MAGNETIC-PROPERTY ENHANCEMENT OF SIZED CONTROLLED COBALT-GOLD CORE-SHELL NANOCRYSTALS

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Cobalt nanoparticles and cobalt-gold core-shell nanoparticles were synthesized via reverse-micelle microemulsion method with emphasis on size control. Cobalt nanoparticles become easily oxidized therefore coating a gold shell on cobalt nanoparticles was necessary and can effectively reduce the oxidation of Co while maintaining most of its magnetic properties. Controlling the size of nanoparticles was performed by adjusting the water to surfactant ratio of reverse micelle solution during synthesis. X-ray diffraction data was used to calculate the crystallinity percentage and percentage of phases presented in Co-Au core-shell nanoparticles. The results from transmission electron microscopy, and field emission electron microscopy combined to energy dispersive x-ray spectroscopy provide direct evidence for shell growth. The average coating layer (shell thickness) in all cases observed to be 4-5 nm. Magnetic properties of samples were investigated using a vibrating sample magnetometer before and after annealing. Magnetic properties enhanced after annealing in all cases. An increase in saturation magnetization after annealing was due to increase in cystallinity percentage. A simple method was applied to measure a totally intrinsic blocking temperature in zero field cooled-warmed (ZFC-W) curves without employing an external magnetic field. The B-field dependence temperature data of Co-Au nanoparticles before and after annealing showed an intrinsic blocking temperature of 45 and 40 K respectively.

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1. Introduction

Nanoscale particles research has recently become an important field in the materials science. Nanoscience and nanothechnology deal with the synthesis, characterization, and exploration of nanostructured materials. Nanostructure is between atomic and finite bulk systems. The vast interest in nanostructured particles mainly arises from the fact that these structures possess novel physical and magnetic properties that differ from those of bulk materials. This is significant in the case of nanoparticles that have a large surface to volume ratio with a high percentage of surface atoms, resulting in unexpected properties. Advance research on nanotechnology bring new structures such as core-shell particles applied in many fields [1]. Coreshell structure nanoparticles have a macrostructure consisting of the surface and internal part. As compared with the single core nanoparticles, core-shell nanoparticles have shown improvement in the functional properties and oxidative stability [2].

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Through the past several decades, amorphous and more recently nanocrystalline materials have been investigated for the application in many fields. An example is high density magnetic recording media technology [3-4]. Increasing the storage density requires more severe control over the morphology of the materials and strong reduction of its dimensions, down to the sizes of the single domain. In nano-region size the crystallinity percentage plays an important role which affects the properties of nanoparticles. Moreover, as a large portion of atoms in nanocrystals is located at the surface, the modification of the surface has been recognized as one of the most advanced methods to improve the reactivity of surface and enhance the stability of the material.

Among magnetic materials cobalt has attracted much attention in magnetic recording media because of very high magnetocrystalline anisotropy and high Curie temperature but it is suffer from oxidation in air. As cobalt nanopaticles are sensitive to oxidation and their sensitivity increases with decreasing the particle size thus they should be coated with materials such as silica [5] [6], metal oxides [7], and gold [8]. Gold particles have high thermal and electrical conductivities, high corrosion and oxidation resistance even in nanometer size region [9]. Therefore coating gold shell on cobalt nanoparticles can effectively reduce the oxidation process of magnetic metal cores and maintain most of the favourable magnetic properties [10-11].

Nanoparticle production by size-controlled and shape-controlled procedure has been a new and interesting research focus. Generally, the shape, size and size distribution of nanoparticles can be controlled by employing different synthetic methods. The most important key is to avoid agglomeration of nanoparticles during the synthesis because the coalescence of the nanoparticles may loss their characteristic properties. It is usually difficult to distinguish between nanoparticles synthesizing methods, however chemical methods are used frequently as a consequence of the production of higher stability and better control over the size and shape of nanoparticles. Among various chemical methods, reverse microemulsion is creating stable colloids with good size dispersion and are typically carried out at room temperature.

