

## ROLE OF PREPARATION PROCEDURE OF GRAPHENE ON THE ELECTROCHEMICAL PERFORMANCE OF FREE-STANDING GRAPHENE/METHYLENE BLUE/SILVER NANOPARTICLE COMPOSITE ELECTRODES

Ezgi Topçu, Oğuz Bayındır, Elif Erçarıkçı, Kader Dağcı, Ayşe Öztürk, Murat Alanyalıoğlu\*

*Atatürk University, Sciences Faculty, Department of Chemistry, Erzurum, Turkey*

*\* Corresponding author, e-mail: malanya@atauni.edu.tr*

### Abstract

We have prepared graphene/methylene blue/silver nanoparticles composite paper electrodes by mixing each precursor in an aqueous solution and then filtering this suspension on a suitable membrane. Graphene suspensions have been prepared by using two different methods: First method includes successive electrochemical intercalation of sodium dodecyl sulfate into graphite (oxidation) and electrochemical exfoliation of this sodium dodecyl sulfate-intercalated graphite electrode (reduction). Second method is called as Hummer's method in the literature. In this method, graphite oxide is obtained by chemical oxidation of graphite and then graphite oxide is dispersed to graphene oxide in a suitable solvent under ultrasonic effect. Characterization of obtained composite papers was performed by using scanning electron microscopy, electron dispersive spectroscopy, powder X-ray diffraction, and cyclic voltammetry techniques. We have tested electrochemical performance of these two composite free-standing electrodes by using as working electrode for reversible ferricyanide/ferrocyanide redox system. The results indicate that the composite electrode which is prepared by using Hummer's method exhibits better electrochemical performance than that of electrochemically prepared Gr composite electrode. This situation is attributed to different exfoliation conditions of both graphene preparation methods.

**Keywords:** graphene, methylene blue, free-standing electrode, composite, electrochemistry

### 1. INTRODUCTION

There is currently a great demand for the development of new economic, flexible, light-weight and environmentally friendly paper-like electrode materials for especially amperometric sensor applications. Carbon-based paper materials e.g. graphene (Gr), carbon nanotubes, fullerenes have raised great interest for different types of applications such as electrochemical energy storage devices [1], catalyst supports and fuel cells [2], sensors and actuators, chemical filters and membranes, and structural composites [3]. A promising building block of intriguing actual scientific and technological interest is Gr, best described as a two-dimensional single-atom thick sheet of  $sp^2$  hybridized carbon atoms arranged in a honeycomb lattice with outstanding electronic, mechanical, thermal and chemical properties [4]. Different noble metal nanoparticles with high conductivity have been successfully used to construct composite papers. Among them, silver nanoparticles (AgNPs) that aroused growing interest due to their specific properties such as small granule diameter, large specific surface area, high catalytic activity, good biocompatibility and conductivity [5]. MB, a derivative of a phenothiazine, is a water-soluble cationic dye. Methylene blue (MB) possesses a  $\pi$  conjugation structure with a highly flat hydrophobic surface. These properties of MB allow Gr to facily interact with some organic compounds through  $\pi$ - $\pi$  electronic and hydrophobic interactions and thus to form new nanostructures [6].

Interaction between Gr and MB has been investigated by different groups [6-8]. Ramesha et al. have determined that graphene oxide (GO) and reduced graphene oxide (rGO) act as good adsorbents for

cationic and anionic dyes from aqueous solutions, respectively. They have proposed that adsorption occurs via electrostatic interaction between graphene sheets and dyes [7]. Zhang et al. have prepared rGO/MB nanocomposite structure by ultrasonication method. They have proposed  $\pi$ - $\pi$  stacking interaction between MB and rGO [8].

In this work, we propose a new approach for preparing functional free-standing Gr/MB/AgNPs composite papers. For this purpose, Gr sheets have prepared by using both chemical (cGr) and electrochemical (eGr) methods. We have also tested electrochemical performance of these two composite free-standing paper electrodes by using as working electrode for a reversible ferricyanide/ferrocyanide redox system in a three-electrode system.

