5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

Influence of surfactants in synthesizing of AgCl-doped silica spheres

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Abstract

Silver chloride-doped silica (AgCl-SiO2) particles with the crystallite size of AgCl ranging from 130 – 240 nm have been prepared via the precipitation of Ag+ and Cl−. The Ag+ were adsorbed onto the silica surfaces during the Stöber process, followed by the addition of Cl− and surfactant for the formation of AgCl-SiO2 particles. Polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) with different molarities were used as surfactants. Samples also were prepared without surfactant. The synthesized samples were characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-visible spectroscopy (UV-Vis). XRD patterns confirmed the formation of AgCl for all samples. For low molarity of surfactants (50 mM), smaller size of 133 nm AgCl was formed by using the PEG while at higher molarity (75 mM), the PVP gives smaller size of 134 nm AgCl particles. From SEM, there is no significant difference in morphology of all samples. The strong absorption in ultraviolet region indicates the presence of AgCl particles.

Keywords: polyvinylpyrrolidone; polyethylene glycol; silver chloride

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1. Introduction

The massive issues on environment pollutant and energy crisis urge the researchers to hunt for efficient semiconductor photocatalyst to minimize the problem. Silver chloride (AgCl) is well identified as a good candidate for photocatalytic activity especially for splitting of water into hydrogen using solar energy and its application in pollutant degradation. Moreover, recent interest in AgCl particles as vital component materials for visible-light-driven photocatalyst has aroused. It also has wide applications in sensitized paper and electroplate due to its indirect gap semiconductor property. Interestingly, it also exhibits a good antimicrobial characteristic that can be used for the fabrication, bone cement and antiseptic catheters. As for photocatalytic application, larger surface area provides more adsorption capacity that can increase the efficiency of the material. Thus, the size of the synthesized AgCl particles plays important roles. In this work, the demonstration via facile route to synthesize AgCl nanoparticles were done by mixing Ag+ ion from AgNO3 and Cl– ion from NaCl in ethanolic medium. Apparently, AgCl nanoparticles have distinctive properties such as catalytic and optical properties in which depend on the shape and the size of produced nanoparticles. However, the evolution of AgCl occurred rapidly and it is challenging to produce small particle especially in nano size.

In order to solve this matter, many research testified on using amorphous silica (SiO2) particles, which were synthesized via Stöber method as a substrate for the deposition of various type of nanoparticles. The properties of silica that is chemically inert and able to conduct high stability against aggregation make it suitable to use as the substrate. Apparently, Stöber method is the most modest and elegant method for preparing monodisperse spherical silica particles. The 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.

Polymers such as polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) are known to have long hydrocarbon chain structures with hydrophobic ends. It is believed that this structure is critical in manipulating particle sizes. The rate of particle aggregation is a major factor that controls the morphology and crystallinity of the final product. Besides that, the discrepancy in the capping behavior between PEG and PVP could be attributed to the difference in adhesion strength. However, PVP has been widely known as a capping reagent for microparticles as the adhesion of PVP was stronger than that of PEG. Thus, the usages of PVP or PEG are expected to results in difference rate of formation, deposition, size and shape of synthesized AgCl particles.

2. Methodology

2.1 Materials

The reagents applied were ammonium hydroxide 25%(NH4OH, J.T Baker), tetraethyl orthosilicate 98% (TEOS, Acros), ethanol 96 % (Altaia), silver nitrate (AgNO3, Sigma-Aldrich), hydrochloric acid 37% (HCl, Sigma-Aldrich), polyvinylpyrrolidone m.w.10,000 (PVP, Sigma-Aldrich), poly(ethylene glycol) (PEG) m.w. 380 and deionized water. All the materials were used without prior purification.

