Synthesis of silver nanoparticles deposited on silica by γ-irradiation and preparation of PE/Ag nano compound masterbatches

Thi Kim Lan Nguyen¹, Thuy Ai Trinh Nguyen², Van Phu Dang¹, Ngoc Duy Nguyen¹, Anh Quoc Le¹ and Quoc Hien Nguyen¹

¹ Research and Development Center for Radiation Technology, Vietnam Atomic Energy Institute, 202A, Street 11, Linh Xuan Ward, Thu Duc District, Ho Chi Minh City, Vietnam
² Ho Chi Minh City University of Technology, Vietnam National University of Ho Chi Minh City, 268, Ly Thuong Kiet, Ho Chi Minh City, Vietnam

E-mail: hien7240238@yahoo.com

Received 14 June 2013
Accepted for publication 17 July 2013
Published 14 August 2013
Online at stacks.iop.org/ANSN/4/045004

Abstract
Silver nanoparticles (AgNPs) deposited on silica were synthesized by gamma Co-60 irradiation of Ag⁺ dispersion in silica/ethanol/water mixture (9/80/20:w/v/v). The reduction of Ag⁺ is occurred by hydrated electron (e⁻ₐq) and hydrogen atom (H•) generated during radiolysis of ethanol/water. The conversion doses (Ag⁺ → Ag₀) were determined by UV–Vis spectroscopy. The synthesized AgNPs/silica were characterized by transmission electron microscopy (TEM) and x-ray diffraction (XRD), which showed the size of AgNPs to be in the range of 5–40 nm for Ag⁺ concentrations from 5 to 20 mM. Masterbatches of PE/AgNPs/silica compound with silver content from 250 to 1000 mg kg⁻¹ were also prepared. These masterbatches can be suitably used for various applications such as antimicrobial food containers and packing films, etc.

Keywords: silver nanoparticles, silica, gamma ray, polyethylene

Classification numbers: 4.02, 5.11

1. Introduction
Silver nanoparticles (AgNPs) have been extensively studied for utilization in different fields as a potential antimicrobial agent owing to their high surface area-to-volume ratio and the unique chemical and physical properties [1–4]. The antimicrobial property of AgNPs is size dependent, the smaller the particles size, the greater the antimicrobial efficacy [5, 6]. Nanocomposite materials of metal particles in particular AgNPs on various solid supports are of great importance for fundamental research and practical applications [7]. A number of reports for the preparation of AgNPs deposited on silica using various methods have been published [8–14]. Gamma Co-60 irradiation is one of the efficient techniques which has been successfully applied for preparation of metal nanoparticles from aqueous corresponding metal ion solutions due to unique ability of γ ray to generate hydrated electron (e⁻ₐq) and hydrogen atom (H•) as powerful reducing agents in water [15–17]. The γ ray irradiation method has distinct advantages compared with conventional chemical methods as described in our previous article [18]. Thus, the γ ray irradiation method is clean and environmentally friendly.

Plastics are widely used to produce biomedical devices and food packaging. However, typically they do not have inherent antimicrobial properties in prevention of infection to humans by microorganisms [19]. Silver-based antimicrobial additives for plastic compounds and consumer products are increasingly applied (www.smartsilver.com/; www.nanotechproject.org/inventories/consumer/analysis_draft/) especially in the medical and healthcare applications [20].

In the present work, the synthesis of AgNPs deposited on silica (AgNPs/silica) by gamma ⁶⁰Co irradiation...
Figure 1. Schematic illustration of the procedure for depositing AgNPs onto silica by γ-irradiation: (a) 5 mM, (b) 10 mM and (c) 20 mM AgNPs.

Figure 2. UV–Vis spectra of AgNPs (a) and optical density (OD) of the irradiated Ag⁺/silica suspension versus doses (b).

was investigated. Masterbatches of polyethylene (PE)/AgNPs/silica compound with different silver content (250–1000 mg kg⁻¹) were also prepared.

2. Experimental

2.1. Materials

Silica (SiO₂) with diameter in the range of 0.2–0.3 μm was purchased from Cabot Co., USA. AgNO₃ and ethanol of analytical grade were from Shanghai Chemical Reagent Co., China. Deionized water from Merck, Germany was used in all preparations of samples. HDPE V1160 was a product from IRPC, Thailand.

