

ELECTRODEPOSITION OF SILVER NANOPARTICLES ON CARBON SPHERE SURFACES BY PULSE CURRENT

Manal A. Hassan^{1*}, Zeinab Abdel Hamid¹, Nabil Nassif¹, Mahmoud rabah²

¹Corrosion Control and Surface Protection Lab, CMRDI

²Chemical and Electrochemical Treatment Lab, mineral processing Dept. CMRDI

¹nmzamanal@yahoo.com, ¹forzeinab@yahoo.com, ¹nabilnassif01@hotmail.com, ²mahmoud.rabah@gmail.com

Abstract- This work studied the effect of applying pulse current ($t_{on}=0$, $t_{off}=1$ s) on the electrodeposition of silver nanoparticles on carbon sphere surface as a substrate. The electrolyte is made of 0.1 M KNO₃, 0.1 M KCN and 0.01M AgNO₃. The pH value has been adjusted in the alkaline region of 9.1 with the help of K(NO₃) addition. Experiments were carried out at room temperature for periods up to 12 minutes. The cell is fitted with a mechanical stirrer to keep the electrolyte in a dynamic state. Product(s) was characterized with the help of SEM and EDX and field emission. Results obtained show that silver nanoparticles has successfully electrodeposited under pulse current conditions with a particle size of 100–400 nm after 2 minutes. Deposition takes place on certain accessible sites of the carbon surface of the substrate forming a monolayer of scattered silver nanoparticles. Formation of macro particles with larger diameter and multilayer in thickness takes place with continuous deposition of silver nanoparticles on the formerly deposited silver. Pulse current helps management of the monolayer deposition as compared to the steady DC application with respect to particle diameter and number of layers.

Keywords: Galvanostatic pulse current silver nanoparticles Homogeneous distribution Electrodeposition.

I. INTRODUCTION

Several techniques had been examined for the synthesis of nanoparticles [1]. Electroplating of silver has been studied applying conventional methods of direct current (DC). The pulse plating technique would be of considerable benefit to the silver deposition especially in jeweler industries. The main benefits of using pulse plating were to significantly reduce the consumption of silver. It also resulting in significant reduction in the production cost, time as well as improving the quality of the coatings [2, 3]. Supported nanoparticles were shown to be important for many applications, including catalysis [4] and electroanalysis [5]. Mahmoud Rabah reported that silver nanoparticles were prepared from E-waste by chemical and electrokinetic process [6]. Nanoparticles of silver can be synthesized by different methods in solution or in gas phase. In case it was required to generate particles firmly attached to a surface, previous methods did not always provide the best solution. Electrochemical deposition has arisen as a promising technique to synthesize nanoparticles because of its high selectivity and cost effectiveness [7]. Several groups have electrodeposited metallic nanoparticles on various substrates such as glassy carbon (GC) [8], highly oriented pyrolytic graphite (HOPG) [9-11], indium doped tin Oxide (ITO) [12, 13] and others [14]. However, the electrodeposition of narrowly dispersed distributions of small nanoparticles was described to be still a challenge. The adhesion of silver nanoparticles to a surface determined the range of applicable techniques to

characterize the substrate surface such as Scanning Electron Microscopy (SEM) [8, 14] or Atomic Force Microscopy/Scanning Tunneling Microscopy (AFM/STM) [9,10]. In practice however, the resolution of a FESEM is limited to particles with diameters larger than 6–7 nm and the AFM/STM. Lateral resolution was affected by the geometry of the tip so the apparent diameters obtained from an AFM image failed to represent the dimensions of the deposited particle. Furthermore, none of these techniques was suitable for high-resolution structural analysis of small nanoparticles. Transmission Electron Microscope (TEM) is the ideal tool for studying the morphological and structural properties of nanoparticles [15]. However, the particles may be supported onto a TEM grid or additional TEM. Sample preparation could alter the properties of the electrodeposited particles. In some cases, particles had been removed from the substrate and dissolved by ultrasonication to be deposited again on a TEM grid [9]. Also, some TEM images of as-electrodeposited nanoparticles have been presented by Penner's group [10] by transferring thin (10–40 nm) HOPG flakes from a working electrode onto TEM grids. However, size distribution and particle density of nanoparticles were studied by TEM. The authors claimed a new and straightforward approach by using carbon coated gold TEM grids as substrates for the electrodeposition of silver nanoparticles. That method enabled to perform conventional FESEM measurements but also allows us to correlate TEM and electrochemical information on early nucleation and growth in a direct manner.

