



*J. Serb. Chem. Soc.* 80 (6) 779–787 (2015)  
JSCS–4757

## Anisotropic silver nanoparticles deposited on zeolite A for selective Hg<sup>2+</sup> colorimetric sensing and antibacterial studies

ALIREZA KHORSHIDI\*, BEHROOZ HEIDARI and HAMIDREZA INANLU

*Department of Chemistry, Faculty of Sciences, University of Guilan,  
P. O. Box 41335-1914, Iran*

(Received 29 July 2014, revised 24 February, accepted 26 February 2015)

**Abstract:** Silver nanoparticles deposited on the surface of zeolite A were prepared *via* the post ion-exchange reduction and reduction–deposition methods. The formation of silver nanoparticles on the surface of zeolite A was verified by surface plasmon spectra using diffuse reflectance spectroscopy and ultra-violet–visible spectroscopy. The morphology of the prepared samples was characterized by X-ray diffraction and scanning electron microscopy. Furthermore, silver nanoparticles deposited on the zeolite A after fixation of rhodamine B dye molecules on them were successful in the selective detection of Hg<sup>2+</sup>. After treatment with the so-obtained sensor, a colour change from colourless to pink was visible to the naked eye for concentrations of the Hg<sup>2+</sup> solution down to 1.0×10<sup>−8</sup> mol L<sup>−1</sup>. Antibacterial tests demonstrated the multi-functional application of the silver nanoparticles deposited on zeolite A.

**Keywords:** sensor; zeolite A; silver; nanoparticle; rhodamine B; mercury.

### INTRODUCTION

Fascinating chemical and physical properties of noble metal nanostructures and their applications, for example, in catalysis,<sup>1</sup> optics<sup>2</sup> and sensing,<sup>3</sup> have attracted extensive attention in recent years. Of the hitherto studied metallic nanoparticles, silver is the most attractive because of its intense nano size related colorimetric effects. The performance of silver nanoparticles in most applications could be significantly enhanced by control of the dimensions and uniformity. Therefore, many approaches have been invented to fabricate silver nanoparticles.<sup>4</sup> One of the most significant aspects of silver nanoparticles is their localized surface plasmon resonance (LSPR), which is derived from interaction of light and metal nanoparticles when the conduction electrons oscillate locally around the nanoparticles at a certain frequency. This optical feature gives rise to captivating colours and is related to particle shape,<sup>5,6</sup> size<sup>7</sup> and environment.<sup>8,9</sup>

\* Corresponding author. E-mail: Khorshidi@guilan.ac.ir  
doi: 10.2298/JSC140729020K

A number of strategies have been devised to control the morphologies of silver nanoparticles.<sup>10–14</sup> Anisotropic silver nanoparticles deposited on various supports have also found application in recent years, for example in the coloration of fabrics.<sup>15,16</sup>

The detection and quantification of heavy metal ions, on the other hand, has been a subject of interest due to its importance in waste management, environmental monitoring and clinical toxicology. Among heavy and transition metals, mercury is a well-known chemical pollutant that can cause serious threats to human health. For the successive detection of  $\text{Hg}^{2+}$ , sensitive optical sensors based on fluorescence were reported, which depend on the change of fluorescence of small organic molecules<sup>17–19</sup> to indicate the concentration of  $\text{Hg}^{2+}$  and usually function in organic media.<sup>20,21</sup> Hence, the development of new and practical chemosensors that offer a promising approach for mercury ion detection is still a great challenge.

Furthermore, zeolite A is one of the most important zeolites that have been used as water softeners in detergents, additives in poly(vinyl chloride) (PVC) plastics, gas drying and separation of linear and branched hydrocarbons. Ongoing interest in the study of transition metals chemistry and ion-exchanged zeolites,<sup>22–24</sup> together with a recent report on rhodamine 6G absorbed on the surface of silver nanoparticles as a probe for the detection of  $\text{Cu}^{2+}$ ,<sup>25</sup> prompted the present evaluation of the sensory response of silver nanoparticles deposited on the surface of zeolite A, as a stable solid support for rhodamine B (RhB) dye molecules, toward the detection of heavy metal ions.

## EXPERIMENTAL

### *Materials*

Zeolite A with the composition  $2.3\text{Na}_2\text{O}:1.0\text{Al}_2\text{O}_3:2\text{SiO}_2:300\text{H}_2\text{O}$  was synthesized according to Salma *et al.*<sup>26</sup> All other chemicals were purchased from Merck and used without further purification.

