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Synthesis and characterization of NiO nanoclusters via thermal decomposition

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ABSTRACT

Thermal decomposition process has been developed to synthesize nickel oxide (NiO) nanoclusters via the reaction between a new precursor, nickel oxalate $[Ni(O_4C_2)(H_2O)_4]$ and oleylamine ($C_{18}H_{37}N$). The combination of triphenylphosphine ($C_{18}H_{15}P$) and $C_{18}H_{37}N$ were added as surfactants to control the particle size. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and ultraviolet–visible (UV–Vis) spectroscopy. The synthesized NiO nanoclusters have a cubic structure with average size 2–10 nm.

1. Introduction

Recently, nanomaterials have attracted extensive interest because of their unique properties in various fields in comparison with their bulk counterparts [1]. A reduction in particle size to nanometer scale results in various interesting properties compared with their bulk properties. Having a large surface area, metal oxide nanomaterials show great advantages over conventional materials in many applications. Nanosized nickel(II) oxide has demonstrated excellence properties such as catalytic [2], magnetic [3], electrochromic [4], optical and electrochemical properties [5]. Furthermore, nickel oxides can be used as a transparent p-type semiconducting layer [6] and are being studied for applications in SMART windows, electrochemical supercapacitors [7] and dye-sensitized photocathodes [8].

In accomplishing the synthesis and manipulation of the nanostructured nickel oxide, a variety of strategies have been employed, such as evaporation [9], sputtering [10], electrodeposition [11], thermal decomposition [12] and sol–gel techniques [13]. Thermal decomposition method has some advantages such as simple process, low cost and easiness to obtain high purity products hence it is quite promising and facile rout for industrial applications.

Many reports have concerned the synthesis of NiO nanocrystals, including NiO nanorings [14], nanosheets [15], nanoribbons [16] and nanoclusters [17]. Recently, Shah reported synthesis of 50–60 nm nickel oxide nanoparticles after 12 h using sonication and hydrothermal methods [18]. More recently, the NiO nanoparticles were synthesized using two different microemulsion approaches by Palanisamy and Raichur. It was reported that $Ni(OH)_2$ particles were first formed which were then calcined at 600 °C to obtain 47 nm nickel oxide NiO particles [19]. Gao and co-workers synthesized NiO nanorods consist of numerous NiO nanoparticles by thermal decomposition of rod-like nickel oxide precursor achieved by microwave-assisted method [20]. Rodríguez-Llamazares et al. synthesized nickel/nickel oxides nanoparticles by a method based on ligand displacement of bis(1,5-cyclooctadiene)-nickel(0), zerovalent organometallic precursor and simultaneous formation of a thiourea inclusion compound [21]. In this study, it is tried to synthesis relatively small NiO nanoclusters from a simple and nontoxic precursor in a short time and with an easy, low temperature, low cost method without using any special instrument.

Nanostructured metal clusters are isolable particles of sizes between 1 and 50 nm. In order to prevent agglomeration, these nanosized entities have to be stabilized by ligand molecules or a whole plethora of "protecting shells" [22]. Nanoclusters are polycrystals in which the size of the individual crystallites is of the order of several nanometers. Therefore, a large fraction of the atoms in nanocluster particles is surface or interface atoms. Any structure sensitive to physical properties is expected to differ between nanocluster particles and bulk materials.

However, an improvement in the thermal decomposition process should be made in preparing NiO nanocrystals with uniform size in order to extend the application areas and satisfy the needs of fundamental research. Although the thermal decomposition of nickel oxalate has been studied in the past, no previous studies have investigated the synthesized nickel oxide nanoclusters. In this paper, we report synthesis of NiO nanoclusters by thermal decom-

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position of $[Ni(O_4C_2)(H_2O)_4]$, without any additional reducing agents. This precursor is a cheap and easy prepared complex with low toxicity.

2. Experimental

All the chemical reagents used in our experiments were of analytical grade and were used as received without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The elemental analysis (carbon, hydrogen and nitrogen) of the materials was obtained from Carlo ERBA Model EA 1108 analyzer. Thermogravimetric-differential thermal analysis (TG-DTA) were carried out using a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 mL min^{-1} and a heating rate of 10 °C min^{-1}. The electronic spectra of the complexes were taken on a Shimadzu UV–visible scanning spectrometer (Model 2101 PC).

Nickel oxalate precursor was synthesized according to this procedure: the $Ni(COOCH_3)_2 \cdot 4H_2O$ was dissolved in 10 mL of distilled water to form a homogeneous solution. A stoichiometric amount of potassium oxalate dissolved in an equal volume of distilled water, was dropwise added into the above solution under magnetic stirring. The solution was stirred for about 15 min and a green precipitate was isolated, washed and dried at 50 ℃. The obtained product was characterized by FT-IR, elemental analyses and thermogravimetric analysis (TGA) [5]. *Anal.* Calc. for $[Ni(O_4C_2)(H_2O)_4]$: C, 10.98; H, 3.69; Ni, 26.83. Found: C, 10.89; H, 3.57; Ni, 26.74%.

