

Nanostructured zirconia@reduced graphene oxide based ultraefficient nanobiosensing platform for food toxin detection

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1. Chemicals and biomolecules: Natural graphite flakes, zirconium ethoxide, N-ethyl-N-(3-dimethylaminopropyl) carbodiimide (EDC), Aflatoxin B1 (AFB1) and bovine serum albumin (BSA) were purchased from Sigma-Aldrich (St. Louis, USA). Sodium hydroxide, cetyltrimethylammonium bromide (CTAB), sodium monophosphate, sodium diphosphate dihydrate and N-hydroxysulfosuccinimide (NHS) were purchased from Fisher Scientific (Maharashtra, India). 3-aminopropyl triethoxy silane (APTES) was procured from Alfa-aesar (Lancashire, UK). These materials were used without further purification. Milli-Q water (resistivity 18 M Ω cm) was used in all the buffer and solution preparation.

2. Characterization: The crystallinity and phase formation of the nanocomposite was examined through X-ray diffraction (XRD) studies [Bruker D-8 Advance] in which the spectrum was recorded through a monochromatic X-ray beam with Cu-k α radiation of wavelength (λ) 1.5406 Å. The structural and morphological studies were conducted through scanning electron microscopy (SEM, Hitachi SN-3700) and transmission electron microscopy (TEM, JEOL-JEM-2100F). Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer, model spectrum ATR accessory) was used to investigate the functional groups and bonds present on APTES/nZrO₂@RGO/ITO and anti-AFB1/APTES/nZrO₂@RGO/ITO electrodes. The electrochemical studies [cyclic voltammetry (CV) and differential pulse voltammetry (DPV)] were performed using Autolab, Potentiostat/Galvanostat (Netherlands). These measurements were conducted using a three-electrode system where modified ITO coated glass substrate was employed as the working electrode, platinum (Pt) as counter electrode and Ag/AgCl as the reference electrode in phosphate buffer saline (PBS) solution (50 mM, 0.9 % NaCl) of pH 7.0 containing 5 mM of [Fe (CN)₆^{3-/4-}] as redox species. All the electrochemical studies were conducted in triplicate.

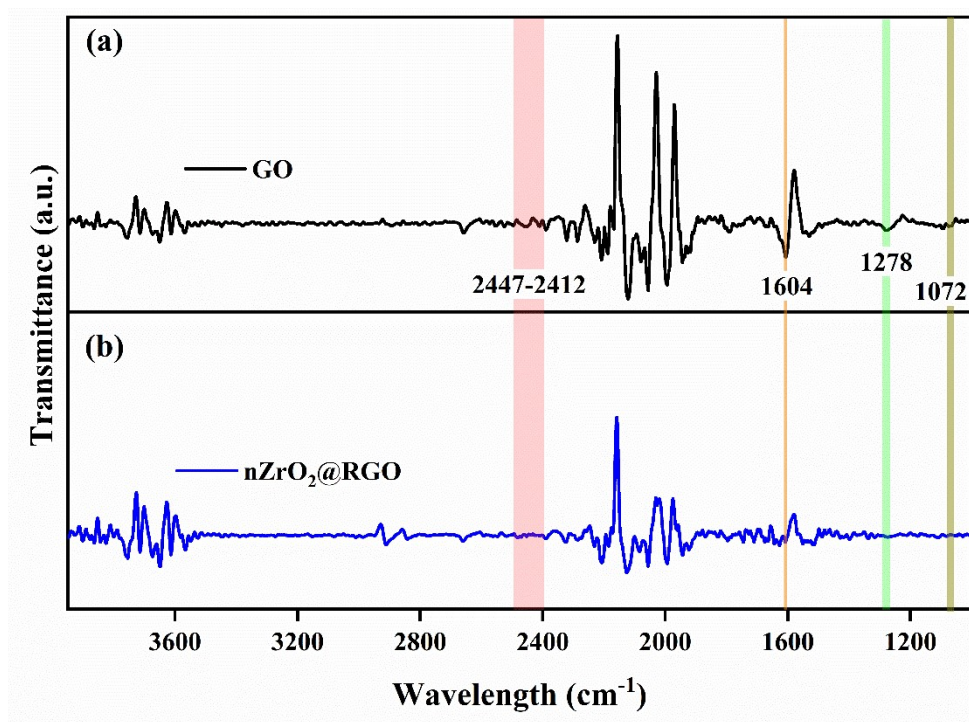


Figure S1: FT-IR spectra of (a) GO and (b) nZrO₂@RGO.

