Solid State Process for Preparation of Nickel Oxide Nanoparticles: Characterization and Optical Study

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ABSTRACT: *In the present work, we report preparation of NiO nanoparticles with well-defined plate morphology by solid-state reaction of $NiCl_2 \cdot 6H_2O$ and the Schiff base ligand N,N′-bis-(3-methoxysalicylidene)benzene-1,4-diamine), as a novel precursor via solid state thermal decomposition method. This method is a simple and environmentally friendly for preparing transition metal oxides. The result of TGA analysis of the precursor showed that the proper calcinations temperature is 450 °C. The NiO product was characterized by XRD, FT-IR and UV-Vis spectroscopy, SEM and TEM. The results indicated that the obtained product is face-centered cubic of nickel oxide, plate shape with average particle size of 10-20 nm. The optical absorption band gap of the nickel oxide nanoparticles was estimated to be 2.1 eV.*

KEYWORDS: *Nickel oxide, Nanoparticles, Solid-state, Schiff base, Thermal decomposition.*

INTRODUCTION

In recent years, transition metal oxide nanostructures have attracted much attention due to their unique chemical and physical properties [1-4]. Among them, nanocrystalline nickel oxide is an important promising material with extensive applications and properties [5-7]. Studies show that NiO nanostructures have better properties than those of their bulk materials. Nickel oxide is an antiferromagnetic oxide p-type semiconductor with wide band gap energy of about 4 eV and is one of the best candidates for gas sensing [8] and anode materials for Li-ion batteries [6]. Recently, many groups are working hard on synthesis and characterization of nickel oxide nanoparticles by various methods such as microwave [7], calcination [6], sol-gel [5], hydrothermal [8] and solvothermal [9] methods. Among them, solid-state thermal decomposition is one of the simplest, lowest cost and environment-friendly method for preparing pure nickel oxides nanoparticles [10-13]. The advantages of this method are no need for solvent, high purity and high yield of products, low energy consumption, the shape and size control of products and no special equipment required.

Herein, the nickel complex as precursor was prepared by solid state reaction between *N,N′*-bis-(3-methoxysalicylidene) benzene-1,4-diamine and nickel(II) chloride (molar ratio, 1:1) in absence of any solvent. Then, we report synthesis of cubic nano-sized NiO nanoparticles by solid-state thermal decomposition of precursor at 450ºC for 3.5 h in absence of any template or surfactant (Scheme 1). The obtained cubic NiO nanoparticles are characterized by FT-IR, PXRD, SEM and TEM.

EXPERIMENTAL SECTION

Materials and characterization

All reagents and solvents for synthesis and analysis

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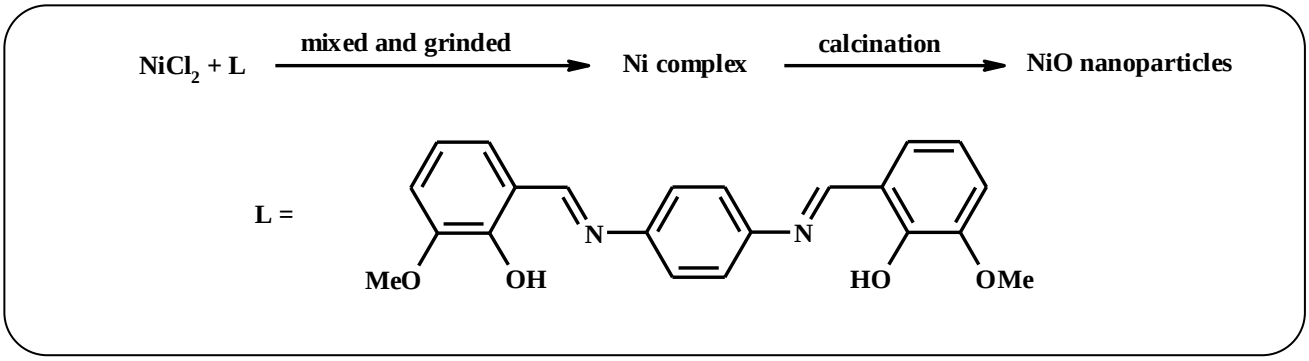

Scheme 1: Synthetic protocol of NiO nanoparticles.

