

## SURFACTANT-FREE SYNTHESIS OF MAGNETIC COBALT PARTICLES WITH HIERARCHICAL NANOSTRUCTURES

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Magnetic cobalt particles with various novel morphologies were prepared via a simple polyol route with a single step and without the assistance of a surfactant. Polyhedral microspheres, bumpy surface microspheres, and unique microspheres with hierarchical nanorod growth on top were synthesized and reported for the first time. Both face centered cubic and hexagonal closed packed phases of cobalt coexisted in these samples, where face centered cubic was the dominant phase. Cobalt microspheres covered with nanorods showed enhanced coercivity compared to their bulk cobalt counterpart most possibly is attributed to shape anisotropy. A possible formation mechanism of the cobalt particles was proposed.

(Received January 28, 2016; Accepted April 1, 2016)

*Keywords:* cobalt; hierarchical nanostructures; magnetic materials.

### 1. Introduction

Cobalt (Co) is an important magnetic material that has always received intensive attention from numerous researchers because of its potential application in microwave absorption [1], catalysis [2], and information storage [3], among others. The development of morphology-controlled synthetic methods has attracted significant interest because of the novel properties of Co that are dependent on its morphology. The diversity of the morphologies of Co have been prepared using various approaches, such as dendritic structure [3], flower-like structure [1,4], hollow structure [5], and microfibers [6], among others. In most cases, the synthesis of Co particles into different shapes or morphologies are surfactant-assisted [1,4,5,7]. Thus, the extra cost of the surfactant is not only involved, but its removal is a tedious and difficult task as well.

In the current study, the preparation of Co particles with three different synthesis conditions without a surfactant was being investigated. Polyhedral microspheres, bumpy surface microspheres, and microspheres with nanorod growth on top have been synthesized via this facile and simple polyol process. To the best of our knowledge, the preparation of Co with these types of morphologies without a surfactant has never been reported. The magnetic properties of Co have been measured and presented. Microspheres covered with nanorods on top showed enhanced coercivity compared to the Co bulk counterpart and other two samples.

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## 2. Experimental details

All chemicals were of analytical grade and used as obtained. In the typical experiment, 1 mmol of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was first dissolved in 50 ml ethylene glycol (EG). Then, 2 mmol sodium hydroxide (NaOH) and 5 mmol of hydrazine hydrate ( $\text{N}_2\text{H}_4$ ) were added into the metal salt solution. The mixture above was magnetically stirred for 15 min prior to being heated to the boiling point of EG. Black powders were obtained after refluxing the mixture for 60 min. After the solution cooled to room temperature, the obtained black powders were collected via centrifugation and were subsequently washed several times with ethanol. The differences in synthesis conditions were denoted as sample A (without stirring during heating) and sample B (with constant stirring during heating). In sample C, the concentration of Co salt was increased to 3.5 mmol (per same volume) with constant stirring during heating.

X-ray diffraction (XRD) was performed using a Bruker D8 Diffractometer with a  $\text{Cu-K}\alpha$  ( $\lambda = 0.154021$  nm) radiation source. Electron micrographs were taken using a ZEISS Leo Supra 50 variable pressure field-emission scanning electron microscope (FESEM) and a FEI (Tecnai G<sup>2</sup> F20) High resolution transmission electron microscope (HRTEM). Elemental analysis was performed using energy dispersive X-ray (EDX) analysis. A hysteresis loop of the sample was obtained using a DMS model 10 vibrating sample magnetometer (VSM).

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the three Co samples synthesized via a polyol route. Both FCC and HCP phases of Co coexisted in these samples, where FCC was the dominant phase. According to the ICDD data file (05-0727), if Co is dominated by the HCP phase, the (101) plane typically emerges as the highest peak. However, none of the three Co samples showed (101) peaks (only sample B showed a very low intensity peak, as pointed out by an arrow). On the other hand, the (111) peak emerged as the highest peak, followed by the (200) and (220) peaks. These results are consistent with the ICDD-data file 15-0806 for FCC Co and are not surprising since FCC Co has been reported earlier despite the HCP cobalt phase being the thermodynamically stable phase [8]. The predominance of FCC Co in the Co samples may be attributed to the dominance of the kinetic chemical reaction rather than the thermodynamic equilibrium [9].

