Synthesis and Characterizations of SiO$_2$-Ag Core-Shell Nanostructure Using Fatty Alcohols as Surface Modifiers

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Abstract. SiO$_2$-Ag core-shell nanostructure with silica core (SiO$_2$) and silver shell (Ag) nanoparticles with spherical morphology were successfully synthesized using a modified self-assembly sol-gel method. Ag nanoparticles at ca.10-50 nm were successfully attached on monodispersed silica spheres (SiO$_2$) with diameter of ca. 450 nm. Renewable resources of palm oil, derived fatty alcohols (octyl-alcohol (C8), decyl-alcohol (C10) and dodecyl-alcohol (C12)) were employed as nonsurfactant surface modifiers prior to coating with Ag nanoparticles. X-ray diffraction (XRD) patterns of calcined SiO$_2$-Ag core-shell nanostructure prepared with surface modifiers exhibited amorphous structure of SiO$_2$ (core) and face-centered cubic (FCC) structure of metallic Ag nanoparticles (shell). The results obtained in the present work demonstrated the feasibility of employing fatty alcohols as potential nonsurfactant surface modifiers in synthesizing SiO$_2$-Ag core-shell.

Introduction

Core-shell nanostructure made-up from dielectric material as core and metal as shell nanostructure constitutes a novel class of materials. This kind of structure has attracted increasing research interest for widespread potential applications ranging from medicine, optical devices, catalysis and biosensing [1-4]. Dielectric materials such as SiO$_2$ were used as core materials by many studies in order to synthesize core-shell nanoparticles due to high chemical and thermal stabilities, good compatibilities with other materials and chemical inertness [5,6]. Comparatively, uniform coating of metal onto SiO$_2$ core exhibited enhanced stability and physical properties relative to their single-component counterparts [7,8].

At present, many synthesis routes were explored to synthesize SiO$_2$-Ag core-shell, such as vapour deposition, plasma-assisted technique, chemical reduction and self-assembly [3,8,9]. Nevertheless, the metal coating was non-uniform and degree of surface coverage was low [10]. Sol-gel method was widely used to prepare nanostructured materials with desired properties because size and shape of the resulting materials can be easily controlled. In addition, sol-gel processing is an effective method for producing core-shell materials because the reactant can be homogeneously mixed at molecular level and the synthesis can be done in "one pot" co-condensation [11]. Conventional sol-gel method used carbon template of surfactants molecules such as triethanolamine (TEA), polyetheyleneimine (PEI), cetyltrimethylammonium bromide (CTAB) and methyltriethoxysilane (MTES) as surface modifiers. However, these surface modifiers were designer compounds that are toxic and expensive [12]. Therefore, we proposed an alternative green route, using palm oil derived fatty alcohols [13,14] which are cheap, renewable and non-toxic to substitute the conventional carbon template of surfactant surface modifiers for the synthesis of SiO$_2$ and SiO$_2$-Ag core-shell materials respectively.

Previously, decyl-alcohol (C10) was successfully employed as surface modifiers in the synthesis of SiO$_2$-CuO core-shell nanostructure using modified sol-gel method [15]. Thus, this paper presents nonsurfactant synthesis of SiO$_2$ and its resulting core-shell nostructure subsequent nonsurfactant

surface modification to produce SiO_2-Ag core-shell nanostructure with similar procedure as reported by our group [15]. In addition, the effects of using fatty alcohols with various carbon chains on the crystallite size and morphology of the materials were also reported.

Materials and Methods

Materials. The silica source used in this study was tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS, 99% Sigma). Fatty alcohols derived from palm oil (octyl-alcohol: C8, decyl-alcohol: C10 and dodecyl-alcohol: C12), 99.7%, Emery Oleochemicals) was used as nonsurfactant template in synthesizing silica spheres and as surface modifiers in the coating process. Ethanol (synthesis grade, J.T. Baker), ammonia water (32%, Merck) and silver acetate (98%, Aldrich) were used in as-received condition.

