Synthesis of Iron Oxide (Fe$_3$O$_4$) Magnetic Nanocrystals by Green Chemistry Approach
(Sintesis Nanohablur Magnet Ferum Oksida (Fe$_3$O$_4$) dengan Pendekatan Kimia Hijau)

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ABSTRACT

In the present study, we report the size distribution study on the iron oxide (Fe$_3$O$_4$) magnetic nanocrystals (NCs), which have been synthesized by using green chemistry approach with palm-oil based carboxylic compound (oleic acid) as capping ligands. The Fe$_3$O$_4$ NCs were prepared by one pot reaction under non-hydrolytic approach. With the assistance of oleic acid that plays the role as effective capping-ligands, we showed that the Fe$_3$O$_4$ NCs that are highly monodispersed in size and shape can be synthesized by scrupulously controlling the reaction time. The diameter of Fe$_3$O$_4$ NCs can be tuned within the range of 4.0-18.0 nm and exhibit very uniform morphology, which are spherical in shape. Current synthetic approach offers a cheap, environmentally benign and excellent repeatability route in large-scale production of high-quality magnetic Fe$_3$O$_4$ NCs if compared to the preceding reports.

Keywords: Fe$_3$O$_4$; iron oxide; magnetic; nanocrystals; synthesis

ABSTRAK

Dalam penyelidikan ini, kami mengkaji taburan saiz ferum oksida (Fe$_3$O$_4$) nanohablur (NH) magnet yang disintesis dengan pendekatan kimia hijau dengan minyak kelapa sawit daripada kumpulan karboksilik (asid oleik) sebagai ligan. Fe$_3$O$_4$ NH disediakan dengan menggunakan tindak balas tunggal dalam keadaan tanpa akueus. Dengan adanya asid oleik yang berperanan sebagai ligan berkesan, kami menunjukkan bahawa Fe$_3$O$_4$ NH yang mempunyai saiz dan bentuk sekata dapat disediakan dengan mengawal tempoh masa tindak balas. Diameter Fe$_3$O$_4$ dapat dikawal dalam julat 4.0-18.0 nm dan menunjukkan morfologi saiz yang sekata, iaitu berbentuk sfera. Pendekatan sintesis ini telah menyediakan satu cara yang murah, mesra-alam dan kebolehulangan untuk penghasilan Fe$_3$O$_4$ NH magnet yang berkualiti tinggi secara besar-besaran berbanding laporan sebelum ini.

Kata kunci: Ferum oksida; Fe$_3$O$_4$; magnet; nanohablur; sintesis

INTRODUCTION

The congruent properties of nanomaterial have attracted much attention from scientific communities to work actively in developing effective synthetic scheme in producing high quality nanocrystals (NCs). Generally, in addition to produce desired-quality nanomaterials, the synthetic scheme nowadays will consider on the aspects of green chemistry and low temperature synthesis. Recently, organometallic synthesis of NCs is relatively successful in the preparation of wide variety of nanomaterials. In organometallic approach, fatty acid was reported to be a facile ligand with excellent tunable reactivity (Chiu et al. 2010, 2008) and able to anchor on the NCs surface for better size control. Also, it is a natural product originated from fatty acid derived from palm oil with low toxicity. Hereby, we extend and modify the existing organometallic approach that have been used in the production of chalcogenide (Yu & Peng 2002) and oxide-based NCs (Jana et al. 2004) to synthesize Fe$_3$O$_4$ NCs by using oleic acid as capping ligand and hexadecane as low boiling point (287°C) solvent. The combinations of oleic acid with hexadecane provide excellent tunability to produce NCs that are highly crystalline and monodispersed in terms of size and shape. Furthermore, current synthetic scheme offer a low synthesis temperature pathway if compared to preceeding organometallic synthesis approach.

MATERIALS AND METHODS

The reaction was carried out in a 250 mL four neck flask equipped with a condenser and a digital temperature controller under vigorous magnetic stirring in an inert atmosphere of Ar gas. In a typical synthesis, 3.00 mmol of Fe(C$_{18}$H$_{33}$O$_2$)$_3$ precursor and 1.50 mmol oleic acid (C$_{18}$H$_{34}$O$_2$) were dissolved in 40 mL hexadecane by heating at 85°C for 1 h and repeatedly evacuated with mechanical pump to eliminate the oxygen and water. In order to accelerate the chemical reaction, the temperature was ramped to 287°C with a constant heating rate of 1.0^{o}C/s and refluxed for various time durations (30, 60, 90, 120

and 180 min) to observe the changes on the sizes of NCs. The aliquots were taken from reaction flask at various time intervals to monitor the growth of NCs.

