UNIVERSITI PUTRA MALAYSIA

PREPARATION, AND ELECTRICAL, MAGNETIC AND THERMAL INVESTIGATION OF POLYPYRROLE-CHITOSAN COMPOSITE AND POLYPYRROLE-CHITOSAN-IRON OXIDE POLYMER NANOCOMPOSITE

JAMILEH AMIN

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By

JAMILEH AMIN

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

June 2013

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Dedicated to my beloved mother, father, my sister Jelveh and her family

Without their understanding and support, I would never have completed this project.

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

PREPARATION, AND ELECTRICAL, MAGNETIC AND THERMAL INVESTIGATION OF POLYPYRROLE- CHITOSAN COMPOSITE AND POLYPYRROLE-CHITOSAN-IRON OXIDE POLYMER NANOCOMPOSITE

By

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June 2012

Chairman: Professor Zainal Abidin Talib, PhD

Faculty: Science

Conducting polymer composite based on Polypyrrole-Chitosan (PPy-CHI) and Polypyrrole-Chitosan-Iron oxide nanoparticles (PPy−CHI−Fe_3O_4) nanocomposite were prepared by using in-situ chemical polymerization method. (PPy−CHI) composites and (PPy−CHI−Fe_3O_4) nanocomposite were prepared with various percentages of CHI and Fe_3O_4 ranging from 0.0% (w/v) to 0.9% (w/v) and 0 wt% to 15wt% respectively. Results from conductivity experiments revealed that the highest conductivity was obtained from PPy−CHI−Fe_3O_4 nancomposite prepared from 0.1 % (w/v) CHI, 3 Molar PPy and 3wt% Fe_3O_4 in 30 minutes at room temperature

The X-ray diffractogram of PPy and CHI illustrated a broad scattering peak for PPy and two scattering peaks of almost equal intensity for CHI which is due to

their highly amorphous and semi-crystallity structure respectively. The XRD spectra for PPy-CHI composite was almost similar to those of PPy with a broad scattering at around 25°-26° indicating an amorphous structure. The XRD spectrum of PPy−CHI−Fe_3O_4 nanocomposite demonstrated similar to those observed from PPy and PPy−CHI composite matrix especially in the lower weight percentage of Fe_3O_4. However, as the nanoparticle loading increased, the characteristic peaks of Fe_3O_4 begun to dominate the nanocomposite spectra indicating to some uncoated Iron oxide nanoparticle which was confirmed by Energy-Dispersive X-ray (EDX) and transmission electron microscopy (TEM). The Fourier transform infrared spectroscopy (FT-IR) spectra of PPy−CHI and PPy−CHI−Fe_3O_4 illustrated almost the same characteristic positions of IR absorption bands similar to those of PPy. The small shift of PPy in the PPy−CHI composites is due to the identical peaks of PPy and CHI while in the PPy−CHI−Fe_3O_4 nanocomposites, the matrix layer of polypyrrole which covered the surface of iron oxide has absorbed most of the IR radiation. The results of Scanning Electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed that the Fe_3O_4 nanoparticles have been coated with the layers of polymeric matrix. A distribution of discrete globular nanoparticles with almost uniform size and dimensions was exhibited in all PPy−CHI−Fe_3O_4 nanocomposite samples. The reduced size of PPy−CHI and PPy−CHI−Fe_3O_4 particles was explained by the effect of Chitosan and iron oxide, the steric stabilization effect of CHI and a core-shell structure for PPy−CHI−Fe_3O_4 nancomposite which was confirmed by SEM and TEM.

The results of Vibrating Sample Magnetometer (VSM) revealed the magnetic properties for various PPy−CHI− Fe_3O_4 nanocomposites strongly depended on the

concentration loading of Fe_3O_4. The hysteresis loops of VSM illustrated superparamagnetic behavior for all the nanocomposite of PPy−CHI−Fe_3O_4 with different loading Fe_3O_4 percentage. The M_s (saturation magnetization) and H_c (coectivity) were monitored for samples with percentage loaded of Fe_3O_4 from 0.1 wt% to 15 wt%. M_s increased from 0.874 emu/g to 5.97 emu/g while Hc decreased from 241.4 Oe to 194.48 Oe.

