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Original Article

Structural, optical and magnetic properties of well-dispersed NiO nanoparticles synthesized by CTAB assisted solvothermal process

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Abstract
We have synthesized without and with cationic surfactant (CTAB) assisted NiO nanoparticles via facile solvothermal process. Their nanostructures as well as physical and chemical properties has been characterized by X-ray powder diffraction (XRD), Fourier transformed infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, transmission electron microscopy (TEM), ultraviolet–visible (UV-vis) spectroscopy, photoluminescence (PL) spectroscopy and vibrating sample magnetometer (VSM). The possible formation mechanism has also been phenomenologically proposed for as-synthesized NiO nanoparticles.

Key words: NiO; Nanoparticles; Structural properties; Optical properties; Magnetic properties.

1. Introduction
Over recent years increasing attention has been focused on the production of novel nanoscale materials. Of particular interest are the nanostructured metal oxide materials. One of the most commonly used transition metal oxides for a wide range of application is NiO. It is a NaCl-type antiferromagnetic oxide semiconductor. Furthermore, it is considered to be a model semiconductor with p-type conductivity films due to its wide band-gap energy range from 3.6 to 4.0 eV [1]. Uniform sized with well-dispersed NiO nanoparticles as a kind of functional material has attracted extensive interests due to its novel optical, electronic, magnetic, thermal, and mechanical properties and potential application in catalyst, battery electrodes, gas sensors, electrochemical films, photo-electronic devices, and so on. In these applications, it is still needed for synthesizing high-quality and ultrafine powders with required characteristics in terms of their size, morphology, optical properties, magnetic properties, and so on, which are the most essential factors which eventually determine the characteristic of the final products.

The particle structural property (particle size, distribution, and morphology) is closely related to the preparation techniques. Several methods have been used and developed for synthesizing crystalline oxide powders in nanoscale dimensions. In many of them, the main objective is to reduce the cost of chemical synthesis, and to produce materials for technological applications. Many researchers have employed NiO nanoparticles by various methods, such as sol–gel [2], surfactant-mediated synthesis [3], thermal decomposition [4], solvothermal [5], and polymer- -matrix assisted synthesis [6] and so on. Among various methods the preparation of metal oxide nanostructures through solvothermal process open a new view for chemists since there are many advantages in it such as: its simple process, low cost, control of process conditions, particles size, particles crystal structure and easiness to obtain high purity products. Hence, it is quite promising and easy to use for industrial applications.

NiO nanoparticles with a uniform size and well dispersion are desirable for many applications. To this day, it is still much more difficult to prepare size-homogeneous and well-dispersed NiO nanoparticles with lesser particles size. Xiang et al. [7] prepared NiO nanoparticles with diameter of 10–15 nm by air-calcination of Ni(OH)2 • NiCO3 • xH2O, while the agglomeration of nanoparticles is a difficult question from the SEM image. Wang yude et al. [8] prepared NiO nanocrystalline with average particle diameter of 18–55 nm using surfactant-mediated. From the TEM image, the NiO nanoparticles were not well-dispersed. Dongliang Tao et al. [9] prepared well-dispersed NiO nanoparticles but the average particle diameter of 30 nm using polyvinylpyrrolidone assisted.

In this paper, presents the results of an investigation into the well-dispersed and lesser NiO nanoparticles by solvothermal processing. Without and with CTAB assisted NiO were studied and compared the effect of the reactant chemistry, average crystallite size, degree of agglomerate...
-eration, optical and magnetic properties were reported and discussed.

2. Materials and Methods

2.1 Synthesis of well-dispersed NiO nanoparticles

All the chemical reagents used in our experiments were of analytical grade and were used as received without further purification. NiO nanoparticles were successfully synthesized by using 1 g of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and 0.5 g of cetyltrimethylammonium bromide (CTAB) dissolved in 80 ml of absolute ethanol. After five minutes of vigorously stirring the solution poured into autoclave capacity of 100 ml. And maintained at 200°C for 24h, then the autoclave was cooled to room temperature. The greenish precipitates were washed with distilled water and absolutely ethanol for six times to remove impurity. The final products were dried in vacuum at 60°C for 6h. The sample named as (b), and without CTAB, NiO nanoparticles prepared with the same procedure as mentioned above and the sample named as (a).

2.2 Characterization of synthesized NiO nanoparticles

The synthesized NiO nanoparticles were characterized by the following. X-ray powder diffraction (XRD) by using a Seifert (JSO-DEBYEFLExX 2002) diffractometer with Cu-Kα radiation (λ=0.1540 nm), Fourier transformed infrared (FT-IR) spectroscopy by using NICOLET 205 spectrometer (as pellets in KBr). Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) analysis (accompanied) performed on a Hitachi S-4500. Transmission electron microscope (TEM) was taken with a JEOL-3010 operating at 200KV. Ultraviolet–visible (UV-vis) absorption spectra were obtained from a Varian Cary 5E spectrophotometer. Photoluminescence (PL) measurements were carried out on a Fluoromax-4 spectrophotometer with a Xe lamp as the excitation light source. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) at room temperature.