RESULTS AND DISCUSSION

According to the TEM image at 30 min (Figure 1(a)), the NCs are very monodisperse in terms of size and shape without any agglomeration. It is uniformly disperse on the surface of the copper grid. Figure 2(a) depicts the histogram for this sample and the mean size of the Fe_3O_4 NCs was determined to be equivalent to 4.56 nm and standard deviation of 0.66 nm. The standard deviation is 14.47%, which is well-complement with the standard of high quality NCs with narrow size distribution (standard deviation less than 15.00%) according to Murray et al. (2000).

Figure 1(b) shows the TEM micrograph for sample prepared by increasing the heating duration to 60 min. As shown in the TEM micrograph, the solids composed of NCs resemble the random packing of hard spheres with soft shells (ligands) filling the interstices and spread over the surface of the copper grid to form a monolayer. The histogram (Figure 2(b)) shows the size distribution of NCs with mean size and standard deviation of 5.20 and 0.75 nm, respectively. The standard deviation is 14.42% of the mean value. As a comparison to the sample with heating duration of 30 min, the mean diameter shows increment of 0.64 nm. With increasing the heating duration, the NCs undergo diffusion-limited growth without undergo secondary nucleation (Reiss 1951). Hence, the narrow size distribution of the NCs is preserved and the growth is spontaneous. The heating process has provides additional kinetic energy to both of the ion Fe^{3+} and O^{2-} that decomposed from precursor and facilitate diffusion across the solvent. This is followed by deposition onto the surface of the existing NCs and subsequently grows into larger crystals.

The TEM micrograph and the histogram of the NCs prepared with heating duration 90 min are depicted in Figures 1(c) and 2(c), respectively. The mean diameter is determined to be 6.04 nm and the standard deviation is 0.99 nm. The standard deviation is 16.39% of the mean value. For this sample, the diameter show increment of 0.84 nm if compared with the sample with heating duration of 60 min.

If compared with previous samples, the percentage of the standard deviation with respect to the mean value begins to show increment and exceeds 15%. This implies the particle size distribution is getting broader. According to Peng et al. (1998) increment of the percentage deviation with respect to the mean value is attributed to the phenomenon of 'defocusing of size distribution'. Broadening of the size distribution is due to the secondary growth approach, known to be 'Ostwald ripening'. At this level, the smaller NCs tend to decompose and dissolve into ionic state due to the high surface energy. These ions will subsequently deposit on the surface of the NCs with larger size. As a result, the mean diameters of the NCs increase, while the total amount of the NCs is decrease with prolong heating duration.

During Ostwald ripening, the concentration of $Fe(C_{18}H_{33}O_2)_3$ precursor is constant due to the changes in the solubility. Hence, there is no decomposition occurs on the $Fe(C_{18}H_{33}O_2)_3$ precursor (Peng et al. 1998). The phenomenon of 'size defocusing' can be explained by using Gibbs-Thomon equation:

$$S_r = S_b \exp(2\sigma V_m / rRT), \qquad (1)$$

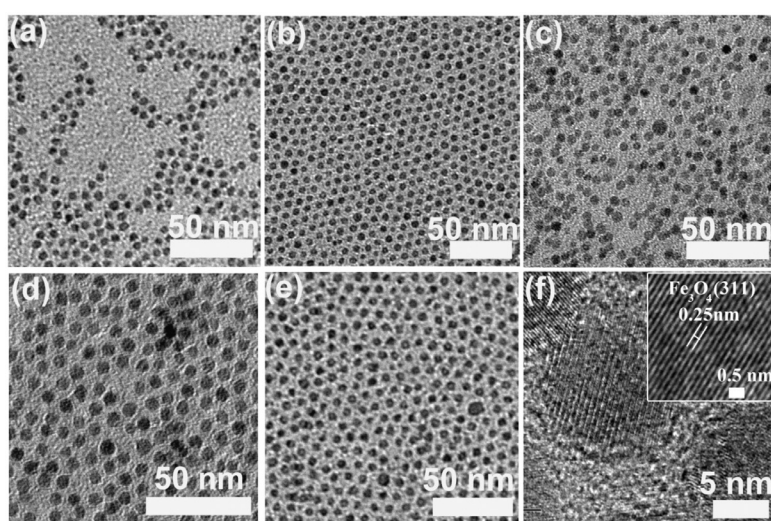where S_r and S_b are the solubility of the NCs and $Fe(C_{18}H_{33}O_2)_3$ precursor, respectively; σ is specific surface

