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Study on the preparation of bimetallic silver-copper nanoparticles by electron beam irradiation

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Abstract: Silver and copper nanoparticles are well-known as good antimicrobial agents. In this study, we reported the preparation and characterization of bimetallic silver-copper nanoparticles (Ag-CuNPs) prepared by the electron beam (EB) irradiation method. Chitosan (CTS) was used as a stabilizer agent. The obtained Ag-CuNPs were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV-Vis spectrophotometry. The influence of the different concentrations in the range of 100–1,000 ppm of Ag^+ and Cu^{2+} ions at the mass ratio of $[Ag^+]:[Cu^{2+}] = 1/1$ on the particle size and particle size distribution of the Ag-CuNPs was investigated. The TEM results showed that the average size of the Ag-CuNPs was 11.02–13.73 nm when the total concentration of Ag^+ and Cu^{2+} ions was 250 – 1,000 ppm, respectively. The EB-irradiation method can be applied in the production of Ag-CuNPs on a large scale.

Keywords: *Ag-Cu nanoparticles, bimetallic, chitosan, electron beam.*

I. INTRODUCTION

Nanomaterials applied in agriculture with a potential to reduce the use of traditional chemical products, which contribute to drug resistance, impact human health, and cause environmental pollution [1]. Nanoscale metallic materials have gained research interest for their high activity against bacteria and fungi [2-5]. Silver nanoparticles (AgNPs) have been extensively studied and applied due to their low toxicity and high antibacterial activity. However, their practical use is still costly. As an alternative, research on applications of copper nanoparticles (CuNPs) has shown promising results, due to lower cost and similar antibacterial and antifungal activity compared with AgNPs [6, 7]. However, the CuNPs are easily oxidized during storage, so many studies have been conducted to fabricate of bimetallic silver and copper nanoparticles (Ag-CuNPs) with superior properties compared to single AgNPs and CuNPs [7-9]. Some studies have reported that the antibacterial and antifungal effectiveness of Ag-CuNPs is higher than that of individual AgNPs or CuNPs at the same concentration [8, 9]. This phenominon is attributed to the surface properties of Ag-CuNPs, which play a role in all proposed antimicrobial mechanisms [8]. Additionally, the bimetallic form helps prevent the oxidation of CuNPs into copper ions, thereby increasing their bactericidal and fungicidal effectiveness. For instance, the results in the study of Hong et al., polyester fabrics coated with a mixture of AgNPs and CuNPs demonstrated that antibacterial property was significantly enhanced compared to fabrics treated with AgNPs alone [10]. Another study comparing AgNPs, CuNPs, and their mixture, CuNPs, and Ag-CuNPs found that the antimicrobial activity of Ag-CuNPs was much higher than that of the other [11]. Likewise, in the study of Wang et al., Ag-CuNPs with the mass ratio [Ag]/[Cu] of 1/1

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exhibited stronger inhibitory activity against the growth of Gram-negative bacteria *E. coli* and Gram-positive *S. aureus* compared to AgNPs or CuNPs [12].

However, manufacturing Ag-CuNPs with a small size, high uniformity, and good stability remains a challenge. Currently, popular methods used to manufacture Ag-CuNPs include chemical reduction, thermal decomposition, polyol, laser irradiation, and biology [13, 14]. Research on the manufacturing of Ag-CuNPs bimetallic nanocolloidal solution using the electron beam (EB) irradiation method seems to be still new, both nationally and globally. In this study, we aim to fabricate Ag-CuNPs using the EB irradiation method. This study offers advantages such as conducting the reaction and fabrication process under normal conditions, resulting in a nano colloidal solution. The resulting Ag-CuNPs exhibit high purity, a small grain size, meet clean production requirements, and enable industrial-scale production at competitive prices. Moreover, there is an urgent need for a new generation of nanoparticle products with small particle sizes, high stability, safety, and high bactericidal and fungicidal efficiency for prevention and treatment applications at low content. Treating plant diseases in agriculture with Ag-CuNPs also contributes to limiting toxic pesticides, contribute to protecting the environment, and developing a safe and sustainable agriculture.

II. EXPERIMENTAL

Copper (II) sulfate ($CuSO_4.5H_2O$), silver nitrate ($AgNO_3$), and lactic acid ($C_3H_6O_3$) used in this study were purchased from Shanghai Chemical Co., China. Chitosan (CTS) with a molecular weight of 600,000 g/mol and a deacetylation degree of about 90% was supplied by the Center for Radiation Technology Research and Development (VINAGAMMA), Vietnam. Distilled water was used in all experiments.

