Renewable Decyl-alcohol Templated Synthesis of Si-Cu Core-Shell Nanocomposite

M A Salim¹, ², H Misran², S Z Othman², N N H Shah³, N A A Razak², A Manap²

²Center of Renewable Energy, Universiti Tenaga Nasional, Selangor, Malaysia.

Email: Musdalilah@uniten.edu.my

Abstract. Monodispersed silica spheres with particles size of ca. 450 nm were successfully synthesized using a modified Stöber method. The synthesized monodispersed silica spheres were successfully coated with copper using modified sol-gel method employing nonsurfactant surface modifiers and catalyst. A renewable palm oil based decyl-alcohol (C10) as nonsurfactant surface modifiers and catalyst were used to modify the silica surfaces prior to coating with copper. The X-ray diffraction patterns of Si-Cu core-shell exhibited a broad peak corresponding to amorphous silica networks and monoclinic CuO phase. It was found that samples modified in the presence of 1 ml catalyst exhibited homogeneous deposition. The surface area of core materials (SiO₂) was at ca. 7.04 m²/g and Si-Cu core-shell was at ca. 8.21 m²/g. The band gap of samples prepared with and without catalyst was calculated to be ca. 2.45 eV and ca. 3.90 eV respectively based on the UV-vis absorption spectrum of the product.

1. Introduction

Metallic materials have attracted increasing interest for their widespread applications in optical, biological, medical, sensors and optoelectronics due to their superior properties [1-2]. In order to obtain high performance metallic material, it is critical to control the size and morphology of nanoparticles. One significant approach is to design the metallic materials in the presence of support materials such as core-shell nanocomposite. Core-shell nanocomposite are widely studied due to their improved physical and chemical properties as compared to their single material [3]. In recent years, many works were conducted on silica as core and metal as shell for the synthesis of various silica-metal core-shell nanocomposite. Silica was extensively used as core materials because it was cheap and relatively easy to produce [4-5]. In addition, the fabrication of silica-metal core-shell utilized only small amount of metals to cover the surfaces of inexpensive core in order to obtain the desired properties [4-5]. At present, many synthesis routes were explored to synthesize core-shell nanocomposite, such as vapour deposition, plasma-assisted technique, chemical reduction and self-assembly [4-6]. However, in most cases the degree of surface coverage was low and metallic coating was non-uniform [6]. Sol-gel processing is an effective method for preparing core-shell materials since the reactant can be homogeneously mixed at the molecular level [7]. However, conventional sol-gel method employs surfactant as surface modifiers such as triethanolamine, polyethylenimine (PEI) and methyltriethoxysilane (MTES) which were toxic and expensive materials. In this study, environmental friendly, cheap and renewable palm oil based fatty alcohol is proposed to substitute the conventional surfactant as nonsurfactant surface modifiers [8]. Si-Cu core-shell nanocomposite will be

¹ To whom any correspondence should be addressed.
synthesized using renewable palm-oil based fatty alcohol (C10) as surface modifiers in the presence of ammonia as catalyst. In addition, the effect of crystallinity and morphology of samples by adding the catalyst during the surface modification process is also reported.

2. Materials and Methods

The silica spheres were prepared according to the method introduced by Misran et al. [9]. In a typical synthesis procedure, C10 was added to ethanolic solution in the presence of ammonia to obtain microemulsion solution under vigorous stirring. Then, silica precursor of tetraethyl orthosilicate (TEOS) was added drop-wise to the microemulsion solution. The resulting white colloidal suspension of silica was filtered and washed several times with water and ethanol. The silica powder were dried at 100 °C overnight and calcined at 550 °C to obtained silica spheres. The processing of Si-Cu core-shell nanocomposite was performed following the reported procedure of Xia and Tang [4] with some modifications. Obtained silica spheres were dispersed and sonicated in ethanol and water to prepare the silica sol prior to surface modification. C10 and ammonia were added to the silica sol followed by copper salt under constant stirring for several hours at 80 °C. The solids were collected, washed with ethanol several times and dried at 100 °C. Then, the samples were calcined at 600 °C to obtain Si-Cu core-shell nanocomposite. The final molar ratio of samples was silica : copper : C10 = 1 : 0.32 : 6.4. The calcined samples were denoted as SiCuD-1 (prepared without catalyst) and SiCuD-2 (with 1 ml ammonia). The optical band gap energy of the product can be determined using the equation 1 [10]:

$$ (αhν)^2 = B(hν - E_g) $$

where \( hν \) is photonic energy, \( α \) is the absorption coefficient, \( B \) is a constant related to materials, and \( E_g \) is the band gap energy.