Methods

Synthesis of SiO_2 Core and SiO_2-Ag Core-Shell. The silica spheres (SiO_2) were prepared according to the method introduced by Misran *et al.* [14]. The processing of SiO_2-Ag core-shell nanostructure was performed following the previous report [15,16]. Obtained SiO_2 spheres were dispersed *via* ultrasonication in ethanol and water to prepare the SiO_2 sol prior to surface modification. Fatty alcohols (C8, C10 and C12) and ammonia, NH_3 were added to the silica sol followed by silver salt under constant stirring for 3 hours at 353 K. The resulting suspension were washed several times with ethanol and dried at 373 K. Then, the samples were calcined at 873 K to obtain SiO_2-Ag core-shell nanoparticles. The final molar composition of samples silica : silver : fatty alcohols = 1 : 0.32 : 6.4.

Characterizations. The powder X-ray diffraction (XRD) analyses were carried out on Shimadzu XRD-6000 diffractometer using Cu-Kα radiation with 30 kV and 20 mA at scan step of 0.2° and scan speed of 3°/min. The crystallite size of Ag nanoparticles were calculated from full width at half maximum (FWHM) of major XRD peak at (111) crystal plane using Debye-Scherrer's equation [16]. The size and morphology of calcined SiO_2-Ag nanostructure samples were investigated using transmission electron microscopy (TEM) was carried out using Technai G2 F20 X-Twin electron microscopy by FEI under 200 kV accelerating voltage and maximum current 0.1 mA. Field emission scanning electron microscopy equipped with an EDX detector (FE-SEM, JEOL JSM-7600F) were used to characterize the morphology and elemental analysis. The acceleration voltage of FESEM and EDX were operated at 5 kV and 20 kV respectively.

Results and Discussion

Structural Characteristics. The X-ray diffraction patterns of calcined SiO_2-Ag core-shell nanostructure prepared with and without surface modifiers are shown in Fig. 1. Sample prepared without surface modifiers exhibited broad peak centered at ca. $2\theta = 22°$ corresponding to the amorphous structure of silica spheres and no other crystalline peak were observed. Several diffraction peaks of sample prepared with surface modifiers and NH_3 were observed at $2\theta = 38.14°$, 44.34°, 64.46° and 77.4°, which corresponded to the (111), (200), (220) and (311) reflection planes of face-centered cubic (FCC) structure of metallic Ag with JCPDS file, No. 04-0783, which was similar to those reported from Tang *et al.* and Jiang *et al.* [6,9]. Any structural transformations of either SiO_2 or Ag were not observed. In addition, no other XRD peaks corresponding to any intermediate compounds formation were observed. These results indicated the presence of Ag in the samples and have a fairly good relative crystallinity of pure Ag product. These results suggested that fatty alcohols had successfully played the role as surface modifier in attaching Ag nanoshell on silica surfaces. However, the carbon chain in fatty alcohols directly affected the crystallinity of Ag as observed when the intensity of diffraction peaks from C10 was higher than C8 and C12. The intensity of the diffraction peaks increased due to the increase of Ag nanocrystals size. The crystallite size of Ag nanoparticles prepared with C8, C10 and C12 was found to be at ca. 29 nm, 49 nm and 39 nm, respectively.
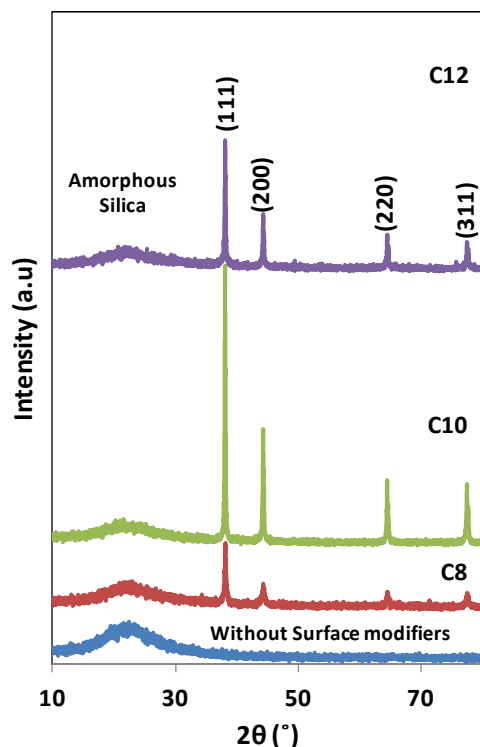
Fig. 1: XRD patterns of SiO_2-Ag core-shell with and without surface modifiers.

