Influence of particle size on Magnetic behavior of nickel oxide nanoparticles

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Abstract: The influence of the particle size on magnetic behaviors of nickel oxide nanoparticles (NiO NPs) was reported. NiO NPs with a uniform particle size were synthesized via a facile sol-gel method, and various sizes of NiO NPs (11, to 49 nm) were achieved by calcination at various temperatures (400, to 700 °C). X-ray diffraction (XRD) analysis revealed that increasing the calcination temperature increased the crystallite size. TEM observations and XRD analysis were used to determine the particle size of the NiO NPs. The field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images showed flake-like morphologies, which consisted of interconnected nanoparticles with a porous channel. The magnetic properties of NiO NPs with different size were studied using vibrating sample magnetometer (VSM). The results suggested that the particle size plays an important role in magnetic property of NiO nanoparticles.

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1. INTRODUCTION

Transition-metal oxides (TMOs) are relevant to a wide range of materials applications. Interest in Transition-metal oxides systems has carried over into the nanoscale regime where novel properties make the nanoscale TMOs attractive for a variety of functions including catalysis, gas sensors, magnetic materials, and biomedical devices. In addition to the particle size and morphology, compositional variability represents a useful method of tailoring nanoparticle properties to the task. The parent NiO system exhibits interesting physical features, such as charge-transfer effects and an interesting antiferromagnetic spin structure[1]. The first investigation of size dependent magnetic properties in NiO was reported by Richardson et al. [2]. In 1961, Néel suggested that the fine particles of NiO should exhibit either weak ferromagnetic or superparamagnetic properties [3, 4]. Kodama et al. in 1997 suggested that anomalous magnetic properties in an antiferromagnetic NiO NPs such as large moments and coercivities can be attributed to a new finite size effect, in which the reduced coordination of surface spins causes a fundamental change in the magnetic order throughout the particle [5]. In 2009, Davar et al. [6] synthesized Ni and NiO NPs by thermal decomposition method and studied their magnetic properties. In 2010, Wesselinowa studied the size and anisotropy effects on the magnetic properties of antiferromagnetic NPs such as NiO by the Heisenberg model. Karthik et al. in 2011 [7] investigated the particle size effect on the magnetic properties of NiO NPs prepared by a precipitation method. Kisan et al. in 2015 [3] investigated the effect of annealing on the magnetic properties of ball milled NiO powders.

2. MATERIALS AND METHODS

The NiO nanoparticles (NiO NPs) were synthesized by sol-gel method as follows. Typically, 5 g of Ni $(NO_3)_2.6H_2O$ was dissolved in 20 mL of deionized water and then stirred for 30 min. Meanwhile, 2 g of gelatine was dissolved in 40 mL of deionized water separately, and then stirred for 30 min at 60 °C to obtain a clear gelatine solution. After that, the nickel nitrate solution was added to the gelatine solution and heated in a water bath at 80 °C under stirring. The stirring was continued for 15 h to obtain a honey like and bright green gel. This gel was rubbed on the inner side of a crucible. The bright green gel was then placed into a horizontal tube furnace (100 cm in length, 5 cm in diameter in the air at 1 atm of pressure). The furnace was heated from room temperature to 300, 400, to 900 °C, at a rate of 30 °C/min. After being held at the final temperature for 1 h, the furnace was cooled down naturally to room temperature[8].

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction and crystallite-size analyses

The XRD patterns of the NiO NPs calcined at different temperatures are shown in Fig. 1. All of the XRD patterns clearly show the diffraction peaks of the (111), (200), (220), (311), and (222) crystal planes, corresponding to face-centred-cubic (fcc) structured NiO (PDF card No. 01-078-0423). The results show that the synthesised NiO NPs had high purity as there was an absence of impurity peaks. It was observed that the intensity of the diffraction peaks increased as the calcination temperature increased because of the increase in the crystallite size of the NiO NPs. Several techniques are available to calculate the crystalline size, such as the Scherrer equation ($D = K\lambda/\beta \cos\theta$), in which D is the grain size, K is the constant of the Scherrer formula related to index (hkl) and the shape of the NPs, λ is the X-ray wavelength, θ is the XRD diffraction angle, and β is the full width at half maximum (FWHM) of the diffraction peak measured in radians [9].
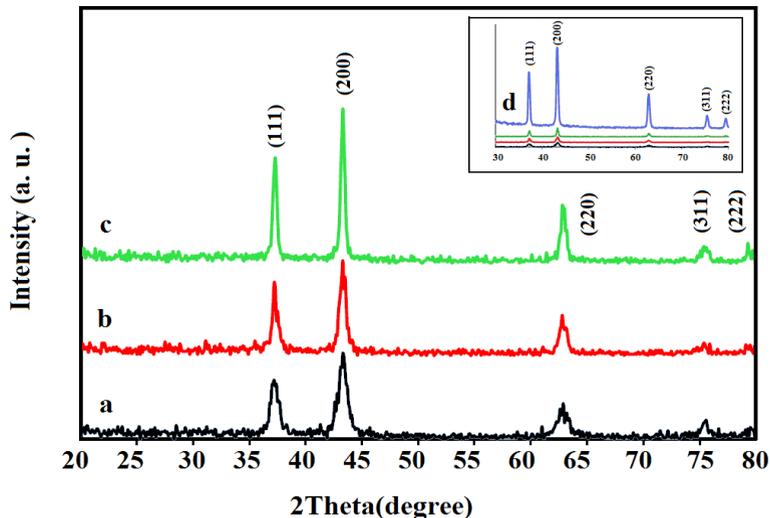

Fig. 1. XRD patterns of nickel oxide particle at different temperatures.