3. Results and Discussions

The X-ray diffraction patterns of pure silica spheres (SiO\(_2\)) as reference (core materials) and Si-Cu core-shell nanocomposite of SiCuD-1 and SiCuD-2 are shown in figure 1. All samples exhibited broad peak centered at ca. 2\( θ \) = 22° corresponding to the amorphous structure of silica spheres. SiCuD-1 and SiCuD-2 samples exhibited ten diffraction peaks attributable to monoclinic structure of CuO. The monoclinic copper oxide phase obtained was in good agreement with result reported by Wu et.al [11] and standard data (JCPDS 5-0661). The addition of 1 ml ammonia in SiCuD-2 had reduced the intensity of CuO peak with relative crystallinity of ca. 42% as compared to SiCuD-1. These results suggested the crystalline structure of CuO deposited on the silica surfaces were affected by the addition of catalyst.

Nitrogen adsorption isotherms of calcined silica spheres (SiO\(_2\)) and Si-Cu core-shell nanocomposite (SiCuD-2) synthesized by modified sol-gel method are shown in figure 2. The adsorption isotherms of both samples exhibited Type II characteristic of nonporous materials where the adsorption occurred on external surface area due to surfaces roughness of nonporous Si-Cu core-shell. The specific surface area of SiO\(_2\) and SiCuD-2 were estimated at ca. 7.04 m\(^2\)/g and 8.21 m\(^2\)/g respectively using BET method. In addition, the surface area of SiCuD-2 was observed to be higher as compared to pure SiO\(_2\) spheres suggesting that copper nanoparticles deposited on the pure SiO\(_2\) resulted in increased surface roughness that caused higher nitrogen uptake. This will increase the surface area accordingly.

The field-emission scanning electron microscopy (FE-SEM) images and energy dispersive X-ray (EDX) of calcined Si-Cu core-shell nanocomposite (SiCuD-2) synthesized by modified sol-gel method are shown in figure 3 (a-c). SiCuD-1 exhibited spherical morphology at ca. 450 nm interspersed with agglomeration of monoclinic CuO as confirm by XRD and EDX. Homogeneous copper nanoparticles at ca. 50 nm to 100 nm were formed on the silica surfaces and the agglomerations were reduced with the addition of 1 ml catalyst (SiCuD-2). These results were in agreement with previous study by Kim and co-workers that reported the addition of ammonia as catalyst at optimum amount resulted homogeneous copper nanoparticles formed on silica surfaces [12]. The formation of CuO in alkaline condition was aided by
ammonia which produced strong nucleophiles that deprotonate hydroxyl ligand in SiOH to generate SiO⁻. Then, electrophilic materials like metal ion (Cu²⁺) can attack and easily bonded with nucleophilic SiO⁻ group [12]. The EDX analysis of SiCuD-1 (figure 3 (d)) and SiCuD-2 (figure 3 (e)) on the surfaces of Si-Cu core-shell exhibited the presence of copper element. These results suggested that ammonia successfully played the role as catalyst in the surface modification using nonsurfactant fatty alcohol (C10) to aid the homogeneous deposition of copper on silica surfaces.

**Figure 1.** X-ray diffraction patterns of calcined SiO₂, SiCuD-1 and SiCuD-2 core-shell.

**Figure 2.** Nitrogen adsorption isotherms of pure SiO₂ and SiCuD-2 core-shell.

**Figure 3.** FE-SEM images of Si-Cu core-shell prepared (a) without catalyst (SiCuD-1), (b) with catalyst (SiCuD-2), (c) different magnification of (b); (d) and (e) EDX spectra of (a) and (b), respectively.
The UV-vis spectra (figure 4 (a)) of as-prepared SiCuD-1 and SiCuD-2 dispersed in ethanol exhibited sharp and broad peak centered at ca. 273 nm and ca. 322 nm respectively. The maximum absorption peak was shifted from ca. 273 nm of SiCuD-1 to ca. 322 nm SiCuD-2. The different morphology of Si-Cu core-shell exhibited absorption at different wavelength. These results suggested that the Si-Cu core-shell prepared in this study have possibilities of manipulating light absorption when the size and shape of copper shell on silica were changed. Based on the relation in equation (1), the plot of $(\alpha h \nu)^2$ vs. $h \nu$ are shown in figure 4 (b). The direct band gap energy of both Si-Cu core-shell (SiCuD-1 and SiCuD-2) are estimated to be at ca. 3.90 eV and 2.45 eV correspondingly.

Figure 4. (a) UV-vis spectra and (b) plots of $(\alpha h \nu)^2$ vs. $h \nu$ for SiCuD-1 and SiCuD-2 core-shell.

4. Conclusions
Si-Cu core-shell nanocomposites at ca. 450 nm were successfully synthesized using a simple and quick method. Decyl-alcohol (C10) successfully played the role as surface modifier for depositing copper onto silica core surfaces. However, in the absence of catalyst, the depositions were not controlled resulting in random formation of monoclinic CuO in between the silica spheres. Addition of catalyst resulted in homogeneous deposition of CuO onto the silica surfaces. The optical properties were highly governed by the morphology of deposited copper.

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