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SYNTHESIS OF SILVER NANOPARTICLES DEPOSITED IN POROUS CERAMIC BY γ-IRRADIATION

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Abstract

Silver nanoparticles (Ag nano) were deposited in porous ceramic (PC) that was functionalized with aminosilane (AS) agent (PC-AS-Ag nano) by gamma Co-60 irradiation of the PC-AS/Ag^+ mixture using polyvinylpyrrolidone (PVP) as stabilizer. Effect of dose on the formation of Ag nano was investigated. Characteristics of the nanocomposite material (PC-AS-Ag nano) were determined by ultraviolet visible spectroscopy (UV-Vis), X-ray diffraction (XRD), transmission electron microscopy (TEM) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Results indicated that Ag nano size was ~9 nm and the Ag nano content in PC-AS-Ag nano material was about of 341 ± 51 mg/kg at dose of 14-20 kGy. Thus, gamma Co-60 irradiation method has the advantage of creation of small Ag nanoparticles with fairly homogenous distribution in PC material.

Keywords. Porous ceramic, silver nano, gamma Co-60.

1. INTRODUCTION

Porous ceramic is a porous filter material with thermal stability, chemical stability and an effectively antimicrobial agent for water treatment [1]. Recently, porous ceramic material has been further developed for point-of-use drinking water treatment. The PC candle filters can be used to treat more than 50 M^3 of drinking water [2]. Furthermore, PC candle filters exhibited antibacterial property for *E. coli* and *coliform* with the efficiency of 80-99.99 %. However, PC has just kept the bacteria on surface but has almost no antimicrobial effect [3]. Silver nanoparticles (Ag nano) are linked to PC for use as highly antimicrobial and anti-biofouling filter materials [4]. Several approaches have been applied to improve Ag nano deposit on to the different types of materials such as polyurethane membrane [5], nonwoven PE/PP [6], zeolite [7], silicon [8], porous ceramic [9-10] etc. for water treatment. Quoc *et al.* [11] reported that the PC-Ag nano candle filter has low content of silver release into filtrated water and highly antimicrobial effect that can be applied for drinking water treatment.

In this paper, we study to deposit silver nanoparticles into porous ceramic that functionalized with aminosilan agent by gamma Co-60 irradiation of the mixture PC-AS/Ag^+. The advantage of the γ-irradiation method is clean, environmentally friendly and capable for large-scale production with competitive price [12].

2. EXPERIMENTAL

2.1. Reagents

Silver nitrate ($AgNO_3$) is a pure-grade product from Shanghai Chemical Reagent Co., China. Polyvinylpyrrolidone (PVP) K90 is a pharmaceutical grade product from BASF, Germany. Absolute isopropanol $(CH_3)_2CHOH$ and aminosilane (AS), namely 3-aminopropyl-triethoxysilaneare, NH_2-C_3H_6-$Si(OC_2H_5)_3$ products of Merck, Germany. Pure water from Merck, Germany was used in all preparations of samples. Porous ceramic samples were supplied by a domestic Ceramic Company, Hai Duong province, Vietnam with the specific surface area of 1.83 m^2/g, the average pore size of 61.9 Å

and total pore volume of 2.8×10^{-3} cm^3/g measured by BET method.

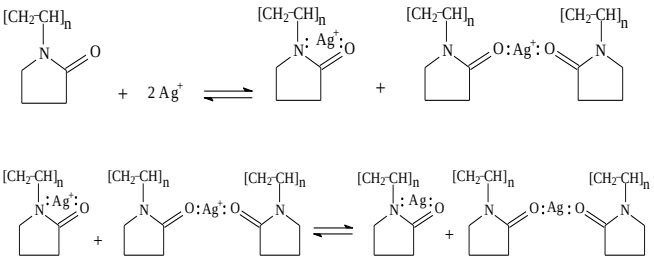
2.2. Methods

PVP and $(CH_3)_2CHOH$ were dissolved in water to prepare solution with the concentration of 2% (w/v) for PVP and 15 % (v/v) for $(CH_3)_2CHOH$. Silver nitrate was then dissolved in the above prepared solution to obtain formulations: 5 mM Ag^+/2% PVP/15% $(CH_3)_2CHOH$. PC functionalized with AS (PC-AS) was prepared as described in our previous study [9]. The PC-AS samples were immersed in Ag^+/PVP solution for 24h and then irradiated by gamma Co-60 for the synthesis of PC-AS-Ag nano. Irradiation was carried out on a Co-60 irradiator at VINAGAMMA Center, Ho Chi Minh City with dose rate of about 1.2 kGy/h measured by the ethanol-chlorobenzene dosimetry system [13]. The irradiated samples were washed three times in ultrasonic bath by water for 15 min. The PC-AS-Ag nano samples were dried in a forced air oven (DNF 410, Yamato, Japan) at 80 ^oC till to dry. Then the PC-AS-Ag nano samples were grinded into fine powder for UV-Vis absorption spectra measurement taken on an UV-vis spectrophotometer model Jasco V-630, Japan. The size of the Ag nano deposited in PC-AS was determined by a transmission electron microscope (TEM) model JEM 1010, JEOL, Japan. The content of Ag nano in PC-AS-Ag nano sample was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer, Optima 5300 DV.

