Electrocatalytic performance of three dimensional electrode Cu/reduced graphene oxide/carbon fiber for nitrate reduction

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A sensitive and reliable three dimensional electrodes consisting of Cu particles/reduced graphene oxide (rGO)/carbon fiber (CF) were development to investigate their performance for nitrate electroreduction. For rGO/CF binary composite, FEG-SEM images showed the characteristic aggregates with irregular and flakes-like shape with high particle density on CF substrate. The Cu deposits depicted small grain morphologies distributed throughout the rGO/CF surface. As expected, Cu deposit rate increased with increasing the deposition time. From X-ray diffraction analyses of the Cu particles, a mixture of phases containing cuprous oxide and metallic copper was identified. Under optimal experimental conditions, the Cu/rGO/CF electrode showed good catalytic activity for nitrate electro-reduction. This behavior can be associated to the presence of rGO and CF with high specific surface area in addition to Cu particle with high electron transfer capability. These results showed that Cu/rGO/CF composite has a great potential as new promising electrode for nitrate electroreduction application.

1. Introduction

Nitrate ions are well-known water toxic inorganic pollutants and also are used as preservatives in the food industry as well as used as fertilizing agents. High concentrations of nitrate ions can cause a serious problem for both aquatic systems and human health [1, 2]. For example, nitrate can react with hemoglobin causing methemoglobinemia which decreases blood oxygen carrying capacity specially in infants and causing eutrophication. Moreover, due to its reduction to nitrite in the digestive system, nitrate may have damaging effect in human health like bladder cancer, gastric cancer, and leukocyte enzyme abnormality [3]. In view of the diverse problems associated with nitrates, it is of great importance to monitor nitrate ions in various kind of source [4]. To date, several analytical methods have been developed for the individual or simultaneous determination of nitrate and nitrite, including electrochemical technique [5-8], spectrophotometry [9, 10], chemiluminescence [11] and chromatography [12, 13]. Most of these analytical technologies require a well-trained technician, expensive equipment, complex detection procedures, and a long analysis time. On the other hand, electrochemical technique offers a simple, rapid, selective, sensitive, inexpensive, safety method for this purpose, not to mention its considered green technology [14]. To improve the nitrate process performance and selectivity, novel electrode materials have been widely investigated. Particularly for nitrate determination, fabrication of modified electrodes is an important issue in

voltammetric sensors because its reduction takes place mutually with the water reduction, getting harder its analysis. To achieve this purpose, more attention has been focused nowadays on mettalic nanoparticles-modified electrodes owing to their small sizes, larger surface area and superior stability, improving the facility of electron transfer between the specific chemical analyte and the electrode surface [15, 16]. Specifically, copper nanoparticle (Cu) has proven to be one of the most effective metal used in recent years, since it possesses the highest performance for nitrate electrochemical sensing [17]. Carbon fiber (CF) appears as a very interesting three-dimensional electrode regarding its application in electroanalysis with large surface area. Recently, graphene has attracted great attention as a new kind of carbon material with a single or a few atomic layer, which has been considered as a promising candidate for electrocatalyst support in electrocatalysis applications [18] and sensors [19] due to its singular properties such as the high surface area (theoretical value of 2620 m^2/g), excellent conductivity, and unique graphitized basal plane structure. Taking into account the presence of rGO and CF with high specific surface area and Cu metal with high electron transfer capability, this work aims to develop a sensitive and reliable three dimensional electrode consisting of Cu particles/reduced graphene oxide (rGO)/carbon fiber (CF) for monitoring nitrate concentration.