## 2. EXPERIMENTAL SECTION

### 2.1. Chemical preparation of Gr (cGr)

GO was prepared by using the modified Hummer's method [9]. Typically, 3 g of graphite powder (325 mesh, Alfa Aesar) was added to 12 ml of concentrated H<sub>2</sub>SO<sub>4</sub> solution containing 2.5 of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 2.5 g of P<sub>2</sub>O<sub>5</sub>. Temperature of the solution was kept at 80 °C for about 5 h, followed by cooling to room temperature and diluting with 500 ml of Milli-Q ultra-pure water (conductivity: 5.5  $\mu$ S m<sup>-1</sup>). The mixture was filtered with a 0.2  $\mu$ m nylon66 membrane (Supelco) and washed to remove residual chemicals. The product was dried and collected as pre-oxidized graphite. The pre-oxidized graphite was re-oxidized by putting into 120 mL of concentrated H<sub>2</sub>SO<sub>4</sub> at 0 °C with gradual addition of 15 g of KMnO<sub>4</sub> under stirring and ice-cooling. The mixture was kept at 35 °C for 3 h and diluted gradually in an ice-bath cooled environment with 250 ml ultra-pure water. The mixture was re-diluted with ultra-pure water, followed by addition of 20 mL H<sub>2</sub>O<sub>2</sub>. The mixture was left for 15 minutes and the color changed to brilliant yellow. The mixture was filtered and washed with 1:10 aqueous HCl solution and ultra-pure water. The obtained graphite oxide powder was dried and dialyzed for one week in 0.5% graphite oxide dispersion. In order to obtain a stable GO dispersion, 200 mg of solid graphite oxide was dispersed in 400 ml of ultra-pure water with ultrasonication treatment, using a high power (340W) ultrasonic pole at room temperature for 2 h. The dispersion was centrifuged at 1000 rpm for 15 min to remove a small quantity of precipitation, forming a black-brown GO aqueous colloid. This homogeneous GO dispersion was tested to be stable for several months.

### 2.2. Electrochemical preparation of Gr (eGr)

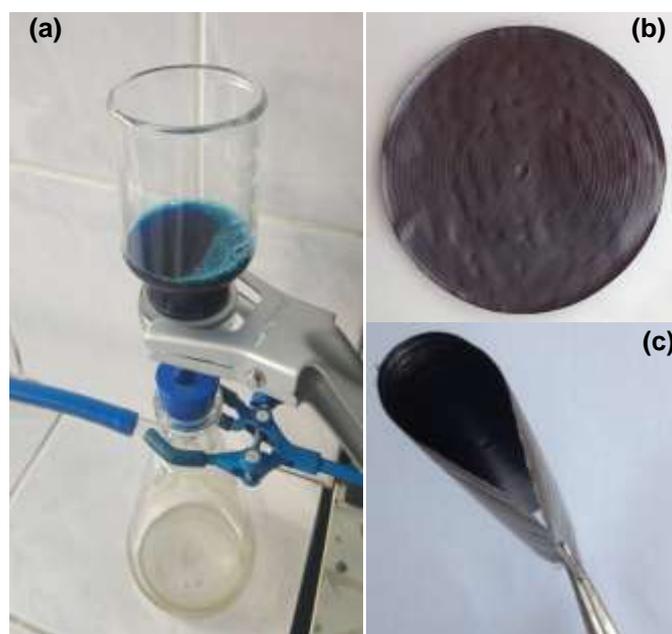
Production of Gr dispersion was performed by using consecutive two step electrochemical processes: First step includes electrochemical intercalation of sodium dodecyl sulfate (SDS) into graphite electrode by oxidation at a constant potential of 2 V for 24 h. This electrochemical procedure was performed in 0.1 M SDS solution by using a graphite rod (Goodfellow, England, 99.997% purity, 1 cm diameter) as working electrode, Pt wire as quasi-reference electrode, and a Pt foil as counter electrode. Second step is electrochemical exfoliation of this SDS-intercalated graphite electrode by reduction at a constant potential of -1 V for 2 h in the same solution [4]. Electrochemical studies were carried out with an Epsilon potentiostat system. The obtained Gr/SDS dispersion was centrifuged at 1000 rpm for 15 min to remove large graphitic agglomerates. These procedures yield a very stable colloidal eGr/SDS suspension.