3. RESULTS AND DISCUSSION

Many methods for the synthesis of Ag nano using different stabilizers have been developed. Du *et al.* [14] reported the results of synthesis of colloidal silver nanoparticles stabilized with PVP by γ-irradiation. The particles size was obtained to be in the range of 6-21 nm for Ag^+ concentration from 1 to 50mM.The mechanism of the gamma Co-6o irradiation method was described by Belloni *et al.* [15]. Polyvinyl pyrrolidon (PVP) is a water soluble polymer, non-toxic, commonly used in the field of health care. This stabilizer is usually added to the Ag^+ solution before irradiating as a protective colloid Ag nano to restrict the size of the Ag^o cluster development [16-18].

The protection mechanism of Ag nano particles by PVP was through co-ordination, electrostatic repulsion and steric effects as described in scheme 1 [19].



Scheme 1: Schematic illustration of stabilization mechanism of Ag nano particles by PVP

Zhang *et al.* reported that PVP stabilized Ag nano particles better than casein protein and dextrin saccharides [20].

3.1. XRD patterns of PC and PC-AS-Ag nano

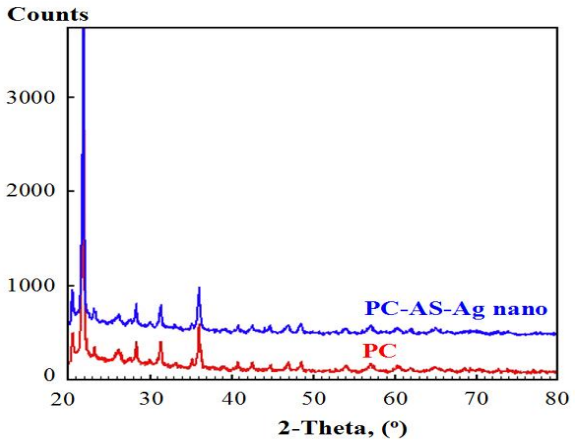


Fig. 1: XRD patterns of PC and Ag nano/AS-PC

Shameli et al. [21] reported XRD patterns of nanocomposite with different Ag nano content from 5000 to 50.000 mg/kg. They confirmed the existence of Ag nano with 4 peaks at 2θ = 38.35, 44.45, 64.70 and 77.64^o, representing the Ag planes of 111, 200, 220 and 311 for crystal Ag nano with typically face-centered cubic (fcc). In Fig. 1, peaks of the crystal Ag nano do not appear, it may be due to the Ag nano content obtained in this study was not enough. Results of ICP-AES analysis indicated that the Ag content in PC-AS-Ag nano was about of 341± 51mg/kg at dose range of 14-20 kGy. The Ag content in PC-AS-Ag sample was higher than that of blank PC (272 mg/kg) without functionalized with AS (data not shown).

3.2. UV-Vis spectra of PC and PC-AS-Ag nano

The maximum absorption wavelength (λ_{max}) of 0.5 % PC-AS-Ag nano measured in 2 % polyvinyl alcohol (PVA) solution was at 422 nm as shown in

Fig. 2. Trinh et al. [9] reported that the λ_{max} values of Ag nano synthesized by γ-irradiation of mixture 5mMAg^+/1%PVP/5%EtOH/water at the conversion dose ($Ag^+ \rightarrow Ag^0$) of 16-20 kGy were in the range of 397-401 nm and the size of Ag nano particles was about 10nm. In addition, Trinh *et al.* also indicated that the content of Ag nano in PC-AS-Ag nano samples prepared by impregnation method of PC-AS samples into Ag nano colloidal solution was of 226 mg/kg, and it was less than that of direct irradiation of PC-AS/Ag^+ mixture (341 mg/kg).

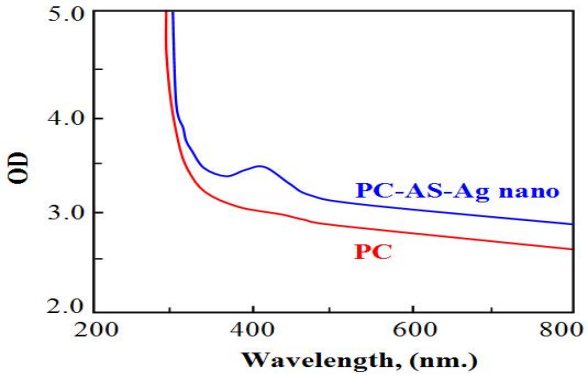
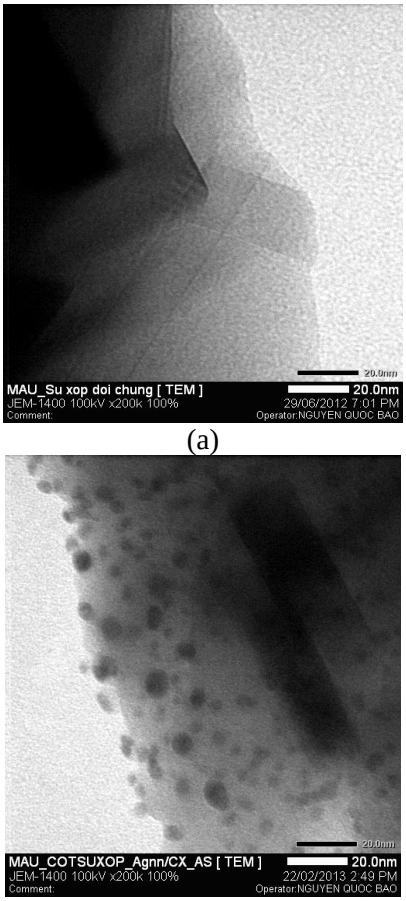


