Jusami
Homepage: http://jusami.batan.go.id
Jurnal Sains Materi Indonesia
Akreditasi LIPI
No.: 602/AU3/P2MI-LIPI/03/2015
Tanggal 15 April 2015
ISSN : 1411-1098

THE 3 HOURS-HYDROTHERMAL SYNTHESIS OF HIGH SURFACE AREA SUPERPARAMAGNETIC Fe_3O_4 CORE-SHELL NANOPARTICLES

Esty Octiana Sari, Ahmad Fadli and Amun Amri
Department of Chemical Engineering Riau University
Jl. HR Subrantas KM 12,5 Panam, Pekanbaru 28293, Riau
E-mail: octiana89@gmail.com

Received: 2 May 2017 *Revised: 27 September 2017* *Accepted: 4 October 2017*

ABSTRACT

THE 3 HOURS-HYDROTHERMAL SYNTHESIS OF HIGH SURFACE AREA SUPERPARAMAGNETIC Fe_3O_4 CORE-SHELL NANOPARTICLES. The monodisperse core-shell Fe_3O_4 nanoparticles have been successfully synthesized by short times (3 hours) hydrothermal method at 220 ^oC from $FeCl_3$, citrate, urea and PEG. The as-synthesized samples have been characterized using X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM), Bruneur-Emmet-Teller (BET) surface area analyzer, and Vibrating Sample Magnetometer (VSM). The XRD result shows the as-synthesized products are pure Fe_3O_4. The TEM image shows the magnetite nanoparticles have monodisperse core-shell shape. The BET result shows the magnetite nanoparticles have 650.757 m^2/g surface area. The hysteresis curve shows the magnetite nanoparticles exhibit super paramagnetic properties. This simple method obtained 60 nm core-shell Fe_3O_4 particles with super paramagnetic, high surface area as well as hydrophilic properties. Those properties are promising for various biomedical application. The advantages of simple and short times methods with high quality of product make this method very promising to be applied.

Keywords: Core-shell, Hydrothermal method, Superparamagnetic, Nanoparticles

ABSTRAK

3 JAM-SINTETIS HIDROTERMAL NANOPARTIKEL *CORE-SHELL* SUPERPARAMAGNETIK Fe_3O_4 DENGAN LUAS PERMUKAAN TINGGI. Nanopartikel monodispersi Fe_3O_4 berbentuk *core-shell* telah berhasil disintesis dengan metode hidrothermal waktu singkat (3 jam) pada suhu 220 ^oC dari $FeCl_3$, sitrat, urea dan PEG. Sampel hasil sintesis telah dikarakterisasi dengan menggunakan difraksi sinar-X (*XRD*), *Transmission Electron Microscopy* (*TEM*), analisis luas permukaan *Bruneur-Emmet-Teller* (*BET*) dan *Vibrating Sample Magnetometer* (*VSM*). Hasil *XRD* menunjukkan bahwa produk adalah Fe_3O_4 murni. Citra *TEM* menunjukkan nanopartikel magnetit memiliki bentuk *core-shell*. Hasil *BET* menunjukkan nanopartikel magnetit memiliki luas permukaan 650,757 m^2/g. Kurva histeresis menunjukkan partikel nano *magnetite* menunjukkan sifat superparamagnetik. Metode sederhana ini menghasilkan Fe_3O_4 berbentuk *core-shell* berukuran 60 nm bersifat superparamagnetik, luas permukaan tinggi serta bersifat hidrofilik. Sifat-sifat tersebut menjanjikan berbagai aplikasi biomedis. Kelebihan metode yang sederhana dan cepat dengan kualitas produk yang tinggi membuat metode ini sangat menjanjikan untuk diterapkan.

Kata kunci: Core-shell, Metode hidrotermal, Superparamagnetik, Nanopartikel

INTRODUCTION

In recent years, magnetite (Fe_3O_4) nanoparticles receive much attention from multidiciplines scientist due to its potential application in various fields. Magnetite nanoparticles have been used as ferrofluids, magnetic recording media, heavy metal removal and various medical application such as contrast agent MRI, hyperthermia and drug delivery [1-5].

