# Supplementary Information

# Sulfonated-Polypyrene aniline/Polyaniline Composite Fortified with Cu-GQD@ZIF8 as the Electrochemical Enzymatic Urea Biosensor

Taşkın Çamurcu[a], Vildan Şanko[b,c], İpek Ömeroğlu[a], Süreyya Oğuz Tümay[d], Ahmet Şenocak[a]*

[a]Department of Chemistry, Gebze Technical University, Gebze 41400, Kocaeli, Türkiye
[b]Department of Chemistry, Hacettepe University, Ankara 06800, Türkiye
[c]METU MEMS Center, Ankara, 06530, Türkiye
[d]Department of Chemistry, Atatürk University, Erzurum 25100, Türkiye

*Corresponding author:

Dr. Ahmet Şenocak

Department of Chemistry, Gebze Technical University, P.O.Box: 141, Gebze 41400, Kocaeli, Türkiye

E-mail: asenocak@gtu.edu.tr

Telephone: +902626503106

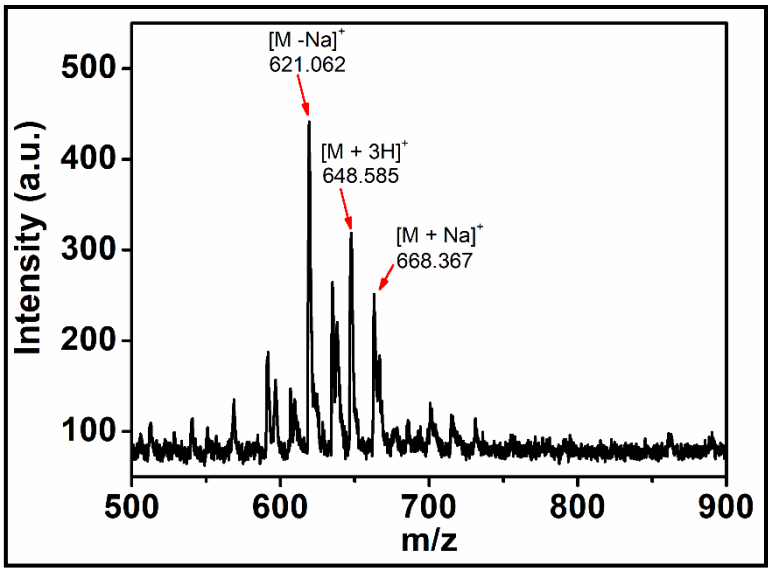


**Fig. S1.** The MALDI-TOF spectrum of compound **3** (Matrix: DHB).

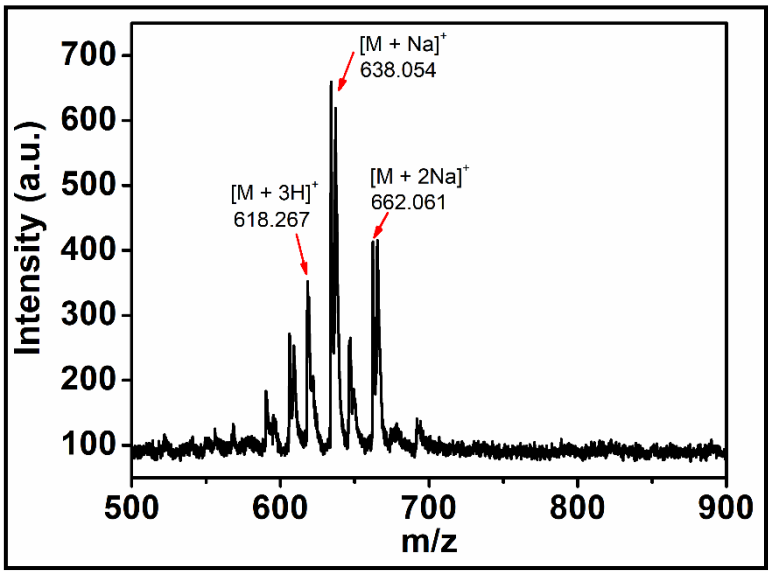


**Fig. S2.** The MALDI-TOF spectrum of compound **4** (No matrix).

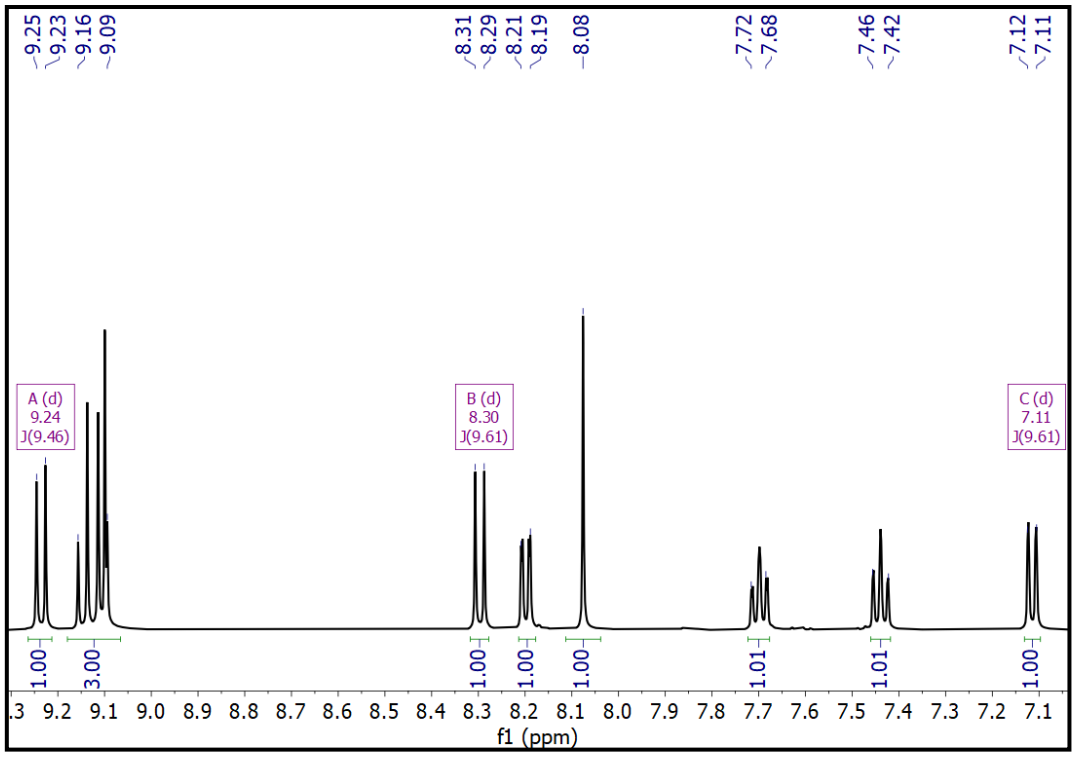


**Fig. S3.** The $^{1}$H-NMR spectrum of compound **3** in DMSO-$d_6$.

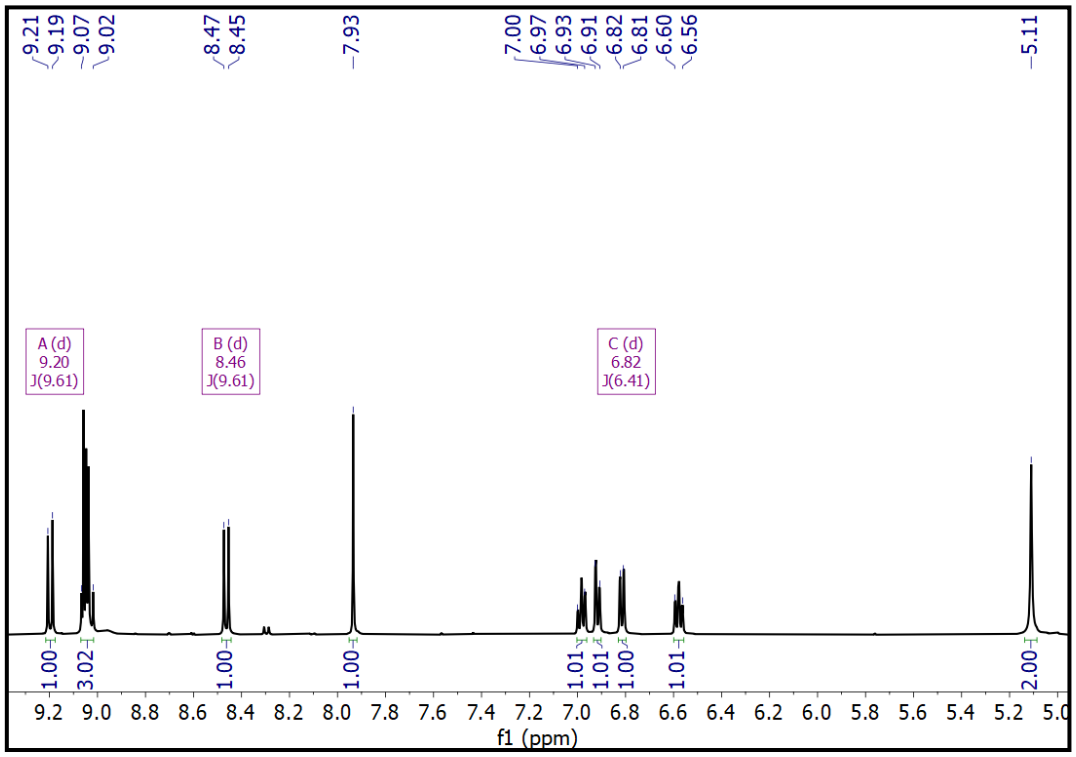


