SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE SUPPORTED ON MESOPOROUS HOLLOW SILICA SPHERE FOR PHOTOCATALYSIS OF SODIUM DODECYLBENZENESULFONATE

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This thesis is dedicated to my beloved family

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ABSTRACT

With the increasing demands of higher living standard accompanied by ever growing of world population and industrial process, the consumption of organic chemicals has been increasing. Most of organic compounds are difficult to be degraded by means of biological and chemical decompositions, making serious damages to the environment. Sodium dodecylbenzenesulfonate (SDBS) is one of the most common surfactants widely used in manufacturing of cleaning products. It can be decomposed through photocatalysis. Among the reported photocatalysts, ZnO is considered as cheap, environmentally friendly and biocompatible material with band gap energy of 3.37 eV. However, the ZnO has low photocatalytic activity due to the formation of aggregates. In this research, a new photocatalyst of zinc oxide immobilized in mesoporous hollow silica spheres (ZnO-MHSSs) have been synthesized for photocatalytic degradation of SDBS under ultraviolet irradiation. ZnO-MHSSs were synthesized via impregnation method applying different temperatures (50 and 85ºC) and ZnO loadings. Zinc acetate dihydrate and tetraethyl orthosilicate were used as precursors of zinc oxide and silica, respectively. In the first attempt, the MHSS was loaded with ZnO (Zn:Si = 1:15, 1:30 and 1:50) at 85ºC. X-ray diffraction (XRD) analysis results confirmed the attainment of mesoporous structure for the obtained composite materials. Nitrogen adsorption-desorption analysis also depicted the formation of mesoporous structure and high surface area for the ZnO-MHSSs compared to bare ZnO. Field emission scanning electron microscopy showed uniform spheres for all samples. The photocatalysis testing was carried out for ZnO-MHSS, ZnO and MHSS by using aqueous solutions of SDBS. The photocatalytic efficiency was determined through tracing the maximum absorption difference of SDBS at fixed time intervals of reaction by using an ultraviolet spectrophotometer. The photocatalysis results demonstrated 14.2-21% efficiency improvement of SDBS decomposition. Applying higher molar ratio of Zn/Si, resulted in formation of zinc silicate (willemite) phase which is not favourable. Therefore, a second procedure was employed in investigating the effect of the higher molar ratio. In the second attempt, ZnO-MHSSs (Zn/Si: 1:1, 1:2, and 2:1) were synthesized at a lower temperature of 50ºC without applying calcination. The XRD analysis confirmed the successful formation of zinc oxide which is not accompanied with the existence of zinc silicate, willemite. Study of the photocatalysis performance was carried out over the prepared samples. The results showed the successful decomposition of SDBS with the highest photocatalytic efficiency improvement (26.7%) for Zn/Si: 1:1 as the best photocatalyst.

ABSTRAK

Dengan pertambahan permintaan terhadap taraf hidup lebih tinggi yang diiringi dengan pertumbuhan penduduk dunia dan proses perindustrian, penggunaan bahan kimia organik juga turut meningkat. Kebanyakan sebatian organik sukar untuk didegradasikan melalui penguraian kimia dan biologi, menyebabkan kerosakan yang serius kepada alam sekitar. Natrium dodesilbenzenasulfonat (SDBS) adalah salah satu surfaktan yang paling biasa digunakan secara meluas dalam penghasilan produk pembersihan. Ia boleh diuraikan melalui fotopemangkinan. Di antara fotomangkin yang telah dilaporkan, ZnO dianggap sebagai bahan yang murah, mesra alam dan bioserasi dengan tenaga luang jalur 3.37 eV. Walau bagaimanapun, ZnO mempunyai aktiviti fotopemangkinan yang rendah akibat pembentukan agregat. Dalam penyelidikan ini, fotomangkin baru zink oksida terpegun dalam sfera silika berongga mesoliang (ZnO-MHSSs) telah disintesis untuk fotopemangkinan SDBS di bawah penyinaran ultralembayung. ZnO-MHSSs telah disintesis melalui kaedah pengisitepuan dengan mengenakan suhu yang berbeza (50 dan 85ºC) dan muatan ZnO. Zink asetat dihidrat dan tetraetil ortosilikat telah digunakan sebagai pelopor zink oksida dan silika, masing-masing. Dalam percubaan pertama, MHSS telah dimuatkan dengan ZnO (Zn:Si = 1:15, 1:30 dan 1:50) pada 85ºC. Keputusan analisis pembelauan sinar-X (XRD) mengesahkan pencapaian struktur mesoliang untuk bahan komposit yang diperoleh. Analisis penjerapan-penyahjerapan nitrogen juga memaparkan pembentukan struktur mesoliang dan luas permukaan yang tinggi untuk ZnO-MHSSs berbanding dengan ZnO. Mikroskopi pengimbasan elektron pelepasan medan menunjukkan sfera yang seragam untuk semua sampel. Ujian fotopemangkinan telah dijalankan ke atas ZnO-MHSS, ZnO dan MHSS dengan menggunakan larutan akueus SDBS. Kecekapan pemfotomangkinan telah ditentukan melalui pencarian perbezaan penyerapan maksimum SDBS pada selang masa tindak balas yang ditetapkan dengan menggunakan spektrofotometer ultralembayung. Keputusan fotopemangkinan menunjukkan peningkatan kecekapan 14.2-21% bagi penguraian SDBS. Penggunaan nisbah molar Zn/Si yang lebih tinggi, mengakibatkan pembentukan fasa zink silikat (willemit) yang tidak diingini. Oleh itu, prosedur kedua telah diaplikasikan untuk mengkaji kesan nisbah molar yang lebih tinggi. Dalam percubaan kedua tersebut, ZnO-MHSSs (Zn/Si: 1:1, 1:2 dan 2:1) telah disintesis pada suhu lebih rendah iaitu 50ºC tanpa pengkalsinan. Analisis XRD mengesahkan kejayaan pembentukan zink oksida yang tidak disertai dengan kewujudan zink silikat, willemit. Kajian prestasi fotopemangkinan telah dijalankan terhadap sampel yang disediakan. Keputusan menunjukkan kejayaan penguraian SDBS dengan peningkatan kecekapan fotopemangkinan tertinggi (26.7%) untuk Zn/Si: 1:1 sebagai fotomangkin terbaik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