The use of magnetite nanoparticles in biomedical application especially for cancer treatment has more challenge because its characteristics have to meet some criterions such as biocompatible, superparamagnetic, monodisperse, 5.5 - 200 nm in diameter [6], and high surface area. Thus, the controllable preparations of this material are needed.

Over the past decades, researchers have proposed several methods for the synthesis of Fe_3O_4 nanoparticles, such as microemulsions, co-precipitation, sol-gel method, pyrolysis, hydrothermal method etc. Among them, the hydrothermal technique can provide highly crystalline Fe_3O_4 nanoparticles with good magnetic properties and highly monodispersity [7, 8]. Cheng *et al.* [9] reported a facile hydrothermal method to prepare the monodiperse and high water solubility of Fe_3O_4 from $FeCl_3$, citrate, polyacrylamide and urea at 200 °C for 12 hours. However, the agglomeration still observed and it makes the nanoparticles size is big (210 nm). This method also time consuming because it takes 12 hours to obtain products.

In this work, we use a high temperature (220 °C) and a short time (3 hours) hydrothermal process to synthesis the core–shell magnetite nanoparticles from $FeCl_3$, citrate and urea. We also added polyethylene glycol as capping agent to overcome agglomeration and enhance the biocompatibility [10-12].

Our method is simple, cheap and environmentally friendly approach for the controllable synthesis of Fe_3O_4 nanoparticles. To the best our knowledge, the magnetite nanoparticles obtained in this work are higher in surface area rather than the magnetite nanoparticles ever prepared before [17-20]. This method also produce magnetite nanoparticles which are ideal in size for biomedical application.

EXPERIMENTAL METHOD

Materials and Tools

All of the chemical reagents used in this experiment are analytical grade and use without further purification. The chemical reagents for prepare magnetite are $FeCl_3$, urea, polyethylene glycol (PEG) (M_W = 950-1050) 99%, sodium citrate ($C_6H_5O_7Na_3 \cdot 2H_2O$), aquades and ethanol 98%. All reagents were purchased from Merck Chemical Industry.

Magnetite nanoparticles were prepared using glass utensils, teflon lined autoclave and oven. X-ray difractometer (XRD) X'PERT POWDER PW 30/40 was used for nanoparticles identification. The morphology of nanoparticle was analyzed by TEM JEOL JEM 1400. The magnetic properties of nanoparticles were determined by *vibrating sample magnetometer* (VSM) type Oxford VSM1.2H. Surface area was analyzed using the Brunauer– Emmett–Teller (BET) tests performed with Quantachrome surface area analyzer.

Synthesis

Synthesis of magnetite nanoparticle has been carried out using the hydrothermal method. A total of 2 mmol $FeCl_3$ (0.05M), 4 mmol of sodium citrate (0.10 M), and 6 mmol of urea (0.15M) was dissolved in 40 mL of distilled water, then polyethylene glycol (PEG) (7.5 g/L) was added until completely dissolved. The solution was then transferred into a teflon lined autoclave which subsequently was putted into oven with temperature was set to 220 °C for 3 hours. Black precipitate was separated by a bar magnet, then washed with water and ethanol, and dried at 60 °C over the night.

Characterization

The crystal structure, purity and crystal size of Fe_3O_4 were determined by XRD. Approximately 200 mg of sample was printed directly on 2 × 2.5 cm of aluminum. Samples were characterized using XRD instrument with Cu radiation light (λ = 1.54 Å) with a voltage of 40 kV and current of 30 mA at $2\theta = 10\text{-}99.97^o$. The particle size, morphology and aggregate were analyzed by transmission electron microscope (TEM JEOL JEM 1400) operated at 5 kV under vacuum. Surface area was analyzed using the Brunauer-Emmett-Teller (BET) test performed with Quantachrome surface area analyzer. The magnetic characteristic of magnetite nanoparticles was analyzed using vibrating sample magnetometer (VSM) type VSM1.2H Oxford. Magnetization curves were measured at room temperature with a magnetic field that varies in the range -1 to 1 Tesla.

