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# Chemical synthesis of the $Co_3O_4$ nanoparticles in presence of CTAB surfactant

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**ABSTRACT:** Sphere-like shaped cobalt oxide nanoparticles ($Co_3O_4$) were synthesized by a simple wet chemical method using cobalt chloride as precursor and cetyl trimethylammonium bromide (CTAB) as surfactant. Their structural and surface morphologial properties were characterized by high resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). XRD measurement exhibited the structure of $Co_3O_4$ nanocrystals for annealed samples. The TEM results showed the sphere-like shaped cobalt oxide nanoparticles with good uniformity in the presence of CTAB surfactant. The SEM images revealed that the particles changed to spherical shape and the size of cobalt oxide nanoparicles increased in the range of 25-45 nm with increasing annealing temperature.

**Keywords:** *Cobalt oxide; CTAB surfactant; Nanocrystals; Synthesis; Wet chemical*

## INTRODUCTION

Metal nanoparticles have been studied for decades as they have properties not found in the same material in bulk form. The nanosize affects greatly the ratio of surface atoms to atoms deep in the crystal matrix. Therefore, surface effects are observed to a much greater extent (Lu, *et al.*, 2007). A notable example is catalysis, where a large surface area to volume ratio is a key parameter. Special nanoeffects are seen in nanomagnets as explained below. In addition, processing techniques like printing are not available or reasonable with micron-sized particles (Gu, *et al.*, 2003, Xu, *et al.*, 2004). Magnetic nanoparticles have received a great deal of attention because of their potential use in various biomedical applications, including contrast agents in magnetic resonance imaging, the magnetic separation and sorting of cells and proteins, immunoassay in pathology laboratories, hyperthermia treatment for cancerous tumors, and the controlled and targeted delivery of pharmaceuticals and therapeutic genes (Gu, *et al.*, 2006, Lee, *et al.*, 2006, Lee, *et al.*, 2007).

Ferromagnetic materials are divided into hard and soft materials. Soft magnetic materials have a low remanent magnetization, a low coercive field, and a high permeability. Hard ferromagnetic materials have a high remanent magnetization, a high coercive field, and a low permeability. Soft ferromagnetic materials are used

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for recording heads and as inductor cores. Hard magnetic materials are used for permanent magnets and recording media.

The magnetic properties change as the particle size decreases. For large particles, magnetic properties are similar to bulk magnetic properties. As particle size decreases, the particles become single domain, as it is not energetically favorable to have a domain wall within the particles. For Co, the single domain diameter is theoretically 58 nm, but the exact particle shape and crystal structure have large effects (Yi, *et al.*, 2005). The coercivity for single domain particles is higher than for the bulk, and saturation magnetization is the same. Very small particles may be in superparamagnetic state. Then, magnetization can randomly change direction due to thermal fluctuations. The time for this direction change is called the Néel relaxation time. In the absence of an external magnetic field, the time used to measure the magnetisation of the nanoparticles is typically much longer than the Néel relaxation time. Then, the magnetization appears to be zero and the particles are said to be in a superparamagnetic state. In this state, an external magnetic field is able to magnetize the nanoparticles. The critical radius for superparamagnetic behaviour is 16 nm for cobalt (Stoeva, *et al.*, 2005).

Even for the particles with the smallest number average particle diameter, the mass fraction of larger particles is significant. The increased saturation moment of Co nanoparticles as compared to the bulk is reported several times for particles less than 10 nm, for example by Chen *et al.* (Chen, *et al.*, 1995). Nanomaterials properties are strongly dependent on the size particle. Consequently, properties of the nanoparticles such as magnetic, optical, thermal or catalytic are different from bulk materials. Chemical solution methods have been widely used to produce nanostructured materials, and different strategies have been applied to achieve monodisperse nanoparticles with controlled size and shape.

However, there is no general strategy to make nanoparticles with narrow size distribution, tailored properties, and desired morphologies, which could be universally applied to different materials. In recent years, much attention has been focused on the synthesis of uniformly sized magnetic nanoparticles (Park, *et al.*, 2007, Dumestre, *et al.*, 2003, Hyeon, *et al.*, 2001, Sun, *et al.*, 2000). However, most of these nanoparticles have been synthesized in organic solvents using hydrophobic capping reagents. Very recently, there have been several reports on the synthesis of water-dispersible magnetic nanoparticles (Wang, *et al.*, 2003, Li, *et al.*, 2004, Kandpal, *et al.*, 2014, Salman, *et al.*, 2014) in which magnetic nanoparticles are functionalized with water-compatible chemical reagents (Pellegrino, *et al.*, 2004).

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 600°C. The structural and optical properties of cobalt oxide have been studied by XRD, HRTEM and FESEM analyses.

