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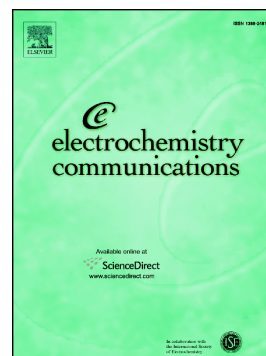
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Electrografting of amino-TEMPO on graphene oxide and electrochemically reduced graphene oxide for electrocatalytic applications

Baiqing Yuan^{a,*}, Chunying Xu^a, Daojun Zhang^a, Renchun Zhang^a, Huimin Su^a, Pei Guan^a, Jiajia Nie^a, Carlos Fernandez^{b,*}

^a Henan Province Key Laboratory of New Optoelectronic Functional Materials, College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang 455000, Henan, China

^b School of Pharmacy and Life Sciences, Robert Gordon University, Garthdee Road, Aberdeen AB10 7GJ, United Kingdom.

*** Corresponding author.**

E-mail: yuanbaiqing@aynu.edu.cn (B. Yuan); baiqingyuan1981@126.com (B. Yuan); c.fernandez@rgu.ac.uk (C. Fernandez)

Abstract

4-amino-2,2,6,6-tetramethyl-1-piperidine N-oxyl (4-amino-TEMPO), an electroactive nitroxide radical, was attached to the surface of graphene oxide (GO) and electrochemically reduced graphene oxide (ERGO) modified glassy carbon electrode by a simple, rapid and green electrografting method. The electroactive interfaces were analyzed by X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV). The calculated surface coverage for 4-amino-TEMPO is up to $1.55 \times 10^{-9} \text{ mol}\cdot\text{cm}^{-2}$. The modified electroactive interface exhibited excellent electrocatalytic activity towards the electro-oxidation of reduced glutathione (GSH) and hydrogen peroxide (H_2O_2).

Key words: 4-amino-TEMPO, Nitroxide radical, Electrochemically reduced graphene oxide, Reduced glutathione, Hydrogen peroxide

Introduction

2,2,6,6-tetramethyl-1-piperidine N-oxyl (TEMPO) is a stable and electroactive radical in both aqueous and non-aqueous solution due to being protected by four α -methyl groups [1,2]. However, this persistent nitroxyl radical can be converted to an oxoammonium cation in a fast and reversible electrochemical process [3]. TEMPO and its derivatives have been widely investigated and employed as electrocatalysts for the oxidation of alcohols [3-7] and amines [8] as well as being used as an anode material [9] or electrolyte [2,10] in batteries.

TEMPO-based electroactive interfaces have attracted great attention due to their enhanced electrocatalytic behavior [11], which has been achieved through immobilization onto various solid surfaces including Si electrodes [12,13], ITO [14], multiwalled carbon nanotubes [15], glassy carbon electrodes (GCE) [11,16], and graphite electrodes [17,18]. Several methods have been employed to achieve immobilization including chemisorption [12], π -stacking [15], electropolymerization [14], and covalent bonding [11,18].

Graphene (G) has emerged as a promising material owing to its unique two-dimensional structure. Graphene oxide (GO) is a highly oxidized derivative of graphene which possesses a large amount of oxygen functional groups (e.g. hydroxyl, epoxide, carboxyl, and carbonyl groups) [19]. TEMPO has been successfully anchored onto GO [20,21] and G [9] via a covalent bonding method. However, we present here for the first time a simple, rapid, and green electrografting method for attaching the TEMPO radical to GO and electrochemically reduced GO (ERGO) by

using 4-amino-TEMPO. The modified TEMPO interface showed excellent redox properties. The methodology was successfully applied to enhance the electrocatalytic oxidation of reduced glutathione (GSH) and hydrogen peroxide (H_2O_2).

2. Experimental

2.1. Chemicals and solutions

4-amino-TEMPO, TEMPO, GSH, and H_2O_2 were purchased from Sigma-Aldrich Co., China. GO and graphene were acquired from Nanjing XFNano Materials Tech Co., Ltd, China. All other chemicals were of analytical reagent grade, and doubly distilled water was used to prepare all the solutions.