To prepare the 2% CTS solution, 2 g CTS was dissolved in 100 ml of 2% lactic acid solution and stirred for 30 minutes. Then, chitosan solution was filtrated using a 100-mesh stainless steel mesh to eliminate undissolved parts. After that, a required amount of $AgNO_3$ and $CuSO_4$ salts dissolved in water was added into the CTS solution to obtain the total concentration of Ag^+ and Cu^{2+} from 100 to 1,000 ppm with the mass ratio $[Ag^+]/[Cu^{2+}]$ of 1/1, and the final CTS concentration of 1.5%. The resulting Ag^+/Cu^{2+}/CTS solution was placed in a plastic bag and irradiated to obtain the Ag-CuNPs solution on an electron beam machine at the VINAGAMMA Center. The prepared Ag-CuNPs solutions were investigated with UV-Vis spectroscopy, TEM imaging, X-ray diffraction (XRD), and infrared spectroscopy (FTIR).

For UV-Vis spectrometry, the Ag-CuNPs solution was diluted in water to a 20 ppm solution, calculated based on the Ag^+/Cu^{2+} concentration. The absorbance of the solution was recorded using a UV-Vis spectrophotometer (UV-2401PC, Shimadzu, Japan).

Transmission electron microscope (TEM) images were taken using the TEM model JEM-1400 from JEOL, Japan. TEM images were used to determine the size of the Ag-CuNPs using Photoshop CS4 software [15].

XRD spectrometry was performed on a diffractometer (D2-Phaser, Bruker, Germany) with CuKa radiation. X-ray diffraction patterns of the Ag-CuNPs were recorded in the 2θ range of 10–80^o.

FTIR spectra was determined on a Jasco FTIR - 4700 spectrometer from Easten, MA, USA. The sample measurement range was from 4000 - 400 cm^{-1}, with a resolution mode of 4.00 cm^{-1}.

III. RESULTS AND DISCUSSION

A. The effect of different total concentration of Ag^+ and Cu^{2+}

Ag-CuNPs solutions were prepared using the EB irradiation method with total Ag^+ and Cu^{2+} concentrations of 100, 250, 500, 750, and 1000 ppm and corresponding absorbed doses of 16, 40, 80, 120, and 160 kGy. The results in Figure 1 indicate that the total Ag^+ and Cu^{2+} concentration significantly affected the characteristics of the Ag-CuNPs solution. Specifically, the solution's color changed from light blue (Figure 1a) to dark brown, with a darker color of the Ag-CuNPs solution observed for higher total Ag^+ and Cu^{2+} concentrations and absorbed doses (Figure 1b).

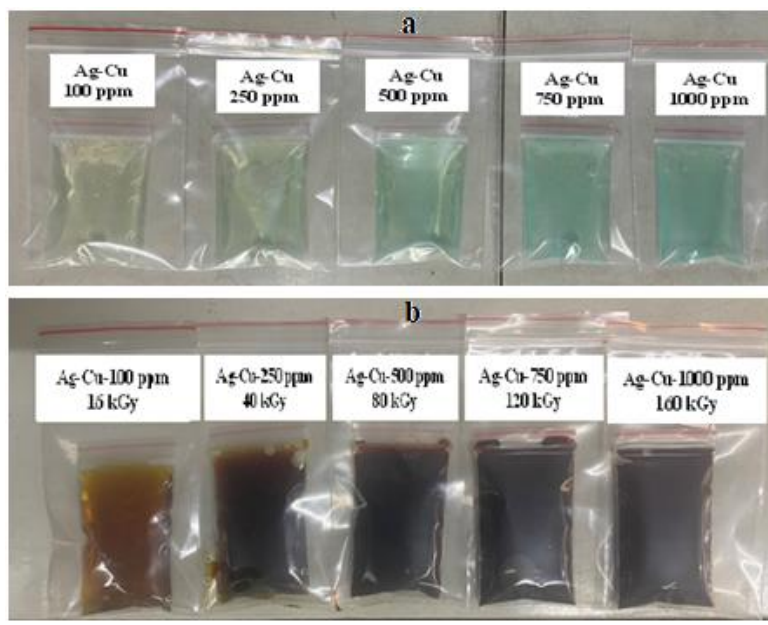

Fig. 1. Ag-CuNPs samples with total Ag^+ and Cu^{2+} concentrations of 100–1,000 ppm, (a) before irradiation; (b) after irradiation