2. Experimental

The CF sample was produced from polyacrylonitrile (PAN) precursor at heat treatment temperature of 1000 ºC using temperature steps of 330ºC h^{-1} under inert atmosphere of nitrogen, reaching their maximum for 30 min up to their cooling down to room temperature. Graphite oxide (GO) was first synthesized from natural graphite powder using modified Hummer´s method [20] and then 180 mg the product GO was dispersed into 30 mL deionized water under ultrasonic homogenizer during 30 min so that the impurities in the GO solution were centrifuged using centrifugal machine 4000 rpm for 15 min. The concentration of GO solution was estimated to be 3 mg L^{-1}. rGO and Cu electrodepositions on CF substrate were performed at room temperature using an Autolab PGSTAT 302 equipment with a conventional three-electrode electrochemical cell consisting of CF (working electrode) Pt mesh (counter electrode), and $Ag/AgCl/KCl_{(sat)}$ as reference electrode. The rGO electrodeposition on CF (with geometric area of 1 cm^2) was performed at a fixed potential of -1.25 V for 10 min in a 20 mL of the graphene oxide (3mg mL^{-1}) + 0.1 mol L^{-1} $LiClO_4$ aqueous solution. The Cu electrodeposition on rGO/CF was carried out at a fixed potential of -0.7 V for 3, 6, 10 s in a 10 mmol L^{-1} $CuSO_4$ + 100 mmol L^{-1} H_2SO_4 aqueous solution. The rGO/CF and Cu/rGO/CF composites morphologies and structures were analyzed by field emission gun scanning electron microscopy (FEG-SEM) from a TESCAN MIRA 3 microscope system, X-ray diffraction mesuarements recorded by a PANanalytical model X'Pert Powder diffractometer with the CuKα (λ = 1.54 Å), set at 45 kV and 25 mA, in the ω/2θ configuration with ω = 1° and 2θ varying from 10 to 100°, and Raman spectroscopy using a Horiba Scientific LabRAM HR Evolution microscope system with laser beam line of 514 nm. Nitrate electro-reduction was evaluated using cyclic voltammetry (CV) at 50 mV s^{-1} in 0.1 mol L^{-1} K_2SO_4 solution (pH = 3.0) with and without the presence of 10^{-2} mol L^{-1} KNO_3.

3. Results and discussion

3.1. Basic characterizations of GO and rGO

Figure 1(A) shows the XRD patterns for GO and rGO/CF films. A clear diffraction peak is observed at 2θ= 10.6° due to the formation of oxygen-containing functional groups associated to the complete oxidation of graphite to the graphite oxide. Afterwards the GO electrochemical reduction on CF substrate, the GO characteristic peak disappeared and a broad (002) diffraction peak at about 2θ = 24.7° was evidenced caused by the removal of some oxygen-containing functional groups, which indicates a successfully reduction of GO on CF substrate. These XRD patterns of the synthesized GO and rGO displayed a typical characteristic peaks reported to the literature [21].

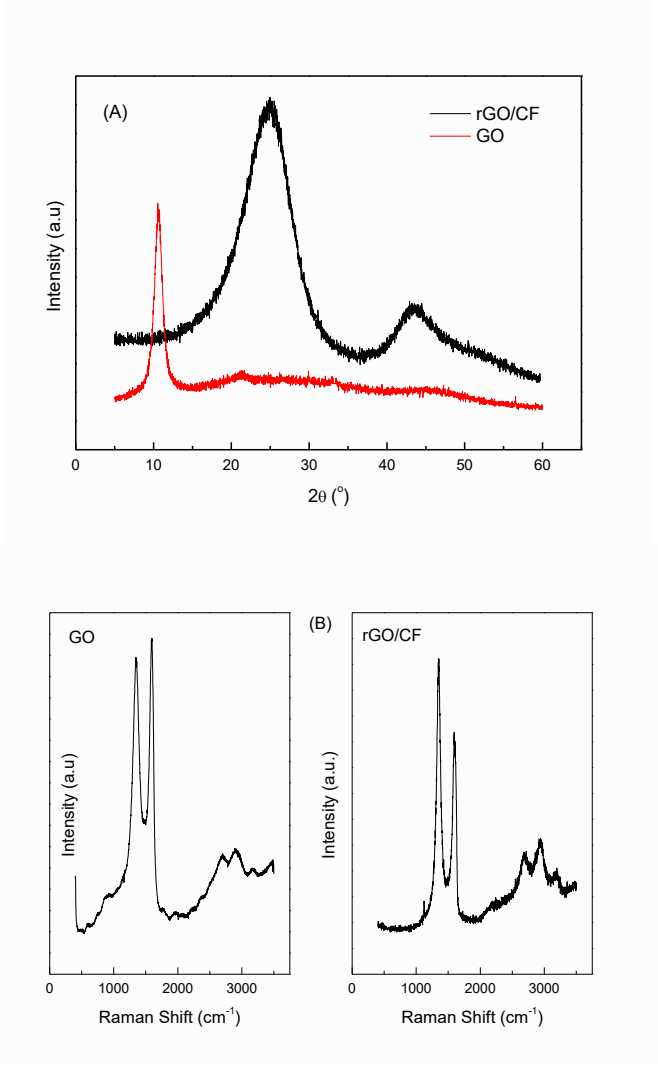

Figure 1- (A) XRD patterns of the GO and rGO/CF films; **(B)** Raman spectra of the GO and rGO/CF films.