2.2. Apparatus

All the electrochemical experiments were carried out on a CHI 842C electrochemical workstation (Austin, TX, USA) with a conventional three-electrode system, which included a glassy carbon working electrode, a platinum coil as an auxiliary electrode, and Ag/AgCl (saturated KCl) as the reference electrode. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB250 spectrometer fitted with a monochromatic Al $\text{K}\alpha$ X-ray source.

2.3. Electrode preparation and modification

Prior to each experiment, the GCE was polished with 1, 0.3, and 0.05 μm alumina paste to a mirror finish. The electrode was then rinsed with water and an ultrasonic treatment in water was applied. GCEs modified with GO and G (GO/GCE and G/GCE) were prepared by dropping 5 μL of 1 mg/mL GO aqueous solution and 1 mg/mL G DMF dispersion, respectively, onto the cleaned electrode, followed by

drying at room temperature. In order to investigate the effect of oxygen-containing species on the grafting of 4-amino-TEMPO, the GO/GCE was electrochemically reduced (ERGO) in 0.1 M acetate buffer (pH = 4) by amperometry for 500 s at different potentials in a range from -0.6 to -1.2 V. Unless otherwise specified, the applied potential refers to -0.9 V. The immobilization of 4-amino-TEMPO on GO/GCE (4-amino-TEMPO-GO/GCE) or ERGO/GCE (4-amino-TEMPO-ERGO/GCE) was achieved in 0.1 M PBS (pH = 7.2) in the presence of 1 mM 4-amino-TEMPO by CV scanning for 50 cycles from 0 to 1.1 V. Control experiments were also performed in 1 mM TEMPO under the same conditions. For comparison, experiments were also conducted by dipping the corresponding electrode in 0.1 M PBS (pH = 7.2) in the presence of 1 mM 4-amino-TEMPO solution for 40 mins without CV scanning. All electrodes were rinsed with water after each step.

3. Results and discussion

Figure 1 shows the CVs of different modified electrodes in 0.1 M PBS (pH = 7.2) at a scan rate of 0.1 V/s. As shown in **Fig. 1A**, the bare GCE exhibited a couple of very weak redox peaks at 0.72 and 0.66 V after CV scanning in 0.1 M PBS (pH = 7.2) in the presence of 1 mM 4-amino-TEMPO, indicating that hardly any 4-amino TEMPO was present on the bare GCE. Compared to the bare GCE, much higher redox peaks were observed at the GO/GCE, although the redox currents diminished dramatically with the number of cycles (**Fig. 1B**, solid lines). This suggested that 4-amino-TEMPO was attached to the surface of GO/GCE, and the surface coverage

was calculated to be 7.26×10^{-11} mol·cm⁻² from Faraday's law by integration of the cyclic voltammograms. It is interesting that no redox peaks appeared for GO/GCE in the background electrolyte when the same experiment was performed in 0.1 M PBS (pH = 7.2) in the presence of 1 mM TEMPO (**Fig. 1C**), indicating that the amino group plays an essential role in the immobilization of 4-amino-TEMPO.

Next, a comparison experiment was carried out to investigate the influence of possible adsorption of 4-amino-TEMPO onto the GO/GCE. Only a couple of very weak peaks occurred at the GO/GCE when the electrode was dipped in 0.1 M PBS (pH = 7.2) in the presence of 1 mM 4-amino-TEMPO for 40 mins and then removed to the background electrolyte, as shown in **Fig. 1D (dotted line)**. A control experiment was also performed at the G/GCE and again only a little 4-amino TEMPO was present on the electrode (**Fig. 1D, dashed line**). This suggested that a very weak adsorption interaction exists between GO or G and 4-amino-TEMPO but not TEMPO. However, more 4-amino-TEMPO was attached to the GO (7.26×10^{-11} mol·cm⁻²) or G (2.58×10^{-10} mol·cm⁻²) surface after CV scanning (**Fig. 1B and Fig. 1D, solid line**) than after adsorption treatment (**Fig. 1D, dotted line and dashed line**) (9.73×10^{-12} mol·cm⁻² and 5.01×10^{-11} mol·cm⁻² for GO and G, respectively). It was found that an enhanced and stable response representing immobilized 4-amino-TEMPO with a high surface coverage of 1.55×10^{-9} mol·cm⁻² was achieved at the ERGO/GCE (**Fig. 1E**), which was obtained by electrochemical treatment of GO/GCE at -0.9 V. For ten repeated cycles, the redox currents remained almost constant (**Fig. 1E, solid lines**) unlike the results obtained with GO/GCE (**Fig. 1B, solid lines**). The effect of the