**Fig. S4.** The $^{1}$H-NMR spectrum of compound **4** in DMSO-$d_6$.

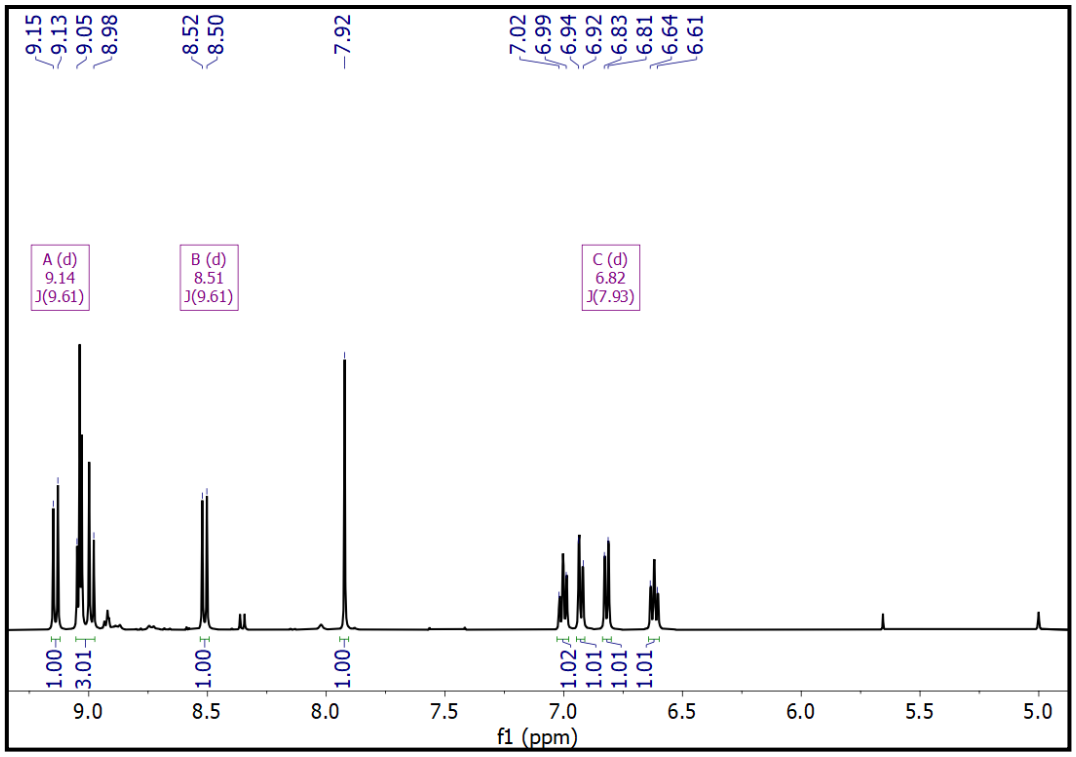


**Fig. S5.** The $^{1}$H-NMR spectrum of compound **4** in DMSO-$d_6$/$D_2O$.

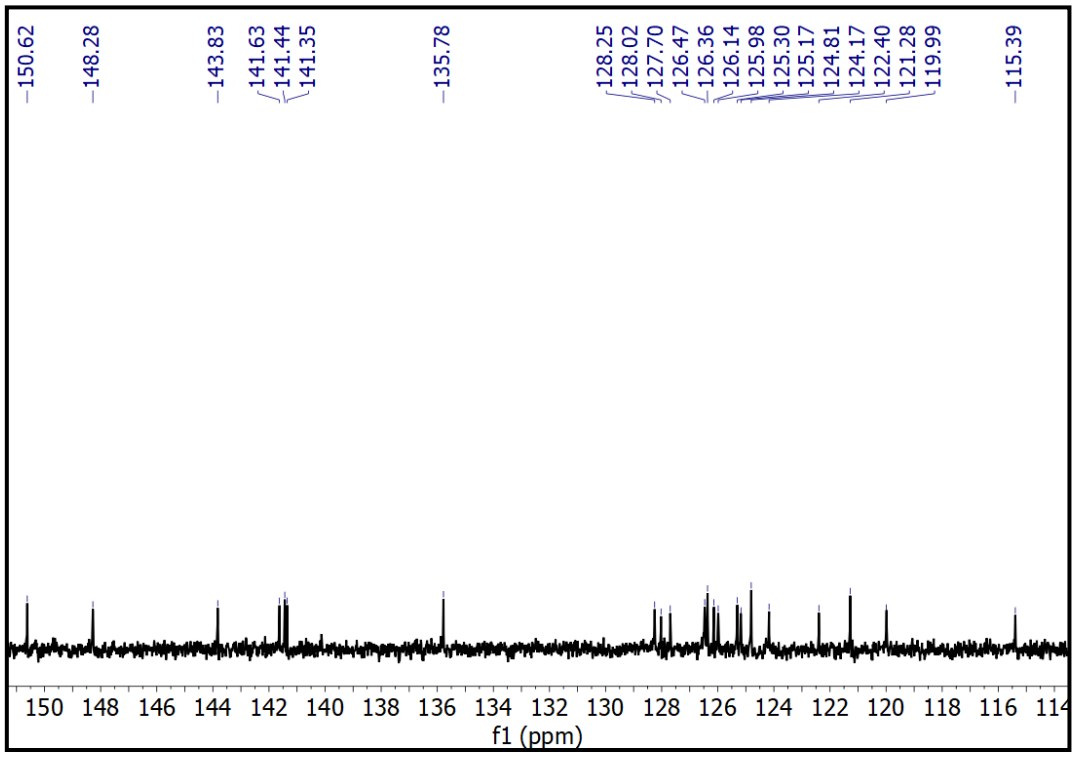


**Fig. S6.** The $^{13}$C-NMR spectrum of compound **3** in DMSO-$d_6$.

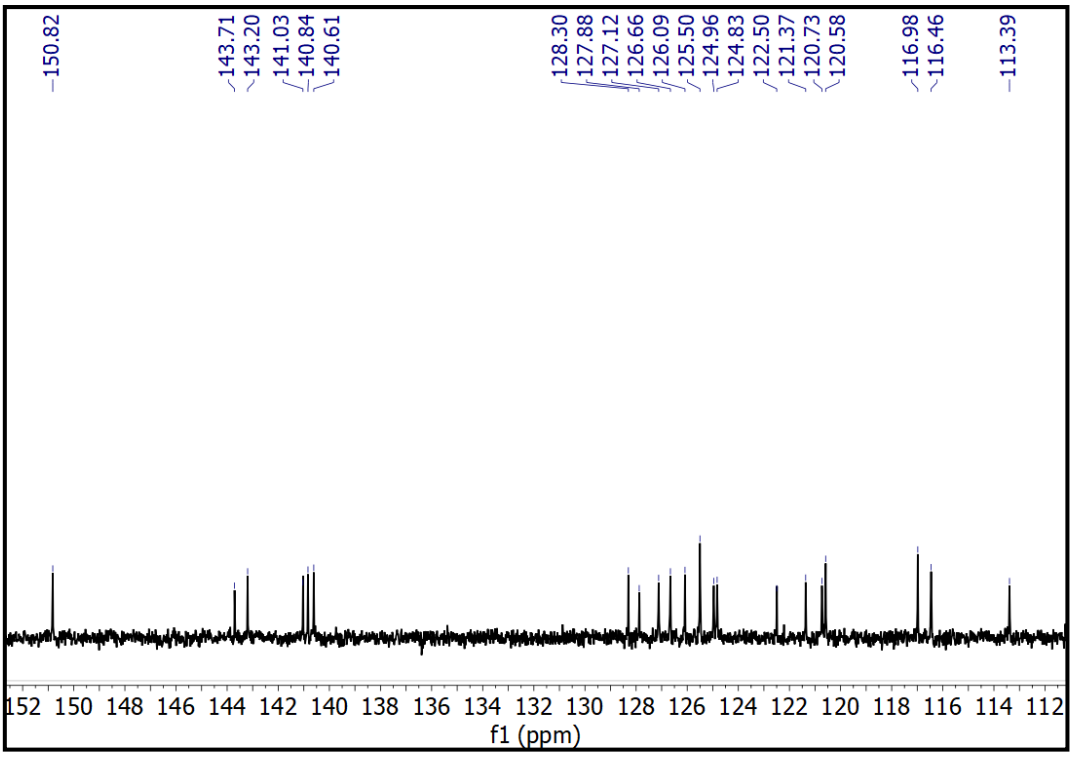