Morphology. Fig. 2 shows TEM images of calcined SiO_2-Ag core-shell nanostructure prepared using nonsurfactant surface modifier, C10 with low (Fig. 2a) and high (Fig. 2b) magnification. The deposition of Ag nanoparticles at ca. 10-50 nm on SiO_2 spheres were clearly observed in Fig. 2. Fig. 3 shows FESEM images of calcined SiO_2-Ag core-shell nanostructure. Samples prepared using surface modifiers exhibited Ag nanoparticles were attached uniformly on monodispersed SiO_2. Sample prepared without surface modifiers exhibited smooth surface of monodispersed spherical particles (SiO_2 core) without any Ag deposition. These results suggested that Ag nanoparticles were not attached on SiO_2 surfaces without the presence of fatty alcohols as nonsurfactant surface modifiers.
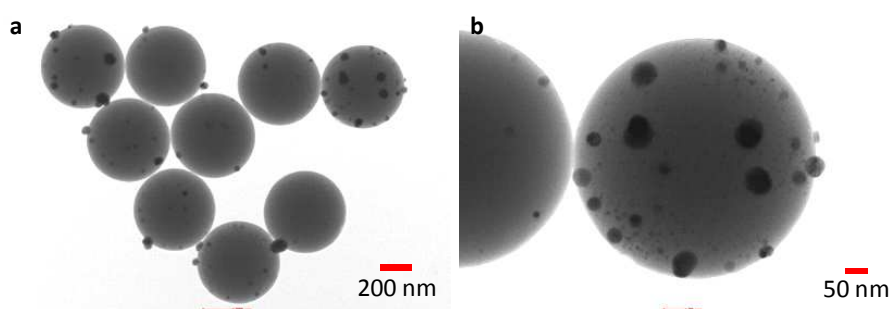

Fig. 2: TEM images of SiO_2-Ag core-shell employed nonsurfactant surface modifier, C10.

Fig. 4 shows the EDX spectra of SiO_2-Ag core-shell nanostructure prepared without surface modifier and with surface modifiers of fatty alcohols with C8, C10 and C12 carbon chains. EDX analyses exhibited strong peaks attributable to O, Si, and Ag peak. These results suggested that Ag was successfully deposited on silica spheres using nonsurfactant surface modifier of fatty alcohols. No other impurities were observed. The appearance of Al peak was originated from the sample support during EDX.
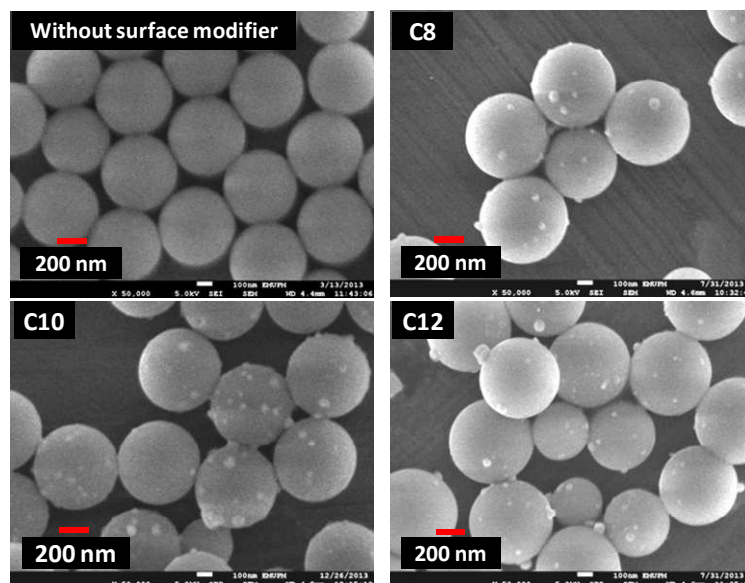
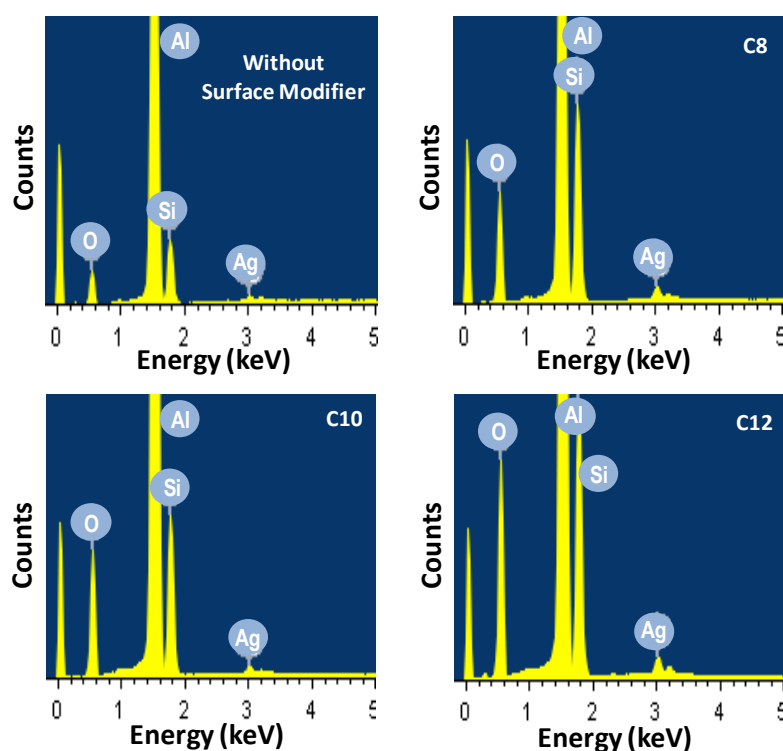Fig. 3: FESEM images of SiO$_2$-Ag core-shell with and without surface modifiers.

