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SYNTHESIS AND CHARACTERIZATION OF STRUCTURE AND MAGNETIC PROPERTIES OF FERRITE NANOPARTICLES PREPARED BY THERMAL TREATMENT METHOD

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By

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DEDICATED TO MY WIFE

Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of requirement for the degree of Doctor of Philosophy

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Spinel ferrite nanocrystals are regarded as one of the most important inorganic nanomaterials because of their electronic, optical, electrical, magnetic, and catalytic properties. These properties are dependent on the chemical composition and microstructural characteristics in which the particle size and shape might be controlled in the fabrication processes. The preparation of spinel ferrite nanocrystals through different routes has become an essential in research and development. But, the most commonly applied synthesis methods are difficult to employ on a large scale because of their complicated procedures, high reaction temperatures, long reaction times, toxic reagents and by-products, and their potential harm to the environment. In this thesis a simple thermal treatment method is described for synthesis of spinel ferrite MFe_2O_4 (M = Ni, Co, Mn, Zn, or their binary metal) nanoparticles. In this method, an aqueous solution of poly (vinyl pyrrolidone) (PVP)

was prepared by dissolving the polymer in deionized water at 343 K before adding iron nitrate and respective metal nitrates and constantly stirring at 353 K for 2 h. The dissolved solution was heated until dried at 353 K for 24 h on a glass Petri dish. The solid and orange coloured transparent remains were crushed and ground in a mortar to form powder before calcinations at different temperatures for 3 h to decompose organic matters and crystallized the ferrite nanparticles. We concluded that the effect and role of PVP in the synthesis of cobalt ferrite nanoparticles by the thermal treatment method is astonishing. Briefly, as was discussed when we considered our XRD results, TEM images, and FT-IR spectra, PVP plays four crucial roles in synthesizing cobalt ferrite nanoparticles, i.e., (1) the control of the growth of the nanoparticles by varying the concentration of PVP; (2) the prevention of agglomeration of the nanoparticles; (3) the enhancement of the degree of the crystallinity of the nanoparticles, and (4) the production of nanoparticles that have a uniform distribution of shapes. Thermo-gravimetry analyses was used to estimate a range of calcination temperature where the polymer mass loss started at 678 K and has the maximum decomposition at 778 K. The optimum calcination temperature was confirmed by Fourier transform infrared spectroscopy (FTIR) measurement by the presence of metal oxide bands at all temperatures and the absence of organic bands at 723 and 823 K for $NiFe_2O_4$ and $CoFe_2O_4$ nanoparticles and at 873 K for, $MnFe_2O_4$, $ZnFe_2O_4$ and $Ni_x\ Co_{1-x}\ Fe_2O_4$ nanoparticles. The transmission electron microscopy (TEM) images showed cubical spinel ferrite nanoparticles that were uniform in both morphology and particle size distribution. The x-ray diffraction (XRD) diffraction patterns showed crystalline phases that confirmed the formation of nanocrystalline single-phase spinel ferrite nanoparticles with a face-centered cubic structure, common structure for nanomaterials. The average particle sizes were

determined from TEM images and found the particle size increased with the calcinations temperature from 7 to 47 nm for $NiFe_2O_4$, from 12.5 to 39 for $CoFe_2O_4$, from 12 to 22 nm for $MnFe_2O_4$, from 17 to 31 nm for $ZnFe_2O_4$ and from 14 to 25 nm for $Ni_x\ Co_{1-x}\ Fe_2O_4$ nanoparticles. These sizes are in a good agreement with XRD results.

