Preparation of Ferromagnetic Co_3O_4 Nanoparticles by Wet Chemical Synthesis Method

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Abstract

Cobalt oxide nanoparticles (Co_3O_4) were synthesized by wet chemical method using cobalt sulfate as precursor and ethylene glycol as surfactant. Their physico-chemical properties were characterized by high resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and vibration sampling magnetometer (VSM) analyses. The crystal structure of samples after annealing was done by XRD analysis. XRD measurement exhibited the structure of Co_3O_4 nanocrystals for annealed samples. The TEM results showed the cobalt oxide nanoparticles with good uniformity. The SEM images revealed that the size of nanoparicles increased in the range of 20-50 nm with increasing annealing temperature. The magnetic results indicated a good coercive field and saturation magnetism around 452 G and 18 emu/g, respectively.

Keywords: Co_3O_4 nanoparticles, wet chemical, crystal properties, synthesis

Introduction

Nanoparticles are generally classified according to their composition: metal oxides, noble metals, transition metals, magnetic metals, etc. [1-27]. Magnetic nanoparticles with unique nanoscale magnetism have long been sought for future data storage, energy storage, and biomedicine [28-31]. While ferromagnetic nanoparticles are tested as building blocks for fabricating magnetic storage media with ultra-high density and nanocomposite permanent magnets with maximum energy product [32-36]. Superparamagnetic nanoparticles are promising probes for biological separation, biosensor, magnetic resonance imaging, magnetic fluid hyperthermia and magnetic particle imaging [37]. To realize their application potentials, magnetic nanoparticles should first be made with controlled dimensions, structure and magnetic properties. Magnetocrystalline anisotropy arises from spin-orbit coupling and energetically favors alignment of the magnetization along a specific crystallographic direction, which is called the easy axis of the material. The magnetocrystalline anisotropy is specific to a given material and independent of particle shape. The coercivity is proportional to the anisotropy constant, so high anisotropy materials are attractive candidates for high-coercivity applications. Cobalt (Co) is typical classes of ferromagnetic materials with high magnetic moment

(1422 emu/cc) and high Curie temperature (1110°C). Magnetic nanoparticles of Co with high magnetic moment should serve as ideal building blocks for various magnetic applications. However, metallic Co nanoparticles are chemically unstable and are oxidized easily to form various oxide nanoparticles with much reduced magnetic moment. The magnitude of the magnetocrystalline anisotropy at room temperature is 7×10^6 erg/cm^3 in cobalt. Co is a well-known ferromagnetic material which is commonly used as an alloying element in permanent magnets [38]. It exists in two forms: HCP (hexagonal close-packed) and FCC (face-centered cubic). HCP is the stable phase at room temperature, whereas FCC is stable at temperatures above 450 °C [39]. In nanosized, Co particles display a wide range of interesting size-dependent structural, electrical, magnetic, and catalytic properties [40]. In particular, because of their large surface area, Co nanoparticles showed high chemical reactivity, which makes them suitable for catalysis [41]. Furthermore, below a critical size of 20 nm, they have as single-domain particles displaying quantum size effects, superparamagnetism, large magnetic anisotropies, and a maximum coercivity. Moreover, at this size range, a new metastable phase can also be formed, called ε-Co and has properties in between the HCP and FCC phases. ε-Co can be prepared by solution chemistry, particularly via organometallic route in the presence of tight binding ligands [42]. Future applications of Co nanoparticles in the fields of separation technology, information storage systems, catalysis, and biomedicine [43] require the nanoparticles to be discrete, identical in size and shape, and uniform in composition and crystal structure. However, formation of nanoparticles satisfying these requirements prove to be difficult due to their high surface energy, their intrinsic magnetic properties, and the inherent limitations of the available processes. In addition, there are also concerns regarding the reproducibility of the existing methods. Therefore one of the biggest challenges in the synthesis of Co nanoparticles is how to stabilize them against fast oxidation. Cobalt nanoparticles have been prepared by various methods including thermal decomposition [44], gas vapor condensation [45], reverse microemulsion [46], sol-gel [47], and precipitation method [48]. In the present work, we focused on synthesis of cobalt oxide (Co_3O_4) nanoparticles system by wet chemical route. 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 samples by wet synthesis technique is reported by $CoSO_4.7H_2O$ precursor and calcined at different temperature. The structural and optical properties of cobalt oxide have been studied by XRD, HRTEM, FESEM and VSM, analyses.

