



# PHYSICAL CHEMISTRY 2016

*13<sup>th</sup> International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry*

*Proceedings  
Volume I*

**BELGRADE**  
**September 26 - 30, 2016**

**ISBN 978-86-82475-34-7**

**Title:** Physical Chemistry 2016 (Proceedings)

**Editors:** Željko Čupić and Slobodan Anić

**Published by:** Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.

**Publisher:** Society of Physical Chemists of Serbia

**For Publisher:** S. Anić, President of Society of Physical Chemists of Serbia

**Printed by:** "Jovan", Printing and Publishing Company; 200 Copies.

**Number of pages:** 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

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*13<sup>th</sup> International Conference on  
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*Organized by*

*The Society of Physical Chemists of  
Serbia*

*in co-operation with*

*Institute of Catalysis Bulgarian Academy of Sciences*

*and*

*Boreskov Institute of Catalysis Siberian Branch of  
Russian Academy of Sciences*

*and*

*University of Belgrade, Serbia:*

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## ELECTROANALYTICAL SENSING OF BROMIDES USING SILVER NANOPARTICLE ELECTOCATALYST

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### ABSTRACT

Silver nanoparticles supported on carbon (AgNP/C) were prepared by the  $\gamma$ -radiation reduction method and characterised using transmission electron microscopy and X-ray diffraction. Subsequently, glassy carbon electrode was modified with the prepared AgNP/C and further characterized using electrochemical methods for possible application for sensing of bromide. AgNP/C proved to be highly active for bromide electrochemical detection.

### INTRODUCTION

Monitoring the level of bromide in water is now a days of great importance for the protection of both human health and environment. For instance, in the oxidative disinfection of drinking water with ozone or chlorine, bromide is oxidised to bromate, which can cause carcinoma [1,2]. Methods so far used or suggested for the detection of bromide (and other halogens) in water include neutron activation analysis, inductively coupled plasma–mass spectrometry and ion chromatography. Herein, electrochemical sensing of bromides is proposed, offering benefits of low cost, simplicity and rapidity.

### EXPERIMENTAL

**Electrocatalyst preparation.** Carbon–supported silver nanoparticles (AgNP/C) were synthesized by the  $\gamma$ -radiation reduction method using poly(vinyl alcohol) (PVA, mean molecular weight of 72 kDa, degree of hydrolysis of 99 %) as a stabilizer. Two aqueous solutions, one 4 wt.% PVA solution and the second with 0.4 M silver nitrate (AgNO<sub>3</sub>) and 0.2 M 2–propanol, were prepared in separated glasses and then mixed so that the weight ratio of Ag to PVA was 1:1. Vulcan XC 72R was added to the solution to obtain the weight ratio of Ag to C of 1:1. The obtained dispersion was homogenized ultrasonically, and then deaerated with argon for 20 min in an air–tight glass vessel, after which it was exposed to  $\gamma$ -rays

( $^{60}\text{Co}$  source) at the temperature of  $22^\circ\text{C}$ . The absorbed dose and the dose rate were  $710\text{ kGy}$  and  $12\text{ kGy h}^{-1}$ , respectively.

**Characterization.** Transmission electron microscopy (TEM) analysis was done using the JEOL JEM-1400Plus device, while the X-ray diffraction (XRD) analysis was done using Bruker D8 Advance Diffractometer ( $\text{Cu K}\alpha_1$  radiation,  $\lambda = 0.1541\text{ nm}$ ).

**Electrochemical Characterization.** The working electrode was prepared as follows:  $0.5\text{ wt.}\%$  solution of gallic acid (GA) was added to the Ag dispersion, to obtain the molar ratio of GA to PVA of  $8.2:1$ , after which the dispersion was diluted and the appropriate volume of  $1\text{ M HCl}$  was added, in order to obtain HCl concentration of  $0.1\text{ M}$  in the final dispersion.  $10\ \mu\text{L}$  of this dispersion was dropped on the glassy carbon electrode (GCE,  $5\text{ mm}$  diameter, Pine Instruments, Co) so that the loading of Ag on the electrode was  $20\ \mu\text{g cm}^{-2}$ . Crosslinking of PVA with GA was achieved by HCl during the drying (under the nitrogen atmosphere), and gel that was formed acted as a binder.

