Краткие сообщения

Brief communications

УДК 546.55/.59

СИНТЕЗ И ИССЛЕДОВАНИЕ БИМЕТАЛЛИЧЕСКИХ НАНОЧАСТИЦ, ПОЛУЧЕННЫХ КОНТАКТНЫМ ВЗАИМОДЕЙСТВИЕМ

Е. А. АВЧИННИКОВА[1)], ***С. А. ВОРОБЬЕВА***[1)], ***А. А. СОХОР***[1)]

[1)]*Учреждение БГУ «Научно-исследовательский институт физико-химических проблем», ул. Ленинградская, 14, 220030, г. Минск, Беларусь*

В результате контактного взаимодействия металлической меди и нитрата серебра получены композиционные наночастицы, содержащие Cu, Cu_2O и Ag. Методами трансмиссионной электронной микроскопии и рентгенофазового анализа исследованы морфология и фазовый состав полученных наночастиц. Показано, что в результате контактного взаимодействия на поверхности наночастиц меди осаждаются дискретные наночастицы серебра диаметром до 15 нм. В соответствии с данными рентгенофазового анализа полученные образцы содержат Cu, Cu_2O, Ag и практически вся металлическая медь окисляется в результате восстановления ионов Ag^+.

Ключевые слова: контактное восстановление; медь; серебро; наноструктуры.

Образец цитирования:
Авчинникова ЕА, Воробьева СА, Сохор АА. Синтез и исследование биметаллических наночастиц, полученных контактным взаимодействием. *Журнал Белорусского государственного университета. Химия.* 2018;2:36–39 (на англ.).

For citation:
Auchynnikava EA, Vorobyova SA, Sohor AA. Synthesis and investigation of the bimetallic nanoparticles prepared by redox-transmetalation interaction. *Journal of the Belarusian State University. Chemistry.* 2018;2:36–39.

Авторы:
Елена Александровна Авчинникова – младший научный сотрудник лаборатории химии конденсированных сред.
Светлана Александровна Воробьева – кандидат химических наук; ведущий научный сотрудник лаборатории химии конденсированных сред.
Алеся Аркадьевна Сохор – младший научный сотрудник лаборатории химии конденсированных сред.

Authors:
Elena A. Auchynnikava, junior researcher of the laboratory of condensed systems.
jenaenta@tut.by
Svetlana A. Vorobyova, PhD (chemistry); leading researcher of the laboratory of condensed systems.
vorobyova@bsu.by
Alesya A. Sohor, junior researcher of the laboratory of condensed systems.
sohor@bsu.by

SYNTHESIS AND INVESTIGATION OF THE BIMETALLIC NANOPARTICLES PREPARED BY REDOX-TRANSMETALATION INTERACTION

E. A. AUCHYNNIKAVA[a], *S. A. VOROBYOVA*[a], *A. A. SOHOR*[a]

[a]*Research Institute for Physical Chemical Problems, Belarusian State University, 14 Lieninhradskaja Street, Minsk 220030, Belarus*

Corresponding author: S. A. Vorobyova (vorobyova@bsu.by)

Composite nanoparticles, containing copper, copper (I) oxide and silver, were prepared by redox-transmetalation interaction of metallic copper and silver nitrate. The morphology and phase composition of the prepared nanoparticles were investigated by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). The TEM investigation shows that discrete spherical silver nanoparticles with an average diameter of 15 nm are formed onto the surface of copper nanoparticles as a result of the redox-transmetalation interaction of copper and silver nitrate. According to X-ray data the prepared samples contain Cu, Cu_2O, Ag and almost all amount of metallic copper are oxidized as a result of Ag^+ reduction.

Key words: redox-transmetalation; copper; silver; nanostructures.

Introduction

In recent years nanocomposites have been extensively investigated due to their practical applications in diverse fields, such as optical and electronic nanodevices, catalysts and sensors for biomedical applications [1–8]. To prepare composite copper/silver nanoparticles that may be used as a component of the effective antimicrobial substances various routes were employed. Specifically, synthesis of Ag-coated copper powders by silver coprecipitation in the presence of copper cores was described in [9; 10]. It was shown that prepared Cu-Ag composite nanoparticles contain Cu_2O phase, indicating that Cu was partially oxidized, but the ratio of the phases Cu/Cu_2O wasn't determined. Another technique for Cu/Ag particles preparation was presented in [11], where the redox-transmetalation reaction was used. At the first stage the aqueous dispersion of Cu NPs was prepared by reduction with an excess of hydrazine hydrate in the presence of polyacrylic acid sodium salt as a protective agent. At the second step, a silver salt was added, and the reduction of silver ions by the copper metal took place directly on the surface of Cu nanoparticles. It was shown that prepared nanoparticles are free of copper oxide.

