
Research Article

Theme- New horizons in chemical sciences.

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Synthesis and Characterization of Cobalt Nanoparticles by Wet Chemical Method.

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ABSTRACT

Cobalt nanoparticles were produced by using the wet phase reduction method. The effect of urea and alkali additives on the formation and growth mechanism of cobalt nanoparticles was investigated. The Co-precipitation method was employed in the laboratory for the synthesis of a cobalt catalyst. The cobalt nitrate salt and urea (1:2) were mixed in little quantity of distilled water and heated at 400°C in a muffle furnace with constant stirring. As obtained cobalt oxide was powdered and reduced to Cobalt nanoparticles in hydrogen gas at different temperatures (700-800°C). The synthesized nano-catalyst was further evaluated using key analytical techniques viz. XRD (X-ray Diffractometry), FTIR (Fourier Transform Infra-Red Spectroscopy), BET and SEM (Scanning Electron Microscopy). Further studies were done to conclude the impact of varying reducing temperatures and the mole ratio of metal salt and Urea.

KEYWORDS

Cobalt nanoparticles, wet phase reduction, Urea decomposition, X-ray Diffractometry, Scanning Electron Microscopy.

1. INTRODUCTION

Nanotechnology is a branch of science that deals synthesis and development of various nanomaterials. In nanotechnology, a particle is defined as a small object that behaves as a whole unit concerning its transport and properties[1]. Different metallic nanomaterials are being produced using copper, zinc, titanium, magnesium, gold, alginate and silver. Of all the metals, Cobalt is proven to be the first catalyst made from non-precious metal with properties closely matching with those of platinum[2]. Cobalt serves as a model system for the macroscopic magnetic response since its slow to moderate crystal anisotropy allows the effects of size, shape, internal crystal structure and surface anisotropy to be observed in a single system [3,4]. The low crystal anisotropy of cobalt also promotes their study as a model system for the effects of size, shape, crystal structure and surface anisotropy on their macroscopic magnetic response.

Cobalt is one of the most important ferromagnetic metals due to its three metastable phases with different crystallographic structures, namely, the hexagonal closed packed (hcp) phase, the face-centered cubic(FCC) phase, and the epsilon phase [5,6].Synthesizing metallic nanoparticles following the wet-chemistry route is a powerful way of obtaining the producible macroscopic amount of homogeneous samples [7]. Several wet-chemical methods have been developed to synthesize cobalt crystals with different morphologies, for example, pyrolysis, solvo thermal and hydrothermal decomposition, microfluidic synthesis; modified polyol processes and template-based methods [8-10].

In the presented study, we applied the co-precipitation method for the synthesis of cobalt oxide nanoparticles. The co-precipitation method is a comparatively simple, cost-effective synthesis method. Further, the cobalt oxide nanoparticles were reduced to cobalt nanoparticles under the influence of hydrogen gas.

The synthesized cobalt oxide nanoparticles and cobalt nanoparticles were characterized by key analytical techniques viz. Fourier Transform Infrared Spectrometer (FTIR); X-ray diffraction technique (XRD); BET Surface area analyzer (SAA) and Scanning Electron Microscopy (SEM).

2. MATERIALS AND METHODS

2.1. Synthesis of Cobalt Oxide Nanoparticles

Approximate quantities of ACS grade Cobalt nitrate hexahydrate (~20g) and AR grade Urea (~40g) were weighed into glass beaker to maintain mole ratio of the composite as 1:2% w/w. Added little quantity of demineralized water in the beaker and the mixture was stirred to make the homogeneous composite. Being oxidizing agent, urea performed as fuel into this synthesis. The beaker was then placed into the muffle furnace which was previously set at 400°C. The blend was shaken intermittently with a glass rod to ensure the formation of cobalt oxide from across the blend. The reaction was allowed to complete for the next three hours with constant stirring.

After three hours, the beaker was removed from the muffle furnace and allowed to cool at room temperature. The outcome of this synthesis was black colored lumps that were broken gently to get powder.

