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**Nanostructure of AgCl/Ag photocatalyst: “ Synthesis,
Characterization and Applications”.**

By

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometer
ccp	Cubic closed-packed
EDS	Energy dispersive spectroscopy
FWHM	Full-width-half-maximum
PEG	Polyethyleneglycol
PVP	Polyvinylpyrrolidone
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TEOS	Tetraethylorthosilicate
UV-Vis	UV-visible spectrometer
VSM	Vibrating sample magnetometer
XRD	X-ray diffraction

LIST OF SYMBOLS

$=\text{Si}(\text{OH})_2$	silanediols
$\equiv\text{Si}-\text{OH}$	silanol
$\equiv\text{Si}-\text{O}-\text{Si}\equiv$	siloxane
α	unit cell length
AgCl	silver chloride
AgNO_3	silver nitrate
Cu	copper
EtOH	ethanol
Fe	pure iron
$\text{Fe}(\text{OH})_2$	iron (II) hydroxide
YFe_2O_3	maghemite
Fe_3O_4	magnetite
FeOOH	iron oxide-hydroxide
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	ferrous sulfate
H_c	coercivity
HCl	hydrochloric acid
KCl	potassium chloride
NaCl	sodium chloride
M_R	remanence
M_s	saturation magnetization
NaOH	sodium hydroxide
NH_4OH	ammonium hydroxide
OH	hydroxyl
SiO_2	silica
TiO_2	titanium dioxide
λ	X-ray wavelength of the source material

Struktur Nano Pemangkin Cahaya AgCl/Ag: “Sintesis, Pencirian dan Aplikasi”

ABSTRAK

Perak klorida/perak (AgCl/Ag) berbentuk nanokubik berjaya disalutkan ke atas permukaan magnetit-silika ($\text{Fe}_3\text{O}_4\text{-SiO}_2$) dan maghemit-silika ($\text{YFe}_2\text{O}_3\text{-SiO}_2$). Dalam proses ini, teras magnetit telah disediakan dengan menggunakan kaedah pemendakan berbalik manakala teras maghemit dihasilkan melalui pengoksidaan zarah magnetit yang telah disintesis. Sementara itu, salutan lapisan silika telah disintesis ke atas zarah magnetik dalam bentuk struktur petala melalui kaedah Stöber yang telah diubah suai. Nanokubik perak klorida dilampirkan ke permukaan luar silika melalui proses penjerapan ion Ag^+ ke permukaan silika diikuti tindak balas dengan ion klorida dan surfaktan untuk membentuk nanokubik AgCl. Kemudian sebahagian daripada AgCl ditransformasi ke zarah Ag melalui pendedahan kepada sinaran gelombang mikro. Penyiasatan ke atas morfologi, fasa, sifat optik dan magnet serbuk yang disintesis dikaji dengan menggunakan mikroskop pengimbasan elektron (SEM), mikroskop pengimbasan medan elektron (FE-SEM), mikroskop pengaliran elektron (TEM), difraksi sinaran-X (XRD), spectrometer Ultraviolet (UV-Vis) dan magnetometer bergetar (VSM). Morfologi zarah AgCl dengan saiz purata 20-30 nm dihasilkan di atas permukaan iron oksida-silika sementara pembentukan zarah Ag bersaiz nano dihasilkan melalui kaedah sinaran gelombang mikro, yang mana saiznya dalam julat 50-60 nm secara purata. Penyerapan yang tinggi dilihat di kawasan UV dan kawasan nyata (panjang gelombang 400 nm) membuktikan kewujudan zarah AgCl/Ag. Zarah-zarah yang disintesis telah digunakan dalam beberapa aplikasi. Zarah-zarah yang disintesis telah diaplikasikan dalam penggunaan fabrik pembersih sendiri (SCF), sebagai pemangkin cahaya dalam penyahgredan metilena biru (MB) dan sebagai penjerap untuk penyingkiran Cu^{2+} di bawah cahaya UV. Zarah AgCl/SiO₂ telah diaplikasikan dalam fabrik pembersih sendiri (SCF) sebagai pemangkin cahaya di mana fabrik kapas berwarna gelap berubah cerah selepas 9 jam didedahkan dibawah cahaya matahari. Sementara itu, zarah $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{/AgCl}$ yang disintesis telah digunakan dalam penyahgredan metilena biru (MB) dan berjaya melunturkan 90% MB selepas didedahkan di bawah cahaya matahari selama 2 jam. Zarah-zarah cecair $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{/AgCl/Ag}$ yang disintesis juga digunakan sebagai penjerap dalam pengalihan ion tembaga di mana kira-kira 99% Cu^{2+} berjaya dikeluarkan daripada larutan. Oleh itu, zarah-zarah yang disintesis ini boleh menjadi pemangkin cahaya dan penjerap yang baik pada masa hadapan yang mana pemangkin ini dapat dikumpulkan semula dengan mudah menggunakan medan magnet luar.