The aim of this article was to prepare bimetallic nanoparticles containing copper and silver by redox-transmetalation reaction without using any protective agents and investigate their composition and morphology.

Experimental method

To achieve the core-shell structure at the first stage copper nanoparticles were prepared by a modified method described in [12]. To do this 2.98 g of copper (II) sulfate pentahydrate was dissolved in 150 ml of distilled water and was vigorously stirred under argon atmosphere for 20 min. Thereafter 1.36 g of sodium borohydride was dissolved in 15 ml of distilled water and was added dropwise with the rate of 1 ml/min to the copper (II) sulfate pentahydrate solution. After the reaction ended, the mixture was vigorously stirred for 10 min, obtained precipitate was washed by decantation until the negative reaction toward SO_4^{2-} ions. The precipitate was sonicated in 100 ml of distilled water in an ultrasonic bath for 15 min. Then, 61 ml of the obtained suspension was placed on a magnetic stirrer under the flow of Ar and solution of 0.34 g $AgNO_3$ in 20 ml of distilled water was added to the copper nanoparticles suspension. Intensive stirring was continued for 30 min. The color of the supernatant turned bluish due to the formation of copper ions Cu^{2+}. Obtained black precipitate was washed by decantation and dried in a desiccator over P_2O_5.

Dispersion and phase composition of the prepared samples were investigated by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). Electron microscopic studies were performed with an electron microscope LEO-906. Samples were prepared by the following manner: the obtained precipitate was sonicated for 10 min in ethanol in an ultrasonic bath SONOREX RK-100H and then a drop of the resulting dispersion was placed on a copper grid coated with carbon film and dried in the air.

XRD measurements were performed on a X-ray diffractometer DRON-3 employing CoK_α-radiation in the angular range $2\theta = 10–90^\circ$. The content of metallic copper, copper oxide (I) and metallic silver in the samples was calculated from corundum numbers in the PDF-2 database:

$$I_{Cu} = 8.86\, I_{Cor}, \quad (1)$$

$$I_{Cu_2O} = 8.28\, I_{Cor}, \quad (2)$$

$$I_{Ag} = 5.20\, I_{Cor}, \quad (3)$$

where I_{Cu}, I_{Cu_2O}, I_{Ag} – the intensity of the peaks of copper, copper (I) oxide and silver on X-ray spectrum, containing 1 g of copper and 1 g of corundum (1); 1 g of copper (I) oxide and 1 g of corundum (2); 1 g of silver and 1 g of corundum (3).

Results and discussion

The results of the XRD investigation of the prepared nanoparticles are displayed in fig. 1, *a*. The particles that were synthesized at the first stage and were used as a core contain the crystalline face-centered cubic metal Cu (JCPDS No. 85-1326, the most intensive peak at 2θ = 50.7º) and fcc copper (I) oxide Cu_2O (JCPDF No. 78-2076, the most intensive peak at 2θ = 42.6º). Calculated contents of Cu and Cu_2O were 71.9 and 28.1 % of the total weight respectively.

After redox-transmetalation reaction (fig. 1, *b*) sample contains metallic fcc silver (JCPDS No. 87-0720) with diffraction peaks at 2θ value of 44.6°, 51.9° and 76.5°. The spectrum also shows Cu_2O peaks (34.5º, 42.6º, 49.5º, 72.7º and 88.1º) and a Cu peak (50.7º). Calculated contents of Cu, Cu_2O and Ag were 4.2, 55.0 and 40.8 % of the total weight respectively.