MHSS	-	Mesoporous hollow silica sphere
AOPs	-	Advanced Oxidation Processes
BET	-	Brunauer, Emmett and Teller
BJH	-	Barrett–Joyner–Halenda
CTAB	-	Cetyltrimethyl Ammonium Bromide
CMC	-	Critical Micelle Concentration
CPC	-	Cetylpyridinium Chloride
DEG	-	Diethylene glycol
DRS	-	Diffuse Reflectance Spectroscopy
EDX	-	Energy dispersive X-ray spectroscopy
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared Spectroscopy
ICP-AES	-	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-OES	-	Inductively Coupled Plasma Optical Emission Spectrometry
IUPAC	-	International Union of Pure and Applied Chemistry
MHSS	-	Mesoporous Hollow Silica Spheres
MWNTs	-	Multi-Walled Carbon Nanotubes
TEOS	-	Tetraethyl ortosilicate
TBOT	-	Tetrabutyl orthotitanate
TEM	-	Transmission electron microscopy

TEA	-	Triethanolamine
SDBS	-	Sodium dodecylbenzenesulfonate
BS	-	Benzene Sulfonate
SEM	-	Scanning Electron Microscopy
SDS	-	Sodium dodecylsulfate
XRD	-	X-ray Diffraction
XPS	-	X-ray Photoelectron spectroscopy
UV-Vis	-	Ultraviolet visible spectrophotometry
NOM	-	Natural Organic Matter
TX- 100	-	Triton X- 100
ALFP	-	Amplified Fragments Length Polymorphism
VB	-	Valence Band
CB	-	Conduction Band
ZSM-5	-	Zeolite Socony Mobile No.5

LIST OF SYMBOLS

^{o}C	-	Degree Celsius
Cm	-	Centimeter
G	-	Gram
K	-	Kelvin
KV	-	Kilo Volt
L	-	Liter
M	-	Molar
M	-	Meter
Mg	-	Mili gram
mL	-	Mili Liter
Min	-	Minute
Mm	-	Mili meter
mM	-	Mili Molar
Nm	-	Nano meter
Ppm	-	Part per million
Rpm	-	Rotation per minute
V	-	Volume
Å	-	Angstrom
Θ	-	Theta
Λ	-	Lambda
β	-	Full Width at half maximum intensity (FWHM) in radian

D	-	Average crystallite size in nm
cm^{-1}	-	Wavenumber
%	-	Percentage
Wt%	-	Weight percentage
R	-	Reflectance
K-M	-	Kubelka-Munk function
S	-	Scattering coefficient
K	-	Absorption coefficient
µ	-	Micro
h^+	-	Positive hole
e^-	-	Electron
e^-/ h^+	-	Electron- hole pair

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

With the increasing demands of higher living standard accompanied by ever growing of world population and industrial process, the consumption of organic chemicals such as cleaning products, cosmetics, stabilizers, artificial fertilizers, fuel, polymers, paints, dyes, pesticides and herbicides is being increased. These compounds are usually resistant to environmental degradation through chemical and biological processes, thus remain in the environment and tend to enter the plants or animals tissue. Besides, organic compounds, preferentially stored in fatty tissue can accumulate in food chain due to slow metabolism [1, 2]. Furthermore, water is a necessary element for all forms of life, pollution from both the atmosphere and soil will eventually enter the aqueous phase through deposition and penetration respectively. Thus, our main concern has to focus on our water reserves [3].