GO/GCE reduction potential (-0.6 to -1.2 V) on the grafting of 4-amino-TEMPO was also investigated, as shown in **Fig. 1F**. It was found that GO/GCE treated at -0.9 V yielded the most efficient immobilization of 4-amino-TEMPO, suggesting that the oxygen-containing species vary with the reduction potential and that these also have an influence on the grafting of 4-amino-TEMPO. It seems that both amino group and CV scanning are essential for the efficient immobilization of the TEMPO radical onto the modified electrode. We proposed that firstly the amine group of 4-amino-TEMPO was intermolecularly oxidized by its active oxoammonium ion (II) and secondly, the product was then attached to some target-specific oxygen-containing groups [22] on ERGO and GO because the oxoammonium salts could oxidize amines to a series of compounds [23].

The 4-amino-TEMPO modified interfaces were further analyzed by XPS (**Fig. 2**). The survey spectra showed obvious C 1s, O 1s, and N 1s peaks, with atomic percentages of 80.02:15.01:4.97 and 71.56:24.93:3.51, for 4-amino-TEMPO-ERGO/GCE and 4-amino-TEMPO-GO/GCE, respectively. There was no observed high binding energy N 1s peak at ca. 405 eV [24] which would correspond to nitroxide adsorbed on G surface, suggesting that 4-amino-TEMPO was attached to GO and ERGO via covalent binding rather than adsorption. The narrow N 1s spectrum of 4-amino-TEMPO-ERGO/GCE gave two fitted peaks with binding energies of 400.4 and 399.8 eV. For 4-amino-TEMPO-GO/GCE, the binding energies were found to be 400.8 and 399.8 eV, respectively. The two binding energy peaks are assigned to the free nitroxide nitrogen atom (400.6 eV) in the thin film [12] and the

amine nitrogen atom (399.3 eV) [25], respectively. As shown in **Fig. 2E**, the C 1s spectrum of GO exhibited four fitted peaks centered at 285.0, 285.7, 287.4, 289.4, indicating the presence of C-C, COH, C-O-C, and COOH, respectively [26]. Comparing the C 1s spectrum of GO/GCE with the C 1s spectrum of 4-amino-TEMPO-GO/GCE (**Fig. 2F**), the COOH peak disappeared and the intensity of the COH peak diminished dramatically. This suggests that 4-amino TEMPO might be grafted to GO via COOH and COH groups.

Figure 3A shows the CVs of 4-amino-TEMPO-ERGO/GCE in 0.1 M PBS (pH 7.2) at different scan rates (0.02 to 0.8 V/s). As can be seen in **Fig. 3A**, both the anodic and cathodic peak currents are proportional to the scan rate, which is indicative of a surface-controlled process. The stability of the coatings was also investigated by repeated cycles. It took more than four hours for 1000 cycles. The oxidation (reduction) peak current diminishes gradually with a loss of 2.9% (1.4%), 48% (46%), and 84% (85%), respectively, after 100, 500, and 1000 cycles. This stability is better than that currently reported in the literature for covalent TEMPO attached to a Si [12] or graphite felt electrode [18] by chemical reactions. For the two reported electrodes, the current response decreased by 33% after 100 cycles and 50% after 50 cycles, respectively.

Next, the 4-amino-TEMPO-ERGO/GCE was employed for enhanced electrocatalytic oxidation of GSH in 0.1 M PBS (pH 7.2), as shown in **Fig. 3B**. It can be seen that, upon addition of GSH to the background electrolyte, an oxidation wave with a peak potential of 0.7 V was observed, suggesting that the immobilized