3.2. Morphological studies

The morphology and structure of NiO samples in the various calcination temperatures are shown by FESEM and TEM images in Fig. 2, and 3. The FESEM images (Fig.2) show a flake-like structure of the NiO samples at 400, 500, 600, and 700 °C respectively. Moreover, the images clearly indicate that the flake structure grows rapidly with increasing the calcination temperature. These observations are in agreement with previous report [10]. The TEM images of the NiO samples at different temperatures in Fig.3 show a similar structure for all samples that consisted nanoparticles with various sizes and porosity, because of

their temperature. The average size of NiO NPs in Figure 3 obtained 11, 19, 36 and 49 nm, of the NiO NPs at 400, 500, 600, and 700 ℃ respectively.
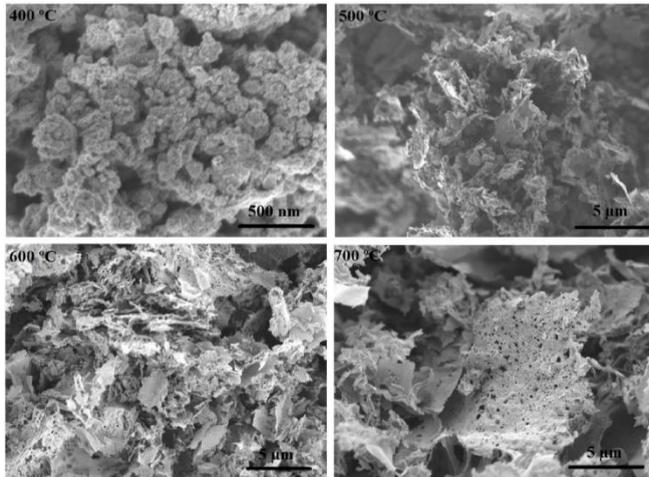

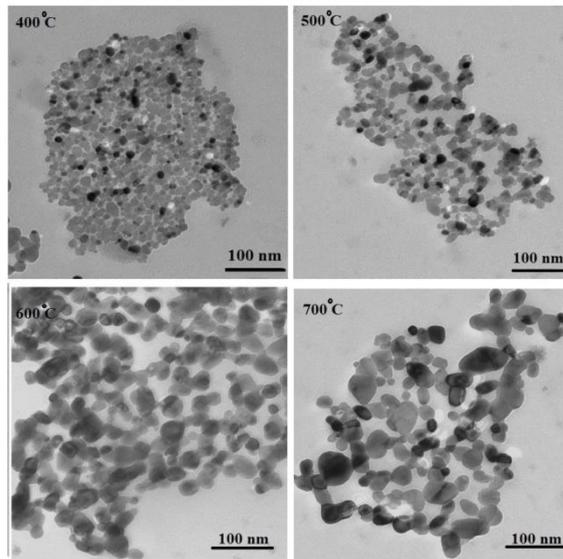Fig. 2. FESEM images of nickel oxide at different calcination temperatures

Fig. 3. TEM images of nanoparticles of nickel oxide at different temperatures.

3. 3. Magnetic properties

Fig.4 shows the magnetization M curves of prepared NiO NPs, after annealing at different temperatures, versus applied field H (between −10 and +10 kOe). The

saturation magnetization (M_s), the coercive force (H_c) and the remanent magnetization (M_r) are showed. It is observed that (i) NiO powder exhibits a weak response to the applied field; (ii) Nature of M-H loops changes significantly for the annealed powders, i.e., superparamagnetic by increasing of annealing temperature up to 400 and 700 °C, respectively; (iii) Saturation magnetization and coercivity decrease by the increase of annealing temperature; (iv) The shape of the hysteresis loop changes too.
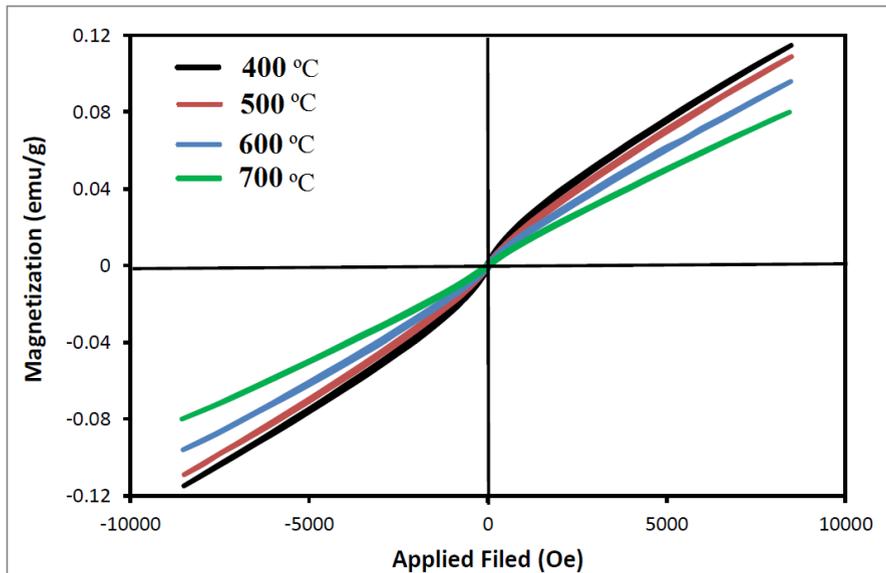