The magnetic properties were determined by vibrating sample magnetometer (VSM), which showed that the calcined samples exhibited ferromagnetic, ferromagnetic or superparamagnetic behaviors. The VSM results displayed ferromagnetic behaviors for $NiFe_2O_4$, $CoFe_2O_4$, and $Ni_x\ Co_{1-x}\ Fe_2O_4$ nanoparticles and super paramagnetic behaviors for $MnFe_2O_4$ and $ZnFe_2O_4$ nanoparticles. The magnetic properties acquired by VSM, such as saturation magnetization and coercivity field are dependent on the calcination temperatures. The magnetic properties were also confirmed by the use of electron paramagnetic resonance (EPR) spectroscopy, which revealed the existence of unpaired electrons and also measured peak-to-peak line width (ΔH_{pp}), resonant magnetic field (H_r), and the g-factor for $MnFe_2O_4$ and $ZnFe_2O_4$ nanoparticles while $NiFe_2O_4$, $CoFe_2O_4$, and $Ni_x\ Co_{1-x}\ Fe_2O_4$ nanoparticles did not exhibit resonance signal. This could be possibly due to the super exchange interaction produces that occurs in these nanoparticles.

Our results show that we have succeeded in fabricating crystalline $NiFe_2O_4$, $CoFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$ and $Ni_x\ Co_{1-x}\ Fe_2O_4$ nanoparticles by a simple thermal treatment method. This method is cost-effective, environmentally-friendly, has low reaction temperatures, and produced no by-product effluents. It can be extended to fabricating other spinel ferrite nanoparticles of interest or other metallic oxides nanocrystals.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebageu memenuhi keperluan untuk ijazah Doktor Falsafah

SINTISIS DAN PENCIRIAN STRUKTUR DAN HARTANAH MAGNETIK FERIT NANOPARTIKEL DISEDIAKAN OLEH KAEDAH RAWATAN TERM

Oleh

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Hablur nano spinel ferit dianggap sebagai salah satu bahan nano bukan organik yang paling penting kerana sifat-sifat elektronik, optik, elektrik, magnetik, dan sebagai pemangkin bergantung kepada komposisi kimia dan ciri-ciri mikrostruktur di mana saiz zarah dan bentuknya mungkin boleh dikawal dalam proses fabrikasi. Penyediaan hablurnano spinel ferit melalui laluan yang berbeza telah menjadi penting dalam penyelidikan dan pembangunan. Tetapi, kaedah sintesis yang biasa digunakan adalah sukar untuk digunakan secara besar-besaran kerana kaedahnya yang rumit, suhu tindakbalas yang tinggi, masa tindakbalas panjang, reagen dan biproduk yang toksik, dan berpotensi membawan kemudaratan kepada alam sekitar. Dalam tesis ini fabarikasi kaedah rawatan haba yang mudah untuk sintesis spinel ferit zarahnano MFe_2O_4 (M = Ni, Co, Mn, Zn, atau binari logam mereka) diketengahkan. Dalam

kaedah ini, penyelesaian berair poli (vinil pyrrolidone) (PVP) telah disediakan dengan melarutkan polimer di dalam air takberion pada suhu 343 K sebelum menambah nitrat-nitrat ferum dan logam lain berkenaan dan sentiasa dikacau pada 353 K selama 2 jam. Kemudian larutan itu dipanaskan sehingga kering pada 353 K selama 24 jam kaca Petri. Sebatian pepejal dan berwarna oren telah dihancurkan dan dikisar menggunakan lesung kepada bentuk serbuk sebelum diapurkan pada suhu yang berbeza selama 3 jam untuk menguraikan bahan organik dan proses penghabluran zarahnano ferit. Kami menyimpulkan bahawa kesan dan peranan PVP dalam sintesis nanopartikel kobalt ferit dengan kaedah rawatan haba memeranjatkan. Secara ringkas, seperti yang telah dibincangkan apabila kita menganggap keputusan XRD kami, imej TEM, dan Spektrum FT-IR, PVP memainkan empat peranan penting dalam sintesis nanopartikel ferit kobalt, iaitu, (1) kawalan pertumbuhan yang nanopartikel dengan mengubah kepekatan PVP; (2) pencegahan pengaglomeratan yang nanopartikel; (3) peningkatan ijazah penghabluran yang nanopartikel, dan (4) pengeluaran nanopartikel yang mempunyai taburan seragam bentuk.

