

Supporting information

Fig. S1. The Raman spectra of GO, NG and Pd₁Ag₁/NG.

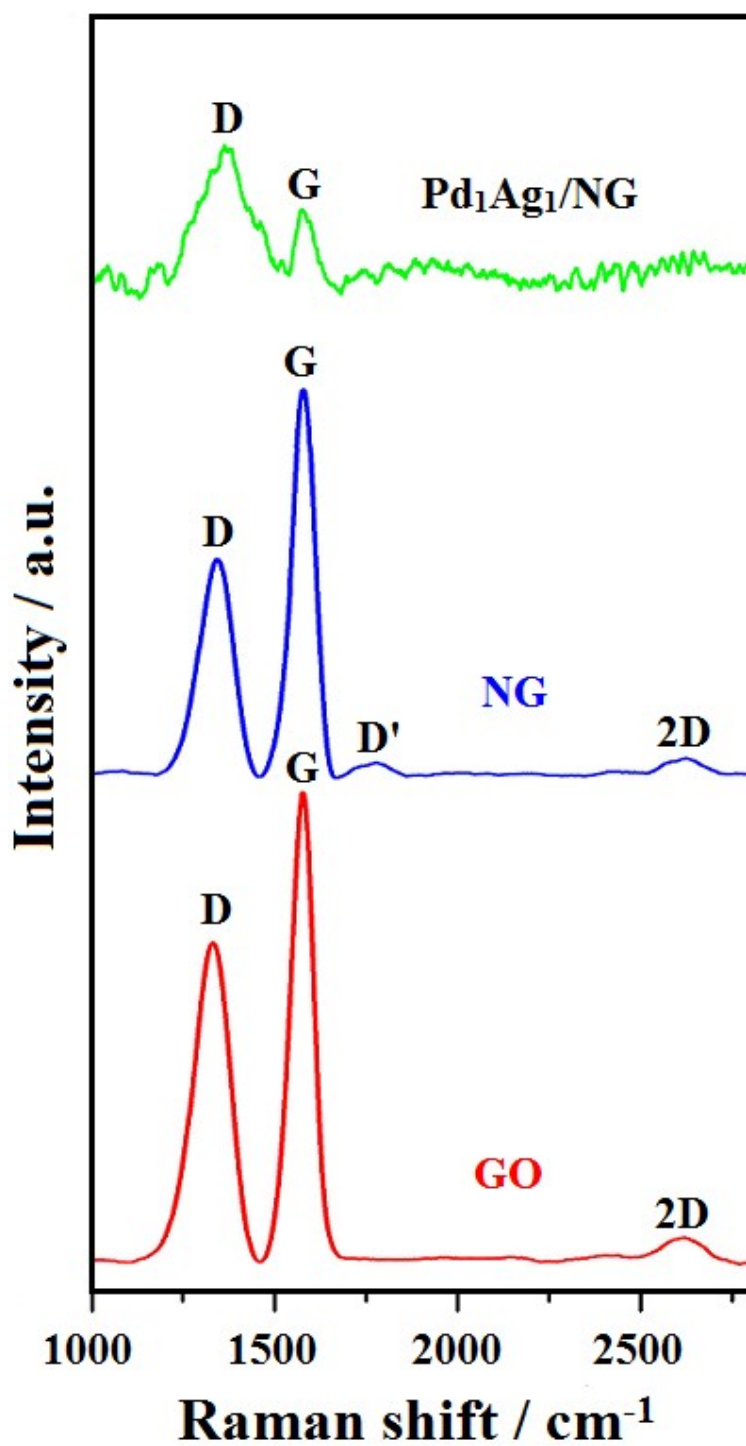
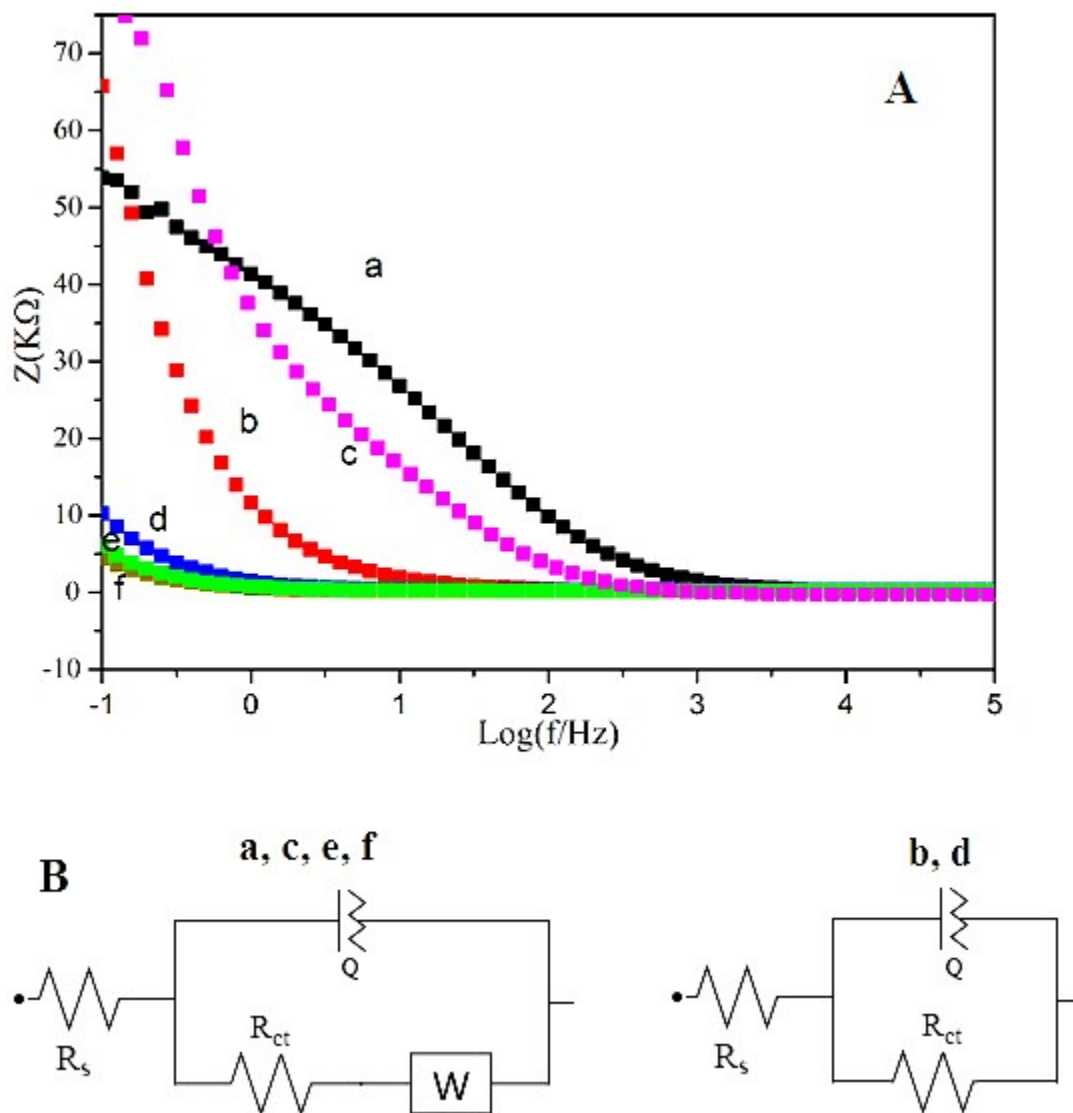