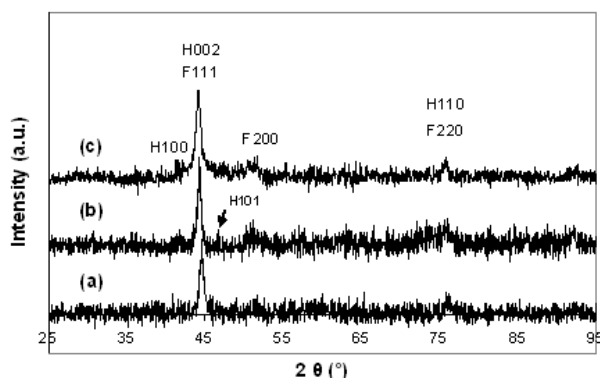
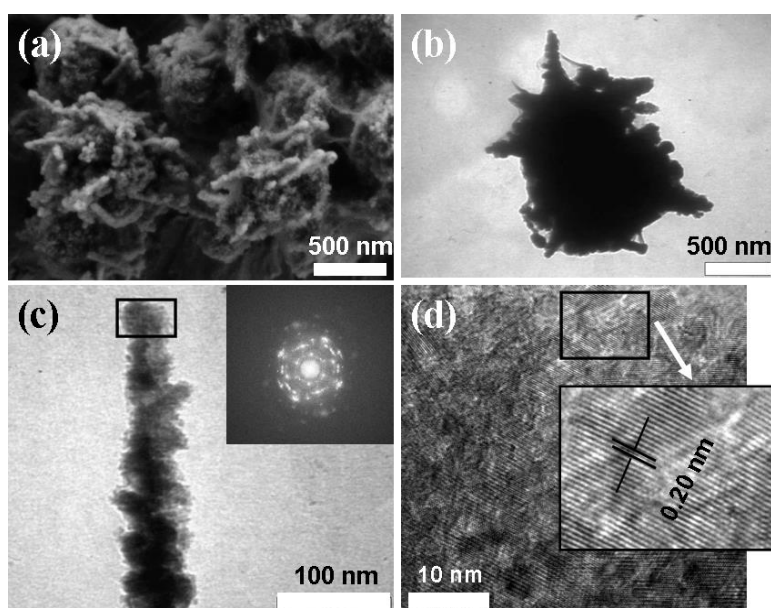


Fig. 1. XRD patterns of the as-prepared samples (a) sample A (b) sample B and (c) sample C. (H=HCP; F=FCC)

Figure 2 shown the electron micrographs for the sample A which is synthesized without stirring. As can be seen from the Fig. 2 (a), nanorods were randomly grown on the body of cobalt particles. From the TEM image presented in the Fig. 2(b), it is clearly notice the nanorods were grown on the surface of the cobalt micropshere. The length of nanorods were ranged from 50nm to 300nm. The hierarchical strcuture of the nanorods were clearly revealed in the Fig. 2(c). One can notice that the whole rod is actually stacking of the smaller nanoparticles. From the fast fourier

transformation (FFT) shown in the inset, it also revealed the nanorod is a polycrystalline. The tip region of the nanorod (marked with square) was also magnified and the lattice resolved image was presented in the Fig. 2 (d). There are many overlapping crystal lattice fringes. On the other words, this indicating that many nanoparticles stacking on one another. This is in agreement with the FFT pattern. The lattice spacing measured was found to be 0.20 nm which can be assigned to the plane F111/H002 of cobalt. This result also in agreement with the XRD pattern where this F111/H002 diffraction peaks show highest intensity. This indicating that sample A has a preferential orientation along the [F111/H002] direction.



*Fig. 2. Electron micrographs of the samples A (a) SEM, (b) TEM, (c) Magnified TEM image of a nanorod, inset shows the FFT of the nanorod tip area and (d) lattice resolved micrograph.*

Figure 3 presented the electron micrographs for the sample B with constant stirring. Sample morphology was more uniform as can be seen from the SEM and TEM images displayed in Figs. 3 (a-b). These particles are clearly self-organized from the smaller nanoparticles and formed a bumpy surface. The particle size measured from the TEM image was roughly 500 to 600nm. From the bumpy surface, a magnified image was presented in the Fig. 3(c) and at a specific selected area (marked with square), the lattice resolved micrograph was obtained and shown in Fig. 3 (d). The well aligned lattice fringes were observed and the lattice spacing was measured. The lattice spacing was 0.20 nm and this is again consistent with the highest diffraction peak (F111/H002) from the XRD pattern.