This paper aims to study the effect of applying pulse current on the catalytic activity of electrodeposited silver nanoparticles on carbon substrate. Parameters affecting the magnitude and properties of the deposited nanoparticles of silver such as current density, time, and the pH value have been investigated.

II. EXPERIMENTAL

A. Materials and Methods

a) Chemicals used in this study were pure grade chemicals.

Silver nitrate 0.1M solution was prepared in a de-ionized water. A standard 0.1 M solution of KNO₃ and KCN were used to adjust and control the pH value of the electrolyte at 9.1 and a complexing agent respectively.

b) The electrolysis cell

It is made of Pyrex glass beaker 250 ml. The cell is fitted with two holders for fixing the electrodes, a magnetic stirrer, precise micrometer and voltmeter. The main power is connected to a sliding resistance. The two electrodes (anode and cathode) were

made of small sheet measuring 30 x10 x 0.3 mm in thickness. Electrodes were made of graphite-doped polypropylene. The carbon electrodes were washed with pure water followed by acetone prior to use. Fig.1 shows a photograph of the cell



Fig, 1 A photograph of the experimental set-up for pulse current

B. Description of the electro deposition process

The pH value was adjusted and kept constant at 9.1 with the help of addition of drops of 0.1M potassium nitrate solution. Experiments were carried out at room temperature. The working area of the cathode was 4 cm². The two electrodes were separated by silk screen diaphragm. The cell is fitted with a separating funnel filled with silver stock solutions. The electro deposition was carried out under galvanostatic conditions using a DC power supply unit Model QJ3005.

C. Methods of measurement the characteristics of the deposited silver

A potentiostat/galvanostat IVIUMSTAT, controlled by personal computer was used for the voltammetric measurements. Weight of deposited silver was recorded by a precise electronic balance. The crystalline structure of silver nanoparticles electrodeposited on carbon was examined by x-ray diffraction (Shimadzu XRD-6000). The surface morphology of the silver nanoparticles was examined with the help of Philip XL-40FEG filed emission SEM.

III. RESULTS

Results reveal that the rate of deposition of silver particles at current density 12 mA dm⁻² amounts to 0.515 mg/cm².min and alleviates to 0.21 and 0.16 mg/cm².min with lower current density conditions of 6 and 5 Adm⁻² respectively. The rate of deposition linearly relates to the current density value and time up to 10 minutes.

Fig.2 shows the weight of the deposited silver as a function of time. It can be seen that the weight deposited increases with time up to 8 minutes after which it decreases with more time. Fig 3 shows the rate of deposition against time. It is seen that the rate of deposition of silver nanoparticles as affected by time of electrodeposition at room temperature. It is seen that the rate decreases with increasing time up to 12 min whereby a minimum value is attained (0.12 mg cm⁻²min⁻¹) with more time, the rate of deposition is kept more or less the same.