4-amino-TEMPO showed a high electrocatalytic activity towards the oxidation of GSH. Electrochemical detection of GSH was achieved using the 4-amino-TEMPO-ERGO/GCE; the linear range is from 1 to 254 μM with a calculated detection limit of 0.6 μM ($S/N = 3$). The electrode was also utilized for the enhanced electro-oxidation of H_2O_2 (**Fig. 4**). No H_2O_2 oxidation peaks were observed at the GO/GCE (**Fig. 4A**) or ERGO/GCE (**Fig. 4B**). However, at the 4-amino-TEMPO-GO/GCE, the oxidation peak of H_2O_2 appeared at 0.8 V (**Fig. 4C**). Among the electrodes studied, the 4-amino-TEMPO-ERGO/GCE electrode exhibited the highest oxidation current for H_2O_2 , and the oxidation current was two times higher than that obtained with 4-amino-TEMPO-GO/GCE. This indicated that the 4-amino-TEMPO immobilized on ERGO has a much higher electrocatalytic activity towards the oxidation of H_2O_2 . H_2O_2 was successfully detected over a linear range from 0.1 to 666.3 μM using amperometry. The detection limit for H_2O_2 was calculated to be 0.04 μM ($S/N =$).

4. Conclusions

A simple, rapid and green electrografting method was successfully demonstrated for the immobilization of amino-TEMPO onto GO and ERGO modified electrodes. The amino group present on TEMPO played an essential role in the immobilization of TEMPO. The 4-amino-TEMPO modified interface exhibited high electrocatalytic activity for the oxidation of GSH and H_2O_2 and the methodology was successfully employed for the sensitive determination of GSH and H_2O_2 . The TEMPO-based electroactive interface has potential for applications in electrocatalysis and electrode

materials.

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Figure captions

Figure 1. CVs of GCE (A) and GO/GCE (B and C) in 0.1 M PBS (pH 7.2) before (dotted line) and after (solid line) CV scanning (*Inset*) in 1 mM 4-amino-TEMPO (A and B) or TEMPO (C) at a scan rate of 0.1 V/s. (D) CVs of GO/GCE (dotted line) and G/GCE (solid line and dashed line) after CV scanning (solid line/*Inset*) or immersion (dotted line and dashed line) in 1 mM 4-amino-TEMPO for 40 mins. (E) CVs of GO/GCE treated at -0.9 V in 0.1 M PBS (pH 7.2) after CV scanning (*Inset*) in 1 mM 4-amino-TEMPO. (F) CVs of GO/GCE treated at different potentials in 0.1 M PBS (pH 7.2) after CV scanning in 1 mM 4-amino-TEMPO. *Insets* are the CVs of the different electrodes including GCE (A), GO/GCE (B,C), G/GCE (D), and ERGO/GCE (E) in 0.1 M PBS (pH 7.2) in the presence of 1 mM 4-amino-TEMPO (A, B, D, E) or TEMPO (C). 0.1 M PBS (pH 7.2) was employed as the electrolyte in all cases.

Figure 2. Survey XPS scan (A and C) and narrow scan of the N 1s (B and D) and C 1s (E and F) region for 4-amino-TEMPO-ERGO/GCE (A and B), 4-amino-TEMPO-GO/GCE (C, D, and F), and GO/GCE (E).

Fig.3 (A) CVs of 4-amino-TEMPO-ERGO/GCE in 0.1 M PBS (pH 7.2) at different scan rates. *Inset* is the plot of redox peak currents vs. the scan rate; (B) CVs of 4-amino-TEMPO-ERGO/GCE in 0.1 M PBS (pH 7.2) in the absence (dotted line) and presence (solid line) of 5 mM GSH at a scan rate of 0.1 V/s. *Inset* (C) is the amperometric response of 4-amino-TEMPO-ERGO/GCE to the successive addition of

GSH in stirred 0.1 M PBS (pH 7.2) at an applied potential of 0.6 V. *Inset* (D) is the amperometric response at low concentrations. *Inset* (E) is the calibration curve for the steady-state current on the addition of different GSH concentrations.

Fig. 4 CVs of GO/GCE (A), ERGO/GCE (B), 4-amino-TEMPO-GO/GCE (C), and 4-amino-TEMPO-ERGO/GCE (D) in 0.1 M PBS (pH 7.2) in the absence (dotted line) and presence (solid line) of 5 mM H₂O₂. (E) Amperometric response of 4-amino-TEMPO-ERGO/GCE to the successive addition of H₂O₂ in stirred 0.1 M PBS (pH 7.2) at an applied potential of 0.75 V with the calibration curve (*Inset*). (F) Amperometric response at low H₂O₂ concentration.

