SILVER - POLY(3-HIDROXY-BUTYRATE) [AG-PHB] NANOCOMPOSITE: A PREPARATIVE EVALUATION

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ABSTRACT

A simple phase transfer method is employed to synthesize silver (Ag) nanoparticles in Poly-3-hidroxy-butyrate (PHB) composite in the presence of TOAB. TOAB act as capping agent for the Ag particles, obtained through the reduction of AgNO$_3$ using NaBH$_4$ in aqueous solution as well as an aqueous to organic phase transfer. Experiments were conducted with and without PHB in the organic phase. Ag organosols were characterized using UV-vis, TEM, FTIR, and AAS techniques. The UV-vis absorption spectra confirmed that silver nanoparticles synthesized in the aqueous phase and subsequently transferred into organic phase with or without PHB. TEM monographs showed the presence of small and highly distributed of Ag particles when the organosol contains PHB as compared to organosol without PHB, where the average particle size and standard deviation (SD) are of $11.3 \pm 4.5$ nm and $5.8 \pm 3.6$ nm respectively. The AAS results showed the Ag particles transfer efficiency in the organosol with PHB with more than 90%. It is therefore demonstrated that Ag-PHB nanocomposites are synthesizable through a biphasic mixture. This work also proves that PHB, a biopolymer, is applicable as matrix for the preparations of inorganic-organic nanocomposites.

Keywords: Silver, Poly-3-hydroxy-butyrate (PHB), Particles, Composites, Preparation

INTRODUCTION

Metal nanoparticles are considerable interest in catalysis, electronic, biomedicine, sensors, optoelectronics and magnetic photoluminescence and electroluminescence devices, since they possess interesting chemical, optical and size dependent properties [1-7]. Among the metals, silver is one of the most studied. Nanosized silver particles exhibit remarkable catalytic activity, and selectivity for the epoxidation of alkenes. Besides, silver nanoparticles also applied in areas such as integrate circuit, cell electrodes, antimicrobial deodorants, and chemical analyses [8]. Other potential applications for silver nanoparticles include diagnostic biomedical optical imaging and biological implants dressings. Moreover, silver is a versatile element with applications in the clothing, appliance and semiconductor industries.

A numbers of synthesis strategies have been developed to synthesize metal nanoparticle in polar or non-polar solvent. The colloidal stability, particle size and its properties depend on the specific method of preparation. The utilization of liquid-liquid phase transfer techniques in synthesis of metal particles are known to exhibits characteristic advantages and disadvantages [3, 9]. We have reported silver nanoparticles aqueous to organic phase transfer synthesis with high particle transfer efficiency [10]. Due to metal nanoparticles easily agglomerate as induce by the van de walls attraction between the particles, therefore, supporting agent, capping molecules or stabilizer are needed to overcome the attraction forces and improve the solubility of nanoparticles in organic media [9].

Synthetic polymers are widely employed as stabilizer in the synthesis of metal nanoparticles compared to natural polymer. However, the detrimental effects of synthetic polymer on the environment have become increasingly evident in recent decades mainly due to the resistance of these materials to degradation by microorganisms, and the associated toxicity to the environment and biological hazards. With the increasing interest in minimization or total elimination of waste and implementation of sustainable processes, development of 'green approaches' for the preparation of advanced materials is desirable. The evolution of the 'green approach' is more evident recently to scientific community. For example, Huang et al. [11] reported a green method for synthesis of polysaccharide-stabilized gold and silver nanoparticle. According to Huang, a green method for synthesis of nanoparticle should evaluate from three aspects: (i) solvent, (ii) reducing agent and (iii) stabilizer. In general, biopolymers are an important consideration in the ecological balance of materials. Poly-3-hydroxybutyrate (PHB) is the most studied among a wide variety of biopolymers. It is 100% biodegradable polyester which is regarded as a new environmentally compatible material and is a microbial thermoplastic [12]. Therefore, in our work, we employed a simple
phase transfer method for the synthesis of silver nanoparticles using biodegradable PHB polymer as stabilizer. An evaluation on the preparation of Ag-PHB composite is described.

EXPERIMENTAL SECTION

Material

Silver nitrate (Johnson Matthey, U. K.), sodium borohydride (Riedel-de Haen), chloroform (Systerm, Malaysia), tetraoctylammoniumbromide 98%, TOAB (Aldrich Chemicals). All solvents and chemicals mentioned were used without further purification. Poly-3-hydroxy-butyrate (PHB) was purified according to purification method of G. L. See [13].

