Deep Eutectic Solvent-Driven Synthesis of La₂NiO₄@rGO Ruddlesden–Popper Hybrids for Ethyl Parathion Sensing Supported with Theoretical Studies

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S.I. 1 Chemical reagents:

Lathanum (III) nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O ≥ 99.0%), nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$.6H$_2$O, ≥ 99.0%), (ACS grade), ethanol (C$_2$H$_5$OH ≥ 99.8%), sodium hydroxide (NaOH ≥ 99.0%), sodium phosphate monobasic (NaH$_2$PO$_4$), sodium phosphate dibasic (Na$_2$HPO$_4$), alumina slurry, and ethyl parathion (EP) were procured from Sigma-Aldrich, Taiwan. Additionally, Choline chloride ([(CH$_3$) $_3$NCH$_2$CH$_2$OH] $^+$Cl$^-$), fructose (C$_6$H$_{12}$O$_6$) and citric acid (C$_6$H$_8$O$_7$), and potassium hydroxide (KOH) were procured from Sigma-Aldrich, Taiwan. All chemicals were of analytical grade with the highest purity available and did not require additional purification. A phosphate buffer solution (PBS) at a concentration of 0.1 M was prepared using Na$_2$HPO$_4$ and NaH$_2$PO$_4$, and pH adjustment was achieved using 0.1 M HCl/NaOH solutions. Distilled water served as the solvent for formulation. Finally, carrot juice, apple juice, cabbage, and orange juice have been purchased in the Taiwan market for the real sample analysis.

S.I. 2 Chemical Methods and Instruments:

High-Resolution Transmission Electron Microscopy (HR-TEM; JEM 2100F) and Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM–6500F) coupled with Energy-Dispersive X-ray Spectroscopy (EDX) were employed to identify the surface morphology of nanomaterials. Furthermore, X-ray Photoelectron Spectroscopy (XPS) with the Thermo Scientific MultiLab 2000 instrument and X-ray Diffraction (XRD, PANalytical X'PERT PRO, Netherlands) using Cu–Kα as the source radiation (λ = 1.5417 Å), Raman analysis was performed within the frequency range of 100 cm^{-1} to 3000 cm^{-1} utilizing a Dong Woo 500i system from Korea and Fourier transform infrared spectroscopy (FTIR) has been studied by the FTIR-6600 spectrometer in the wavenumber range between 4000 and 400 cm^{-1} were utilized to scrutinize the elemental composition and surface characteristics. In the realm of electrochemical studies, a three-electrode system was utilized, comprising a glassy carbon electrode (GCE, 0.071 cm²) as the working electrode, a platinum electrode as the counter electrode, and an Ag/AgCl electrode as the reference electrode (ALS Co., Ltd, Japan). Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) were conducted in a nitrogen gas atmosphere using phosphate buffer solution, with a potential range of 0.6 to -1.2 V (vs Ag/AgCl) and a scan rate of 100 mV/s. Additionally,