Fig.1

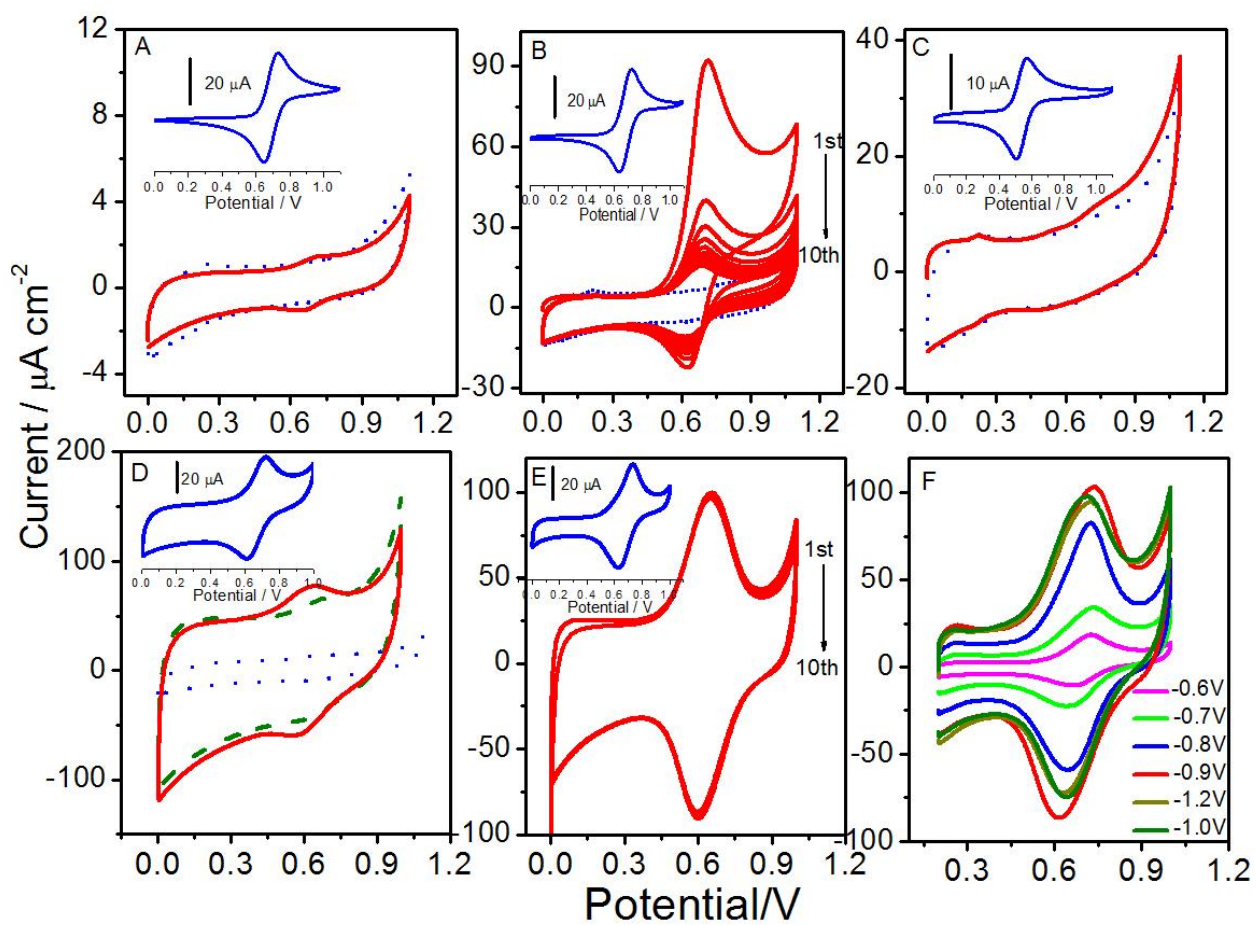


Fig.2

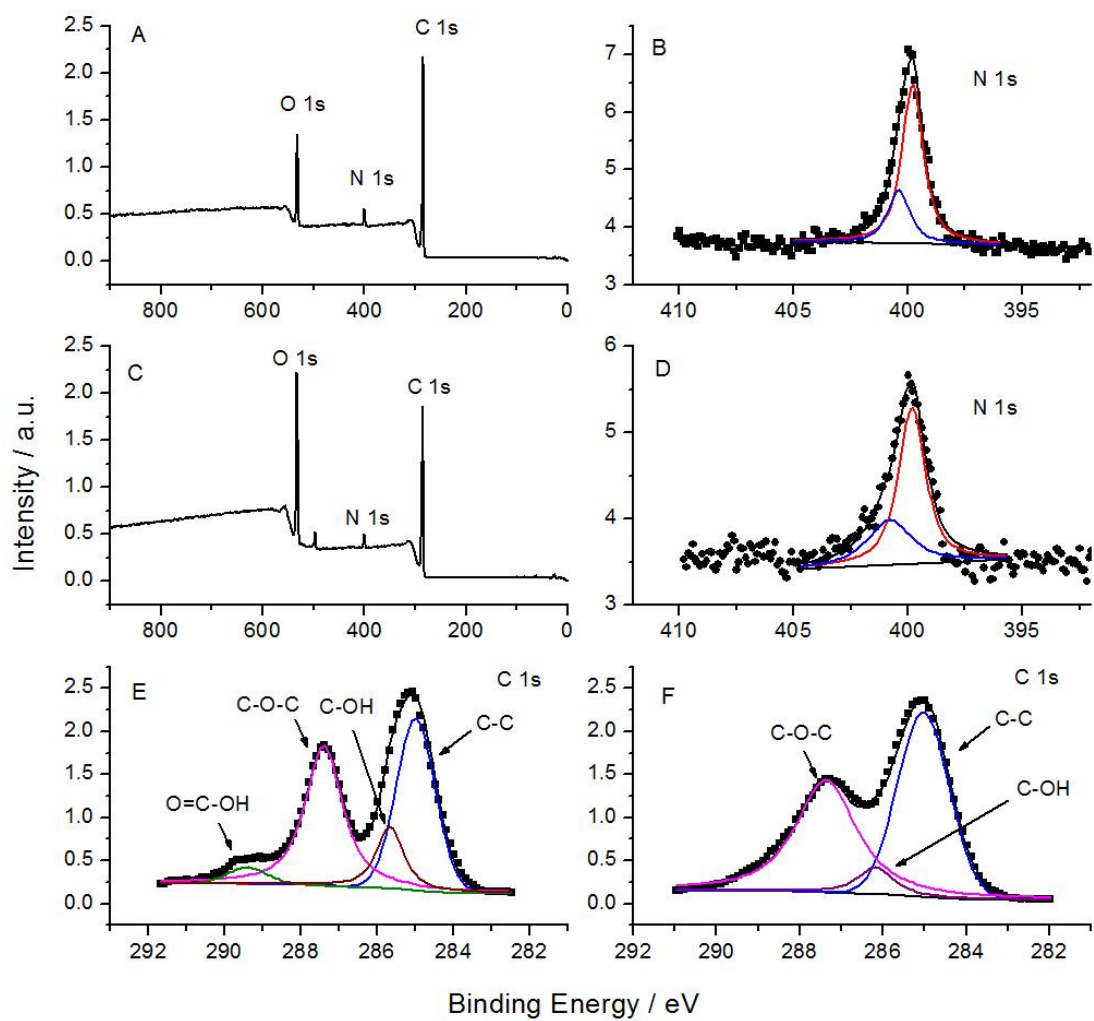


Fig.3

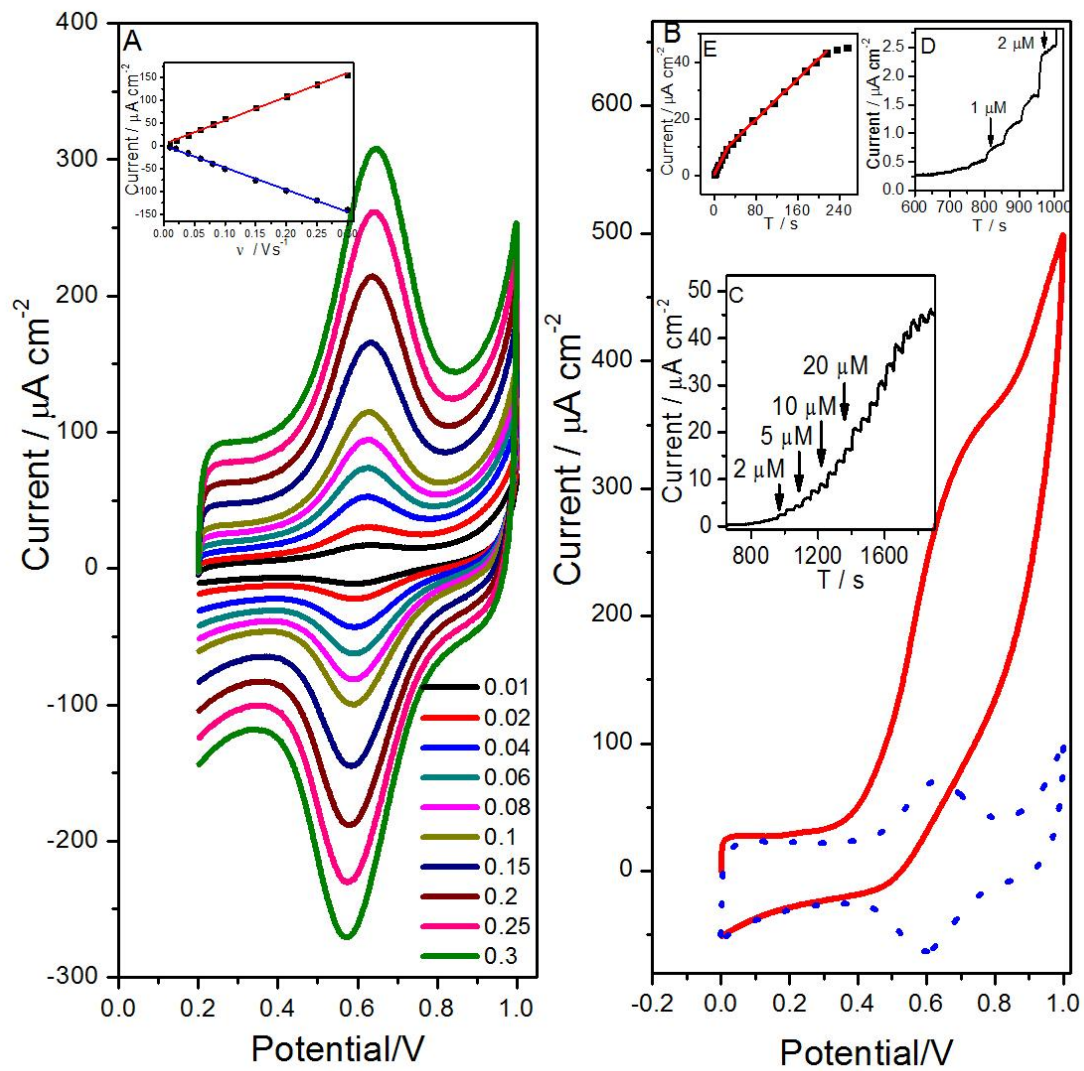