Surfactants are considered as one principal source of pollution due to their widely presence in different commercial products such as emulsifiers, industrial and domestic cleaning products. Surfactants are amphiphilic organic compounds, as they possess both hydrophobic groups and hydrophilic groups. Therefore, a surfactant molecule contains both water insoluble and water soluble component. Due to their characteristics, surfactants have the tendency to form micelles in water, followed by increasing the solubility and making the removal of organic compounds more difficult from waste waters [4]. Usually the surfactants have the ability of easy accumulation on surface waters, reducing surface tension and quality of water. They also can be adsorbed onto and penetrate the cell membrane of aquatic organisms [5].

Although they are biodegradable to some extent, some of the products obtained from biodegradation such as alkyl phenols are much more problematic than the original compounds. Therefore, efficient methods are strongly needed for omitting persistent organic compound. Sodium dodecylbenzenesulfonate (SDBS) is one of the most common surfactants widely used in manufacturing of cleaning products. Plenty of SDBS is produced all over the world to be consumed as industrial detergents and household cleaning products. Therefore, huge amounts of SDBS effluent are released into the environment, as wastewater, causing serious pollution problems. There are a lot of attempts made by different researchers for removal of SDBS such as adsorption and various techniques of advanced oxidation process. Taffarel and Rubio [6] investigated the adsorption efficiency for the removal of SDBS from aqueous solution by applying cetyl trimethylamunium bromide (CTAB) modified zeolite as an adsorbent. However, through applying the adsorption process, the contaminants are only transferred to the adsorbent without any molecular destruction, consequently secondary pollution occurs.

Advanced Oxidation Processes (AOPs) are defined as near ambient temperature and pressure for contaminants removal processes. It includes different methods of oxidation such as H_2O_2, ozone, ultra-sonication, Fenton oxidation reaction and semiconductor-based photocatalysis. In all AOP methods, the process of contaminant removal is conducted by using energy to produce highly reactive species with high reducing or oxidizing potential, which then attack and destroy the targeted compounds [7]. The main advantages of AOP methods are high rates of pollutant oxidation while, the most important disadvantages are relatively high costs of treatment as well as the special safety needed for using highly reactive chemicals and high-energy sources [8].

Among all methods of AOPs, semiconductor photocatalysis, a kind of heterogeneous catalysis has attracted more attention than the others. The advantages of this method are milder operating condition of temperature and pressure, lower cost of photocatalysts and possibility of using solar energy to drive the process. The catalyst itself is unchanged during the process and no consumable chemicals are required. This can benefit to considerable savings and a simpler operation of the

equipment involved. Furthermore, compared to the other methods, heterogeneous photocatalysis is considered as a green treatment approach. Since is no chemical reagent applied and the only requirement to drive the process is photocatalyst under light irradiation [8].

Semiconductor photocatalysis is a surface-related application. The reaction takes place on the surface of catalyst in which the organic compounds are adsorbed on the surface of photocatalyst during the process. Therefore, surface properties of catalyst are key point to achieve a better performance. Properties such as porosity, total surface area, pore volume as well as structural uniformity and stability of catalyst are crucial to achieve a better performance of photocatalyst [9-11]. It was reported that by decreasing particle size of nanoparticles, surface to volume ratio of the particles increased, lead to enormously increase of surface free energy and subsequently change in phase stability. The more smaller of particle size, the surface role to the total energy grows significantly due to highly increased free energy [12, 13]. This property induces nanoparticles to stick to each other, forming aggregates of nanoparticles and disqualifying their performance.

Zinc oxide nanoparticles have become very well established as good semiconductor in the photocatalytic approaches because of their high photosentivity and stability in degrading various toxic substances [14] . However, due to the as-mentioned phenomenon, ZnO nanoparticles tend to aggregate forming irregular shapes of the morphology and disqualify nanoparticles properties [15]. In order to resolve the problem, distribution of them over a high surface area support appears to be an effective approach [16] . Different supports have been employed in this regard [17, 18]. Among them, silica spheres have applied as supports due to the easy preparation, compatibility with other materials and good environmental stability [19-22]. Mesoporous Hollow silica Spheres (MHSS) are considered to be more efficient supports than solid and Mesoporous spheres due to lower density and toxicity, larger surface area and more stability. Different methods have been applied to synthesize mesoporous hollow silica spheres. Deposition of silica layer on latex or colloid templates and subsequent removal of the hard templates by calcination or corrosion has been known to be the conventional approach for preparation of MHSSs [23, 24].

