Supporting Information

Promoting the signal reliability of non-invasive biosensors *via* N-doped graphene quantum dot modified Prussian blue analogue protective layer for glucose monitoring

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EXPERIMENTAL

Materials

The uric acid (≥99.0%) were purchased from Acros Organics. Disodium phosphate (Na_2HPO_4, ≥98.0%) were acquired from J.T.Baker. Urea (99.0-100%), hydrogen peroxide (30%), glutaraldehyde (50%) , glucose oxidase, monosodium phosphate (NaH_2PO_4, ≥98.0%), sodium chloride (NaCl, ≥99.9%), D-(+)-Glucose ($C_6H_{12}O_6$, ≥99.5%), Nafion® 117 solution (~5%), aniline (>99 %) and L-Lactate (98.0%) were supplied from Sigma-Aldrich. Ascorbic acid (99.5%) was bought from Pub Chem. Hydrochloric acid (HCl, 37%) was obtained from Scharlau.

Preparation of PBS

To make 0.01 M Phosphate Buffered Saline (PBS), first, dissolve 0.2641 g NaH_2PO_4 and 1.15 g Na_2HPO_4 in 800 mL DI water. After that, 7.4451 g of KCl was added to the solution along with 1000 mL of DI water. Finally, NaOH and HCl were used to adjust the pH to 7.2.

Preparation of PB nanocomposites on the SPCEs

The PB layer was synthesized by cyclic voltammetry method with three-electrode systems (a platinum foil counter electrode, an Ag/AgCl (3.0 M) reference electrode, and a working electrode made of screen-printed carbon electrodes (SPCEs) coated with polyethylene terephthalate (PET) (0.1256 cm^2)). The process was performed within the voltage range of 0 to 1 V, with a sweep rate of 0.02 V/s for one cycle. The solution for electrodeposition consisted of 2.5 mM $FeCl_3$, 100 mM KCl, 2.5 mM $K_3Fe(CN)_6$, and 100 mM HCl with DIW. Following the electrodeposition, the mixture was purified with DIW to eliminate extra components.

Preparation of enzymatic electrode

2 wt% of acetic acid and 0.5 wt% of chitosan were dissolved into 0.01 M PBS (pH=7.5), the chitosan solution was mixed thoroughly with glucose oxidase solution (20 mg ml^{-1} in PBS of pH 7.5) in the ratio 2:1 (volume by volume). After that, adding 4.8 μL of GOx solution onto fabricated electrode *via* drop cast method and dry at 40^{o}C oven. The solutions and the fabricated electrode were stored at 4 °C when not in use.

Material characterization

A field-emission scanning electron microscope (FE-SEM, JSM-6500F, JEOL) has been used to obtain images of mophology to evaluate the shape and composition of the produced nanomaterials. A cold field-emission transmission electron microscope (TEM, JEM 2100F, JEOL) with an accelerating voltage of 200 kV was used for the TEM procedure. The chemical state of the as-prepared materials was examined using X-ray photoelectron spectroscopy (XPS) measurements utilizing an X-ray photoelectron spectroscope (JPS-9030, JEOL). The spot size was 400 nm, and the X-ray source had an energy of 12 kV, 72 W, and was monochromated Al K at 1486.6 eV. At room temperature, aqueous dispersion of GQDs and N-GQDs was subjected to photoluminescence (PL) spectroscopy experiments. A commercial spectrometer (Horiba Jobin Yvon Nanolog-3 spectrofluorometer) with a 20 nm bandpass for both emission and excitation and an InGaAs NIR detector was used to record the excitation and emission spectra. According to the measured excitation power, the PL spectra were scaled. Fourier transforms infrared (FTIR) spectra were captured in the 500–4000 cm^{-1} wavelength range using a PerkinElmer instrument. With a micro-Raman system (UniNanoTech UniRAM) outfitted with a wavelength of 532 nm and a CCD detector, the Raman spectra were conducted to define the defect inside materials. Room temperature was used to collect the spectra.