Experimental detail

Cobalt oxide nanoparticles were successfully synthesized according to the following manner. First, 10 mL solution of ethylene glycol (0.035 M) was added drop wise into 100 mL de-ionized water with stirring. Then, 2g of cobalt sulfate ($CoSO_4.7H_2O$) was slowly added to the solution and stirred for 5 min at room temperature. By adding NaOH (1.5 M) the color of solution changed from brown color to black color and the volume of the solution reached to 160 mL. The pH was maintained to 14 during the process. Resulting Co solution were

dried at 55 °C for 2 h and cooled to room temperature and then calcined at 1000 °C for 3 hours. The black Co powder was later obtained. The samples were characterized without any washing and purification.

The specification of the size, structural, magnetical and optical properties of the as-synthesized and annealed cobalt oxide nanoparticles were carried out to study of their morphology. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were 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. All the measurements were carried out at room temperature.

Results and discussion

X-ray diffraction (XRD) at 40Kv was used to identify crystalline phases and to estimate the crystalline sizes. Figure 1 shows the XRD morphology of Co oxide nanoparticles at 1000°C for 3 hours and indicates the structure of Co_3O_4 phase. Well-defined diffraction peaks at about 19.08°, 31.35°, 36.93°, 38.65°, 44.89°, 55.76°, 59.43°, 65.31°, 74.79°, 77.39°, and 78.48° are observed at figure 3(c), corresponding to the (111), (220), (311), (222), (400), (422), (511), (440), (620), (533) and (622) planes of Co_3O_4 crystals. The mean crystallite size of the ordered Co_3O_4 nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula [49] according to equation the following:

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

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 size of annealed Co_3O_4 nanocrystals was calculated about 27 nm.