3. Results

The purity and crystallinity of the as-synthesized NiO nanoparticles were examined by using powder X-ray diffraction (XRD) as shown in Fig.1. Fig.2 shows the FT-IR spectra of NiO nanoparticles, which showed several significant absorption peaks. The surface morphological studies and composition analysis of the nickel oxide nanoparticles were carried out using SEM and EDX images shown in Fig. 3a-c. The size and morphology of primary nanoparticles can be further confirmed from imaging by TEM analysis shown in Fig.4a and 4b. Selected area electron diffraction pattern of the samples shown in Fig.5a and 5b. Fig. 6 shows the UV-Vis absorption spectra of the as-synthesized NiO nanoparticles. The band gap was determined by using extrapolating the linear portion of the plot shown in Fig.7a and 7b. Fig.8 shows the room-temperature photoluminescence spectra of the samples. The magnetic property of NiO nanoparticles has been measured by VSM shown in Fig. 9.

4. Discussion

The XRD patterns of the product confirm that the formed material is nickel oxide. It can be seen from XRD patterns that the diffraction peaks are low and broad due to the small size effect. The peaks positions appearing at 2θ = 37.20°, 43.20°, 62.87°, 75.20°, and 79.38° can be readily indexed as (111), (200), (220), (311), and (222) crystal planes of the bulk NiO, respectively. All these diffraction peaks can be perfectly indexed to the face-centered cubic (FCC) crystalline structure of NiO, not only in peak position, but also in their relative intensity of the characteristic peaks, which is in accordance with that of the standard spectrum (JCPDS, No. 04-0835). The XRD pattern shows that the samples are single phase and no any other impurities distinct diffraction peak except the characteristic peaks of FCC phase NiO was detected. This result shows that the physical phases of the NiO nanoparticles have higher purity prepared in this work.
Fig. 3 SEM images of as-synthesized (a) without and (b) with CTAB assisted NiO nanoparticles; (c) EDX spectrum of CTAB assisted samples.

Fig. 4 TEM images of as-synthesized (a) without and (b) with CTAB assisted NiO nanoparticles, corresponding particles size distribution inserted.

Fig. 5 SAED pattern of (a) without and (b) with CTAB assisted NiO nanoparticles.
**Fig. 6** UV-Vis absorption spectra of as-synthesized (a) without and (b) with CTAB assisted NiO nanoparticles.

**Fig. 7** $(Ahv)^n$ versus $(hv)$ spectra of as-synthesized (a) without and (b) with CTAB assisted NiO nanoparticles.

**Fig. 8** Room temperature photoluminescence spectra of as-synthesized (a) without and (b) with CTAB assisted NiO nanoparticles.

**Fig. 9** Magnetization vs. applied at 300 K for NiO nanoparticles obtained for CTAB assisted sample.

The crystallite size of the as synthesized nickel oxide nanoparticles calculated from the diffraction peaks using the Debye-Scherrer’s formula:

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where $K$ is a constant (0.9); $\lambda$ is the X-ray wavelength used in XRD (0.15418 nm); $\theta$ is the Bragg angle; $\beta$ is the FWHM (full width at half maximum intensity), that is, broadening due to the crystallite dimensions. The diameter of the nanoparticles calculated by the Debye-Scherrer’s formula are 27 and 25 nm for without and with CTAB assisted NiO nanoparticles, respectively, which are good agreement with TEM analysis.

In the FT-IR spectra, the broad absorption band centered at 3440 cm$^{-1}$ is attributable to the band O–H stretching vibrations and the band near 1606 cm$^{-1}$ is assigned to H–O–H bending vibrations mode were also presented due to the adsorption of water in air when FT-IR sample disks were prepared in an open air. The peaks near 2930 and 2365 cm$^{-1}$ are associated with the CH stretching vibrations.
mode on the surface of the products. The absorption band at 1396 and 1098 cm$^{-1}$ indicates the existence of carbonates. The broad absorption band in the region 430 – 530 cm$^{-1}$ is assigned to Ni-O stretching vibration mode [10]; the broadness of the absorption band indicates that the NiO powders are nanocrystals and well crystallized. The size of samples used in this study was much less than the bulks form NiO, so that NiO nanoparticles had its IR peak of Ni-O stretching vibration and shifted to blue direction. Due to their quantum size effect and spherical nano-structures, the FT-IR absorption of NiO nanoparticles is blue-shifted compared to that of the bulk form.

SEM images show the without and with CTAB assisted NiO nanoparticles. From the SEM analyses, one can conclude the formation of nanoparticles spherical structure. Moreover, in the Fig. 3a shows the highly aggregated spherical nanoparticles compared than the 3b. Fig. 3b shows the loosely aggregated image due to the effect of cationic surfactant (CTAB). The EDX spectrum for the CTAB assisted NiO nanoparticles shown in Fig. 3(c) revealed that the presence of Ni and O as the only elementary species in the sample, without CTAB assisted NiO also showed Ni and O as the only elementary species in the sample (not shown). Moreover, no additional peaks corresponding to any other elements except Ni and O were observed.