## MATERIALS AND METHODS

Cobalt oxide nanoparticles were successfully synthesized according to the following manner. First 2 g of cetyl trimethylammonium bromide (CTAB) surfactant was dissolved into 70 mL de-ionized water with stirring. Then, 1gr of cobalt chloride ($CoCl_2.6H_2O$) was slowly added to the solution and stirred for 5 min at room temperature. By adding the solution of NaOH (2 M) the solution changed from pink color to blue color and the volume of the solution reached to 100 mL. The pH was maintained at 6.5 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 nanoparticles were carried out to study of the 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-$K_\alpha$: λ = 1.54 Å. The morphology was characterized by field emission scanning electron microscopy (FESEM) with type KYKY-EM3200, 25 kV and field emission transmission electron microscopy (FETEM) with type Zeiss EM-900, 80 kV.

## RESULTS AND DISCUSSION

X-ray diffraction (XRD) at 40Kv was used to identify crystalline phases and to estimate the crystalline sizes. Fig. 1 shows the XRD morphology of $Co_3O_4$ nanoparticles and indicates the nanostructure of $Co_3O_4$. Well-defined diffraction peaks at about 19.52°, 31.50°, 37.05°, 38.77°, 44.96°, 55.80°, 59.53°, 65.30°, 74.55°, 77.50°, and 78.60° are observed, corresponding to the (111), (220), (311), (222), (400), (422), (511), (440), (620), (533) and (622) planes of $Co_3O_4$ crystals. The mean size of the ordered $Co_3O_4$ nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula 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 size of annealed $Co_3O_4$ nanoparticles was in the range of 20-50 nm from this Debye-Sherrer equation.

Scanning electron microscope (SEM) was used for the morphological study of nanoparticles of $Co_3O_4$. These Figures show high uniformity emerged in the samples surface by increasing annealing temperature. Fig. 2(a) shows the SEM image of the as-prepared cobalt oxide nanoparticles prepared by wet chemical method. It can be seen that the particles were aggregated together with particle size in the range of 25-45 nm. Fig. 2(b) shows the SEM image of the annealed $Co_3O_4$ nanoparticles at 600°C for 3 hours in presence of CTAB surfactant. Fig. 2(c) shows the SEM image of the annealed $Co_3O_4$ nanoparticles at 600°C for 3 hours without CTAB surfactant. It can be seen the sphere-like shaped $Co_3O_4$ nanocrystals were formed with good uniformity when CTAB surfactant was used. The average crystallite size of annealed nanocrystals is about 35 nm. In fact surfactants have capping agent to stabilize the nanoparticles to prevent agglomeration. Repulsive Steric hindrance is appeared between particles in atomic scale to prevent attractive inter-atomic interaction for stabilization of the particles.

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

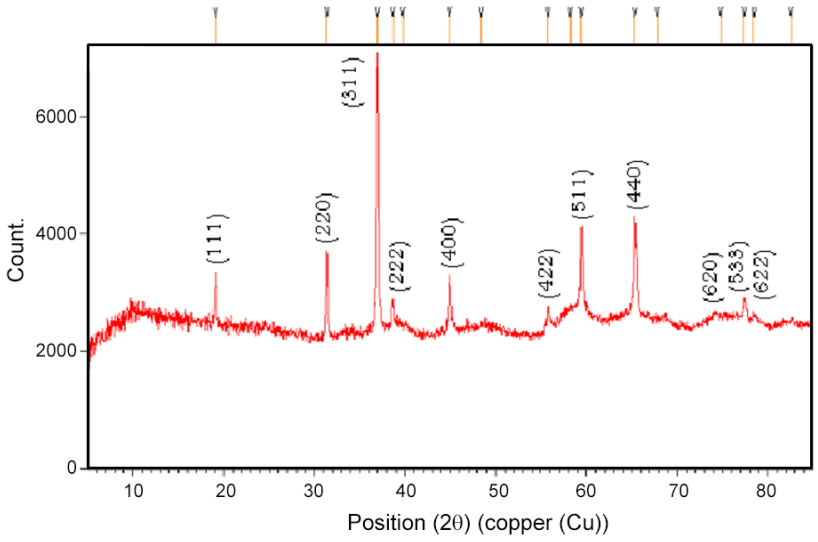


Fig. 1: XRD pattern of annealed Co3O4 nanoparticles after annealing at 600oC for 3 hours

