

Supporting Information

An efficient way to reduce graphene oxide by water elimination using phosphoric acid

Engin Er ^a, Hüseyin Çelikkan ^{b,*}

^a Department of Analytical Chemistry, Faculty of Pharmacy, Ankara University, Ankara, Turkey

^b Department of Chemistry, Faculty of Science, Gazi University, Ankara, Turkey

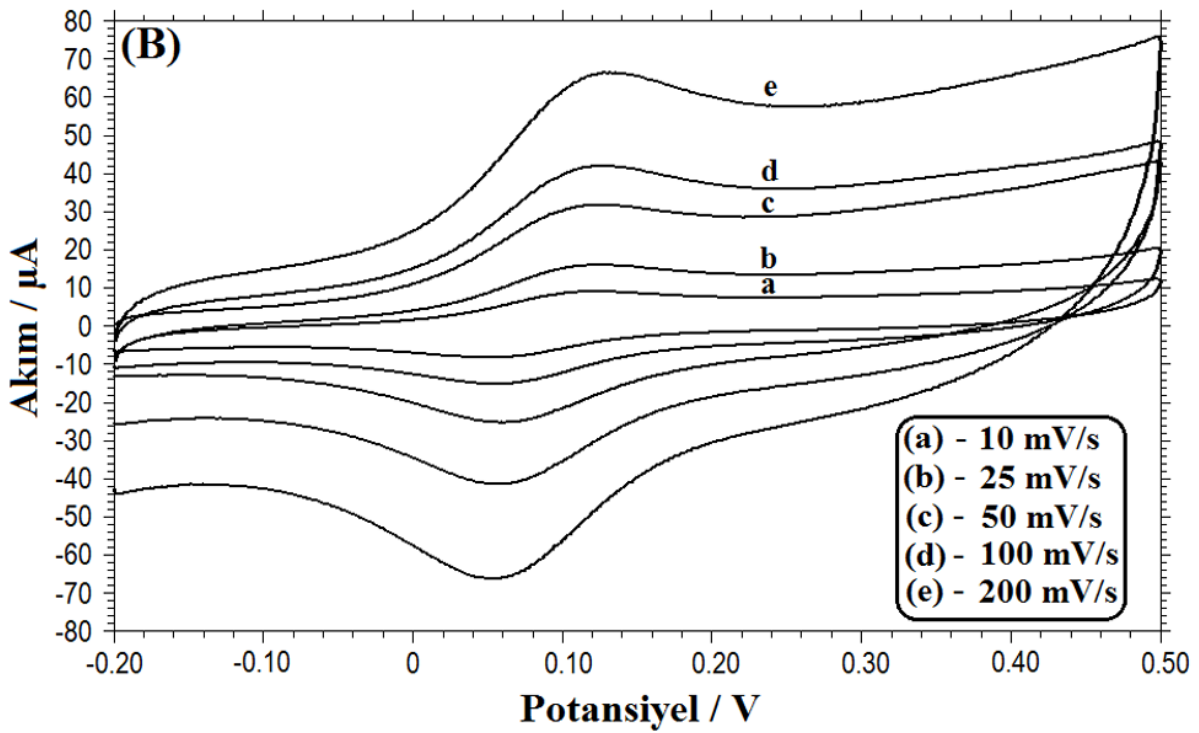
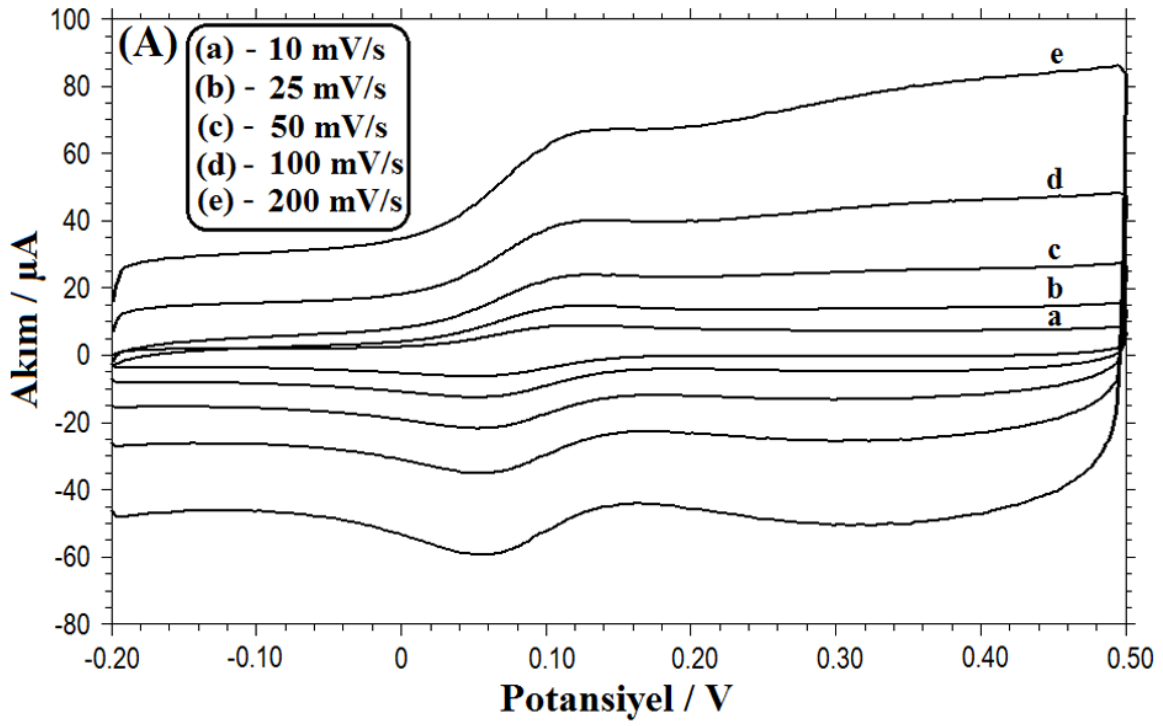
* E-mail: celikkan@gazi.edu.tr