RESULTS AND DISCUSSION

The crystallographic structure of the sample was identified by XRD. The XRD pattern of the typical sample is depicted in Figure 1. It is found that the peaks in XRD pattern match well with the Fe_3O_4 (ICSD no.01-089-0950). However, there are not typical ε-Fe_2O_3 peaks such as (013), (122), (210) (ICSD no.01-076-8881) existing in the XRD pattern, confirm the as-synthesized sample are pure Fe_3O_4 phase. ε-Fe_2O_3 is a ferromagnetic orthorhombic iron oxide, while Fe_3O_4 nanoparticle is superparamagnetic cubic iron oxide [21]. The superparamgnetic properties are expected for drug delivery application to overcome particles agglomeration because of residual magnetization after exposed by external magnet [22].

The calculation using Scherrer's formula for the strongest peak (3 1 1) reveals that the crystal size of the sample is 9.68 nm. The Miller indices ((311) and (440)) are combination of all odds or all even numbers, indicating the crystal structure of as-synthesized sample is Face Centered Cubic (FCC) [16].

The morphologies and particle size of typical sample were examined by TEM. The TEM images in

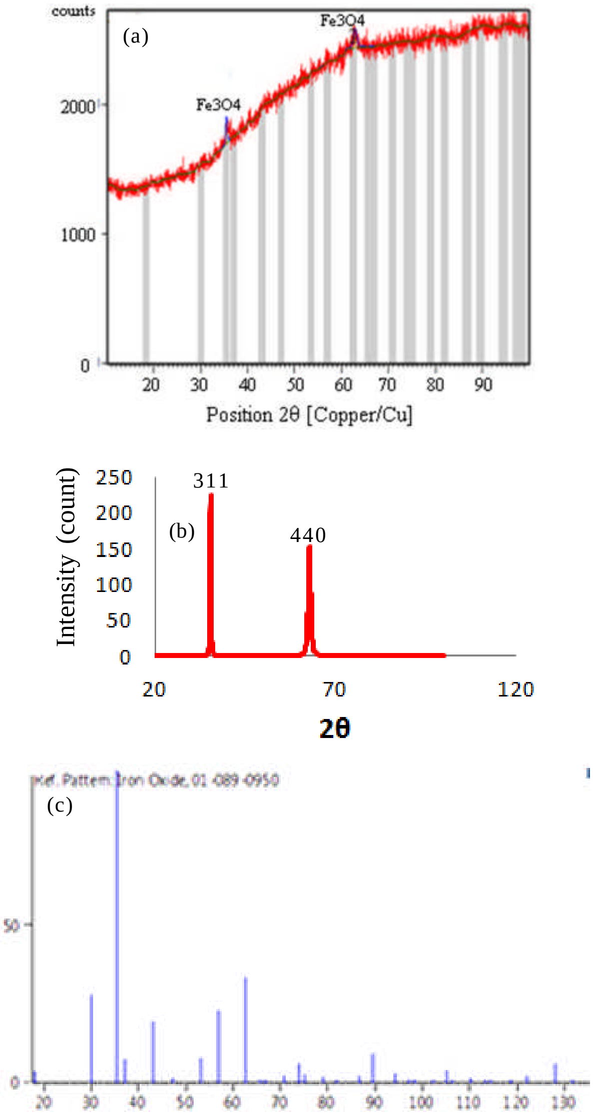

Figure 1. XRD pattern of as-syntesized sample (a). original XRD pattern before noise reduction and (b). XRD pattern after noise reduction match well with (c). Fe_3O_4 standard pattern.

Figure 2(a) and 2(b) show that the product are monodispers and no aglomeration detected. In high magnification (Figure 2c and 2d) it can be clearly observed that the particles have a core-shell shape. It is identified from the dark image in core and the light image in shell area. The dark image indicates a higher christallinity, meanwhile the light image indicates an amorphous phase [9]. The core-shell shape gives some advantages, the shell can be act as protector from air oxidation and can be place for ligan attachment as well [13-14]. From the TEM images, the average particle size of the as-synthesized sample is about 60 nm. This size is suitable to the cryteria of ideal drug delivery where the particles size must be in range of 5 - 200 nm. It is reported that under 5 nm the drug delivery will be released fastly by renal, and if it is bigger than 200 nm it will be deposited in liver [6].

