

SUPPLEMENTARY INFORMATION

A Novel Electrochemical Sensor for Nitroguanidine Determination Using a Glassy Carbon Electrode Modified with Multi-Walled Carbon Nanotubes and Polyvinylpyrrolidone

Abdoul Kader Alassane Moussa^{1,2}, Şener Sağlam², Ayşem Üzer^{2,*}, Reşat Apak^{2,3,}**

¹Institute of Graduate Studies, Chemistry Department, Istanbul University–Cerrahpaşa, Avcılar, Istanbul, Turkey

²Engineering Faculty, Chemistry Department, Istanbul University–Cerrahpaşa, Avcılar, Istanbul, Turkey

³Turkish Academy of Sciences (TUBA), Bayraktar neighborhood, Vedat Dalokay st. No:112, 06670, Cankaya, Ankara, Turkey

* Corresponding author, **Co-corresponding Author

E-mail: auzer@iuc.edu.tr, rapak@istanbul.edu.tr

Supplementary information file contains; (i) The Quantity of PVP Used in GCE Modification, (ii) Investigation of the Supporting Electrolyte, (iii) pH Investigation of Phosphate Buffer, (iv) Investigation of the Acetonitrile Amount, (v) Characterization of GC/PVP/MWCNTs Modified Electrode, (vi) Impedance Measurements of GC, GC/PVP and GC/PVP/MWCNTs Electrodes, (vii) Recovery Results for Synthetic Mixtures of Energetic Materials and Real Sample Analysis

(i) The Quantity of PVP Used in GCE Modification

The GCE surface was modified with 0.1 – 1.0 % PVP (w/v) and 1 mg mL⁻¹ of MWCNTs (*i.e.* used as the maximum amount that could be dissolved homogeneously in DMF media) that were dissolved in 5 mL volumetric flask using DMF, and 2 μ L of this solution was dropped onto the electrode surface, respectively. The prepared GC/PVP/MWCNTs electrodes were used for 100 mg L⁻¹ NG determination using SWV method within the potential range of 0.0 V to -1.8 V, and the reduction peak current was obtained *vs.* Ag/AgCl/3M KCl.

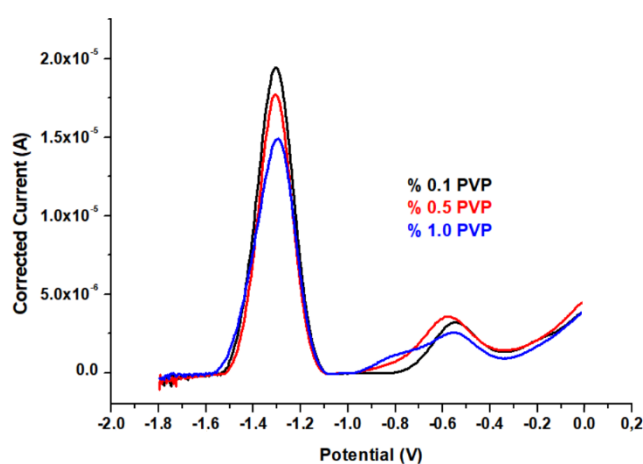


Figure S1: The square wave voltammograms of 100 mg L⁻¹ NG in 0.1 mol L⁻¹ pH 7 phosphate buffer (5 mL) using 0.1 – 1.0 % PVP (w/v) modified working electrode

As seen in Fig. S1, the highest reduction current value was obtained at about -1.32 V with 0.1 % (w/v) PVP modified working electrode for 100 mg L⁻¹ NG analysis, and therefore 0.1% PVP was selected as the optimal amount for the working electrode modification. The corrected current values were calculated using the Nova 2.1.4 programme of Metrohm Autolab potentiostat/galvanostat (PGSTAT204, Switzerland).

(ii) Investigation of the Supporting Electrolyte

NG at 10 mg L^{-1} was measured separately in 5 mL of 0.1 mol L^{-1} pH 7 phosphate buffer, and distilled water containing 0.5 mol L^{-1} LiClO_4 , 0.5 mol L^{-1} NaCl , and 0.5 mol L^{-1} KCl using the SWV method within the potential range of 0.0 V to -1.8 V by the GC/PVP/MWCNTs electrode. The highest reduction current value was obtained at about -1.32 V for 10 mg L^{-1} NG in the 0.1 mol L^{-1} pH 7 phosphate buffer, as shown in Figure S2.

