



Ionic Liquid-Assisted Synthesis of Nickel Oxide Magnetic Nanoparticles

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In this paper, the synthesis of nickel oxide nanoparticles using a novel synthesis medium namely 1-*n*-butyl-3-methylimidazolium trifluoromethane sulfonate [BMIM][TfO] ionic liquid. Ionic liquids have been used as a potential electrolyte/medium for the nanoparticle synthesis, especially for their suitability at high temperature withstandability. During the NiO nanoparticle synthesis, Ni(OH)₂ precipitates first consequently NiO nanoparticles is formed upon calcinations at 400 °C. Nickel hydroxide and oxide formation was confirmed by XRD, FT-IR and TGA results of the NiO as precipitated and calcinated samples. The SEM image of the calcinated sample shows the average particle size is 45 nm with small rock salt-like morphology. The synthesized NiO nanoparticle exhibits an excellent superparamagnetic behaviour without showing any coercivity. The magnetic property of NiO nanoparticle was studied with vibrating sample magnetometer.

Key Words: Oxides, Chemical synthesis, Thermogravimetric analysis, X-Ray diffraction, Magnetic properties.

INTRODUCTION

Now-a-days, nanostructured materials have been attracted more interest in both fundamental as well as applied research owing to their extraordinary physical and chemical properties. Nickel oxide nanoparticle is considered to be a proto-typical *p*-type semiconductor with wide band gap of 3.6-4.0 eV¹. Nickel oxide nanoparticle is demonstrated for their excellent optical, electronic, magnetic, thermal, catalytic and mechanical properties². Important applications of NiO nanoparticles include cathode materials for alkaline batteries, electrochemical supercapacitors, smart windows, active layer for gas sensors and dye-sensitized photocathodes³. In the recent years, for the synthesis of NiO nanoparticles, chemical methods such as sol-gel, hydrothermal, precipitation, emulsion, electrodeposition and sputtering techniques have been developed⁴⁻⁶.

Room-temperature ionic liquids (RTILs) provide a new route for the preparation and processing of materials owing to their special properties such as low vapour pressure, high fluidity, low melting temperature, air and water stability, low toxicity, strong solvent power for organic and inorganic compounds, nonflammability and high ionic conductivity⁷. For the past couple of years, ionic liquids have been used for the preparation of nanomaterials. Inorganic oxides including flower-like and shuttle-like ZnO nanoparticles⁸, CuO nanosheets⁹, nanoneedle of manganese oxide¹⁰ *etc.*, have been successfully synthesized in room temperature ionic liquids.

This is the first effort made to synthesize NiO nanoparticles *via* precipitation method using *n*-butyl-3-methylimidazolium trifluoromethane sulfonate [BMIM][TfO] ionic liquid as medium.

EXPERIMENTAL

Synthesis of NiO nanoparticles: All the chemicals used in this study were purchased from E-Merck and were used as received without further purification. For the synthesis of NiO nanoparticle, 0.75 % of [BMIM][TfO] ionic liquid was prepared using deionized water under constant stirring for 0.5 h to get homogenous solution. Nickel nitrate tetrahydrate (0.1 M) solution was added slowly to the above [BMIM][TfO] ionic liquid solution with continuous stirring. Then, a concentrated solution of sodium hydroxide was quickly added to the above reaction mixture to adjust the pH 11. After the addition of NaOH, the colour of the solution becomes light green and consequently precipitate was formed. The obtained precipitate was magnetically concentrated and removed by centrifugation at 8000 rpm. The precursor (nickel hydroxide) residue was washed with water and ethanol for several times dried in a vacuum. The as-synthesized sample was interrogated for TGA analysis to confirm the NiO nanoparticle formation and further the particles was calcinated at 250 and 400 °C for 3 h in air.

The as-prepared and calcined particles at 250 and 400 °C were subjected to TGA analysis of a heating rate of 20 °C/min using S11X* TG/DTA 6300 instrument. The synthesized

materials were characterized by powder X-ray diffraction using PANalytical X'Pert PRO Diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$) in the range of $10\text{--}80^\circ$. The Fourier Transform infrared (FT-IR) spectra of the samples were recorded in the range of $4000\text{--}400 \text{ cm}^{-1}$ on a Shimadzu 8400-S Fourier transform infrared (FT-IR) spectrometer using KBr pellet method. The surface morphology of the synthesized nanoparticle was observed through FEI Quanta FEG 200-High Resolution Scanning Electron Microscope. The magnetic measurement was carried out in a vibrating sample magnetometer at room temperature using VSM, Lakeshore-7404 instrument.

RESULTS AND DISCUSSION

The thermal behaviour of synthesized $\beta\text{-Ni(OH)}_2$ particles and calcinated samples at 250 and 400°C were investigated by TGA analysis and the results are presented in Fig. 1. The as-prepared and calcinated at 250°C samples underwent a two step weight loss due to the dehydration and decomposition of water and residual hydrocarbons associated with nanoparticles. The weight loss is around 11% upto 110°C and which consequently increases to 16% upto 300°C . However, the sample calcinated at 250°C shows only 7 and 10% weight loss in the first and second stages at increased temperature range. The temperature for the decomposition of hydroxide depends on the synthesized method. In room temperature ionic liquid assisted synthesis of NiO nanoparticles, the complete dehydroxylation is obtained at 400°C . TGA analysis of sample calcinated at 400°C confirmed the complete hydroxide ion removal by the formation of NiO as a black powder.