2.2. Synthesis of Cobalt Nanoparticles

About 500mg of a powdered sample as obtained cobalt oxide were taken into two different quartz boats. To synthesize the cobalt nanoparticles, Lenton's Split Tube Furnace equipped with a one-meter long quartz tube was used (Figure 1). The hydrogen gas outlet was terminated into the water reservoir. It was ensured that both the ends of the quartz tube were closely packed to avoid the interference of atmospheric conditions while the synthesis of cobalt nanoparticles under the influence of hydrogen gas. The temperature of the furnace was set at 700°C and 800°C stepwise. After achieving the desired temperature, quartz boats having samples were kept into the tube. The ends of the tube were firmly sealed again. The hydrogen gas was allowed to flow through the tube for about two hours with controlled pressure.

After two hours reduction under a hydrogen atmosphere, the quartz boats were allowed to cool into the tube itself. After achieving room temperature, samples were collected and stored into the glass bottles.

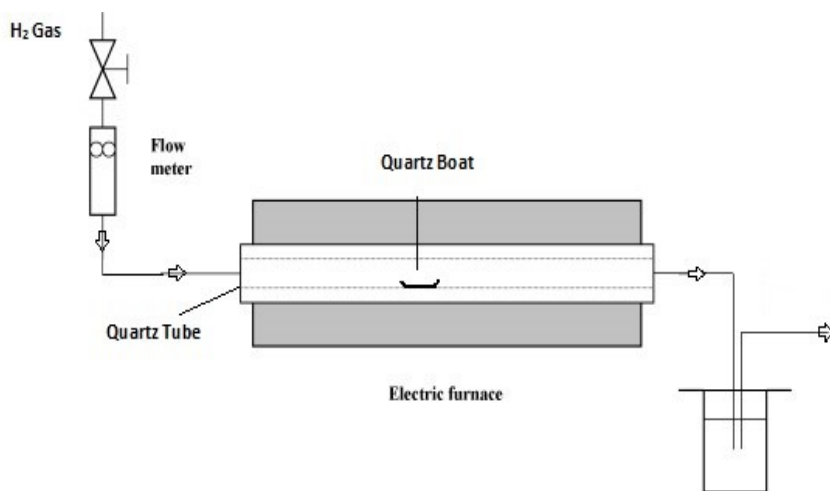


Fig. 1. Schematic Diagram of Lenton's Split Tube Furnace.

2.3. Characterizations

The Cobalt nanoparticles were characterized by the KBr pellet method of the Perkin-Elmer FTIR Spectrometer with the spectrum-one model. X-ray diffraction (XRD) analysis was performed using Phillips analytical X-ray diffractometer with Cu K α radiation running at 45 KV/40 mA in the 2θ range 2°–100°. With a step size of 0.02, Specific surface areas were measured using the SmartSorb-92/93 model of Smart Instruments Co. Pvt Ltd. by low-temperature nitrogen adsorption using the Brunauer-Emmett-Teller (BET) single point method. The samples were degassed at 150°C for 2h before analysis. The morphological analysis was performed with a Phillips SEM 505 scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Cobalt Oxide Nanoparticles

FTIR spectrum of cobalt oxide nanoparticles so obtained in experiment 2.1 (Figure 2) was recorded. The broadband at 3251cm^{-1} has been attributed to N-H stretch. The band at 650cm^{-1} was assigned to the bridging vibration of the O-Co-O bond [11]. The weak band near 1635cm^{-1} was assigned to H-O-H bending vibration mode and was presented due to the adsorption of moisture when FTIR sample disks were prepared in an open-air atmosphere.