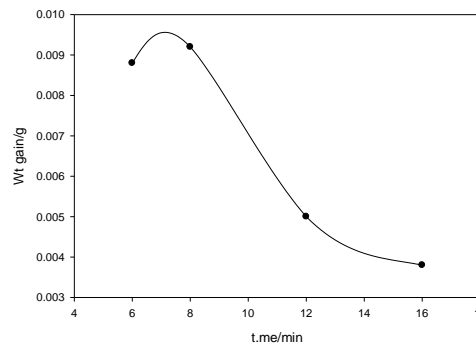


Fig. 2: relationship between weight gain/gm of deposition of silver nanoparticles on porous graphite against time/min at current density 6Adm⁻², room temperature, and pH9.1 under pulsed condition (T_{on}=T_{off}=1sec)

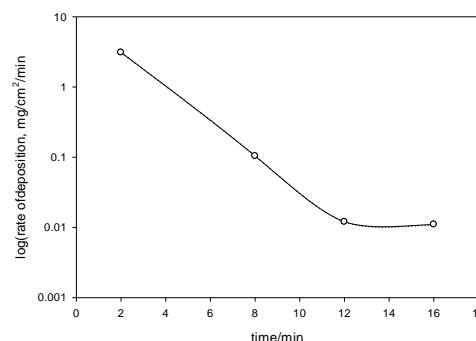


Fig.3 Rate of deposition of Ag as function of time at 6A/dm² current density, room temp, and pH 9.1 under pulsed condition (T_{on}, T_{off} =1sec)

Fig 4 shows the rate of electro deposition as a function of current density. It can be seen that the rate of electro deposition of silver increases with increasing current density value passing through a maximum at (6Adm⁻²). With further increase in current density, the rate value decreases drastically to reach a minimum value of (3 mg cm⁻²min⁻¹)

Fig.5 shows the effect of pH value of the silver electrolyte on the rate of silver electrodeposition at room temperature. It is seen decreases slightly within the pH range 8.4 – 9.1. With more basic electrolyte (pH ≥ 9.2 to 9.9, the rate of electrodeposition of silver exhibits pronounced decrease

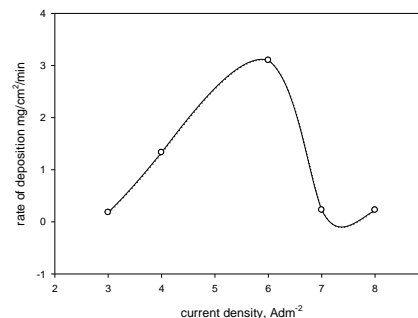


Fig.4 Rate of deposition of Ag as function of current density at time 2min, room temperature and pH 9.1 under pulsed condition(T_{on},T_{off} =1sec)

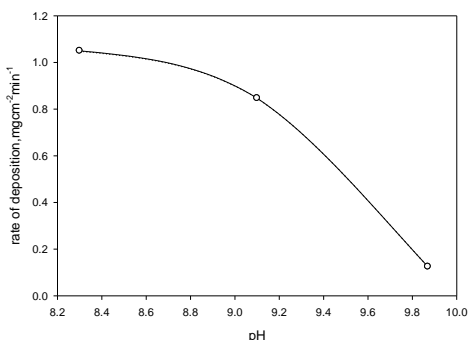


Fig.5 Rate of deposition of Ag as function of pH at current density 8 Adm⁻², time 2min ,room temperature and under pulsed condition(T_{on},T_{off}=1sec)

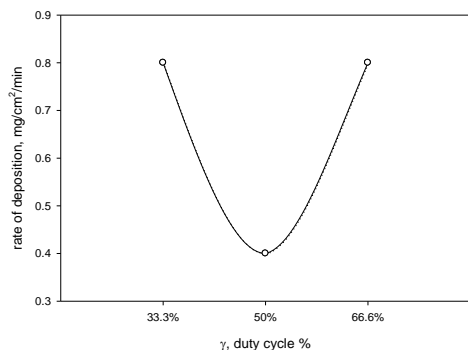


Fig.6 Rate of deposition and duty cycle % (γ). 8 A/dm², time 2 min ,room temperature, pH 9.1

Fig.6 shows the rate of electrodeposition of silver as influenced by the duty cycle percent (γ). It can be seen that the rate curve displays a parabolic shape with its maximum of 0.8 mg/cm²/ min while its minimum value amounting to 0.4 mgcm⁻² min⁻¹ with (γ) value of 50%..