### *Preparation of silver nanoparticles deposited on the surface of zeolite A: Reduction–deposition method*

Anisotropic silver nanoparticles were prepared according to the Mirkin method.<sup>27</sup> Briefly, aqueous solutions of  $\text{AgNO}_3$  (0.1 mM, 200 mL), trisodium citrate (100 mM, 3.6 mL), PVP (poly(vinyl pyrrolidone), 0.24g), and hydrogen peroxide (30 wt. %, 0.48 mL) were mixed and vigorously stirred under ambient condition. A freshly prepared aqueous  $\text{NaBH}_4$  solution (0.65 mL, 100 mM) was then rapidly injected into the mixture. After approximately 30 min, a yellow silver colloid was obtained. To this colloid, 500 mg of zeolite A was added and the mixture was stirred. After 15 min, the zeolite was colorized to pale yellow. Eventually, the treated zeolite was centrifuged at 1000 rpm, rinsed with deionised water and dried at 373 K.

### *Preparation of silver nanoparticles deposited on the surface of zeolite A: Post ion-exchange reduction*

Zeolite A (500 mg) was ion-exchanged with  $\text{AgNO}_3$  solution (0.1 mM, 200 mL) overnight under stirring at room temperature. The resulting solid was filtered and rinsed with

deionised water (three times), then suspended in 200 mL of deionised water. To this suspension, trisodium citrate (100 mM, 3.6 mL), PVP (0.24 g) and hydrogen peroxide (30 wt. %, 0.48 mL) were added and the mixture stirred vigorously. NaBH<sub>4</sub> solution (0.65 mL, 100 mM) was then rapidly injected into the mixture. After approximately 45 min, the colour of zeolite had changed to yellow. This product was separated by centrifuge at 1000 rpm, rinsed with deionised water and dried at 373 K.

#### Sensor studies

5 mL of rhodamine B dye (RhB,  $1 \times 10^{-6}$  mol.L<sup>-1</sup>) was gradually added to a 5 mL aqueous suspension of 500 mg of the product obtained by post ion-exchange reduction, and magnetically stirred. After 30 min, colour of the solution had faded and the mixture was centrifuged at 1000 rpm. The yellow product (RhB–Ag–ZeoA) was rinsed with deionised water (three times) and dried at 373 K. To 100 mg of this sample, 3 mL of the test solution containing metallic ions, such as Fe<sup>2+</sup>/Cu<sup>2+</sup>/Zn<sup>2+</sup>/Hg<sup>2+</sup>/Mg<sup>2+</sup> of concentration  $1 \times 10^{-6}$  mol.L<sup>-1</sup> was added and stirred for 30 min. The best response, however, was obtained for Hg<sup>2+</sup>, and the pink colour of RhB developed into the solution during 20 min. To investigate the sensitivity effect of the RhB–Ag–ZeoA toward Hg<sup>2+</sup>, various concentrations of Hg<sup>2+</sup> ( $10^{-5}/10^{-6}/10^{-7}/10^{-8}/10^{-9}$  mol L<sup>-1</sup>) was studied by recording UV–Vis spectra of the supernatant liquid obtained after filtration of the mixture.

#### Characterizations

UV-Vis spectra were recorded on a Perkin Elmer LAMBDA 25 spectrophotometer. The diffuse reflectance spectra were recorded at room temperature using a Shimadzu UV-2100 spectrophotometer in the reflectance mode by investigating the evolution of the absorbance. X-Ray powder diffraction (XRD) measurements were performed using a Philips diffractometer with mono chromatized CuK<sub>α</sub> radiation at 40 kV and 20 mA (Ni filter,  $2\theta$  10 to 70° with a step size of 0.05° and a count time of 1 s). Morphology of the synthesized samples was characterized using a Philips XL30 ESEM scanning electron microscope (SEM).

#### Antibacterial activity of extracts

**Bacteria and culture.** The bacteria *Staphylococcus aureus* (PTCC 1764) and *Pseudomonas aeruginosa* (PTCC 1074) were purchased from the Persian Type Culture Collection (PTCC, Tehran, Iran) and used as test microorganisms. The strains were cultured on Nutrient Broth medium and incubated at 37 °C for 24 h.