Precipitation in water-in-oil microemulsion has been shown to be a very promising technique for preparing monodispersed, ultrafine particles. By this method, the precipitation occurs in nanosize droplets water in oil that is embedded with a surfactant and co-surfactant. Nanoparticles were precipitated during coalescence between water droplets of metal ions and reducing agent ions in the main phase (oil) composed of CTAB/n-octane/1-butanol. Water droplet size was controlled via the molar ratio of water to surfactant by changing concentration of CTAB (surfactant) in solution. Water pools of these reverse-micelles act as nano-reactors for performing simple reaction of synthesis.

We applied reverse microemulsion method for the synthesis of magnetic cobalt and cobalt-gold core-shell nanoparticles. XRD, EDX, TEM, FESEM, and VSM were used for analysis and characterization of magnetic nanomaterials. Moreover the effect annealing and ω (the molar ratio of water to surfactant) on particle size, structure, crystallinity percentage and magnetic properties of cobalt-gold nanoparticles were investigated.

2. Methodology

Preparation of cobalt and cobalt-gold core-shell NPs: Co-Au core-shell nanoparticles were fabricated in a two-step route: initial synthesis of core (or cobalt) nanoparticles and the subsequent shell growth reaction. The compositions of the used microemulsion systems are summarized in Table 1. To prepare cobalt core nanoparticles microemulsions I and II were used. Microemulsion II was slowly added into microemulsion I under argon atmosphere during stirring, and continuously mixed for 20 minutes. The formation of cobalt nanoparticles can be observed by black colour precipitates. In the next step of shell growth reaction, microemulsion III followed by microemulsion II were slowly added into the cobalt mixed solution under argon gas during stirring for 20 minutes. The resulting precipitates were centrifuged and washed with a mixture of methanol and chloroform (volume ratio 1:1) several times and dried at room temperature. Some part of the as-prepared cobalt nanoparticles washed and dried to compare with core-shell nanoparticles as well.

Table 1. Composition of the microemulsions.					
	Surfactant phase	Oil phase	Aqueous phase		
Microemulsion I	CTAB+1-butanol	n-octane	$Co(NO_3)_2.6H_2O$		
Microemulsion II	CTAB+1-butanol	n-octane	NaBH ₄		
Microemulsion III	CTAB+1-butanol	n-octane	AuCl ₃		

CTAB: N-cetyl-Trimethylammonium Bromide

Size controlled nanoparticles: Controlling the size of nanoparticles using microemulsion method was performed by varying the molar ratio of water to surfactant (ω =[water]/[surfactant]) from 5 to 20 to control the water droplet size in the main phase (oil).

Both cobalt and cobalt-gold NPs were subjected to this procedure. However, there was an exception for the core-shell nanoparticles: controlling the shell thickness was performed by calculation of the required amount of shell precursor. Assuming all the shell material is used for deposition on the existing core nanoparticles, the amount of precursor for the growth of a shell with the desired thickness of δ can be calculated as follows [2, 12]:

$$V_{shell} = \frac{nM}{N_{core}\rho_{shell}} = \frac{\pi}{6}((d_{core} + 2\delta)^3 - d_{core}^3)$$
(1)

where V_{shell} is the shell volume, d_{core} is the core diameter, *n* is the number of moles of shell material that can form by reaction, *M* and ρ_{shell} are the molecular weight and density of shell material, respectively, and N_{core} is the number of core nanoparticles.

Heat treatment of NPs: After synthesizing Co and Co-Au nanoparticles, some part of the as-prepared powders were sintered at 400°C for 2 hours under argon gas.

Characterizations methods: X-ray diffraction (XRD) spectra was recorded using Philips Diffractometer model 7602 EA Almelo, equipped with a graphite monochromator, operating at 40 kV and 30 mA CuK α radiation source with $\lambda = 1.5418$ Å. The scanning was performed at a scanning rate of 5°/min in the 2 θ range 4-90°. Transmission electron microscopy (TEM) was performed by a Hitachi (H-7100) electron microscopy with an accelerating voltage of 120 keV. Particle size measurement and distribution graphs were calculated over at least 150 particles per sample. Energy dispersive x-ray spectroscopy (EDX) and field emission electron microscopy (FESEM) measurements were carried out on powder sample by Joel-Jsm-7600F field emission SEM. Hysteresis loops measurements were obtained using Lake Shore model 7407 vibrating sample magnetometer (VSM) at room temperature with the maximum applied magnetic field of 10 kOe on powder form samples. The blocking temperature was measured at a cusp of the produced magnetic field by the sample (B) versus the temperature curve during warming up the sample from a very low temperature ($\leq 15K$) to room temperature in the absence of applied magnetic field.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of as prepared cobalt nanoparticles for four different ω ratios. Although the peak for pure cobalt (ICDD PDF 89-4307) was observed at 20: 52.5° but most of the peaks was referred to cobalt oxide. The peaks at 20: 31°, 38.2°, 44.4°, 58.3° and 64.6° were related to (220), (222), (400), (511) and (440) crystalline plans of cubic Co₃O₄ (ICDD PDF 78-1969), respectively.