### 2.3. Preparation of free-standing Gr/MB/AgNPs paper electrodes

AgNPs were synthesized according to related literature study [10] Firstly, Gr/MB/AgNPs composite prepared through filtration of a suspension which includes 40 mL of 1 mg/mL Gr, 25 mL of 1.0 mM MB and 40 mL of 0.25 mM AgNPs on a filter membrane as seen in Fig. 1.a. Highly flexible and free-standing Gr/MB/AgNPs composite paper was obtained by chemical reduction of GO/MB/AgNPs paper with HI (Fig. 1.b) [11]. The composite paper is mechanically stable, flexible and can be shaped into desired structures and bent into large angles as shown in Fig. 1.c.

## 2.4. Instrumentation

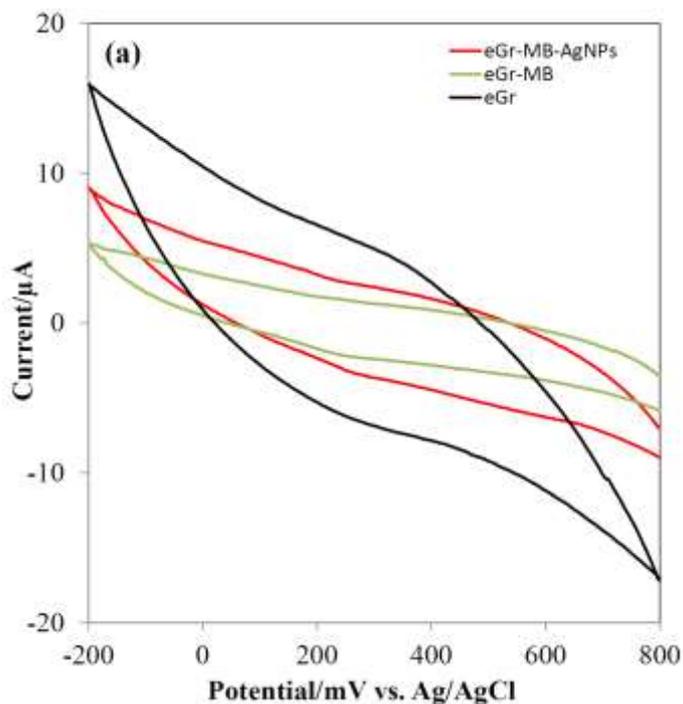
Electrochemical characterization of the prepared samples was acquired with an Epsilon (Bioanalytical Systems) potentiostat system connected to a three electrode cell. In this system, Gr/MB/AgNPs composite electrode was working electrode, while a Pt wire and Ag/AgCl (3.5 M KCl) were served as counter and reference electrode, respectively. The SEM analysis and elemental composition determination of the samples were collected by electron dispersive spectroscopy (EDS) with a ZEISS system coupled to the SEM instrument. The powder X-ray diffractograms (XRD) of the papers were collected by using a Rigaku (miniflex) powder X-ray diffractometer by using Cu  $K\alpha$  radiation ( $\lambda=1.54050 \text{ \AA}$ ). The identification of the diffraction profiles were performed with the help of the JCPDS (Joint Committee on Powder Diffraction Standards) cards.



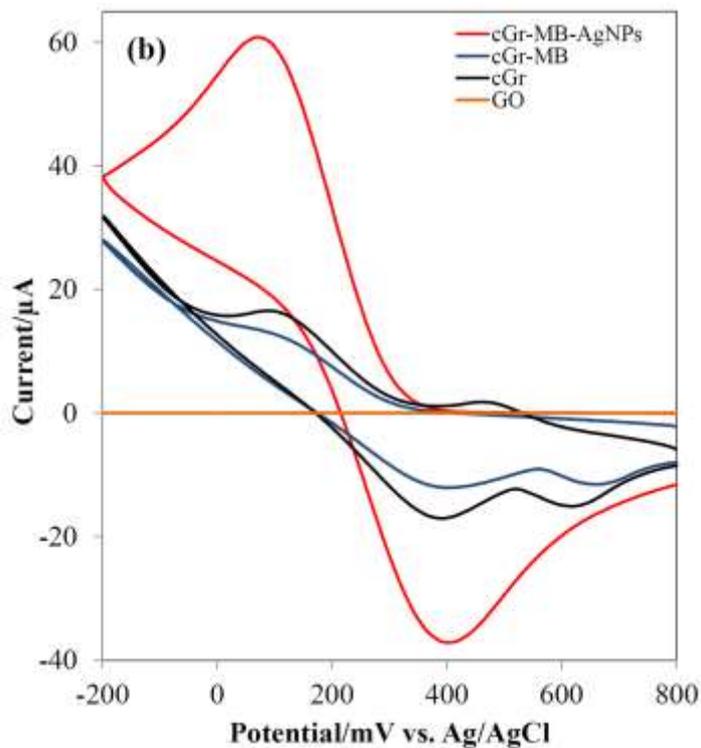
**Fig. 1.** Digital photographs of **a)** filtration system, **b)** free-standing cGr/MB/AgNPs paper, and **c)** flexibility of Gr/MB/AgNPs paper.

