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Nickel oxide nanoparticles: Synthesis and spectral studies of interactions with glucose ☆

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ABSTRACT

Nickel oxide (NiO) nanoparticles were successfully synthesized by the reaction of nickel chloride with hydrazine at room temperature and thermal decomposition of the precursor nickel hydroxide ($Ni(OH)_2$) nanoparticles. The products were characterized by X-ray diffraction, Transmission electron microscopy, Fourier transform infrared spectroscopy, and UV–vis absorption spectroscopy. The result of thermogravimetric analysis showed that the $Ni(OH)_2$ nanoparticles are calcinated at ~400 °C. The interactions between NiO nanoparticles and glucose have been studied using UV–vis absorption and fluorescence spectroscopy. The zeta-potential of NiO nanoparticles was used to gain insight about the interaction mode between NiO nanoparticles and glucose.

1. Introduction

Nickel oxide NiO is an important transition metal oxide with cubic lattice structure. It has attracted increasing attention owing to potential use in a variety of applications such as: catalysis [1], battery cathodes [2,3], gas sensors [4], electrochromic films [5] and magnetic materials [6,7]. It can also be extensively used in dye sensitized photocathodes [8]. It exhibits anodic electrochromism, excellent durability and electrochemical stability, large spin optical density and various manufacturing possibilities [9]. Also for low material cost as an ion storage material, NiO semiconductor becomes a motivating topic in the new area of research. Because of the volume effect, the quantum size effect, the surface effect and the macroscopic quantum tunnel effect, nanocrystalline NiO is expected to possess many improved properties than those of micrometer-sized NiO particles.

With advancements in all areas of industry and technology, the interest has been focused on nanoscale materials, which stems from the fact that new properties are required at this length scale and, equally important, that these properties change with their size and morphology. Thus, many methods have been attempted to prepare nanosized nickel oxide, including nanoparticles [10], nanorings [11], nanosheets, and nanoribbons [12]. However, there are only few biosensor applications. Li et al. developed a novel amperometric glucose sensor based on NiO hollow nanosphere [13]. The NiO is suitable for electrostatic immobilization of proteins having low ionization potential because the ionization potential of NiO is about 10.7 eV and the hollow-sphered NiO was good responsible for high loading of glucose oxidase and showed fast electron transfer with a sensitivity of 3.43 μA mM^{-1} and a detection limit of 47 μM (S/N=3) [13]. Fluorescence based glucose sensors have appeared in the literature as an alternative way of continuous monitoring of glucose levels. These sensors are highly specific towards analytes but require built-in probes [14]. It has been reported that glucose is used as a reducing agent in preparation of metal nanoparticles [15]. So it could be assumed that glucose in blood serum would affect the optical properties of NiO nanoparticles when they are used in the organism. In the last decade the use of glucose biosensor was constructed by using metal nanoparticles [16–18] and metal-oxide including zinc oxide, copper oxides,

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manganese dioxide, titanium oxides, cerium oxide and silicon dioxide [19].

In the present work, we report the synthesis of NiO nanoparticles by the chemical reduction of nickel chloride with hydrazine at room temperature and thermal decomposition of the precursor nickel hydroxide nanoparticles. Also, the interactions between NiO nanoparticles and glucose have been discussed using UV–vis absorption and fluorescence spectroscopy. The zeta-potential measurements are used to assess the interaction mode. Experimental results have demonstrated that the optical properties of glucose solution can be altered by the addition of nickel oxide nanoparticles. This finding is significant for optical glucose sensors.

2. Experimental

2.1. Materials

All chemicals used in this experiment were of reagent grade and used without any further purification. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was purchased from Wilinson–Vickers Ltd., hydrazine monohydrate ($N_2H_4 \cdot H_2O$) solution was purchased from Merck, potassium hydroxide (KOH) was purchased from Sigma-Aldrich. Ethyl alcohol and acetone were received from Merck. All solutions were prepared with deionized water.

