UNIVERSITI PUTRA MALAYSIA

RADIATION SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYANILINE AND POLYANILINE/SILVER NANOPARTICELS

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RADIATION SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYANILINE AND POLYANILINE/SILVER NANOPARTICELS

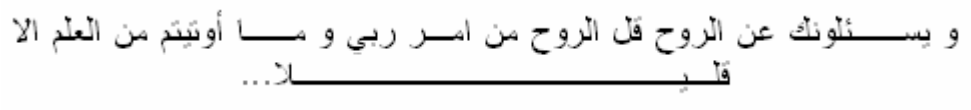
By

MOHAMMED AHMED ALI OMER

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

September 2007

UPM

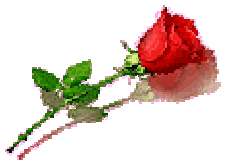


Dan mereka bertanya kepadamu tentang roh. Katakan: “Roh itu dari perkara urusan tuhanku dan kamu tidak diberikan ilmu pengetahuan melainkan sedikit sahaja”
(Al-Israa – 85)

DEDICATION

To the Soule of my parent mum Maddeina M.O. and Ahmed Ali O. who were sincerely encourage and foster me through out my study-hood, I dedicate the benefits of this humble work. To the Soule of Uncle Abdelrahman Ali O., Omer Awad O. and my brother Alfatih Shaikh Alddin Ali, Allah rewards them with paradise.

To my friend as well as my Uncle Salahualdinn Ali O, whose generous help and sincere encouragement motivated me to go ahead for further study, to my patientful wife Omsalam Mohamed Ismail, our son Ahmed Mohammed Ahmed and those who are sincerely pray for my success.



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

RADIATION SYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYANILINE AND POLYANILINE/SILVER NANOPARTICELS

By

MOHAMMED AHMED ALI OMER

September 2007

Chairman: **Professor Elias Saion, PhD**

Faculty: **Science**

The conducting polymer PANI nanoparticles were synthesized from polyvinyl alcohol PVA and aniline hydrochloride (AniHCl) blend films at different AniHCl monomer concentrations (0.5, 1.0, 1.5 and 2.0 g or as 9.0, 16.7, 23.1, and 28.6 wt %) and irradiated with gamma radiation at different doses (0, 10, 20, 30, 40, and 50 kGy) at ambient conditions. Upon irradiation AniHCl undergoes dechlorination by the loss of Cl^- that acts as an oxidant and 'in situ' polymerizing aniline into conducting PANI nanoparticles. The formation of conducting PANI has been observed by the change of colour from colourless to dark green due to the formation of polaron species characterized by the defect in molecular structure of the polymer and was confirmed by Raman scattering at 1637 cm^{-1} Raman shift assigned for C=N stretching of imines group. The SEM morphology of PVA/PANI composites reveals the spherical structure of nanoparticles, 50 – 100 nm in diameter which then

transformed into globular clusters of conducting PANI with good environmental stability.

The optical properties of PANI nanoparticles were measured by means of UV-visible spectrophotometry and found that the absorbance at 790 nm band of conducting PANI increased exponentially with the increase of dose and fitted the expression of the form: $y = y_0 \exp(D/D_0)$, where D is the absorbed dose and D_0 is the dose sensitivity. The results reveal that the optical parameters such as absorption edge, activation energy, and band gap energy decreased with the increase of dose and AniHCl concentration. When the dose increased from 10 kGy to 50 kGy the absorption edge decreased from 1.0 to 0.91 eV for 9.0% AniHCl and from 0.82 to 0.44 eV for 28.6% AniHCl, the activation energy decreased from 2.25 to 1.5 eV for 9.0% AniHCl and from 0.8 to 0.69 eV for 28.6% AniHCl, and the band gap energy decreased from 1.36 to 1.18 eV for 9.0% AniHCl and from 1.12 to 1.00 eV for 28.6 wt% AniHCl. The electrical conductivity was determined by an impedance analyzer and found the conductivity increased with the increase of dose and AniHCl concentration. The conductivity is mainly the direct current (dc) component attributed to the creation of polarons in the PANI structure and they are the charge carriers of conducting PANI which are set in motion in a form of electron hopping within the backbone of the composites. The dc conductivity increased from 5.75×10^{-6} S/m to 1.32×10^{-3} S/m for 9.0 wt% and from 7.76×10^{-5} S/m to 1.17×10^{-1} S/m for 28.6 wt% AniHCl when the dose was increased from 10 kGy to 50 kGy. The dc conductivity is therefore governed by the exponential relation of the form: $\sigma_{dc} = \sigma_0 \exp(D/D_0)$, where σ_0 and D_0 were found varied with different AniHCl concentration.

