Supporting Information

Polyaniline nanoflowers grafted onto nanodiamond via soft template guided secondary nucelation process for high-performance glucose sensing

S. Komathi[1,#], A-I. Gopalan[2,3,#], N. Muthuchamy[1] and K-P. Lee[1,3,*]

[1]Deparment of Chemistry Education, Kyungpook National University, Daegu, S.Korea

[2]Research Institute of Advanced Energy Technology, Kyungpook National University, Daegu, S.Korea

[3]Department of Nanoscience and Nanotechnology, Kyungpook National University, Daegu, S.Korea

[#] Authors contributed equally to this work

*Corresponding author: kplee@knu.ac.kr

SI-1. Electrochemical Properties of Prepared Electrodes

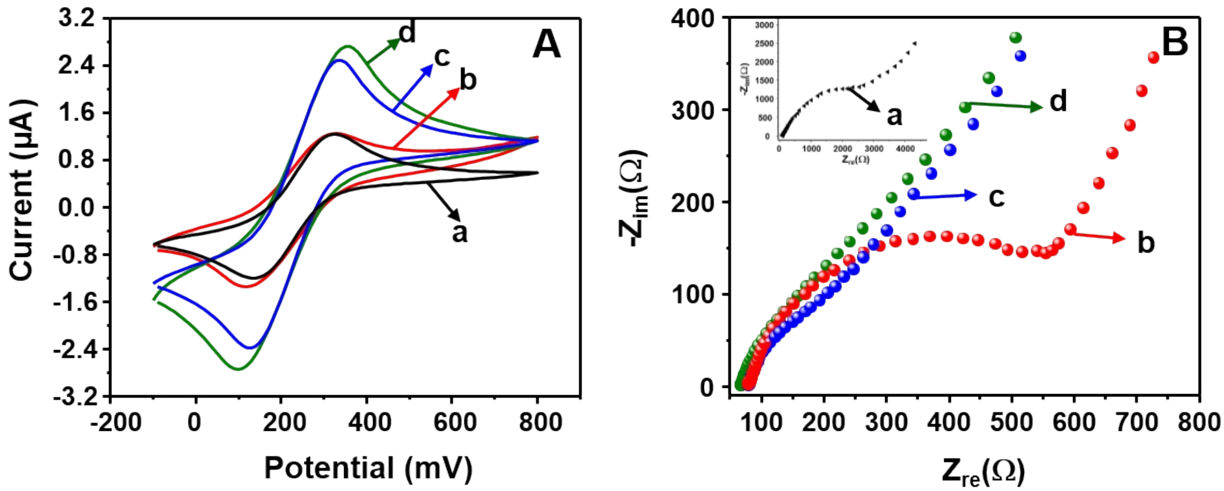
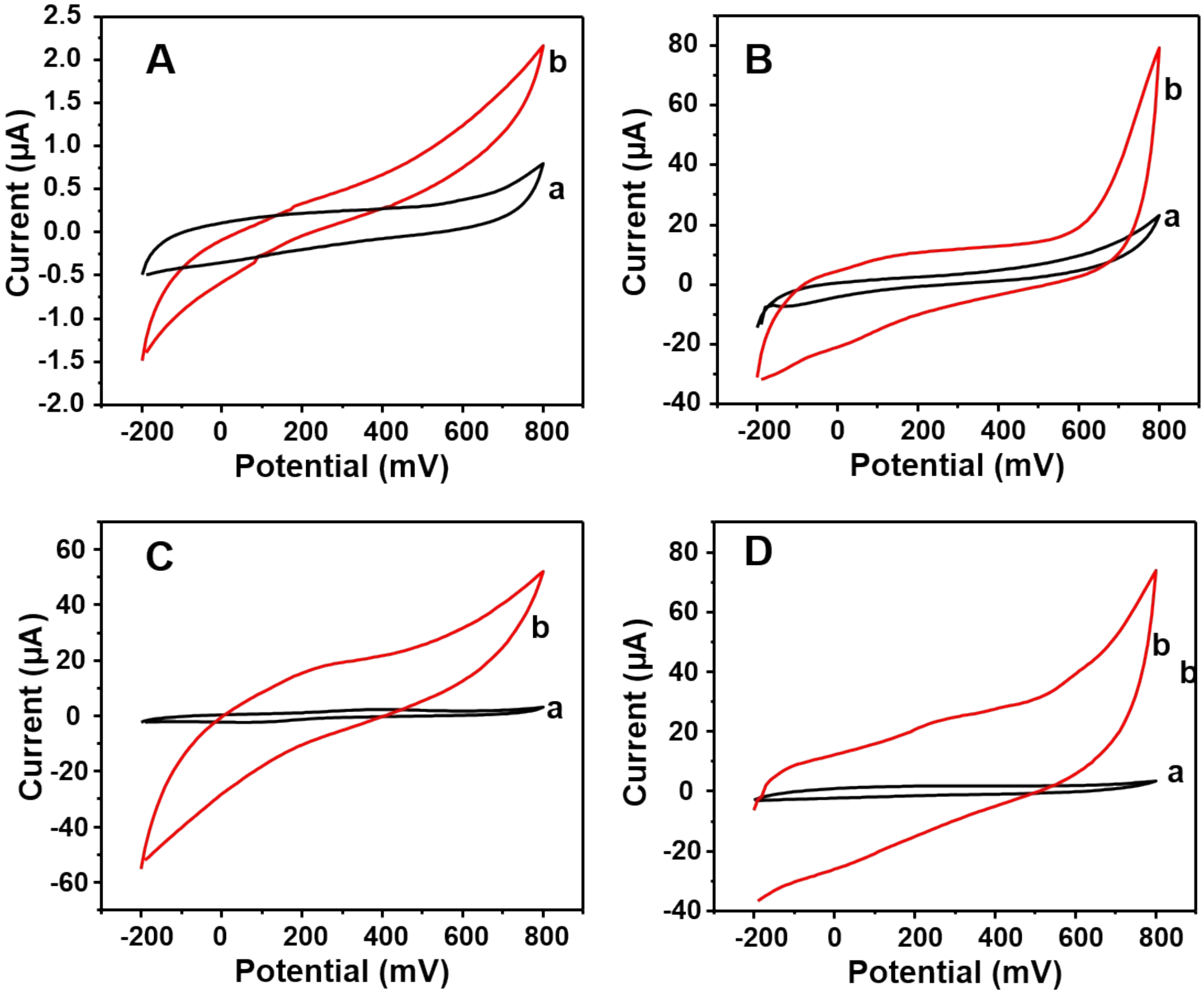


