

*Supplementary Information*

**Au nanoparticle decorated graphene nanosheets for electrochemical  
immunosensor of p53 antibodies for cancer prognostics**

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## Experimental section

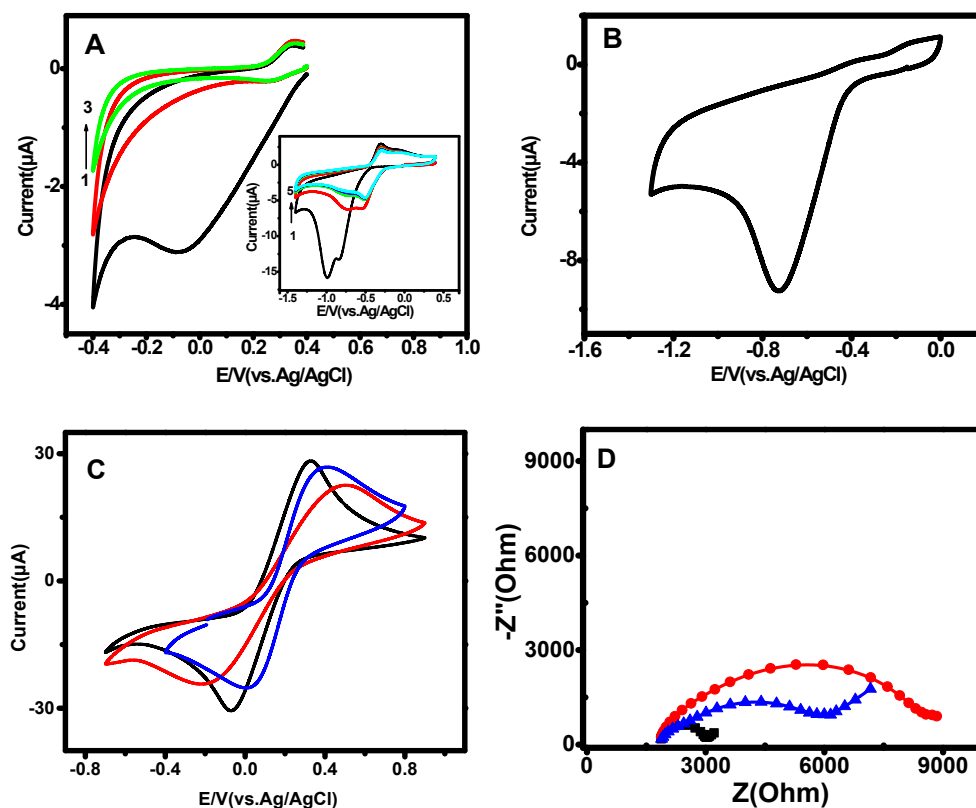
### Electrochemical characterization of GO and ERGO modified electrodes

The assembly of GO and ERGO through p-aminophenyl (p-AP) moiety occurs through electrostatic interactions and  $\pi$ - $\pi$  stacking. The grafting of p-nitrophenylamine (p-NP) was carried out by cyclic voltammetry. A sharp irreversible peak at approximately  $-0.073$  V vs. Ag/AgCl was recorded during the first cycle, followed by a significant decrease of the current during the subsequent cycles (Fig. S1). This response is similar to that observed for other diazonium salts <sup>1</sup>. The grafted p-NP was then subjected to electrochemical reduction to produce amino terminated phenyl, as illustrated by the reduction peak at  $-1$  V vs. Ag/AgCl during the first cycle (Fig. S1, inset).

After assembling of the GO sheets onto the SPCE surface, the electrochemical reduction of GO to ERGO was performed, and this process can be illustrated by the sharp reduction peak at  $-0.87$  V as shown in Fig. S1, panel B. This voltammetric profile is similar to the one previously reported for the reduction of GO sheets on glassy carbon electrode surfaces <sup>2</sup>.

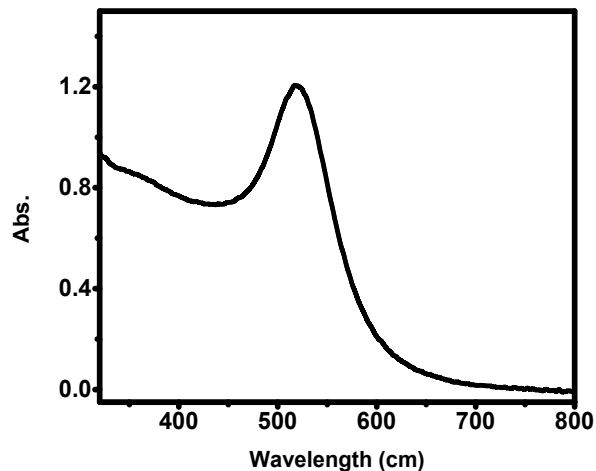
The characterization of GO and ERGO modified surfaces was then performed by recording the corresponding CVs and electrochemical impedance spectra in the presence of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox probe. A significant decrease in the peak current and an increase in the peak separation were observed upon assembly of GO sheets as compared to bare SPCE. This behaviour was confirmed by impedance spectroscopy where the diameter of the semi-circle in the Nyquist plot increases as the result of the higher electron transfer resistance ( $R_{\text{et}}$ ) on the GO surface with respect to the SPCE (Fig. S1, C, D, red curves). Such behaviour may be attributed to the lower conductivity of GO with respect to the SPCE substrate and to the electrostatic repulsion of negatively charged GO sheets and  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ . The typical CV of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  was partially

