**Lysimachia christinae** polysaccharide mediated facile synthesis of gold-silver alloy nanoparticles for catalytic reduction of 4-nitrophenol

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**Abstract.** We report here an environmentally benign and facile approach for the synthesis of gold-silver alloy nanoparticles. This approach involves the co-reduction of HAuCl₄ and AgNO₃ by employing *Lysimachia christinae* polysaccharide as both reductant and stabilizer without the introduction of any other surfactant. The formed gold-silver alloy nanoparticles exhibited relatively narrow distribution and good stability. Generation of the gold-silver alloy nanoparticles were observed by UV-vis spectroscopy, transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The reaction of 4-nitrophenol reduction was employed to evaluate the catalytic property of gold-silver alloy nanoparticles, and it was found that the alloy nanoparticles (χAu = 0.5) have better catalytic performance than the corresponding monometallic nanoparticles.

1. **Introduction**

Noble metal nanoparticle (NP) has recently attracted great attention owing to their excellent physicochemical properties and wide potential applications in sensing, catalysis and bio-imaging [1, 2]. Particularly, the complex compositions and structures of alloy NPs can combine the functions of their monometallic counterparts, and thus usually exhibit enhanced physical and chemical properties [3, 4]. For instance, in the field of catalysis, the preparation of alloy NPs is of great importance due to their better catalytic performance that arise from the synergistic effect between the metals [5, 6].

Several synthetic methodologies such as thermal evaporation, plasma spraying, radiation-induced synthesis, electrochemical synthesis have been used recently to generate alloy NPs. Wet chemical synthesis through the co-reduction of noble metal salts using appropriate reductant and stabilizer has gained much interest due to its convenience and controllability [7-10]. In most cases, chemical reductants or traditional organic solvents, such as sodium borohydride, hydrazine or oleylamine, were involved in the synthetic process, which would pose some environmental or biological risks [11]. Therefore, it is highly desirable to develop reliable environmentally benign protocols to synthesize bimetallic alloy nanoparticles. Biological methods for NPs preparation using proteins [12], microorganisms [13], plant extracts [14] and polysaccharides [15] have been considered as a class of
possible environmentally friendly alternatives to traditional chemical methods. Generally, biosynthesis of NPs has many advantages in the perspective of decreasing the introduction of harmful chemicals and minimizing risks during the industrial and biomedical applications.

Among the various biological materials, polysaccharide is a class of significant natural biopolymer resource for the preparation of metal NPs. Since Raveendran et al. first used starch to prepare silver NPs in a completely green way [16], many studies have studied the effect and mechanism of different polysaccharides on the generation of metal NPs. For instance, Emam used Arabic gum as biosynthesizer for the generation of Ag-Au bimetallic NPs [17]. Gao et al. synthesized Au NPs with narrow size distribution and good stability through the reduction of HAuCl₄ using konjac glucomannan in a one-pot manner [18]. Moreover, cellulosic solid support was also employed as reductant and stabilizer for the production and deposition of bimetallic catalytic nanostructures [5]. During these synthesis processes, polysaccharides usually served as reductant or stabilizing agent because of their abundant functional groups and diverse structural characteristics. In our previous research, a water-soluble polysaccharide, Lysimachia christinae polysaccharide (LCP), has been extracted from a widely distributed plant which is commonly known as “Jinqiancao” in China, and explored as moisturizing agent during processing of agricultural products [19]. Moreover, LCP has been extensively studied for its diverse important functions in healthcare and pharmacology, such as clearing heat, diuresis, anti-inflammation and analgesia [20]. Herein, we attempt to employ LCP for the preparation of metal NPs and thus further promoting its application in nanotechnology.

In the present study, LCP was utilized for the facile and green synthesis of gold-silver (Au–Ag) alloy NPs by serving as both reductant and stabilizer through the co-reduction manner (Figure 1). Various techniques such as UV-vis absorption spectroscopy (UV-Vis), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were adopted to observe the nature of the alloy NPs. Furthermore, catalytic activity of the synthesized alloy NPs was evaluated through the reduction of p-nitrophenol (4-NP) into p-aminophenol (4-AP).

![Figure 1. Schematic of the procedure followed to prepare Au–Ag alloy NPs and its application in catalytic reduction of 4-NP](image)

2. Materials and methods

2.1. Materials
Silver nitrate (AgNO₃), Chloroauric acid (HAuCl₄) and sodium borohydride (NaBH₄) were purchased from Aladdin Reagent Company (Shanghai, China). LCP and 4-NP (99%) were purchased from Sinopharm Chemical Regent Co., Ltd (Shanghai, China). Deionized water was used for all the experiments.

