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COMMUNICATION

# A Highly Active Based Graphene Cathode for Electro-Fenton Reaction

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Abstract. Reduced Graphene Oxide (rGO) was coated on Carbon Felt (CF) in order to design a novel cathode applied in Electro-Fenton (EF) reaction for decontamination of wastewater polluted with Persistent Organic Pollutants (POPs). The new cathode was fabricated by an electrophoretic deposition of Graphene Oxide (GO) followed by its electrochemical reduction at a current density of -1.5 mA.cm^{-2} for 10 min. The modified electrode and GO were characterized by SEM, AFM, XRD and XPS, showing the presence of rGO after optimization of the electrochemical conditions of synthesis. Electrode modification has improved CF electrochemical properties as proved by the decrease of the charge-transfer resistance (R_{ct}) determined by electrochemical impedance spectroscopy (EIS) and the increase of the CV response (2.5 times) of the couple Fe^{III}/Fe^{II} used as a redox probe. Degradation of Acid Orange 7 (AO7), a model pollutant molecule, was monitored by UV-Vis spectrophotometry at the selected single wavelength $\lambda = 485$ nm. Results show that the degradation kinetic was 2 times higher on graphene modified cathode compared to raw carbon felt proving the efficiency of this modification process.

Electro-Fenton (EF) process is one of the most popular electrochemical advanced oxidation processes (EAOPs) for mineralization of persistent organic pollutants (POPs). In this system, the hydroxyl radical (•OH), a highly powerful oxidizing agent, is produced electrochemically and regenerated throughout the reaction between iron catalyst and hydrogen peroxide[1].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^- \quad (1)$$
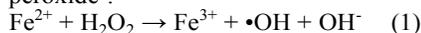
Hydrogen peroxide in aqueous solution can be electro-generated by the two-electron reduction of dissolved oxygen on a cathode.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$
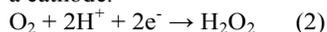
Carbonaceous materials are usually used as cathode, such as three-dimensional graphite[2], reticulated vitreous carbon[3,4], carbon sponge[5], graphite-felt[6,7] or activated carbon fiber (ACF)[8,9,10].

Among the carbon materials, graphene is a two-dimensional (2-D), one-atom thick sheet composed of sp^2 carbon atoms arranged in a honeycomb structure. The isolation of free-standing single-layer graphene was first achieved in 2004[11]. Graphene presents outstanding physical properties, such as high intrinsic mobility, high thermal and electrical conductivity. With Young's modulus of 1 TPa and ultimate strength of 130 GPa, single-layer graphene is the strongest material ever measured. Two main divisions can be distinguished for the graphene preparation methods: bottom-up and top-down. A number of bottom-up approaches have been developed for graphene synthesis, including chemical vapor deposition[12], arc discharge, epitaxial growth on electrically insulating surfaces (as for SiC), chemical conversion, reduction of CO, unzipping carbon nanotubes and self-assembly of surfactants. In top-down processes, graphene or modified graphene sheets are produced by separation/exfoliation of graphite or graphite derivatives (such as GO and graphite fluoride). The advantage of this approach is that it enables high yield production and, hence, it is a cost-effective and scalable process, as required for different applications[13,14].

In this study, rGO produced by exfoliation of graphite will be electrochemically deposited on Carbon Felt (CF) in order to enhance the rate decomposition of dye compound at modified cathode by electro-Fenton reaction because of the possibility to improve the electroactive surface area of raw CF. This new cathode provides an alternative cathode material for future designing of water treatment system using EF technology.

The XRD patterns of graphite powder and graphene oxide are shown in Figure 1a. A strong and sharp diffraction peak (002) at $2\theta = 26.5^0$ was presented for the high ordered structure of graphite powder. On the other hand, XRD of GO exhibited a reflection at approximately 12.5^0 attesting of the high degree of oxidation of the obtained GO materials. The XRD shows as

well the absence of a peak at around 26° confirming that all the graphite powders have been converted to GO[15]. Moreover, the much higher d-spacing of GO comparing to graphite powder demonstrated the formation of oxygenated functional groups

such as hydroxyl, epoxy and carboxyl after the oxidation which could be seen clearly on XPS spectrum (Figure 1b).