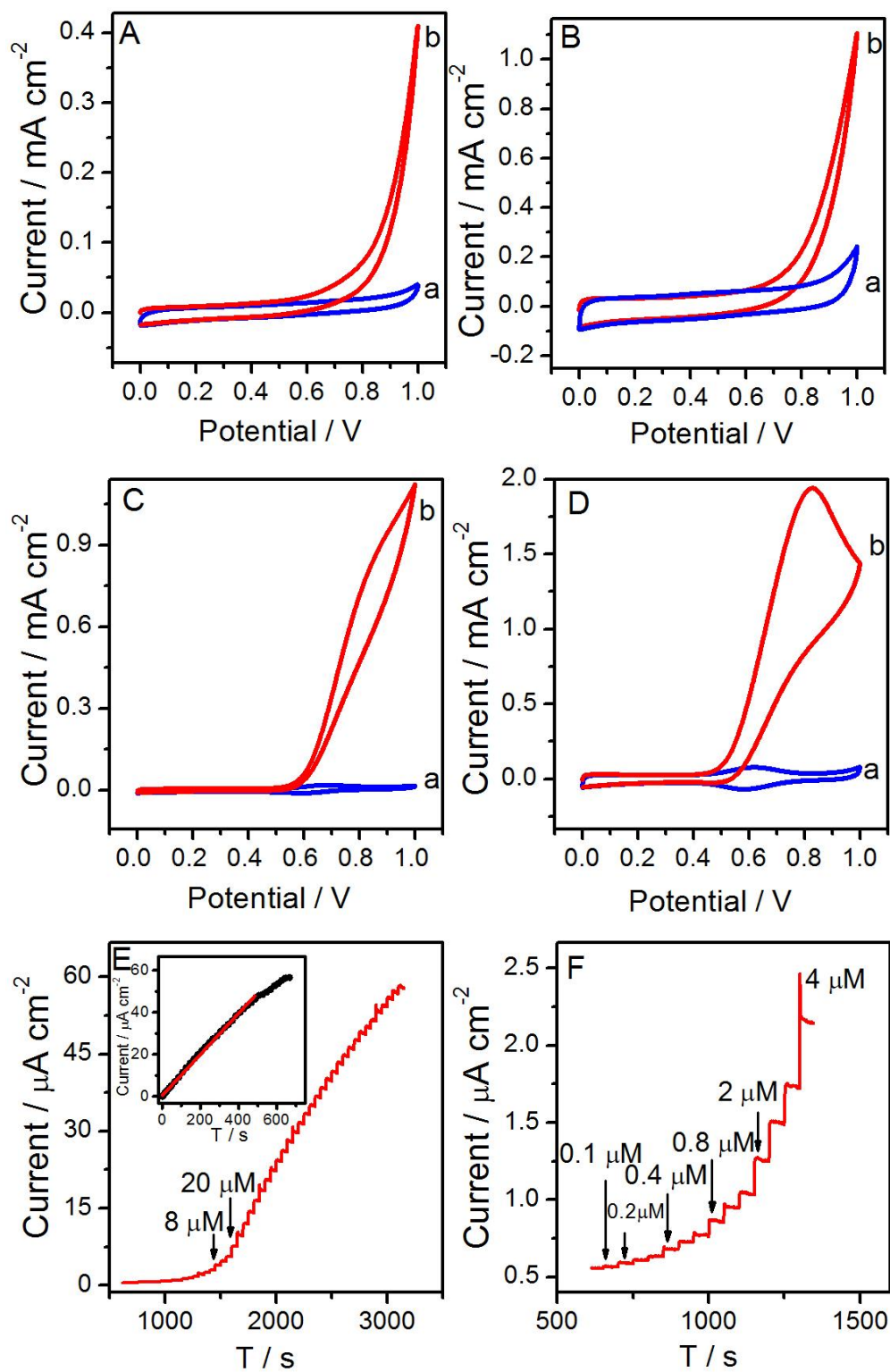
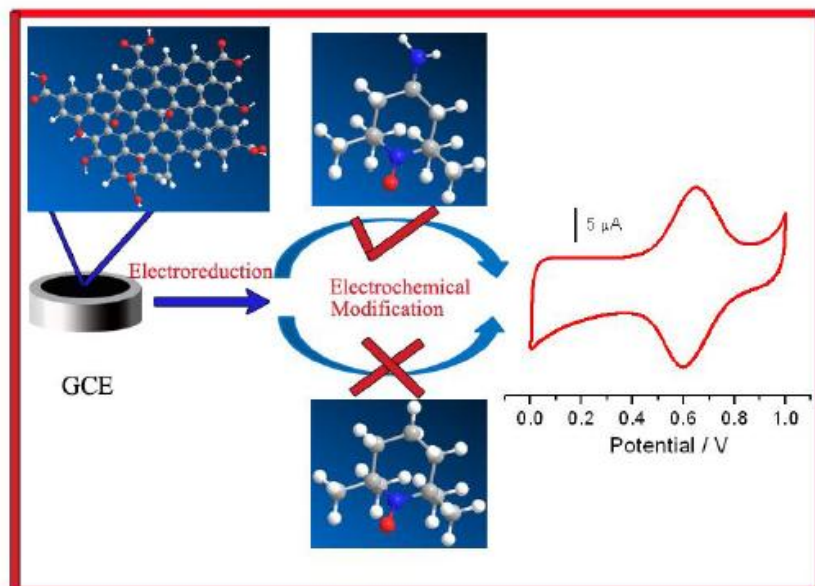


Fig.4





Graphical abstract

Highlights

- Grafting of 4-amino-TEMPO onto GO and ERGO by a simple electrochemical method.
- The 4-amino-TEMPO surface coverage is up to $1.55 \times 10^{-9} \text{ mol cm}^{-2}$.
- The modified TEMPO interface showed high electrocatalytic activity for GSH and H_2O_2 .