**Fig. S7.** The $^{13}$C-NMR spectrum of compound **4** in DMSO-$d_6$.

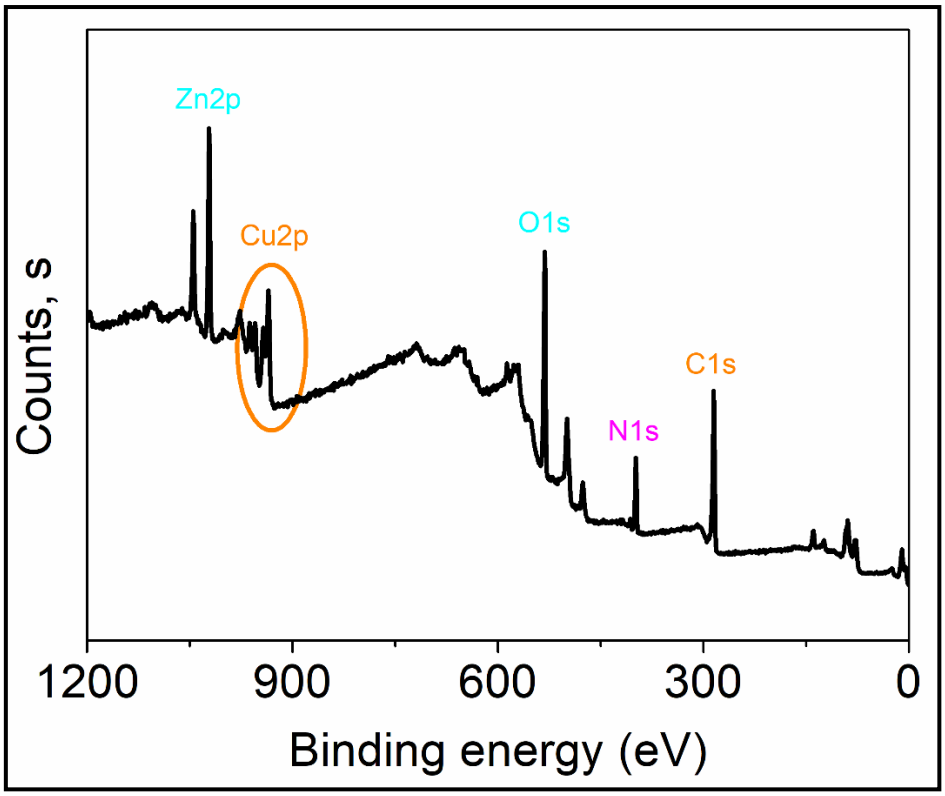


**Fig. S8.** XPS spectrum of Cu-GQD@ZIF8 materials.

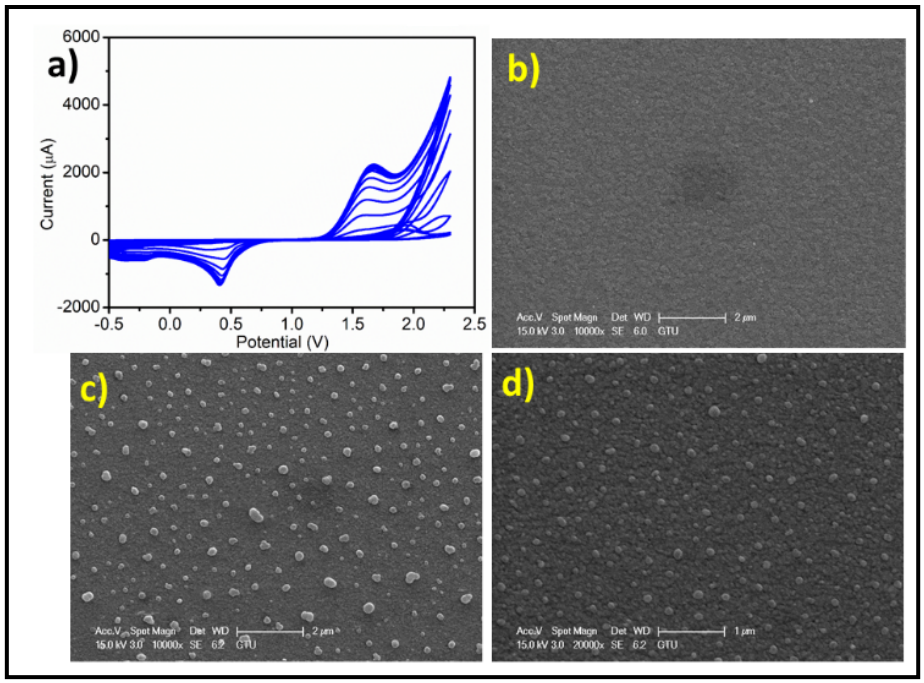


**Fig. S9**. a) Electropolymerization of pyranine aniline compound onto the ITO glass surface with 15 cycles using