are commercially available and used without further purifications. The Schiff base ligand *N*,*N*′-bis-(3-methoxysalicylidene)benzene-1,4-diamine was prepared following published procedure [14]. Fourier Transform Infrared spectra (FT-IR) are recorded as a KBr disk on a Perkin–Elmer FTIR spectrometer. Optical absorption spectra were recorded on a Cary 100 UV-Visible Spectrophotometer, VARIAN EL 12092335 in a wavelength range of 200 – 700 nm at room temperature. The sample for UV-Vis studies was well dispersed in distilled water by sonication for 10 min to form a homogeneous suspension. Elemental analyses are carried out using a Heraeus CHN-O-Rapid analyzer. X-Ray powder Diffraction (XRD) pattern of the nickel oxide nanoparticles are recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-Kα radiation with nickel beta filter in the range $2\theta = 10^{o}$–80^{o}. Scanning Electron Microscopy (SEM) images are obtained on Philips XL-30ESEM. Transmission Electron Microscopy (TEM) images were obtained on a Zeiss - EM10C transmission electron microscope with an accelerating voltage of 80 kV.

Preparation of NiO nanoparticles

$NiCl_2{\cdot}6H_2O$ (1 mmol) and Schiff base ligand (1 mmol) were ground separately for 5 min in an agate mortar. Then, the powders were mixed and grinding for 30 min. The product washed with ethanol and dried at 70 °C in an oven and the resultant solid was subsequently annealed in the electrical furnace at 450 °C for 3 h. Nanoparticles of NiO are produced after 3 h, washed with ethanol and dried at room temperature. The synthesized NiO nanoparticles are characterized by FT-IR and UV-Vis spectroscopy, XRD, SEM and TEM.

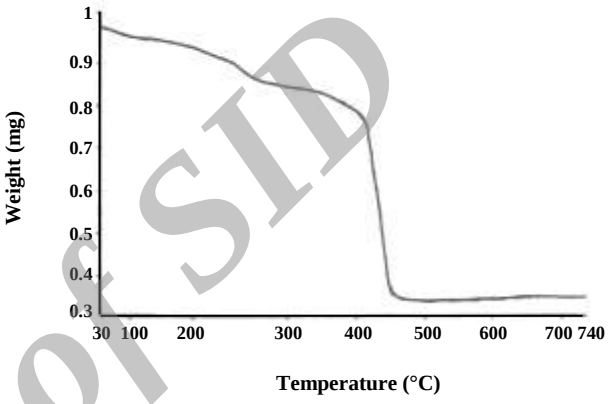

Fig. 1: TGA and DTA curves of the nickel complex.

RESULTS AND DISCUSSION

TGA

The TGA curve of the nickel(II) complex is shown in Fig. 1. It can be seen that there are three distinct weight loss steps. The first stage occurs at 29–252 ^{o}C, which corresponds to the evaporation of water molecules. The second stage occurs at 252–379 ^{o}C and may be ascribed to the partial decomposition of the complex. The third stage is the main step of weight loss occurs at 379–453 ^{o}C and ascribed to the partial decomposition of the complex, followed by the formation of NiO. The sharp exothermic peak at about 440 ^{o}C can be explained by the explosive decomposition of nickel complex.

FT-IR and UV-Vis spectra

In the FT-IR spectrum of NiO nanoparticles, the broad bond peak at 3450 cm^{-1} is representative of adsorbed water on the external surface of the NiO nanoparticles. The strong band at 420 cm^{-1} is belongings to the spinal structure of NiO [10-12].

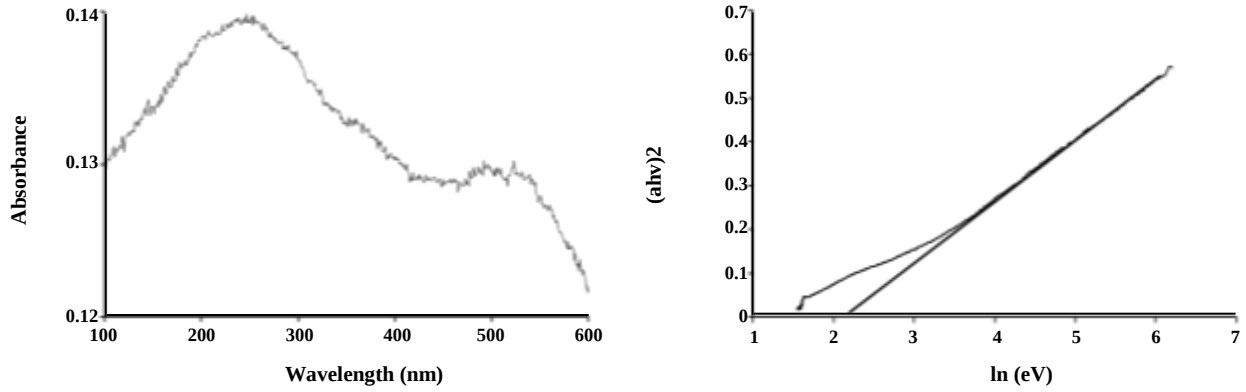

Fig. 2: UV-Vis spectrum (top) and $(ahv)^2$ – hv curve (bottom) of the NiO nanoparticles.

