Syntheses and Characterization of Silica Nanoparticles Grafted with Selected Heterocyclic Derivatives

Syed Salman Shafqat

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Syntheses and Characterization of Silica Nanoparticles Grafted with Selected Heterocyclic Derivatives

Syed Salman Shafqat

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. It is original and is the result of my work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted at Universiti Malaysia Sarawak or to any other academic institution or non-academic institution for any other degree or qualification.

Name of Student: Syed Salman Shafqat

Student ID No: 13010043

Program Degree: PhD, Mechanical and Manufacturing Engineering

Faculty: Faculty of Engineering

Thesis Title: Syntheses and Characterization of Silica Nanoparticles Grafted with Selected Heterocyclic Derivatives

Signature of Student: ________________________________

Date: November 31, 2016.
DEDICATION

I would like to dedicate my research to my beloved parents; my brother and my sisters whose support always remain as a source of help for me. They are my source of inspiration and will remain my source of inspiration. In all achievements of my life especially in my PhD, I could never oversight their cordial role and support which make me accomplish this research work.
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ABSTRACT

Sol-gel process has been used to synthesize amino functionalized silica nanoparticles by using gelator precursor tetraethylorthosilicate (TEOS) as well as tetramethoxyorthosilicate (TMEOS) and surface modifier, 3-Aminopropyltriethoxysilane, 3-Aminopropyltrimethoxysilane, separately. Sol-gel methodology is the best alternative protocol to synthesize mesoporous nanoparticles as the classic ways to obtain silica from natural sources are unable to produce silica with high purity and uniform size distribution. Amino functionalized silica nanoparticles were then grafted with Furfural as well as Coumarin derivatives to produce organic/inorganic hybrid materials. Furfural and its derivatives find applications in cosmetic, color and paint industries. To synthesize furfural derivatives, Meerwein arylation of furfural at 5th position with o-nitroanilin, m-nitroanilin and p-nitroanilin was carried out separately which gave 5-arylfurfurals. These 5-aryl furfural derivatives are bright colored compounds in the visible light. Coumarin, especially Coumarin-3-carboxylic acid and coumarin-3-carboxylic acid ethyl ester find their applications in medicinal chemistry. Coumarin and Furanacrylic acid are usually prepared by Knoevenagel condensation using health hazards organic bases. In another part of this research, green catalysts viz amino acids and aqueous extract of Acacia concinna were investigated in order to synthesize Furanacrylic acid and Coumarin derivatives. Green approach for the syntheses of Triarylimidazols and Biginelli compounds is also a part of this thesis. All of these organic syntheses were carried out in mild conditions with excellent yields using natural and less expensive and environmental benign catalysts. Finally, the syntheses of silica nanoparticles grafted with Furfural and Coumarin derivatives were conducted via co-condensation as well as post grafting methods. These organically modified silica nanoparticles found their eventual applications in cosmetics as well as paint industries, medical fields and as adsorbents in water treatment, respectively.
Characterization of all these synthetic products was carried out at several stages of syntheses, by using Thin Layer Chromatography (TLC), Fourier Transform Infra-Red spectroscopy (FTIR), Gas Chromatography-Mass Spectroscopy (GC-MS), Nuclear Magnetic Resonance Spectroscopy (NMR), Scanning Electron Microscope (SEM), X-Rays Diffraction (X-RD) and Thermogravimetric analysis (TGA) accordingly.

**KeyWords:** Sol-Gel, Silica Nanoparticles, Heterocyclic Derivatives, Green Approach, Co-condensation
**ABSTRAK**

Proses Sol-gel telah digunakan untuk mensintesis nanopartikel silika dengan menggunakan tetraetilortosilikat gelator pelopor (TEOS) serta tetrametoksiosilikat (TMEOS) dan pengubahsuai permukaan, 3-aminopropiltrietaksi 3-aminopropiltrimetoksilana, secara berasingan. Proses Sol-gel adalah protokol alternatif terbaik untuk mensintesis nanopartikel mesoporous sebagai cara klasik untuk mendapatkan silika daripada sumber semula jadi tidak dapat menghasilkan silika dengan kesucian yang tinggi dan taburan saiz seragam Nanopartikel silika kemudian dicantumkan dengan furfural serta terbitan koumarin untuk menghasilkan bahan hibrid organik / bukan organik. Furfural dan terbitan koumarin diaplikasikan dalam industri kosmetik, warna dan cat. Untuk mensintesis terbitan furfural, Pengarilan Meerwein pada posisi kelima gelang furfural dengan o-nitroanilina, m-nitroanilina dan p-nitroanilina telah dijalankan secara berasingan yang menghasilkan 5-arilfurfural. terbitan furfural 5-aril adalah sebatian berwarna terang di bawah cahaya yang boleh dilihat. Koumarin, terutamanya asid koumarin-3-karboksilik dan koumarin-3-asid karboksilik etil ester boleh diaplikasi dalam kimia perubatan. Koumarin dan asid furanoakrilik biasanya disediakan secara kaedah Knoevenagel pemeluwapan menggunakan asas organik yang berbahaya kepada kesihatan. Terdapat satu bahagian dalam penyelidikan ini, pemangkin hijau iaitu asid amino dan ekstrak akueus Acacia concinna telah dikaji untuk mensintesis asid furanoakrilik dan terbitan koumarin. Pendekatan hijau untuk sintesis daripada triarilimidazol dan sebatian Biginelli juga merupakan sebahagian daripada kajian tesis ini. Semua sintesis organik telah dijalankan dalam keadaan sederhana dengan hasil yang sangat
baik dengan menggunakan mangkin tidak berbahaya semula jadi, murah dan baik kepada alam
sekitar. Kesimpulannya, sintesis nanopartikel silika yang digabungkan dengan furfural dan
derivatif koumarin telah dijalankan melalui pemeluwapan-bersama serta kaedah cantuman
pos. Nanopartikel silika organik yang diubahsuai berpotensi untuk digunakan dalam bidang
kosmetik, industri cat dan bidang perubatan. Pencirian semua produk-produk sintetik telah
dijalankan di beberapa peringkat sintesis, dengan menggunakan Thin Layer Chromatography
(TLC), Fourier Transform Infra-Red spectroscopy (FTIR), Gas Chromatography-Mass
Spectroscopy(GC-MS), Nuclear Magnetic Resonance Spectroscopy (NMR), Scanning Electron
Microscope (SEM), X-Rays Diffraction (X-RD) dan Thermogravimetric analysis (TGA)
accordingly.

Kata Kunci: Sol-Gel, Silika Nanopartikel, Terbitan Heterocyclic, Pendekatan Green, Co-
pemeluwapan
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<tr>
<td>AP-TMS</td>
<td>3-Aminopropyltrimethoxysilane</td>
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<td>AEAP-TMS</td>
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<td>ORMONNAN</td>
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<td>Monodispersed Mesoporous Silica Spheres</td>
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<tr>
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