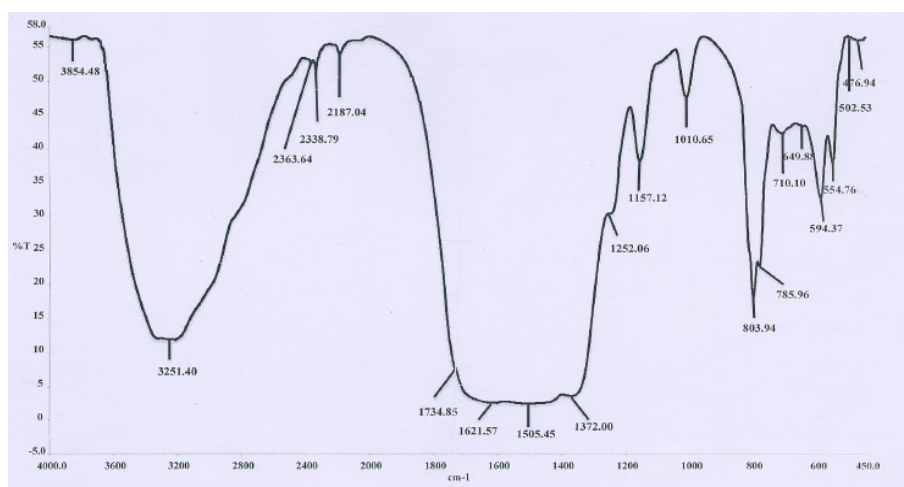


Fig. 2. FTIR Spectrum of Cobalt Oxide Nanoparticles.

The obtained XRD pattern (Figure 3) exhibits a non-crystalline pattern which indicates that the size of granules into the synthesized cobalt oxide nanoparticles was too small to detect by the X-ray diffraction technique.

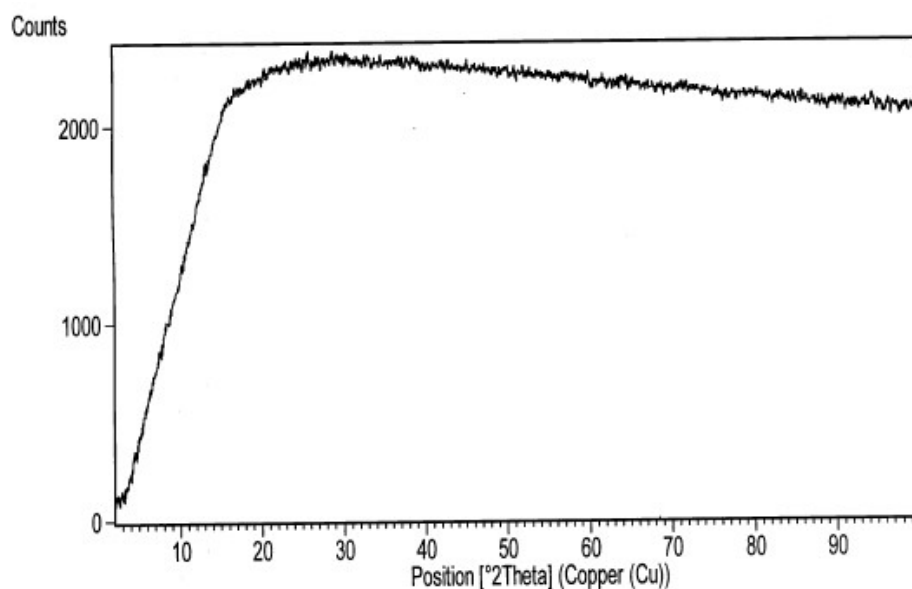


Fig. 3. XRD Pattern of Cobalt Oxide Nanoparticles.

The surface area of cobalt oxide nanoparticles was determined (Figure 4) and surface area value was $4.65\text{m}^2/\text{g}$ which indicates the formation of nanosized particles.