Fig. SI-1. (A) CV and **(B)** Nyquist EIS plots of (a) PANI (b) ND_1-g-PANI, (c) ND_5-g-PANI and (d) ND_{10}-g-PANI electrodes in 0.1M KCl containing 5 mM of $Fe(CN)_6^{3-/4-}$ in the scan rate range from 50 $mV.s^{-1}$.

The electroactivity of (a) PANI (b) ND_1-g-PANI, (c) ND_5-g-PANI and (d) ND_{10}-g-PANI electrodes was investigated by cyclic voltammetry (CV) in a solution of $Fe(CN)_6^{3-/4-}$ (5 mM) in 0.1M KCl. CVs of the prepared electrodes exhibited symmetrical anodic and cathodic peaks that are associated with the redox $Fe(CN)_6^{3-/4-}$ transitions. The anodic-cathodic peak potential separation at the (a) PANI (b) ND_1-g-PANI, (c) ND_5-g-PANI and (d) ND_{10}-g-PANI electrode was +0.19 V, +0.21 V, +0.11 V and +0.13 V, respectively, which indicates a quasireversible reaction at these electrodes. The comparison of peak current at the $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$ redox transition reveals the effectiveness of surface modifications. The peak current at ND_{10}-g-PANI (d) electrode was 1.1, 2.1 and ~2.18 times higher than ND_5-g-PANI, ND_1-g-PANI and PANI electrodes, respectively. The ND_{10}-g-PANI showed much higher peak current and the least anodic-cathodic peak separation value among the other three electrodes investigated.

The modified electrodes were characterized by electrochemical impedance spectroscopy (EIS), The Nyquist plots of for the (a) PANI (b) ND_1-g-PANI, (c) ND_5-g-PANI and (d) ND_{10}-g-PANI electrodes recorded in 0.1M KCl containing 5 mM of $Fe(CN)_6^{3-/4-}$ are shown in Fig SI-1B. The Nyquist plots show a semicircular region at higher frequencies followed by a long tail at lower frequencies. The semicircle part and linear part correspond to the electron transfer limited and diffusion processes respectively. The diameter of the semicircle determines the charge transfer resistance (R_{ct}) at the electrode. R_{ct} values of (a) PANI (b) ND_1-g-PANI, (c) ND_5-g-PANI and (d) ND_{10}-g-PANI electrodes were obtained by fitting the EIS data into the Randles circuit, as 3766 Ω, 642 Ω, 278 Ω and 190 Ω respectively. R_{ct} value is the least for ND_{10}-g-PANI (190 Ω) among the electrodes investigated. The lowest R_{ct} at ND_{10}-g-PANI (190 Ω) suggests an efficient electron conduction pathway between the electrode and electrolyte at the ND_{10}-g-PANI modified electrode.