2.2. Methods

AgNPs deposited onto SiO₂ (AgNPs/SiO₂) were synthesized by gamma ⁶⁰Co irradiation of Ag⁺/SiO₂/ethanol/water mixture that was prepared by adding AgNO₃ with desired concentration of 5, 10 and 20 mM into dispersion of SiO₂/ethanol/water (9/80/20:w/v/v) while stirring. The prepared mixtures above were poured into glass bottles and capped. γ-Irradiation was carried out on a ⁶⁰Co irradiator with dose rate of 1.3 kGy h⁻¹ at VINAGAMMA Center, Ho Chi Minh City. After irradiation with different doses up to 40 kGy, UV-Vis spectra of irradiated Ag⁺/SiO₂ suspensions were recorded on an UV-2401PC, Shimadzu, Japan to determine optical absorption properties and conversion doses (Ag⁺ → Ag⁰). The size of AgNPs was evaluated by transmission electron microscopy (TEM) images on a JEM 1010, JEOL, Japan. X-ray diffraction (XRD) of AgNPs/SiO₂ as prepared was performed on an X Per’Pro, PANalytical, Netherlands for characterization of crystalline structures. In addition, the size of AgNPs was also calculated from XRD patterns according to Debye–Schererrer equation as described elsewhere [11]. The overall process for the synthesis of AgNPs deposited on silica by γ-irradiation was shown in figure 1.

After irradiation, AgNPs/SiO₂ suspension was dried in force air oven at 60°C to obtain AgNPs/SiO₂ powder. Masterbatches of PE/AgNPs/SiO₂ compound were prepared by mixing AgNPs/SiO₂ powder into PE with desired content of silver on an Extruder Brabender, Germany. Melt flow index (g per 10 min) was carried out on an ATS Faar machine, Italy according to ASTM D 1238.

3. Results and discussion

The absorption spectra of the irradiated Ag⁺/silica suspension were shown in figure 2. It can be observed that the maximum absorption wavelength (λmax) values are of 418.5, 439.0 and 447.5 nm (figure 2(a)) at conversion dose of 12, 24 and 36 kGy (figure 2(b)) for 5, 10 and 20 mM Ag⁺ in silica suspension, respectively. Adsorption of Ag⁺ on the silica surface occurs by adding silver ions to a silica suspension. Lawless et al [15]
Figure 3. TEM images of AgNPs/silica from: (a) 5 mM, (b) 10 mM and (c) 20 mM of Ag⁺.

Figure 4. XRD patterns of bare silica (a) and AgNPs/silica from sample of 10 mM Ag⁺.

Figure 5. Pictures of AgNPs/silica, PE and PE/AgNPs/silica with silver content of 500 ppm.

Table 1. Results of melt flow index (MFI) of PE/AgNPs/silica compounds with different silver content.

| Sample | PE 250 ppm | PE 500 ppm | PE 1000 ppm | PE 10000 ppm |
|--------|-------------|-------------|-------------|--------------|
| MFI, g per 10 min | 15.00 | 15.58 | 16.86 | 16.78 |

described the equilibrium of the adsorption process of Ag⁺ on the SiO₂ surface (Ag⁺ad) and free Ag⁺ in solution as follows: 

\[
\text{Ag}^+ + (\text{SiO}_2) \rightleftharpoons (\text{SiO}_2) \text{Ag}^+ (= \text{Ag}_{\text{ad}}^+) \]

The equilibrium constant, 

\[
K = [\text{Ag}^+]_{\text{ad}}/[\text{Ag}^+][\text{SiO}_2] \]

for this adsorption is \((3.4 \pm 1.5) \times 10^5\). In these experimental conditions, Ag⁺ ion was less than 20 mM and silica content was about 9% (w/v), therefore almost all Ag⁺ was adsorbed on the silica surface as shown in figure 1.

From TEM images shown in figure 3, the AgNPs size was estimated to be of 5–20, 15–30 and 20–40 nm for samples with Ag⁺ concentration of 5, 10 and 20 mM, respectively. The results indicated that the average AgNPs size can be selected by changing Ag⁺ concentration, the lower the Ag⁺ concentration the smaller the AgNPs size that could be obtained. The content of silver in AgNPs/SiO₂ powder that was typically analyzed for the sample with Ag⁺ concentration of 10 mM was from 10000 to 11000 ppm (equivalence to 1.0–1.1% w/w).