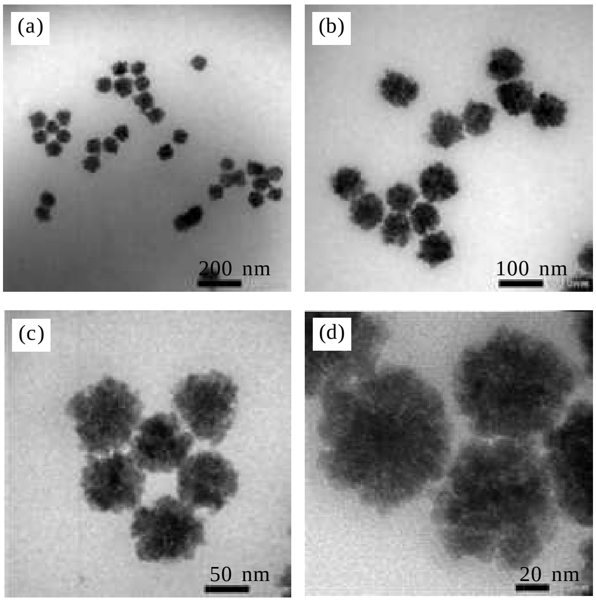

Figure 2. low magnification (a and b) and high magnification (c and d) TEM image of typical sample.

Surface area of sample was determined by the Brunaeur-Emmet-Teller (BET) test. The BET plot is shown in Figure 3. From the calculation, the specific surface area of sample is 650.575 m^2/g. This surface area is greater than the surface area of magnetite nanoparticles from literatures. It was reported that Cheng et al. have prepared magnetite with the specific surface area was 56.7 m^2/g [9]. Rahman et al. have prepared magnetite with the specific area was 23.1 m^2/g [17]. Mascolo et al. prepared magnetite with the specific surface area were 89.4-167.9 m^2/g [18]. Ma et al. prepared magnetite with the specific area was 286.9 m^2/g [19]. On 2016, Jianfang et al. prepared magnetite with the specific area was 68 m^2/g [20].

The magnetic properties of as-synthesized sample were measured on Vibrating Sample Magnetometer (VSM) at 300K. The magnetic hysteresis

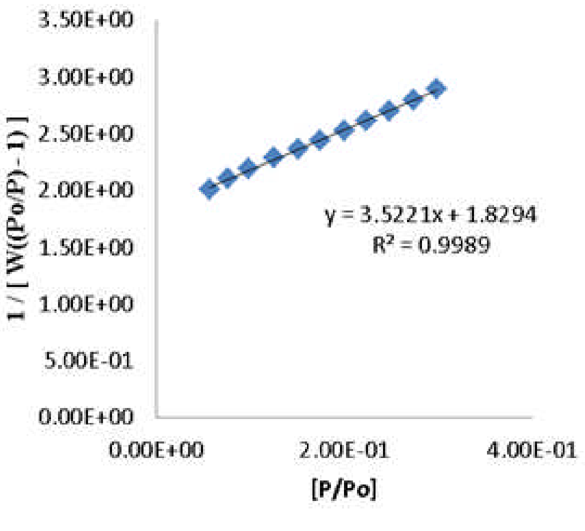

Figure 3. BET curve of typical sample

curve depicted in Figure 4 shows no coercivity and slightly hysteresis loop indicate a typical superparamagnetic sample. This superparamagnetic behavior gives some advantages in biomedical application, such as easy to be controlled and guided to the parts of body [15].

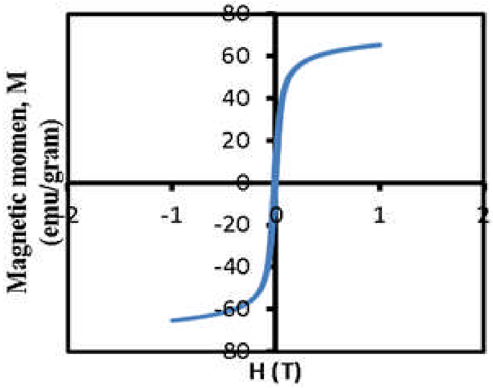

Figure 4. Magnetic hysteresis curve of typical sample

Not only has superparamgnetic property, the as-synthesized magnetite is also water soluble (Figure 5).The presence of PEG that has an -OH group on the surface of the nanoparticles makes the nanoparticles are hydrophilic and negatively charged. Thus, it makes the nanoparticles have a longer residence time in the bloodstream (high bioavailability) because it corresponds to the nature of the plasma proteins which are also hydrophilic and negatively charged. In general, phagocytosis will occur in particles of non-polar and positively charged as it is considered as a substance foreign to the body [6].