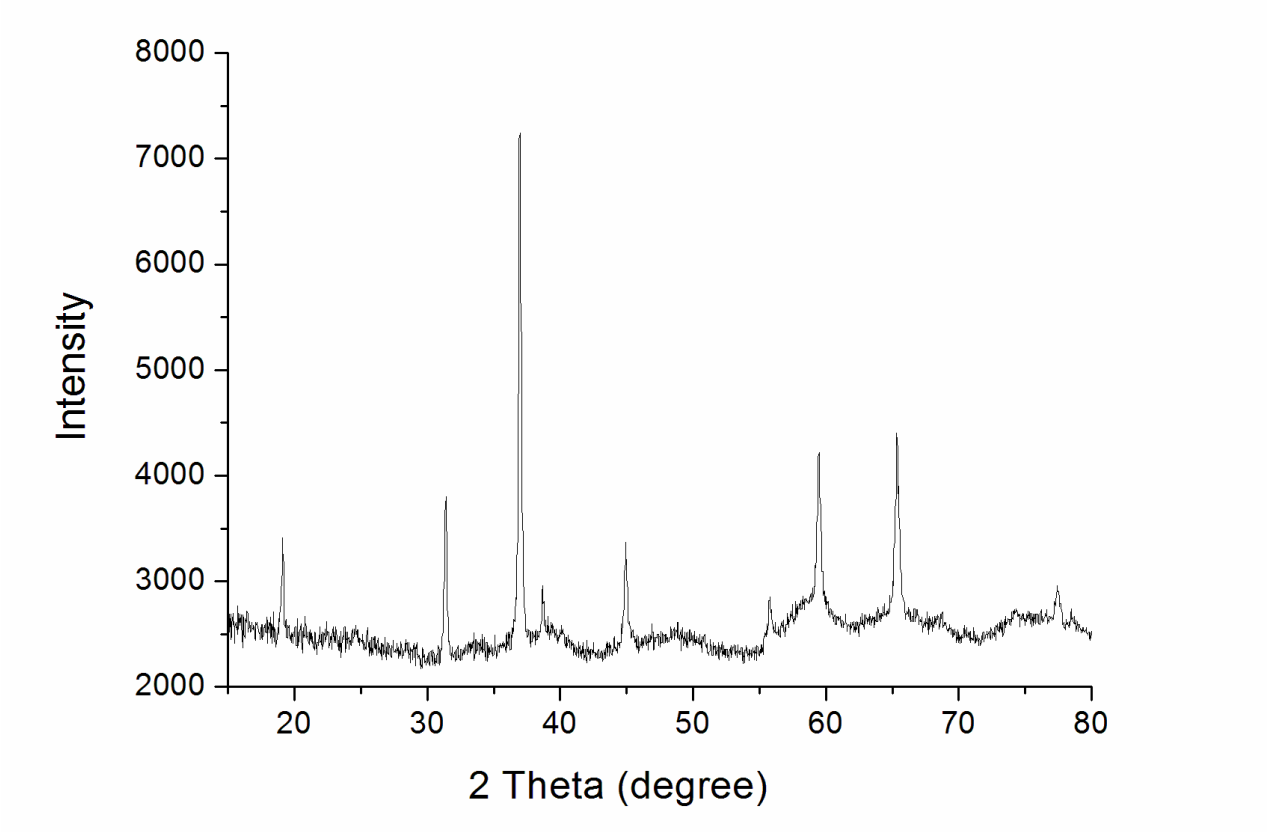

Figure 1. XRD pattern of as-prepared and annealed Co_3O_4 nanoparticles

Scanning electron microscope (SEM) was used for the morphological study of nanoparticles of Co_3O_4. These figures show high aggregation 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. In this figure small particles are observed in the range size of 20-50 nm. Figure 2(b) shows the SEM image of the annealed Co_3O_4 nanoparticles at 1000°C for 3 hours. As you can see from this image, the Co_3O_4 nanocrystals formed with less agglomeration.

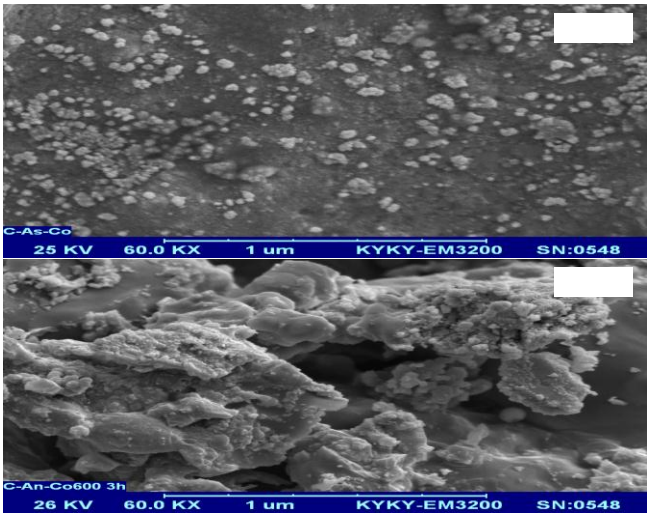

Figure 2. SEM images of the Co_3O_4 nanoparticles (a) as-prepared and (b) annealed at 1000 °C

The transmission electron microscopic (TEM) analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. 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. The uniform Co_3O_4 particles have sphere-like shapes with weak agglomeration. As can be seen in the inset of Figure 3, the as-prepared particle sizes possess a broad distribution in a range of 10 - 40 nm, and the mean particle diameter is about 25 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.

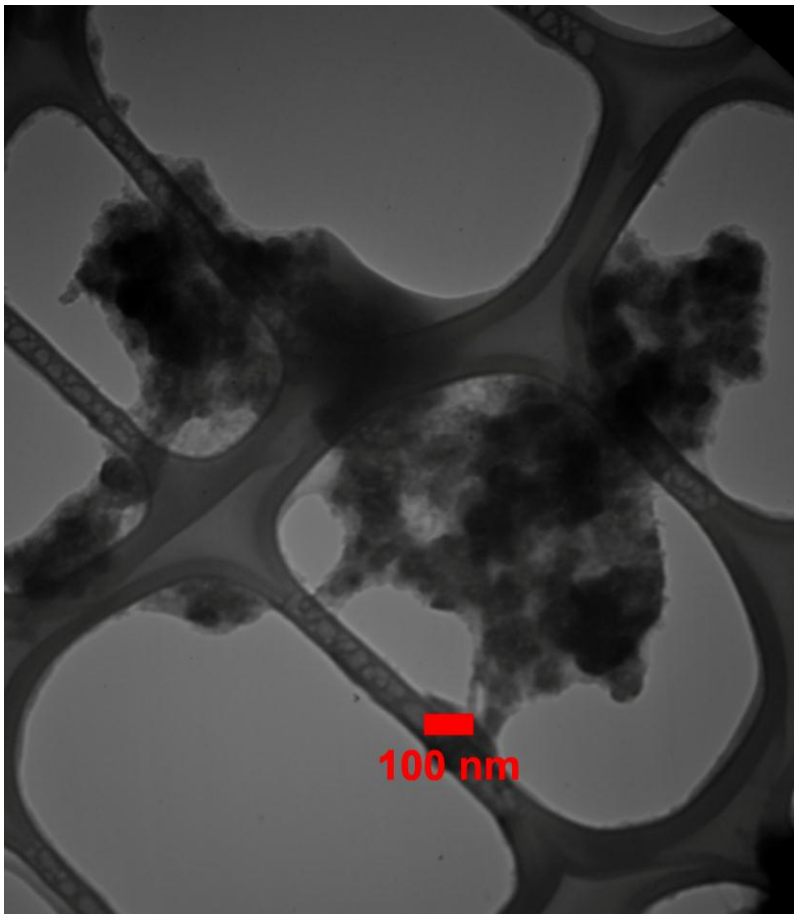

Figure 3. TEM image of the as-prepared Co_3O_4 nanoparticles

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 loop for annealed samples. The results of magnetic