Use of TEM for determining the particle is preferred over X-ray line broadening. This technology is more direct and less likely to be affected by experimental errors and/or other properties of the particles such as strain or a distribution in the size. Fig. 4a and 4b depicts the well-dispersed NiO nanoparticles for without and with CTAB assisted samples. The figures indicate that most particles are fine and spherical while some are elongated. The average particles size was measured to be 27 and 25 nm for without and with CTAB assisted samples, which was in good agreement with calculated particles size by XRD analysis. The corresponding particles size distribution was inserted, its can be seen that the particles are narrowly dispersed. From the images, the nanoparticles are composed of smaller nanoparticles. This indicates that there is a hierarchy, which NiO nanoparticles at smaller level self-assemble into larger nanoparticles. A typical SAED patterns taken from the individual nanoparticles was shown in Fig. 5, for without and with CTAB assisted samples, indicating that the NiO nanoparticles were polycrystalline structure.

The absorption edges are seen to be shifted slightly towards lower wavenumber (blue shift). This shift indicates an increase in the band gap, which can be attributed to a decrease in particle size. The value of the absorption edge of without and with CTAB assisted samples was 318 and 316 nm respectively, blue shift was observed due to the quantum confinement effects. According to the data of the absorption spectra, the optical band gaps ($E_g$) of NiO nanoparticles can be estimated by using the following equation:

$$(Ahv)^n = B (hv - E_g)$$

where $h\nu$, $A$, $B$ and $n$ are photo energy, absorbance, constant relative to the material and either 2 for direct transition or 1/2 for an indirect transition, respectively. Hence, the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the $(Ahv)^n$ – $hv$ curve to zero shown in Fig. 7a and 7b. The band gap is determined by extrapolating the linear portion of the plot to the energy axis. The corresponding band gap energy to be calculated 3.89 and 3.92 eV for without and with CTAB assisted samples, which was good agreement with the value of 3.6i-i4.0 eV for the NiO nanoparticles [11]. The increasing trends of the band gap energy upon the decreasing particles size are well presented for the as-synthesized samples. This effect is likely due to the chemical defects or vacancies present in the intergranular regions generating new energy level to reduce the band gap energy [12]. No linear relation was found for $n = 1/2$, suggesting that the as-synthesized NiO nanostructures are semiconducting with direct transition at this energy [13].

The resulting emission characteristics show the origination of one main strong emission peak centered at around 3.59 eV (345 nm) and seven shoulder emission peaks observed nearby 370, 395, 410, 450, 467, 481 and 493 nm. The origin of the main strong peak attributed to the electronic transition of the Ni$^{2+}$ ions. Optical absorption study reveals the existence of several transitions at energies below band gap in NiO [14]. Adler and Feinleib [15] reported a series of absorption peaks below 4 eV as purely intraionic 3d$^8$-3d$^9$ transitions of Ni$^{2+}$. The study of electron energy loss spectroscopy (EELS) and spin polarized electron energy loss spectroscopy (SPEELS) also confirm the existence of this kind of transition of the 3d$^9$ electrons in NiO [16]. The property of strong room temperature UV emission should be attributed to the high purity and perfect crystallinity of the as-synthesized cubic NiO nanostructures. The other shoulder emission peaks might be attributed to near band-to-band transition and oxygen-related defects.

The magnetic property of NiO nanoparticles has been measured. Fig. 9 shows the hysteresis loops of NiO nanoparticles at 300 K (CTAB assisted sample). It can be seen that NiO nanoparticles present a superparamagnetic behavior although NiO bulk material is antiferromagnetic [17]. The pure NiO nanoparticles also observed the same properties (not shown).

Here, a possible mechanism for the NiO nanoparticles is as follows: CTAB is a cation surfactant and ionizes completely in ethanol. The resulted cation is also a tetrahedron with a long hydrophobic tail [18]. Therefore, ion-pairs between Ni(OH)$_2$$^+$ and CTA$^-$ could form due to electrostatic interaction [18]. In the crystallization process, surfactant molecules adsorbed on the crystal nuclei not only serve as a growth director but also as a protector to prevent from aggregation of the product. As a result, NiO nanospheres were produced. According to above results, the smallest sized and well-dispersed NiO nanoparticles were obtained successfully with cationic surfactant (CTAB) assisted by the solvothermal process.

5. Conclusions

Without and with cationic surfactant (CTAB) assisted NiO nanoparticles were successfully synthesized via facile solvothermal process. The average particles size was
calculated to be 25 and 27 nm from XRD analysis and confirmed by TEM. The spherical morphologies of the samples were observed by SEM analysis. Optical properties of the samples were studied by UV-vis absorption and photoluminescence spectroscopy. The synthesized NiO nanoparticles present the superparamagnetic behavior although NiO bulk material is antiferromagnetic. We hope that the procedure mentioned in experimental section can be a suitable route for high-grade synthesis of NiO nanoparticles.

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