Fig. 4: EDX spectra of calcined SiO$_2$-Ag core-shell prepared with and without surface modifier.

Conclusions

Metallic Ag nanoparticles were successfully attached onto the monodispersed silica spheres using fatty alcohols (octyl-alcohol (C8), decyl-alcohol (C10) and dodecyl-alcohol (C12)) as nonsurfactant surface modifiers. Additionally, fatty alcohols were necessary ingredient and played the role of similar to surfactant in the synthesis of facile and low-cost SiO$_2$-Ag core-shell nanostructure. Thus, from these preliminary results, Ag nanoparticles can only be attached onto the surfaces of silica spheres with the aid of fatty alcohol as surface modifiers.

References

[1] P.N.R. Kishorer and P. Jeevanandam, J. Alloy and Compd. 522 (2012) 51-62

[2] S. Kalele, R. Dey, N. Hebalkar, J. Urban, S.W. Gosavi and S.K. Kulkarni, Indian Ecademy of Science 65 (2005) 787-791

[3] H.L. Xia and F.Q. Tang, J. Phys. Chem. B 107 (2003) 9175-9178

[4] S. Son, S.H. Hwang, C. Kim, J.Y. Yun and J. Jang, ACS Appl. Mater. Interfaces 5 (2013) 4815-4820

[5] K. Nischala, T.N. Rao, N. Hebalkar, Colloids Surf., B: Biointerfaces 82 (2011) 203-208

[6] S. Tang, Y. Tang, S. Zhu, H. Lu, X. Meng, J. Solid State Chem. 180 (2007) 2871–2876

[7] Z. Nan, N. Liu, C. Wei, Mater. Sci. Eng. C 29 (2009) 1124–1127

[8] F. Caruso, Adv. Mater. 13 (2001) 11-22

[9] Z.J. Jiang and C.Y. Liu, J. Phys. Chem. B 107 (2003) 12411-12415

[10] R.A. Caruso and M. Antonietti, Chem. Mater. 13 (2001) 3272-3282

[11] K. Han, Z. Zhao, Z. Xiang, C. Wang, J. Zhang and B. Yang, Mater. Lett. 61 (2007) 363-368

[12] M.A. Lewis, Wat. Res. 25 (1991) 101-113

[13] H. Misran, R. Singh and M.A. Yarmo, Micropor. & Mesopor. Mater. 112 (2008) 243-253

[14] H. Misran, M. A. Yarmo and S. Ramesh, Ceram. Inter. 39 (2013) 931-940

[15] M.A. Salim, H. Misran, S.Z. Othman, N.N.H. Shah, N.A.A. Razak and A. Manap, Appl. Mech. Mater. 465-466 (2014) 813-818

[16] M.A. Salim, H. Misran, S.Z. Othman, N.N.H. Shah, N.A.A. Razak and A. Manap, IOP Conf. Sciences: Earth and Environmental Science 16 (2013) 012054