**Preparations of extracts.** 5 ml of distilled deionised water were added to 15 mg of zeolite A, Ag<sup>+</sup> ion-exchanged zeolite A (Ag<sup>+</sup>A), silver nanoparticles deposited on the zeolite A via the reduction–deposition method (AgA–RD) and silver nanoparticles deposited on the zeolite A via the post ion-exchange method (AgA–PX), and stirred for 3 h at 150 rpm. Then, after centrifuging at 4000 rpm for 10 min, the supernatants were collected. Finally, 112, 225 and 450 μL volumes, each in triplicate, were chosen for antibacterial assessment.

**Antibacterial test.** Antibacterial activities of each extraction were assessed by the well diffusion method.<sup>28</sup> The prepared extracts were separately transferred into the wells punched in the inoculated plates using a 0.5-cm sterile cork borer and incubated at 37 °C for 24 h. The antibacterial activities were determined by measuring the diameter of the inhibition zone (mm). Drug references, *i.e.*, tetracycline (30 μg disc<sup>-1</sup>), chloramphenicol (30 μg disc<sup>-1</sup>) and cefotaxime (30 μg disc<sup>-1</sup>), were used as positive controls.

### Statistical analysis

Data were analyzed using SPSS version 19 in Windows 7. The differences between the various treatments were assessed using one-way ANOVA followed by the Duncan test at a confidence level of 95 %. There were three triplicates in all the experiments. All data are presented as the mean  $\pm$  SD.

## RESULTS AND DISCUSSION

Formation of anisotropic silver nanoparticles is associated with a colour change of the solution to light yellow. The in-plane dipole LSPR band of the silver nanoparticles is responsible for this color,<sup>14</sup> and in the present experiments, it occurred at 490 nm, as is obvious from UV-Vis spectra of the solution (Fig. 1, curve a). These anisotropic silver nanoparticles were deposited on the surface of zeolite A *via* the reduction-deposition method, resulting in a pale yellow powder. The same characteristic band of the silver nanoparticles at 490 nm was observed in the diffuse reflectance spectra (DRS) of this powder (Fig. 1, curve b).

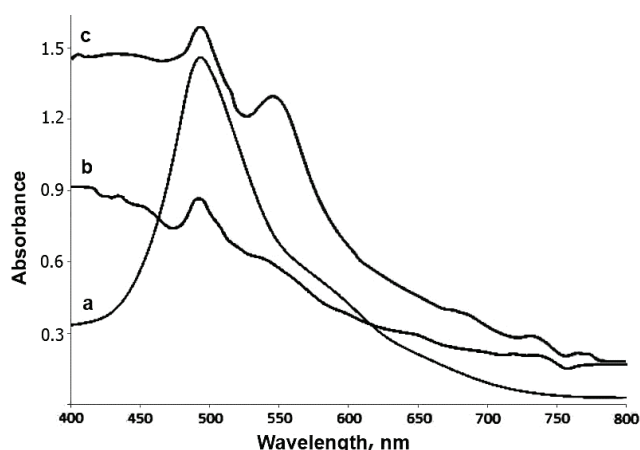


Fig. 1. a) UV-Vis spectra of silver nanoparticles, b) DRS spectra of Ag-ZeoA and c) DRS spectra of RhB-Ag-ZeoA.

The SEM technique was used to clarify the evolution of silver nanoparticles and their deposition on the surface of the zeolite. As shown in Fig. 2a, silver nanoparticles with different sizes and shapes were formed along with some aggregates. The post ion-exchange reduction method, however, resulted in more uniform semi spherical particles (Fig. 2b) with a narrower size distribution. A closer observation by TEM further confirmed this result, as could be seen in Fig. 2c.

The crystalline character of the prepared samples was analyzed by X-ray diffraction (XRD). The XRD patterns of the dried samples obtained *via* the reduction-deposition method and *via* the post ion-exchange reduction method are shown in Fig. 3, curves a and b, respectively. Both patterns, showed three index peaks at 37.9, 44.0 and 64.4°, associated with the (111), (200) and (220) reflect-

ions of fcc silver, based on the standard values given in the JCPDS card (file No. 04-783). The XRD patterns also showed that the crystal structure of the zeolite A (JCPDS card No. 73-2340) was retained after deposition of the silver nanoparticles.

