Vietnam Journal of Chemistry, International Edition, **55**(2): 211-215, 2017
DOI: 10.15625/2525-2321.2017-00446

Synthesis of gelatin stabilized gold nanoparticles with seed particles enlargement by gamma Co-60 irradiation

Nguyen Ngoc Duy[1], Doan Thi Thu Thao[2], Hoang Thi Dong Quy[2], Dang Van Phu[1], Bui Duy Du[3*], Nguyen Quoc Hien[1]

[1]*Research and Development Center for Radiation Technology, Viet Nam Atomic Energy Institute*

[2]*University of Science*

[3]*Institute of Applied Materials Science, Vietnam Academy of Science and Technology*

Received 31 October 2016; Accepted for publication 11 April 2017

Abstract

Gold nanoparticles (AuNPs) with size from 13 to ~36 nm were synthesized by γ-irradiation method using gelatin as stabilizer. The AuNPs with controllable size were prepared using various concentration of Au^{3+} from 0.5 to 2 mM and seed particle enlargement with different ratios of $[Au^{3+}]/[Au^{o}]$ up to 50. Maximum absorption wavelength (λ_{max}) was measured by UV-Vis spectroscopy, and particle size was determined from TEM images. Results showed that the size of AuNPs increased with the Au^{3+} concentration. The seed enlargement approach is efficient to control the size of AuNPs. The value of λ_{max} shifted from 527.5 nm (seed particles) to 537.5 nm, and the size of AuNPs increased from 13 nm (seed particles) to ~36 nm for concentration ratio of $[Au^{3+}]/[Au^{o}]$ up to 40. Thus, γ-irradiation method is favorable for production of AuNPs with controllable size and high purity. The AuNPs/gelatin synthesized by γ-irradiation with the advantages of environmental friendly and mass production process may be potentially promising for applications in medicines, cosmetics and in other fields as well.

Keywords. Gold, Nanoparticles, Gelatin, γ-irradiation.

1. INTRODUCTION

Gold nanoparticles (AuNPs) with different sizes and shapes have unique optical [1-2], antioxidant [3-4], catalytic [5], and chemical [6] properties. A number of methods have been reported for the synthesis of AuNPs, such as chemical reduction [3, 7], photochemical [8], sonochemical [9], and radiolytic [10-12] method. In comparison with other methods, gamma Co-60 ray irradiation is considered as an effective method with several advantages such as: (1) the reaction is carried out at room temperature; (2) the yield of AuNPs is high; (3) AuNPs can be purely prepared without contamination of excessive chemical reductant and Au^{3+} ions residue; (4) the size of AuNPs is easily controlled by varying Au^{3+} ions or seed enlargement approaches; (5) mass production can be carried out and (6) processing is satisfied to requirement of clean production [12]. According to Chmielewski et al. [13], the use of radiation (gamma, electro and ion beams) has proved to be an essential technique for fabrication of nanostructure with high resolution and furthermore, they reported that three groups of products could be considered to be fabricated by radiation techniques: nanoparticles, nanogels and nanocomposites.

Synthesis of AuNPs with desired size and shape has enormous importance in scientific research and practical application because small changes in the size or shape of nanoparticles can have great effect on a variety of physical properties of the material. Changes in size cause the AuNPs to have different applications, therefore some approaches were used to adjust size of AuNPs such as change of concentration of Au^{3+} ion, stabilizer or molecular weight of stabilizer, pH, reduction rate, and reducing agent.

AuNPs can be used in biological applications such as DNA sensor [14] drug delivery [15], in cosmetic, in cancer diagnostic and therapy [1] should be biocompatible and nontoxic. Thus, besides the "green" synthesis method, natural polymers such as chitosan [3, 8, 16], alginate [11], hyaluronan [12], soluble starch [17], gum arabic [18], heparin [19], and gelatin [20] have been used as stabilizers. Gelatin is a water soluble polypeptide derived from insoluble collagen and has been widely used for

food, pharmaceutical, and medical application [21]. Due to the presence of functional groups including $–NH_2$, –SH and –COOH, and biocompatibility, biodegradability, and nontoxicity [20, 21], gelatin is an ideal natural protein (polypeptide) to use as stabilizer for the synthesis of noble metal nanoparticles.

In this work, gelatin was used as a stabilizer for radiolytic synthesis of AuNPs with controllable size by varying Au^{3+} concentration and by seed enlargement by varying $[Au^{3+}]/[Au^o]$ concentration ratio.