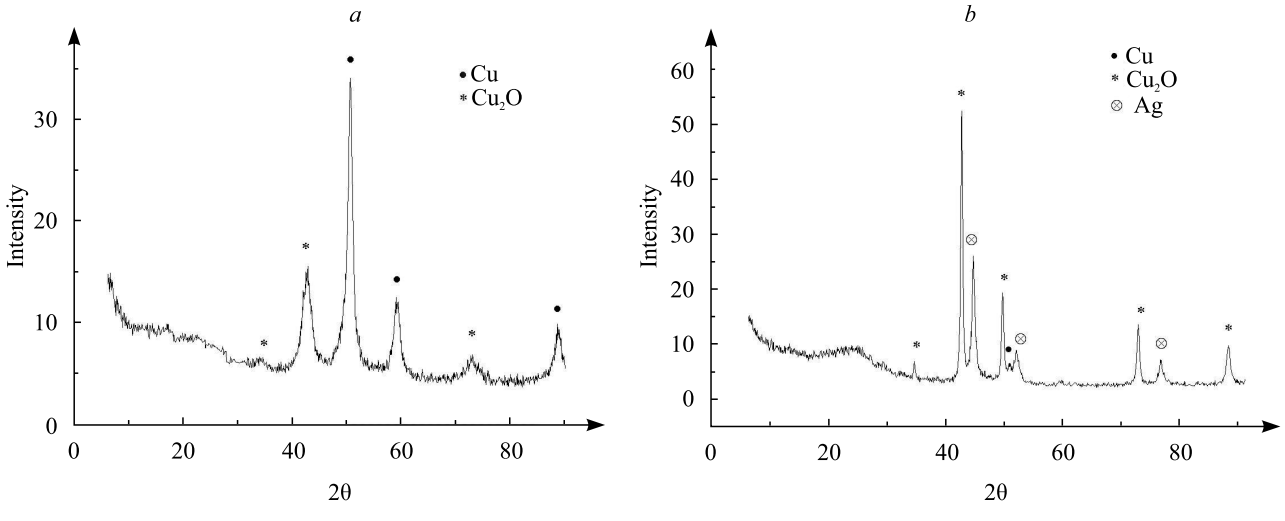

Fig. 1. X-ray diffraction pattern of nanoparticles prepared at the first stage (*a*) and after redox-transmetalation interaction (*b*)

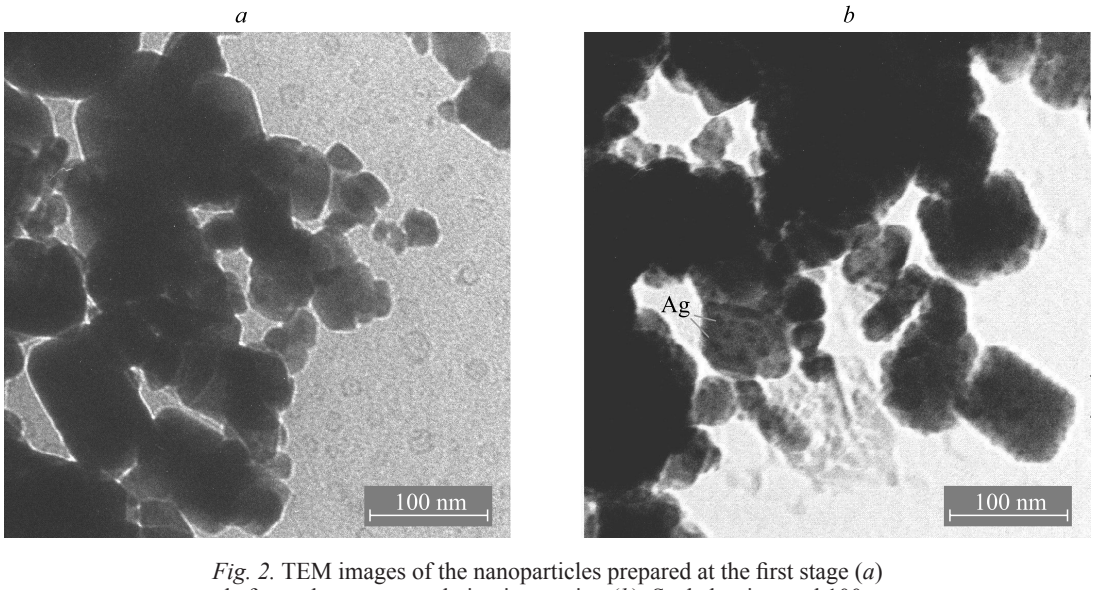

Fig. 2. TEM images of the nanoparticles prepared at the first stage (*a*) and after redox-transmetalation interaction (*b*). Scale bar is equal 100 nm

As it is clearly seen from a comparison of the TEM images displayed in fig. 2, *a*, *b*, both Cu/Cu_2O and $Cu,Cu_2O/Ag$ nanoparticles have spherical and rectangular shape in diameter up to 150 nm. As shown, small spherical particles are occurred at the surface of the Cu/Cu_2O nanoparticles after copper redox-transmetalation interaction with silver nitrate (fig. 2, *b*). Their size varies from 7 to 15 nm. When taken into account that redox-transmetalation reaction takes place onto the surface of the metallic core and according to results of morphology and composition investigation it can be suggested that small particles at the surface of copper are the silver nanoparticles. Evidently, the presence of copper (I) oxide on the metallic copper particles surface prevents formation of the continuous silver shell at copper core.