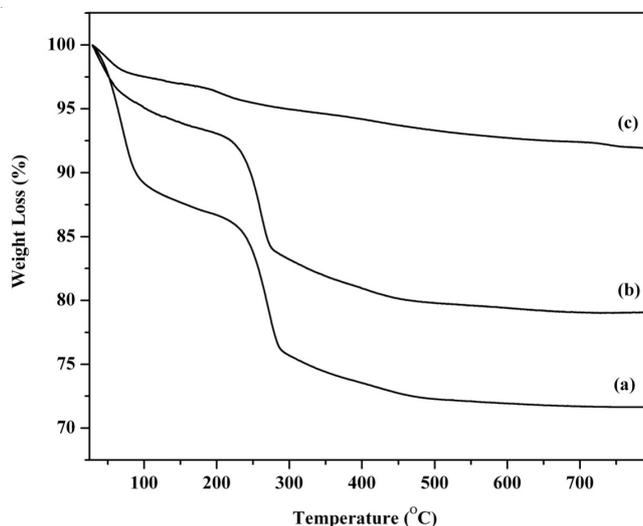


Fig. 1. TGA graph of (a) as-synthesized Ni(OH)_2 particles synthesized using 0.75% [BMIM][TfO] ionic liquid (b) the as-prepared sample calcinated at 250°C (c) the as-prepared sample calcinated at 400°C

The particle calcinated at 400°C shows only a gradual negligible weight loss in contrast to the as-prepared and calcinated at 250°C samples. It is in good agreement for the NiO nanoparticle formation at 400°C ^{11,12}.

The purity and phase of NiO nanoparticles were analyzed by powder X-ray diffraction method. The XRD patterns are represented in Fig. 2. The XRD of as-prepared Ni(OH)_2 and

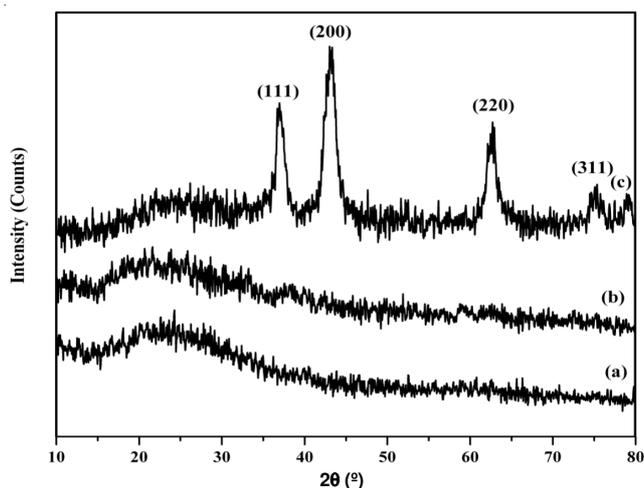


Fig. 2. XRD patterns of as-prepared (a) and calcinated nanoparticles at 250°C (b) and 400°C (c)

calcinated Ni(OH)_2 at 250°C shows poor crystallinity which indicates that there is no complete formation of NiO nanoparticles. But the as-prepared sample calcinated at 400°C produce cubic phase bunsenite nanostructured NiO nanoparticles with higher purity¹³. The diffraction peaks at 37.019 , 43.075 , 62.575 and 74.869° , corresponds perfectly to crystal planes such as (111), (200), (220) and (311), respectively. The absence of impurity peak implies that NiO nanoparticles are in ultra pure state. The lattice constant of synthesized NiO nanoparticle is 4.197 \AA which is in close correlation with the reported JCPDS data (JCPDS 78-0429).

FT-IR spectra of as-prepared and calcinated at 250 and 400°C reveals that the existence of functional groups which is depicted in Fig. 3. The spectra of as-prepared shows a strong narrow band at 3645 cm^{-1} characteristic of the stretching vibration of $\nu(\text{-OH})$ and also confirms the existence of hydroxyl group in a free configuration. A strong band at 534 cm^{-1} corresponding to the lattice vibration of -OH group for calcinated as-prepared sample at 250°C . It implies that the as-prepared particle is not completely dehydroxylated at 250°C . The spectra of NiO nanoparticles calcinated at 400°C shows a weak band at 462 cm^{-1} corresponds to lattice vibration of $\nu(\text{Ni-O})$ and the absence of peak characteristic of hydroxyl group indicates that the complete dehydroxylation occurred to produce pure NiO nanoparticles. The Ni-O stretching vibration is shifted to blue direction which is due to the reduction of the particle size compared to bulk NiO¹⁴⁻¹⁹.

