Borohydride Reduction of Cobalt Oxide (Co_3O_4) Nanoparticles

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Abstract

Recently, magntic nanomaterials have been used in wide range of applications such as medicine and electronic. In this research, rod-like shaped cobalt oxide magnetic nanoparticles (Co_3O_4) were synthesized by simple co-precipitation method using cobalt chloride as precursor and sodium borohydride ($NaBH_4$) as reducing agent. Their structural and surface morphological properties were characterized by high resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and vibration sampling magnetometer with (VSM). XRD measurement exhibited the structure of Co_3O_4 nanocrystals for annealed samples. The TEM results showed the cobalt oxide nanoparticles with good uniformity in the range size of 10-40 nm. The SEM images revealed that the particles changed from spherical shape to rod-like shape with increasing temperature. Magnetic measurements showed coercive field of around 84.5G and saturation magnetization of annealed of around 9.83 emu/g.

Keywords: cobalt oxide, nanocrystals, wet chemical, sodium borohydride, co-precipitation

Introduction

Nanometer size particles display many properties which are both quantitatively and qualitatively different from the respective bulk materials [1-8]. It is possible to tune specific properties of nanoparticles, such as geometric and electronic structure, by varying the particle size [9-15]. Recently, the study of size effects of metal nanoparticles has intensified with the promise of utilizing novel properties in new materials and devices [16-23]. Recently, magnetic nanoparticles have been used as the active component of ferrofluids, magnetic recording devices, electronic components, solar energy transformers, and chemical catalysts [24-27]. Furthermore, superparamagnetic nanoparticles have also found applications in medicine, for example, in drug delivery and restriction of blood flow to a selected part of the body [28-32]. For high-density magnetic recording applications, new magnetic materials require particles of small size, narrow size distribution, as well as control of size and shape. The fabrication methods used to organize magnetic nanoparticles are also becoming increasingly important. Numerous physical and chemical methods have been developed for the preparation of magnetic nanoparticles [32]. The magnetic properties of nanoparticles, for example, depend strongly on the size of the particles. Typically, nanosized particles show superparamagnetic properties and magnetic materials, such as cobalt, become very important for their applications in magnetic storage technology. The synthesis of nanoparticles has been intensively pursued not only for their fundamental scientific interest but also for many technological applications [26-32] monodisperse nanoparticles with controlled particle sizes are of key importance because the electrical, optical, and magnetic properties of these nanoparticles depend strongly on their size.[33-35]. In the present paper, Co oxide nanorods were successfully fabricated by using cobalt chloride as precursor and sodium borohydride ($NaBH_4$) as reducing agent. This method has novel features which are of considerable interest due to its low cost, easy preparation and industrial viability. Synthesis of Co_3O_4 nanorods is reported by wet synthesis technique and calcined at 600 °C. The morphology properties of the samples have been studied by XRD, TEM, SEM and VSM analyses.

Experimental detail

Cobalt oxide nanoparticles were successfully synthesized according to the following manner. First, 3g of cobalt chloride ($CoCl_2.6H_2O$) was compleately dissolved in 100 ml distilled water for 10 min with stirring at room temperature. After that, 3g $NaBH_4$ was slowly added to the solution and synthesis temperature was increased to 85 °C. By adding $NaBH_4$ the solution changed from pink color to black color. The pH was adjusted around 8-9 during the process. Resulting Co solution were dried at 85°C for 2 hours and cooled to room temperature and then calcined at 600 °C for 3 hours. The Cobalt oxide nanocrystals powder was later obtained. The samples were characterized without any washing and purification.

The specification of the size, structure and surface morphological properties of the as-synthesized and annealed cobalt nanoparticles were carried out to study of the cobalt morphology. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern was recorded with 2θ in the range of 4-85° with type X-Pert Pro MPD, Cu-K_α: λ = 1.54 Å. The morphology was characterized by field emission scanning electron microscopy (FESEM) with type KYKY-EM3200, 25 kV and transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV. Magnetic measurements were carried out using vibration sampling magnetometer with type VSM 7400 Lake Shore.