2.2. Facile and green synthesis of Au-Ag alloy NPs
LCP powder (1.0 g) was dispersed in 600 mL water at 60 °C by stirring for 1 hour. Afterward, the dispersion was filtered to remove foreign nucleation sources and stored for further experiments. The preparation of Au-Ag alloy NPs involves the chelating adsorption of metal ions onto the functional
groups of LCP and the subsequent co-reduction process. During a typical procedure, 2 mL of AgNO₃ (1 mM) and 2 mL of HAuCl₄ were sequentially injected into a 40 mL LCP solution that preheated at 85 °C. The mixture was further heated at 85 °C under intense agitation for 0.5 hour before cooling down to room temperature. After that, the alloy NPs hydrosol was obtained by collecting supernatant after centrifugation at 4000 rpm for 15 min. The composition of Au-Ag alloy NPs can be regulated by altering the molar ratios of metal precursors (Au:Ag ratios were 1:3, 1:1, and 3:1, respectively). Meanwhile, as a control, monometallic Ag and Au NPs were also synthesized according to the same procedure by substituting the AgNO₃/HAuCl₄ mixture with single AgNO₃ or HAuCl₄ solution, respectively.

2.3. Catalytic reduction of 4-NP

The catalytic property of the synthesized metal NPs was investigated by employing the reduction of 4-NP as a model reaction system according to our previously reported method [21]. In a typical experiment, 0.1 mL of the as-prepared metal NPs dispersion was added into a mixed solution containing 7 mL of water and 0.75 mL of 4-NP (3 mM). Subsequently, 1 mL of fresh NaBH₄ solution (0.3 M) was injected under continuous stirring at 308.15 K to start the reduction reaction. At specific time interval, an appropriate volume of the reaction solution was transferred into a quartz cuvette to record the UV-vis absorption spectra for monitoring the reaction progress.

2.4. Characterization techniques

UV-vis absorption spectra of the synthesized metal NPs was recorded using a TU-1810 (Persee, China) spectrometer. Micromorphology and size distribution of the Au–Ag alloy NPs were characterized using transmission electron microscope (TEM, JEM-2100F, 200 kV) equipped with an EDX analysis attachment. X-ray diffraction (XRD) analysis was performed by employing a D/max 2500 XRD spectrometer (Rigaku, Japan). X-ray photoelectron spectra (XPS) characterization of the Au–Ag NPs was carried out on an electron spectrometer (ESCALAB 250Xi, Thermo) equipped with an Al Kα radiation (hv = 1486.6 eV).

3. Results and discussion

3.1. UV-Vis spectral analysis

The synthetic procedure for the preparation of Au–Ag alloy NPs, namely, through a co-reduction process of AuCl₄⁻ and Ag⁺ in the presence of LCP under 85 °C was illustrated Figure 1. By altering the molar ratio of the initial metal precursors, Au-Ag alloy NPs with different compositions or monometallic Au and Ag NPs were obtained. Figure 2a shows the solutions of the synthesized pure Ag, Au and three alloy NPs with different gold molar fractions (χAu). A gradual color changes from yellow to yellowish-brown to pink and purple can be observed with an increase in the Au/Ag ratio. UV-vis spectroscopy was used to characterize the optical property of as-prepared NPs [22]. In fact, UV-vis is a convenient method to distinguish whether the structural feature of bimetallic NPs are mixed alloys or core-shells. Figure 2b shows the corresponding UV-Vis spectra of the NPs solutions that shown in Figure 2a. The spectra of pure Ag and Au NPs exhibit the characteristic surface plasmon resonance (SPR) absorption peak around 416 nm and 544 nm, respectively. This result confirmed LCP could reduce metal precursor into NPs owing to its abundant functional groups. At the same time, only a single absorption peak that located between the absorption peaks of pure Au and Ag NPs is observed for each bimetallic Au–Ag NPs sample. This phenomenon indicates the structure of co-reduced bimetallic Au–Ag NPs is mixed alloy rather than core-shells or a simple mixing of pure Ag and Au NPs [23].

Figure 2c exhibits the plot of maximum absorbance wavelength (λmax) of NPs versus the χAu, and a good linear relationship was observed. This result was ascribed to the different high-frequency dielectric constants of Au and Ag, which led to a perturbation of the D-band energy levels and subsequently a shifting of the absorption band during the alloy formation [24]. Moreover, the
relationship between the position of the absorption peak and the Au/Ag ratio strongly confirmed the alloy pattern of the bimetallic NPs.