The peaks located between 800 and 1800 cm^{-1} could be assigned to the presence of anions, which have not probably been completely eliminated during the washing stage. The peaks observed at 1540 , 1400 and 1055 cm^{-1} are assigned to various vibrational modes of the carbonate groups orienting from the adsorption of atmospheric CO_2 .

FE-SEM image of the Ni(OH)_2 calcinated at 400°C is presented in Fig. 4. The FE-SEM picture shows that the sample consists of small rock salt-like morphology. It can be seen that the aggregates of the smaller particles with average size is in the range of $25\text{--}60 \text{ nm}$.

Fig. 5 is the hysteresis loop of NiO nanoparticles synthesized in [BMIM][TfO] ionic liquid. The nanoparticle exhibits

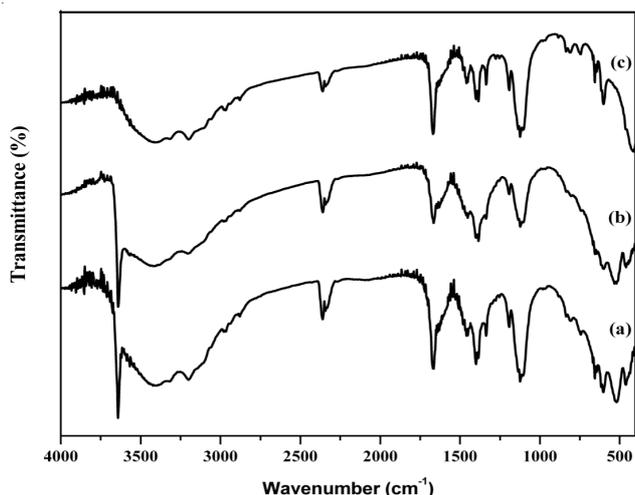


Fig. 3. FT-IR spectra of as-prepared (a) and calcined NiO nanoparticles at 250 °C (b) and 400 °C (c)

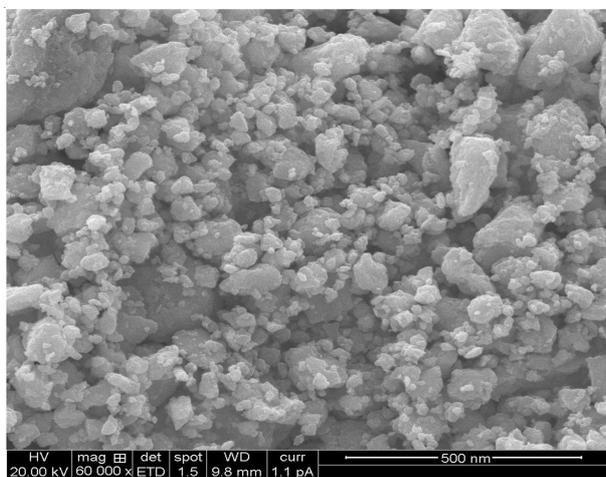


Fig. 4. SEM image of NiO nanoparticles calcined at 400 °C

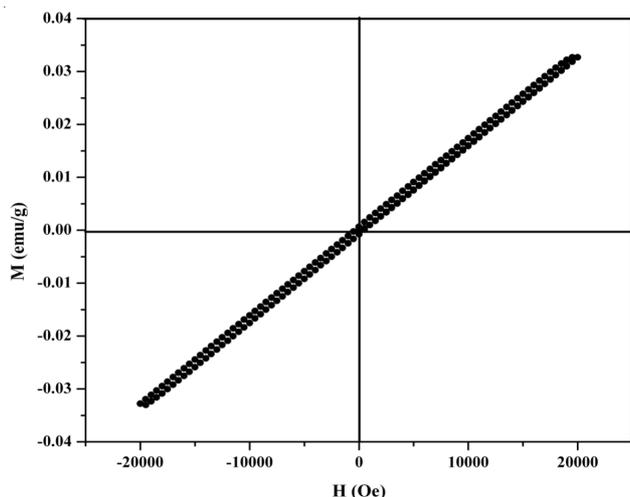


Fig. 5. Hysteresis loop of NiO nanoparticles calcined at 400 °C

superparamagnetic behaviour although the NiO bulk material is antiferromagnetic²⁰. The existence of superparamagnetic

behaviour of synthesized NiO nanoparticle is mainly because of the reduction in size through the use of room temperature ionic liquid which helps to bind the cations and releasing slowly for the NiO nucleation. Thus [BMIM][TfO] ionic liquid is very much useful in controlling the size and designing the required property of the materials.

Conclusion

Nickel oxide nanoparticles were synthesized successfully through a novel method of using 1-*n*-butyl-3-methylimidazolium ionic liquid medium. A well crystalline nanoparticles of NiO are formed at 400 °C when calcinated the Ni(OH)₂ which is confirmed by the TGA and XRD analysis. The formed products exhibits the cubic phase evidenced by XRD and FT-IR spectra show Ni-O bond clearly without the bond for H₂O/O-H for the calcinated sample. FE-SEM image of NiO nanoparticles are in the range of 25-60 nm in size and rock-salt like structure with super structure on the particles. An increase of superparamagnetic behaviour is obtained with increasing the calcinations temperature.

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