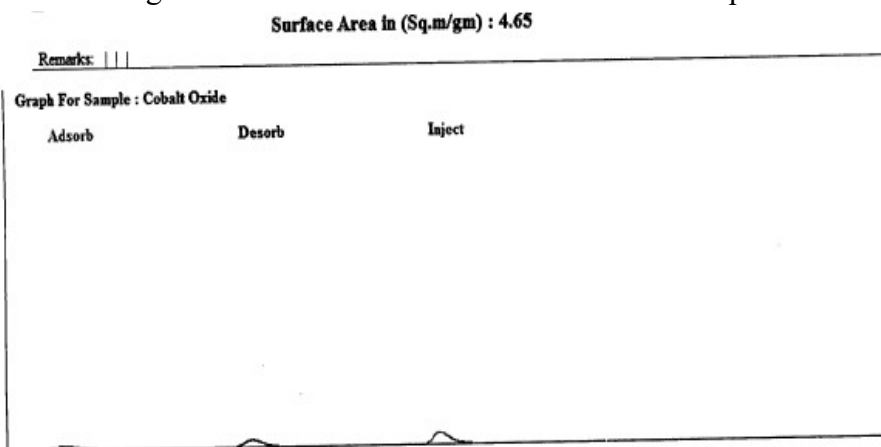


Fig. 4. BET Surface Area of Cobalt Oxide Nanoparticles.

3.2. Cobalt nanoparticles

FTIR spectra of cobalt nanoparticles calcined at 700°C (Figure 5a) and 800°C (Figure 5b) were recorded. The FTIR spectra of cobalt nanoparticles collected at varying calcination temperatures (700°C & 800°C) are comparable and indicate the absence of characteristic bands that were present in the FTIR spectrum of cobalt oxide nanoparticles. This confirms the changes at a molecular level using a loss of different oxides during calcination experiments. However, there is an enhancement in the FTIR transmittance of nanoparticles obtained at 800°C in comparison with the nanoparticles obtained at 700°C . This affirms the development of pure cobalt nanoparticles at elevated temperatures.

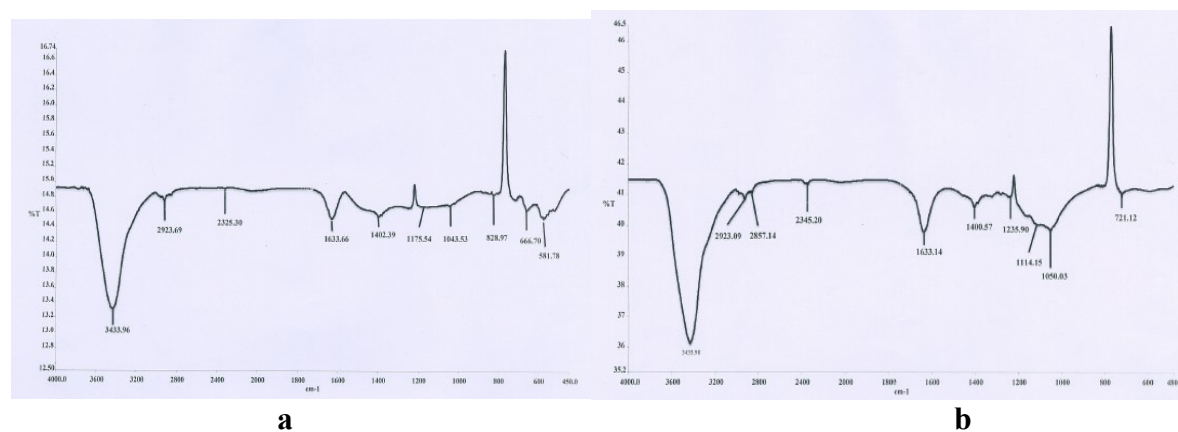


Fig. 5. FTIR Spectra of Cobalt Nano-Catalyst obtained at a) 700°C b) 800°C .