Thus, the morphology and phase composition of nanoparticles prepared by redox-transmetalation interaction of metallic copper and silver nitrate were investigated. It was shown that silver does not form a continuous shell, but small discrete silver nanoparticles cover bigger copper nanoparticles. X-ray analysis shows that the samples contain Cu, Cu_2O and Ag.

References

1. Chattopadhyay DP, Patel BH. Preparation, characterization and stabilization of nanosized copper particles. *International Journal of Pure and Applied Sciences and Technology*. 2012;9(1):1–8.

2. Yang G, Zhang Z, Zhang S, Yu L, Zhang P. Synthesis and characterization of highly stable dispersions of copper nanoparticles by a novel one-pot method. *Materials Research Bulletin*. 2013;48(4):1716–1719. DOI: 10.1016/j.materresbull.2013.01.025.

3. Zhu H, Zhang C, Yin Y. Novel synthesis of copper nanoparticles: influence of the synthesis conditions on the particle size. *Nanotechnology*. 2005;16(12):3078–3087. DOI: 10.1088/0957–4484/16/12/059.

4. Wang Y, Chen P, Liu M. Synthesis of well-defined copper nanocubes by a one-pot solution process. *Nanotechnology*. 2006;17(24):6000–6006. DOI: 10.1088/0957-4484/17/24/016.

5. Studer AM, Limbach LK, Duc LV, Krumeich F, Athanassiou EK, Gerber LC, et al. Nanoparticle cytotoxicity depends on intracellular solubility: comparison of stabilized copper metal and degradable copper oxide nanoparticles. *Toxicology Letters*. 2010;197(3):169–174. DOI: 10.1016/j.toxlet.2010.05.012.

6. Chatterjee AK, Sarkar RK, Chattopadhyay AP, Aich P, Chakraborty R, Basu T. A simple robust method for synthesis of metallic copper nanoparticles of high antibacterial potency against *E. coli. Nanotechnology*. 2012;23(8):085103. DOI: 1088/0957-4484/23/8/085103.

7. Ramyadevi J, Jeyasubramanian K, Marikani A, Rajakumar G, Rahuman AA. Synthesis and antimicrobial activity of copper nanoparticles. *Materials Letters*. 2012;71:114–116. DOI: 10.1016/j.matlet.2011.12.055.

8. Jeyaraj M, Rajesha M, Arunb R, MubarakAlic D, Sathishkumara G, Sivanandhana G, et al. An investigation on the cytotoxicity and caspase-mediated apoptotic effect of biologically synthesized silver nanoparticles using podophyllum hexandrum on human cervical carcinoma cells. *Colloids and Surfaces B: Biointerfaces*. 2013;102:708–717. DOI: 10.1016/j.colsurfb.2012.09.042.

9. Zhao J, Zhang D, Zhao J. Fabrication of Cu–Ag core-shell bimetallic superfine powders by eco-friendly reagents and structures characterization. *Journal of Solid State Chemistry*. 2011;184(9):2339–2344. DOI: 10.1016/j.jssc.2011.06.032.

10. Chen KT, Ray D, Peng YH, Hsu YC. Preparation of Cu–Ag core-shell particles with their anti-oxidation and antibacterial properties. *Current Applied Physics*. 2013;13(7):1496–1501. DOI: 10.1016/j.cap.2013.05.003.

11 Grouchko M, Kamyshny A, Magdassi S. Formation of air-stable copper-silver core-shell nanoparticles for inkjet printing. *Journal of Materials. Chemistry*. 2009;19:3057–3062. DOI: 10.1039/B821327E.

12. Auchynnikava AA, Vorobyova SA. Synthesis and properties of the copper nanoparticles, stabilized with polyethylene glycol. *Vestnik BGU. Seriya 2, Khimiya. Biologiya. Geografiya*. 2013;3:12–16. Russian.

Received by editorial board 25.06.2018.