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Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode

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Abstract

Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5}M Na_2HPO_4 solution is carried out by sweep rate variation studies. Two specific anodic current peaks at 0.25V and 0.32V were observed in current-potential curves. It was concluded that 0.32V was due to the incomplete oxidation of Ag_2O to AgO under the anodic sweep or due to the partial decomposition of AgO layer, and 0.25V was due to the catalytic reaction of AgO followed by the electrochemical oxidation of Ag_2O to AgO. Studies of various scan rates from 10-100 mV/s were carried out. By comparing, 0.25 Ip vs **v** gives better linearity than Ip vs $\mathbf{v}^{0.5}$ indicating the surface adsorption controlled process are operative. But at 0.32V Ip vs $\mathbf{v}^{0.5}$ gives better linearity when compared to Ip vs **v** indicating diffusion controlled process are operative.

1. Introduction

Nanoparticle research has become an immense developing field due to its wide range of applications in different areas of science and technology. Nanomaterials are gaining interest and prominence due to their many new-fangled properties in contrast to that in traditional bulk materials. Among the metal nanoparticles (NPs), transition metal NPs, in particular the nanoparticles of cobalt (Farhadi *et al .,* 2013), nickel (Abdelhalim *et al .,* 2012; Huang *et al .*,2007; Nejati and Zabihi 2012), palladium (Xiong *et al .,* 2005), platinum(Cuenya *et al .,* 2011; Zhang *et al .*,2008), gold (Merza *et al .,* 2012), and titanium (Misra *et al .,* 2013), have attracted much attention of the researchers for a long time due to their size-induced properties and application-oriented importance in many industries as well as in advanced technologies. Among these transition metal nanoparticles, silver nanoparticles (Ag NPs) have been extensively studied due to their surface enhanced properties with fascinating structures and unique electrical, chemical, optical and antimicrobial properties. Several synthesis aspects have been reported for formation of silver oxide on to silver metal. Murray *et al.*, (2005) have reported the synthesis of Ag_xO with diameters ranging from 0.7 to 1.1 µm by electrochemical step edge decoration on highly oriented pyrolytic graphite electrode surface. Wei *et al.,* (2011) have synthesized

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oriented silver oxide nanostructures through a template free electrochemical route. De Mott et al employed dual pulse programmed electro deposition of silver oxide on silver disc electrode in the flow system from sodium hydroxide or sodium hydroxide with traces of sodium phosphate for the amperometric detection of carbohydrates, aminoacids (De-Mott *et al .,* 2005), and related compounds (De-Mott *et al .,* 1998).

Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5} Na_2HPO_4 solution is carried out (Subha *et al .,* 2013).

2. Materials & Methods

2.1 Instruments and reagents

Electrochemical experiments were performed at room temperature in a three electrode cell using a potentiostat/galvanostat-Autolab system (Ecochemie, The Netherlands). The system was run on a PC using GPES 4.9 software. Working electrode was polycrystalline Ag disc of surface area of 0.0314cm^2. Reference electrode and counter electrode [Elico Ltd] were Ag/AgCl (in saturated KCl solution) and platinum sheet respectively.

Analytical reagent grade chemicals were used throughout the experiments. NaOH, Na_2HPO_4 chemicals were of analytical reagent grade (Merck, Mumbai, India). Working solutions were prepared using double distilled water.

3. Results and Discussion

Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5}M Na_2HPO_4 solution is carried out. Figure 1 shows the cyclic voltammetric curves of nano structured silver oxide film formation on polycrystalline silver electrode in1M NaOH + 5 x 10^{-5} Na_2HPO_4 solution (pH 11.8.). Studies of various scan rates from 10-100 mV/s were also carried out.

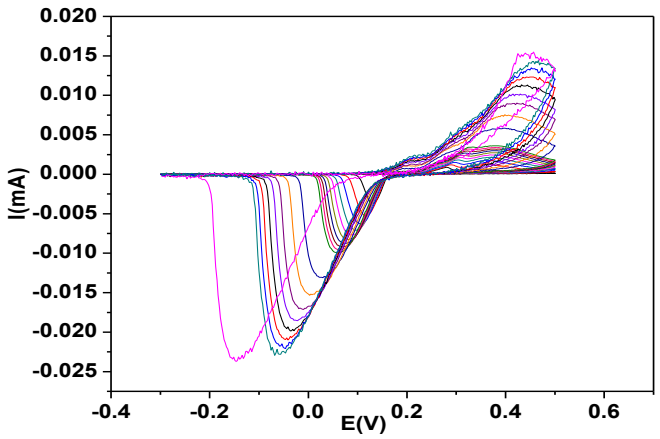

Fig. 1: Cyclic voltammetric curves of nano structured silver oxide film modified polycrystalline silver electrode in1M NaOH + 5 x 10^{-5} Na_2HPO_4 solution (pH 11.8.). Potential sweep rates from 10, 20, 30, 40, 50, 60, 70, 80, 80, 90 and 100 mVs^{-1}.