Fig. 1. XRD pattern of Cobalt NPs as prepared and crystallinity percentage (Crl%) for ω: 5, 10, 15 and 20.

The oxidation problem was thus expected to be severe; therefore the appropriate experimental move was to abandon any characterization of the oxidized cobalt nanoparticles which were not the desired material in this work. Instead to protect these particles from oxidation, a sequential synthesis was used in order to form a passivation layer of gold on cobalt nanoparticles. To fabricate Co-Au core-shell nanoparticles two critical issues must be considered during the growth of Au shell, The elimination of the nucleation of the Au and homogeneous growth of Au shell onto all Co core nanocrystals in solution were two critical issues that must be considered during the growth of Au shell [13] [14]. XRD patterns of cobalt nanoparticles coated with gold for different ω ratio is shown in Figure 2 (a) and (b) respectively before and after annealing. The main diffraction peaks are assigned to (111), (200), (220), (311) and (222) planes of cubic Au (ICDD PDF 89-3697 before and after annealing) at 20 value of 38.18°, 44.33°, 64.64° and 77.5° respectively. Two characteristic peaks for pure Co was observed and indexed to (111) and (200) at 20: 44.38° and 51.77° accordingly. No peaks for cobalt oxide was detected which conclude that Co particles were perfectly coated with Au shell.



Fig. 2. XRD patterns of (a) as-prepared and (b) annealed Co-Au core-shell NPs and calculated crystallinity percentage (Crl%) for ω : 5, 10, 15 and 20

The peaks observe at 20: 19.9°, 25.5°, 32°, 39.9° and 42.8° from reflection plans of (101), (011), (002), (112) and (00) are related to cobalt derivatives like orthorhombic cobalt borate $(Co_3(BO_3)_2)$ which was due to reduction of cobalt ions by sodium borohydride. The presented phase percentage was calculated by the sum of observed intensities for each phase to the sum of observed intensities which contains all the crystalline and amorphous phase together (equation 2). The rest is the percentage of impurities in the sample. The percentage of each presented phases for four different ω ratios before and after annealing and their crystallographic parameters are reported in Table 2.

Presented phase percentage =
$$\frac{\sum I_{(crystalline \ phase)}}{\sum I_{(crystalline + \ amorphous \ phases)}} \times 100$$
 (2)

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Sample	Dhasa prosont	Lattice	Density	Volume	ω			
Sample	i nase present	(Å)	(g/cm^3)	Cell (Å ³)	5	00 10 11% 35% 54% 10%	15	20
	Co (cubic)	a=b=c=3.54	8.79	44.52	16%	11%	17%	20%
As prepared	Co ₃ (BO ₃) ₂ (orthorhombic)	a=8.43 b=4.52 c=5.46	4.68	208.68	8%	35%	-	-
	Au (cubic)	a=b=c=4.07	19.26	67.85	%76	54%	83%	80%
Annealed	Co (cubic)	a=b=c=3.55	8.90	44.89	18%	10%	20%	20%
	Co ₃ (BO ₃) ₂ (orthorhombic)	a=8.43 b=4.52 c=5.46	4.68	208.68	-	30%	-	-
	Au (cubic)	a=b=c=4.06	19.30	67.90	82%	60%	80%	80%

Table 2. Crystallographic parameters and Percentage of phases presented in samples for fourdifferent ω before and after annealing.

Scherer's equation was used to calculate the crystalline size (equation 3) [15-17]:

$$D = k\lambda / \beta \cos \theta \tag{3}$$

where *D* is the average crystallite size, *k* is particle shape factor that varies with the method of taking the breadth and shape of crystallites (0.89<*K*<1) [18], λ is the X-ray wavelength used (0.1542 nm), β is the angular line width of half-maximum intensity, θ is the Bragg's angle in degrees. The crystalline size of the Co-Au was calculated using (111) reflection of the XRD patterns and estimated sizes are listed in Table 3.