Results and discussion

X-rar diffraction (XRD) at 40Kv was used to identify crystalline phases and to estimate the crystalline sizes. Figure 1 shows the annealed XRD morphology of Co oxide nanoparticles. Well-defined diffraction peaks at about 18.58°, 24.69°, 26.32°, 31.35°, 34.46°, 36.93°, 38.57°, 55.80 and 65.27° are observed, corresponding to Co_3O_4 crystals. The mean size of the ordered Co_3O_4 nanocrystals has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula [36] according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \quad (1)$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The average crystalite size of annealed sample was about 30 nm from this Debye-Sherrer equation.

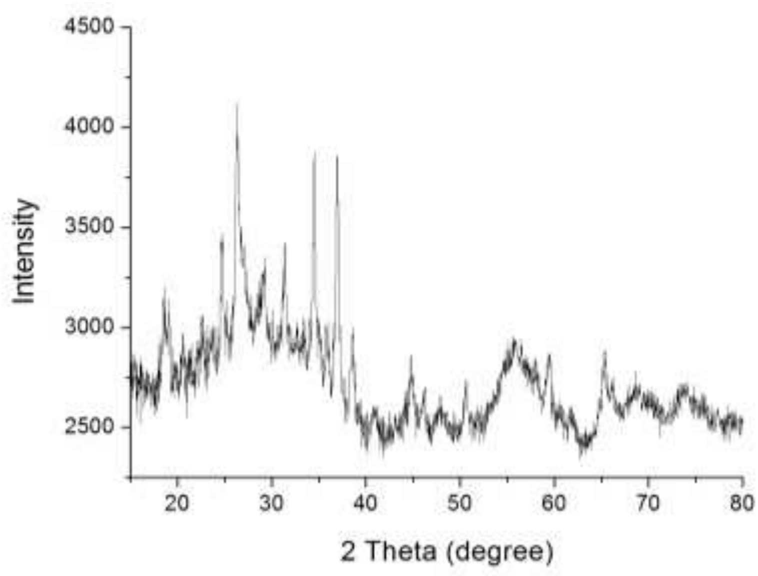

Figure 1. XRD pattern of annealed Co_3O_4 nanoparticles

Scanning electron microscope (SEM) was used for the morphological study of nanoparticles of Co_3O_4. Results show the formation of nanorods emerged in the samples surface by increasing annealing temperature. Figure 2(a) shows the SEM image of the as-prepared cobalt oxide nanoparticles prepared by wet chemical method. It can be seen the particles were aggregated together. Figure 2(b) shows the SEM image of the annealed Co_3O_4 nanoparticles at 600ºC for 3 hours. It is realized that with increasing temperature the sphere-like shape nanoparticles change to nano-rod shaped because of the interaction. In fact by increasing temperature, the stabilizers around the particles are removed and the interactions between particles increase and finally the particles change from spherical to rod shape [31].