On the basis of the slopes of the linear dependence of the anodic peak currents with the potential sweep rates, by the equation,

$$Ip = \frac{n^2F^2\Gamma A\nu}{4RT}$$

where Ip is the peak current, A is the electrode surface area, Γ is surface coverage

On the basis of the slopes of the linear dependence of the anodic peak currents on the square root of the potential sweep rates, by Randel-Sevcik equation,q2

$$Ip = (2.99x10^5)\ \alpha^{1/2}\, n^{3/2} A C D^{1/2} v^{1/2}$$

where Ip is the peak current, A is the electrode surface area, D is the diffusion co-efficient and C is the bulk concentration.

Studies of various scan rates from 10-100 mV/s were carried out. During silver oxide film formation two anodic peaks were obtained i.e., at 0.25V and 0.32V and one reduction peak at 0.02V. By comparing Figure 2 (1) & 2 (II) at 0.25 Ip vs **v** gives better linearity compared to Ip vs $\mathbf{v}^{0.5}$ indicating surface adsorption controlled process are operative. But in Figure 3 (I) & 3(II) at 0.32V Ip vs $\mathbf{v}^{0.5}$ gives better linearity compared to Ip vs **v** indicating diffusion controlled process are operative.

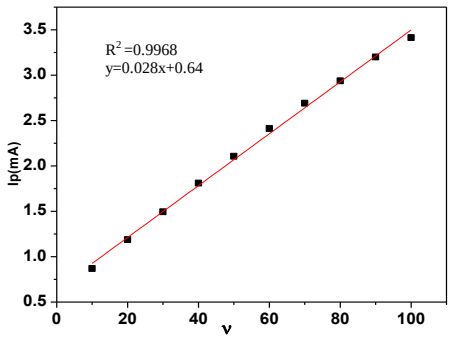

Fig. 2 (I): Plot of Ip vs v for nano structured silver oxide film modified polycrystalline silver electrode at 0.25V.

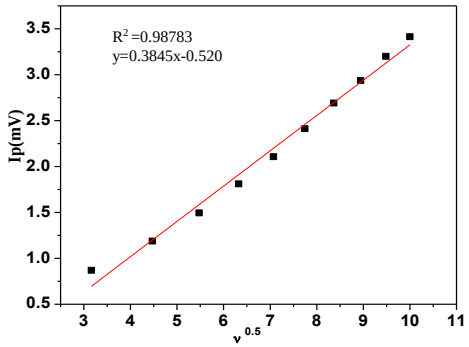

Fig. 2 (II): Plot of Ip vs $v^{0.5}$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.25V.

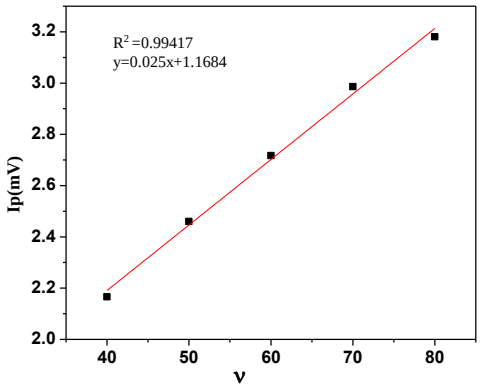

Fig. 3 (I): Plot of Ip vs v for nano structured silver oxide film modified polycrystalline silver electrode at 0.32V.

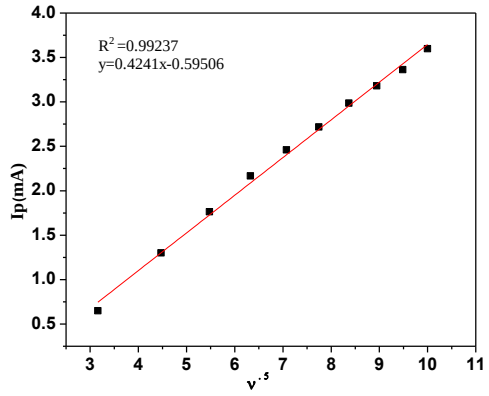

Fig. 3 (II): Plot of Ip vs $v^{0.5}$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.32

Tafel plot

In order to obtain information about the rate determining step, the Tafel plot (b) was drawn using the following equation, for a diffusion controlled process,

$$Ep = (b/2) \log v + \text{constant}$$

Based on the above equation, from the Tafel plot (Fig.4) the slope of Ep vs. log v is b/2 where b indicates the Tafel slope. The slope of Ep vs. log v for nano structured silver oxide film modified polycrystalline silver electrode at 0.32V was found to be 0.044. In this work, thus b= 0.044 x 2 = 0.088. This slope indicates an electron transfer co-efficient of α = 0.6715 for a one electron transfer process, which is the rate determining step. Figure 4 shows the slope of Ep vs. log v for nano structured silver oxide film modified polycrystalline silver electrode at 0.02 V was found to be 0.0107 in this work, thus b = 0.0107 x 2 = 0.0214.