Nanostructure of AgCl/Ag photocatalyst: "Synthesis, Characterization and Applications".

ABSTRACT

The silver chloride/ silver (AgCl/Ag) nanocubes were successfully doped onto the surface of magnetite-silica ($\text{Fe}_3\text{O}_4\text{-SiO}_2$) and maghemite-silica ($\text{YFe}_2\text{O}_3\text{-SiO}_2$) coreshell particles. In the process, the magnetite-core was prepared by using a reverse co-precipitation method while maghemite-core was prepared via the oxidation of the synthesized magnetite particles. Meanwhile, the coating of the silica layer onto the magnetic nanoparticles in the form of coreshell structure were done through a modified Stöber method. The silver chloride nanocubes were doped onto the surface of the silica-shell by the adsorption of Ag^+ onto the surface of silica followed by the reaction with chloride ions and surfactant to form the AgCl nanocubes. Then part of the AgCl was reduced to Ag nanoparticles via microwave irradiation. The investigation on morphology, phase, optical and magnetic properties of the synthesized powders were characterized by using scanning electron microscopy (SEM), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Ultraviolet visible spectrometer (UV-Vis) and vibrating sample magnetometer (VSM). The cubic morphology of AgCl particles with the average size of 20-30 nm were found to deposit on the iron oxide-silica surfaces while the formation of Ag nanoparticles after microwave radiation was found to be 50-60 nm in average. The absorption peaks in UV and visible region (400nm of wavelength) indicate the existence of the AgCl/Ag particles. The synthesized particles were used in application of self-cleaning fabric (SCF), as photocatalyst for the degradation of methylene blue (MB) and as an adsorbent for removal of Cu^{2+} under UV light. The AgCl/ SiO_2 particles applied in self-cleaning fabric (SCF) turned the stained cotton fabric colorless after 9 hours of exposure under the sunlight. Meanwhile, the synthesized $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{/AgCl}$ coreshell particles were used in the degradation of methylene blue (MB) solution and was successful to degrade 90 % of MB after 2 hours of sunlight exposure. The synthesized $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{/AgCl/Ag}$ coreshell particles were also applied as adsorbents in the removal of copper ions where approximately about 99% of Cu^{2+} were removed from the solution. Therefore, these synthesized coreshell particles could be a promising photocatalyst and adsorbent in the future that can be easily recovered by the external magnetic field.

CHAPTER 1: INTRODUCTION

1.0 Research Background

Development of novel and cost-effective nanomaterials for environmental remediation, pollution detection and other applications has attracted considerable attention. Photocatalysis has recently become a popular and various products using photocatalytic functions have been commercialized while semiconductor photocatalysis has aroused much interest. This is due to its promising applications in environmental remediation and clean energy generation. Typical examples include hydrogen production, degradation of pollutants and conversion of carbon dioxide to solar fuels (Spanhel et al., 1987).

Initially, single nanoparticles were studied by researchers due to their better properties compared to the bulk materials. However, in the late 1980s it was found that sandwich colloidal, composite or heterogeneous semiconductor nanoparticles have better efficiency than their corresponding single nanoparticles. For instance, there are some cases that showed their development into some new properties (Hao et al., 1999); (Taylor et al., 2012). In the early 1990s, concentric multilayer semiconductor nanoparticles were synthesized with the aim to improve the property of previously produced semiconductor materials. Consequently, the expression or terminology “coreshell” was adopted (Gu et al., 2008); (Zhou et al., 1996).