2. MATERIALS AND METHODS

Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4.3H_2O$) and pure water obtained from Merck, Germany. Gelatin was purchased from Sigma-Aldrich.

For the synthesis of AuNPs seed, 2 ml of 10 mM $HAuCl_4$ was added to 10 ml of 2 % (w/v) aqueous gelatin, then the mixture was filled with water to the final volume of 20 ml for preparing solution of 1 mM Au^{3+}/1 % gelatin. The same process was used for preparing solution of 0.5 and 2 mM Au^{3+}/1% gelatin. Irradiation was carried out on a Co-60 irradiator at VINAGAMMA Center, Ho Chi Minh City with dose of about 8 kGy and dose rate of 1.3 kGy/h measured by the ethanol-chlorobenzene (ECB) dosimetry system from mean value of absorbed doses of three dosimeters at 25 °C (ASTM International, 2004) [22].

The obtained AuNPs solution from irradiated solution of 1 mM Au^{3+}/1 % gelatin was used as seeds for further particle enlargement. One volume of as-synthesized 1 mM AuNPs/1 % gelatin solution was mixed 10, 20, 30, 40 and 50 part of 1 mM Au^{3+}/1% gelatin solution. The overall gold concentration ($[Au^{3+}] + [Au^o]$) in these mixtures was again of 1 mM, but the Au^{3+} concentration was from 10 to 50 times larger than that of AuNPs. Irradiation was carried out as the same as above description.

The UV-Vis spectra of the obtained AuNPs solutions which were diluted by water to 0.1 mM calculated as Au^{3+} concentration were recorded using UV-Vis spectrophotometer model UV-2401PC, Shimadzu, Japan. The size of AuNPs was characterized by a transmission electron microscope (TEM) model JEM 1010, JEOL, Japan operating at 100 kV.

3. RESULTS AND DISCUSSION

3.1. Effect of Au^{3+} concentration

In the first experiment, AuNPs were prepared from samples containing 1 % (w/v) gelatin with different Au^{3+} concentrations particularly 0.5, 1 and 2 mM. The UV-Vis absorption spectra (Fig. 1) of AuNPs solutions showed the maximum absorption wavelengths (λ_{max}) at 527, 527.5 and 530 nm for Au^{3+} concentrations of 0.5, 1 and 2 mM, respectively. The TEM images and size distributions of three AuNPs samples were showed in Fig. 2. The average diameters for the AuNPs were of 12, 13 and 17 nm for Au^{3+} concentrations of 0.5, 1 and 2 mM, respectively. Results showed that with the increase of Au^{3+} concentration the AuNPs became bigger and λ_{max} shifted to longer wavelengths. The similar results were also observed earlier by Anh et al. in the study on synthesis of AuNPs by γ-irradiation using alginate as a stabilizer [11].

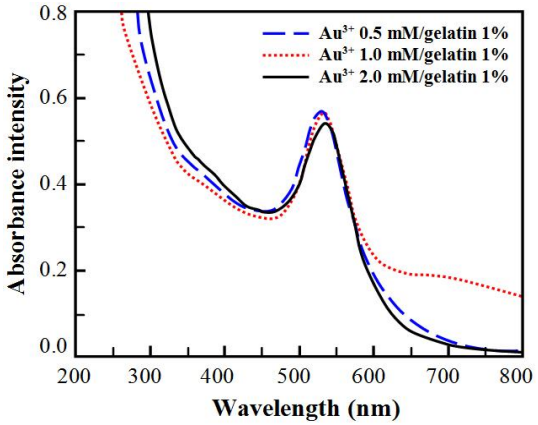

Figure 1: UV-Vis spectra of AuNPs stabilized by 1 % gelatin with Au^{3+} 0.5, 1 and 2 mM

3.2. Enlargement of seed particles

Our attempt is to develop a "green" γ-irradiation synthetic method for the enlargement size of AuNPs. In the first step, the AuNPs with diameter of 13 nm prepared from solution of 1 mM Au^{3+}/1% gelatin were used as seeds for preparation of AuNPs with the larger size. In the enlargement step, appropriate amounts of precursor Au^{3+} ions and AuNPs solution were mixed and irradiated for the growth of the seeds diameter. In this approach the seeds act as nucleation centers and become larger ones due to the reduction of the Au^{3+} ions absorbed on surface of the seeds [10, 11].