Table 1. Atomic percentage in the synthesized samples

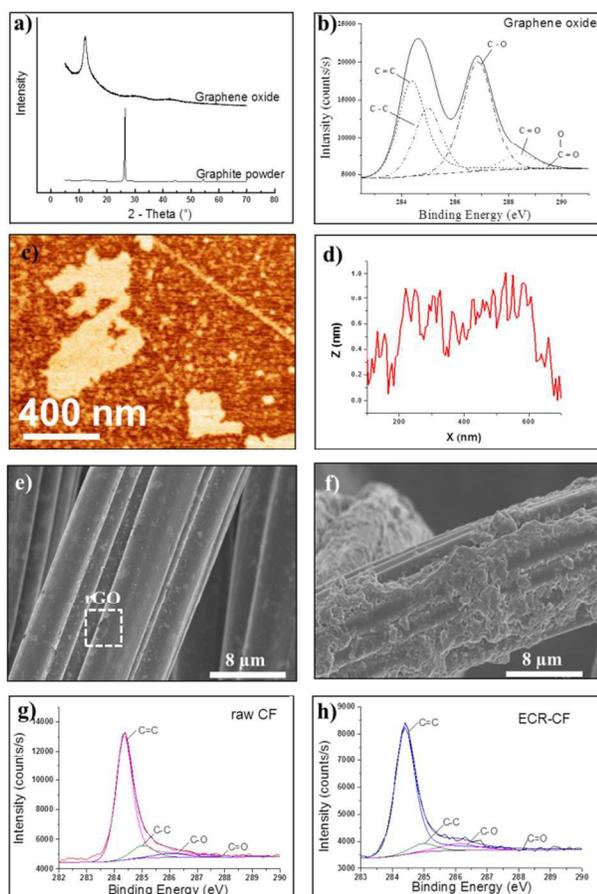|	*Name*	*Peak BE*	*Height Counts*	*FWHM eV*	*Area (P) CPS.eV*	*Area (N)*	*At. %*
GO	C1s	284.66	18061.79	1.60	56275.23	1.30	73.33
	O1s	532.71	27099.56	1.96	58213.40	0.47	*26.67*
RawCF	C1s	284.37	8486.01	0.73	8312.01	0.19	92.26
	O1s	532.23	609.67	2.62	1985.18	0.02	*7.74*
ECR-CF	C1s	284.40	4838.88	0.74	4951.55	0.11	87.67
	O1s	531.99	652.03	2.98	1981.68	0.02	*12.33*

Figure 1. (a) X-ray diffraction patterns of graphite powder and graphene oxide, (b) X-ray photoelectron spectroscopy of graphene oxide, (c) AFM topographic image and (d) Height profile of a single layer from the suspension of graphene oxide, (e) SEM image of CF after 10 min and (f) after 2h of GO deposition, (g) XPS of raw-CF and (h) XPS of ECR-CF electrode.

Atomic Force Microscopy (AFM) image (Figure 1c and 1d) indicated that the thickness of GO is around 1 nm demonstrating that the suspension of graphene oxide are consisting of monolayers of graphene oxide.

The C/O ratio obtained by XPS measurement (Table 1) was 2.75, proving that the synthesized GO has very good properties because it is generally accepted that the conversion of graphite to GO is completed when the C/O ratio becomes higher than 2.0 as reported by Kovtyukhova *et al*[16].

Electrochemical Reduction-Carbon Felt (ECR-CF) electrode was manufactured by electrophoretic deposition and electrochemical reduction of a suspension of GO. The SEM graphs (Figure 1e) shows a well adhesive layer of rGO coated on the CF surface to create uniform structure. As the CF was decorated by rGO, the roughness of the electrode increased, leading to the enhancement of the specific surface area. We note here that due to the low quantity of GO deposited on the surface of CFs, Brunauer-Emmett-Teller (BET) experiments could not be performed to determine quantitatively the specific surface area.

Deconvolution of the C1s peak in the XPS spectrum (performed on ECR-CF surface) in Figure 1g and 1h showed the presence of four types of carbon bonds: C=C (284.2 eV), C-C (285 eV), C-O (286.3 eV), and C=O (288.2 eV). Compared to GO, intensity of C-O or C=O peaks of ECR-CF decreased significantly, which confirms that most of the oxygen functionalities were removed. There was 12.33% oxygen retaining in modified samples because of 7.74 % in initial CF and only 4.59% from the residual hydroxyl, epoxy or carboxylic groups that still existed in the structure of rGO (Table 1). However, these defects become useful when ECR-CF was applied in EF process, owing to induce an improved hydrophilic characteristic.