Eventually, coreshell nanoparticles have received significant attention recently and rapidly investigated owing to their broad potential for a variety of applications. Previously, photocatalyst made up from titania has become the most advance photocatalyst. However, the combination of AgCl/Ag as a photocatalyst has been reported to be more stable than titania (Lu et al., 2008). In this work, coreshell structure of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AgCl/Ag}$ and $\text{YFe}_2\text{O}_3\text{-SiO}_2\text{-AgCl/Ag}$ nanoparticles were synthesized.

Silver chloride (AgCl) particles are also known to be good candidates for photocatalytic activity, especially in water splitting and decomposition of organic compounds (Choi et al., 2010). In addition, there has been interest recently in AgCl particles as vital component materials for visible-light-driven photocatalyst (Liang et al., 2015). However, the AgCl particle only absorbs light in the ultraviolet range (180-380 nm) due to its semiconductor indirect band gaps of 5.15 eV (~240 nm) and 3.25 eV (~380 nm) (Mahmed et al., 2013). Therefore, one of the solutions is by the nucleation of Ag nanoparticles onto AgCl surface. The AgCl/Ag composite is a good candidate for plasmonic photocatalyst applications as their absorption can be extended in the visible-light wavelength due to the surface plasmon resonance of Ag nanoparticles that is around 400 nm that covered a wide absorption range of visible light (Fei et al., 2016). Specifically, the improved catalytic activity was originated from the enhanced adsorption for visible light, electron-hole separation, and the formation of chloride atoms in silver chloride/silver nanostructured materials.

Kim et al. (2010) demonstrated the usage of silver chloride/silver (AgCl/Ag) composite in the formation of plasmonic photocatalytic system, where AgCl nanocubes was synthesized by controlling the molar ratio of the silver (Ag^+) and chloride (Cl^-) ions in order

to expand the functionality of these composites in catalyst recovery. Apart from that, Choi et al., (2010) synthesized AgCl/Ag nanostructure by reacting silver nitrate (AgNO_3) with hydrochloric acid (HCl) using polyvinyl alcohol (PVA) as a dispersing agent followed by inducing the Ag nanoparticles on the AgCl surfaces by microwave irradiation method. Despite of the enhancement of the absorption of visible light due to the present of silver atoms in silver chloride/silver nanostructured materials, the composite AgCl/Ag particles also exhibit a good antimicrobial property as it promotes a slow release of Ag ions that can be used for the fabrication of antiseptic catheters, bone cements and fabrics (Adams et al., 1999).

However, the evolution of AgCl occurred rapidly and it is challenging to produce AgCl as small particle especially in nano size. Thus, one of the method to overcome this problem is by controlling the ratio of the precursor (Ag^+ ions) and catalyst (Cl^- ions). Apart from that, many research has testified on using amorphous silica (SiO_2) particles, which were synthesized via Stöber method as a substrate for the deposition of various type of nanoparticles (Ghosh and Paria, 2012).

Silica was chosen to coat the magnetic core synthesized in this research due to its properties that is chemically inert and able to conduct high stability against aggregation. Apparently, Stöber method is the modest and elegant method for preparing monodisperse spherical silica particles. Therefore, the Stöber process has been used to make the core-shell structure of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-AgCl/Ag}$ and $\text{YFe}_2\text{O}_3\text{-SiO}_2\text{-AgCl/Ag}$ nanoparticles.

The Stöber process involved hydrolysis and condensation of a silica precursor, tetraethyl orthosilicate (TEOS) in an ethanol as the solvent with the presence of ammonia at room temperature (Lee et al., 2007). During the hydrolysis reaction, the ethoxy group of

TEOS reacts with the water molecule to form the intermediate $[\text{Si}(\text{OC}_2\text{H}_5)_{4-x}(\text{OH})_x]$ with hydroxyl group substituting ethoxy groups, while ammonia works as a basic catalyst to this reaction (Brinker, 1990). Consequently, following the hydrolysis process, the condensation reaction occurred immediately to form Si-O-Si bridges (Ismail et al., 2010).