The results of electron spin resonance (ESR) spectroscopy revealed a reduction in the Peak-to-peak line-width (ΔH_{pp}) value between PPy and PPy−CHI. The adding of Fe_3O_4 have resulted in (ΔH_{pp}) values increased in the order PPy−CHI <PPy−CHI−Fe_3O_4 (1wt%) < PPy−CHI−Fe_3O_4 (3wt%) > PPy−CHI−Fe_3O_4 (5wt %) < PPy−CHI−Fe_3O_4 (7wt %) < PPy−CHI−Fe_3O_4 (10wt %) < PPy−CHI−Fe_3O_4 (15wt %) at room temperature. The spin concentration (N_s) measurement of PPy−CHI−Fe_3O_4 with the various Fe_3O_4 content revealed to be larger than PPy−CHI (8×10^6, 1.59×10^7, 3×10^7, 2.29×10^7, 2.43×10^7 and 2.49×10^7 spin g-1 for PPy-CHI and 1wt%, 3wt%, 5wt%, 7wt% and 10wt%, of Fe_3O_4 respectively). The increase in percentage loading of iron oxide also resulted in better thermal stability of the nanocomposites.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENYIASATAN DAN PENYEDIAAN, ELEKTRIKAL, MAGNETIK DAN TERMAL BAGI POLIPYRROLE-KITOSAN KOMPOSIT POLIPYRROLE-KITOSAN OKSIDA POLIMER KOMPOSIT NANO

Oleh

JAMILEH AMIN

Jun 2012

Pengerusi : Profesor Zainal Abidin Talib, PhD

Fakulti: Sains

Penyediaan komposit polimer berasaskan ke atas Polipyrrole-Kitosan (PPy-CHI) dan partikel nano Polipyrrole-Kitosan-Besi oksida (PPy−CHI−Fe_3O_4) komposit nano telah disediakan menggunakan kaedah pempolimeran kimia setempat. Komposit (PPy−CHI) dan komposit nano (PPy−CHI−Fe_3O_4) telah disediakan menggunakan pelbagai peratusan CHI dan Fe_3O_4 masing-masing dari 0.0% (w/v) sehingga 0.9% (w/v) dan 0 wt% kepada 15wt%. Dapatan daripada eksperimen kekonduksian mendapati bahawa konduksi tertinggi diperolehi daripada komposit nano PPy−CHI−Fe_3O_4 disediakan daripada 0.1 % (w/v) CHI, 3 Molar PPy dan 3wt% Fe_3O_4 dalam 30 minit pada suhu bilik.

X-ray difraktogram bagi PPy dan CHI ditunjukkan pada puncak tertinggi serakan terluar bagi PPy dan dua puncak serakan bagi hampir sama keamatannya bagi