Fig.7 shows the strength of adhesion of the deposited silver on the carbon substrate expressed as the weight removed upon agitation with water at room temperature. It can be seen that weight removed of the deposited silver nanoparticles increase with increasing current density till reach to 5Adm⁻², passing through that value the rate of deposition decrease to reach 6Adm⁻² then slightly decrease.

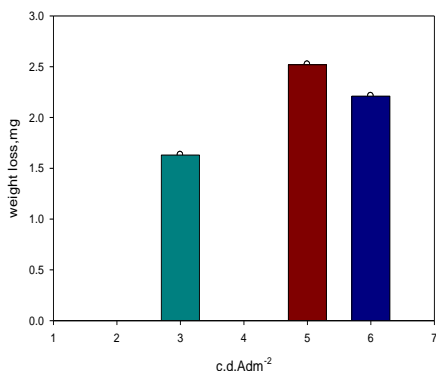


Fig.7 Relation between weight loss and current density, 2min., room temperature, pH 9.1 and under pulsed condition(T_{on},T_{off}=1sec)

Fig.8 shows the Anodic cyclic voltammetry curves (CV) of ethanol oxidation in alkaline solution using Ag on nonporous carbon surface with various scanning rates (5, 25, 50, and 100) mVs⁻¹. It can be seen that the four peaks are displayed at 0.5, 3.7, 6 and 8.2 mA.cm⁻² with 0.5, 0.58, 0.69 and 0.80 mV respectively. Fig. 9 shows the plots of current density peak (I) against square root of scan rate of Ag/C electrode in KOH+5M ethanol. It is seen that the current peak value is linearly related to the scan rate. The slop of the linear relation amounts to mA/scan rate.

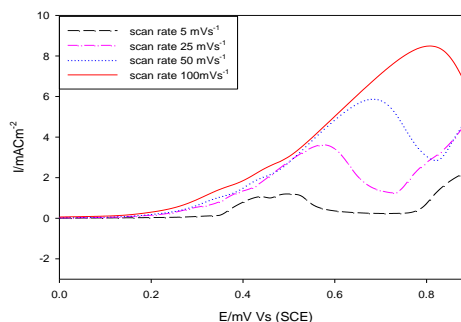


Fig.8: The anodic cyclic voltammetry curves (CV) of oxidation of ethanol in alkaline solution at Ag/C electrode (deposited at the optimum conditions) with various scan rate (5, 25, 50, 100) mVs⁻¹.

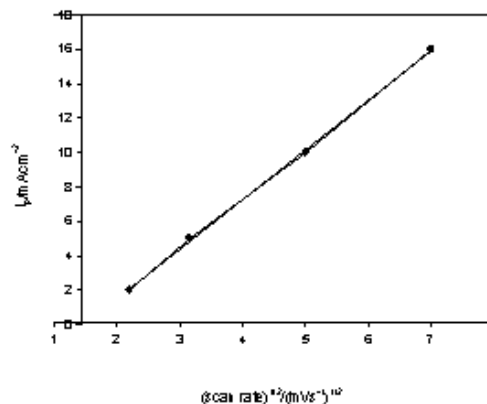


Fig.9: Plots of peak current density (I) against square root of scan rate f Ag/C electrode in KOH+5M ethanol.

Figure 10 shows the anodic cyclic voltammetry curves (CV) of oxidation of ethanol (5M) in alkaline solution (1MKOH) at 5 mVs⁻¹ scan rate using porous and nonporous carbon electrodes. It can be seen that the anodic cyclic voltammetry value displays more or less the same value of 0.15 mA/cm² with increasing the potential up to 0.38 mV. With higher potential > 0.38 mV, the anodic cyclic voltammetry displays a rapid increase to reach a peak of 3 mA/cm² at 0.46 mV with porous graphite electrodes. The corresponding values obtained with nonporous graphite electrodes displays a broad maximum of about 1 mA/cm² at the same potential. It is worth noting that the standard reduction potential of (OH) group amounts to +0.8277 mA [R].