Besides coating the magnetic core with silica layer, surfactant polyvinylpyrrolidone (PVP) and polyethyleneglycol (PEG) were used as capping agent to control the size and shape of AgCl dopant. Both surfactants were used to investigate the effect of using different types of capping agents to synthesize AgCl-doped silica nanoparticles. Another role of PVP and PEG is that it could promote the reaction of positive ions, Ag^+ with silica by generating the OH^- groups in the mixture solution containing TEOS and ethanol. Basically, PVP is a non-ionic surfactant and it would be partially charged. However, PVP charged strongly due to its positively charged nitrogen. The concentration of PVP used influenced in the rate of formation, deposition, shape and size of the synthesized AgCl particles.

Meanwhile, synthesis and applications of iron oxide nanoparticles have received tremendous attention in recent years due to their potentials for position sensing, information storage devices as well as medical applications (Khalil, 2015). Besides that, the present of magnetic core enable the synthesized coreshell particle to be reuse as the powder can be collectible by using external magnetic field. In this work, magnetite (Fe_3O_4) is synthesized by reverse co-precipitation process (Mahmed et al., 2013) while maghemite (YFe_2O_3) nanoparticles will be synthesized through oxidation of the synthesized Fe_3O_4 nanoparticles. Both iron oxide will act as the magnetic core of the synthesized coreshell structure of Fe_3O_4 - SiO_2 -AgCl and YFe_2O_3 - SiO_2 -AgCl nanoparticles.

Eventually, the increasing of industrial activities such as mining, battery manufacturing industries, and chemical manufacturing have led to severe environmental pollution where various type of toxic metals that are non-biodegradable were released and they tend to accumulate in streams or drainages (Natalie et al., 2014). Apart from that, many industries like textiles, cosmetics, paper, printing, plastics and leather used many synthetic dyes to color their products. These synthetic dyes are known to be a common water pollutants and frequently be found in trace quantities in industrial wastewater. Hence, in order to curb this problem, the synthesized photocatalyst can act as adsorbent to degrade and remove the pollutants (George et al., 2013). Interestingly, the synthesized photocatalyst can be reused back since it can be recovered easily through the application of external magnetic field.

1.1 Problem Statement

The main challenge in the synthesis of silver chloride nanocubes is in controlling the particle size. This is due to the highly reactive reaction between Ag^+ and Cl^- ions. Thus, modification on parameter in term of concentration of Ag^+ and Cl^- ions was made in order to obtain smaller AgCl with the nanocubes structure. The advantages of AgCl nanocubes is due to their larger surface area to volume ratio and their surface plasmon resonance at different wavelength (Hadi and Irene, 2015).

For the deposition of AgCl/Ag dopant on the silica surface, a problem in getting full deposition of AgCl/Ag nanocubes was addressed. Regarding this matter, the chemistry and understanding the mechanism involved between the AgCl/Ag and SiO_2 surface is necessary in investigating the perfect synthesis condition of AgCl/AgCl doped SiO_2 particle within the size range of 50 nm.

Consequently, for the enhancement of the synthesized photocatalyst, magnetic component is used as the core for the coreshell photocatalyst. The use of both magnetic components (magnetite and maghemite) help in the mobility and recyclability of the synthesized coreshell photocatalysts as they act as the core particle. However, the challenges in controlling the size of the magnetic core is also addressed. Therefore, the knowledge on both magnetite and maghemite particles are needed to be further investigated.

Besides that, numerous environmental problems such as water pollution resulted from dye waste water pollution, waste from textile industry and the problem regarding excessive usage of detergents lead to the idea for the synthesis of this magnetic coreshell photocatalyst. Three specific applications were emphasized in this work, in which the synthesized coreshell photocatalyst were used in the application of self-cleaning fabric (SCF), as a photocatalyst for degradation of methylene blue (MB) and as an adsorbent for the removal of copper ions (Cu^{2+}).