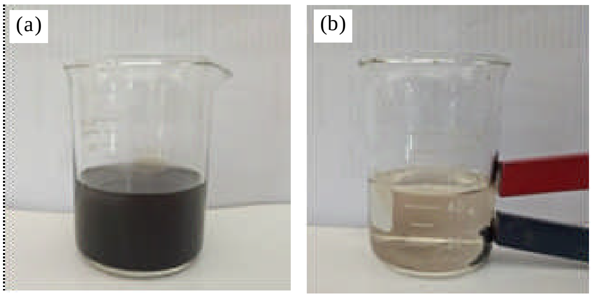

Figure 5. Photoghraph of the as-synthesized core-shell magnetite nanoparticles dispersed in water (a) without magnet and (b) after applied an external magnetic field for 45 seconds explain.

CONCLUSION

The magnetite core-shell nanoparticles have been successfully synthesized from environmental friendly starting material $FeCl_3$, citrate, urea and polyethylene glycol (PEG) using a facile and economical hydrothermal method. The core-shell magnetite synthesized in this process has ideal size for drug delivery (60 nm), high surface area (650.575 m^2/g), water soluble and exhibit superparamagnetic properties. Those all properties will render them as ideal candidates for biomedical applications.

ACKNOWLEDGEMENT

We acknowledge the ministry of Ristekdikti Republic of Indonesia for the research grant.

REFERENCES

[1]. M. Mustafa, A. Musthtaq, T. Hayat and A. Al-saedi. “Rotating Flow of Magnetite-Water Nanofluid Over a Stretching Surface Inspired by Non-Linear Thermal Radiation.” Plos One, vol. 11, pp. 1-16, 2016.

[2]. Y. Grosu, A. Faik, I. O. Fernandez and B. D'aguanno. “Natural Magnetite for Thermal Energy Storage : Excellent Thermophysical Properties, Reversible Latent Heat Transition and Controlled Thermal Conductivity.” Solar Energy Materials and Solar Cells, vol. 161, pp.170-176, Dec.2016.

[3]. A. Suhada, A. R. Arifin, I. Ismail, A. H. Abdullah, I. R. Ibrahim and F. N. Shafiee. “Magnetite Nanoparticles in Wastewater Treatment.” Pertanika Journal of Scholarly Research Reviews, vol. 2, pp. 108-122, 2016.

[4]. R.A. Revia and M. Zhang. “Magnetite Nanoparticles for Cancer Diagnosis, Treatment, and Treatment Monitoring : Recent Advance.” Materials Today, vol. 19, pp. 157-168, Apr. 2016.

[5]. J. C. R. Hurtado, E. M. M. Ramos, A. Z. Cruz, D. and A. C. Hernandez. “Mechanosynthesis as a Simple Method to Obtain a Magnetic Composite (Activated Carbon/Fe_3O_4) for Hyperthermia Treatment.” Journal of Biomaterials and Nano Biotechnology, vol. 7, pp. 19-28, Jan. 2016.

[6]. M. Colombo, S. C. Romero, M.F. Casula, L.Gutierrez, M. P. Morales, J. B. Bohm, J. T. Heverhagen , D. Prosper and W. J. Parak. “Biological Applications of Magnetic Nanoparticles.” Chemical Science Review, vol. 41, pp. 4306-4334, 2012.

[7]. N. Mizutani, T. Iwasaki, and S. Watano. “Response Surface Methodology Study on Magnetite Nanoparticle Formation Under Hydrothermal Formations.” Nanomaterial Nanotechnology, vol. 5, pp. 1-7, April 2015.

[8]. W. Wu, Z. Wu, T. Yu, C. Jiang and W. S. Kim. “Recent Progress on Magnetic Iron Oxide Nanoparticles: Synthesis, Surface Functional Strategies And Biomedical Applications.” Science and Technology of Advanced Materials, vol. 16, pp. 1-43, Apr. 2015.