CV technique, b) SEM image of unmodified ITO glass, c-d) SEM images of electropolymerized PA compound.

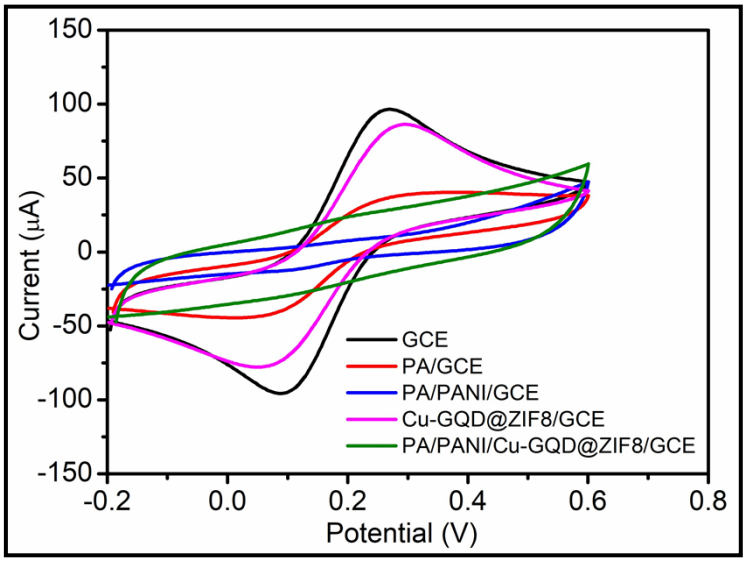


**Fig. S10.** CV voltammograms of bare GCE compared to PA, PANI, GQD@ZIF8, and PA/PANI/Cu-GQD@ZIF8/Urs/GCE carried out in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ a solution containing 0.1 M KCl.