Further information obtained from XRD data is crystallinty percentage which was calculated by the net area under the peaks to the total area. Crystalline diffraction pattern was obtained after removing the linear background and scaling the amorphous sample spectrum [19]. The results show that the crystallinity percentage was increased with increase in ω from 5 to 20 and also enhanced after annealing. A reduction in crystallinity percentage in smaller particle size was due to the larger proportion of non-crystalline (or structurally disordered content). Size reduction from micronmeter to nanometer size particles denotes a decrease in grain size (which contained crystalline phase), while the grain boundaries contain amorphous phase remained constant [20]. In was observed that the crystallinity percentage increases while the intensity and integrated intensity rises accordingly.

Sample	ω	FWHM	Crystallite size(nm)	Intensity (cts)	Integrated Intensity	Crl%
As prepared	5	1.55	5.6	130.0	199.9	7
	10	0.77	11.2	292.0	234.3	8
	15	0.51	16.9	431.1	331.4	10
	20	0.38	22.5	493.9	379.7	12
Annealed	5	0.77	11.5	408.5	209.3	7.3
	10	0.51	17	458.2	704.5	8.1
	15	0.38	22.5	501.8	771.5	10.4
	20	0.25	33.8	522.6	803.5	13.0

Table 3. Crystallite size, full width half maximum (FWHM), Intensity and Integrated intensity of the mean peak with the Crystallinity percentage (Crl %) for different ω .

TEM micrographs for cobalt nanoparticles coated with gold are revealed in Figure 3. The average size was in good agreement with the crystalline size calculated from Scherer formula. The average size of nanoparticles also closely agrees with the calculated ω ratio. In some cases, the smaller size derived from XRD compared with the size obtained from TEM, should be described to the presence of polycrystalline gold and amorphous portion of gold dispersed both on the outer surface of the nanoparticles and at the interface between Co cores and the gold shells. Afetr annealing at 400°C the average particle size was increased from 9, 12, 14 and 19 nm to 12, 16, 18 and 32 nm respectively. The results after annealung are shown in Figure 4.



Fig.3. TEM images of as-prepared cobalt-gold nanoparticles and their size distribution analysis for different $\omega = [H_2O]/[CTAB]$ (a) ω :5, (b) ω :10 (c) ω :15, (d) ω :20.

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Fig. 4. TEM images of cobalt-gold nanoparticles after annealing at 400°C for 2 hours and their size distribution analysis for different $\omega = [H_2O]/[CTAB]$ (a) ω :5, (b) ω :10 (c) ω :15 and (d) ω :20.

Figure 5 gives the high magnification TEM images of Co-Au core shell nanoparticles. The dark grey or black color around the cores presents the gold shell, while the small grey particles are assigned to be Co cores. The average coating layer (shell thickness) in all cases observed to be 4-5 nm.



Fig. 5. High magnification TEM image of gold shell thickness of core-shell Co-Au nanoparticles.

Formation of core-shell structure was furthermore confirmed by FESEM and EDX results. FESEM result of as-prepared cobalt nanoparticles coated with gold is shown in Figure 6. Although the secondary electron mode is usually used for elemental analysis but in our case the backscattered electron mode was used to observe both Co and Au elements since backscattered electrons were reflected from the deeper part of specimen and could analysis the element of core as well. The atomic percentage of Co and Au was 64 and 26% respectively.



Fig. 6. (a) FESEM and (b) EDX image of as-prepared cobalt-gold core-shell

Vibrating sample magnetometer was used to study magnetic properties of Co-Au coreshell nanoparticles. The purpose was to see the effect of annealing on morphology and magnetic properties with variation in particle size. Figure 7 shows the hysteresis loops for Co-Au core shell nanoparticles at room temperature before and after annealing. The shape of hysteresis indicates superparamagnetic behavior for Co-Au core shell nanoparticles as-prepared with low value of coercivity. Usually in particles with the size below the critical size, domain walls are not stable and cause unstable magnetocrystalline anisotropy so the samples behave like superparamagnetic. The single domain size of cobalt nanoparticles was reported in literatures to be 70 nm [21-22] or 68 nm [23]. The coercivity, saturation magnetization and remanent of the as prepared samples are given in Table 5.