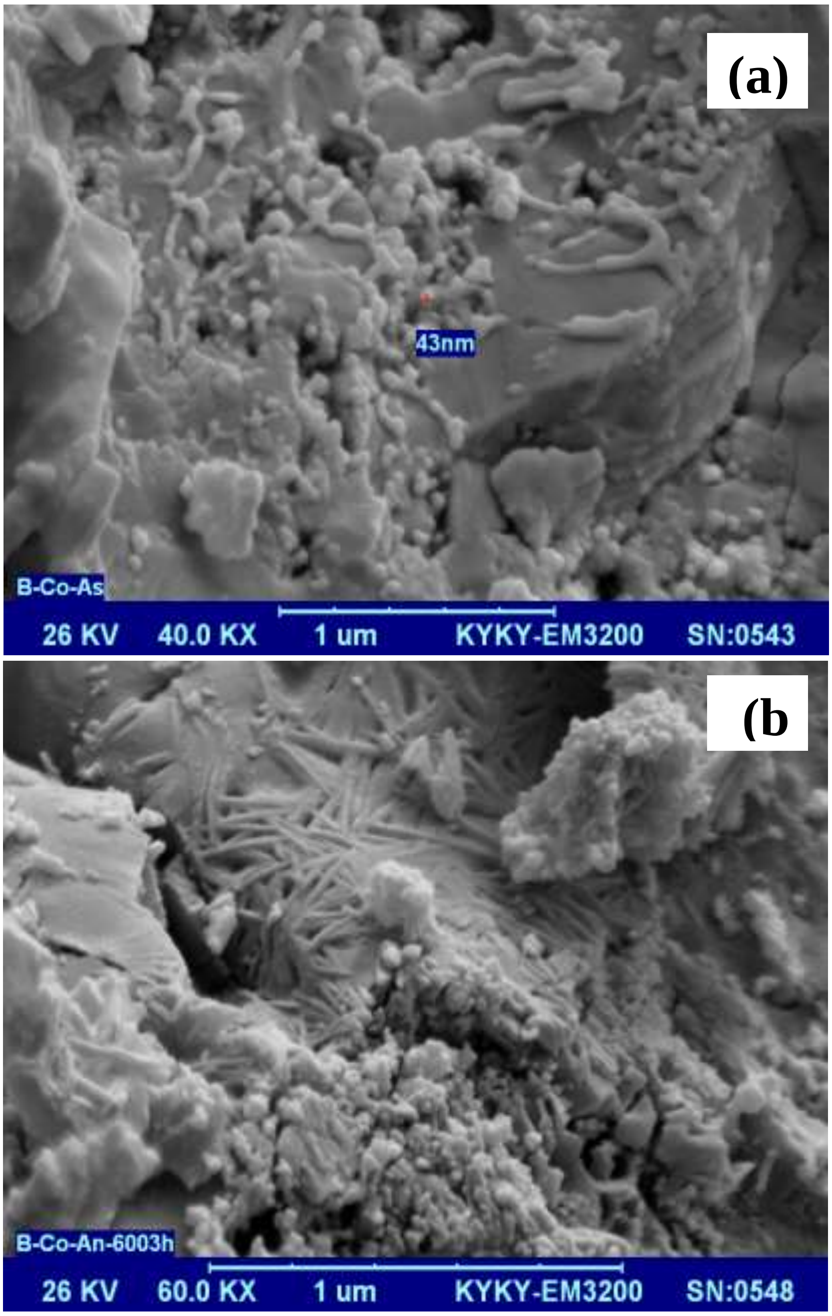

Figure 2. SEM images of (a) as-prepared and (b) annealed Co_3O_4 nanoparticles

The TEM sample was prepared by dispersing the powder in ethanol by ultrasonic vibration. It can be seen that the product was formed from extremely fine spherical particles which were loosely aggregated [37]. The as-made Co_3O_4 particles have sphere-like shape with weak agglomeration. As can be seen in the inset of Figure 3, the particle sizes possess a narrow distribution in a range of 10-40 nm. In fact, the mean particle size determined by TEM is very close to the average particle size calculated by the Debye-Scherer formula from the XRD pattern.