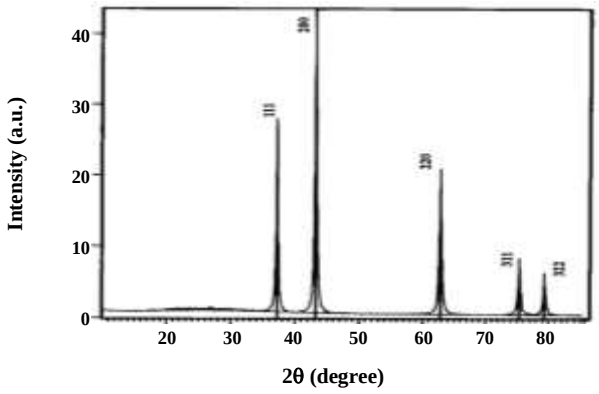

Fig. 3: XRD pattern of NiO nanoparticles.

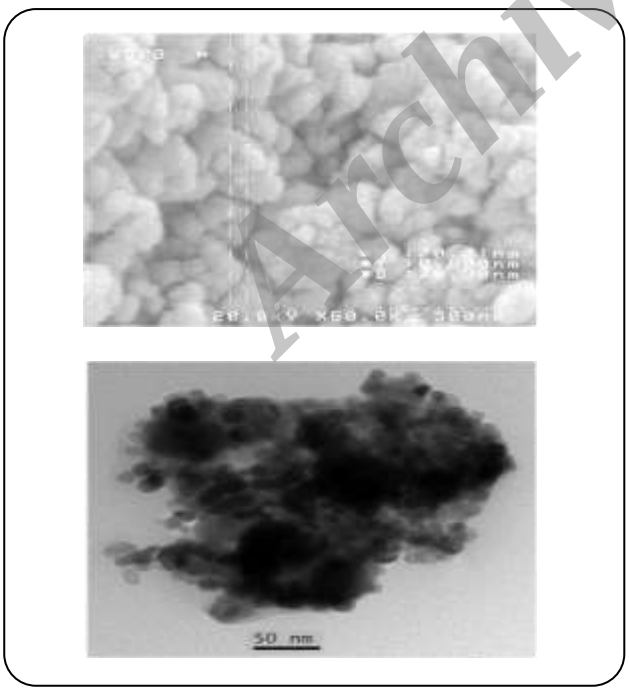

Fig. 4: SEM (left) and TEM (right) images of NiO nanoparticles.

As shown in Fig. 2, the optical property of the NiO product was investigated by UVvis spectroscopy. Two bands at about 250 and 500 nm are observed on the UV-Vis spectrum of the NiO nanoparticles. The direct band gap (*E*g) of the NiO nanoparticles can be calculated by (*ahv*)2 = B(*hv*-*Eg*) equation. Fig. 2, show the plot of (*ahv*)2 versus *hv* for the NiO product. By the extrapolation on the linear region of this curve, the band gap was estimated to be about 2.1 eV.

Characterization of NiO: XRD

The structure and the phase composition of NiO nanoparticles, obtained after calcination at 450 °C for 3 h, have been characterized by powder XRD analysis (Fig. 3). The diffraction peaks were observed at 2θ values of 37.23º, 43.31º, 62.84º, 75.34º and 79.32º, can be indexed to (111), (200), (220), (311) and (222) crystal planes of the pure nickel oxide nanocrystalline phase with space group Fm3m [10-12]. The average size of NiO nanoparticles calculated from X-ray line broadening, using the Debye-Scherrer formula ($Dc = K\lambda / \beta\cos\theta$), is 15 nm.

Microscopy analysis of NiO: SEM and TEM

In addition to the XRD studies, the morphology, structure and size of the NiO nanoparticles have been investigated by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) (Fig. 4). The detailed of SEM and TEM images clearly indicate similar morphologies and size of NiO nanoparticles. The TEM images show the formation of NiO nanoparticles with the diameter distribution of 10-20 nm.

CONCLUSIONS

In this research work, nickel oxide nanoparticles were prepared by solid-state thermal decomposition of nickel complex. The crystalline structure, optical property and morphology of the synthesized NiO nanoparticles have been studied by FT-IR, UV-Vis, XRD, SEM and TEM. The absence of any residual complex traces or other phases indicated the as-prepared NiO samples to have high purity. Solid state thermal decomposition method is introduced as an environment-friendly and facile for the synthesis of nanoparticles of NiO.

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