However, the use of hard templates in the synthesis process has always introduced impurity in the resulted materials. In order to prepare MHSS, sol–gel emulsion method, in which stable and uniform emulsion droplets act as templates, has been applied as an alternative method [25-28].

This study aimed to synthesize mesoporous hollow silica spheres (MHSS) as supporting material for nano zinc oxide photocatalyst. However, there is no information in the modification of mesoporoos hollow silica spheres with zinc oxide. Therefore, the focus of study is on simple production of modified MHSS for photodegradation of sodium dodecylbemzene sulfonate (SDBS). Two procedures were applied for modification of MHSSs. The characterizations based on phase determination, surface analysis and electron microscope imaging were carried out.

1.2 Problem Statement

Due to the growing consumption of laundry detergents, there is a necessity for a quick and effective degradation of SDBS. Photocatalytic degradation by using semiconductor nanoparticles such as TiO_2 and ZnO has attracted a lot of attention for decomposition of organic compounds. However, by decreasing size, particles tend to stick and form irregular shape of aggregates which can affect their performance.

Despite reports on preparation of supported zinc oxide nanoparticles, there is still lack of simple and affordable method for immobilization of zinc oxide nanoparticles onto a support with high surface area, porosity and stability as well as low toxicity. Mesoporous hollow silica spheres (MHSS) have been attracted lots of attention as support for immobilization of nanoparticles, drugs and enzymes owing to having all these requirements. However, zinc oxide supported on MHSS has not been reported.

It is well-known that in order to prepare highly crystalline zinc oxide, calcination at high temperatures is commonly applied [29, 30] . However, calcination results in increase of crystal sizes and decrease of surface areas due to aggregation of

nanoparticles at higher synthesis temperatures [29, 31, 32]. Furthermore, by applying high amount of ZnO precursor followed by calcination, a reaction between silica phase and zinc oxide occurred which led to formation of binary oxide of zinc silicate, willemite [33, 34]. Therefore, procedure to prepare zinc oxide immobilized MHSS without applying heat treatment at elevated temperatures is highly desired.

1.3 Research Objectives

The research objectives of this study were:

1. To synthesize nanosized zinc oxide immoblized mesoporous hollow silica Spheres (ZnO-MHSS)
2. To characterize ZnO/MHSS by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and nitrogen adsorption-desorption analysis.
3. To evaluate the photocatalytic performance and kinetic behaviour of the materials.

1.4 Scope of Study

Mesoporous hollow silica spheres were synthesized by using sol-gel/emulsion method followed by immobilization with zinc oxide in two attempts through impregnation method using zinc acetate dihydrate as ZnO precursor. In the first attempt, lower molar ratios of Zn/Si precursors (1:15, 1:30 and 1:50) were applied with heat treatment at high temperature, whereas, in the second attempt high molar ratios of Zn/Si precursors (1:2, 1:1 and 2:1) were employed without heat treatment at high temperature.

In order to obtain physicochemical properties of all photocatalysts, characterizations were carried out comparing with zinc oxide nanoparticles and MHSS. The characterization methods included X-ray Diffraction (XRD) for phase determination, Fourier transform infrared spectroscopy (FTIR), Nitrogen adsorption-desorption analysis for textural properties study, Transmission electron microscopy (TEM) and Field Emission Scanning Electron Microscopy (FESEM) for morphological properties, Energy-dispersive X-ray spectroscopy (EDX) and inductively coupled plasma optical emission spectrometry (ICP-OES) for elemental analysis. In the last part, the photocatalytic activity of materials was tested through the photocatalytic degradation of SDBS under UV irradiation. Photodegradation reaction was traced through determination of the concentration at proper intervals of time applying UV-Vis absorbance considering maximum wavelength of SDBS at 224 nm. The kinetic study was carried out to ascertain the order of reaction.

1.5 Significance of Study

The importance of this study is due to successful preparation of ZnO-MHSS by two simple, quick and affordable procedures. In the first attempt, low zinc oxide loadings allowed to obtain well-distribution of ZnO nanoparticles over MHSS with high monodispersity and uniformity and no aggregation, while, high loadings of zinc oxide were applied for clear observation of crystalinity of ZnO nanoparticles in the second attempt.

Possibility of using solar light suggests a green inexpensive approach for degradation of waste water treatment. This work presents two procedures for preparation of ZnO immobilized MHSS support. Through employing the best photocatalyst in the first procedure, nearly 80% photodegradation was achieved within two hours of irradiation using a 16 W Uvc lamp and 0.1 g catalyst in 500 mL of SDBS solution. Meanwhile, in the case of second attempt, by applying the best photocatalyst, 85% photodegradation was obtained in two hours with the same reaction condition as the first attempt. The small amount of the catalyst used in these experiments proposed an economic approach for degradation of organic compounds.

The reusability was tested for five cycles and showed no significant drop in the efficiency of catalyst.

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