The redox wave $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ is sensitive to surface chemistry of carbon-based electrodes[17], so it was used to optimize the conditions for the deposition as well as the reduction of GO as shown in Figure 2a and 2b. The current response toward $[Fe(CN)_6]^{3-/4-}$ of the modified electrode increased strongly as the current density deposition changed from 0.75 to 1.5 mA/cm^2 or time deposition climbed from 5 min up to 10 min. In fact the higher current either time was, the more quantity of GO came and reduced on the surface of CF, forming an homogeneous graphene-layer which induced the acceleration of the electrochemical action as a consequence of the excellent electrical property of graphene[18]. Nevertheless a slight decline was observed continuously from 3.0 to 6.0 mA/cm^2 which results from the agglomeration of the GO sheets, as observed on SEM (Figure 1f), and uncompleted reduction. This decreased phenomenon was also observed if the

time of deposition was extended over 10 min (*i.e.* 40 min) with the similar reason as too much rGO overlapped on CF. Therefore, we suggest choosing the best deposition condition at 1.5 mA/cm^2 for 10 min (Table S2 (SI)).
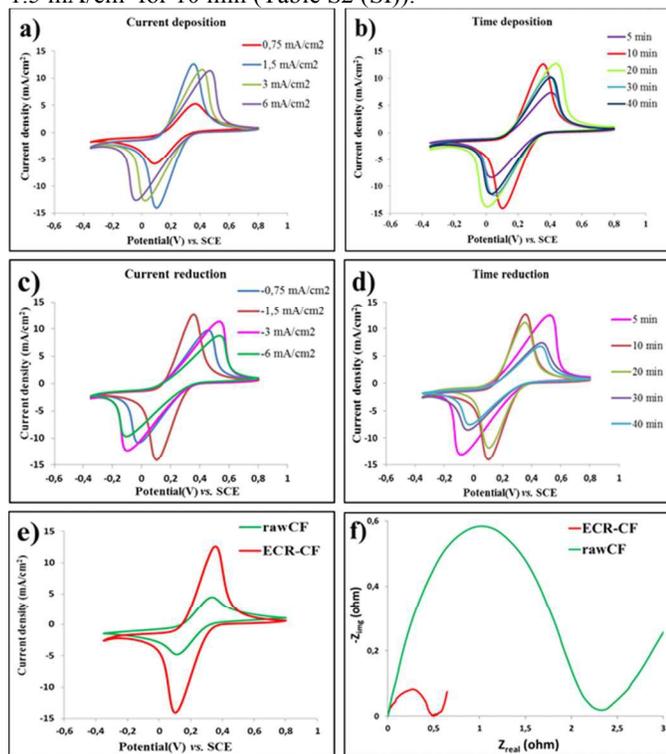

Figure 2. (a) Cyclic voltammograms (CVs) of ECR-CF at different currents deposition, (b) at different times deposition, (c) different currents reduction, and (d) different times reduction. (e) CVs and (f) Electrochemical impedance spectroscopy (EIS) of the modified (in optimal conditions) and the unmodified electrodes in 10mM $K_3[Fe(CN)_6]$ + 1M KNO_3 solution. Scan rate 10 mV/s.

The oxygen-containing groups of GO was electrochemical reduced directly from an aqueous suspension of GO at the CF electrode surfaces to form rGO[19]. Most of these groups were reduced at applied current density of -1.5 mA/cm^2 in 10 min. Exceeding these values, the high of the peak current on redox probe $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ fell down quickly (Figure 2c and 2d). Particularly, the peak current density of modified electrode went up and the anodic and cathodic peak separation was smaller when the current density reduction increased from -0.75 to -1.5 mA/cm^2 or the time reduction prolonged from 5 min to 10 min, because the GO staying on CF needed enough the power as well as the time to be reduced fully. However, these results were changed badly if we continued extending the current density reduction up to -3 mA/cm^2 and -6 mA/cm^2 or time reduction up to 40 min. It could come from the reason that the reverse of CF electrode polarity from anode for GO deposition to cathode for the reduction made the adsorbed GO on the CF partly moved back to the opposite electrode of Pt, which might be causing the loss amount of rGO on the surface electrode during the reduction process. Therefore, the more current and time reduction were, the more rGO was mislaid. In fact, a yellow-brown color layer of GO was formed on the surface of Pt electrode after experiment, so it hindered

somewhat the reduction reaction of GO at the CF when current and time reduction exceeded the optimal value.