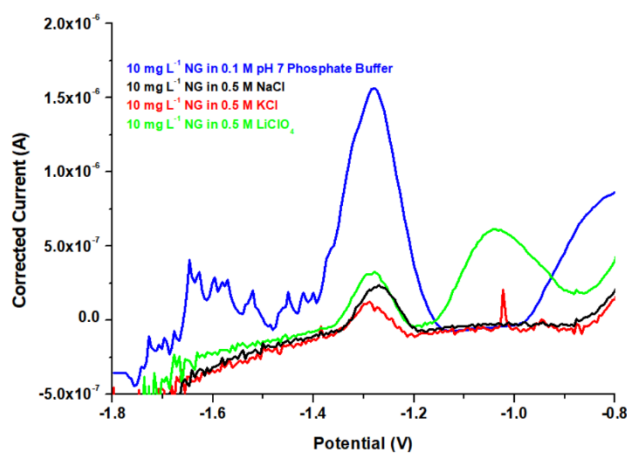


Figure S2: The square wave voltammograms of 10 mg L^{-1} NG in 0.1 mol L^{-1} pH 7 phosphate buffer, and distilled water containing 0.5 mol L^{-1} LiClO_4 , 0.5 mol L^{-1} NaCl , and 0.5 mol L^{-1} KCl using the GC/PVP/MWCNTs electrode.

(iii) pH Investigation of Phosphate Buffer

NG at 10 mg L^{-1} was measured separately in 5 mL of 0.1 mol L^{-1} pH 3, 5, 6, 7, 8 and 10 phosphate buffer using the SWV method within the potential range of 0.0 V to -1.8 V by the GC/PVP/MWCNTs electrode. The best reduction current value was obtained at about -1.32 V for 10 mg L^{-1} NG in the 0.1 mol L^{-1} pH 7 phosphate buffer (Figure S3).

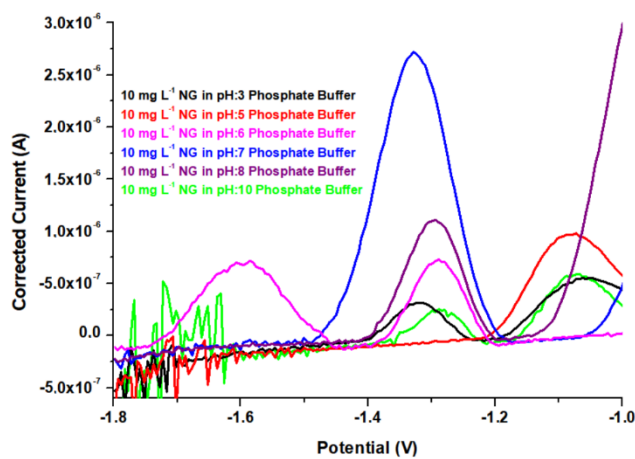


Figure S3: The square wave voltammograms of 10 mg L^{-1} NG in different pH of phosphate buffer with GC/PVP/MWCNTs electrode

(iv) Investigation of the Acetonitrile Amount

Selective NG determination is very important in the presence of nitro-aromatic and nitramine type explosives such as TNT, DNT, RDX, Tetryl, PETN and HMX (as they can interfere with the analysis of NG). However, the solubility of nitro-aromatic and nitramine type energetic materials in water are very low, while high in acetonitrile¹. For this reason, by adding acetonitrile to the phosphate buffer solution as the NG measurement medium, NG was determined using the proposed SWV method. In order to examine the effect of acetonitrile amount, 50 ppm NG determination in 0.1 mL, 0.25 mL and 0.5 mL acetonitrile and phosphate buffer medium (phosphate buffer was added to a total volume of 5 mL) was performed using the developed GC/PVP/MWCNTs electrode and the SWV method. As a result of the SWV measurements, the highest current value was obtained in 0.5 mL acetonitrile + 4.5 mL phosphate buffer medium, and this ratio was maintained for all measurements (Fig. S4).