2.2. Synthesis of nickel oxide nanoparticles

NiO nanoparticles were synthesized by thermal decomposition of $Ni(OH)_2$ by modification of the method reported by GangWu et al. [20]. Nickel chloride hexahydrate (0.111 M) in absolute ethanol were used as precursors, and were added to hydrazine monohydrate solution (6.73 ml of molar ratio 5). The pH was adjusted from 8.0 to 12 using potassium hydroxide. The reaction was stirred for 2 h at room temperature. The resultant product was washed thoroughly with deionized water for removal of reaction residues followed by washing with acetone. Finally, deep green nanoparticles [$Ni(OH)_2 \cdot 0.5H_2O$] were formed, and dried in vacuum. The nickel hydroxide nanoparticles were converted to NiO via thermal decomposition at 600 °C. During the synthesis of NiO nanoparticles, the following reactions are reasonable to propose:

$$NiCl_2 \cdot 6H_2O + 6C_2H_5OH \rightarrow [Ni(C_2H_5OH)_6]Cl_2 \quad (1)$$

$$[Ni(C_2H_5OH)_6]Cl_2 + m\ N_2H_4 \rightarrow 6C_2H_5OH + [Ni(N_2H_4)_m]Cl_2 \quad (2)$$

$$[Ni(N_2H_4)_m]Cl_2 + 2KOH \rightarrow mN_2H_4 + Ni(OH)_2 \quad (3)$$

$$Ni(OH)_2 \overset{25-600\ ^\circ C}{\rightarrow} NiO \quad (4)$$

2.3. Equipment

UV–vis absorption spectra were measured on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorometer. The Fourier-transform infrared (FT-IR) spectra were measured with a JASCO spectrometer 4100 using the KBr pellet technique. The X-ray diffraction (XRD) measurements were conducted by using a Shimadzu 6000-XRD X-ray diffractometer using CuKα radiation ($\lambda = 1.54056$ Å). Transmission electron micrographs (TEM) were obtained using a JEOL 2010 microscope operating at an accelerating voltage of 200 kV. Zeta potential results were carried out on Brookhaven zeta potential/particle size analyzer.

2.4. Spectral measurements

It should be emphasized that when the interaction of particles with glucose was conducted at constant concentration of NiO nanoparticles, the absorption and emission data show little spectral changes. However, considerable spectral changes were observed when the interactions of the nanoparticles with glucose were performed at different concentrations of NiO nanoparticles and constant glucose concentration. This was likely because the reactions occur on the surfaces of NiO nanoparticles. Increasing the surface area of nanoparticles generally increases the rate of chemical reactions. The pH of the aqueous solutions was adjusted by phosphate buffer. All experiments were performed at pH 6.8, unless otherwise specified.

3. Results and discussions

3.1. Characterization of nanoparticles

In order to reveal the changes that occurred during heat treatment of the precursor powders, TGA analysis were carried out from 25 to 600 °C in atmosphere (Fig. 1). It is readily seen that the TGA curve showed two steps of weight loss. The first weight loss (found 8.6 wt%, Cal. 8.8 wt%) in a temperature range of 25–210 °C can be ascribed to the evaporation of half water molecule of crystallization. The second weight loss (found 17.8%, Cal. 17.7%) is due to the elimination of one water molecule in the range of 210–400 °C and associated with the thermal decomposition of Ni $(OH)_2$ to NiO nanoparticles. When temperature is above 400 °C, weight loss becomes fairly slight; indicating the

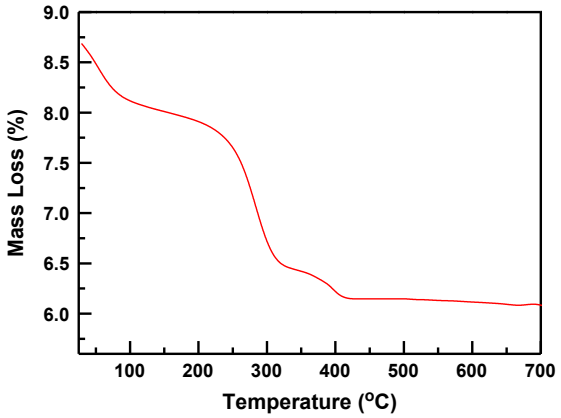

Fig. 1. TGA of $Ni(OH)_2$ nanoparticles.