Fig. 4 Hysteresis loop at room temperature for nickel oxide nanoparticles with different cooking temperatures

According to the reports, the variation of magnetic properties is related to structural properties [11]. The magnetic properties of NiO powder changes as follows: Bulk NiO materials are antiferromagnetic. The structure of antiferromagnetic NiO is determined by the dominating super-exchange interactions in linear Ni–O–Ni atomic chains, which the spins along the (1 1 1) direction are opposite [12]. The spins are compensated and hence show a weak response to the applied field. The exchange interaction between two neighboring Ni+2 ions is mediated by an oxygen ion (superexchange). By missing an oxygen ion from the surface, the exchange bond would be broken and the interaction energy would be reduced. Coordination number at the surface for Ni+2 ions are less than in the bulk. This fact can result in a distribution of exchange interaction energies for the surface spins. Also the superexchange is sensitive to bond lengths

and bond angles, which are likely to be different at the surface compared to the bulk. As the particle size decreases, the fraction of atoms lying on the surface of the particles increases, which may lead to increasing of surface spin disorder [21]. When the size of the particles is reduced to the nanoscale in NiO materials, they can exhibit different magnetic properties like, superparamagnetism[3, 13]. The superparamagnetic property in NiO is attributed to the incomplete compensation between antiferromagnetic sublattices[5].
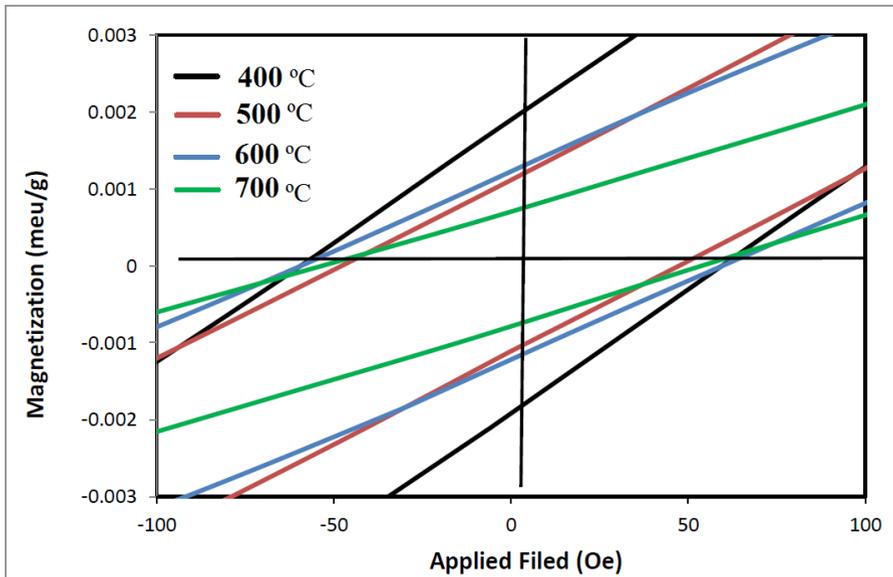

Fig. 5. The amount of residual magnetization and coercivity according to particles size

Fig. 5 shows M_s and H_c versus annealing temperature. The decrease of M_s as well as H_c observed with the increasing annealing temperature as a result of increasing of crystallite size. Moreover, the uncompensated surface spins, finite size effect, surface strain and defects could be the reasons of the observed behavior. These results are in a good agreement with the experimental results of Makhlouf et al. [14], Karthik et al. [7], Kisan et al. [4], Thota et al. [15] and theoretical results of Wesselinowa[16]. According to the reports, the magnetic properties of nanomaterials have been believed highly dependent on the sample preparation method, shape, crystallinity, magnetization direction and so on [17].

4. CONCLUSION

In this work, the size effect of NiO NPs on the Magnetic behavior of nickel oxide nanoparticles was studied. Various sizes of NiO NPs (11, 19, 36, and 49 nm) were synthesized via a facile sol–gel method using gelatin as a green polymerizing agent, followed by calcination at various temperatures (400, 500,600, and 700 °C). Magnetic properties of the well-characterized NiO NPs of antiferromagnetic oxides reveals the presence of superparamagnetic behavior, as evidenced by the decreasing saturation magnetization and coercivity as well as the increasing crystallite size with increasing annealing temperature. This is attributed to finite size effect and uncompensated spins at the surface.

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