In Raman spectra, two characteristic bands of the carbonaceous materials designated of D and G band was observed at about 1352 cm^{-1} and 1592 cm^{-1}, respectively. The D band corresponds to the disordered structural defects and G band is associated with the in-plane vibration of sp^2 bonded carbon atoms. Afterwards the GO electrochemical reduction to rGO, the I_D/I_G value increased from 0.95 to 1.05, respectively, confirming

its deoxygenation process [21]. For rGO/CF binary composite, FEG-SEM images, Figure 2, showed the characteristic aggregates with irregular and flakes-like shape with high particle density on CF substrate.

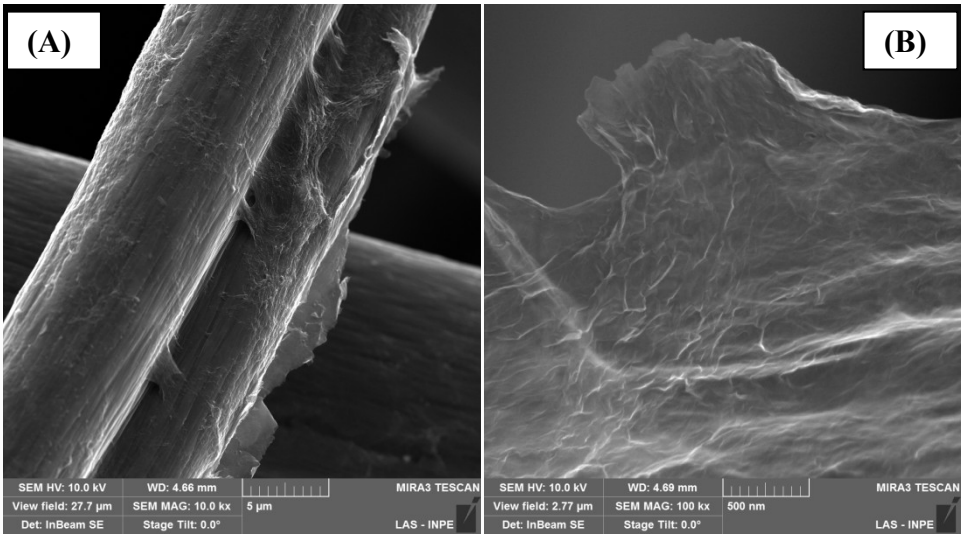

Figure 2- FEG-SEM images: **(A)** rGO/CF film covering CF fibers; **(B)** rGO/CF film with higher magnification evidencing rGO morphology.

3.2. Morphologies and characterization of Cu/rGO/CF electrodes

The top view FEG-SEM images of the Cu deposits on rGO/CF electrodes are depicted in Figure 3, which is related to the small white spots. The Cu deposits presented small grain morphologies distributed throughout the rGO/CF surface. As expected, Cu deposit rate increased from (A) to (C) images, where Cu grain kept similar shapes, but their grain size and density increased as a function of the deposition time.

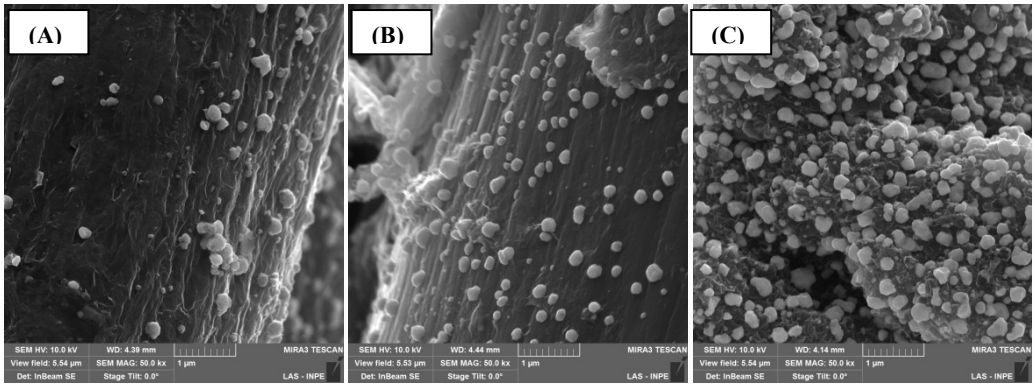

Figure 3- FEG-SEM images of the Cu/rGO/CF films: (A) 3s, (B) 6s, (C) 10s deposition time of Cu.