The heterogeneous electron transfer rates of NaBH₄-G, H₂SO₄-G and H₃PO₄-G were determined with Nicholson¹ method using the cyclic voltammograms of Fe(CN)₆³⁻. The GC electrodes covered by NaBH₄-G, H₂SO₄-G and H₃PO₄-G gave heterogeneous electron rate constants (k^0) of 0.00313 ± 0.00043 , 0.0122 ± 0.0096 and 0.0305 ± 0.00293 cm.s⁻¹ by the use of Equation 1 for 1.0 mM Fe(CN)₆³⁻ solution in 1.0 M KNO₃. These results showed that the electron transfer kinetics of H₂SO₄-G and H₃PO₄-G were significantly faster than graphene prepared by the classical method and the other carbonaceous materials are shown in Table S1. The fact that the rate of electron transfer for graphene electrodes prepared by the acidic method was higher means that they have lower polarizability and therefore higher electrocatalytic activity. Accordingly the k^0 values are in good accordance with the specific capacitance values listed in Table 2. It is observed that NaBH₄-G electrode with high capacitance values have lower electron transfer rate values which verifies this fact.

$$k^0 = \Psi \left(\frac{D_0 \pi \nu F}{RT} \right)^{1/2} \quad (1)$$

Table S1. The heterogeneous electron rate constants (k^0) of various carbonaceous materials.

Carbonaceous Materials	Heterogeneous Electron Rate Constants (k^0), $\text{cm}\cdot\text{s}^{-1}$	Reference
Graphite (Surface defects free)	10^{-6}	[2]
Basal HOPG	2.26×10^{-5}	[3]
Edge HOPG	5×10^{-3}	[3]
Glassy carbon	3×10^{-3}	[3]
Single sheet graphene	1.2×10^{-3}	[4]
Few layer graphene	7×10^{-4}	[4]
Bulk graphene (Thermally reduced)	5×10^{-3}	[3]
Bulk graphene (Electrochemically reduced)	2.8×10^{-3}	[3]
Bulk graphene (Chemically reduced)	3.9×10^{-3}	[3]
Graphene oxide (GO)	5.43×10^{-5}	[3]
H ₂ SO ₄ -G	0.0122 ± 0.0096	In this study
H ₃ PO ₄ -G	0.0305 ± 0.00293	In this study