The silver nanoparticles were synthesized from PVA/silver nitrate ($AgNO_3$) blend films at different $AgNO_3$ dopant concentration of 0.01 wt % and irradiated with gamma radiation at different doses (0, 10, 20, 30, 40, and 50 kGy) at ambient conditions. Upon gamma irradiation, the released electrons interact with silver ions Ag^+ which reduce to silver nanoparticles Ag^0. The formation of Ag^0 nanoparticles has been observed by the colour changed from colourless to golden yellow due to the presence of Ag^0 nanoparticles and was confirmed by XRD analysis. Further, the presence of metal nanoparticles was verified with the UV-visible absorption measurement that reveals the absorption peak at 425 nm due to surface plasmon resonant phenomenon at the conduction band of Ag^0 nanoparticles where the absorbance increased with the increase of dose and fitted the expression of the form: $y = y_0 \exp(D / D_0)$.

The composites of PVA/PANI/Ag^0 nanoparticles were radio-synthesized with the concentration of AniHCl at 28.6 wt%. The concentrations of $AgNO_3$ dopant are different (0.01, 0.03, 0.05, and 0.07 wt %) and different radiation doses (0, 10, 20, 30, 40, and 50 kGy). The results from optical absorption measurement reveal two absorption bands at 415 nm due to surface plasmons of Ag^0 nanoparticles and at 600 nm due to polarons of low conducting PANI. The absorption band shifted from 425 nm to 415 nm crrosponds to decreasing diameter of Ag^0 nanoparticles in the presence of PANI in the composites. The band gap increased with the increase of $AgNO_3$ dopant, from 1.72 eV for 0.01 wt% to 2.58 eV for 0.07 wt% dopant irradiated at 50 kGy. The dc conductivity increased with the increase of dose and decreased with the increase of dopant concentration Ag^+. The dc conductivity for 0.01 wt% dopant increased from 9.77×10^{-6} S/m at 10 kGy to 8.51×10^{-4} S/m at 50 kGy. For dopant

concentration at 0.07 wt%, however, the dc conductivity increased from 1.07×10^{-7} S/m at 10 kGy to 1.23×10^{-5} S/m at 50 kGy. The dc conductivity of PVA/PANI/Ag^0 nanocomposites was found to have an exponential expression of the form: $\sigma_{dc} = \sigma_0 \exp(D / D_0)$.

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

SINTESIS SINARAN DAN PENCIRIAN POLIANILINA KONDUKTOR DAN ZARAH NANO POLIANILINA/ARGENTUM DISEBARKAN

Oleh

MOHAMMED AHMED ALI OMER

September 2007

Pengerusi: Profesor Elias Saion, PhD

Fakulti : Sains

Zarah nano bagi polimer konduktor PANI telah disintesiskan daripada film adunan PVA/aniline hidroklorida (AniHCl) pada kepekatan monomer AniHCl berbeza (9.0, 16.7, 23.1, and 28.6 wt%) dan disinarkan dengan sinaran gama pada dos berbeza (0, 10, 20, 30, 40, and 50 kGy) dalam keadaan ambien. Setelah disinarkan AniHCl mengalami nyahklorin dengan kehilangan Cl^- yang bertindak sebagai pengoksidan dan secara ‘in situ’ mengpolimerkan anilina kepada zarah nano PANI konduktor. Pembentukan PANI konduktor telah diperhatikan sebagai perubahan warna daripada tak berwarna kepada hijau gelap kerana pembentukan spesis polaron yang dikaitkan sebagai kecacatan struktur molekul polimer dan telah disahkan oleh pengukuran serakan Raman pada anjakan Raman 1637 cm^{-1} yang dipadankan kepada rengangan ikatan C=N dalam kumpulan amina. Morpologi SEM bagi komposit PVA/PANI menunjukkan struktur zarah nano berbentuk sfera berdiameter 50 – 100 nm dan

kemudian struktur zarah nano PANI bertukar kepada kulster PANI dengan mempunyai kestabilan alam sekitar yang baik.