The CV peak current on the ECR-CF was 2.5 times stronger than on the raw CF in Figure 2e. This result obviously pointed out that the electroactive surface area was increased, indeed it helped to create a rise of electrochemical active sites for redox reactions of the couple Fe^{III}/Fe^{II} on the surface CF, relying on the large surface area of graphene, as mentioned in previous studies for graphene-modification[20,21,22]. Additionally, the interfacial charge-transfer resistance (R_{ct}) of ECR-CF determined by EIS is lowered by 1.88 Ω, comparing to 2.38 Ω of raw CF (Figure 2f), which demonstrated that rGO could accelerate the electron transfer efficiency, proving the good conductivity of modified electrode as compared to raw CF thus aided to encourage the cathode performance in EF reaction.

The modification by rGO upgraded remarkably the performance of the new cathode applied to treat azo dye AO7 by EF reaction, depending on the improvement of the charge transfer resistance of the raw CF. This feature is very important to H_2O_2 production, the Fenton's reagent, since the acceleration of the electron transfer rate could promote the reduction of the dissolved oxygen at the cathode according to Eq. (2)[23]. From that more hydroxyl radicals (•OH) were generated in the medium following Eq. (1)[24]. Figure 3a described the decay kinetics of AO7 by electro-Fenton process on the modified cathode. The complete degradation of 0.1 mM AO7 was achieved in 6 min on the ECR-CF instead of more than 12 min on the unmodified one. It could be seen from Figure 3b that absorption band related to azo bond (wavelength $\lambda = 485$ nm) disappeared totally after 6 min treatment, so the color orange of initial solution was destroyed completely (Figure 3c). The absorption peak at 228, 254, and 310 nm in the initial solution were rapidly weakened due to the damage of aromatic ring structure. Apparent rate constants for the degradation of AO7 were determined by plotting the Ln($[AO7_0]/[AO7]$) against time[25,26,27]. The values of 0.5688 min^{-1} was obtained for ECR-CF more than 2 times of the pristine one (Table 2).
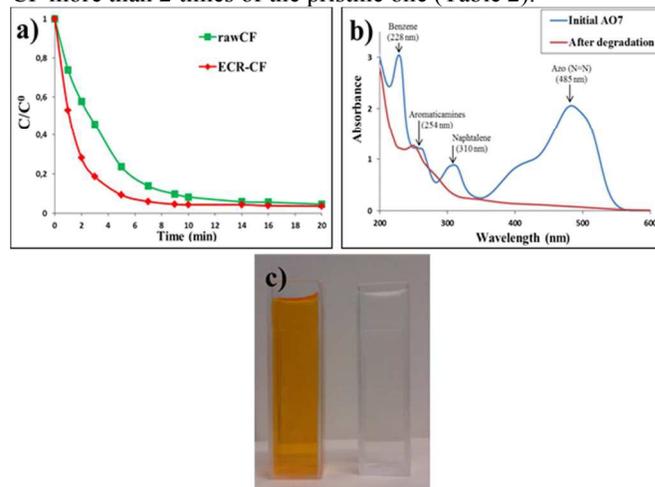

Figure 3. Degradation kinetics of AO7 by the electro-Fenton process on raw CF and ECR-CF cathode. Conditions: 30 mL AO7 (0.1 mM) aqueous solution in 50 mM Na_2SO_4 with 0.20 mM Fe^{2+} of pH 3.0, Pt anode, and 40 mA constant current electrolysis. (b) The absorption spectrum of initial AO7 and treated solution after 6 min. (c) Color of AO7 solution before and after decontamination.

Table 2. Apparent first order rate constants and abatements for the degradation kinetics of AO7.

Catod	k_{app} (min^{-1})	Abatement (%) after 3 min
rawCF	0.2596	54.29
rGO-CF	0.5688	81.44

Conclusions

In summary, a novel cathode fabricated from a suspension of GO by electrophoretic deposition at 1.5 mA/cm^2 in 10 min and electrochemical reduction at -1.5 mA/cm^2 with the same time was used in EF process to eliminate the azo dye AO7 in aqueous medium. This method is very simple, rapid without using supporting electrolyte, toxic reductor or binder. The XRD, AFM and XPS indicated that GO was synthesized successfully from oxidation of graphite and most of them was changed to rGO on the surface of CF after reduction. This modification raised the electroactive surface area of ECR-CF which is proved by CVs and EIS results. Therefore, AO7 degradation rate using ECR-CF cathode is 2 times quicker than on the non-modified CF. In the future research, ECR-CF will be a good choice for the treatment of wastewater accommodating POPs by EF process.

Notes and references

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