CHI yang mana disebabkan masing-masing oleh struktur amorphous yang tinggi dan semi-hablur mereka yang tinggi masing-masing. Spektra XRD bagi komposit PPy-CHI adalah hampir sama dengan PPy yang serakan luasnya adalah pada 25°-26° menunjukkan struktur amorfus. Spektrum XRD spectrum bagi komposit nano PPy−CHI−Fe_3O_4 menunjukkan hasil sama dengan yang telah diperhatikan daripada matrik komposit PPy dan PPy−CHI khasnya dalam peratusan berat yang lebih rendah bagi Fe_3O_4. Walaubagaimanapun, semakin bebanan partikel nano bertambah, karekter puncak bagi Fe_3O_4 mula mendominasi spektrum komposit nano menunjukkan yang beberapa partikel nano Besi oksida tidak diselaputi yang telah disahkan oleh Energy-Dispersive X-ray (EDX) dan transmisi mikroskopi elektron (TEM). Fourier merubah spektrum infra merah spektroskopi (FTIR) bagi PPy−CHI dan PPy−CHI−Fe_3O_4 menunjukkan hampir sama karekter kedudukannya bagi penyerapan jalur IR adalah sama dengan PPy. Perubahan kecil PPy dalam komposit PPy−CHI adalah disebabkan kepada puncak yang sama bagi PPy dan CHI sementara dalam komposit nano PPy−CHI−Fe_3O_4, lapisan matrik bagi polipyrrole yang telah diselaputi dengan permukaan besi oksida telah menyerap kebanyakan radiasi IR. Hasil daripada mikroskopi Scanning Electron (SEM) dan transmisi mikroskopi elektron (TEM) mengesahkan yang partikel nano Fe_3O_4 telah dilaputi dengan lapisan matrik polimerik. Taburan bagi partikel nano diskret globular dengan hampir saiz uniform dan dimensi yang sama telah ditunjukkan dalam semua sampel komposit nano PPy−CHI−Fe_3O_4. Pengurangan saiz bagi PPy−CHI dan partikel PPy−CHI−Fe_3O_4 telah diterangkan dengan kesan oksida Kitosan dan besi , kesan penstabilan sterik bagiCHI dan struktur teras-luaran bagi komposit nano PPy−CHI−Fe_3O_4 telah disahkan dengan SEM dan TEM.

Dapatan bagi Vibrating Sample Magnetometer (VSM) menunjukkan yang sifat magnetik bagi pelbagai komposit nano PPy−CHI−Fe_3O_4 secara kuatnya bergantung kepada bebanan tumpuan bagi Fe_3O_4. Histeresis lilitan bagi VSM berasaskan tingkah laku superparamagnetik bagi kesemua komposit nano PPy−CHI− Fe_3O_4 dengan peratusan berbeza bebanan Fe_3O_4. M_s (penepuan pemagnetan) dan H_c (koektiviti) telah diperhatikan kepada sampel dengan peratusan yang mengandungi Fe_3O_4 daripada 0.1 wt% kepada15 wt%. M_s meningkat daripada 0.874 emu/g kepada 5.97 emu/g sementara Hc berkurangan daripada 241.4Oe kepada 194.48 Oe.

Dapatan dari putaran resonan elektron (ESR) spektroskopi menunjukkan pengurangan dalam nilai Peak-to-peak line-width (ΔH_{pp}) antara PPy dan PPy−CHI. Penambahan Fe_3O_4 telah menyebabkan dalam nilai (ΔH_{pp}) meningkat dalam turutan PPy−CHI <PPy−CHI−Fe_3O_4 (1wt%) < PPy−CHI−Fe_3O_4 (3wt%) > PPy−CHI−Fe_3O_4 (5wt %) < PPy−CHI−Fe_3O_4 (7wt %) < PPy−CHI−Fe_3O_4 (10wt %) < PPy−CHI−Fe_3O_4 (15wt %) pada suhu bilik. Pengukuran putaran tumpuan (N_s) bagi PPy−CHI−Fe_3O_4 dengan pelbagai kandungan Fe_3O_4 menunjukkan ianya lebih besar daripada PPy−CHI (8×10^6, 1.59×10^7, 3×10^7, 2.29×10^7, 2.43×10^7 dan 2.49×10^7 spin g-1 kepada PPy-CHI dan1wt%, 3wt%, 5wt%, 7wt% dan10wt%, of Fe_3O_4 masing-masing). Peningkatan dalam peratusan bebanan oksida besi turut menyebabkan kestabilan terma bagi komposit nano yang lebih baik .

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I certify that an Examination Committee has met on 4 June 2013 to conduct the final examination of Jamileh Amin on her Doctor of Philosophy thesis entitled "Peparation, and Electrical, Magnetic and Thermal Investigation of Polypyrrole–Chitosan Composite and Polypyrrole– Chitosan–Iron Oxide Polymer Nanocomposite" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at University Putra Malaysia or other institutions.

2013/8/14

JAMILEH AMIN

Date: 4 June 2013

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