Ciri optik zarah nano PANI telah diukur dengan menggunakan kaedah spektrophotometri UV-tampak dan didapati penyerapan pada 790 nm bertambah secara eksponen dengan pertambahan dos berpadanan dengan bentuk: $y = y_0 \exp(D / D_0)$, yang mana D ialah dos terserap dan D_0 ialah kepekaan dos. Keputusan menunjukkan parameter optik seperti penyerapan pinggir, tenaga pengaktifan dan tenaga jalur celah didapati berkurangan dengan pertambahan dos dan kepekatan AniHCl. Apabila dos ditingkatkan daripada 10 kGy kepada 50 kGy didapati penyerapan pinggir berkurangan daripada 1.0 kepada 0.91 eV untuk 9.0% AniHCl dan daripada 0.82 kepada 0.44 eV untuk 28.6% AniHCl, tenaga pengaktifan berkurangan daripada 2.25 kepada 1.5 eV untuk 9.0% AniHCl dan daripada 0.8 kepada 0.69 eV untuk 28.6% AniHCl, serta tenaga jalur celah berkurangan daripada 1.36 kepada 1.18 eV untuk 9.0% AniHCl dan daripada 1.12 kepada 1.00 eV untuk 28.6% AniHCl. Kekonduksina elektrik telah ditentukan secara analisis impedans dan didapati kekonduksian bertambah dengan pertambahan dos dan kepekatan AniHCl. Kekonduksian dipengaruhi oleh komponen arus terus (dc) kerana kewujudan polaron dalam struktur PANI dan ia adalah pembawa cas bagi PANI. Kekonduksian arus terus dc bertambah daripada 5.75×10^{-6} S/m kepada 1.32×10^{-3} S/m untuk 9.0% dan daripada 7.76×10^{-5} S/m kepada 1.17×10^{-1} S/m untuk 28.6% AniHCl dimana dos ditingkatkan daripada 10 kGy kepada 50 kGy. Kekonduksian dc dipengaruhi oleh hubungan eksponen dalam bentuk $\sigma_{dc} = \sigma_0 \exp(D / D_0)$, dimana σ_0 dan D_0 didapati berubah dengan kepekatan AniHCl.

Zarah argentum nano telah disentisis daripada film adunan PVA/argentum nitrat ($AgNO_3$) pada kepekatan dopan $AgNO_3$ ialah 0.01 wt % dan disinarkan dengan sinar gama pada dos berbeza (0, 10, 20, 30, 40, and 50 kGy) dalam keadaan ambient. Semasa penyinaran gama electron yang dihasilkan bersaling tindak dengan ion argentum Ag^+ lalu menghasilkan zarah argentum nano Ag^0. Pembentukan zarah argentum nano Ag^0 telah diperhatikan sebagai perubahan warna daripada tak berwarna kepada kuning emas kerana kehadiran zarah argentum nano Ag^0 dan telah disahkan secara analisis XRD. Seterusnya kehadiran zarah argentum nano Ag^0 telah ditentusahkan secara kaedah penyerapan UV-tampak yang menghasilkan puncak penyerapan pada 425 nm kerana kehadiran plasmon pada jalur konduksi zarah nano argentum Ag^0. Penyerapan bertambah dengan pertambahan dos dan berpadanan dengan hubungan eksponen dalam bentuk $y = y_0 \exp(D / D_0)$.

Komposit zarah nano PVA/PANI/Ag^0 telah disentisis dengan kepekatan AniHCl 28.6 wt%. Kepekatan dopan $AgNO_3$ berbeza (0.01, 0.03, 0.05, and 0.07 wt %) dan berbeza dos sinar gama (0, 10, 20, 30, 40, and 50 kGy). Keputusan daripada pengukuran penyerapan optik menunjukkan dua jalur penyerapan pada 415 nm bersumber daripada plasmon dipermukaan zarah argentum nano Ag^0 dan pada 600 nm disebabkan oleh polaron pada PANI konduksi rendah. Jalur penyerapan beranjak daripada 425 nm kepada 415 nm yang menunjukkan bahawa diameter zarah argentum nano Ag^0 telah berkurangan kerana kehadiran PANI dalam komposit. Tenaga jalur celah bertambah dengan pertambahan dopan $AgNO_3$ daripada 1.72 eV untuk 0.01 wt% kepada 2.58 eV untuk 0.07 wt% pada dos 50 kGy. Kekonduksian dc bertambah dengan pertambahan dos dan berkurangan dengan pertambahan kepekatan dopan. Kekonduksian dc untuk dopan 0.01 wt% bertambah daripada 9.77×10^{-6} S/m

pada 10 kGy kepada 8.51×10^{-4} S/m pada 50 kGy. Untuk dopan 0.07 wt% kekonduksian dc bertambah daripada 1.07×10^{-7} S/m pada 10 kGy kepada 1.23×10^{-5} S/m pada 50 kGy. Kekonduksian dc komposit nano PVA/PANI/Ag^0 didapati mempunyai hubungan eksponen dalam bentuk $\sigma_{dc} = \sigma_0 \exp(D / D_0)$.

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I certify that an Examination Committee has met on September 18, 2007 to conduct the final examination of Mohammed Ahmed Ali Omer on his Doctor of Philosophy thesis entitled "Radiation Synthesis and Characterization of Conducting Polyaniline and Polyaniline/Silver Nanoparticles" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the relevant degree.

Members of the Examination Committee are as follows:

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Date: 24 October 2007

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

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Date:15 November 2007

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