Sample	ω	Particle size (nm)	H _C (Oe)	M _S (emu/g)	M_r/M_S	Crl%
As prepared	5	9	37.2	0.09	0.03	7
	10	12	83.1	0.34	0.07	8
	15	14	250	0.38	0.10	10
	20	19	199	2.36	0.17	12
Annealed	5	12	137.7	0.27	0.10	7.3
	10	16	281.2	0.66	0.20	8.1
	15	18	515.8	0.71	0.25	10.4
	20	32	456.7	4.75	0.30	13.0

Table 5. Magnetic data for as-prepared and heat-treated Co-Au nanoparticles.

Enhancement in magnetic properties was observed in all the samples with different ω ratio after annealing (Table 5). The enhancement in coercivity was due to increase in magnetocrystalline anisotropy and the interaction between moments [24]. Furthermore, the increase in saturation magnetization after annealing was attributable to crystallinity percentage increment. It is observed that with increasing the ω ratio, the volume of the particles increases so the percentage of amorphous phase at the grain boundaries decreases. The crystallinity percentage and saturation magnetization versus ω is illustrated in Figure 8. Both Crl% and Ms enhanced after annealing with respect to different ω ratios.

Magnetic properties of nanomaterials have been believed to be highly depend on the sample shape, crystallinity and magnetization direction [13]. The results obtained by XRD showed that both Co and Au has cubic structure with the moments align to [001] crystal direction; but combination of two different magnetic phase (diamagnetic and ferromagnetic) will lead to new properties different from un-coated cobalt. The effect of surface anisotropy in addition gives an overall picture of anisotropy for Co-Au nanoparticles. After annealing the samples showed higher coercivity and behaved as ferromagnetic materials.





Fig. 7. Hysteresis loops of: a) as-synthesised, and b) heat-treated, Co-Au for ω ratios: 5, 10, 15 and 20 at room temperature with applied field H=100000e.



Fig. 8. Saturation magnetization and Crystallinity percentage (Crl%) as a function of ω .

It is well known that in small size particles both superparamagnetic and single domain ferromagnetic domains exist simultaneously. In superparamagnetic and paramagnetic materials the moments are random as a consequence of thermal fluctuation at room temperature. At this point thermal energy overcomes the interaction energy between moments and causes random alignment of the moments. It is interesting to know about the transition temperature (blocking temperature) when almost all the superparamagnetic domains behave like pure ferromagnetic domains. The intrinsic blocking temperature was measured for Co-Au nanoparticles by cooling the sample in the absence of external magnetic field called zero-field-cooled (ZFC) from room temperature to 15 K. The B-field produced by the sample as a function of temperature was measured in the warming process to a temperature well above the blocking temperature called zero-field-warmed (ZFW). The peaks in Figure 9 indicate the blocking temperature (T_B) around 45 and 40 K for Co-Au nanoparticles before and after annealing. At the blocking temperature the energy barrier is equals to thermal energy ($E=K_UV=25k_BT$). Above T_B sample behave like superparamagnetic materials and below that behave like single domain ferromagnetic materials. A decrease in blocking temperature after annealing is due to an increase in coercivity and inter-particle interactions between Co nanoparticles.



Fig. 9. B-Field vs. temperature measured at zero field cooled-warmed state for Co-Au nanoparticles before and after annealing.

4. Conclusion

Magnetic property enhancement of cobalt nanoparticles was successfully performed in this work. Cobalt nanoparticles were protected from oxidation via coating them by a gold shell with the average shell thickness of 4-5 nm. TEM and EDX results were an evidence of core-shell structure formation. Crystallinity percentage of Co-Au core-shell nanoparticles were calculated using XRD data. The crystallinity percentage of nanoparticles increases with increasing the particle size and enhanced after annealing. An increase in saturation magnetization was attributed to crystallinity percentage. An increase in crystalline phase was due to particle size growth after annealing. Blocking temperature was measured using a simple method and showed a transition from superparamagnetic to ferromagnetic at 45 and 40 K for Co-Au nanoparticles respectively before and after annealing.

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