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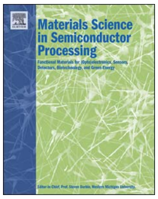

Effect of calcination temperature on Cu doped NiO nanoparticles prepared via wet-chemical method: Structural, optical and morphological studies

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ABSTRACT

In the present study, NiO and Cu-doped NiO nanoparticles were successfully synthesized by wet chemical method at room temperature using sodium hydroxide (NaOH) as precipitating agent. The as-prepared Cu-doped NiO powder samples were subjected to three different calcination temperatures such as, 350 °C, 450 °C and 550 °C in order to investigate the impact of calcined temperatures on the phase formation, particle size and band gap evolution. The phase formation and crystal structure information of the prepared nanomaterials were examined by X-ray powder diffraction (XRD). XRD revealed the face-centered cubic (FCC) structure. Average crystalline size of pure and doped samples estimated using Scherer formula was found to be 15 nm and 9 nm respectively. With increase in the calcination temperature from 350 °C to 550 °C for the Cu doped NiO samples the particle size of the nanoparticles was found to increase from 4 nm to 9 nm respectively. The optical study for both pure and doped NiO nanoparticles was performed using an UV–Vis spectrophotometer in the wavelength range of 200–800 nm. The strong absorption in the UV region confirms the band gap absorption in NiO and was estimated from the UV–Vis diffuse reflectance spectra via Tauc plot. Systematic studies were also carried out to study the effect of calcination on the optical transmittance. Samples were also investigated using Raman and Fourier Transform Infrared Spectroscopy (FTIR). Furthermore, morphology of the pure NiO and Cu-doped NiO Nanoparticles were examined by scanning electron microscope (SEM).

1. Introduction

Nanometer sized nickel oxide materials has received great attention in research and various application purposes. Nickel oxide (NiO), a p-type oxide semiconductor is an important transition metal oxide which exhibits a wide band gap of 3.6–4.0 eV [1]. The nanomaterial system also serves as an alternative material for energy applications, such as p-type semiconductor material for solar cells, electrochemical capacitors, photocatalysts, smart windows and organic light emitting diodes [2,3]. However, high resistivity of NiO has always been a concern in many applications. To overcome this limitation, doping of NiO with mono-valent impurities, such as copper (Cu) and lithium (Li) has been done. This kind of doping helps to improve the properties of NiO making it suitable in a variety of applications. For instance, enhanced electrochromic behaviour leads to better smart windows and good catalysis.

NiO nanoparticles (NPs) can be synthesized by different techniques, such as hydrothermal, microemulsion, solvothermal, chemical precipitation, sol-gel, thermal decomposition, combustion and microwave irradiation [4–10]. Using solvothermal technique, Anandan group obtained different morphologies of NiO NPs by using single precursor (Nickel acetate) in different solvents. The obtained nanoparticles were found to be around 25–30 nm [11]. Another work showed that $Ni(OH)_2$ precursor was first prepared by using microwave assisted hydrothermal technique and subsequently thermal decomposition was used to prepare NiO NPs [12]. NiO NPs prepared by using sol-gel method at pH 11 and calcination temperature 450 °C, revealed amorphous phase before calcination and crystalline phase after calcination (~32.9 nm average diameter) in XRD results [13]. Annealing study of NiO carried out by Kisan B et al. showed no changes in XRD peak upto 300 °C, whereafter, the peak width decreased. According to them, the annealing process not only increased the average crystallite size, but dislocations/defects were also reduced with increase in the calcinations temperature [14]. Nadeem et al. reported structural and magnetic study of NiO with respect to annealing temperature from 400 °C–800 °C. Results showed that at lower annealing temperature Ni phase was dominant and oxidation did not occur to form NiO. Moreover the particles were found to remain separated. At higher temperature, the particles became agglomerated and XRD data revealed