Electrochemical Impedance Spectroscopy (EIS) was carried out over a frequency range of $(10^2\text{-}10^5)$ Hz in a solution containing potassium chloride and $[Fe\,(CN)_6]^{3-}/^{4-}$. These electrochemical methods provided valuable insights into the material's electrochemical behavior and properties. Real sample validation carried out by Ultimate 3000 RS UHPLC Systems with Ultimate 3000 Analytical column.
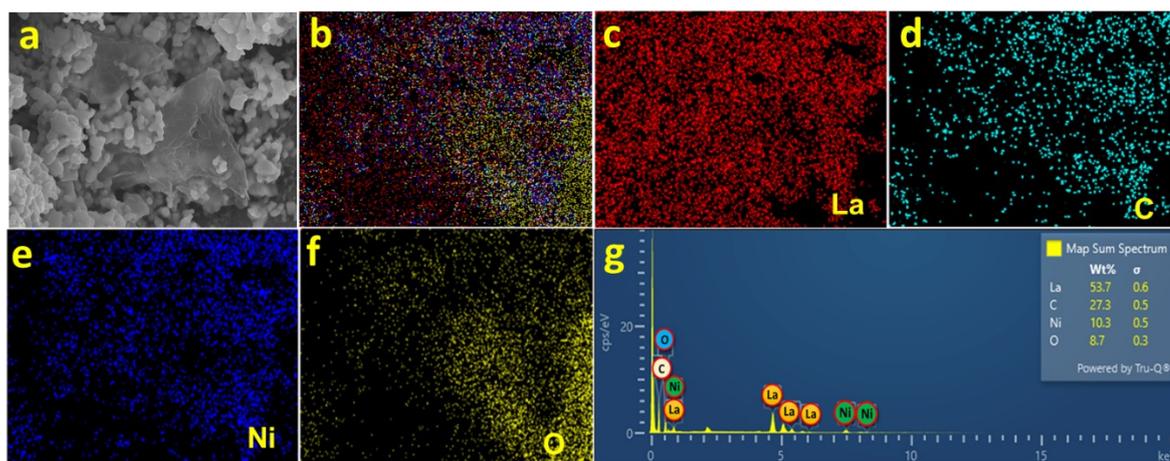