Fig. 2: UV-Vis spectra of PC and PC-AS-Ag nano suspended in solution of PVA 2 %

3.3. TEM images PC and PC-AS-Ag nano

From TEM images in Fig. 3, the size distribution of Ag nano particles deposited on surface of PC-AS sample was estimated as shown in Fig. 4. On the AS functionalized PC surface, siloxane (Si-O-Si) of molecules AS was linked with silanol groups (Si-OH) of PC [9]. Thus in the irradiated PC-AS/Ag^+ mixture, it was believed that the obtained PC-AS-Ag nano material also had the coordination bonds between $–NH_2$ (Si–O–Si–NH_2) groups and Ag atoms on the PC surface due Ag nano has high affinity with $–NH_2$ functional groups of AS. Thus, $–NH_2$ groups play a role of chemical bridge (binder or coupler) on the surface of PC-AS as an linking agent between the PC substrate and Ag nano particles [9]. This mechanism has been reported by Lv et al. [22]. In addition, Trinh *et al.* also reported the results of AS functionalized domestic commercialized porous ceramic product used for fixing Ag nano by impregnation method in colloidal Ag nano solution. The product PC-AS-Ag nano candle filters with the silver content of 200-250 mg/kg and the specific surface area of 1.51 m^2/g, average pore size of 48.2 Å and pore volume of 1.8×10^{-3} cm^3/g showed highly antimicrobial effect that can be applied for point-of-use drinking water treatment [9].



(a)

(b)

Fig. 3: TEM images of PC (a); PC-AS-Ag nano (b)

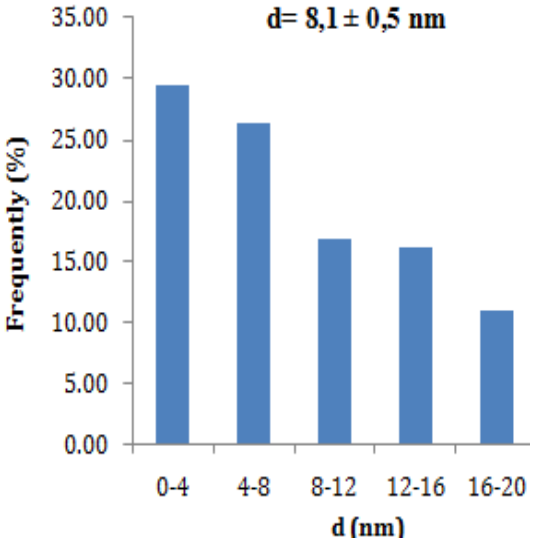


Fig. 4: Histogram of size distribution of Ag nano in PC-AS sample

The size distribution of Ag nanoparticles deposited onto PC-AS prepared was presented in Fig. 4. As a result, the average size of Ag nano deposited onto PC-AS prepared by direct γ-irradiation was about 9 nm that was smaller than that of the Ag nano imbedded into PC by sintering method [10]. According to results reported by Li *et*

al. [13] the size of Ag nano prepared by gamma irradiation was smaller compared with that by chemical reduction method using PVP as a stabilizer [13]. In the study of Lu *et al.* [23], different size of Ag nano also displayed different antibacterial activity against an aerobic oral pathogenic bacteria. The size of Ag nano of about 5 nm exhibited the best antibacterial activity [23]. Phu *et al.* [24] reported that the Ag nano of 10 nm at 5 ppm proved to be the best treatment for reducing bacteria by more than 99.9 %. Due to the rather small size of Ag nano obtained in PC-AS (9 nm) by direct γ-irradiation, the resultant PC-AS-Ag nano product may exhibit highly bactericidal activity that can be favorably applied for water treatment.

4. CONCLUSION

The synthesis of Ag nano deposited into PC functionalized with aminosilan by directly γ-irradiation Co-60 was carried out. Results indicated that the Ag nano size was of 9 nm and the Ag nano content in PC-AS-Ag nano sample was of 341±51 mg/kg at dose of 14-20 kGy. Thus, gamma Co-60 irradiation method has the advantage of creation of small size of Ag nanoparticles with fairly homogenous distribution in PC material. The obtained nanocomposite material namely PC-AS-Ag nano can be favorably applied for point-of-use drinking water treatment.

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