Fig. S2 (A). Bode plots showing excellent agreement between the experimental results and the parameters obtained from: (a) bare electrode, (b) GO, (c) NG, (d) Pd/NG, (e) Ag/NG and (f) Pd₁Ag₁/NG. **S2 (B).** The proposed equivalent circuits for bare electrode, NG, Ag/NG and Pd₁Ag₁/NG modified electrodes, GO, Pd/NG where the chi-squared (χ^2) is minimized at 10^{-4} .



Two different circuits were used to simulate the data. In the case of Fig. S2. (a and c), the samples showed a normal behavior and Randles circuit in parallel with Warburg were used for extracting the data. In Fig. S2. (e and f) at high frequency ranges, the semicircles with very small diameter were observed. And in Fig. S2. (b and d), the semicircle did not fully formed but after

simulation, the diameters were achieved. In the later samples, a simple Randles circuit without Warburg was used for simulation. Figure S2 (A) shows the Bode diagram of the samples and confirms the proposed R_{ct} order. Fig S2 (B) show the equivalent circuits.

Fig. S3. Effect of pH on the (A) anodic peak currents and (B) anodic peak potential.

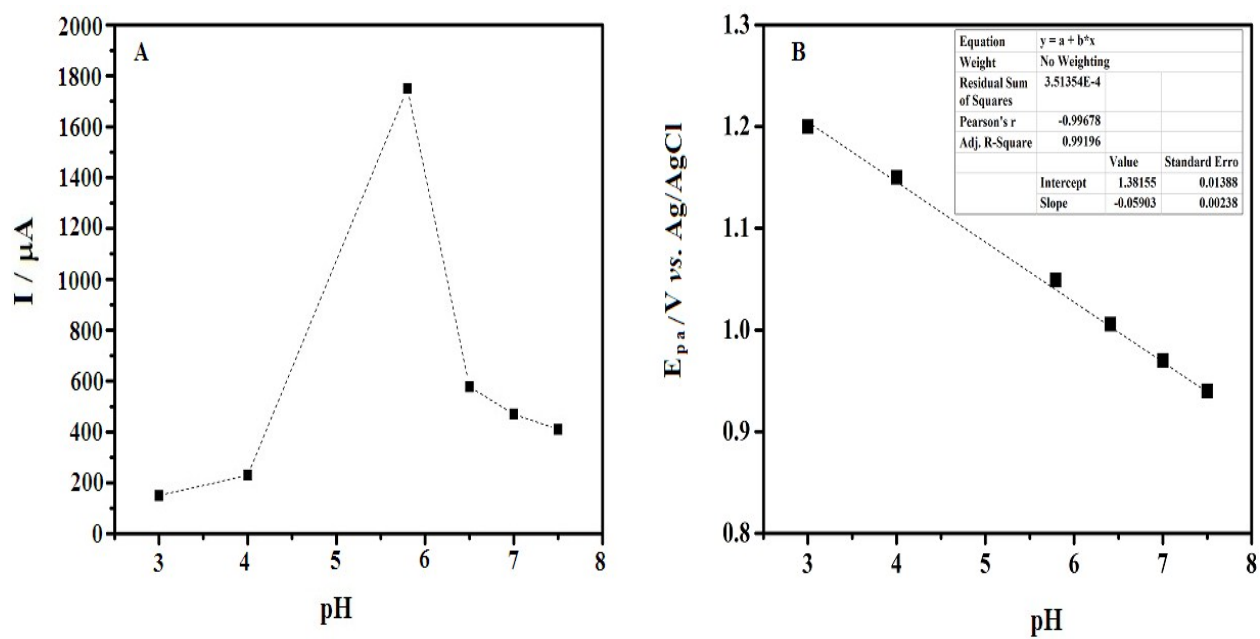


Fig. S4. Long term stability of the Pd₁Ag₁/NG–GCE studied in 3 weeks.

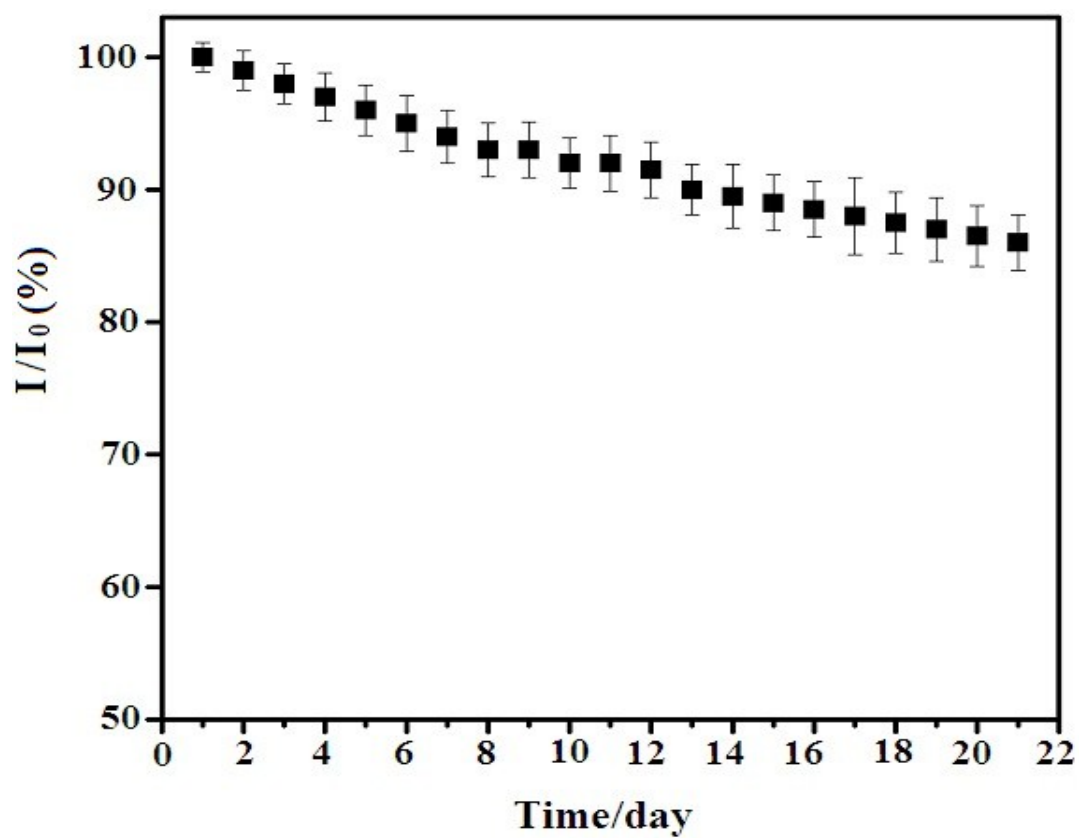


Table S1. Determination of MTX in human urine samples with Pd₁Ag₁/NG–GCE (n=3)

Sample	MTX (μM)		RSD (%)	Recovery (%)
	Added	Found		
1	5	4.96	2.21	99.2
2	10	9.97	2	99.7
3	20	19.9	1.3	99.5