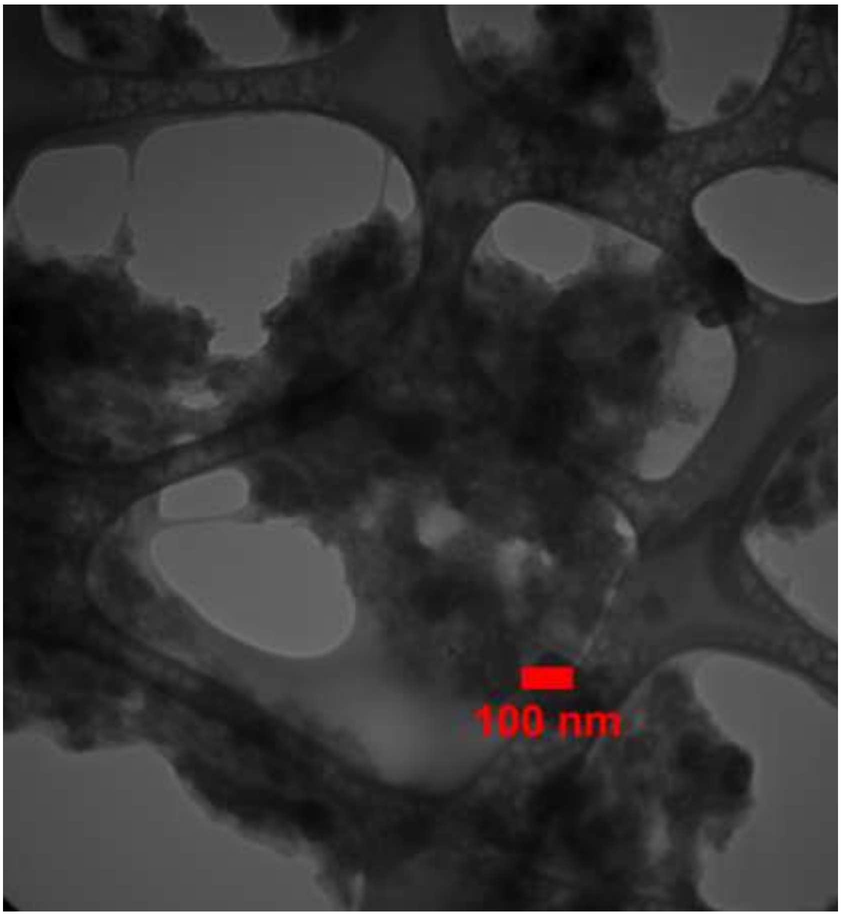

Figure 3. TEM image of the as-prepared Co_3O_4 nanoparticles

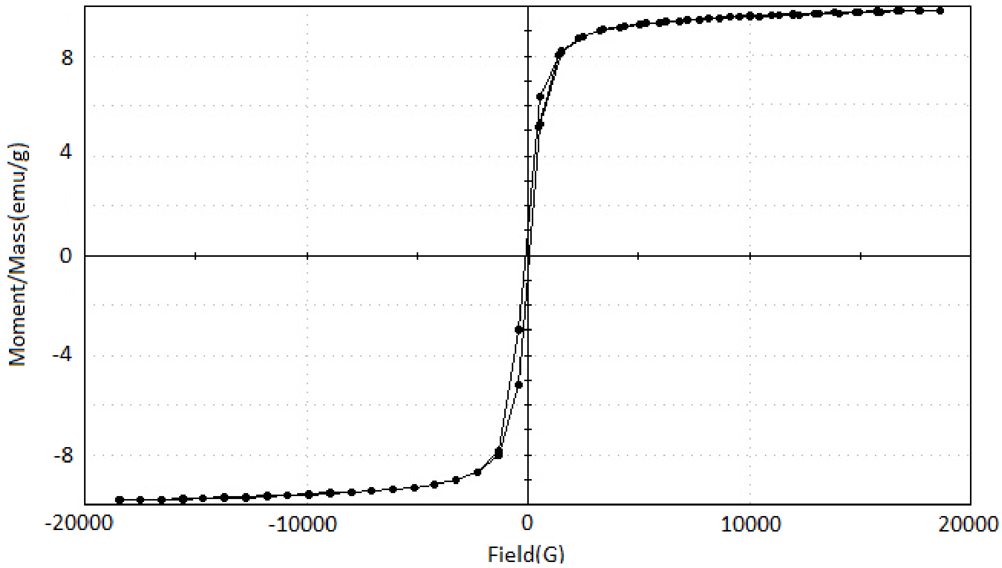

Figure 4. Magnetic hysteresis loops of the annealed cobalt oxide nanoparpticles

The classification of a material's magnetic property is based on magnetic susceptibility. Magnetizations *M* versus applied magnetic field *H* for powders of the samples are measured at room temperature by cycling the magnetic field between -20k to 20k G. Figure 4 shows the magnetization curve hysteresis of annealed sample. The results of magnetic measurements showed coercive field and saturation magnetism of annealed one around 84.5 G and 9.83 emu/g, respectively.

Conclusion

Cobalt oxide (Co_3O_4) nanorods were successfully synthesized by simple co-precipitation method using cobalt chloride as precursor and sodium borohydride ($NaBH_4$) as reducing agent. SEM images revealed that the particles changed from spherical shape to nanorod shaped with less agglomeration by increasing annealing temperature. XRD pattern of cobalt oxide samples exhibited the structure of Co_3O_4 nanoparticles. TEM image revealed high uniformity of the cobalt oxide nanoparticles with particle size in the range of 10-40 nm. VSM measurement indicated the ferromagnetic behavipr of the cobalt oxide nanoparticles.

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