Synthesis and aqueous to organic phase transfer of silver nanoparticles with or without PHB

Silver nanoparticles were prepared by the reduction of silver nitrate (AgNO₃) using borohydride, NaBH₄ as reducing agent. Typically tetraoctylammonium bromide, TOAB was added into the 5ml of 1x10⁻⁶mol AgNO₃ solution with vigorous stirring at room temperature. Under vigorous stirring, 1ml of 1x10⁻⁵mol NaBH₄ was introduced drop wise to prepare Ag hydrosol. A yellow-brown colloidal solution was obtained. 5ml of 5 x 10⁻⁴PHB in chloroform was added to silver colloidal solution. The stirring was stopped after several minutes and the mixture was left standing for separation.

Characterization

The resultant nanoparticles were characterized by UV-vis absorption using a U-2000 (Hitachi, Japan) spectrophotometer to determine its optical property. The particles size was determined by TEM using a Philip CM12 electron microscope operated at an accelerating voltage of 80kV. The residual silver content of the aqueous phase samples was determined using Perkin-Elmer atomic absorption spectroscopy (AAS). The FTIR spectrum was collected in the range 4000-400 cm⁻¹ using a Thermo Nicolet IR200 spectrometer.

RESULT AND DISCUSSION

Effect of TOAB as transferring agent

Aqueous AgNO₃ solution is colourless. However, upon reduction silver ions with NaBH₄, a yellowish-brown coloured solution was observed. This colour is symptomatic of the formation of silver nanoparticles. The equation of typical borohydride reduction of silver is as follow [14]:

\[
8\text{Ag}^+ + 8\text{OH}^- + 2\text{BH}_4^- \rightarrow 8\text{Ag}^{0} + 5\text{H}_2\text{O} + 2\text{BO}_3^{2-}
\]

The PHB/chloroform was added into the above silver hydrosol with vigorous stirring. Upon standing, the reaction mixture separated into two layers. The upper aqueous layer becomes colorless and the bottom organic layer adopt the yellow-brownish coloration, (density of chloroform is 1.485g/cm³ ) [15], see Figure 1a. However, when TOAB is excluded in the preparation, the organic phase remains colorless. This indicates that phase transfer of Ag nanoparticles occur only in the presence of TOAB. observed that the yellow-brownish coloration of organic phase and the aqueous phase lost its colour for sample which is added TOAB. For a series of silver organosols prepared with different volume of TOAB (0.1, 0.2, 0.4, 0.6, and 1.0 ml),the color of organosol are almost the same. However, the colour of these organosols gradually fade day to day, and the rates of fading are proportional to the volume of TOAB used.

Table 1 shows the AAS result on the particle transfer efficiency at different volume of TOAB. Regardless of the volume of TOAB used, high percentage of efficiency of phase transfer, (i.e >90) is obtained. There is no significant enhancement of particles transfer efficiency while increasing the volume of TOAB.

The surface plasmon resonance (SPR) of silver nanoparticles can be detected at the visible wavelength range of 350-500 nm [16]. UV-vis absorption spectra of silver organosol with different volume of TOAB used are shown in Fig. 2. The strong absorptions are observed to occur at ~ 410- 430 nm in all spectra depicting a typical plasmon resonance of silver nanoparticles. Figure 2(b) exhibits UV-vis absorbencies of silver organosols that decrease after 3 days preparation. This decreament is related to the amouth of TOAB used. Thus the stability of samples tends to decrease when the volume of TOAB is increased.

Table 1: Silver particles transfer efficiency w.r.t. volume of TOAB used.

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<tr>
<th>Volume of TOAB</th>
<th>% efficiency of phase transfer</th>
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<tbody>
<tr>
<td>0.1ml</td>
<td>93.16</td>
</tr>
<tr>
<td>0.2ml</td>
<td>93.28</td>
</tr>
<tr>
<td>0.4ml</td>
<td>93.37</td>
</tr>
<tr>
<td>0.6ml</td>
<td>93.37</td>
</tr>
<tr>
<td>1.0ml</td>
<td>N/A</td>
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From the result of AAS and analyses of the UV-vis absorption spectra, 0.1ml of TOAB affords the best result in silver particles transfer and exerts a positive influence towards the stability of silver nanoparticles. Therefore, the volume of TOAB was fixed at 0.1ml for further experiment and characterization described in this work.