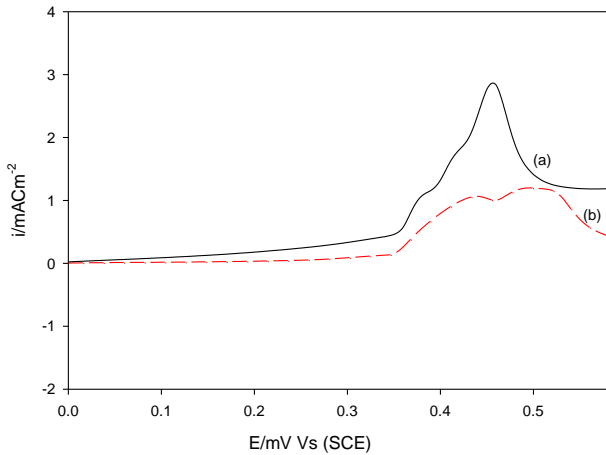


Fig. 10: Anodic cyclic voltammetry curves (CV) of oxidation of ethanol (5M) in alkaline solution (1MKOH) at 5 mVs⁻¹ scan rate using different electrodes: (standard (OH) oxidation $+0.8277 \text{ mA/cm}^2 \text{ [R]}$)

- a) Silver/ porous graphite electrode.
- b) Silver/ non-porous graphite electrode

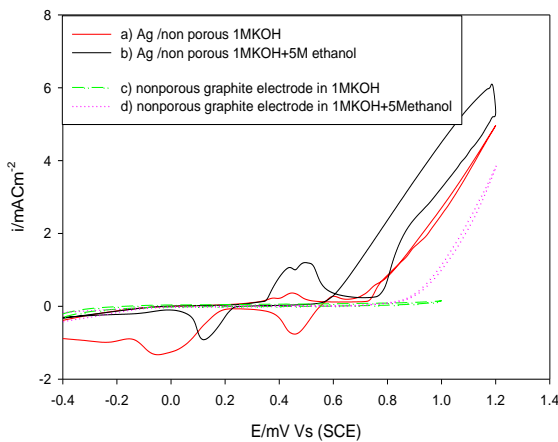


Fig.11: Cyclic voltammograms at 5 mVs⁻¹ scan rate for

- a) Silver / non porous graphite electrode in 1M KOH solution.
- b) Silver / non porous graphite electrode in 1M KOH +5M ethanol solution.
- c) Non porous graphite electrode in 1M KOH solution.
- d) Non porous graphite electrode in 1M KOH +5M ethanol solution

Figure 11 shows the Cyclic voltammetry CV of silver nanoparticles electrodeposited on porous and nonporous carbon substrate in 1 M KOH. Parallel experiments were carried out in presence of 5 M ethanol. It is seen that the silver on porous carbon displays more catalytic effect in oxidizing ethanol as compared to silver on nonporous substrate. Silver oxidative peak appeared at 0.47 mV. The catalytic activity becomes very pronounced with higher potential values >0.6 mV.

Fig 12 shows SEM photograph of the electrodeposited silver on porous and nonporous carbon substrate. The particle size amounts to 117 um.