UV-Vis absorption spectra of AuNPs solution (Fig. 3) showed that the λ_{max} value of AuNPs shifted from 527.5 nm (seeds) to 533, 535, 536, 537.5 and 538 nm, and the size of AuNPs also increased particularly to 21 nm (Fig. 4A,a), 23 nm (Fig. 4B,b), 33 nm (Fig. 4C,c), 36 nm (Fig. 4D,d) and ~36 nm

(Fig. 4E,e) for $[Au^{3+}]/[Au^{o}]$ = 10, 20, 30, 40 and 50, respectively. In addition, it was observed in Figs. 2B, 2C & Fig. 4 for as-synthesized AuNPs that beside the spherical AuNPs, triangle AuNPs were also formed not only for seed AuNPs (Fig. 2B) but also for enlarged AuNPs (Fig. 4). The results also indicated that the AuNPs size was almost not increased further for the $[Au^{3+}]/[Au^{o}]$ ratio from 40 to 50. This $[Au^{3+}]/[Au^{o}]$ ratio range may be considered as a critical ratio for seed enlargement of AuNPs synthesized by γ-irradiation method using gelatin as a stabilizer.

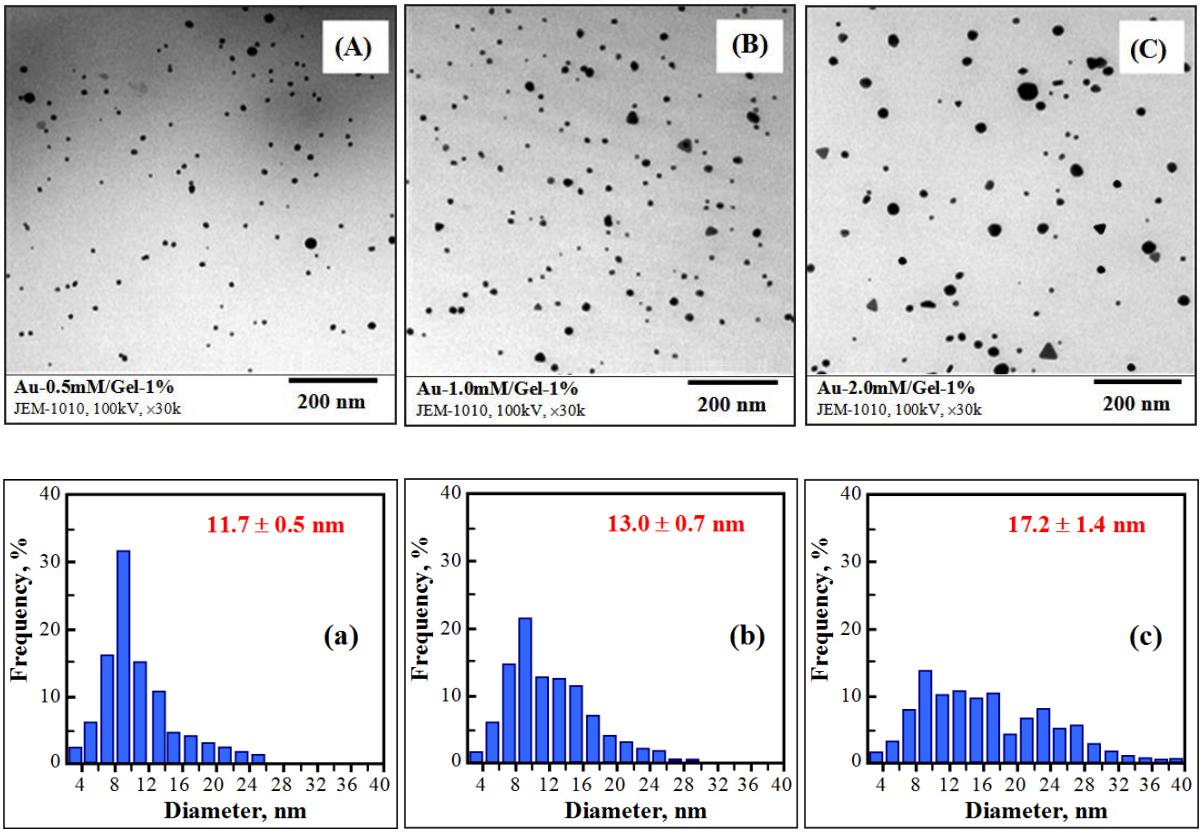

Figure 2: TEM images and size distribution histograms of AuNPs stabilized by 1 % gelatin with Au^{3+} 0.5 mM (A, a); 1 mM (B, b) and 2 mM (C, c)