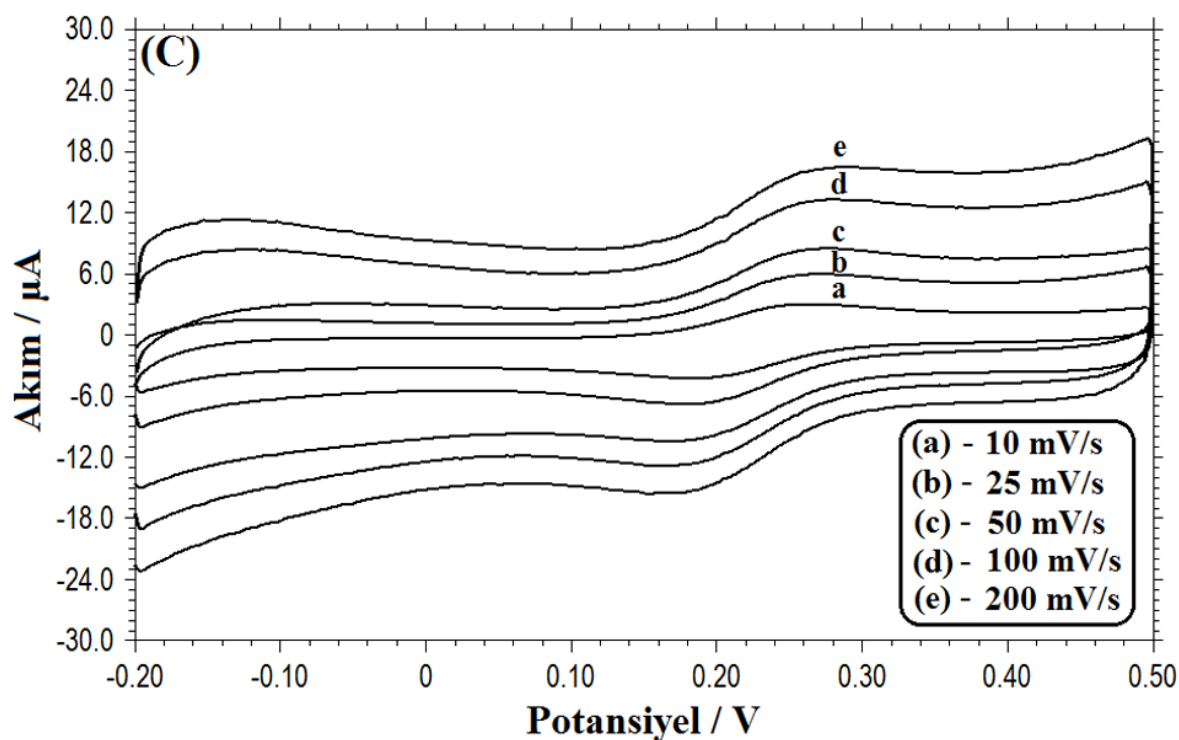


Figure S1. Cyclic voltammograms of 1.0 mM ferricyanide in 1.0 M KNO₃ at various scan rates on H₂SO₄-G (A), H₃PO₄-G (B) and NaBH₄-G (C) modified electrodes