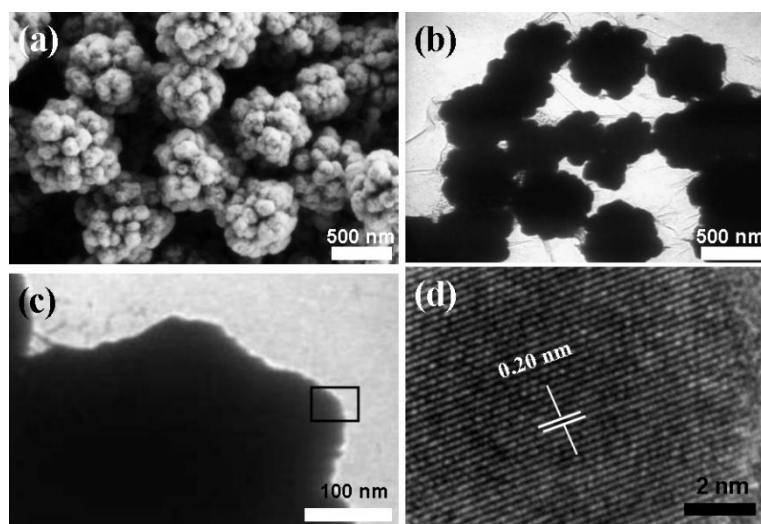


Fig. 3. Electron micrographs of the samples B (a) SEM, (b) TEM, (c) Magnified TEM image and (d) lattice resolved micrograph.

When the cobalt salt concentration increased to higher value while the stirring kept constant, the electron micrographs obtain for the sample C were presented in the Fig. 4. Interestingly, the morphology of the sample C was developed into a polyhedral microspheres. The size of the particles were roughly 600-700nm. From the SEM and TEM images shown in the Fig. 4 (a-b), the surface of the particles was “rough” other than the polyhedral morphology. This rough surface also indicating that they are self-organized from the smaller nanoparticles. The magnified image of the rough surface was presented in the Fig. 4 (c). There are many nanoparticles can be observed which can proved the speculation of the self-organized of nanoparticles into the polyhedral morphology. The lattice resolved micrograph presented in the Fig. 4 (d) also further proved that F111/H002 is the preferred orientation since the measured lattice spacing is 0.20nm. The single particle that marked in the circle is about 5-6 nm.

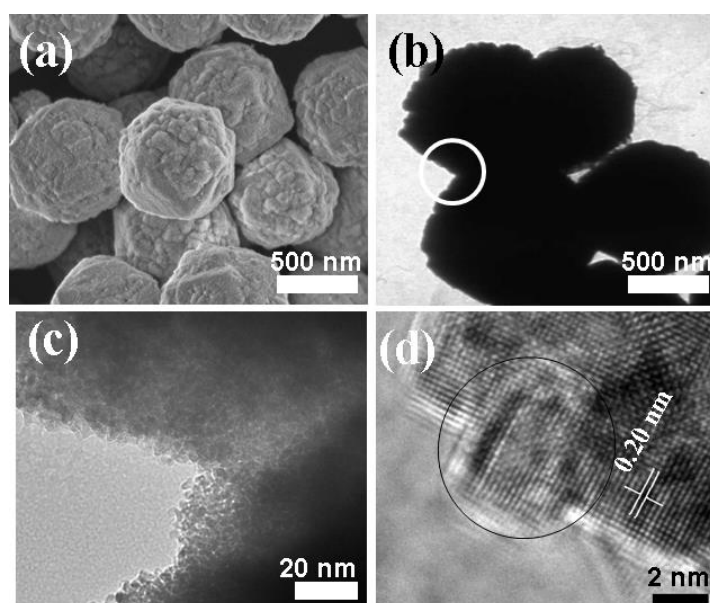


Fig. 4. Electron micrographs of the samples C (a) SEM, (b) TEM, (c) Magnified TEM image and (d) lattice resolved micrograph.