The main synthetic procedure in order to approach to final products is a modified version of the method developed by Hyeon and others for the synthesis of metal nanocrystals that employ the thermal decomposition of transition metal complexes [23,24]. In current synthesis, NiO nanoclusters were prepared by the thermal decomposition of nickel oxalate as precursor. First 0.6 g of $[Ni(O_4C_2)(H_2O)_4]$ and 5 mL of $C_{18}H_{37}N$ were mixed to produce $[Ni(O_4C_2)(H_2O)_2]$–oleylamin as suggested intermediate precursor. The solution was placed in a 50 mL three-neck distillation flask and heated up to 140 ℃ for 60 min. Then 5 g of $C_{18}H_{15}P$ was injected into the resulting metal-complex solution at 240 ℃. The color of the solution changed from green to black, indicating generation of colloidal products. The black solution was aged at 240 ℃ for 45 min, and was then cooled to room temperature. The black products were precipitated by adding excess C_2H_5OH to the solution. The NiO nanoclusters were washed with C_2H_5OH. These products could easily be re-dispersed in nonpolar organic solvents, such as C_6H_{12} (Scheme 1). The synthesized nanoclusters were characterized by XRD, TEM, FT-IR and UV–Vis techniques.

3. Results and discussion

In order to make sure of the precursor composition, elemental analysis was done. The TGA curve of the as-prepared precursor is shown in Fig. 1. It can be seen that there are two distinct weight loss steps. The first weight loss occurs at 110–190 ℃, which corresponds to the evaporation of crystallized water, that is to say, nickel oxalate in the stage. The second weight loss step occurs at the temperature range 210–370 ℃. The weight loss at 210–370 ℃ may be ascribed to the decomposition of the oxalate. The weight loss of two steps is about 17.80% and 41.18%, which is close to the theoretical value.

The XRD diffraction patterns of the sample of nickel oxides were recorded for the identification of the products (Fig. 2). The main diffraction peaks were observed at 37.18°, 43.42°, 62.82°, 74.20° and 79.2° in the XRD pattern of the nickel oxide which confirm that the formed material is nickel oxide. The diffraction peaks match with the standard values and they can be indexed to pure cubic phase of NiO (*Fm3 m*) with lattice parameter $a = 4.1771$ Å (JCPDS: 78-0429). The crystal size of the NiO nanoclusters was estimated by Debye–Scherrer equation ($d = 0.9\lambda/\beta\cos\theta$) and it was about 2.7 nm, which is in agreement with the other observation results. The diffraction peaks are clearly broadened, which can be the result of the reduced particle size.

To investigate whether the surface of the nanoparticles was capped with organic surface, the Fourier transformed infrared (FT-IR) of the as-synthesized samples was performed. Fig. 3 shows the FT-IR spectra of NiO nanoclusters and progressive formatted

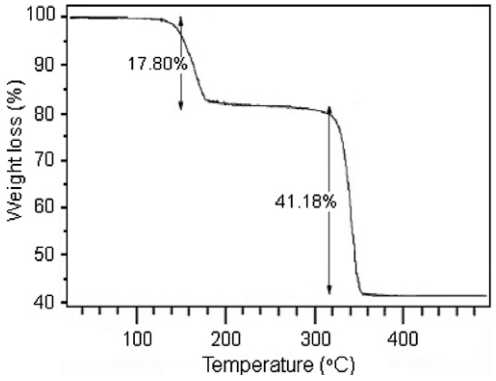
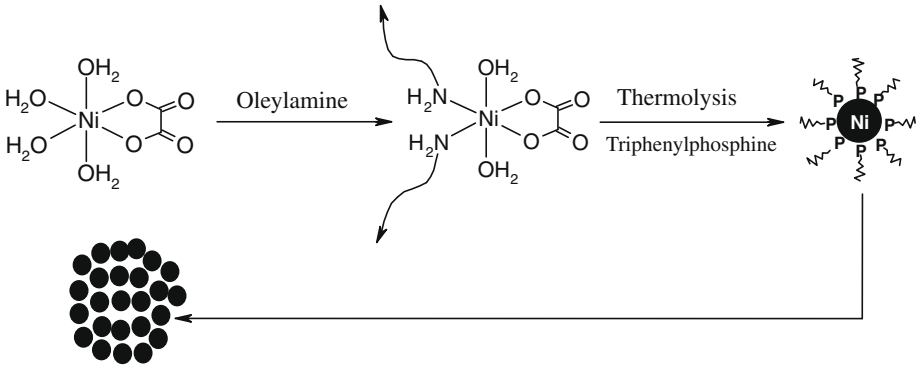


Fig. 1. TGA of the nickel oxalate precursor.



Scheme 1. Schematic diagram illustrating the formation of NiO nanoclusters.