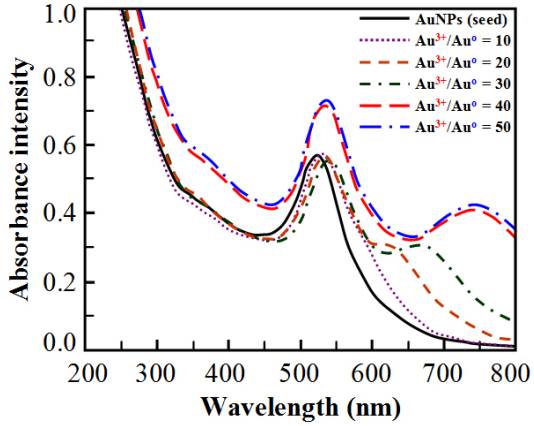

Figure 3: UV-Vis spectra of of AuNPs obtained by enlargement of AuNPs seed for ratio of $[Au^{3+}]/[Au^{o}]$ = 10, 20, 30, 40 and 50

The obtained results were relatively compatible with the results reported by Henglein & Meisel when AuNPs were synthesized by γ-irradiation with enlargement of seed particles using polyvinyl alcohol as stabilizer [10]. In our previous works, AuNPs were also synthesized with enlargement size by γ-irradiation using alginate and water soluble chitosan as stabilizer [11, 16]. For alginate, the size of AuNPs increased from 20 nm (seeds) to 39 nm, and the critical ratio of $[Au^{3+}]/[Au^{o}]$ was of 6 [11]. While for water soluble chitosan, the size of AuNPs increased from 10 nm (seeds) to 20, 38 and 53 nm for $[Au^{3+}]/[Au^{o}]$ = 2.5, 5 and 10, respectively and then decreased to 42 nm and 19 nm for $[Au^{3+}]/[Au^{o}]$ = 20 and 40 with particle size dispersed in two size ranges (small size and large size) [16]. The reason may be due to the formation of new nucleation centers from reduction of Au^{3+} to Au^{o} in solution and the reduction Au^{3+} adsorbed onto the "seed" particles surface to enlarge the particle size of AuNPs occurred simultaneously at high

concentration ratio of $[Au^{3+}]/[Au^{o}]$. Thus, by using seed enlargement approach, the increase of AuNPs size depends not only on the synthetic method but also on a certain particular stabilizer.

