UNIVERSITI PUTRA MALAYSIA

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL PROPERTIES OF SILVER NANOPARTICLES IN CLAY AND ORGANIC POLYMERS AS NANOCOMPOSITES

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By

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

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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL PROPERTIES OF SILVER NANOPARTICLES IN CLAY AND ORGANIC POLYMERS AS NANOCOMPOSITES

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Chairman : Associate Professor Mansor bin Hj Ahmad @ Ayob, PhD

Faculty : Science

In this study, silver nanoparticles (Ag NPs) with the small size (2.12–30.63 nm) were successfully synthesized in the lamellar space of montmorillonite (MMT), montmorillonite/chitosan (MMT/Cts), porous zeolite framework and external surface layer of talc by chemical reducing agent in the absence of heat treatment. The most favourable experimental condition for the synthesis of Ag NPs in the MMT, talc, zeolite nanocomposites (NCs) and silver/montmorillonite/chitosan bionanocomposites (Ag/MMT/Cts BNCs) are described in terms of the initial concentrations of $AgNO_3$. The mean diameters and standard deviation of Ag NPs in all of solid supports increased gradually with the increase of silver ions concentration. The external morphologies indicate that there are no noteworthy morphological distinctions between solid substrates and Ag NPs incorporated to them. The Ag NPs by the physical synthetic route were synthesized in the lamellar space of MMT/Cts utilising the UV-irradiation reduction method in the absence of

reducing agent or heat treatment. The properties of Ag/MMT/Cts BNCs were studied as the function of UV-irradiation times. UV-irradiation disintegrated the Ag NPs into smaller size until a relatively stable size and size distribution were achieved. The silver nanocrystals were also synthesized by another physical method into the interlamellar space of MMT by using γ-irradiation in the absence of reducing agent or heat treatment. The properties of Ag/MMT NCs and the diameters of Ag NPs were studied as a function of γ-irradiation doses. The results from the UV-visible spectroscopy and TEM demonstrated that increasing the γ-irradiation doses enhanced the concentration of Ag NPs. In addition, the particle size of Ag NPs gradually increased from 1 until 20 kGy. When the γ-irradiation doses increased from 20 to 40 kGy, the particle diameters decreased suddenly as a result of the induced fragmentation for Ag NPs. Moreover silver/poly(lactic acid) nanocomposites (Ag/PLA NCs) films were investigated, while Ag NPs were synthesized into the biodegradable PLA as a polymeric matrix and stabilizer in the presence of sodium borohydride as a chemical reduction agent in diphase solvent. In all preparation, MMT, talc and zeolite were used as the inorganic solid supports and poly(lactic acid) was used as organic polymeric matrix. The silver nitrate, chitosan, and sodium borohydride were used as the silver precursor, natural and biodegradable polymeric stabilizer, and the reduction agent respectively. The crystalline structure of Ag NPs for all of samples, average size and size distributions, surface plasmon resonance, surface morphology, and functional groups were studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible spectroscopy (UV-vis), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) respectively. The XRD analysis confirmed that the crystallographic planes of the silver crystals were the face-centred cubic (fcc) types. The UV-visible absorption

spectra showed the peaks characteristic of the surface plasmon resonance (SPR) bonds of Ag NPs. The antibacterial activities of Ag NPs were investigated against Gram-negative and Gram-positive bacteria by the disk diffusion method using Mueller-Hinton Agar (MHA) at different sizes and amounts of Ag NPs. Results show that the antibacterial activity of Ag NPs can be modified with the particle size of Ag NPs.