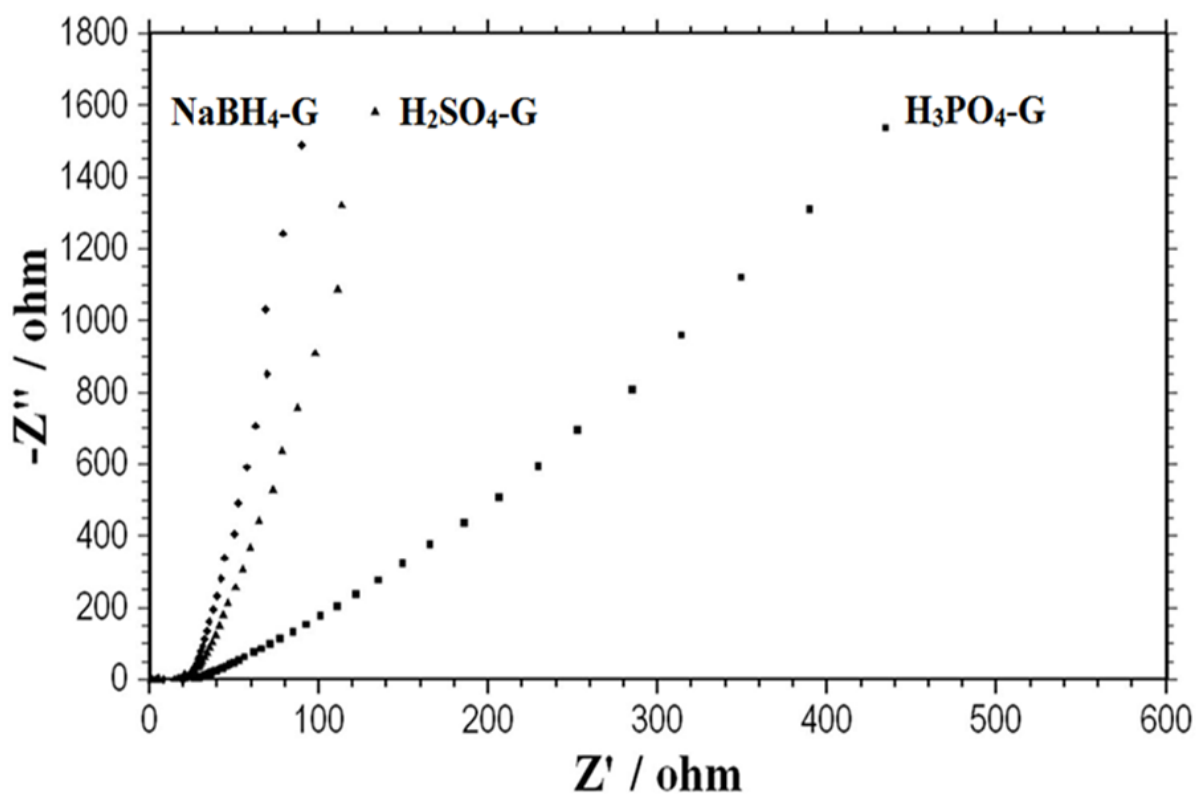


Figure S2. Electrochemical impedance spectra of graphene samples obtained at frequencies of 100,000 to 1 Hz in 1.0 M KCl.

Capacitance property of an electrode can be described with steepness of the impedance plots. The ideal situation for a capacitor is 90° . The angle is much steeper for $\text{NaBH}_4\text{-G}$ compared to other two materials namely $\text{H}_2\text{SO}_4\text{-G}$ and $\text{H}_3\text{PO}_4\text{-G}$ shown in Figure S2. The suitability of a material for the electrochemical applications is inversely related to its capacitance feature. Therefore it can conveniently be claimed that $\text{H}_3\text{PO}_4\text{-G}$ is the most suitable material for the electroanalytical applications.

References

- (1) R.S. Nicholson, Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics, *Anal. Chem.*, 1965, **37**, 1351-1355.
- (2) R.S. Robinson, K. Sternitzke, M.T. McDermott and R.L. McCreery, Morphology and Electrochemical Effects of Defects on Highly Oriented Pyrolytic Graphite, *J. Electrochem. Soc.*, 1991, **138**, 2412– 2418.
- (3) A. Ambrosi, A. Bonanni, Z. Sofer, J.S. Cross and M. Pumera, Electrochemistry at Chemically Modified Graphenes, *Chem. Eur. J.*, 2011, **17**, 10763–10770.
- (4) A.T. Valota, I.A. Kinloch, K.S. Novoselov, C. Casiraghi, A. Eckmann, E.W. Hill and R.A.W. Dryfe, Electrochemical Behavior of Monolayer and Bilayer Graphene, *ACS Nano*, 2011, **5**, 8809–8815.