Electrochemical measurement

A conventional three-electrode electrochemical cell was used for the cyclic voltammetry and amperometry, with a modified SPCE participating as the working electrode (WE), a Pt foil acting as the counter electrode (CE), and an Ag/ AgCl (3 M KCl) acting as the reference electrode (RE). With an applied voltage of -0.1 V inside 0.01 M PBS (pH = 7.2), the electrochemical impedance spectroscopy (EIS) analysis was carried out in the frequency range of 7 MHz to 0.1 Hz with an AC amplitude of 10 mV with 1 mM H_2O_2

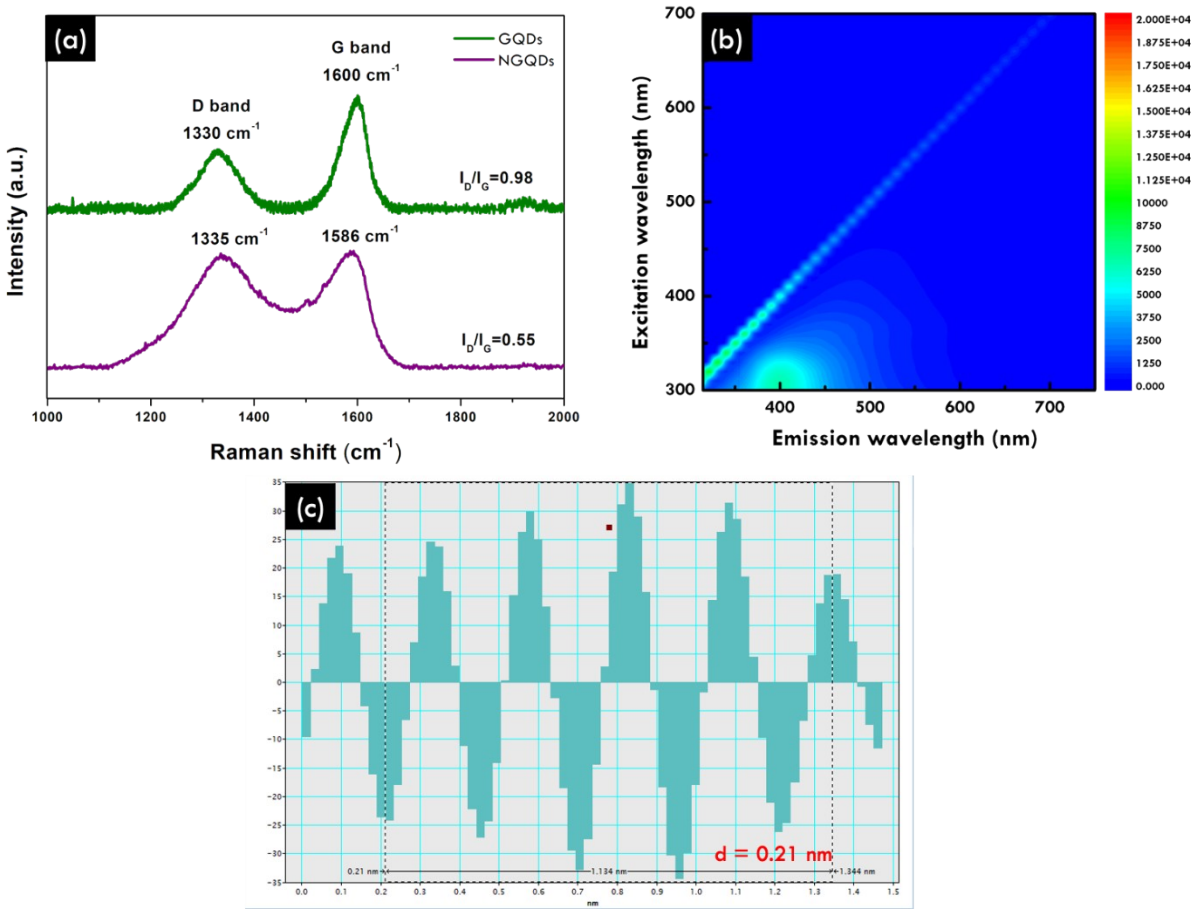

Figure S1 (a) Raman spectroscopy of GQDs and NGQDs; (b) PL excitation-emission mapping of GQDs, (c) Lattice spacing of NGQDs.