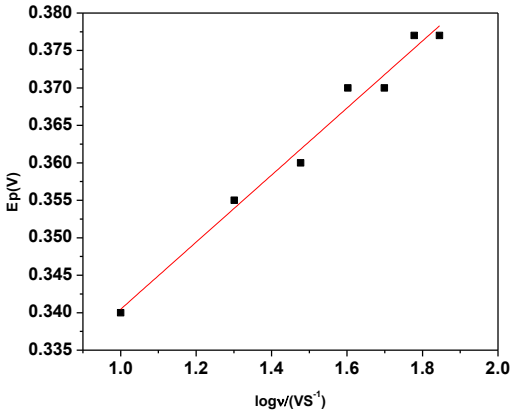

Fig. 4: Plot of Ep vs log v for nano structured silver oxide film modified polycrystalline silver electrode at 0.32V.

4. Conclusion

Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10-5M Na2HPO4 solution is carried by sweep rate variation studies. Two specific anodic current peaks at 0.25V and 0.32V were observed in current-potential curves. It was concluded that 0.32V was due to the incomplete oxidation of Ag_2O to AgO under the anodic sweep or due to the partial decomposition of AgO layer, and 0.25V was due to the catalytic reaction of AgO followed by the electrochemical oxidation of Ag_2O to AgO. Studies of various scan rates from 10-100 mV/s were carried out. On comparison, 0.25 Ip vs **v** gives better linearity than Ip vs $\mathbf{v}^{0.5}$ indicating surface adsorption controlled process are operative. But at 0.32V Ip vs $\mathbf{v}^{0.5}$ gives better linearity as compared to Ip vs **v** indicating diffusion controlled process are operative. Nano structured silver oxide film modified polycrystalline silver electrode is first of its kind with superior electrochemical performance, characteristics towards sub-picomolar level sensing of endosulphan.

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6. References

Abdelhalim, M.A.K., Mady, M.M., Ghannam, M.M. (2012). Physical Properties of Different Gold Nanoparticles: Ultraviolet-Visible and Fluorescence Measurements. *J Nanomed Nanotechol.*, 3: 133.

Cuenya, B.R., Ortigoza, M.A., Ono, L.K., Behafarid, F., Mostafa, S., Croy, J.R., Paredis, K., Shafai, G., Rahman, T.S., Li, L., Zhang, Z., Yang, J.C. (2011). Thermodynamic properties of Pt nanoparticles: Size, shape, support, and adsorbate effects. *Phys. Rev.*, 84:245-438.

De Mott, J.M.(Jr), Tougas, T.P. and Jahngen, E.G.E. (1998). Optimization of Response of the Silver Oxide Electrode for the

Detection of Carbohydrates and Related Compounds. *Electroanal*. 10: 836-841.

De Mott, J. and Jahngen, E. (2005). Determination of Amino Acids at a Silver Oxide/Silver Phosphate Electrode and the Analysis of Structure-Response Relationships. *Electroanalysis,* 17: 599-606.

Farhadi, S., Safabakhsh, J. and Zaringhadam, P. (2013). Synthesis, Characterization, and Investigation of Optical and Magnetic Properties of Cobalt Oxide (Co3O4) Nanoparticles. *Journal of Nanostructure in Chemistr.* 3: 69.

Huang, X., Jain, P.K., El-sayed, I.H., El-sayed, M.A. (2007). Gold nanoparticles: interesting optical properties and recent applications in cancer diagnostics and therapy. *Nanomedicine.* 2(5): 681–693.

Merza, K., Al-Attabi, H., Abbas, Z., and Yusr, H. (2012). Comparative Study on Methods for Preparation of Gold Nanoparticles. *Green and Sustainable Chemistry*. 2: 26–28

Misra, N., Biswal, J., Dhamgaye, V.P., Lodha, G.S., Sabharwal, S., (2013). A comparative study of gamma, electron beam, and synchrotron X-ray irradiation method for synthesis of silver nanoparticles in PVP. *Adv Mat Lett.,* 4(6): 458–463.

Murray, B.J., Li, Q., Newberg, J.T., Hemminger, J.C., Penner, R.M. (2005). Reversible Resistance Modulation in Mesoscopic Silver Wires Induced by Exposure to Amine Vapor. *Anal. Chem.*, 77: 5205-5214.

Nejati, K. and Zabihi, R. (2012). Preparation and magnetic properties of nano size nickel ferrite particles using hydrothermal method. *Chem Cent J.,* 6:23.

Subha, P.V., Saumya, V., Rao, T.P. (2013). International publication No.2013/114404 A1.

Wei, W.F., Mao, X.H., Ortiz, L.A., Sadoway, D.R. (2011). Oriented silver oxide nanostructures synthesized through a template-free electrochemical route. *Journal of Materials Chemistry*. 21: 432–438.

Xiong, Y., Chen, J., Wiley, B., Xia, Y., Yin, Y., Li, Z.Y. (2005). Size-dependence of surface plasmon resonance and oxidation for Pd nanocubes synthesized via a seed etching process. *Nano Lett.,* 5(7): 1237–1242.

Zhang, L., Fang, Z., Zhao, G.C., Wei, X.W. (2008). Electrodeposited platinum nanoparticles on the multi-walled carbon nanotubes and its electrocatalytic for nitric oxide. *Int J Electrochem Sci.,* 3: 746–754.