The purity of the as-prepared samples via the polyol process was verified using EDX, as shown in Fig. 5. The EDX analysis shows that the obtained Co was of high purity. Low-intensity carbon and oxygen peaks were detected in the spectrum because of some small amounts of organic molecules, i.e., ethylene glycol absorbed on the surface of Co particles.

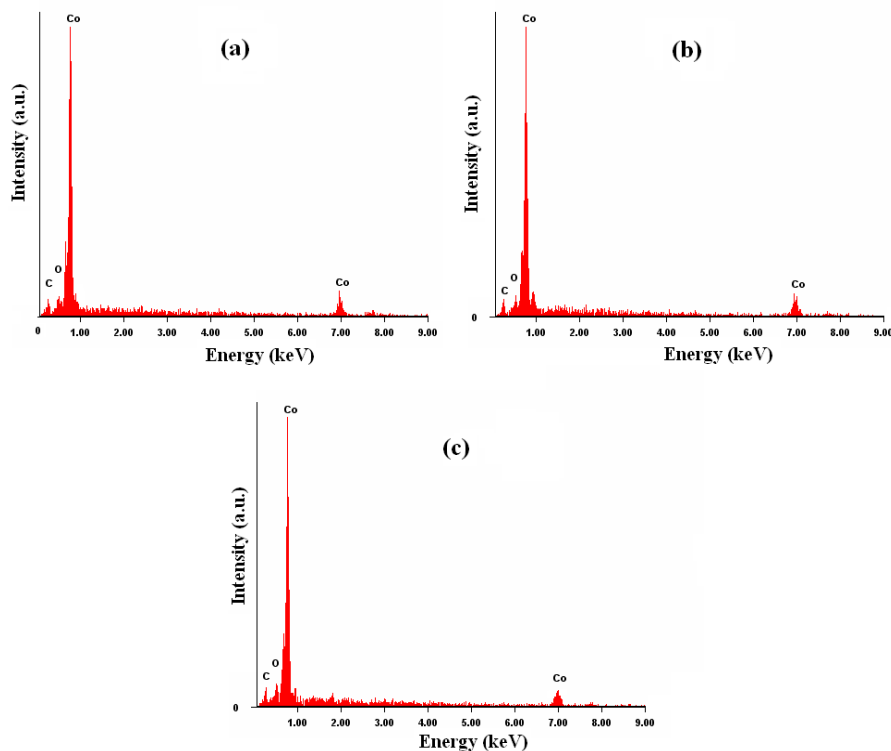


Fig. 5. EDX spectral of the sample (a) sample A (b) sample B and (c) sample C.

A possible formation mechanism based on experimental results and observations was proposed. The effects of stirring and hydrazine were assumed to play crucial roles in the formation of the Co particles with different morphologies. Based on observations, a pink emulsion formed initially when the Co ions reacted with hydrazine (cobalt-hydrazine complexes) [9]. This pink emulsion was relatively stable in room temperature. The excessive hydrazine converted the complexes to Co metal when the temperature increased. Nucleation started at the boiling point of the EG (solution started to turn black). Large amount of Co nanoparticles formed initially and aggregated to form larger spherical particles driven by the minimization of the surface energy and magnetic force of the Co nanoparticles. The reaction rate slowed down with increasing reaction time because of the decrease in concentration of the Co-hydrazine complex. Therefore, the concentration of Co atoms was insufficient for the growth of spherical particles, and Co atoms randomly formed on the top of the pre-formed Co particles. The small spots with high surface energies function as “active sites” for particle growth. Preferential orientation growth started when the nuclei formed at the active sites. As a result, non-uniform nanorods were randomly grown and arranged. Co particles formed were more uniform and close to a spherical shape under constant stirring because the particles underwent more constant collisions and distributed more evenly on the surface of the pre-formed Co particles. Therefore, spherical bumpy surface microspheres were formed due to a better environment for diffusion of nuclei.