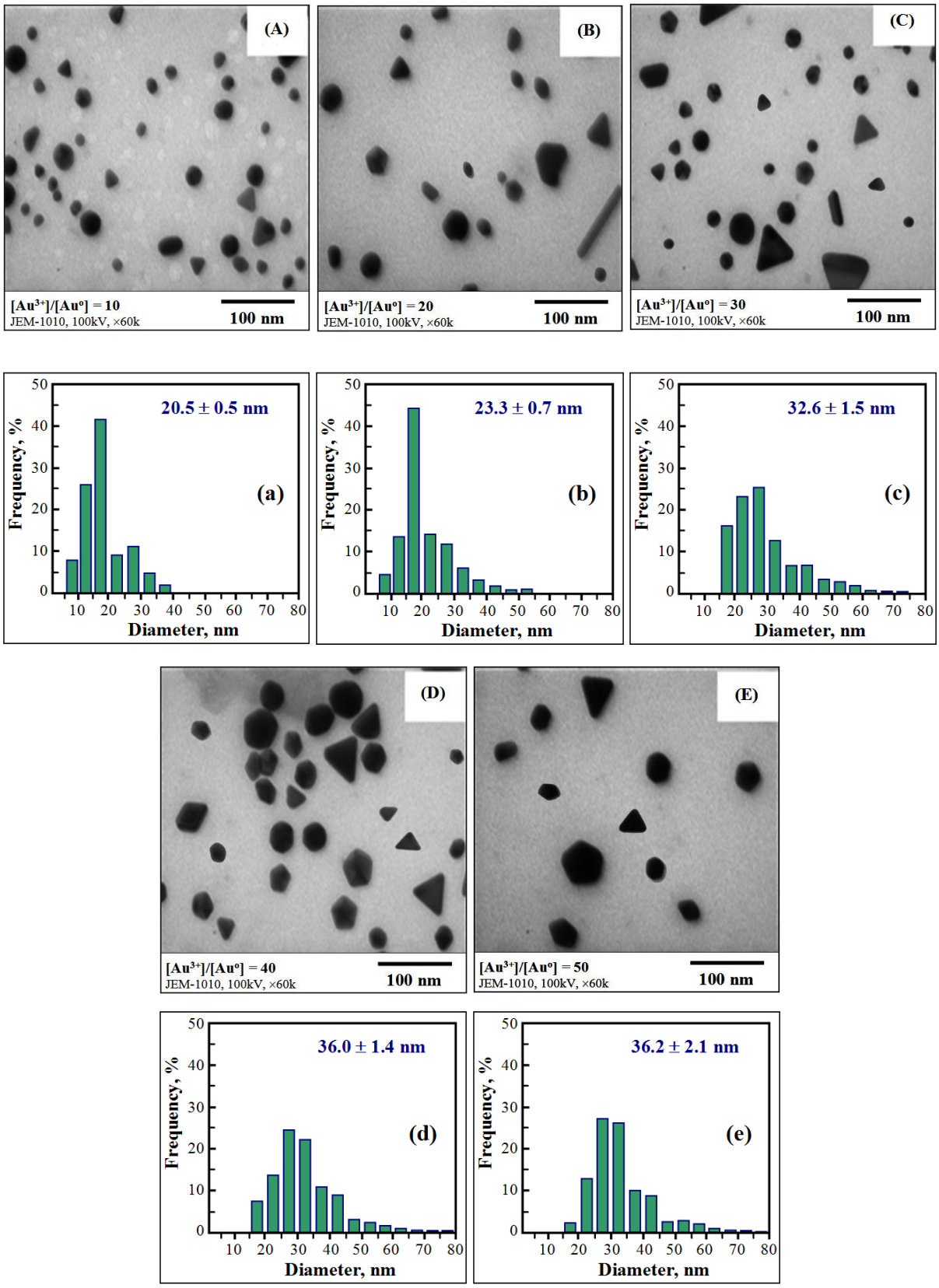

Figure 4: TEM images and size distribution histograms of AuNPs obtained by enlargement of seed for ratio of $[Au^{3+}]/[Au^{o}]$ = 10 (A,a), 20 (B,b), 30 (C,c), 40 (D,d) and 50 (E,e)

4. CONCLUSION

AuNPs were successfully synthesized by γ-irradiation using gelatin as stabilizer and controllable size by seed enlargement approach. The size of AuNPs was desirously increased from 13 nm (seeds) to ~36 nm by adjusting concentration ratio of $[Au^{3+}]/[Au^{o}]$ to 40. Thus, based on the compatibility of gelatin and the unique attribute of AuNPs, the pure colloidal AuNPs/gelatin solution synthesized by γ-irradiation, a facile and environmental friendly process can be potentially applied in biomedicines, cosmetics, and in other fields as well.