FIGURE 1. TEM micrographs of Fe_3O_4 NCs annealed for different time duration: (a) 30 min (b) 60 min (c) 90 min (d) 120 min (e) 180 min (f) HRTEM image of Fe_3O_4 NCs annealed at 180 min with magnification of 800,000× (inset: lattice spacing of (311) plane with d-spacing of 0.25 nm as-observed at magnification of 1,500,000×)

energy; r is the radius of the NCs; V_m is the molar volume of the materials; R is the gas constant and T is the temperature.

If the solubility of the $Fe(C_{18}H_{33}O_2)_3$ precursor is greater than solubility of the NCs, the grow is occurring by diffusion limited growth. Hence, $2\sigma V_m/rRT \leq 1$ and the diffusion limited growth rate can be represented by:

$$dr/dt = K(1/r + 1/\delta)(1/r^* - 1/r), \qquad (2)$$

where K is a constant that is proportional to the diffusion constant of the $Fe(C_{18}H_{33}O_2)_3$ precursor. δ is the thickness of the diffusion layer. r^* is the critical radius for NCs when the solubility of the NCs is exactly the concentration of the $Fe(C_{18}H_{33}O_2)_3$ precursor (with zero growth rate).

According to the Sugimoto model (Sugimoto 1987), the critical size exists in any concentration of $Fe(C_{18}H_{33}O_2)_3$ precursor, which is in equilibrium. NCs with radius less than r^* have negative growth rate, which implies the dissolution occurs. However, for NCs with radius greater than r^*, the grow rates is strictly dependent on the instantaneous radius. Focusing of the size distribution occurs when $1 \leq r/r^* \leq 1.5$ and the smaller NCs in the distribution grow faster than the larger ones at this moment. When the concentration of the $Fe(C_{18}H_{33}O_2)_3$ precursor is depleted due to the growth, the r^* is getting increase than the average radius and broaden the size distributions because some smaller NCs are shrinking and eventually disappear, while the larger ones are still continue to grow. Under this condition, the Ostwald ripening or defocusing has occurred (Chiu et al. 2007).

As a result, it is observed that for sample prepared with heating duration 90 min, the standard deviation increase to 0.99 nm. The standard deviation for this sample is 16.39%, which is deviate from narrow distribution range (15% of mean value). Further increase of the heating duration to 120 min causes the 'defocusing' phenomenon to become more obvious. The TEM micrograph and histogram are shown in Figures 1(d) and 2(d), respectively. The mean diameter was determined to be 6.79 nm, while the standard deviation for this sample increase to 1.17 nm and this value is 17.23% of the mean value.

With increasing the heating duration to 180 min, the mean diameter increase to 17.67 nm and the standard deviation was determined to be 2.23 nm (Figure 2(e)). The standard deviation is 13.19% of the mean value. Due to the cumulative heating duration, the existing NCs continue to grow, while the amount of the smaller NCs that dissolve to form ion Fe^{3+} and O^{2-} decrease. Therefore, the mean diameter of the NCs continue to increase by consuming both ion Fe^{3+} and O^{2-} and develop into well-order crystal lattice onto the preform Fe_3O_4 NCs (Murray et al. 1993). The statistical analysis data for the as-synthesized Fe_3O_4 NCs is depicted in Table 1.