![Figure 2. (a) UV-vis spectra of the as-prepared NPs with different initial Au/Ag molar ratios. (b) Plot of the λ_max versus χ_{Au}.](image)

3.2. Morphology and structure analysis

The morphology and size distribution of the synthesized Au–Ag alloy NPs were characterized by TEM measurement. Some typical TEM images of the alloy NPs (χ_{Au} = 0.5) are shown in Figure 3a, b, which demonstrate that the NPs exhibit approximately spherical shape with several big particles. However, lattice fringes can be hardly seen from the high magnification TEM image (Figure 3b), maybe due to the capping effect of LCP biomacromolecule on NPs surface. Figure 3c shows the histogram of size distribution of alloy NPs viewed from TEM images. The particle sizes distribute in the range of 2.4 to 10.6 nm, with an average diameter of 5.68 nm. More than 80% of the particles are in the range of 2.9 to 7.5 nm, indicating a relatively narrow distribution of the Au–Ag alloy NPs. Generally speaking, small nanoparticles in solution tend to self-aggregation due to their high surface energy [25]. Actually, the synthesized NPs dispersion in this work exhibited good stability without visible aggregation or precipitation occurring even after storage for two months. This indicated that the LCP could serve as stabilizer to protect nanoparticles from aggregation after the reduction of metal precursors. Furthermore, the elemental composition characterized by EDX (Figure 3d) simultaneously shows the characteristic peaks of Au and Ag, which also confirm the formation of alloy nanoparticles.
Figure 3. (a, b) Representative TEM images of the morphology of the Au–Ag alloy NPs ($\chi_{Au} = 0.5$). (c) The particle size distribution histogram of the corresponding NPs. (d) EDX elemental analysis of alloy NPs.

The XRD pattern of the as-prepared Au–Ag alloy NPs is presented in Figure 4. Bragg reflection peaks at $2\theta = 38.5^\circ$ and $44.3^\circ$ could be readily indexed to the (111) and (200) reflections of face-centered cubic structure, respectively. In order to confirm the construction and valence state of elements in the Au–Ag alloy NPs, the XPS measurements were performed. The survey scan spectrum of LCP stabilized Au–Ag alloy NPs is shown in Figure 5a which exhibits the presence of Au 4f, C 1s, Ag 3d, O 1s, and Ag 3p core levels without significant impurities. The existence of C and O indicating the capping effect of LCP on the surface of NPs. Moreover, Figure 5b and c show the Au 4f and Ag 3d core-level XPS spectra. Two peaks at 84.0 and 87.7 eV corresponded to Au 4f$_{7/2}$ and Au 4f$_{5/2}$ binding energies, respectively, which is in agreement with characteristic peaks for metallic Au$^0$[26]. In the Ag spectra, the doublet Ag 3d peaks exhibit the 367.8 (Ag 3d$_{5/2}$) and 373.8 eV (Ag 3d$_{3/2}$) binding energies with a spin-orbit separation equal to 6.0 eV, indicating that Ag exist in the Ag$^0$ metal state [27]. This observation indicates that the metal precursors were completely reduced by LCP and the Au$^0$ and Ag$^0$ were coexisted in the generated alloy NPs.

Figure 4. XRD patterns of Au–Ag alloy NPs ($\chi_{Au} = 0.5$).

Intensive studies have shown that polyphenols, reducing sugars and protein could be used to synthesize Au or Ag NPs [11, 28]. A common feature of these substances is that they contain hydroxyl or carboxyl groups. In this work, LCP was employed both as reductant and stabilizer for the formation of Au–Ag alloy NPs. The hydroxyl and carboxyl groups of biomacromolecule were expected to...
possess the ability to bind and enrich metal ions [18, 22]. Then the chelated Au(III) and Ag(I) could be simultaneously reduced to atoms by the specific functional groups of LCP under an elevated temperature. The continuous accumulation of metal atoms led to the growth of nuclei and formation of Au-Ag alloy NPs. At the same time, the generated alloy NPs were capped and stabilized by the LCP molecules to prevent further agglomeration and to enhance the stability in solution. Therefore, the introduction of LCP here provides a facile and environmentally friendly method for the synthesis of Au–Ag alloy NPs with good stability.