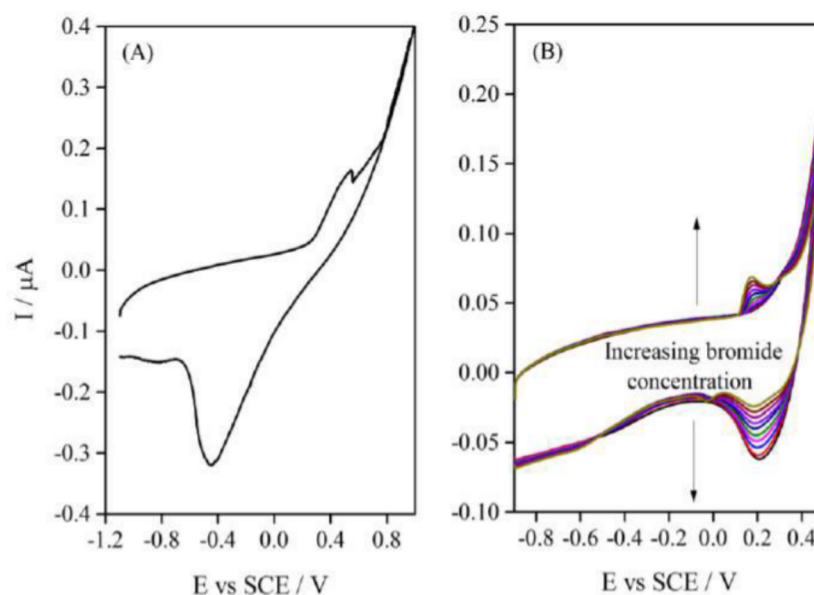
The electrochemical characterisation of AgNP/C electrocatalyst was done by cyclic voltammetry (CV) in a conventional one-compartment glass cell of  $100\text{ mL}$  volume connected to Gamry PCI4/750 potentiostat/galvanostat. Pt foil was employed as the counter electrode and a saturated calomel electrode (SCE, Radiometer Analytical) as a reference. All potentials within the paper are reported relative to the SCE. Electrochemical characterisation was performed in  $0.1\text{ M}$  phosphate buffer, while bromide sensing was performed in  $0.1\text{ M K}_2\text{SO}_4$  as supporting electrolyte.

## RESULTS AND DISCUSSION

A major advantage of radiation methods for the synthesis of metal nanoparticles is a homogenous reduction of metal ions throughout the solution. The radiation induced reduction of  $\text{Ag}^+$  starts with the radiolysis of water and formation of hydrated electrons, hydrogen and hydroxyl radicals ( $\text{H}^\bullet$  and  $\text{OH}^\bullet$ ). Hydrated electrons and  $\text{H}^\bullet$  radicals reduce  $\text{Ag}^+$  to  $\text{Ag}^0$ , which further dimerize when they encounter or associate with  $\text{Ag}^+$  and progressively grow yielding the formation of metal clusters and particles. The detailed mechanism of Ag NP formation by radiation methods has been explained by Belloni[3]. Since the  $\text{OH}^\bullet$  radicals can oxidize the metal atoms into a higher oxidation state and thus counterbalance the reduction, 2-propanol is used as a scavenger to convert them to 2-propanol radicals, which further act as strong reducing species.

The detailed XRD and TEM analysis of the carbon-supported Ag NPs obtained by the  $\gamma$ -radiation method was reported in our previous publication

[4], in which different Ag/C samples were investigated as electrocatalysts for the oxygen reduction and borohydride oxidation reaction. TEM analysis of Ag/C sample corresponding to the one prepared in this work in terms of the synthesis parameters and components content, revealed a crystallite size of 13.9 nm. XRD analysis revealed the formation of face centred cubic crystal structure of bulk metallic Ag (JCPDS File No. 89-3722). Furthermore, crystallite size determined by XRD was found to be 15 nm, which is in good agreement with the crystallite size obtained by TEM.



**Figure 1.** (A) CV of AgNP/C in pH 7 phosphate buffer at scan rate of  $200 \text{ mV s}^{-1}$ . (B) CVs of AgNP/C in  $0.1 \text{ M K}_2\text{SO}_4$  solution at scan rate of  $100 \text{ mV s}^{-1}$  with increasing bromide concentration.