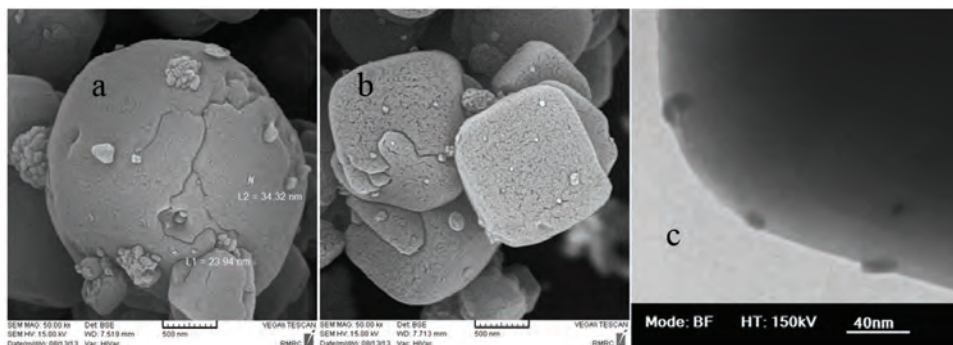


Fig. 2. SEM image of the silver nanoparticles deposited on the surface of zeolite A *via*: a) the reduction–deposition method and b) the post ion-exchange reduction method and c) a TEM image of the latter.

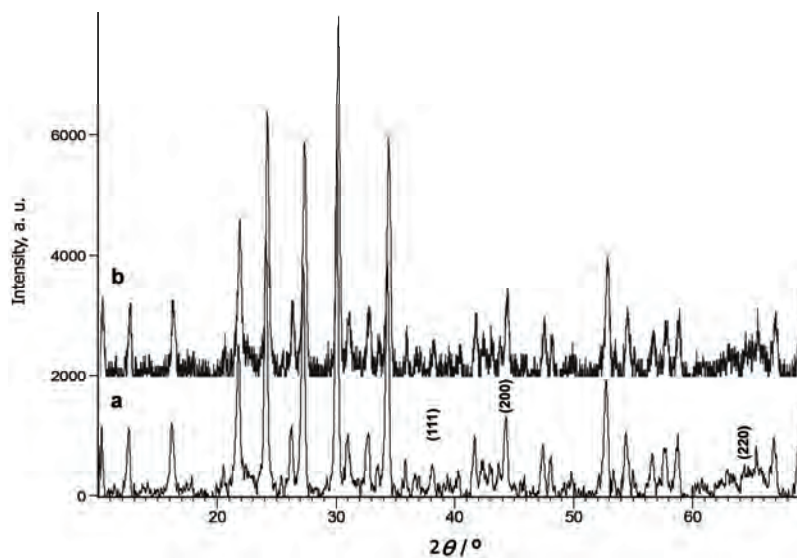


Fig. 3. XRD pattern of Ag–ZeoA obtained *via* a) the reduction deposition method and b) the post ion-exchange reduction method.

*Sensor studies*

Based on the morphological properties, the silver nanoparticles deposited on the surface of zeolite A *via* the post ion-exchange reduction method were chosen for sensor studies. Fixation of the RhB dye molecules over the surface of silver

nanoparticles deposited on zeolite A (RhB–Ag–ZeoA) was evident from the DRS spectra of the product. As shown in Fig. 1, curve c, the characteristic band of the silver nanoparticles at 490 nm and that of RhB at 550 nm are present simultaneously. Heavy metal sensing could be attributed to the replacement of dye moieties by metallic ions, according to Kirubaharan *et al.*<sup>25</sup> Among the different cations tested ( $\text{Fe}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}/\text{Hg}^{2+}/\text{Mg}^{2+}$ ), only  $\text{Hg}^{2+}$  resulted in the release of dye moiety as a visual colorimetric sensor. A dilute solution of RhB dye in water is pink and this colour develops into the solution upon addition of  $\text{Hg}^{2+}$  solution to the RhB–Ag–ZeoA, as  $\text{Hg}^{2+}$  start to adhere to the surface of the silver nanoparticles by replacing RhB dye molecules. A colour change from colourless to pink was visible to the naked eye for concentrations of  $\text{Hg}^{2+}$  in the solution down to  $1.0 \times 10^{-8} \text{ mol L}^{-1}$ . The proposed sensing mechanism is given in Fig. 4.

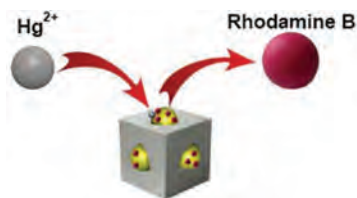


Fig. 4. The mechanism of sensing  $\text{Hg}^{2+}$  ions by RhB–Ag–ZeoA.