**Effect of PHB as stabilizer**

Synthesis and transfer of silver nanoparticles were carried out in the sample with and without PHB to determine the ability of PHB as stabilizer. Figure 3 shows the UV-vis absorbencies of silver organosols with and without PHB on the first day and the third day of preparation. The silver organosols show absorbencies at 433 nm for PHB-stabilized and at the 426nm for those without PHB. This indicates that silver nanoparticles are transferred even without PHB. Meanwhile, the maximum absorption gives rise to the red shift in the optical absorption. There are many research reports mentioned that red shift may indicate the particle size increased and large silver aggregates formed during the phase transfer process [9, 17]. However, these conclusions from the absorption spectra are not suitable in this study. It is due to the TEM result exhibit that particle size decreases for the sample with larger maximum wavelength. Therefore, the slight shiftment might be due to the decreasing solvent polarity [18].

The absorbance exhibited by the organosols without PHB tends to be broader and decreased greatly on the 3rd day. A broader absorbance is indicative of large particles while a sharp absorbance is usually caused by smaller particles [6]. This could be explained as below: as for the absent of stabilizer, Ag nanoparticles are unstable and easier to aggregate and form larger particles. On the other hand, no significant time-dependent changes in the UV-vis absorbencies of PHB-stabilized colloidal silver particles are observed. The presence of PHB thus stabilized the Ag particles from aggregation. Therefore, PHB functioned as stabilizer among colloidal silver particles.

Typical transmission electron microscope (TEM) image and the histograms of particle size distribution of silver nanoparticles in the organosols are showed in Figure 4. As illustrate in the micrograph, grid is uniformly covered different sizes of silver nanoparticles. The TEM images, Figure 4(A) revealed that the majority of the particles are spherical. Small Ag particles are nevertheless aggregated. It is due to the absent of PHB and result in no protection for the silver nanoparticles. However, smaller and disperse Ag nanoparticles are observed for PHB-stabilized organosols, Figure 4 (C). An average particles size and standard deviation of 11.3 ± 4.5 nm were obtained for the silver nanoparticles without PHB while 5.8 ± 3.6 nm for the silver nanoparticles, Table 2. Obviously, the size of silver nanoparticles in sample with PHB as a stabilizer is definitely smaller than it is in sample without PHB. Hence, it is believed that silver nanoparticles were protected from phenomenon of Ostwald Ripening by PHB.
Figure 4 (a) TEM monograph and (b) size distribution of Ag nanoparticles for sample with and without PHB as stabilizing agent.

Table 2 The mean diameter and standard deviation for Ag nanoparticles synthesized in the absent and presence of PHB.

<table>
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<tr>
<th>Sample</th>
<th>Mean diameter (nm)</th>
<th>Standard Deviation(nm)</th>
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<tbody>
<tr>
<td>Without PHB</td>
<td>11.3</td>
<td>4.5</td>
</tr>
<tr>
<td>With PHB</td>
<td>5.8</td>
<td>3.6</td>
</tr>
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</table>

It is observed that the colourless PHB-stabilized organosols (i.e., samples without TOAb eventually become yellow in colour after 3 weeks of experiment was carried out, Figure 5(a, b). It indicates that silver nanoparticles are gradually transferred to organic phase. This observation is further enhanced by the UV-vis absorbance at 406 nm of the said organosol, Figure 5(C). Therefore, PHB also has ability to act as transfer agent but at a much weaker capacity.

Figure 6 show FTIR spectra of PHB, TOAB and the organosol. In Figure 6(b), the peaks at 1723, 1279 cm\(^{-1}\) are the equivalent for C=O stretching, and 1381 cm\(^{-1}\) for CH\(_2\) group of PHB. The intense bands at 1000-1300 cm\(^{-1}\) are those of C-O stretching of the ester group of PHB too. The bands at 2850-2920 showed that CH\(_2\) groups of TOAB are present on the organosol. The methylene (-CH\(_2\)-) groups appears in the 721 cm\(^{-1}\) region are also and the methyl groups,(CH) in the 1400 cm\(^{-1}\) regions also arise from the presence of TOAB. These spectra are expected due to presence of TOAB and PHB in silver organosol.

**CONCLUSION**

Aqueous to organic silver particles transfer is possible with and without PHB stablilizer in the presence of TOAB as transferring agent. A small size of silver nanoparticles were successfully synthesized by the phase transfer method with PHB as a stabilizer in organic phase. The synthesis in the presence of PHB also affords smaller size distribution of silver nanoparticles (5.8 ± 3.6) as compare to size distribution of silver nanoparticles without PHB-stabilized (11.3 ± 4.5). The volume of transferring agent at 0.1ml of TOAB gave good result in term of stability of Ag organosol and afford a high transfer efficiency, ca. >90%. PHB also act as transferring agent but in much less effective as compared to TOAB.
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