Figure 5. Survey scan (a) and Au 4f (b) and Ag 3d (c) core-level XPS spectra of Au–Ag alloy NPs

3.3. Catalytic property analysis

The bimetallic composition and small particle size of synthesized Au–Ag alloy NPs was expected to promise catalytic activity. Here, the reduction of 4-NP into 4-AP in the presence of NaBH₄ was employed as a target system to evaluate and compare the catalytic properties of as-prepared NPs. The conversion of 4-NP has attracted great attention due to its water pollution problem, while its derivative, 4-AP, is an important intermediate for drug manufacture [27, 29]. Although this reduction reaction is thermodynamically favorable, it does not proceed without catalysts due to the kinetic barrier caused by the large potential difference between the donor and acceptor molecules [30]. In this respect, metal nanocatalyst could catalyze this reaction by acting as an electronic relay system to overcome the kinetic barrier. This reduction reaction could be easily monitored by tracking the variations in the absorbance peak of 4-nitrophenolate ions at 400 nm and therefore was often chosen as a model reaction to evaluate the catalytic activity of various nanocatalyst [1, 21, 30-32].

Figure 6a presents the time-dependent evolution of UV-vis absorption spectra for the reduction of 4-NP with Au–Ag alloy NPs (χ Au = 0.5) as catalyst. A successive intensity decreases of the absorption peak at 400 nm along with a concomitant increase in the new peak at 300 nm is observed because of the consumption of 4-NP, resulting in the fading and ultimate bleaching of the yellow-green colour of 4-nitrophenolate ions. Moreover, all the UV-vis spectra intersect each other at two points, demonstrating that the 4-NP was gradually reduced into 4-AP without the formation of by-product [33]. The completion of the reduction reaction was also visualized by the ultimate discoloration of the characteristic yellow-green color solution. Meanwhile, the catalytic activity of pure Au and Ag NPs was also tested using this reaction for comparison. All these metal NPs could enable the reaction by acting as catalyst to transfer electrons from BH₄⁻ to 4-NP during the reduction process. Figure 6b shows the C_t/C₀ versus reaction time for the reduction of 4-NP over the Au–Ag alloy, pure Au and Ag NPs, where C_t and C₀ are the concentrations of 4-NP at intervals and the initial stage. The reactions were almost completed within 240s, 600 s and 1200 s, respectively.
Figure 6. Catalytic conversion of 4-NP using as-prepared nanocatalysts.
(a) Time-dependent UV-vis absorption spectra for the catalytic reduction of 4-NP to 4-AP over Au–Ag alloy NPs ($\chi_{Au} = 0.5$); (b) Comparison of $C_t/C_0$ versus reaction time over alloy, pure Au and Ag NPs; (c) Plots of $\ln(C_t/C_0)$ versus time for different nanocatalyst; (d) Reaction rate constants calculated from the plots for the as-prepared catalysts.

Since the concentration of NaBH$_4$ in the system was much higher in comparison with that of 4-NP, the reaction rate was reasonably independent of NaBH$_4$ concentration. In this context, the kinetics could be regarded as pseudo-first-order with respect to 4-NP [8]. As expected, the linear correlation between $\ln(C_t/C_0)$ and time is obtained (Figure 6c). The kinetic rate constant is estimated from the slope to be 0.0170, 0.00671, and 0.00275 s$^{-1}$ for Au–Ag alloy, pure Au and Ag NPs respectively (as shown in Figure 6d). This result demonstrates that the Au–Ag alloy NPs possess higher catalytic activity than the corresponding monometallic NPs, revealing the synergistic catalytic effect of Au and Ag species. Meanwhile, the activity of LCP mediated Au–Ag alloy NPs here is comparable to that of other biomolecule stabilized Au-Ag alloy NPs and even Au-Ag alloy-decorated graphene [11]. Generally, the composition and size of NPs are the main factors that affect the catalytic property [27]. In this study, the synergistic electronic effect of alloy NPs may facilitate the electrons transfer and increase the electron density on the surface of nanocatalysts. On the other hand, Au-Ag alloy NPs with small size stabilized by LCP may also contribute to the high catalytic activity, since they could provide higher specific surface area and more potential catalytic sites.