Figure S1. Elemental mapping of La2NiO4@rGO nanocomposite. (a) La2NiO4@rGO nanocomposite, (b) whole elemental distribution, (c) La, (d) C, (e) Ni, (f) O.
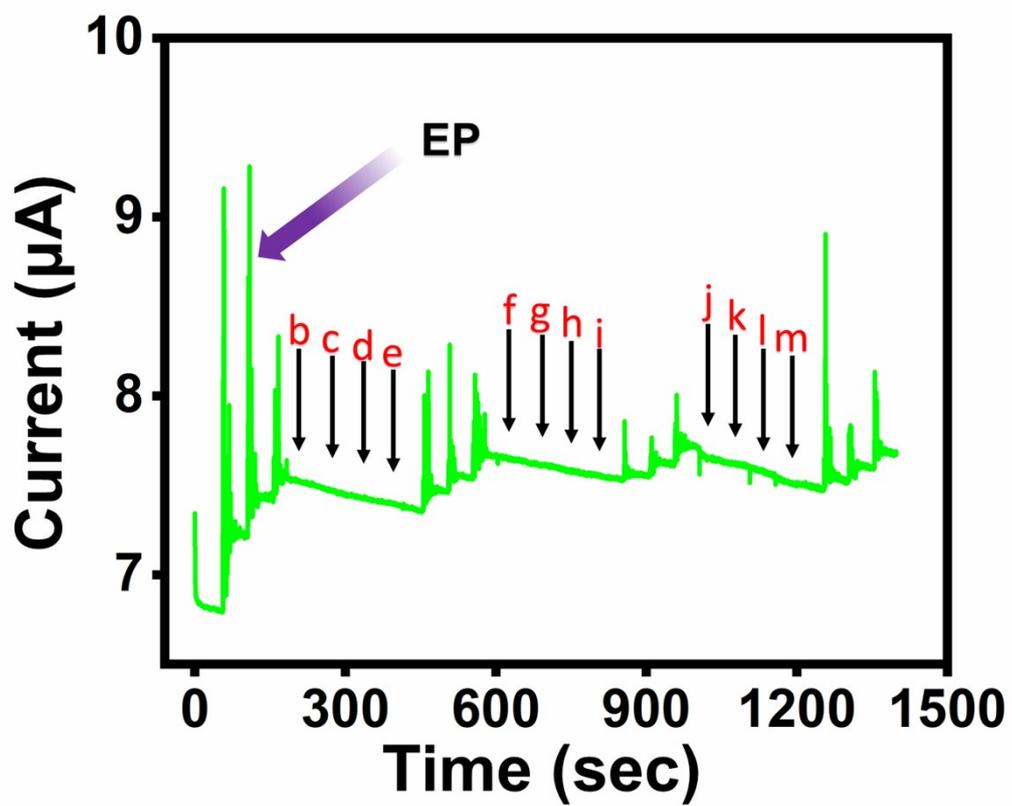
Figure S2. Anti-interference study with five-fold excess concentration
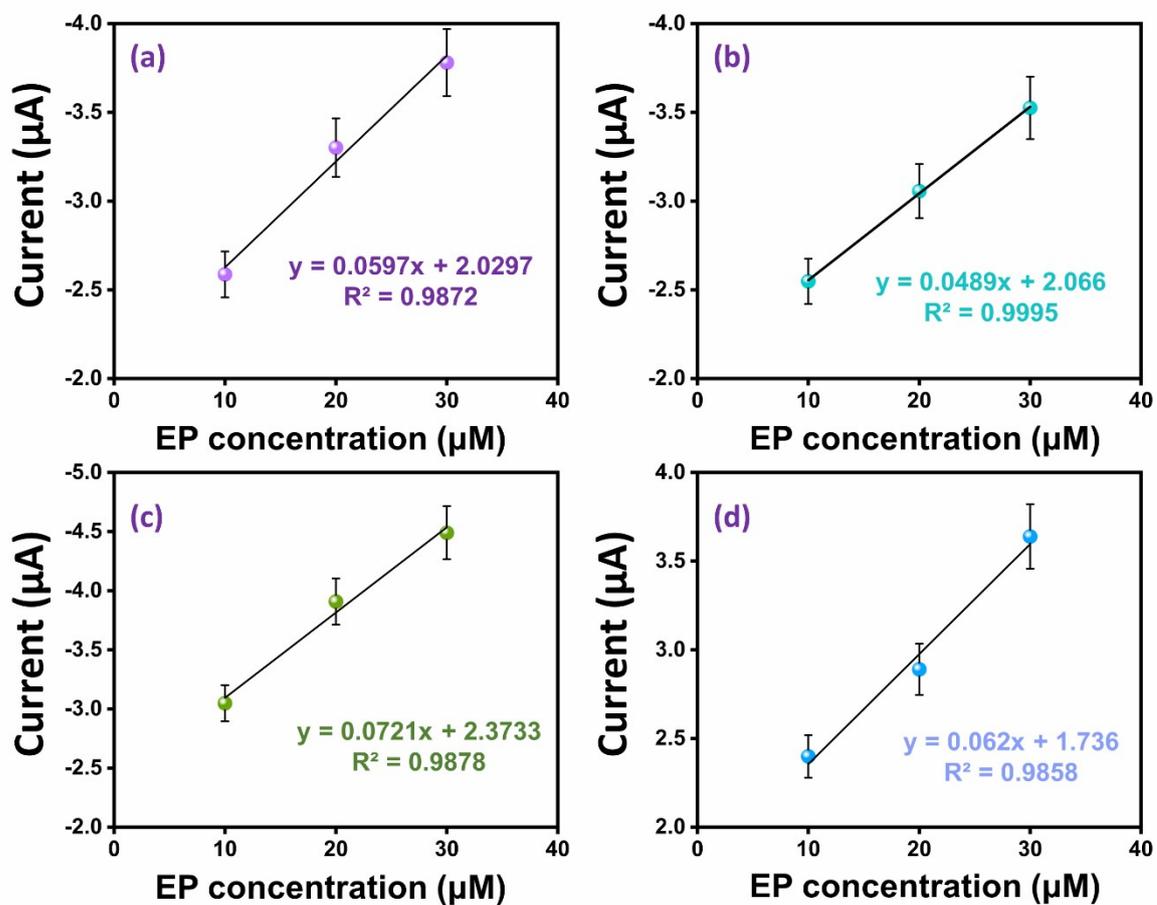
Figure S3. Calibration plot for the real samples, carrot juice (a), cabbage juice (b), apple juice (c), orange juice (d).