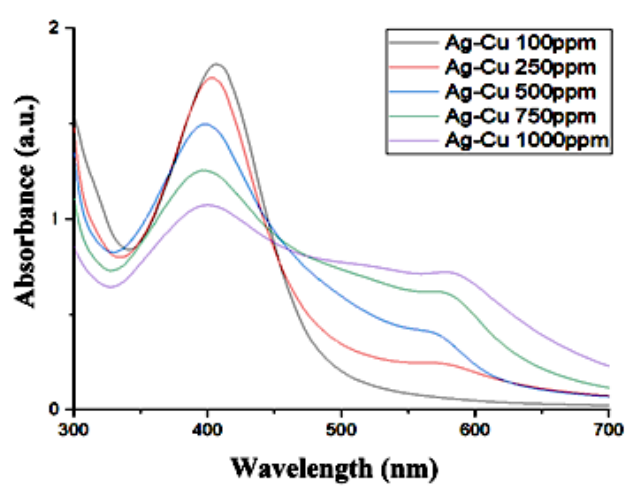

Fig. 2. UV-Vis spectra of Ag-CuNPs solutions with total Ag^+ and Cu^{2+} concentrations of 100–1,000 ppm

The results of Figure 2 demonstrate that the absorbance at the λ_{max} specified for AgNPs decreased when total concentration increased from 100 ppm to 1,000 ppm. Meanwhile, the absorbance at the λ_{max} specified increased. The UV-Vis spectrum of Ag-CuNPs exhibited two absorption peaks, with characteristic wavelengths ranging 380–420 nm for AgNPs and 570–600 nm for CuNPs,

except the 100 ppm sample that did not appear the peak of CuNPs. The results demonstrated that the bimetallic Ag-CuNPs were formed in the solution.

The effect of total Ag^+ and Cu^{2+} concentration on the size of Ag-CuNPs particles is also presented in Figure 3.

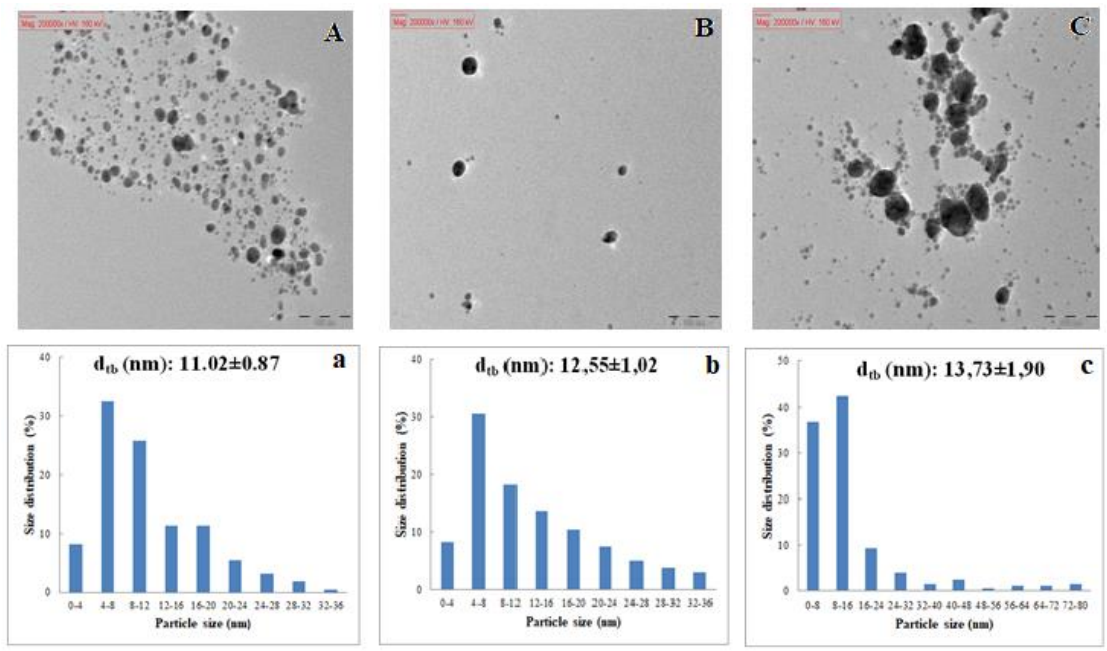

Fig. 3. TEM images and size distribution of Ag-CuNPs with total Ag^+ and Cu^{2+} concentrations of 250 (A,a), 500 (B,b) and 1000 ppm (C,c)

Based on the recorded data in Figure 3, it can be observed that as the total concentration of Ag^+ and Cu^{2+} increased, the particle size also increased. Specifically, at the total Ag^+ and Cu^{2+} concentration of 250 ppm, the average particle size of Ag-CuNPs was 11.02 nm. However, when the total Ag^+ and Cu^{2+} concentration increased to 500 and 1000 ppm, the average sizes Ag-CuNPs increased to 12.55 and 13.73 nm, respectively. These TEM results align with the findings of Zain et al. [16], in which the size of Ag-CuNPs/CTS increased with increasing the total concentration of Ag^+ and Cu^{2+} ions.