recovered at the ERGO modified SPCE with a decrease in  $R_{et}$  due to the higher conductivity of ERGO with respect to GO and to a less number of exposed negatively charged oxygen containing groups after reduction (Fig.S1, C, D, blue curves).



**Fig. S1.** (A) Cyclic voltammograms of the in-situ generated p-nitrophenyl diazonium salt in the diazotation mixture (1.0 mM NaNO<sub>2</sub>+1.0 mM 4-nitroaniline in 0.5 M HCl) on a SPCE. Inset, successive CVs of the p-nitrophenyl modified SPCE in 0.1 M KCl; scan rate 100 mV s<sup>-1</sup>.(B) electrochemical reduction of GO/SPCE surface (in 0.5 M NaCl) at a scan rate of 50 mV s<sup>-1</sup>. (C) CVs and (D) Nyquist plots of 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> redox couple in PBS, pH 7.4, for bare SPCE electrode (black), SPCE/GO (red), SPCE/ERGO(blue). The CV was performed at a scan rate of 100 mV s<sup>-1</sup>, and the EIS was performed at a frequency range of 10<sup>5</sup> to 3Hz, dc potential of +0.16 V, and ac amplitude of 10 mV.

## Au NPs UV characterization

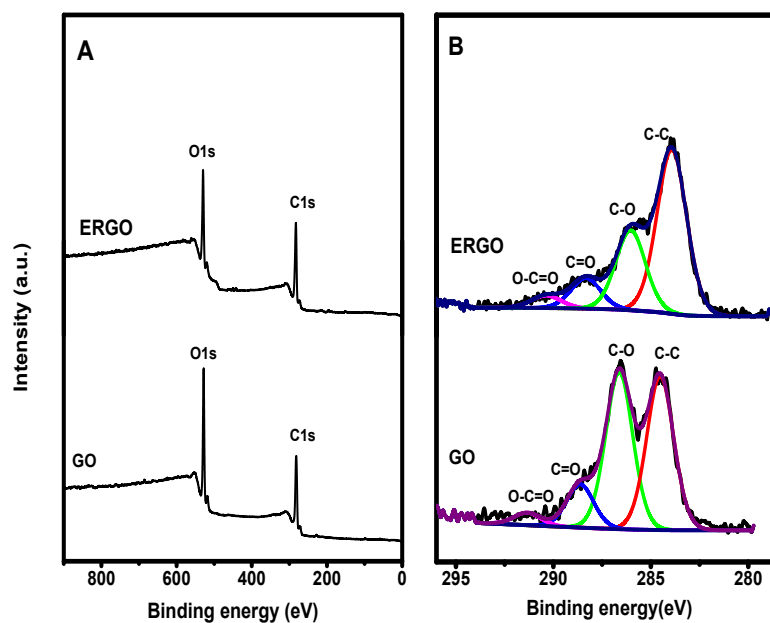


**Fig. S2.** UV-vis spectrum of the prepared Au NPs.

## Result and discussion

XPS survey of GO and ERGO surfaces show two peaks at 284.4 eV and 531 eV, respectively, corresponding to the C1s and O1s (Fig.S3, A). After the GO electroreduction to ERGO, the intensity of O1s peak decreases with respect to that of C1s, which is translated by a lower O/C ratio (0.057 for ERGO vs. 0.123 for GO).

High resolution C1s spectra of GO and ERGO (Fig. S3, B) are also analyzed. Four components of carbon in different functional groups can be fitted for GO and ERGO. The peaks occur at 284.5, 286.6, 287.8 and 289.4 eV, corresponding to graphitic (C-C), epoxy (C-O), carbonyl (C=O) and carboxylic acid (O-C=O) groups. For ERGO, the last three peaks show lower intensities indicating lower percentage of oxygen functional groups, which supports the reduction of GO.



**Fig. S3.** X-ray photoelectron spectroscopy spectra for GO and ERGO (A) Survey and (B) C1s core-level spectra.

## References

- 1 A.-E. Radi, X. Muñoz-Berbel, M. Cortina-Puig, J.-L. Marty, *Electroanalysis* 2009, 21, 1624–1629.
- 2 Z. Wang, X. Zhou, J. Zhang, F. Boey, H. Zhang, *The Journal of Physical Chemistry C* 2009, 113, 14071–14075.