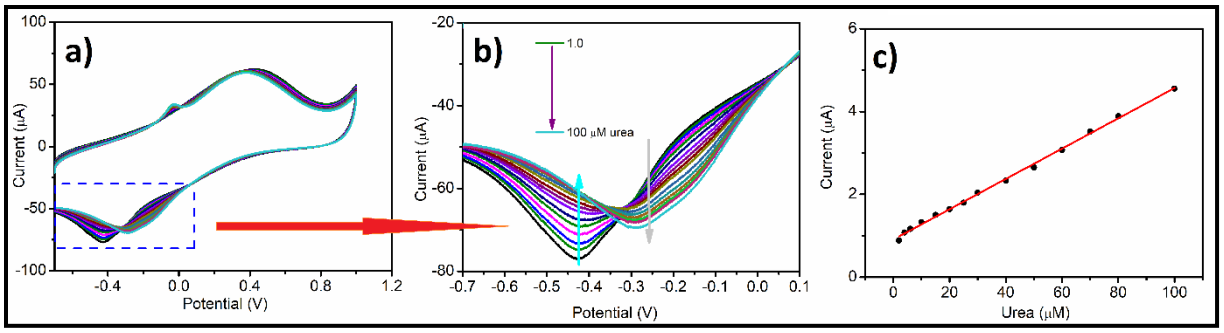


**Fig. S11.** a) CV responses for different urea concentrations on PA/PANI/Cu-GQD@ZIF8/Urs/GCE b) Close-up view of a plot (a) and c) linear relationship between urea concentrations and peak currents.

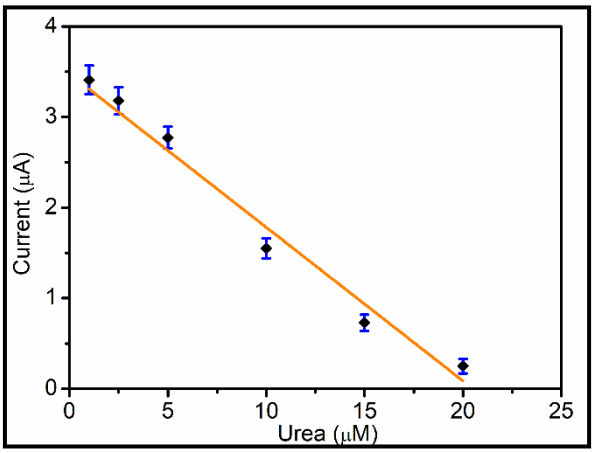


**Fig. S12.** Linear relationship between urea concentrations and peak currents by decreasing peaks on DPV measurement at -0.42V.