The XRD patterns of rGO/CF and Cu/rGO/CF films are shown in Figure 4 where rGO/CF displayed three characteristic peaks at about $2\theta = 25^{o}$, 43^{o} and 80^{o}. For Cu particle additions forming the ternary composites, four peaks at about $2\theta = 43^{o}$, 50^{o}, 74^{o} and 90^{o} are detected corresponding to the Cu metal. Furthermore, for Cu/rGO/CF_10s a mixture of phases containing cuprous oxide ($2\theta = 36^{o}$) and metallic copper was also identified. These patterns confirmed that prepared ternary composites

of crystalline Cu metal particles were successfully decorated on CF as well as on rGO sheets.

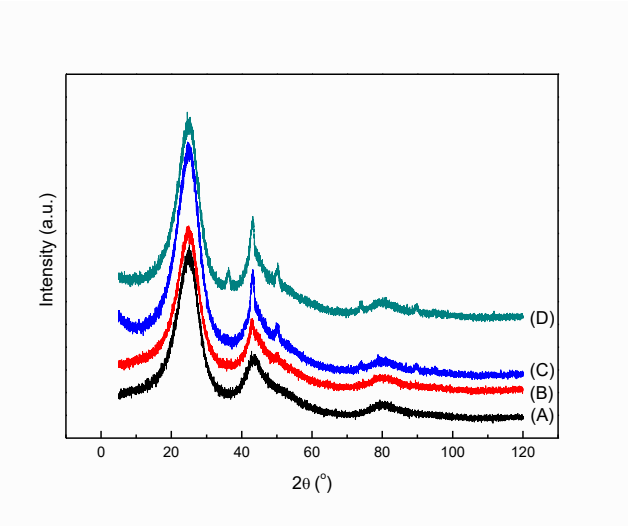

Figure 4- XRD patterns of the (A) rGO/CF and Cu/rGO/CF films: (B) 3s, (C) 6s, (D) 10s of Cu deposition time.

3.3. Electrochemical behavior for nitrate reduction

To investigate the performance of the modified electrodes, the electrochemical behavior for nitrate reduction was studied using CV method. Figure 5 depicts the CV curves obtained in 100 mmol L^{-1} K_2SO_4/H_2SO_4 solution (pH = 3.0) with and without the 10 mmol $L^{-1}KNO_3$. It is important to point out that the electrochemical behavior in the absence of nitrate was similar for all used electrodes. Therefore, we presented only the CV curve for Cu/rGO/CF_10s (blank curve) in Figure 5.

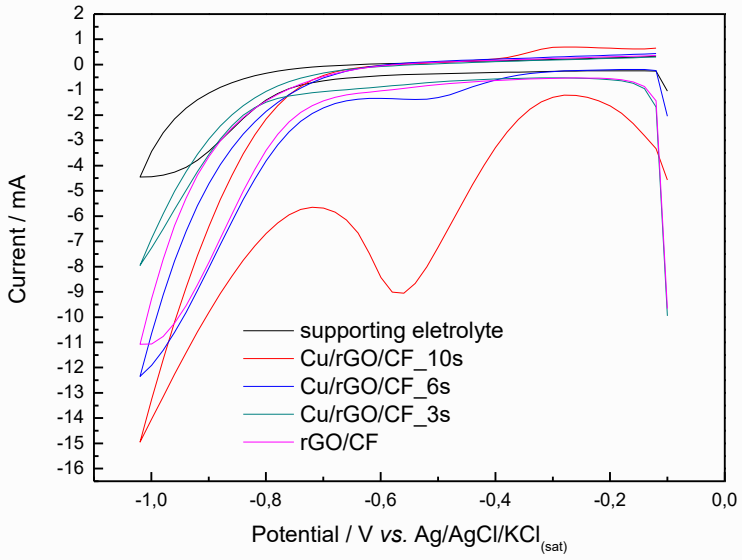

Figure 5- CV curves on rGO/CF and Cu/rGO/CF electrodes in 100 mmol L^{-1} K_2SO_4/H_2SO_4 solution (pH = 3.0) + 10 mmol $L^{-1}KNO_3$ (50 mV s^{-1}).