[9]. W. Cheng, K. Tang, Y. Qi, J. Sheng, and Z. Liu. “One-Step Synthesis of Superparamagnetic Monodisperse Porous Fe_3O_4 Hollow and Core-Shell Sphere.” Journal of Material Chemistry, vol. 2, pp.1799-1805, Jan. 2010.

[10]. J. Markhulia, V. Mikelashvili, S. Kekutia, L. Saneblidze, Z. Jabua, D. Daraselia and D. Jafa-ridze. “Some Physical Parameters of PEG-Modified Magnetite Nanofluids.” Journal Pharmacy and Applied Chemistry, vol. 2, pp.33-37, 2016.

[11]. X. Cao, B. Zhang, F. Zhao, and L. Feng. “Synthesis and Properties of MPEG-Coated Super paramagnetic Magnetite Nanoparticles.” Journal of Nanomaterial, vol. 607296, pp.1-6, 2012.

[12]. M. Yu, S. Huang, K. Yu, and A. M Clyne. “Dextran and Polymer Polyethylene Glycol (PEG) Coating Reduce Both 5 and 30 nm Iron Oxide Nanoparticle Cytotoxicity in 2D and 3D Cell Culture.” International Journal Molecular Science, vol.13, pp. 5554-5570, 2012.

[13]. K.S. Kumar , V. B. Kumar, and P. Paik. “Recent Advancement in Functional Core-Shell Nanoparticles of Polymers: Synthesis, Physical Properties, and Applications in Medical Biotechnology.” Journal of Nanoparticles, vol 2013, pp. 1-24, Feb. 2013.

[14]. K. Luszczyk, J. Kaleta, dan R. Mech. “Magnetic Core-shell Structures as Potential Carriers in Drug Delivery System.” International journal of Engineering Science, vol. 2, pp.1-4, 2014.

[15]. M. Arruebo, F.R Pacheco, R.M. Ibarra, and J. Santamaría. “Magnetics Nanoparticles for Drug Delivery.” Nanotoday, vol. 2, pp. 22-32, Jun. 2007.

[16]. M. Ladd and R. Palmer. “Structure Determination by X-Ray Crystallography: Analysis by X-Rays and Neutrons.” New York, Springer Sciences Bussiness Media, pp. 1-109, 2013.

[17]. O. U. Rahman, S. C. Mohapatra and S. Ahmad. “Fe_3O_4 Inverse Spinal Super Paramagnetic Nanoparticles.” Materials Chemistry and Physics, vol.132, pp. 196-202, Nov. 2011.

[18]. M. C. Mascolo, Y. Pei and T. A. Ring. “Room Temperature co-Precipitation Synthesis of Magnetite Nanoparticles in a Large pH Window with Different Bases.” Materials, vol. 6, pp. 5549-5567, Nov. 2013.

[19]. J. Ma, L. Wang, Y. Wu, X. Dong, Q. Ma, C. Qiao, Q. Zhang and J. Zhang. “Facile Synthesis of Fe_3O_4 Nanoparticles with a High Specific Surface Area.” Materials Transactions, vo.l 55, pp.1900-1902, Oct. 2014.

[20]. J. Jianfang, H. Chunyang, X. Jun, J. Hao, T. Wenya. “Preparation and Characterization of Nano Fe_3O_4/ Carboxylation Chitosan/Alginate Sodium Magnetofluid by One Pot Method.” Nanoscience and Nanotechnology Letters, vol. 8, pp.1089-1094, Des. 2016.

[21]. M. Chirita and L. Grozescu. “Fe_2O_3-Nanoparticles, Physical Properties and Their Photochemical and Photoelectrochemical Applications.” Chemistry Bulletin POLITECHNICA University of Timisoara, vol. 68, pp.1-8, Jan. 2009.

[22]. Wahajuddin and S. Arora. “Superparamagnetic Iron Oxide Nanoparticles: Magnetic Nanoplatforms as Drug Carriers.” International Journal of Nanomedicine, vol. 7, pp. 3445-3471, Jul. 2012.

.