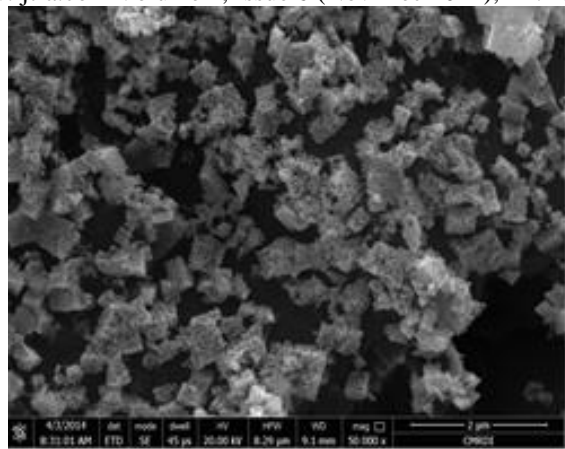
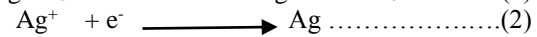
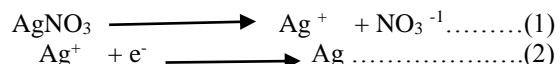


Fig. 12 SEM of silver deposit on graphite-PP substrate, mag.x 50,000

IV. DISCUSSION

Electrodeposition of silver nanoparticles has its importance from the fact that the metal is used as a catalyst. Nanoparticles of the Nobel metal acquire high catalytic activity as compared to the common regular silver particles. In this context, the method used in this work, investigated the application of pulse current technique to help deposition of silver on carbon with a slow rate to accomplish deposition of fine particles of nano size. Results revealed that the used silver nitrate solution is a suitable electrolyte to carry out silver electro deposition. The addition of potassium nitrate helps to keep the silver solution at constant pH value of 9.1. The process of deposition takes place according to the following equation



Reaction 2 would be enhanced by controlling the potential of the electrolysis process across the solution bulk and the surface of the cathode to establish a concentration gradient at the cathode vicinity. Adjustment of the current density, the concentration of the silver ions in solution and the temperature promote the successful deposition of silver in nano size. The use of pulse current prevails the time enough for silver ions to diffuse through the established concentration gradient to be available for deposition. Results given in Figs 2 and 3 are in a good agreement with this model. The effect of current density (Fig.3) can be explained in the light of a model which suggested that at low current density, the rate of silver deposition is low due to deficiency of electrons (equation 2). With gradual increase in current density, excessive silver ions are liable to be discharged and deposited. The maximum rate of deposition takes place with 6 A/dm². With further increase in current density, rapid deposition of silver particles takes place with less significant adhesion forces on the carbon substrate. In other words, the deposited silver is loose without enough adhesion forces to cement to the cathode surface and fall down in the bottom of the electrolyzing cell. The effect of pH (Fig.4) on the rate of silver deposition revealed that high OH⁻ groups would inhibit silver ion diffusion from the solution bulk to the cathode. Results of Figures 8 and 9 show that silver particles display catalytic activity to oxidize ethanol. Such activity becomes very

pronounced with silver on porous graphite substrate as judged from the increasing value in current density peak value as compared to the value with silver on nonporous graphite (Fig. 10). This phenomenon finds support from the fact that porous substrate provide larger surface area of the silver catalyst to help more catalytic activity. SEM investigations of the silver metal deposited on graphite-doped PP (mag.x500) supports this model. Porous graphite provides the silver catalysis with increasing sites accessible for deposition. Catalytic activity of the deposited silver is further improved by using pulse current technique for electro deposition of silver nano particles. A proper time necessary for diffusion of silver ions and discharging before deposition seems available in the cathode vicinity. In other words, silver ions in nanoparticles size are successfully deposited under pulse current density conditions and room temperature on sites of the graphite surface. The use of current density 6 Adm^{-2} prevail the optimum conditions to deposit silver in nano size. Higher current density implies that silver ions are discharged simultaneously and would aggregate to form particles larger in size. Excessive high current density is not in favor of nano particles deposition as particles of silver will deposit in loose grains falling on the bottom of the electrolyzing cell. It is worth noting that the applied potential may affect the current density value (Fig.7). This is legitimate on the basis of the fact that the power (VA) only suitable for silver ions discharge would be highly recommended.

