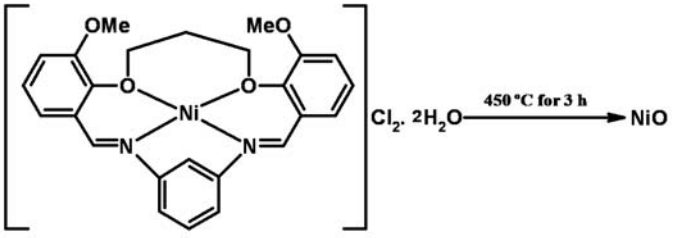

Figure 1: *The chemical structure of nickel(II) macrocyclic Schiff base complex and the preparation of NiO nanoparticles.*

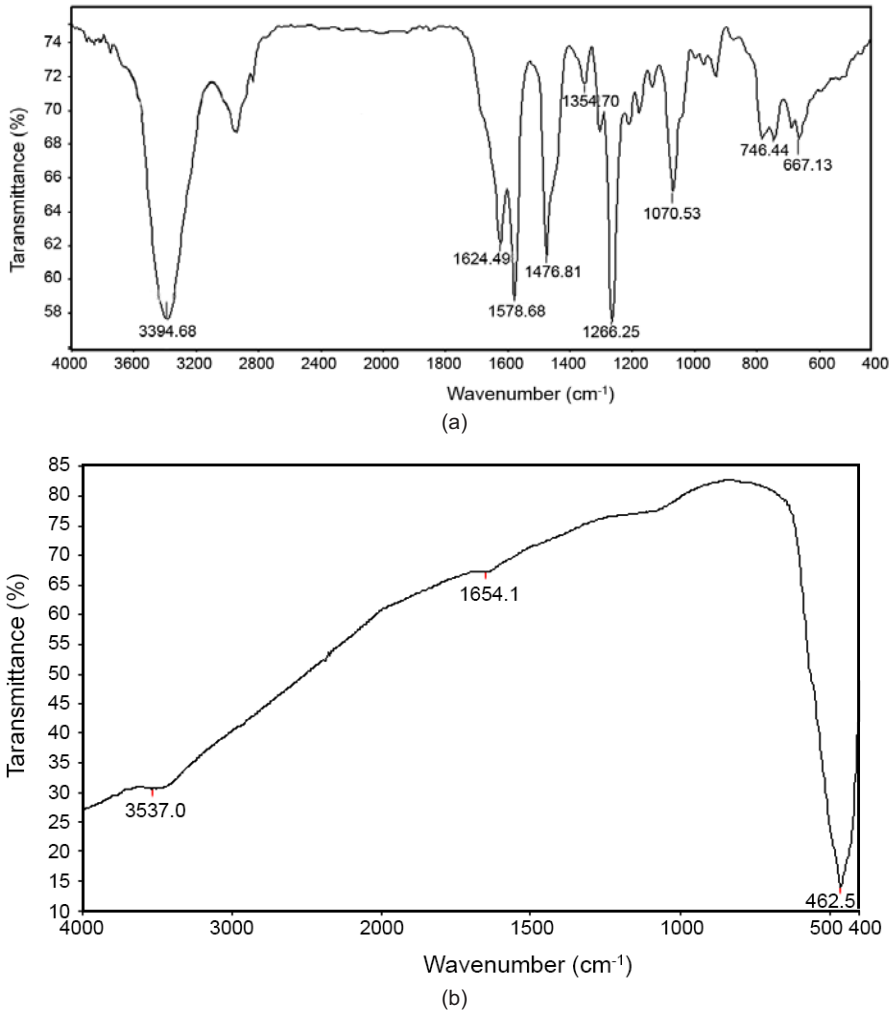

Figure 2: *FT-IR spectra of complex (top) and NiO nanopartilces (bottom).*

3. RESULTS AND DISCUSSION

3.1. Synthesis

The mononuclear nickel(II) macrocyclic Schiff base complex was synthesis by methanolic solution of nickel(II) chloride, 1,2-bis(2-formyl-3-methoxyphenyl)propane and 1,3-phenylenediamine in molar ratio 1:1:1 at room temperature for 2 h and characterized by FT-IR and elemental analyses (CHN). The proposed structure of the complex is presented in Figure 1, and is similar to the nickel(II) macrocyclic complexes that reported by Ilhan and co-workers [4].

3.2. FT-IR spectrum

The FT-IR spectra of complex and its decomposition product at 450°C are shown in Figure 2. In the FT-IR spectrum of complex, the characteristic band of the H_2O molecules is observed at 3394 cm^{-1}, while the characteristic band of C=N and C=C groups are observed at 1624 and 1578-1476 cm^{-1}, respectively, confirmed the coordination of macrocycle Schiff base ligand to Ni(II) ion. These bans disappeared in the FT-IR spectrum of NiO product. In the FT-IR spectrum of NiO products (Figure 2), the broad bonds peaks at 3537 (hydroxyl group) and 1654 cm^{-1} (H-OH bending vibration), are due to adsorbed water molecules on the external surface of NiO nanoparticles during handling to record the spectrum. The characteristic wide peak at 462 cm^{-1} was attributed to the Ni-O stretching vibration of spinal structure of NiO [19].