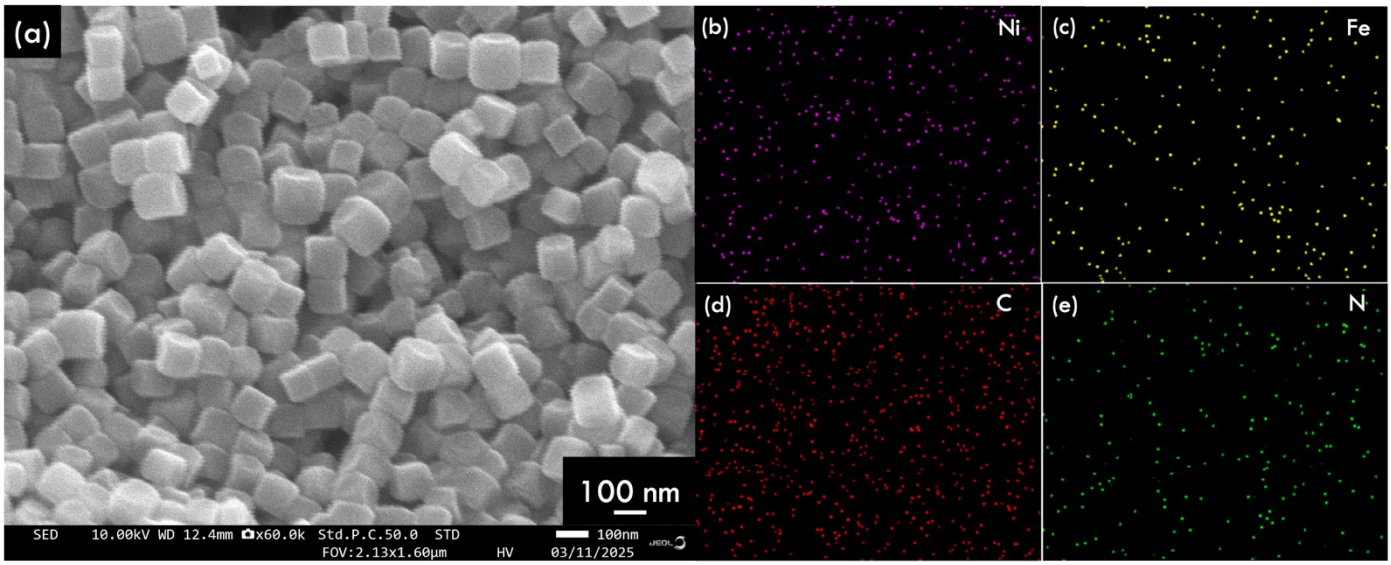

Figure S2 (a). SEM image, (b). SEM-EDX of PB/PBA/NGQDs

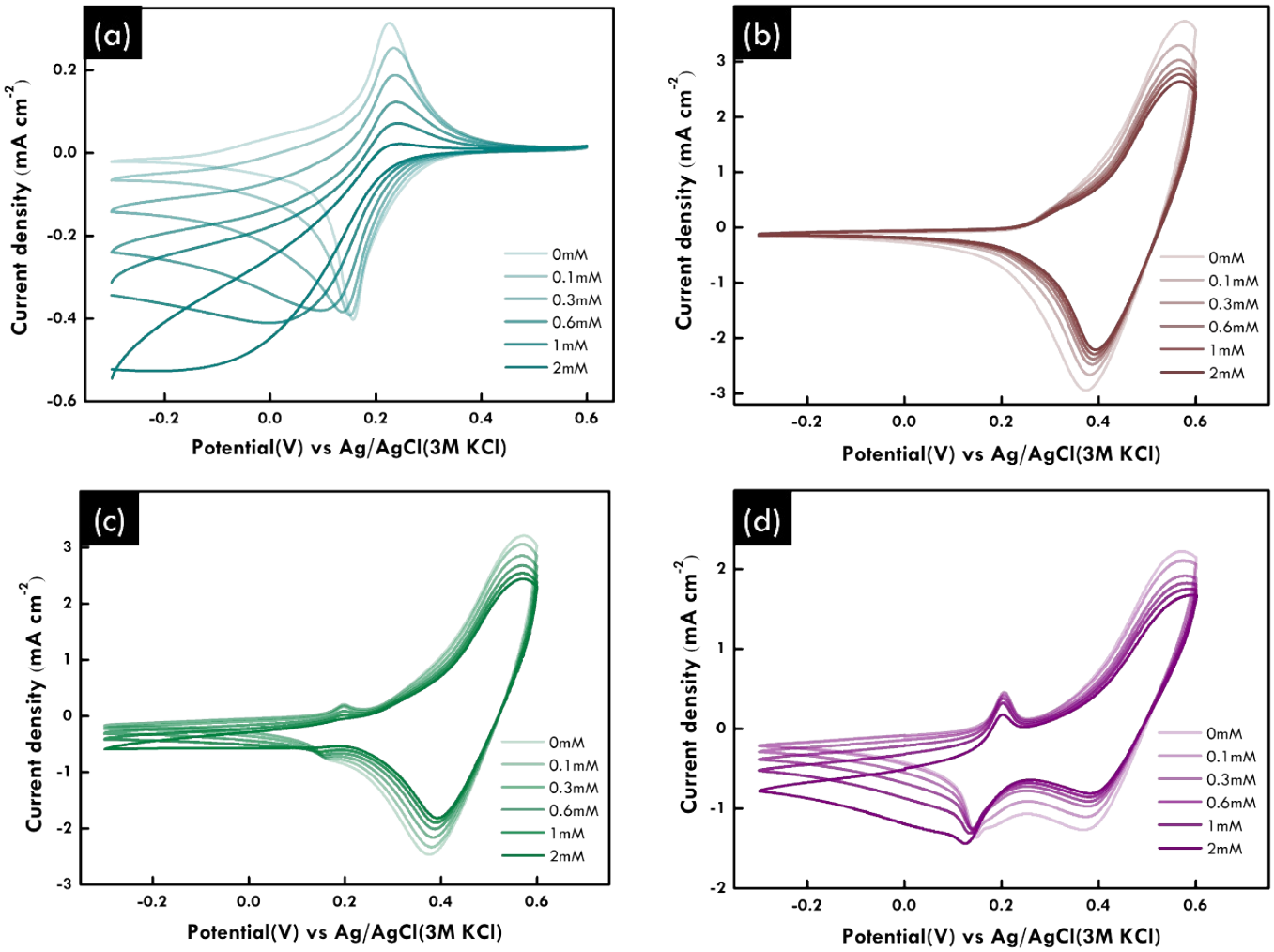

Figure S3 The cyclic voltammetry of (a) PB, (b) PBA, (c) PBA/PB, and (d) NGQDs/PBA/PB on SPCEs with a linear range of 0-2 mM H_2O_2 for H_2O_2 detection in 0.01 M PBS (pH=7.2).