For all electrodes, the cathodic currents in the absence of the analyte are associated with water reduction. When the nitrate is added, a shift toward more positive potential and an increase of cathodic current are observed, for rGO/CF and Cu/rGO/CF_3s electrodes. This behavior implies that part of the process involved in the cathodic current is associated with water reduction reaction, and another part refers to the nitrate reduction. Thus, these electrodes do not demonstrate good electroactivity response for nitrate reduction. On the other hand, for Cu/rGO/CF_6s a small shoulder appears at around −0.4 V, while for Cu/rGO/CF_10s a well-defined analyte cathodic peak was observed. This potential refers to the nitrate to nitrite reduction, where the catalytic effect and strong enhancement in the electron transfer rate of the analyte on Cu/rGO/CF_10s surface took place. In summary, the Cu/rGO/CF_10s electrode exhibited an excellent electrocatalytic activity toward the nitrate reduction with the highest nitrate cathodic current also demonstrating significant over potential reduction up to ~200 mV.

4. Conclusions

In this paper, stable solid state electrodes of Cu/rGO/CF were successfully produced and characterized using suitable techniques. Then, these electrodes were employed to nitrate reduction. Singular properties such as excellent conductivity and high surface area were obtained for the ternary electrodes attributed to the graphene layer addition enhancing their performance. FEG-SEM images showed the metal deposition density increase as a function of the deposition time. For the novel Cu/rGO/CF eletrodes, the nitrate potential response was stable, rapid, and sensitive. Furthermore, an acceptable selectivity and the highest cathodic current were achieved for Cu/rGO/CF_10s electrode, which means that the metal electrocatalytic activity was the dominant contribution. Preliminary tests indicated that our electrode presented low cost, easy fabrication process, simple to use, and environmentally friendly, suggesting to be promise electrode for nitrate monitoring in various sources.

Acknowledgments

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5. References

[1] R. Gürkan, N. Altunay, J. Food Composition Anal., 2016.
[2] K. Fajerwerg, V. Ynam, B. Chaudret, V. Garçon, D. Thouron, M. Comtat, Electrochem. Commun. 12 , 2010.
[3] G.E. Badea, Electrochim. Acta 54, 2009.
[4] Q. Wang, L. Yu, Y. Liu, L. Lin, R. Lu, J. Zhu, L. He, Z. Lu, Talanta 165, 2017.
[5] F. Manea, A. Remes, C. Radovan, R. Pode, S. Picken, J. Schoonman, Talanta 83 2010.
[6] M. Bonyani, A. Mirzaei, S.G. Leonardi, G. Neri, Measurement 84, 2016.
[7] L. Mattarozzi, S. Cattarin, N. Comisso, R. Gerbasi, P. Guerriero, M. Musiani, E. Verlato, Electrochimica Acta 230, 2017.
[8] J. Hu, J. Sun, C. Bian, J. Tong, X. Shanhong, Electroanalysis 25, 2013.
[9] M.A. Ferree, R.D. Shannon, Water Res. 35 2001.

[10] E. Murray, E. P. Nesterenko, M. McCaul, A. Morrin, D. Diamond and B, Moore, Anal. Methods 9, 2017.
[11] M. Yaqoob, B. Folgado Biot, A. Nabi, P.J. Worsfold, Luminescence 27, 2012.
[12] Y. Zuo, C. Wang, T. Van, Talanta 70, 2006.
[13] I. Ferreira, S. Silva, Talanta 74, 2008.
[14] J. Martínez, A. Ortiz, I. Ortiz, Applied Catalysis B: Environmental, 207, 2017.
[15] M. N. Bui, J. Brockgreitens, S. Ahmed, A. Abbas, Biosensors and Bioelectronics 85, 2016.
[16] M. Kato, M. Okui, S. Taguchi, I. Yagi Journal of Electroanalytical Chemistry, 2017.
[17] H. Bagheri, A. Hajian, M. Rezaei, A. Shirzadmehr, Journal of Hazardous Materials 324, 2017.
[18] W. Ye1, X. Zhang, Y. Chen, Y. Du, F. Zhou, C. Wang, Int. J. Electrochem. Sci. 8 2013.
[19] J. Luo, S. Jiang, H. Zhang, J. Jiang and X. Liu, *Anal. Chim. Acta*, 709, 2012.
[20] B. Yang, H. Wang, J. Du, Y. Fu, P. Yang, Y. Du, Colloids and Surfaces A: Physicochemical and Engineering Aspects 456, 2014.
[21] Y. Ji, Q. Liu, M. Cheng, L. Lai, Z. Li, Y. Peng, Y. Yang, Materials Science & Engineering C 33, 2013.