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

SINTESIS, PENCIRIAN DAN ANTIBAKTERI SIFAT-SIFAT NANOKOMPOSITS NANOZARAH PERAK DI DALAM POLIMER ORGANIK DAN TAK ORGANIK

Oleh

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Dalam kajian ini, nanozarah perak (Ag NPs) bersaiz kecil berjaya disintesis dalam ruangan pipih montmorilonit (MMT), montmorillonit/kitosan (MMT/Cts), rangka zeolit berliang dan lapisan permukaan luar talk dengan agen penurun kimia tanpa rawatan pemanasan. Keadaan percubaan yang paling sesuai untuk sintesis Ag NP dalam MMT, talk, nanokomposit zeolit (NCs) dan bionanokomposit perak/montmorilonit/kitosan (Ag/MMT/Cts BNCs) dijelas berdasarkan kepekatan awal $AgNO_3$. Purata diameter dan sisihan piawai Ag NPs di semua sokongan pepejal meningkat secara berperingkat dengan peningkatan kepekatan ion perak. Morfologi luaran menunjukkan bahawa tidak ada perbezaan morfologi penting antara substrat pepejal dan Ag NPs yang dimasukkan ke dalam mereka. Hablur perak dengan laluan sintetik hijau fizikal disintesis dalam ruangan pipih MMT/Cts dengan menggunakan kaedah penurunan UV-penyinaran tanpa agen penurun atau rawatan pemanasan. Sifat Ag/MMT/Cts BNCs dikaji sebagai fungsi tempoh masa UV- penyinaran. UV-

penyinaran menghancurkan Ag NPs ke saiz yang lebih kecil sehingga ke paras yang relatif stabil dan pengedaran saiz telah dicapai. Nanokristal perak juga disintesis dengan kaedah fizikal yang lain dalam ruangan antara pipih MMT dengan menggunakan γ- penyinaran tanpa agen penurun atau rawatan pemanasan. Sifat Ag/MMT NCs dan diameter Ag NPs dikaji sebagai fungsi dos γ- penyinaran. Keputusan spektroskopi UV-tampak dan TEM menunjukkan bahawa peningkatan dos γ-iradiasi meningkatkan kepekatan Ag NPs. Selain itu, saiz zarah Ag NPs meningkat secara perlahan-lahan dari 1 hingga 20 kGy. Apabila dos γ-iradiasi meningkat dari 20 hingga 40 kGy, diameter zarah menurun secara mendadak akibat fragmentasi Ag NPs. Tambahan pula, kepingan nanokomposit perak/poli(asid laktat) (Ag/PLA NCs) juga dikaji, sementara Ag NPs disintesis dalam PLA terbiodigradasi sebagai matriks polimer dan penstabil dengan kehadiran borohidrida natrium sebagai agen penurun kimia di dalam pelarut dwifasa. Dalam kesemua penyediaan, MMT, talk dan zeolit digunakan sebagai sokongan pepejal tak organik dan poli(asid laktat) digunakan sebagai matrik polimer organik. Perak nitrat, kitosan dan borohidrida natrium digunakan sebagai prekursor perak, semula jadi dan penstabil polimer terbiodigradasi, dan agen penurunan masing-masing. Struktur hablur Ag NPs untuk kesemua sampel, purata saiz dan saiz edaran, resonans permukaan plasmon, morfologi permukaan, dan kumpulan-kumpulan berfungsi dikaji dengan menggunakan belauan sinar-X (XRD), mikroskopi penghantaran elektron (TEM), spektroskopi UV-tampak (UV-vis), mikroskopi imbasan elektron (SEM) dan infra-merah jelmaan fourier (FT-IR). Analisis XRD menegaskan bahawa bidang kristalografi dari kristal perak adalah jenis kubus berpusat muka (fcc). Spektrum serapan UV-tampak menunjukkan puncak ciri-ciri permukaan plasmon resonan (SPR) Ag NPs. Aktiviti antibakteria Ag NPs diselidik terhadap bakteria Gram-

negatif dan Gram-positif dengan kaedah pembauran cakera dengan menggunakan Mueller-Hinton Agar (MHA) pada pelbagai saiz dan kuantiti Ag NPs. Keputusan kajian menunjukkan bahawa aktiviti antibakteria Ag NPs boleh diubahsuai dengan saiz zarah Ag NPs.

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I certify that Examination Committee has met on date of viva voce to conduct the final examination of Kamyar Shameli on her Degree of Doctor of Philosophy thesis entitled "Synthesis, characterization and properties of silver nanoparticles in inorganic and organic polymer nanocomposites" 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 Degree of Doctor of Philosophy.

Member of the Examination committee were as follows

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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 Supervisory committee were as follows:

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DECLARATION

I hereby 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, and it is not concurrently, submitted for any other degree at University Putra Malaysia or at any institutions.

KAMYAR SHAMELI

Date: 8 April 2011

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