## 3. RESULTS AND DISCUSSION

We have first investigated electrochemical responses of prepared composite electrodes those include eCr and cGr. Fig. 2 shows electrochemical behaviors of free-standing eGr, eGr/MB, and eGr/MB/AgNPs electrodes in 10 mM  $K_3Fe(CN)_6$  solution containing 0.1 M  $KNO_3$ . It is clear that electrochemical response of these three electrodes is very poor and these electrodes are not suitable for electrochemical applications. Electrochemical responses of GO, cGr, cGr/MB, and cGr/MB/AgNPs are also presented in Fig. 3. GO paper exhibit no electrochemical response through ferricyanide/ferrocyanide redox system while its reduced form (cGr) and cGr/MB paper reveal peaks at about +100/+400 mV. In these voltammograms, a redox pair at around +450/+600 mV arises and are attributed to electrochemical response of iodine which is contaminated during chemical reduction of the papers with HI. Best electrochemical response is obtained for cGr/MB/AgNPs paper electrode as shown in Fig. 3. cGr/MB/AgNPs paper electrode presents a redox pair at about +100/+400 mV with a very high current value.



**Fig. 2.** Electrochemical responses of different free-standing electrodes prepared with electrochemically synthesized graphene in 10 mM  $K_3Fe(CN)_6$  solution containing 0.1 M  $KNO_3$ . Scan rate: 50  $mV \cdot s^{-1}$ .



**Fig. 3.** Electrochemical responses of different free-standing electrodes prepared with chemically synthesized (modified Hummer's method) graphene in 10 mM  $K_3Fe(CN)_6$  solution containing 0.1 M  $KNO_3$ . Scan rate: 50  $mV \cdot s^{-1}$ .

Because the electrochemical response of eGr, eGr/MB, and eGr/MB/AgNPs are very poor through ferricyanide/ferrocyanide reversible system, we have not further characterized eGr and its related composite papers. We have investigated morphological properties of cGr/MB/AgNPs composite papers by SEM. Chemical composition was studied by EDS, while crystal structure determination was performed by XRD technique. Fig. 4 presents SEM image of free-standing cGr/MB/AgNPs paper. This image shows wrinkled structure which is characteristics of 2-D materials [12]. There are randomly dispersed and localized nanoparticles on the graphene surface which may be due to MB interacted with graphene via electrostatic or  $\pi$ - $\pi$  stacking forces. AgNPs are not assigned by using only this morphological image which may be because of the concentration of AgNPs are very low in this study or preferentially intercalation of AgNPs into graphene layers.

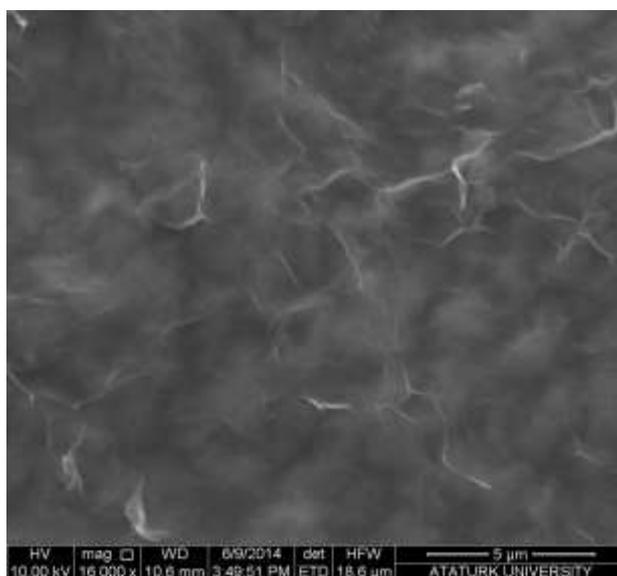


Fig. 4. SEM image of free-standing cGr/MB/AgNPs paper.