The XRD patterns of cobalt nanoparticles obtained at 700°C (Figure 6a) and 800°C (Figure 6b) exhibit interesting features, showing diffraction peaks at 2-theta $\sim 44.9^\circ$, 52.4° , 77.4° , and 92.5° . These 2-theta reflections are the characteristic of cobalt nanoparticles (JCPDS Card No. 73). However, the intensity counts on 2-theta peaks were decreased in the XRD pattern of

nanoparticles obtained at 800 °C compared with the intensity counts of nanoparticles obtained at 700°C. The crystallite size was calculated by Debye Scherer equation as,

$$D = K\lambda / \beta \cos\theta \quad \text{---Equation 1}$$

Where, D = the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;

K = shape factor, with a value close to unity;

λ = X-ray wavelength;

β = line broadening at half the maximum intensity (FWHM);

θ = the Bragg angle.

Table-1 indicates the comparison of intensity counts and average crystallite size of cobalt nanoparticles obtained at 700°C and 800°C.

Table 1. Comparison of XRD intensity counts and Average Crystallite Size.

2-theta (°)	Nanoparticles obtained at 700°C		Nanoparticles obtained at 800°C	
	Intensity Counts (cts)	Average Crystallite Size (nm)	Intensity Counts (cts)	Average Crystallite Size (nm)
44.3	650	35	375	24
51.6	307		190	
76.0	250		127	
92.4	209		152	

From Table-1 it is seen that the intensity counts of 2-theta reflections collected from the XRD pattern of nanoparticles obtained at 700°C are comparatively more than that of nanoparticles obtained at 800°C. This indicates the development of amorphicity in the cobalt nanoparticles with increasing temperatures.

Further, the average crystallite size of nanoparticles obtained at 700°C is greater than the average crystallite size of the catalyst obtained at 800°C. It reveals that increasing calcination temperatures have an impact on the average crystallite size of the cobalt nanoparticles.

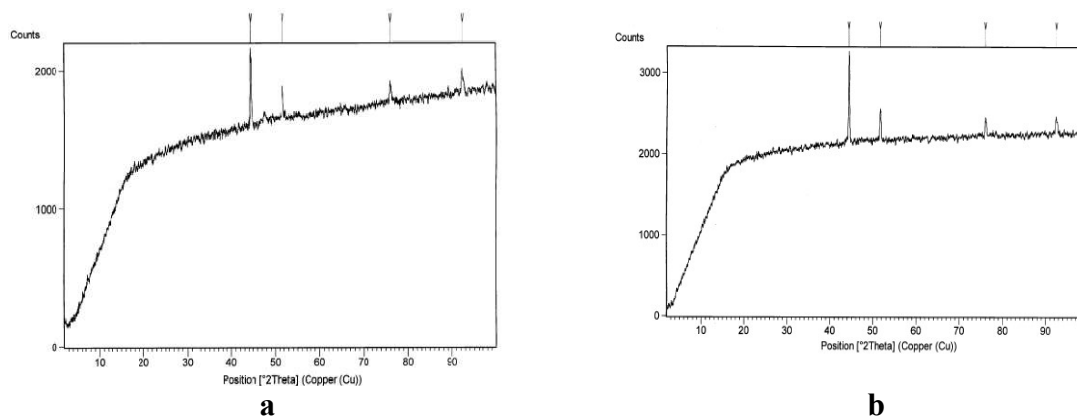


Fig. 6. XRD Patterns of Cobalt Nanoparticles obtained at a) 700°C b) 800°C.

Figure 7a and figure 7b shows BET plots of cobalt nanoparticles obtained at 700°C and 800°C respectively. The specific surface area was calculated as 12.15m²/g for the nanoparticles obtained at 700°C whereas 16.54m²/g for the nanoparticles obtained at 800°C. The difference in the specific surface area at two temperatures indicates the impact of calcination temperature on the surface area of cobalt nanoparticles.