1.2 Objectives

This study was focused on the synthesized of nanocubic AgCl/Ag coreshell photocatalyst which consisted of magnetic core as the anchor for recyclability purpose and silica interlayer for the deposition of AgCl/Ag dopant. The specific objectives of this research are stated as follow:

- 1) To synthesize silver chloride nanocubes using different type of surfactant, PVP and PEG.
- 2) To synthesize magnetite and maghemite in nanosize

3) To induce the mobility for recyclability of the synthesized coreshell photocatalyst by depositing these particles onto the surface of the magnetic-silica coreshell structure.

4) To evaluate the ability of the synthesized coreshell particles as a photocatalyst and an adsorbent.

1.3 Research Study /Scope of study

The expression of coreshell is used for a structure that consists of material that is coated by an outside layer forming a shell or layer around the core. This structure consists of Fe_3O_4 or YFe_2O_3 nanoparticles that act as core that will be coated with an amorphous silica in the form of coreshell structure. Then, there will be AgCl/Ag nanoparticles as the dopants.

After the preliminary study on cubical AgCl was succeed, the first stage will be started with synthesizing of Fe_3O_4 and YFe_2O_3 core nanoparticle where YFe_2O_3 nanoparticles were synthesized by heating process of the Fe_3O_4 nanoparticle. The second stage would be synthesizing of silica interface layer via modified Stöber method. The next stage is the doping of AgCl nanocubes on the surface of $\text{Fe}_3\text{O}_4\text{-SiO}_2$ and $\text{YFe}_2\text{O}_3\text{-SiO}_2$ particles.

The synthesis parameter of AgCl included the concentration of both Ag^+ and Cl^- ions precursor, type of Cl^- ions, stirring time while the rotation per minute (rpm) of centrifugation process that needed to be controlled.

In order to confirm the existence and morphology of AgCl , the synthesized AgCl will undergo X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) characterization before being deposited on the surface of silica. Once the deposition of AgCl

nanocubes on the surface of the silica shell is succeed, the Ag nanoparticles will be induced on the coreshell surfaces via microwave irradiation technique. Finally, microscopy studies will be conducted by using different microscopic techniques. The morphology and particle size observation of the synthesized AgCl/Ag doped SiO₂- Fe₃O₄ and SiO₂- γ Fe₂O₃ coreshell structure will be conducted by using a scanning electron microscope with energy dispersive spectroscopy (SEM-EDS). Transmission electron microscope (TEM) will be used to differentiate the phase structure of both nanoparticles. Digital Micrograph and J-image software will be used for the particle size calculation from TEM images.

The synthesized coreshell particles have been used in several applications, where AgCl/SiO₂ particle was used in self-cleaning fabric (SCF), while Fe₃O₄-SiO₂-AgCl has been used as recyclable photocatalyst for the degradation of methylene blue. Apart from these two particles, (Fe₃O₄ & γ Fe₂O₃)-SiO₂/AgCl/Ag coreshell particles were applied in the removal of Cu²⁺.

2.1 Iron oxide nanoparticles

Iron oxide nanomaterials have attracted great attention from many research fields. They are widespread in nature and also have been synthesized in the laboratory. Iron oxide nanoparticle can be synthesized by various methods such as thermal decomposition, coprecipitation, ultrasound irradiation and sol gel. They have been found versatile and have high efficiency in the application in various field such as catalysis, supercapacitor, lithium ion batteries, labeling and sorting of cells as well as for the separation of biochemical products (Yang et al., 2015; Ge et al., 2009). Iron oxides exist in various states, including hydroxides, oxides and oxide-hydroxides.

In general, hematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4) and maghemite ($\gamma\text{Fe}_2\text{O}_3$) nanoparticles are the most commonly used in many diverse technological applications (Robinson et al., 2010). Hematite is colored blood-red in fine powder form, while in the coarsely crystalline state the color of hematite is grey or black (Schwertmann, 2008). It is also be responsible for the red color of many minerals (Torrent et al., 1980). Hematite has the corundum ($\alpha\text{-Al}_2\text{O}_3$) structure that is based on hexagonal closed-packed (hcp) anion packing, with Fe (III) ions occupying the octahedral sites (De Grave et al., 1988). At temperature of 650 °C, hematite turns into magnetite with a high energy loss. Hematite has strong antiferromagnetic properties (Chirita et al., 2009).