measurements showed a good coercive field and saturation magnetization of annealed samples around 452 G and 18 emu/g, respectively.

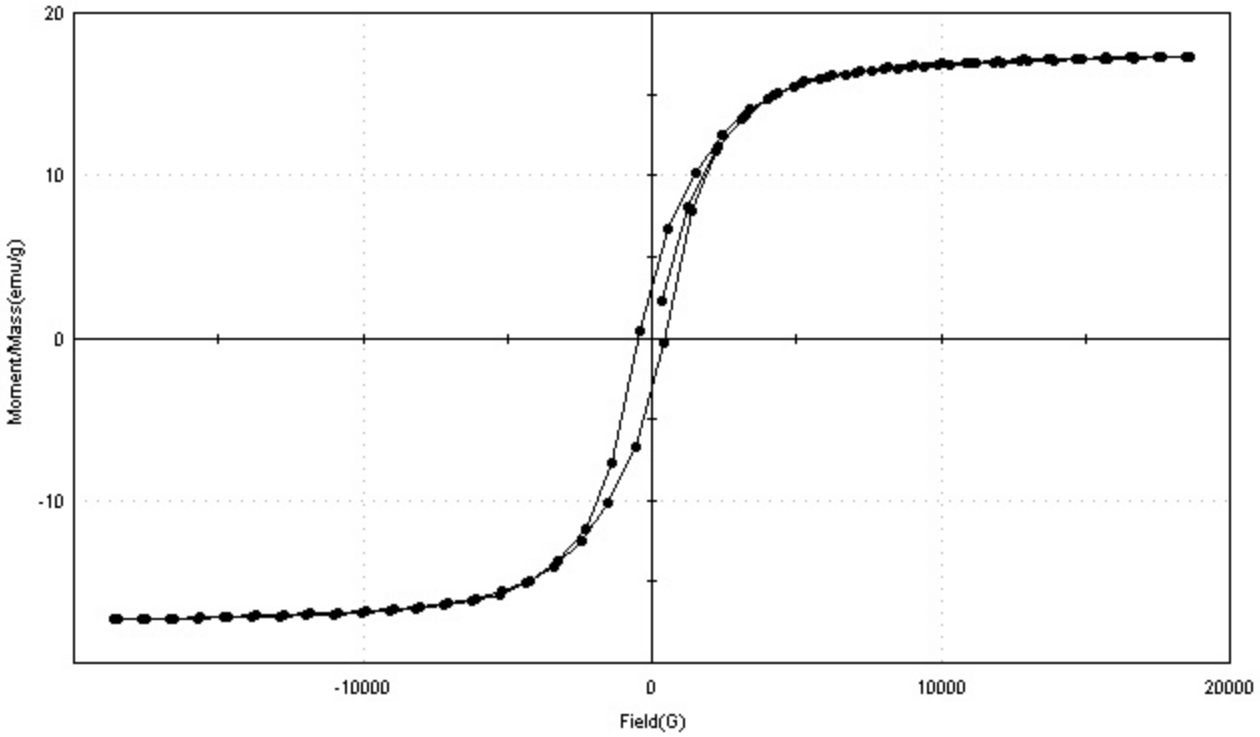

Figure 4. Magnetic hysteresis loops of annealed cobalt oxide nanoparpticles

Conclusion

Cobalt oxide (Co_3O_4) nanoparticles were successfully prepared by a simple wet synthesis method using cobalt sulfate as precursor and ethylene glycol as surfactant. The particle size Co_3O_4 was measured in the range of 20-50 nm for as-prepared particles and 25 nm for of annealed one. SEM images revealed that the particles were less aggregated by increasing annealing temperature. XRD pattern of cobalt oxide samples nanoparticles exhibited the structure of Co_3O_4 nanoparticles. Magnetic measurements studies showed a good coercive field and saturation magnetism around 452 G and 18 emu/g, respectively.

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