The limit of detection, however, was determined by recording the UV–Vis spectrum of the supernatant liquid obtained after filtration of the mixture. The spectroscopic responses of 100 mg of RhB–Ag–ZeoA against 5 mL of  $\text{Hg}^{2+}$  solutions of concentrations  $10^{-5}/10^{-6}/10^{-7}/10^{-8}/10^{-9} \text{ mol L}^{-1}$  are shown in Fig. 5a. The absorbance intensity is dependent upon the concentration of  $\text{Hg}^{2+}$  and

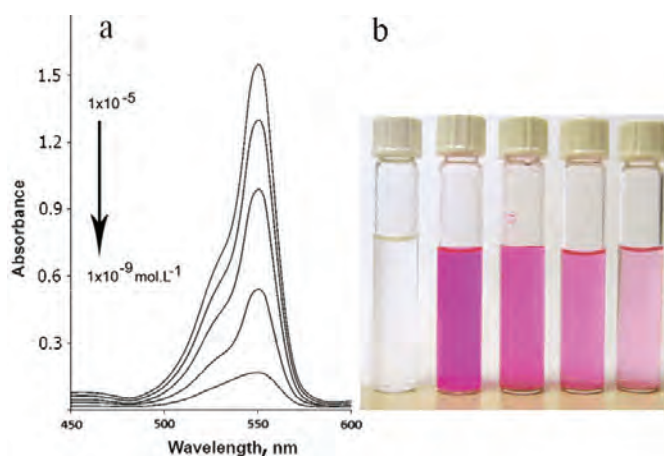


Fig. 5. a) Spectroscopic response of RhB–Ag–ZeoA upon the addition of  $1.0 \times 10^{-5}/10^{-6}/10^{-7}/10^{-8}/10^{-9} \text{ mol L}^{-1}$  of  $\text{Hg}^{2+}$  and b) the corresponding colour changes in solutions containing four concentrations ( $1.0 \times 10^{-5}/10^{-6}/10^{-7}/10^{-8} \text{ mol L}^{-1}$ ) against  $\text{Hg}^{2+}$  solution ( $1.0 \times 10^{-5} \text{ mol L}^{-1}$ ) as blank (from right to left).

minimal concentration of mercuric ions ( $1.0 \times 10^{-9}$  mol L<sup>-1</sup>) was detectable. The corresponding colour changes of solutions containing the four upper concentrations of Hg<sup>2+</sup> are presented in Fig. 5b.

*The results of the antibacterial test*

Assessment of antibacterial test of the extracts using well diffusion method showed significantly different inhibitory effects on the growth of *S. aureus* and *P. aeruginosa*. Since the extract volume of 112 μL well<sup>-1</sup> had no effect on the growth of the bacteria, it is not mentioned in the results.

*Effects of the extracts on S. aureus.* Similar inhibitory effects were observed for the extracts with extract volumes of 225 and 450 μL well<sup>-1</sup> (Figs. S-1 and S-2, given in the Supplementary material to this paper). Zeolite A had no effect on *S. aureus* while the other extracts showed significant inhibitory effects on the bacteria ( $p < 0.05$ ). The diameter of inhibition zone of Ag<sup>+</sup>A and AgA–RD were significantly higher than that of AgA–PX ( $p < 0.05$ , Fig. S-1). The maximum diameter of inhibition zone was measured in AgA–RD in both extract volumes.

*Effects of the extracts on P. aeruginosa.* Significant differences in the growth of *P. aeruginosa* ( $p < 0.05$ ) were observed between the extracts with extract volumes of 225 and 450 μL well<sup>-1</sup> (Figs. S-3 and S-4 of the Supplementary material).

With an extract volume of 225 μL well<sup>-1</sup>, zeolite A, Ag<sup>+</sup>A and AgA–PX had no inhibition effects but AgA–RD showed an inhibitory effect on the growth of the bacteria with an inhibition zone diameter of  $8.33 \pm 1.15$  mm (Fig. S-3). With an extract volume of 450 μL well<sup>-1</sup>, Ag<sup>+</sup>A had the largest diameter of the inhibition zone ( $14 \pm 0$  mm) in relation to AgA–PX ( $12 \pm 0$  mm) and AgA–RD ( $8 \pm 1.73$  mm,  $p < 0.05$ ), while zeolite A had no effect (Fig. S-4).