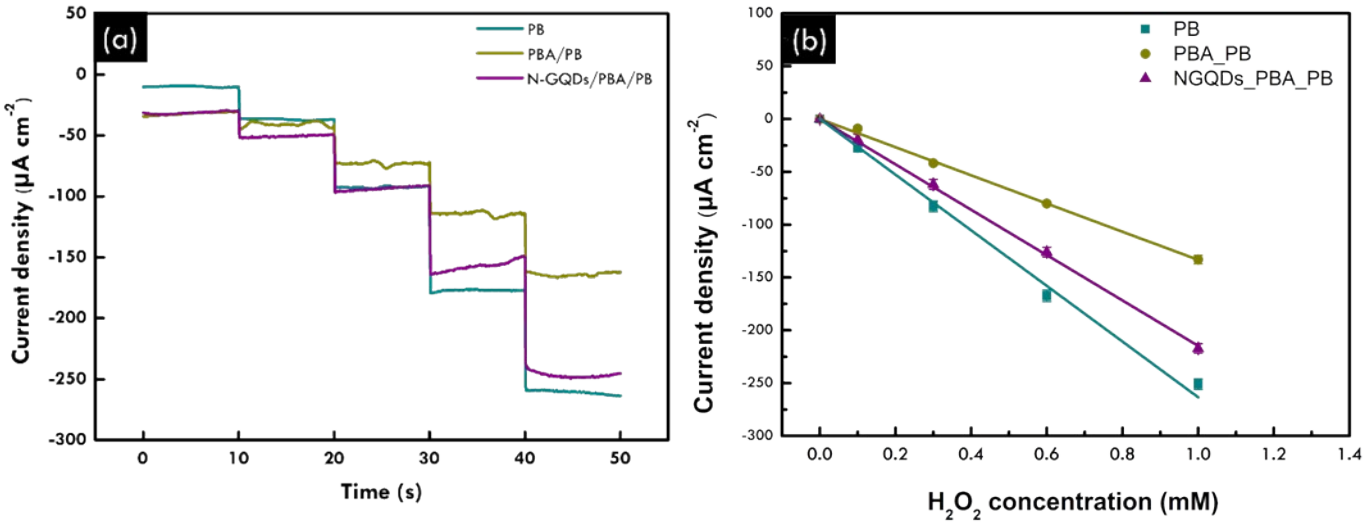

Figure S4 (a) The amperometry curve of PB, PBA/PB, and NGQDs/PBA/PB on SPCEs; (b) The calibration curve of PB, PBA/PB, and NGQDs/PBA/PB on SPCEs with a linear range of 0-1 mM H_2O_2 for H_2O_2 detection in 0.01 M PBS (pH=7.2).