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increase in NiO phase with temperature [15]. NiO synthesized using chemical precipitation method indicated blue shift in optical study with increase in calcination temperatures. Thermogravimetric study revealed weight loss of precursor at calcinations temperatures of 50°C-350°C and complete decomposition of precursor to form NiO at 400 °C [16]. NiO/RGO composites prepared by hydrothermal method and treated at different calcinations temperatures (250 °C, 300 °C, 400 °C and 500 °C) showed that the intensity of diffraction peak in XRD increased with temperature. The particles size of NiO in NiO/RGO was 2.62, 3.60, 5.75 and 9.94 nm at 250 °C, 300 °C, 400 °C and 500 °C, respectively. Additionally, lower temperature calcined composites exhibited enhanced electrochemical performance due to small crystallite size and high surface area [6].

Research work was also carried out to prepare 1-D NiO-RuO_2-carbon composite nanofibers using thermal assisted electrospinning technique [17]. The fabricated composite nanofibers were further utilized in the application of asymmetric supercapacitors and Li-cyclic studies. Preparation of vertically aligned single crystalline NiO nanowalls on a Ni foil using simple and efficient method of plasma assisted oxidation method was reported by Sow et al. group [18]. They have demonstrated the application of these NiO nanowall films in electron field emission and Li-ion battery application (turn-on field of 7.4 V/μm, maximum current density of ~160 μA/cm^2). G. R. Balakrishna group [19] utilized gel combustion technique synthesized NiO nanoparticles using various weight ratios of oxidizer (O), nickel nitrate hexahydrate and fuel (F) such as cassava starch respectively. Their result showed that when the oxidizer to fuel ratio is 1:1, the photocatalytic degradation of MB dye performed in sunlight exhibited higher degradation efficiency (94%) as compared to UV light. The prepared nanoparticles were tested for energy storage where electrochemical studies depicted a reversible capacity of 940 and 785 mA h/g when O:F ratio was taken as 1:0.5 and 1:1 respectively. Antibacterial activity was also performed against a fungal strain and two bacterial strains.

A few researchers synthesized NiO and Cu doped NiO NPs by using chemical co-precipitation technique. The reported $Ni_{1-x}Cu_xO$ (6.52–13.4 nm) exhibited decreased particle size with increasing doping concentration. They showed that doping at lower concentration was suitable electrode material for super capacitor application [20,21]. Cu doped ZnO co-doped Ni ($Zn_{0.96-X}Ni_{0.04}Cu_XO$) NPs synthesized by sol-gel method showed well agglomerated rod like morphology [22]. In literature, un-doped, Fe, Mn and Zn doped NiO NPs synthesis by chemical co-precipitation method were also documented [9,23,24]. Recently researchers have also reported the application of electrospun NiO-SnO_2 nanofibers in the electrical and humidity sensors [25].

In addition to NiO, few other Binary Oxides MO (M = Co, Fe, Cu, Mn) systems of significant interest is also reported in literature. M. V. Reddy et al. [26] utilized urea combustion method nitridation and cabothermal reduction methods to prepare Co_3O, CoN and CoO respectively. Their results of CV and galvanostatic cyclic tests indicated that the prepared materials showed negligible capacity fading. Also CoN proved to be the best anode material with higher theoretical capacity of 1100 mAh g^{-1} due to formation of Co metal and Li_3N.The same group also reported nano/submicrometer and micrometer sized CuO prepared by molten salt method at different temperatures for Li-ion battery (LIB) applications. They concluded that at the end of 40th cycle the CuO prepared at 750 °C exhibited high and stable capacity of ~620 mAh g^{-1} [27]. Other application of energy storage studies on CuO is also well documented [28–31]. Formation of exfoliated graphene oxide (EG)/Iron (II) oxide FeO composite using a novel and new graphenothermal reduction process is also reported in literature [32]. This one pot synthesis process is eco-friendly, scalable and the synthesized composite material proved to be a suitable alternate anode material for LIB's. The capacity and cyclic stability was much higher when compared with their individual counterpart. The same technique was utilized even to prepare EG/MnO Manganese (II) oxide composite which exhibited a high reversible capacity of 936 mAh g^{-1}at a current rate of 75 mAg^{-1} [33]. In addition capacity retention of ~84% (784 mAh g^{-1}) was observed even at the 100th cycle.