SI-2. Enzymatic Glucose Oxidation

Fig. SI-2. (A) CVs of (A) PANI/GOx **(B)** ND_1-g-PANI/GOx, **(C)** ND_5-g-PANI/GOx and **(D)** ND_{10}-g-PANI/GOx electrodes in **(a)** 0.1 M PBS containing **(b)** 1 mM of glucose solution in the scan rate range from 50 mV.s^{-1}.

Fig. SI-2. shows typical CV results for (A) PANI/GOx **(B)** ND_1-g-PANI/GOx, **(C)** ND_5-g-PANI/GOx and **(D)** ND_{10}-g-PANI/GOx electrodes in **(a)** 0.1 M PBS and in the presence of 1mM glucose **(b)** at a scan rate of 50 mV.s^{-1}. In the absence of 1 mM glucose, no prominent catalytic redox peaks were observed for PANI/GOx**,** ND_1-g-PANI/GOx, ND_5-g-PANI/GOx and ND_{10}-g-PANI/GOx electrodes except for an increases in background current. ND_5-g-PANI/GOx and ND_{10}-g-PANI/GOx electrodes exhibits a redox peak around +0.40 V (anodic) and −0.1 V (cathodic) in the presence of 1 mM glucose. No redox peaks were observed for PANI/GOx **(B)** ND_1-g-PANI/GOx (**Fig. SI-2 (A-B)**, curve b). Amperometric measurements were further performed to study the influence of applied potentials (from +0.25 V to +0.65 V) on the sensitivity of ND_{10}-g-PANI/GOx for 1 mM solution of glucose in 0.1 M PBS. The ND_{10}-g-PANI/GOx electrode (**Fig. SI-3**) showed a well-defined electrocatalytic oxidation peak at +0.40 V with a high peak current. As a result, the electrochemical oxidation of glucose can be followed at ND_{10}-g-PANI/GOx electrode at a much lower potential.

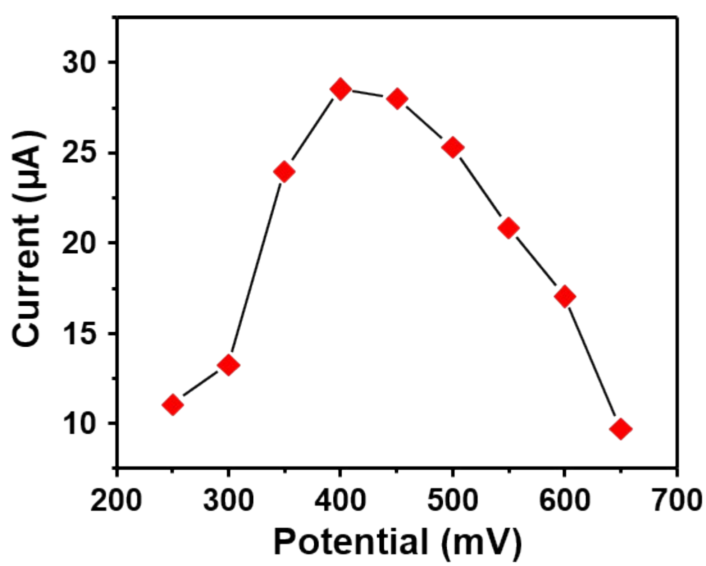


Fig. SI-3. Amperometric current responses observed at ND_{10}-g-PANI/GOx in 1 mM of glucose (in 0.1 M PBS) solution on various applied potentials.

SI-3. Reproducibility, repeatability and stability

The reproducibility of the electrode was analyzed by using six similarly fabricated ND_{10}-g-PANI/GOx biosensing electrodes. The reproducibility of the current responses of 5 mM glucose in PBS using the ND_{10}-g-PANI/GOx biosensor electrode at +0.40 V determined for the six electrodes. The root of mean square standard derivation (R.S.D) value of 1.2% was noticed for the six electrodes.

The repeatability of the ND_{10}-g-PANI/GOx biosensor was also checked by performing four repeated amperometric measurements at +0.40 V for 5 mM glucose solution in PBS. R.S.D. value of 1.42% was obtained. The value is indicative of the good repeatability of the ND_{10}-g-PANI/GOx biosensor.

The stability of the ND_{10}-g-PANI/GOx biosensor was investigated by performing amperometric measurements (+0.40 V) with 5 mM glucose in PBS over a period of 30 days. The electrode was stored at 4 °C in a PBS, whenever not in use. The mean value of the current responses was noted every day. There was no significant change in the mean value of current responses for the first three weeks. However, a small (<3%) decrease in current response was observed in the fourth week up to 30 days.