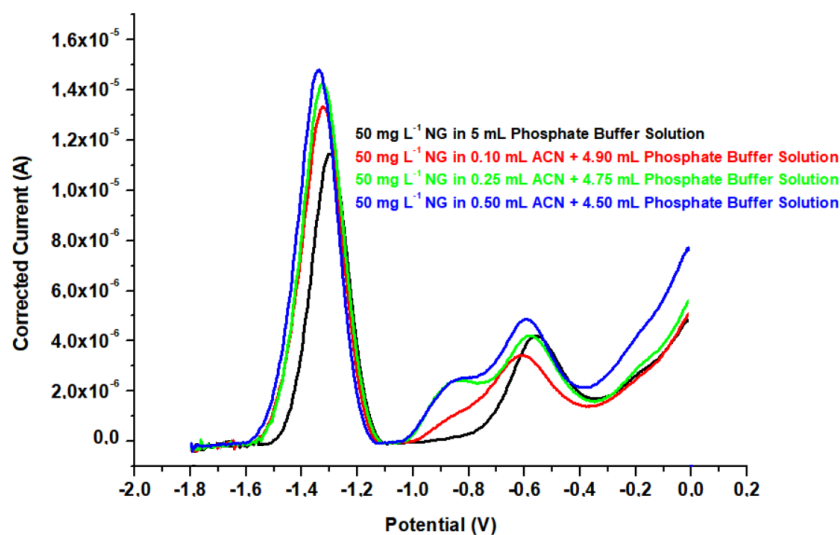


Figure S4: The square wave voltammograms of 50 mg L⁻¹ NG in different compositions of acetonitrile and phosphate buffer medium with GC/PVP/MWCNTs electrode

(v) Characterization of GC/PVP/MWCNTs Modified Electrode

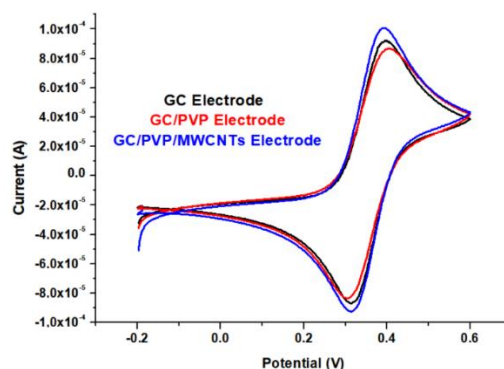


Figure S5: The cyclic voltammograms of GC, GC/PVP and GC/PVP/MWCNTs in 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution (containing 0.10 mol L⁻¹ KCl and 0.10 mol L⁻¹ HCl)

(vi) Impedance measurements of GC, GC/PVP and GC/PVP/MWCNTs electrodes

The Randles equivalent circuit was created using "fit and simulation" in Nova 2.1.4 programme of Metrohm Autolab for impedance measurements of the GC, GC/PVP and GC/PVP/MWCNTs electrodes, and the fitted data can be seen in Figure S6.

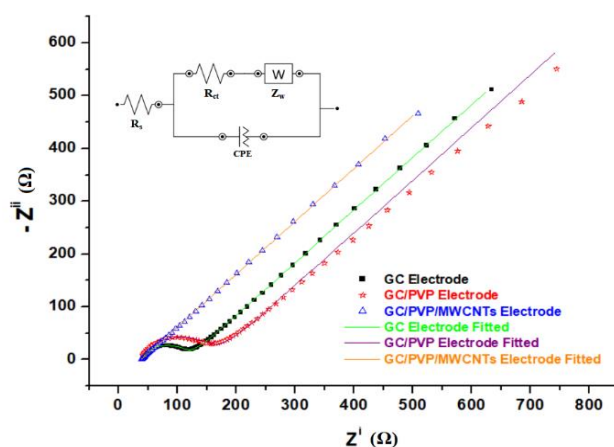


Figure S6: Impedance measurements of the GC, GC/PVP and GC/PVP/MWCNTs electrodes using the Potentiostat EIS method in 0.1 mol L⁻¹ HCl containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ media, and the Randles equivalent circuit was given as inset figure (constant phase element (CPE) and Z_w is Warburg impedance).

(vii) Recovery Results for Synthetic Mixtures of Energetic Materials and Real Sample Analysis

Table S1: Recovery (%) values of 10 mg L⁻¹ NG in the presence of a 10-fold concentration of TNT, DNT, RDX, Tetryl, PETN, HMX, NTO, NH₄NO₃, Comp B, Octol and Comp C4.

Sample (mg L⁻¹)	Recovery (%)
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ TNT	97.03
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ DNT	101.46
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ Tetryl	98.84
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ RDX	94.56
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ HMX	102.12
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ PETN	94.86
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ NTO	98.46
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ NH ₄ NO ₃	100.62
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ Comp. B	97.01
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ Octol	96.26
10 mg L ⁻¹ TNT + 100 mg L ⁻¹ Comp. C4	104.79

References

- 1 J. Yinon, *Forensic and Environmental Detection of Explosives*, 1999.