XRD patterns were shown in figure 4 typically for AgNPs/silica from a sample of 10 mM Ag⁺ and bare silica. In figure 4(a), the peak at 2\(\theta\) = 21.5° is consistent with the amorphous structure of silica [15], whereas figure 4(b) confirmed the existence of AgNPs with four peaks at 2\(\theta\) = 38.0°, 44.2°, 64.2° and 77.2°, representing the Ag planes of 111, 200, 220 and 311 for crystal AgNPs with typically face-centered cubic (fcc) (ASTM No. 4-783). The obtained result of XRD for AgNPs/SiO₂ was also in accordance with the results reported by Ramnani et al [14] and Jiang et al [15]. From the XRD pattern in figure 4(b), the average size of the metallic AgNPs deposited on silica obtained from sample 10 mM Ag⁺ was calculated using the peak at 2\(\theta\) = 38.0° and based on Scherrer’s formula: 

\[
t = 0.9 \lambda / B \cos \theta
\]

where \(\lambda\) is the wavelength of the X-rays, \(B\) is the full width at half maximum (FWHM) of the peak measured in radians, and \(\theta\) is the Bragg angle. The calculated size of AgNPs was of 23 nm which was in good agreement with the particles size estimated from TEM image in figure 3(b).

Results in table 1 showed that MFI of masterbatches of PE/AgNPs/silica compound was slightly increased with the increase of AgNPs content compared to that of the original PE sample (15 g per 10 min). Accordingly, these masterbatches can be suitably used to mix with original PE to produce antimicrobial plastic products such as antimicrobial food containers and packing films, etc [21]. A typical picture of PE/AgNPs/silica compound contained 500 ppm silver is shown in figure 5. For a typical formulation, 1 kg of this masterbatch can be used to mix with 9 kg PE for preparing antimicrobial plastic products. Furthermore, the prepared AgNPs/silica powder can be also used for production of antimicrobial toothpaste, soap and water-based paints as well as for treatment of water for aquaculture of shrimps.
4. Conclusion

γ-Irradiation is an effective method for the synthesis of AgNPs deposited onto the surface of silica at room temperature. The size of AgNPs deposited on silica increased with the increasing Ag⁺ concentration. Masterbatches of PE/AgNPs/silica compound as prepared can be potentially used for the production of antimicrobial plastic devices and/or food containers. In addition, the resultant AgNPs/SiO₂ powder can also be used for other products such as antimicrobial toothpaste, soap, and water-based paints, etc.

References

[1] Rai M, Yadav A and Gade A 2009 Biotechnol. Adv. 27 76
[2] Zhang F, Wu X, Chen Y and Lin H 2009 Fiber Polym. 10 496
[3] Panacek A et al 2006 J. Phys. Chem. B 110 16248
[4] Phu D V et al 2010 J. Exp. Nanosci. 5 169
[5] Martinez-Castanon G A, Nino-Martinez N, Martinez-Gutierrez F, Martinez-Mendoza J R and Ruiz F 2008 J. Nanopart. Res. 10 1343
[6] Baker C, Pradhan A, Pakstis L, Pochan D J and Shah S I 2005 J. Nanosci. Nanotechnol. 5 244
[7] Zhang L et al 2003 Langmuir 19 10372
[8] Muniz-Miranda M 2003 Colloids Surf. A 217 185
[9] Hornebeq V, Antonietti M, Cardinal T and Treguer-Delapiere M 2003 Chem. Mater. 15 1993
[10] Tuval T and Gedanken A 2007 Nanotechnology 18 255601
[11] Jiang L, Wu Z, Wu D, Yang W and Jin R 2007 Nanotechnology 18 185603
[12] Li T, Moon J, Morrone A, Mecholsky J, Talham R and Adair H 1999 Langmuir 15 4328
[13] Tang S, Tang Y, Gao F, Liu Z and Meng X 2007 Nanotechnology 18 295607
[14] Rammani S P, Biswal J and Sabharwal S 2007 Radiat. Phys. Chem. 76 1290
[15] Lawless D, Kapoor S, Kennepolh P, Meisel D and Serpone N 1994 J. Phys. Chem. 98 9619
[16] Belloni J and Mostafavi M 1998 New J. Chem. 22 1239
[17] Hund F, Bertino F G., Zhang G, Sotiriou-Leventis C, Leventis N, Tokuhiro T and Farmer J 2003 J. Phys. Chem. B 107 465
[18] Du B D et al 2008 J. Exp. Nanosci. 3 207
[19] Marin-M, Niederhausern S D, Iseppi R, Bondi M, Sabia C, Toselli M and Pilati F 2007 Biomacromolecules 8 1246
[20] Markarian J 2009 Plast. Add. Compound. 11 18
[21] Llorens A, Lloret E, Picouet P A, Trbojevich R and Fernandez A 2012 Trends Food Sci. Technol. 24 19