In this work, we have synthesized pure NiO and Cu doped NiO NPs (NiO:Cu) by wet chemical method successfully. Although researchers have used NiO and Cu doped NiO films prepared by other methods for different studies, such as physical, optical, electrochemical, magnetic; [34–37] no proper investigation has been done on the effect of calcination temperature on NiO NPs and NiO:Cu NPs. In the present work, a systematic study has been done on the effect of calcination temperature on the structural, morphological and optical properties of NiO and Cu doped NiO nanoparticles.

2. Experimental details

2.1. Synthesis of NiO and Cu doped NiO nanoparticles

All chemicals used in this experimental work were of analytical reagent grades and used without any further purification. NiO and NiO:Cu NPs were prepared by chemical co-precipitation method [8]. $NiCl_2 \cdot 6H_2O$ (2.37 g) and $CuSO_4 \cdot 5H_2O$ (2.49 g) were used as the sources of Ni and Cu, respectively. For pure NiO NPs synthesis, $NiCl_2 \cdot 6H_2O$ and NaOH(0.39 g) were taken in desired molarity of 0.1 M. Then aqueous solution of $NiCl_2 \cdot 6H_2O$ was stirred for 20 min. The pH value was adjusted to 10 by using NaOH solution. Once pH value of solution has attained 10, allow this solution to stir for 4 h. Samples were washed by DI water several times and dried for 8 h at 80 °C in hot air oven. Finally, dried powders were calcined at 550 °C to obtain NiO NPs. Cu doped NiO samples were prepared using the same procedure as described for NiO except desired quantity of $CuSO_4 \cdot 5H_2O$ solution were added into $NiCl_2 \cdot 6H_2O$ to prepare 4% doping samples. As dried NiO:Cu powder samples were calcined for three different temperatures 350 °C, 450 °C and 550 °C respectively.

2.2. Sample characterization

The crystallinity and phase formation of NiO and NiO:Cu NPs were identified by using a Bruker X ray diffractometer with Cu Kα (1.54 Å) radiation source over a range of 2θ from 20° to 80°. Optical properties were analyzed by Specord 210 plus UV–visible absorption spectra instruments in the range of 200–800 nm. Transmittance and Diffuse reflectance study was performed by V-670 JAASCO. Surface morphology of the samples was analyzed by using Scanning Electron Microscope (SEM; FEI Quanta FEG 200–High Resolution Scanning Electron Microscope) coupled with energy dispersive X-ray spectroscopy (EDS). Atomic Absorption Spectroscopy (AAS) was utilized to estimate the amount of Cu doping in NiO. Raman spectra were measured at room temperature using 532 nm green laser beam (ENWaveoptronicsezRaman pro) while Fourier Transform Infrared (FTIR; IRAffinity-1 Shimadzu) were also utilized to characterize the prepared NPs.

3. Results and discussion

3.1. Optical properties

The UV-Vis absorption spectra for the NiO and NiO:Cu samples recorded in the wavelength range of 200 nm to 800 nm is shown in Fig. 1. Both the samples showed strong absorption peaks in the UV region which is blue shifted from the absorption edge of bulk NiO [38]. Pure NiO exhibited the absorption peak at 344 nm while Cu doped NiO NPs showed peak at 323 nm (Fig. 1(a)). This lower wavelength shift or blue shift in the latter case is attributed to Burstein – Moss effect, which confirms the quantum confinement effect and Fig. 1(b) shows the absorption data for the NiO:Cu samples calcined at different temperatures viz. 350 °C, 450 °C and 550 °C. The absorption peaks in the UV region appeared at wavelengths of about 262 nm, 280 nm and 328 nm,