Termal-analisis gravimetri telah digunakan untuk menganggarkan julat suhu proses mengapur di mana kerugian jisim polimer bermula pada 678 K dan penguraian maksimum pada 778 K. Suhu proses mengapur optimum telah disahkan oleh pengukuran spektroskopi Fourier inframerah (FTIR) dengan kehadiran spectrum jalur oksida logam pada semua suhu dan ketiadaan spectrum jalur organik di 723 dan 823 K masing-masing untuk zarahnano $NiFe_2O_4$ dan $CoFe_2O_4$ dan pada 873 K untuk zarahnano $MnFe_2O_4$, $ZnFe_2O_4$ dan $Ni_x\ Co_{1-x}\ Fe_2O_4$. Imej mikroskopi elektron transmisi (TEM) menunjukkan struktur spinel ferit berkubus yang seragam dalam kedua-dua morfologi dan taburan saiz zarah. Corak pembelauan daripada pembelauan sinar-x (XRD) menunjukkan fasa hablur yang mengesahkan

pembentukan hablurnano fasa tunggal dengan struktur kubus muka berpusatkan (fcc) lazim bagi struktur bahan nano. Purata saiz zarah ditentukan dari imej TEM dan mendapati saiz zarah meningkat dengan suhu dari 7 hingga 47 nm untuk $NiFe_2O_4$, 12.5-39 nm untuk $CoFe_2O_4$, dari 12 hingga 22 nm untuk $MnFe_2O_4$, dari 17 hingga 31 nm untuk $ZnFe_2O_4$ dan 14-25 nm untuk $Ni_x\ Co_{1-x}\ Fe_2O_4$ nanopartikel. Saiz ini memenuhi pengukuran dengan keputusan XRD. Sifat-sifat magnet telah ditentukan oleh magnetometer sampel bergetar (VSM), yang menunjukkan bahawa sampel mempamerkan feromagnet, ciri-ciri feromagnet atau superparamagnetic. Keputusan VSM mempamirkan ciri-ciri feromagnet untuk zarahnano $NiFe_2O_4$, $CoFe_2O_4$, dan $Ni_x\ Co_{1-x}\ Fe_2O_4$ dan ciri-ciri super paramagnet untuk zaraqhnano $MnFe_2O_4$ dan $ZnFe_2O_4$. Ciri-ciri magnet yang diperolehi oleh VSM, seperti kemagnetan tepu dan medan coercivity bergantung kepada suhu proses mengapur. Sifat-sifat magnet telah juga disahkan oleh penggunaan spektroskopi resonans paramagnet elektron (EPR), yang mendedahkan kewujudan elektron berpasangan dan juga diukur talian puncak-ke-puncak lebar (ΔH_{pp}), salunan medan magnet (H_r), dan factor-g untuk zarahnano $MnFe_2O_4$ dan $ZnFe_2O_4$ manakala zarahnano $NiFe_2O_4$, $CoFe_2O_4$, dan $Ni_x\ Co_{1-x}\ Fe_2O_4$ tidak menunjukkan isyarat resonans. Ini mungkin disebabkan oleh interaksi pertukaran super berlaku dalam zarahnano. Keputusan kami menunjukkan bahawa kita telah berjaya dalam fabrikasi hablur zarahnano $NiFe_2O_4$, $CoFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$ dan $Ni_x\ Co_{1-x}\ Fe_2O_4$ oleh kaedah rawatan kaedah haba yang mudah. Kaedah ini adalah kos efektif, mesra alam, mempunyai suhu tindak balas yang rendah, dan tidak menghasilkan produk efluen. Ia boleh diperluaskan kepada fabrikasi zarahnano spinel ferit yang berkepentingan atau fabrikasi hablurnano oksida logam lain.

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