V. CONCLUSION

Nano particles of silver have wide range of applications in the fields of energy, environmental, and medical technologies due to their unique properties determined primarily by its size, composition, and structure. Silver nano particles have been of considerable interest because of their unusual and fascinating properties. The electrolyte conditions are controlled by addition of potassium nitrate and potassium cyanide. The optimum electro deposition conditions for silver in nano size are current density = 6 Adm^{-2} , pH 9.1, silver concentration 0.04 N, pulse $t_{\text{on}} = t_{\text{off}} = 1$ at room temperature. Nano particles of silver deposited successfully on graphite substrate and its catalytic activity increases when porous graphite demonstrated as a substrate. Pulse current helps to deposit silver in nano size particles from silver nitrate at alkaline pH value with higher catalytic activity to oxidize ethanol.

REFERENCES

- [1.] U. Mohanty, "Electrodeposition: a versatile and inexpensive tool for the synthesis of nanoparticles, nanorods, nanowires, and nanoclusters of metals," *J.Appl. Electrochem*, 41 (2011) 257.
- [2.] Canning W, *The Canning Handbook of Surface Finishing Technology* (CBS publishers and Distributors, New Delhi), 2005.
- [3.] Nasser Kanani, *Electroplating- Basic Principles, Processes and Practice* (Elsevier Ltd., Berlin, Germany), 2004.
- [4.] J.M. Campelo, D. Luna, R. Luque, J.M. Marinas, A.A. Romero, Sustainable preparation of supported metal nanoparticles and their applications in catalysis, *ChemSusChem* 2 (2009) 18–45.
- [5.] C.W. Welch, R.G. Compton, The use of nanoparticles in electroanalysis: A review, *Anal. Bioanal. Chem.* 384 (2006) 601–619.
- [6.] Mahmoud A. Rabah, "Preparation of size controlled silver on carbon from E-waste by chemical and electrokinetic process" *Int. J. of chem., Mater. Science and engineering*, vol 7 (8) (2013) 75-80.
- [7.] G. Staikov, *Electrocrystallization in Nanotechnology*, WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.
- [8.] A.A. Isse, S. Gottardello, C. Maccato, A. Gennaro, Silver nanoparticles deposited on glassy carbon: Electrocatalytic activity for reduction of benzyl chloride, *Electrochem. Commun.* 8 (2006) 1707–1712.
- [9.] J.V. Zoval, R.M. Stiger, P.R. Biernacki, R.M. Penner, Electrochemical deposition of silver nanocrystallites on the atomically smooth graphite basal plane, *J. Phys. Chem.* 100 (1996) 837–844.
- [10.] J.V. Zoval, J. Lee, S. Gorer, R.M. Penner, Electrochemical preparation of platinum nanocrystallites with size selectivity on basal plane oriented graphite surfaces, *J. Phys. Chem. B* 102 (1998) 1166–1175.
- [11.] H. Liu, F. Favier, K. Ng, M.P. Zach, R.M. Penner, Size-selective electrodeposition of meso-scale metal particles: A general method, *Electrochim. Acta* 47 (2001) 671–677.
- [12.] M. Ueda, H. Dietz, A. Anders, H. Kneppel, A. Meixner, W. Plieth, Double-pulse technique as an electrochemical tool for controlling the preparation of metallic nanoparticles, *Electrochim. Acta* 48 (2002) 377–386.
- [13.] X.A. Dai, R.G. Compton, Direct electrodeposition of gold nanoparticles onto indium tin oxide film coated glass: Application to the detection of arsenic(III), *Anal. Sci.* 22 (2006) 567–570.
- [14.] E. Sheridan, J. Hjelm, R.J. Forster, Electrodeposition of gold nanoparticles on fluorine-doped tin oxide: Control of particle density and size distribution, *J. Electroanal. Chem.* 608 (2007) 1–7.
- [15.] Z.L. Wang, *Characterization of Nanophase Materials*, Wiley–VCH, 2000.