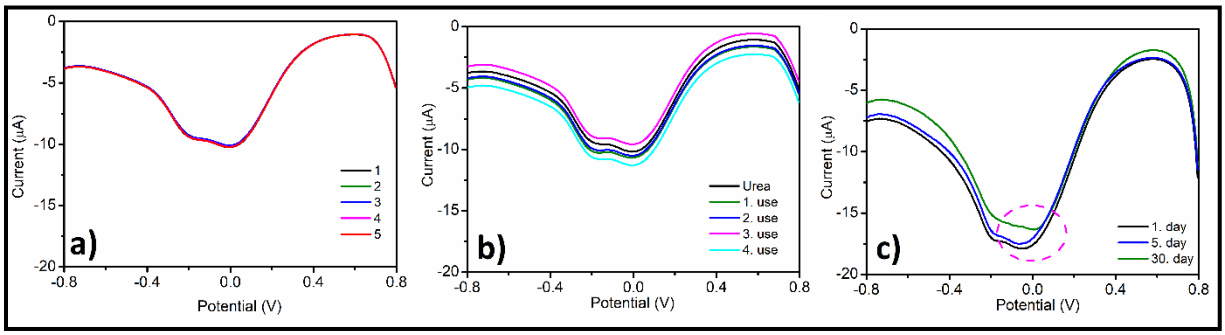


**Fig. S13.** a) Repeatability, b) reusability, and c) lifetime analyses of the PA/PANI/Cu-GQD@ZIF8 sensor.

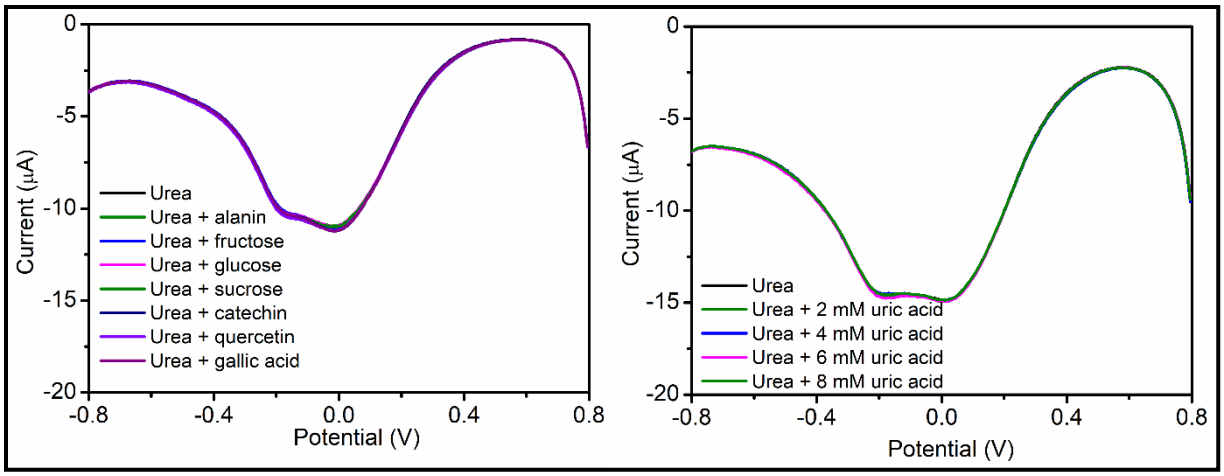


**Fig. S14.** The effect of (a) bioanalytes and (b) different concentrations of uric acid on the voltammetric response of PA/PANI/Cu-GQD@ZIF8/urease biosensor to urea.

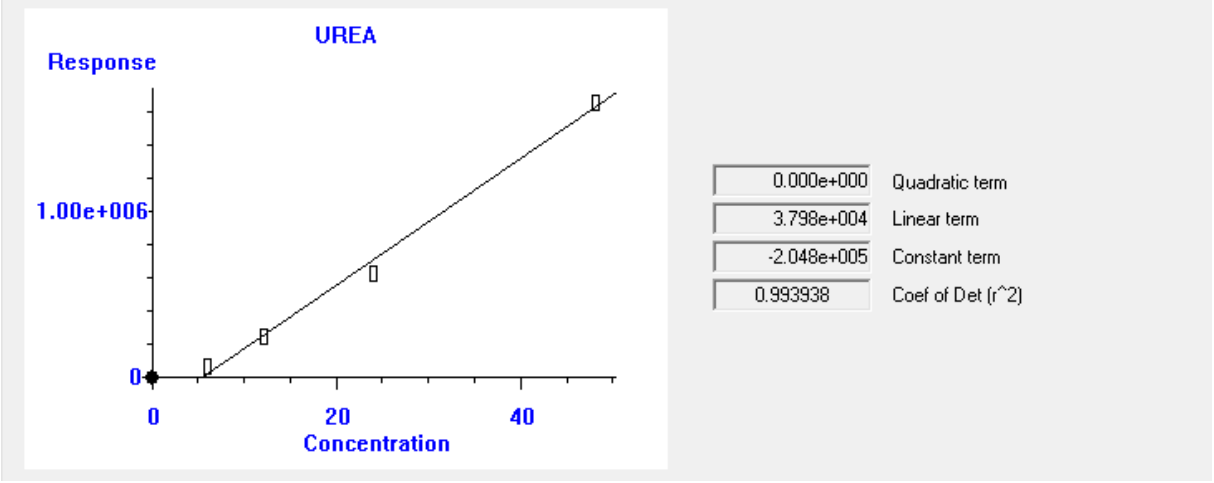


**Fig. S15.** GC-MS calibration curve for urea.

**Table S1:** Spike/recovery tests for electrochemical determination of urea in serum sample.

| | Presented electrochemical method | | | GC-MS |
|---|---|---|---|---|
| | **Added (µM)** | **Detected (µM)** | **Recovery (%)** | **Detected (µM)** |
| Serum | 0 | - | - | ND[a] |
| | 20.0 | 19.62±1.10 | 98.10 | |
| | 40.0 | 39.22±1.64 | 98.05 | |

**a:** Not detected.