The AgNP/C electrocatalyst was characterised by recording CV in  $0.1 \text{ M}$  phosphate buffer in the potential range from  $-1.1 \text{ V}$  to  $1.0 \text{ V}$  at scan rate of  $200 \text{ mV s}^{-1}$ . A peak of Ag surface oxide formation at ca.  $0.50 \text{ V}$  (Fig. 1A) could be observed on the anodic scan. Subsequently, a well-defined peak corresponding to the reduction of this oxide was observed at  $-0.44 \text{ V}$  on the cathodic scan [5].

The detection of bromide was initially studied in  $0.025 \text{ M KBr} + 0.1 \text{ M K}_2\text{SO}_4$  scanning the potential from  $-1.0 \text{ V}$  to  $0.9 \text{ V}$  at a rate of  $100 \text{ mV s}^{-1}$ . A peak originating from the formation of AgBr could be seen at ca.  $0.20 \text{ V}$  on the anodic scan (Fig. 1B) [5]. Accordingly, a well defined cathodic peak

was observed at ca. 0.16 V corresponding to the reduction of formed AgBr. Subsequently, the possibility of quantitative determination of bromides with AgNP/C was addressed. Thereafter, 10 subsequent 50  $\mu\text{M}$  additions of KBr to 0.1 M  $\text{K}_2\text{SO}_4$  were done, with the solution being stirred after each addition by the electrode rotation. Increase of peak current ( $I_p$ ) could be observed with increase of KBr concentration ( $c$ ), with  $I_p$  vs  $c$  dependence resulting in a straight line. The limit of detection (LOD) of bromide with AgNP/C electrocatalyst was evaluated using the 3 sigma method

$$\text{LOD} = 3\sigma/b \quad (1)$$

where  $\sigma$  is the standard deviation of the  $y$ -coordinates from the line of best fit and  $b$  the slope of the same line. Thus the LOD was found to be 1.8  $\mu\text{M}$ . The obtained LOD is comparable or lower than LODs obtained using different electrode substrates (1.2 – 20  $\mu\text{M}$  range) [5], thus indicating high activity of AgNP/C electrocatalyst studied herein for bromide sensing.

## CONCLUSION

In this work synthesis of AgNP/C electrocatalyst was presented, followed by characterisation using transmission electron microscopy, X-ray diffraction and electrochemical techniques. AgNP/C demonstrated high activity for bromide electrooxidation, enabling its determination with low limit of detection of 1.8  $\mu\text{M}$ .

## Acknowledgement

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support within projects III-45014 and III-45005.

## REFERENCES

- [1] K. Tagami, S. Uchida, *Chemosphere*, 2006, **65**, 2358–2365.
- [2] K. Tagami, S. Uchida, I. Hirai, H. Tsukada, H. Takeda, *Ana. Chim. Acta*, 2006, **570**, 88–92.
- [3] J. Belloni, *Catal. Today*, 2006, **113**, 141–156.
- [4] I. Stoševski, J. Krstić, J. Milikić, B. Šljukić, Z. Kačarević–Popović, S. Mentus, Š. Miljanić, *Energy*, 2016, **101**, 79–90.
- [5] B. Šljukić, R. Baron, C. Salter, A. Crossley, R. G. Compton, *Anal. Chim. Acta*, 2007, **590**, 67–73.



544(082)  
66.017/.018(082)  
502/504(082)  
663/664:658.56(082)  
615.31:547(082)

INTERNATIONAL Conference on Fundamental and Applied Aspects of Physical Chemistry (13 ; 2016 ; Beograd)

Physical Chemistry 2016 : proceedings. Vol. 2 / 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry, Belgrade, 26-30 September 2016 ; [editors Željko Čupić and Slobodan Anić]. - Belgrade : Society of Physical Chemists of Serbia, 2016 (Belgrade : Jovan). - IV, 507-930 str. : ilustr. ; 24 cm

Tiraž 200. - Bibliografija uz svaki rad.

ISBN 978-86-82475-33-0

1. Society of Physical Chemists of Serbia (Beograd)

а) Физичка хемија - Зборници б) Наука о материјалима - Зборници с) Животна средина - Заштита - Зборници д) Животне намирнице - Контрола квалитета - Зборници е) Фармацеутска хемија - Зборници  
COBISS.SR-ID 225802508

08.09.2016