Figure 1(f) shows the HRTEM image of the sample annealed for 180 min and the lattice fringes of the NCs are clearly seen, which implies the highly crystalline in nature. Such well- and order-atomic array of crystal plane after cumulative annealing period of 180 min implies the excellent compability of the selected raw materials that
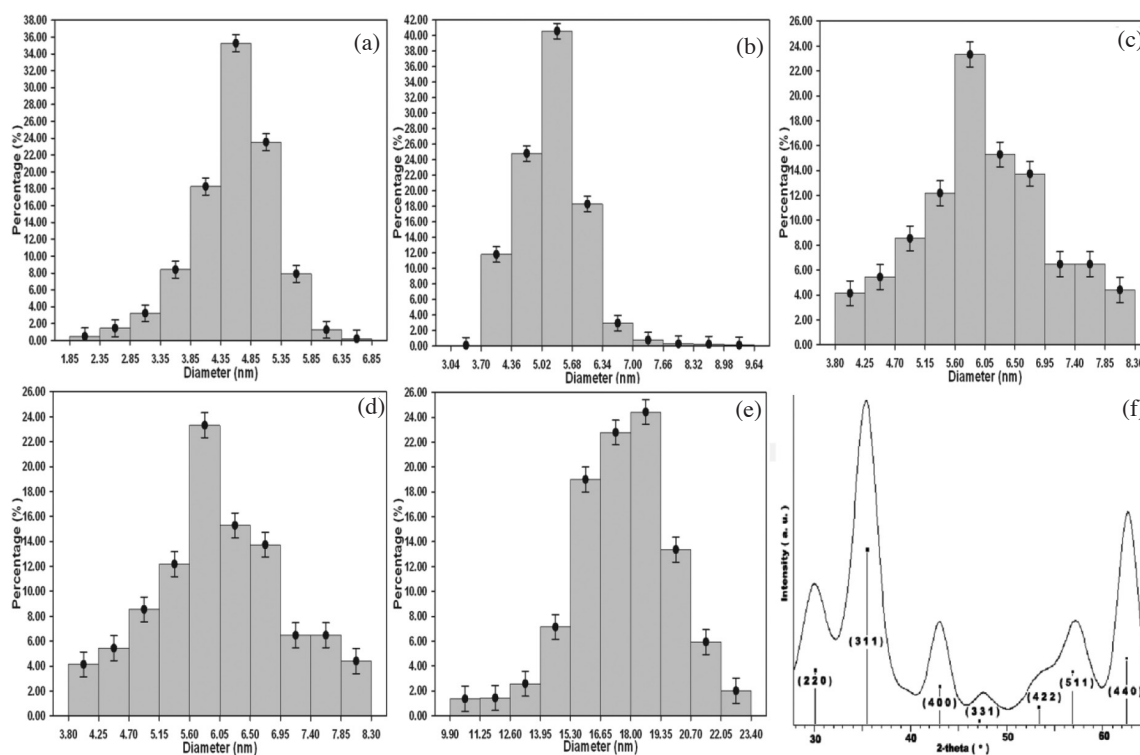

FIGURE 2. Size distribution of Fe_3O_4 NCs that have been annealed at different time duration: (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min, (e) 180 min and (f) XRD powder diffraction pattern of Fe_3O_4 NCs

TABLE 1. The statistical analysis data for the as-synthesized Fe_3O_4 NCs

Annealing duration (min)	Mean size (nm)	Standard deviation	Percent of standard deviation (%)
30	4.56	0.66	14.47
60	5.20	0.75	14.42
90	6.04	0.99	16.39
120	6.79	1.17	17.23
180	17.67	2.23	13.19

facilitate the well-controlled crystallinity. Further zooming into the selected area with the magnification up to 1.5 million times showed that the lattice spacing is equal to 0.25 nm, which is well-correlated with the standard plane of (311) for $Fe_3O_{4.f}$.

Figure 2(f) shows the XRD pattern of the Fe_3O_4 NCs. According to the spectrum, all the peaks are well-indexed with a face-centre-cubic phases (with space group *Fd-3m*) internal structure according to JCPDF files (72-2303) and the spectrum shows evidence of finite size broadening in all reflections due to small crystallite sizes. Additionally, there is no any unknown peak from impurities or other compounds are observed.

CONCLUSION

As a summary, the monodispersed Fe_3O_4 NCs is successfully synthesized by thermal pyrolysis of $Fe(C_{18}H_{33}O_2)_3$ compound in the presence of oleic acid as capping ligands. The use of environmentally-benign metal-oleate precursor and oleic acid together with low boiling point solvents in growing Fe_3O_4 NCs enable the continuous size- and shape-control synthesis of high quality Fe_3O_4 NCs by varying the annealing duration. Thus, the current approach would open a new route to prepare other nanostructure materials with desired morphology and congruent properties.

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