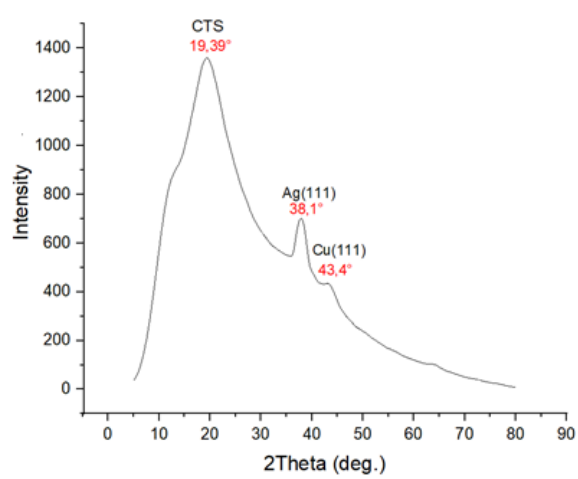

Fig. 4. XRD pattern of Ag-CuNPs

The XRD pattern of the Ag-CuNPs is presented in Figure 4. The pattern exhibited a peak at 2θ position of 43.4°, which is a characteristic crystal peak corresponding to the (111) face in the face-centered cubic structure of Cu metal [17]. In addition, a characteristic crystal peak of silver also appeared at the 2θ position of 38.1°, corresponding to the (111) plane in the

face-centered cubic structure of Ag metal [18]. These parameters indicated the formation of silver and copper crystals in the solution after the EB-irradiating. The XRD pattern also displayed a peak at the 2θ of 19.39°, corresponding to the crystal of CTS [19].

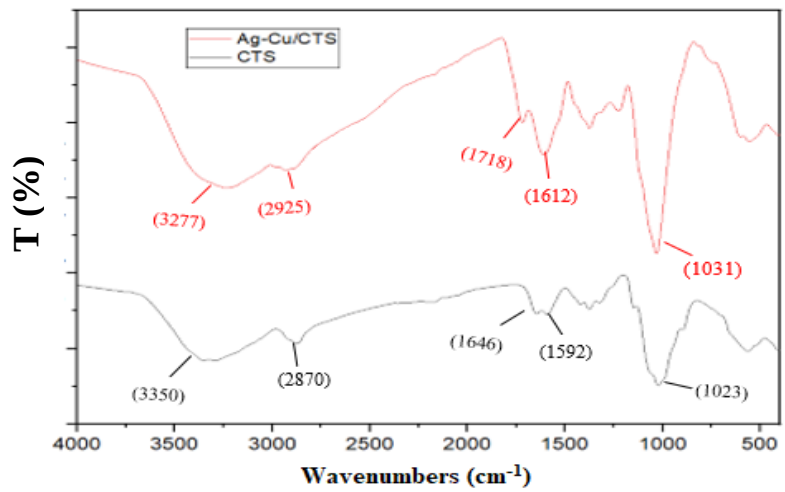

Fig. 5. FTIR spectra of CTS and Ag-CuNPs/CTS samples

The FTIR spectra of the Ag-CuNPs and CTS are shown in Figure 5. In the spectrum of CTS, its characteristic peaks appeared including one at 3350 cm^{-1} corresponds to the vibration of the hydroxyl (-OH) group, 2870 cm^{-1} characterizes the the C–H bond, 1592 cm^{-1} represents the vibration of the primary amine group ($–NH_2$), and 1023 cm^{-1} corresponds to the C–O bond [20]. In the FTIR spectrum of Ag-CuNPs/CTS, characteristic peaks of CTS also appeared. However, there were shifts of wavenumber at the specific peaks. Typically, the peak at 3350 cm^{-1}, characterizing vibration of –OH groups (CTS), was shifted to the lower wavernumber at 3277 cm^{-1} for Ag-CuNPs/CTS. Concurrently, the peak at 1592 cm^{-1} of $–NH_2$ vibration (CTS) was also shifted to 1612 cm^{-1} in the case of Ag-CuNPs/CTS.The changes in wavenumber of peaks can be explained by the participation of Ag-CuNPs in formation of coordination bonds with oxygen and nitrogen on the CTS chain. These bond help prevent flocculation to stabilize the Ag-CuNPs effectively.

CONCLUSIONS

Bimetallic Ag-CuNPs with a size of about 11 – 14 nm were successfully prepared by electron beam irradiating. The size of Ag-CuNPs depended on the initial total concentration of Ag^+ and Cu^{2+} ions, the higher the concentration, the larger the size of Ag-CuNPs. The synthesized Ag-CuNPs with EB-irradiation method with small particle size were convenient for production. Therefore, this material has great potential for use as an antimicrobial agent.

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