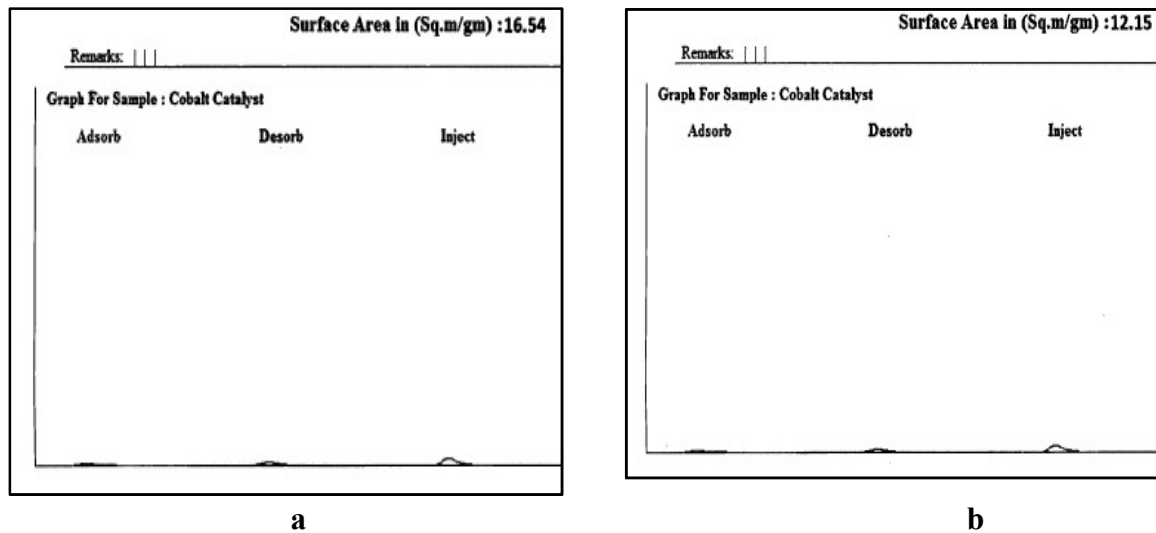


Fig. 7. BET Surface Area of Cobalt Nanoparticles obtained at a) 700°C b) 800°C.

SEM images of cobalt nanoparticles calcined at 700°C and 800°C were collected. It was observed from the image comparison that, the SEM image of cobalt nanoparticles obtained at 800°C exhibits the more clarified picture in comparison with the SEM image of cobalt nanoparticles obtained at 700°C. The particle size of nanoparticles calcined at 800°C ranges between 26nm to 37nm. Thus further supports our hypothesis that the elevated calcination temperature resulted in pure cobalt nanoparticles. Figure 8a and figure 8b show SEM images of cobalt nanoparticles obtained at 700°C and 800°C respectively.

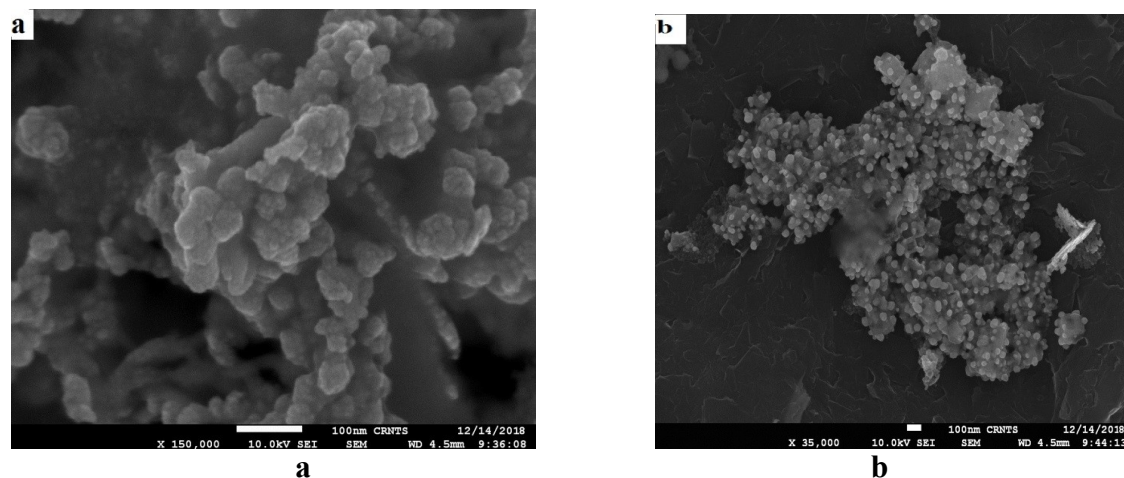


Fig. 8. SEM Data of Cobalt Nanoparticles obtained at a) 700°C b) 800°C.