4. Conclusions
In summary, we have reported the facile synthesis of Au-Ag alloy NPs by using LCP as both reductant and stabilizer under a moderate temperature. Compositions of the Au-Ag alloy NPs could be controlled by adjusting the molar ratio of initial metal precursors, and was also evidenced by the SPR wavelength of alloy NPs. The as-prepared Au-Ag alloy NPs ($\chi_{Au} = 0.5$) with an average diameter of 5.68 nm exhibited good stability owing to the capping effect of LCP. Moreover, the alloy NPs possessed better catalytic performance toward the reduction of 4-NP than the corresponding monometallic NPs. This reported method represents a facile approach for the synthesis of alloy-structured NPs for the potential application in catalysis as well as in the other fields.
Acknowledgements

This work was supported by the Science and Technology Project of Henan Province (No. 182102110113), the “Three District” Talents Support Program of Henan Province (No. Yuke[2017]107) to LM, and the Research Foundation of Zhengzhou University of Light Industry (Nos. 2014BSJJ067, 2018ZCKJ325).

References

[1] Sun L., D. Zhang, Y. Sun, et al. (2018) Facile Fabrication of Highly Dispersed Pd@Ag Core−Shell Nanoparticles Embedded in Spirulina platensis by Electroless Deposition and Their Catalytic Properties. Adv. Funct. Mater., 28: 1707231.

[2] Liang M., R. Su, W. Qi, et al. (2014) Reduction of Hexavalent Chromium Using Recyclable Pt/Pd Nanoparticles Immobilized on Procyanidin-Grafted Eggshell Membrane. Ind. Eng. Chem. Res., 53: 13635-13643.

[3] Elemike E.E., D.C. Onwudiwe, N. Nundkumar, et al. (2019) Green synthesis of Ag, Au and Ag-Au bimetallic nanoparticles using Stigmaphyllon ovatum leaf extract and their in vitro anticancer potential. Mater. Lett., 243: 148-152.

[4] Kuppusamy P., S. Ilavenil, S. Srigopalram, et al. (2017) Synthesis of Bimetallic Nanoparticles (Au–Ag Alloy) Using Commelina nudiflora L. Plant Extract and Study its on Oral Pathogenic Bacteria. J. Inorg. Organomet. P., 27: 562-568.

[5] Emam H.E., M.M. El-Zawahry, H.B. Ahmed. (2017) One-pot fabrication of AgNPs, AuNPs and Ag-Au nano-alloy using cellulosic solid support for catalytic reduction application. Carbohyd. Polym., 166: 1-13.

[6] Zhang X., Z. Su. (2012) Polyelectrolyte-Multilayer-Supported Au@Ag Core-Shell Nanoparticles with High Catalytic Activity. Adv. Mater., 24: 4574-4577.

[7] Wang C., S. Peng, R. Chan, et al. (2009) Synthesis of AuAg Alloy Nanoparticles from Core/Shell-Structured Ag/Au. Small, 5: 567-570.

[8] Jiang H.-L., T. Akita, T. Ishida, et al. (2011) Synergistic Catalysis of Au@Ag Core–Shell Nanoparticles Stabilized on Metal–Organic Framework. J. Am. Chem. Soc., 133: 1304-1306.

[9] Shin Y., A. Dohnalkova, Y. Lin. (2010) Preparation of Homogeneous Gold–Silver Alloy Nanoparticles Using the Apoferritin Cavity As a Nanoreactor. J. Phys. Chem. C, 114: 5985-5989.

[10] Pal A., S. Shah, S. Devi. (2007) Synthesis of Au, Ag and Au–Ag alloy nanoparticles in aqueous polymer solution. Colloid Surface. A, 302: 51-57.

[11] Sun L., Y. Yin, P. Lv, et al. (2018) Green controllable synthesis of Au–Ag alloy nanoparticles using Chinese wolfberry fruit extract and their tunable photocatalytic activity. RSC Adv., 8: 3964-3973.

[12] Pang S., S. Liu. (2017) Lysozyme-stabilized bimetallic gold/silver nanoclusters as a turn-on fluorescent probe for determination of ascorbic acid and acid phosphatase. Anal. Methods, 9: 6713-6718.

[13] Godipurge S.S., S. Yallappa, N.J. Biradar, et al. (2016) A facile and green strategy for the synthesis of Au, Ag and Au–Ag alloy nanoparticles using aerial parts of R. hypocrateriformis extract and their biological activity. Enzyme. Microb. Tech., 95: 174-184.

[14] Meena Kumari M., J. Jacob, D. Philip. (2015) Green synthesis and applications of Au–Ag bimetallic nanoparticles. Spectrochim. Acta A, 137: 185-192.