2.2. Synthesis of AgCl-doped SiO2 spheres

The synthesis of the silica spheres was based on the modified Stöber method. An amount 200 ml ethanol and 2 ml of tetraethylolsolicate (TEOS) was mechanically mixed in 500 ml beaker for 5 minutes, followed by the addition of 14 ml of ammonium hydroxide (NH4OH) dropwise. Then, the solution was stirred for 15 minutes followed by the addition of 10 ml of 20 wt% AgNO3 solutions. The solution was stirred under mechanical mixing for 1 hour to ensure the adsorption of Ag⁺ species onto the silica surfaces. After that, 10 ml of 50 mM polyvinylpyrrolidone (PVP) and a certain amount of 300 mMCl⁻ was added simultaneously into the Ag⁺–rich silica solution. The solution was continued to stir for 2 hours. The sample was washed with deionized water for the removal of excess PVP by centrifuge, dried in vacuum oven at 323 K and ground. This step is repeated for other samples with different parameters as shown in Table 1.
2.3. Characterization

The phases of the synthesized samples were determined by using X-ray diffraction (XRD). D8 Advance Bruker AXS diffractometer using Cu-Kα radiation (λ = 0.15406 nm) over a 2θ range 20°–90°, with the acceleration voltage of 30 kV and emission current of 10 mA. The average crystallite sizes of silver chloride particles were calculated according to the Scherrer formula as shown in Eq. (1) by using the FWHM data of each phase after correcting the instrumental broadening.

\[
t = \frac{0.9\lambda}{B\cos\theta}
\]

Where,

\( t = \) estimate of the crystallite size

\( \lambda = \) X-ray wavelength of the source material

\( \theta = \) Bragg angle.

\( B = \) Spectral breadth due to the crystallite size effect.

The morphology and elemental analysis of the AgCl-doped silica powders were identified by using a scanning electron microscope (SEM) with an energy dispersive analyzer (JEOL JSM 6010-LV). The absorption of AgCl particles in the UV-visible region (200–800 nm) were studied by using UV-visible spectrometer (Hitachi spectrophotometer).

3. Results and Discussion

In this paper, PVP and PEG were used as a surfactant or the capping agent that prevents the agglomeration and controls the AgCl particles growth while NaCl was used as a chloride ion (Cl\(^-\)) source that will induce the formation of AgCl particles. Before inducing the AgCl particles formation onto the SiO\(_2\)-shell surfaces, the Ag\(^+\) was first adsorbed on the surface of SiO\(_2\) spheres by mixing of Ag\(^+\) salts together with the SiO\(_2\) solution as described in the experimental section. When Ag\(^+\) were inserted into the SiO\(_2\) solution, the ammonium ions in the solution, NH\(_4^+\) reacted with Ag\(^+\) and formed Ag(NH\(_3\))\(_2^+\) complexes. These complex ions were attracted to the hydroxyl groups (OH\(^-\)) of SiO\(_2\) spheres by electrostatic interaction and tightly bound on its surface. When the PVP/PEG-containing the Cl\(^-\) is added, the nucleation of AgCl will occur by the reaction of Ag\(^+\) and Cl\(^-\) and the growth of the particles was controlled by the PVP/PEG. There are two different concentrations of PEG/PVP that have been used as shown in Table 1 and the effectiveness of these concentrations were observed from the XRD patterns of the final products. Samples also were prepared without surfactants for references.

The existence of AgCl phases (PDF 00-031-1238) after the synthesis can clearly be observed from the XRD patterns of all the samples in Fig. 1. There are clear peaks of AgCl at 27° (111), 32° (200), 46° (220), 54° (311), and 57° (222). No silica peaks can be observed from the XRD patterns since the Stöber silica is an amorphous. As seen in Table 1, the full width half maximum (FWHM) values for samples with surfactants are higher compared to the samples without the surfactant. This situation indicates that the surfactants did have influence on controlling the growth of the AgCl. From the crystallite size analysis, when low concentration of the PEG and PVP were used, i.e., 50 mM, the crystallite size of AgCl are 133 nm and 178 nm, respectively. However, as the concentration of the surfactants was increased to 75 mM, the AgCl from PVP is smaller in size, 130 nm compared to the PEG that is 145 nm. Specifically, increasing PEG concentration results in longer tie line length in which all mixture compositions lying on the same tie line that give identical compositions of the equilibrium phase. Thus, increasing phase divergence which lead to particle agglomeration for the samples with PEG\(^12\). In addition, there might be the existence of massive chloride ion reacting with PEG particle in the process. Cl\(^-\) ion act as a stabilizer against the clump of particles and it could sufficiently retard the particle growth of AgCl. In contrast, smaller AgCl-doped SiO\(_2\) particles were obtained when slightly higher
concentration of PVP is used. This is might be due to the selected bounding of PVP molecules on the AgCl particle. PVP plays two important roles in this system. Firstly, the PVP could promote the reaction of positive ions, Ag⁺ with silica by generating the OH groups in the solution. This phenomenon promoted reactions and grain growth of AgCl particle. Secondly, PVP showed greater action as a stabilizer or capping agent than PEG. Although both PEG and PVP are non-ionic surfactants, they would be partially charged. In particular, oxygen in PVP would be charged more strongly than oxygen in PEG because of positively charged nitrogen in PVP. Moreover, PVP would electrostatically adhere to the surface of products more strongly than PEG. Therefore, slightly increment in the concentration of PVP resulted in smaller size AgCl doped SiO₂ particles.