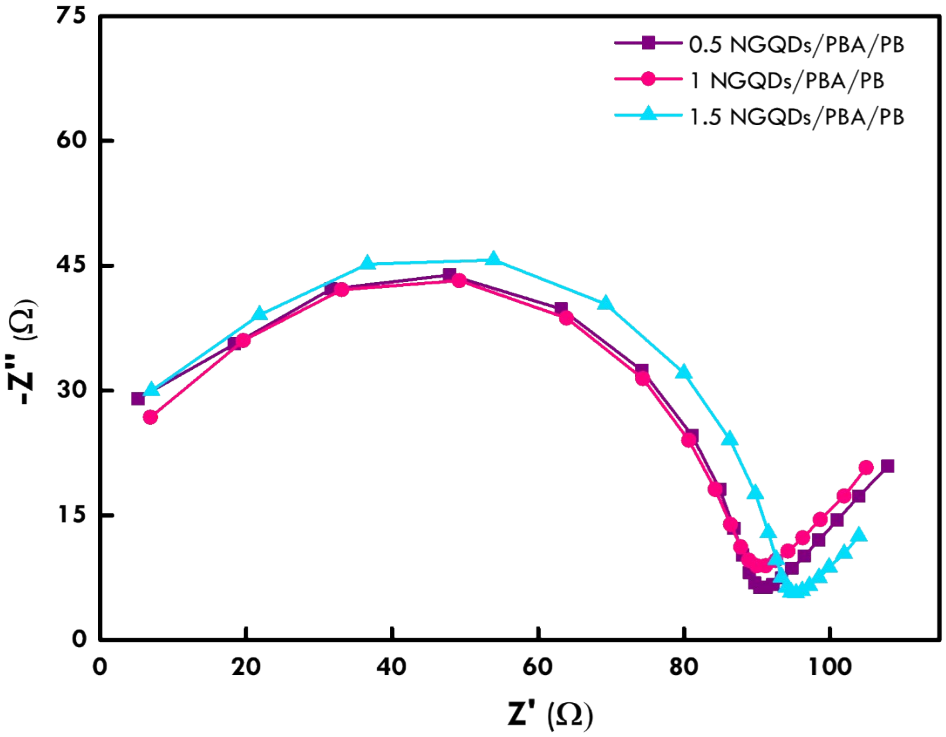

Figure S5 The Nyquist plot of 0.5 PBA/PB, 1 PBA/PB, and 1.5 PBA/PB on SPCEs.

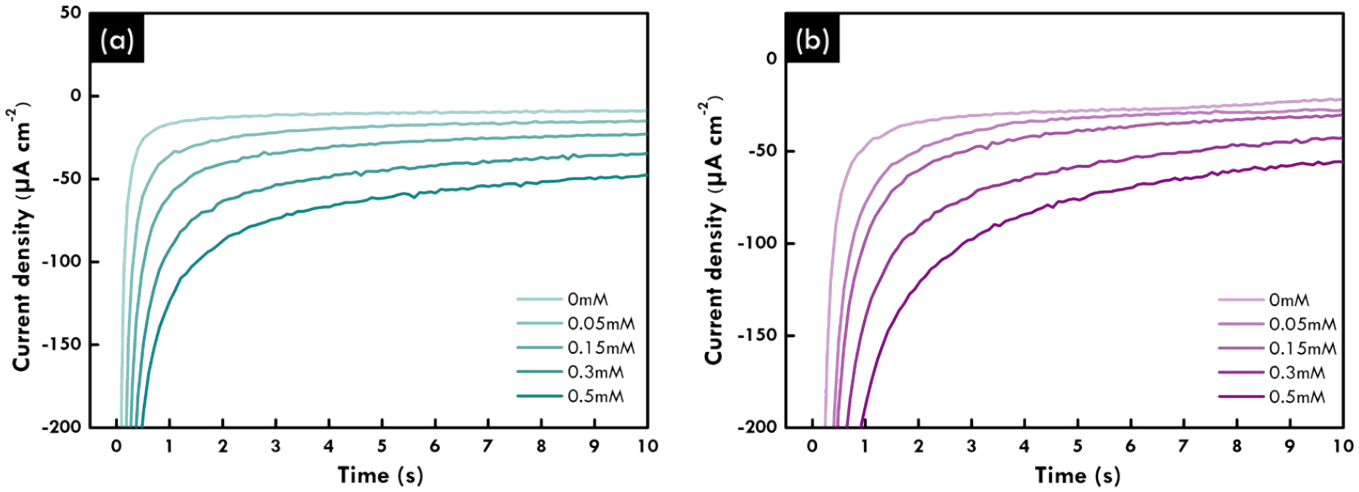

Figure S6 The amperometry curve of (a) GOx/PB and (b) GOx/NGQDs/PBA/PB on SPCEs with a linear range of 0-0.5 mM glucose for glucose detection in 0.01 M PBS (pH=7.2).