*The drug references test.* The results of inhibitory effects of the drug references, *i.e.*, Tetracycline (30 μg disc<sup>-1</sup>), Chloramphenicol (30 μg disc<sup>-1</sup>) and Cefotaxime (30 μg disc<sup>-1</sup>), as positive controls on the growth of the bacteria, are given in Table I. Although the results showed that all antibiotics had larger inhibitory effects compared to those of the extracts, some extracts gave comparable values for bacterial inhibition as the antibiotics (data in Fig. S-4).

TABLE I. Antibacterial tests (diameter of inhibition zone, mm) of the extracts and positive controls on *S. aureus* (*S. a.*) and *P. aeruginosa* (*P. a.*); mean values bearing different superscripts in each column are significantly different ( $p < 0.05$ )

Extract	Extract volume, μL well <sup>-1</sup>						30 μg/disc	
	112		225		450		<i>S. a.</i>	<i>P. a.</i>
	<i>S. a.</i>	<i>P. a.</i>	<i>S. a.</i>	<i>P. a.</i>	<i>S. a.</i>	<i>P. a.</i>		
Zeolite A	0	0	0 <sup>c</sup>	0 <sup>b</sup>	0 <sup>c</sup>	0 <sup>d</sup>	–	–
Ag <sup>+</sup> A	0	0	9±1 <sup>a</sup>	0 <sup>b</sup>	10±2 <sup>a</sup>	14±0 <sup>a</sup>		

TABLE I. Continued

Extracts	Extract volume, $\mu\text{L well}^{-1}$						30 $\mu\text{g/disc}$	
	112		225		450			
	Bacterium							
	<i>S. a.</i>	<i>P. a.</i>	<i>S. a.</i>	<i>P. a.</i>	<i>S. a.</i>	<i>P. a.</i>	<i>S. a.</i>	<i>P. a.</i>
AgA–RD	0	0	9.66 $\pm$ 2.08 <sup>a</sup>	8.33 $\pm$ 1.15 <sup>a</sup>	11 $\pm$ 2 <sup>a</sup>	8 $\pm$ 1.7 <sup>c</sup>	–	–
AgA–PX	0	0	7 $\pm$ 2 <sup>b</sup>	0 <sup>b</sup>	9.33 $\pm$ 2.33 <sup>b</sup>	12 $\pm$ 0 <sup>b</sup>	–	–
Antibiotics								
Tetracycline	–	–	–	–	–	–	12 $\pm$ 0.1	12 $\pm$ 0.2
Chloramphenicol	–	–	–	–	–	–	13 $\pm$ 0.2	13 $\pm$ 0.1
Cefotaxime	–	–	–	–	–	–	14 $\pm$ 0.1	14 $\pm$ 0.2

## CONCLUSIONS

In conclusion, an easy to preserve, stable and reliable colorimetric chemosensor for the successful detection of  $\text{Hg}^{2+}$  ions in solution was developed. Antibacterial activity of silver nanoparticles deposited on zeolite A, also, promises multifunctional usage of this type of material.

## SUPPLEMENTARY MATERIAL

The effects of extracts at different concentrations on the bacteria, Figs. S-1–S-4, are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

*Acknowledgment.* Partial support of this study by the Research Council of the University of Guilan is gratefully acknowledged.

## ИЗВОД

ИСПИТИВАЊЕ СЕЛЕКТИВНЕ КОЛОРИМЕТРИЈСКЕ ДЕТЕКЦИЈЕ  $\text{Hg}^{2+}$  И  
АНТИБАКТЕРИЈСКОГ ДЕЈСТВА АНИЗОТРОПНИХ НАНОЧЕСТИЦА СРЕБРА  
НАНЕТИХ НА ЗЕОЛИТ

ALIREZA KHORSHIDI, BEHROOZ HEIDARI и HAMIDREZA INANLU

*Department of Chemistry, Faculty of Sciences, University of Guilan, P. O. Box 41335-1914, Iran*

Наночестице сребра нанете на површину зеолита А припремљене су редукијом након јонске измене и редукионо–депозиционом методама. Формирање наночестица сребра на површини зеолита А је потврђено спектрима површинских плазмона применом дифузне рефлексионе спектроскопије и UV–Vis спектроскопије. Морфологија припремљених узорака је одређена дифракцијом X-зрачења и скенирајућом електронском микроскопијом. Наночестице сребра нанете на зеолит А на којима су фиксирани молекули родамин Б боје су успешно примењене за селективну детекцију  $\text{Hg}^{2+}$ . Након третмана са сензором добијем на наведени начин, промена боје од безбојне до розе била је видљива оком за концентрације раствора  $\text{Hg}^{2+}$  до  $1,0 \times 10^{-8} \text{ mol L}^{-1}$ . Антибактеријски тестови су показали мултифункционалну примену наночестица сребра нанети на зеолит А.