Table 1. Synthesis parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of surfactant</th>
<th>Molarity of Surfactant [mM]</th>
<th>Reference Pattern</th>
<th>FWHM</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PEG</td>
<td>50</td>
<td>PDF 00-031-1238</td>
<td>0.084</td>
<td>133</td>
</tr>
<tr>
<td>B</td>
<td>PVP</td>
<td>50</td>
<td>PDF 00-031-1238</td>
<td>0.071</td>
<td>178</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>-</td>
<td>PDF 00-031-1238</td>
<td>0.047</td>
<td>244</td>
</tr>
<tr>
<td>D</td>
<td>PEG</td>
<td>75</td>
<td>PDF 00-031-1238</td>
<td>0.077</td>
<td>145</td>
</tr>
<tr>
<td>E</td>
<td>PVP</td>
<td>75</td>
<td>PDF 00-031-1238</td>
<td>0.082</td>
<td>134</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>-</td>
<td>PDF 00-031-1238</td>
<td>0.049</td>
<td>240</td>
</tr>
</tbody>
</table>

The morphologies of all synthesized samples are shown in Fig. 2. For samples synthesized at 50 mM of concentration, there is no significant difference in morphology of the samples for both PEG and PVP used (Fig. 2a and b). Similar morphology also observed from the surfactant-free sample (Fig. 2c and 2f). Samples C and F were synthesized using a similar synthesis condition, to indicate that the experiment is repeatable, i.e., there is still no changes.
in crystallite size and morphology after a repetition of the experiment.

Same situation occur for the higher concentration of surfactant (Fig. 2d and e) used. Only the irregular morphology with some agglomeration can be observed. The spherical shape in all images represents the Stöber silica spheres. Thus, by using different surfactants (with different molarity) or without surfactant, do not have a major influence on the morphology of the particles, except controlling the growth (based on crystallite size) of the AgCl particles. The confirmation of the Ag and Cl elements in the SEM images is shown in Fig. 3. All the samples reflect the same peaks as sample C. The platinum (Pt) peaks represent the coating material that has been used during the SEM sample preparation.

Fig. 2. SEM images for all samples
The UV–vis spectra for all samples of AgCl-doped silica particles exhibit a strong absorbance peak in ultraviolet (250 – 380 nm), which support the formation of AgCl phase as observed in XRD patterns. There is also a broad absorption peak in the visible light region (400-800 nm) for all samples are also detected, as shown in Figure 4. The absorption from 400 – 500 nm wavelength might due to the existence of the silver clusters from the reduction of AgCl particles when exposed to the light, since the surface plasmon excitation of Ag particles appears at ~ 400 nm.
4. Conclusion

Based on results, when low concentration of surfactants was used, i.e., 50 mM, the smallest size of AgCl (133 nm) was obtained when using the PEG. As the concentrations of the surfactants were increased to 75 mM, PVP gives the smaller size of AgCl, i.e., 134 nm compared to the PEG which is 145 nm. For surfactant-free samples, the size of the AgCl is 240 nm in average. There are no significance effects on the morphology of the particles when using different surfactants or without surfactant. All the samples show an irregular morphologies and agglomerates. From the optical properties study, the absorption peaks in ultraviolet region confirm the existence of AgCl particles. Nevertheless, this experiment is a good start to study the optimum concentration of PEG and PVP to be utilized in the formation of AgCl-doped SiO₂ particles.

5. Acknowledgements

This work was financially supported by the Fundamental Research Grant Scheme (FRGS) (Grant No. 9003-00445). The supports from School of Materials Engineering, Universiti Malaysia Perlis (UniMAP) are greatly acknowledged.

References