The higher specific surface area of cobalt nanoparticles obtained at increased calcination temperature demonstrates the impact of calcination temperature on the surface area of cobalt nanoparticles.

4. CONCLUSION

Co-precipitation (Wet) is the practically simple and cost-efficient method for the synthesis of cobalt nanoparticles. The reduction of cobalt oxide nanoparticles to cobalt nanoparticles under the influence of hydrogen gas is an innovative approach. The enhancement in FTIR transmittance of cobalt nanoparticles calcined at 800°C in comparison with nanoparticles obtained at 700°C affirms the development of pure cobalt nanoparticles at elevated temperatures. The crystallite size of nanoparticles obtained at 700°C is greater than the crystallite size of nanoparticles obtained at 800°C. This reveals the impact of increasing calcination temperatures on the crystallite size of cobalt nanoparticles.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. Batista, C. A. S., Larson, R. G., & Kotov, N. A. (2015). Non additivity of nanoparticle interactions. *Science*, *350*(6257), 1242-1247.
2. Yu, Y., Mendoza-Garcia, A., Ning, B., & Sun, S. (2013). Cobalt-substituted magnetite nanoparticles and their assembly into ferrimagnetic nanoparticle arrays. *Advanced Materials*, *25*(22), 3090-3094.
3. Puntès, V. F., Krishnan, K. M., & Alivisatos, A. P. (2001). Colloidal nanocrystal shape and size control: the case of cobalt. *Science*, *291*(5511), 2115-2117.
4. Skumryev, V., Stoyanov, S., Zhang, Y., Hadjipanayis, G., Givord, D., & Nogués, J. (2003). Beating the super paramagnetic limit with exchange bias. *Nature*, *423*(6942), 850.
5. Pandey, B. K., Shahi, A. K., Swarnkar, R. K., & Gopal, R. (2012). Magnetic property of novel cobalt sulfate nanoparticles synthesized by pulsed laser ablation. *Science of Advanced Materials*, *4*(3-4), 537-543.
6. Lu, A. H., Salabas, E. E., & Schüth, F. (2007). Magnetic nanoparticles: synthesis, protection, functionalization, and application. *Angewandte Chemie International Edition*, *46*(8), 1222-1244.
7. Puntès, V. F., Krishnan, K., & Alivisatos, A. P. (2002). Synthesis of colloidal cobalt nanoparticles with controlled size and shapes. *Topics in Catalysis*, *19*(2), 145-148.

- 8.** Guo, L., Liang, F., Wen, X., Yang, S., He, L., Zheng, W., & Zhong, Q. (2007). Uniform magnetic chains of hollow cobalt mesospheres from one-pot synthesis and their assembly in solution. *Advanced Functional Materials*, *17*(3), 425-430.
- 9.** Liu, S. H., Gao, H., Ye, E., Low, M., Lim, S. H., Zhang, S. Y., & Han, M. Y. (2010). Graphitically encapsulated cobalt nanocrystal assemblies. *Chemical Communications*, *46*(26), 4749-4751.
- 10.** Wang, X., Yuan, F., Hu, P., Yu, L., & Bai, L. (2008). Self-assembled growth of hollow spheres with octahedron-like Co nanocrystals via one-pot solution fabrication. *The Journal of Physical Chemistry C*, *112*(24), 8773-8778.
- 11.** Wu, S. H., & Chen, D. H. (2003). Synthesis and characterization of nickel nanoparticles by hydrazine reduction in ethylene glycol. *Journal of Colloid and Interface Science*, *259*(2), 282-286.