As the concentration of the  $\text{CoCl}_2$  increased, the pH of the solution decreased due to the acidic nature of the  $\text{CoCl}_2$  solution. The pH of the solution dropped continuously from 11.4 to 9.1 when the concentration of  $\text{CoCl}_2$  used was increased. Hence, the decreased in the pH caused the reduction rate to slow down (due to hydrazine reduction power decreased). This meaning that cobalt nuclei will only supplied slowly into the reaction solution. However, due to the higher

degree of saturation of the high concentration of cobalt ions, the diffusion of cobalt nuclei formed is largely restrained. This condition is favourable for the generation of many spots and imperfections in the nanoparticles formed later [10] and also further led to the formation of faceted nanoparticles as can be seen from HRTEM. According Wang and Feng [11], during the self-organization, these faceted nanoparticles will preferred to rotate themselves in order to arrange in same faces because of less lattice mismatched and the interface energy will be minimized. With this general principle, the faceted nanoparticles will later self organized to form a larger hierarchical polyhedral shape particles where the Van der Waals and magnetic forces were the driven force. Formation of micron size faceted or polyhedral particles caused by the slower reaction rate also has been reported previously [12].

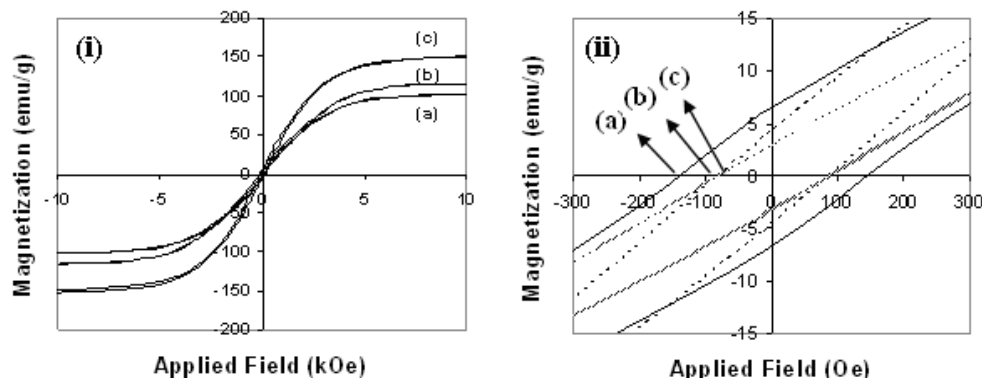


Fig. 6. (i) magnetic hysteresis loops for the three samples with different morphologies (ii) the magnified view at the lower applied field. (a), (b) and (c) is denoted sample A, B and C respectively.

The magnetic hysteresis measurement of the Co particles with different morphologies was conducted at room temperature in the applied field of 10 kOe. These particular samples exhibited ferromagnetic behaviour. Figure 6 shows the open hysteresis loop of the samples. Magnetic saturations ( $M_s$ ) for samples A, B and, C were 104, 116, and 153 emu/g, respectively (Fig. 6 (i)), which were all less than the  $M_s$  for bulk cobalt (168 emu/g) [13]. However, among the three samples, sample C with polyhedral microspheres showed the highest  $M_s$  and closest  $M_s$  to that of the bulk value because it had the largest size and most compact structure. Overall, the decrease in  $M_s$  may be attributed to the surface spin disorder and adsorbed species on the surface of the Co particles [14,15]. As can be seen in the elemental analysis in Fig. 5, the adsorbed polyol molecules on the particle surface may have contributed to the decrement of  $M_s$ .

The coercivities ( $H_c$ ) of samples A, B, and C were 143, 83, and 86 Oe, respectively (Fig. 6(ii)). The sample with nanorods that grew on the surface of the microspheres showed much higher  $H_c$  value than the other two samples. This  $H_c$  also showed an enhanced value compared to the  $H_c$  of bulk cobalt (10 Oe) [16], Co hierarchical microspheres with flower-like structures (95 Oe) [4], and 1D chain-like structures (77 Oe) [17]. This phenomenon may be attributed to shape anisotropy [18,19], which is related to the elongated hierarchical structures of the nanorods that grew on the surface of the microspheres.

#### 4. Conclusions

In summary, magnetic Co particles with various morphologies were successfully prepared via a simple polyol route without the assistance of a surfactant. Polyhedral microspheres, bumpy surface microspheres, and unique microspheres with hierarchical nanorod growth on the surface were reported for the first time. Co microspheres covered with nanorods showed enhanced coercivity compared to bulk cobalt. This surfactant-free polyol process can be extended to prepare other metals with hierarchical nanostructures.

## Acknowledgements

The authors would like to acknowledge USM, and the Short Term Internal Research Funding (STIRF) from Universiti Teknologi PETRONAS for the financial support.

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