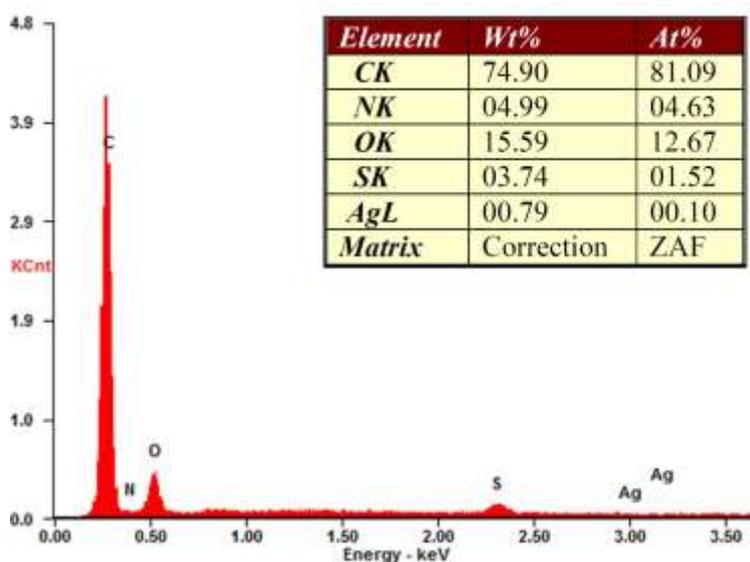
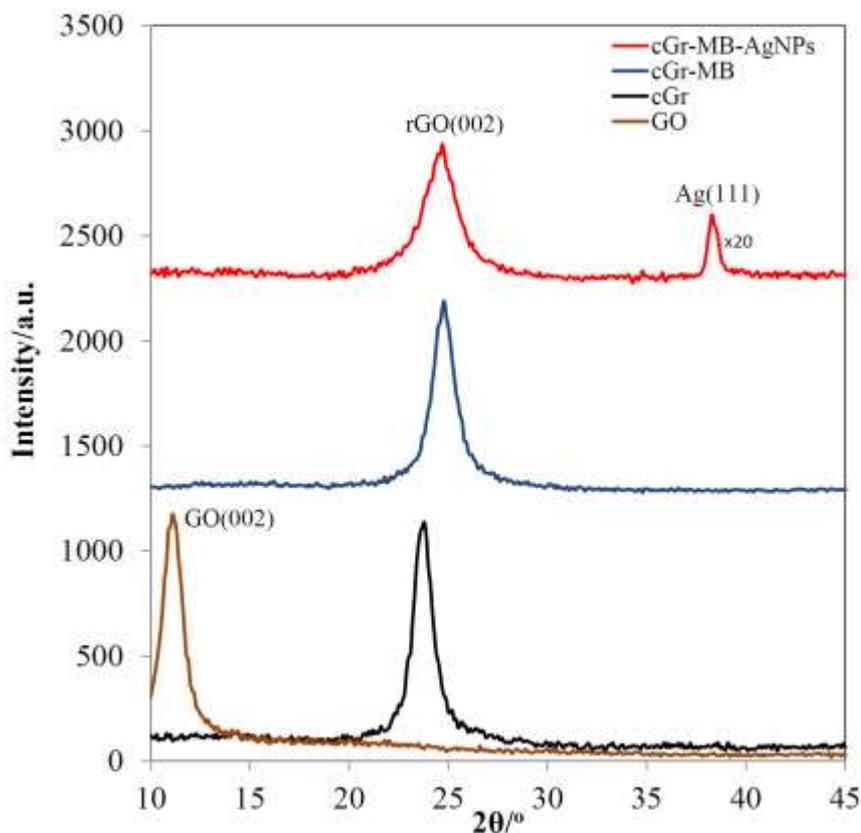


Fig. 5. EDS spectrum of free-standing cGr/MB/AgNPs paper.

In order to verify SEM structure, we have performed EDS study and the results are exhibited in Fig. 5. It is open that composite structure includes only C, N, O, S, and Ag atoms. C and O comes from Gr. However, we have performed chemical reduction, there is still oxygen atoms in the structure. This situation shows that all of the oxygen and/or oxygen-containing groups cannot be removed by chemical reduction method. N and S atoms are indicative of the presence of MB in the composite structure. It is clear that Ag nanoparticles are also seen in the free-standing electrode with a very low amount.