REFERENCES

1. I. H. El-Sayed, X. Huang, M. A. El-Sayed. *Selective laser photo-thermal therapy of epithelial carcinoma using anti-EGFR antibody conjugated gold nanoparticles*, Cancer Lett., **239**, 129-135 (2006).
2. I. L. Maksimova,, G. G. Akchurin, B. N. Khlebtsov, G. S. Terentyuk, G. G. Akchurin, I. A. Ermolaev, A. A. Skaptsov, E. P. Soboleva, N. G. Khlebtsov, V. V. Tuchin. *Near-infrared laser photothermal of cancer by using gold nanoparticles: Computer silmulations and experiment*, Med. Laser Appl., **22**, 199-206 (2007).
3. K. Esumi, N. Takei, T. Yoshimura. *Antioxidant-potentiality of gold-chitosan nanocomposites*, Coll. Surf. B: Biointerfaces, **32**, 117-123 (2003).
4. N. O. Yakimovic, A. A. Ezhevskim, D. V. Guseinov, L. A. Smirnova, T. A. Gracheva, K. S. Klychkov. *Antioxidant properties of gold nanoparticles study by ESR spectroscopy*, Russ. Chem. Bull., **57**, 520-523 (2008).
5. J. Kim, Z. Dohnalek, B. D. Kay. *Cryogenic CO_2 formation on oxidized gold clusters synthesized via reactive layer assisted deposition*, J. Am. Chem. Soc., **127**, 14592-14593 (2005).
6. W. S. Cho et al. *Size-dependent tissue kinetics of PEG-coated gold nanoparticles*, Toxicol. Appl. Pharmacol., **245**, 116-123 (2010).
7. H. Huang, X. Yang. *Synthesis of polysaccharide-stabilized gold and silver nanoparticles: a green method*, Carbohydr. Res., **339**, 2627-2631 (2004).
8. T. K. Sau, A. Pal, N. R. Jana, Z. L. Wang, T. Pal. *Size controlled synthesis of gold nanoparticles using photochemically prepared seed particles*, J. Nanopart. Res., **3**, 257-261 (2001).
9. K. Okitsu, Y. Mizukoshi, T. A. Yamamoto, Y. Maeda, Y. Nagata. S*onochemical synthesis of gold nanoparticles on chitosan*, Mater. Lett., **61** 3429-3431 (2007).
10. A. Henglein, D. Meisel. *Radiolytic control of the size of colloidal gold nanoparticles*, Langmuir **14**, 7392-7396 (1998).
11. N. T. Anh, D. V. Phu, N. N. Duy, B. D. Du, N. Q. Hien. *Synthesis of alginate stabilized gold nanoparticles by g-irradiation with controllable size using different Au^{3+} concentration and seed particles enlargement*, Rad. Phys. Chem., **79**, 405-408 (2010).
12. N. Q. Hien, D. V. Phu, N. N. Duy, L. A. Quoc. *Radiation synthesis and characterization of hyaluronan capped gold nanoparticles*, Carbohyd. Polym., **89**, 537-541 (2012).
13. A. G. Chmielewski, D. K. Chmielewska, J. Michalik, M. H. Sampa. *Prospects and challenges in application of gamma, electron and ion beams in processing of nanomaterials*, Nucl. Inst. Meth. Phys. Res. B, **265**, 347-351 (2007).
14. T. Liu, J. Tang, L. Jiang. *Enhancement effect of gold nanoparticles as a surface modifier on DNA sensor sensitivity*, Biochem. Biophys. Res. Commun., **313**, 3-7 (2004).
15. Y. C. Yang, C. H. Wang, Y. K. Hwu, J. Ho. Je. *Synchrotron X-ray synthesis of colloidal gold particles for drug delivery*, Mater. Chem. Phys., **100**, 72-76 (2006).
16. N. N. Duy, D. Xu. Du, D. V. Phu, L. A. Quoc, B. D. Du, N. Q. Hien. *Synthesis of gold nanoparticles with seed enlargement size by γ-irradiation and investigation of antioxidant activity*, Coll. Surf. A: Physicochem. Eng. Aspects, **426**, 633-638 (2013).
17. S. T. Hussain, M. Iqbal, M. Mazhar. *Size control synthesis of starch capped gold nanoparticles*, J. Nanopart. Res. **11**, 1383-1391 (2009).
18. C. C. Wu, D. H. Chen. *Facile green synthesis of gold nanoparticles with gum Arabic as a stabilizing agent and reducing agent*, Gold Bull. **43**, 234-240 (2010).
19. Y. Guo, H. Yan. *Preparation and characterization of heparin-stabilized gold nanoparticles*, J. Carbohydr. Chem., **27**, 309-319 (2007).
20. Y. Liu, X. Liu, X. Wang. *Biomimetic synthesis of gelatin polypeptide-assisted noble metal nanoparticles and their interaction study*, Nanoscale Res. Lett., **6**, 22 (2011).
21. M. Darroudi, M. B. Ahmad, M. Hakimi, R. Zamiri, A. K. Zak, H. A. Hosseini, M. Zargar. *Preparation, characterization, and antibacterial activity of γ-irradiated silver nanoparticles in aqueous gelatin*, Int. J. Min. Met. Mater., **20**, 403-409 (2013).
22. ASTM International, *Standard practice for use of the ethanol-chlorobenzene dosimetry system*. ISO/ASTM 51538:2002(E), Standards on dosimetry for radiation processing, 2004, p. 87.

Corresponding author: **Bui Duy Du**
Institute of Applied Materials Science - VAST
01 Mac Dinh Chi Steet, District 1, Ho Chi Minh City
E-mail: vina9802@gmail.com; Telephone number: 0931797968.