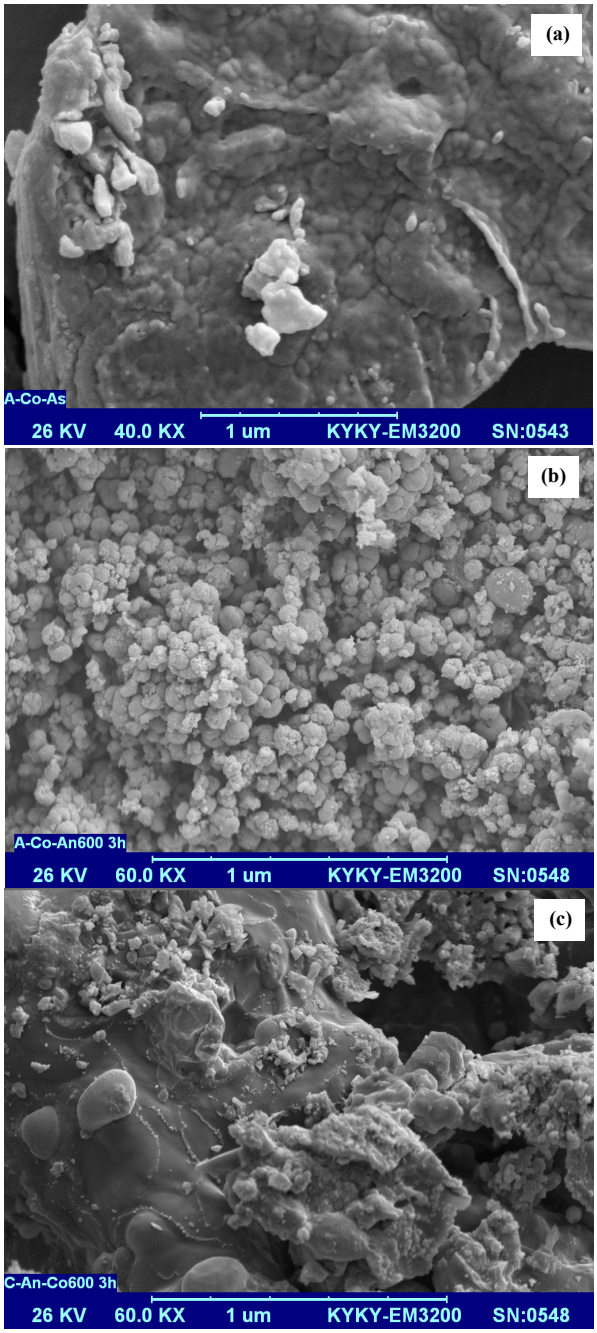


Fig. 2: SEM images of the as-prepared and annealed $Co_3O_4$ nanoparticles: (a) as-prepared cobalt oxide nanoparticles (b) annealed $Co_3O_4$ in presence of CTAB surfactant (c) annealed one without surfactant

aggregated. The uniform $Co_3O_4$ particles have sphere-like shaped with less agglomeration. As can be seen in the inset of Fig. 3, the particle sizes possess a narrow distribution in a range of 25 to 55 nm, and the mean particle diameter is about 35 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.

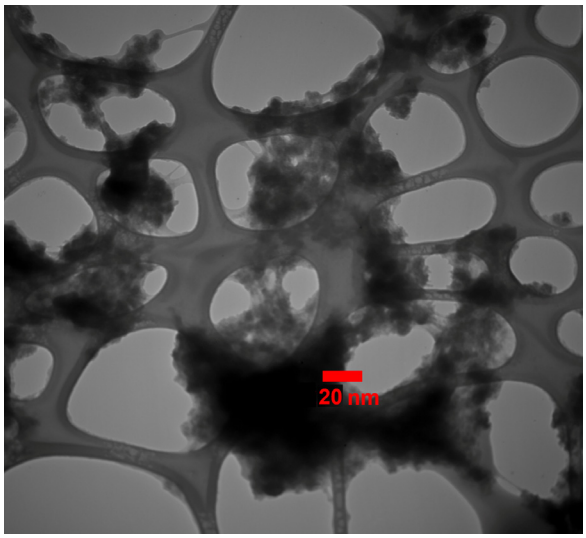


Fig. 3: TEM image of the as-prepared $Co_3O_4$ nanoparticles

## CONCLUSIONS

Cobalt oxide ($Co_3O_4$) nanoparticles were successfully made by simple wet synthesis method using cobalt sulfate as precursor and CTAB as surfactant. The particle size of $Co_3O_4$ was measured in the range of 25-45 nm for as-prepared particles and 35 nm for of annealed one. FESEM images revealed that the particles changed to spherical shape with less agglomeration by increasing annealing temperature. XRD pattern of cobalt oxide samples nanoparticles exhibited the structure of $Co_3O_4$ nanoparticles. TEM image revealed high uniformity of the sphere-like shaped cobalt oxide nanoparticles by increasing annealing temperature

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