**Fig. 6.** XRD patterns of free-standing cGr and its related paper electrodes.

We have performed XRD works to determine the crystal structure of cGr and its related composite papers (Fig. 6). GO paper shows a well-defined diffraction peak at  $2\theta=10.8^\circ$  with 0.81 nm d-spacing. Graphite has a strong peak at  $2\theta=26.1^\circ$  for (002) diffraction which indicates an interlayer spacing of 0.34 nm (JCPDS card no: 41-1487). The expansion of d-spacing of GO is probably due to the presence of oxygen-containing functional groups on the graphene surface, causing an atomic-scale roughness [13]. It is known that the XRD pattern of rGO (cGr in this work) includes a band with a maximum at around  $2\theta=24^\circ$  which is much higher than that of GO, confirming the recovery of ordered graphitic crystal structure after chemical reduction process. Because MB layers presents amorf structure, there is no diffraction peak due to MB. When XRD pattern of cGr/MB paper compared to that of cGr, a broadening and shift to higher  $2\theta$  values are observed which may be due to intercalation of MB species into Gr structure. The diffraction peaks of AgNPs are not observed because we used AgNPs with a very low concentration in this study. So, we have prepared cGr/MB/AgNPs free-standing papers with 20 times more concentration of AgNPs and its XRD pattern is shown in Fig. 6. AgNPs reveals a diffraction peak at  $2\theta=38.3^\circ$  corresponding to (111) crystalline face of Ag (JCPDS file No. 04-0783). If XRD pattern of cGr/MB/AgNPs paper is compared to that of both cGr and

cGr/MB papers, a broadening are seen and can be attributed to intercalation of AgNPs besides MB into cGr structure.

#### 4. CONCLUSION

Gr/MB/AgNPs papers were prepared successfully with a traditional filtration method. For this purpose, Gr were prepared by using electrochemical (eGr) and chemical (cGr) methods. The cyclic voltammetry results indicated that the composite electrode which is prepared by using chemical method exhibits better electrochemical performance than that of electrochemically prepared Gr composite electrode. Electrochemical procedure for the preparation of Gr results with both one-layer or a-few layers Gr formation while high amount of one-layer thick Gr is produced in the chemical method [4,9]. Conductivity of Gr is hardly related to number of layers and defect density. So, this result can be attributed to different exfoliation (oxidation) conditions of both graphene preparation methods.

#### ACKNOWLEDGEMENTS

*This study was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK), project no: 113Z342 and Scientific Research Projects Unit of Ataturk University, project no: 2014/69*

#### LITERATURE

- [1] RA, J., RAYMUNDO-PINERO, E., LEE, Y. H. et al., Carbon 2009, 47, 2984.
- [2] WAJE, M. M., WANG, X., et al., Nanotechnology 2005, 16, 395.
- [3] YUAN, C. J., WANG, C. L., et al., Biosensors and Bioelectronics 2011, 26, 2858.
- [4] ALANYALIOGLU, M., SEGURA, J. J., ORO-SOLE, J., CASAN-PASTOR, N., Carbon 2012, 50, 142.
- [5] HELI, H., et al., Biosensors and Bioelectronics 2009, 24, 2328.
- [6] ERCARIKCI, E., DAGCI, K., TOPCU, E., ALANYALIOGLU, M., Materials Research Bulletin 2014, 55, 95.
- [7] RAMESHA, G. K., KUMARA, A. V., MURALIDHARA, H. B., SAMPATH, S., J. Colloid Interface Sci. 2011, 361, 270.
- [8] ZHANG, D., FU, L., LIAO, L., DAI, B., ZOU, R., ZHANG, C., Electrochimica Acta 2012, 75, 71.
- [9] HUMMERS, W. S., OFFEMAN, E., et al., J. Am. Chem. Soc. 1958, 80, 1339.
- [10] SOLOMON, S., et al, Journal of Chemical Education 2007, 84, 322.
- [11] ZAN, X., FANG, Z., WU, J., XIAO, F., HUO, F., DUAN, H., Biosensors and Bioelectronics, 2013, 49, 71
- [12] DUAN, W. H., GONG, K., WANG, Q., Carbon 2011, 49, 3107
- [13] ANSARI, S., NEELANCHERY, M. M., USHUS, D., J. Appl. Polym. Sci. 2013, 130, 3902.