(Примљено 29. јула 2014, ревидирано 24. фебруара, прихваћено 26. фебруара 2015)



## REFERENCES

1. F. Zhang, G. B. Braun, Y. F. Shi, Y. C. Zhang, X. H. Sun, N. O. Reich, D. Y. Zhao, G. Stucky, *J. Am. Chem. Soc.* **132** (2010) 2850
2. K. Gude, R. Narayanan, *J. Phys. Chem., C* **114** (2010) 6356
3. A. Saha, S. K. Basiruddin, R. Sarkar, N. Pradhan, N. R. Jana, *J. Phys. Chem., C* **113** (2009) 18492
4. D. P. Perez, *Silver nanoparticles*, In-Teh, Vukovar, 2010, p. 35
5. L. J. Sherry, R. C. Jin, C. A. Mirkin, G. C. Schatz, R. P. van Duyne, *NanoLett.* **6** (2006) 2060
6. L. J. Sherry, S. H. Chang, G. C. Schatz, R. P. van Duyne, B. J. Wiley, Y. N. Xia, *NanoLett.* **5** (2005) 2034.
7. C. L. Haynes, R. P. van Duyne, *J. Phys. Chem., B* **105** (2001) 5599
8. J. J. Mock, D. R. Smith, S. Schultz, *NanoLett.* **3** (2003) 485
9. M. Hu, J. Chen, M. Marquez, Y. Xia, G. Hartland, *J. Phys. Chem., C* **111** (2007) 12558
10. R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **294** (2001) 1901
11. C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi, T. Li, *J. Phys. Chem., B* **109** (2005) 13857
12. Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem. Int. Ed.* **48** (2008) 60
13. E. Hao, K. L. Kelly, J. T. Hupp, G. C. Schatz, *J. Am. Chem. Soc.* **124** (2002) 15182
14. B. Tang, S. Xu, J. An, B. Zhao, W. Xu, *J. Phys. Chem., C* **113** (2009) 7025
15. B. Tang, M. Zhang, X. Hou, J. Li, L. Sun, X. Wang, *Ind. Eng. Chem. Res.* **51** (2012) 12807
16. F. M. Kelly, J. H. Johnston, *ACS Appl. Mater. Interfaces* **3** (2011) 1083
17. G. Hennrich, H. Sonnenschein, U. Resch-Genger, *J. Am. Chem. Soc.* **121** (1999) 5073
18. E. M. Nolan, S. J. Lippard, *J. Am. Chem. Soc.* **125** (2003) 14270
19. A. G. Lista, M. E. Palomeque, B. S. Fernández Band, *Talanta* **50** (1999) 881
20. K. Rurack, U. Resch-Genger, J. L. Bricks, M. Spiele, *Chem. Commun.* **21** (2000) 2103
21. D. S. McClure, *J. Chem. Phys.* **20** (1952) 682
22. A. Khorshidi, *Chin. Chem. Lett.* **23** (2012) 903
23. A. Khorshidi, *Ultrason. Sonochem.* **19** (2012) 570
24. A. Khorshidi, K. Tabatabaeian, *J. Mol. Cat., A: Chem.* **344** (2011) 128
25. C. J. Kirubakaran, D. Kalpana, Y. S. Lee, A. R. Kim, D. J. Yoo, K. S. Nahm, G. Kumar, *Ind. Eng. Chem. Res.* **51** (2012) 7441
26. M. Tarek Salama, O. Ibraheem Ali, I. Ahmed Hanafy, M. Waffa Al-Meligy, *Mat. Chem. Phys.* **113** (2009) 159.
27. G. S. Metraux, C. A. Mirkin, *Adv. Mater.* **17** (2005) 412
28. N. Kiani, B. Heidari, M. Rassa, M. Kadkhodazadeh, B. Heidari, *J. Basic Clin. Physiol. Pharmacol.* **25** (2014) 367.