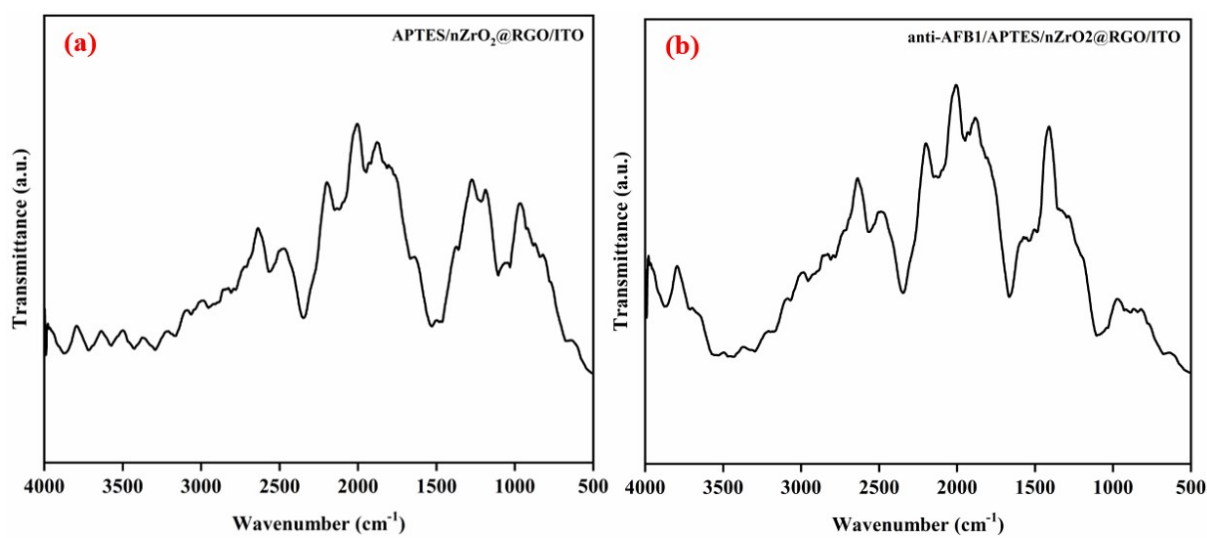


Figure S2: FT-IR spectra of (a) APTES/nZrO₂@RGO/ITO and (b) anti-AFB1/APTES/nZrO₂@RGO/ITO electrodes.

Equations

$$I_{pa} \text{ (APTES/nZrO}_2\text{@RGO/ITO) (mA) = [0.048} \pm \text{0.0004 (mA mV}^{-1/2} \text{ s}^{1/2}) \nu^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2})] + [0.141 \pm \text{0.004 mA}], \quad R^2 = 0.99 \dots \dots \dots \text{(S1)}$$

$$I_{pc} \text{ (APTES/nZrO}_2\text{@RGO/ITO) (mA) = -[0.033} \pm \text{0.0003 (mA mV}^{-1/2} \text{ s}^{1/2}) \nu^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2})] - [0.155 \pm \text{0.003 mA}], \quad R^2 = 0.99 \dots \dots \dots \text{(S2)}$$

$$I_{pa} \text{ ((BSA/anti-AFB1/APTES/nZrO}_2\text{@RGO/ITO) (mA) = [0.047} \pm \text{0.0003 (mA mV}^{-1/2} \text{ s}^{1/2}) \nu^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2})] + [0.136 \pm \text{0.003 mA}], \quad R^2 = 0.99 \dots \dots \dots \text{(S3)}$$

$$I_{pc} \text{ (BSA/anti-AFB1/APTES/nZrO}_2\text{@RGO/ITO) (mA) = -[0.035} \pm \text{0.0002 (mA mV}^{-1/2} \text{ s}^{1/2}) \nu^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2})] - [0.127 \pm \text{0.002 mA}], \quad R^2 = 0.99 \dots \dots \dots \text{(S4)}$$

$$\Delta E_p \text{ (APTES/nZrO}_2\text{@RGO/ITO) (V) = [0.024} \pm \text{0.0002 (V}^{1/2} \text{ mV}^{-1/2} \text{ s}^{1/2}) \nu^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2})] + [0.1536 \pm \text{0.002 V}], \quad R^2 = 0.99 \dots \dots \dots \text{(S5)}$$

$$\Delta E_p \text{ (BSA/anti-CYFRA-21-1/APTES/nZrO}_2\text{@RGO/ITO) (V) = [0.032} \pm \text{0.0004 (V}^{1/2} \text{ mV}^{-1/2} \text{ s}^{1/2}) \nu^{1/2} \text{ (mV}^{1/2} \text{ s}^{-1/2})] + [0.185 \pm \text{0.004 V}], \quad R^2 = 0.99, \dots \dots \dots \text{(S6)}$$