3.3. XRD analysis

The phase composition of NiO products has been characterized by powder XRD analysis (Figure 3). The

Table 1: *The crystal sizes of NiO nanoparticles calculated based on the FWHM of all diffraction peaks.*

Pos. [2θ]	d-spacing [A]	Rel. Int. [%]	Height [cps]	FWHM [2θ]	Crystallite Size [nm]
37.256(2)	2.41155	54.46	287.08	0.244616	24.2
43.290(2)	2.08834	100.00	527.19	0.239636	25.2
62.865(4)	1.47709	30.02	158.24	0.339064	19.4
75.376(9)	1.25998	11.33	59.72	0.397633	17.8
79.33(2)	1.20684	7.61	40.13	0.314134	23.2

XRD pattern reveals diffraction peaks were observed at about 2θ values of 37º, 43º, 63º, 75º and 79º that are assigned to the (111), (200), (220), (311) and (222) crystal planes of the pure nickel oxide nanocrystalline phase, respectively. All the diffraction peaks are in good agreement with the JCPDS card No. 47-1049 of the NiO nanoparticles with space group Fm3m [25, 26]. This result confirms that the complex is decomposed completely into the NiO at 450°C. The XRD result is in good agreement with the FT-IE result. No characteristic peaks of other impure phase, like NaOH, could be detected, indicating that the product is highly pure NiO. The crystal sizes of the NiO nanoparticles based on the FWHM of the all diffraction peaks are in the range of 17.8 to 25.2 nm (Table 1).

3.4. SEM and TEM images

The morphology of the NiO products was investigated by SEM (Figure 4) and TEM (Figure 5). From the SEM micrograph, it was observed that the nanoparticles were similar and uniform sizes but these particles were agglomerates.

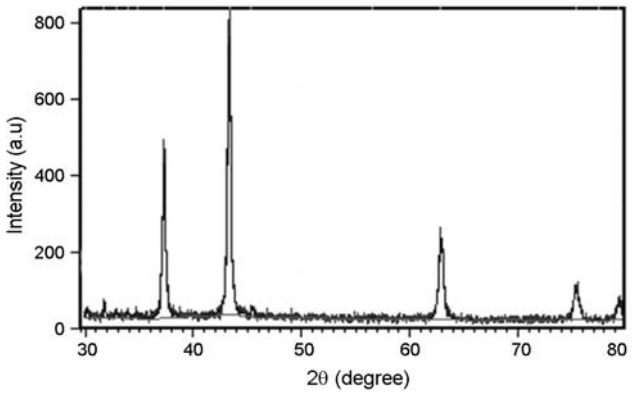

Figure 3: *XRD pattern of NiO nanoparticles prepared.*

The TEM sample was prepared by dispersing the powder in ethanol by ultrasonic vibration. The uniform of the NiO nanoparticles have plate-like shapes with weak agglomeration. The nanoparticles of NiO with an average size about 15-25 nm are seen inside TEM image. The SEM and TEM results confirm that the mononuclear nickel(II) macrocyclic Schiff base complex is suitable precursor for the preparation of NiO

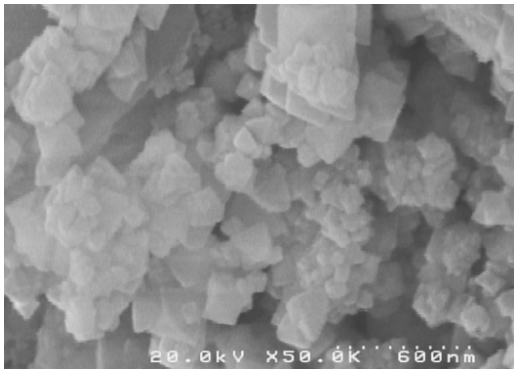

Figure 4: *SEM image of NiO nanoparticles prepared.*

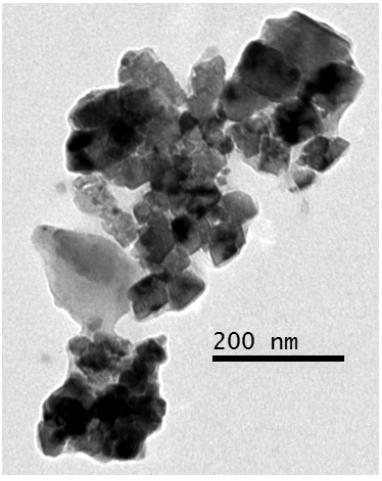

Figure 5: *TEM image of NiO nanoparticles prepared.*

nanoparticles.

4. CONCLUSIONS

In this paper, we used mononuclear nickel(II) macrocyclic Schiff base complex as new precursor for preparation of NiO nanoparticle by solid-state thermal decomposition. The NiO products obtained at 450ºC for 3.5 h. 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 indicated the as-prepared NiO samples to have high purity. The results (XRD and TEM) shows the formation of NiO nanoparticles with almost plate shape with anaverage size ranges from 20-150 nm.

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