[15] Sun L., P. Lv, H. Li, et al. (2018) One-step synthesis of Au–Ag alloy nanoparticles using soluble starch and their photocatalytic performance for 4-nitrophenol degradation. J. Mater. Sci., 53: 15895-15906.

[16] Ravendran P., J. Fu, S.L. Wallen. (2003) Completely “Green” Synthesis and Stabilization of Metal Nanoparticles. J. Am. Chem. Soc., 125: 13940-13941.

[17] Emam H.E. (2019) Arabic Gum as Bio-Synthesizer for Ag–Au Bimetallic Nanocomposite Using Seed-Mediated Growth Technique and Its Biological Efficacy. J. Polym. Environ., 27: 210-
[18] Gao Z., R. Su, R. Huang, et al. (2014) Glucomannan-mediated facile synthesis of gold nanoparticles for catalytic reduction of 4-nitrophenol. Nanoscale Res. Lett., 9: 404.

[19] Liang M., P. Hou, C. Lu, et al. (2019) Effect of Lysimachia christinae Polysaccharide (LCP) on the Drying Kinetics Characteristics of Flue-cured Tobacco Lamina. Journal of Yunnan Agricultural University (Natural Science), 34: 70-77.

[20] Wu N.-h., Z.-q. Ke, S. Wu, et al. (2018) Evaluation of the antioxidant and endothelial protective effects of Lysimachia christinae Hance (Jin Qian Cao) extract fractions. BMC Compl. Altern. M., 18: 128.

[21] Liang M., G. Zhang, Y. Feng, et al. (2018) Facile synthesis of silver nanoparticles on amino-modified cellulose paper and their catalytic properties. J. Mater. Sci., 53: 1568-1579.

[22] Zhang M.-X., R. Cui, J.-Y. Zhao, et al. (2011) Synthesis of sub-5 nm Au–Ag alloy nanoparticles using bio-reducing agent in aqueous solution. J. Mater. Chem., 21: 17080-17082.

[23] Raveendran P., J. Fu, S.L. Wallen. (2006) A simple and “green” method for the synthesis of Au, Ag, and Au–Ag alloy nanoparticles. Green Chem., 8: 34-38.

[24] Mulvaney P. (1996) Surface Plasmon Spectroscopy of Nanosized Metal Particles. Langmuir, 12: 788-800.

[25] Tian H., H. Fan, J. Ma, et al. (2018) Pt-decorated zinc oxide nanorod arrays with graphitic carbon nitride nanosheets for highly efficient dual-functional gas sensing. J. Hazard. Mater., 341: 102-111.

[26] Ruan D., J. Xue, M. Fujitsuka, et al. (2019) Ultrafast spectroscopic study of plasmon-induced hot electron transfer under NIR excitation in Au triangular nanoprisms/g-C3N4 for photocatalytic H2 production. Chem. Commun.

[27] Miao L., S. Rongxin, H. Renliang, et al. (2014) Facile in situ synthesis of silver nanoparticles on procyandin-grafted eggshell membrane and their catalytic properties. ACS Appl. Mater. Inter., 6: 4638-4649.

[28] Goyal D., A. Saini, G.S.S. Saini, et al. (2019) Green synthesis of anisotropic gold nanoparticles using cinnamon with superior antibacterial activity. Mater. Res. Express., 6: 075043.

[29] Chang W., S. Liu, A. Qileng, et al. (2018) In-situ synthesis of monodispersed Au nanoparticles on eggshell membrane by the extract of Lagerstroemia speciosa leaves for the catalytic reduction of 4-nitrophenol. Mater. Res. Express., 6: 015002.

[30] Bouazizi N., J. Vieillard, P. Thebault, et al. (2018) Silver nanoparticle embedded copper oxide as an efficient core–shell for the catalytic reduction of 4-nitrophenol and antibacterial activity improvement. Dalton. T., 47: 9143-9155.

[31] Schlichter S., M. Rocha, A.F. Peixoto, et al. (2018) Copper mesoporous materials as highly efficient recyclable catalysts for the reduction of 4-nitrophenol in aqueous media. Polyhedron, 150: 69-76.

[32] Liu Z., J. Du, X. Jin, et al. (2019) Polyurethane/Keratin/AgNPs nanofibrous mats as catalyst support for 4-nitroaniline reduction. Mater. Lett., 237: 9-13.

[33] Ravula S., J.B. Essner, W.A. La, et al. (2015) Sunlight-assisted route to antimicrobial plasmonic aminoclay catalysts. Nanoscale, 7: 86-91.