

SUPPLEMENTARY MATERIALS

Electrocatalytic Oxidation of Nitrophenols via Ag Nanoparticles Supported on Citric-Acid-Modified Polyaniline

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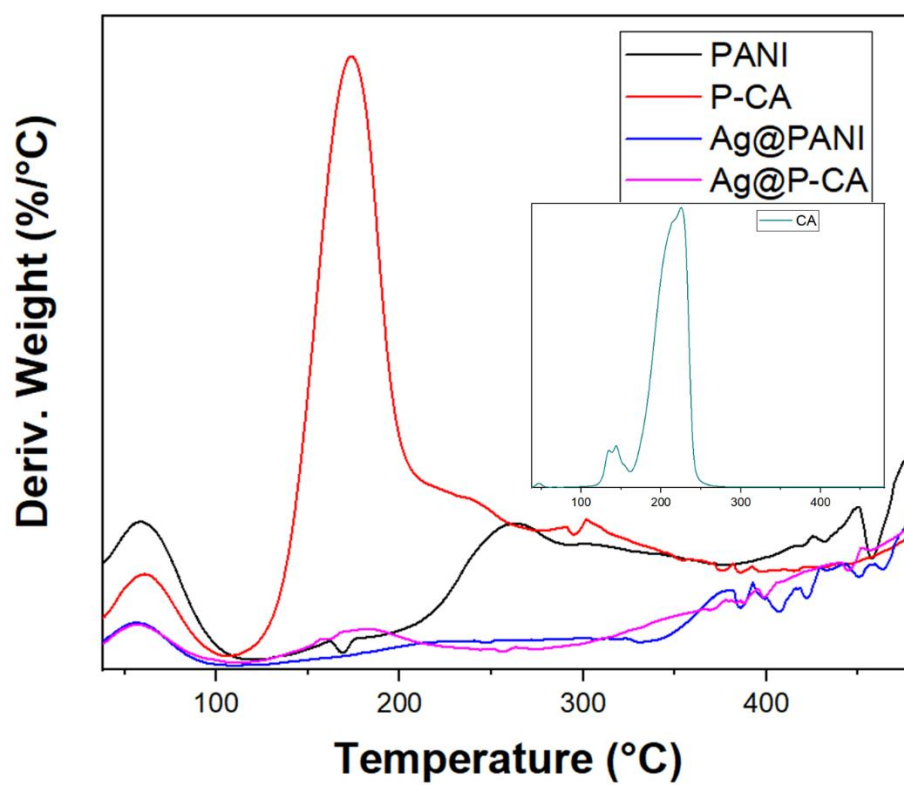


Figure S1. First derivative TGA of modified PANI-based composites and their precursors. The TGA profile is shown as an inset.

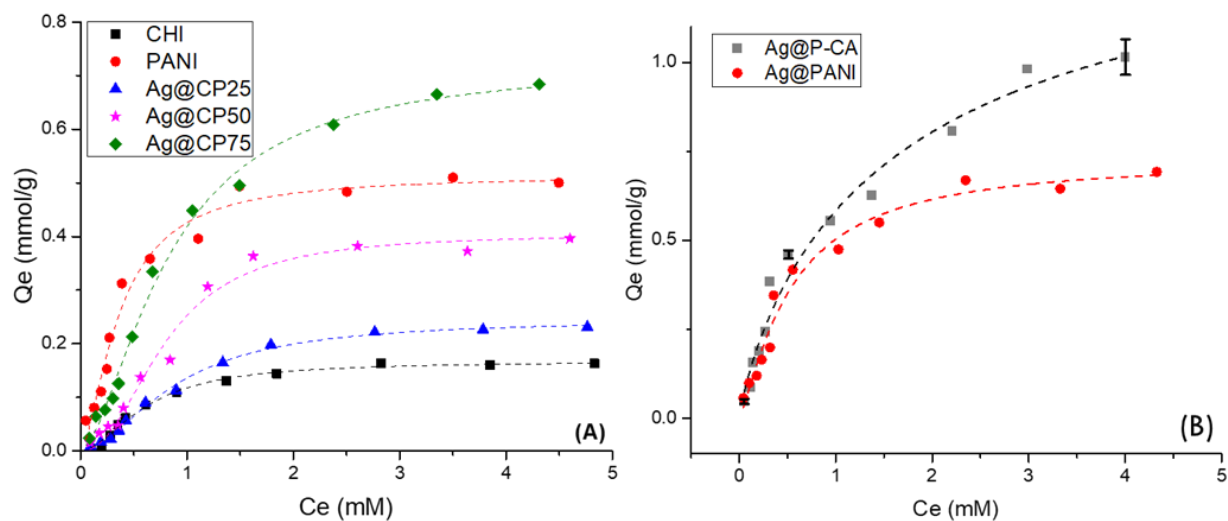


Figure S2. 2-NP adsorption study of modified PANI-based composites and their precursors and fitted isotherms at 295 K and pH = 7 (PBS-7 buffer solution). Dashed lines represent fitted Sips models for each isotherm at 295 K. The plots are based on the amount of dye adsorbed for a given weight of adsorbent (Q_e) vs the dye residual equilibrium concentration (C_e). Panel (A) refers to CHI-based composites and panel (B) refers to non-CHI-based composites. In panel (B), error bars are shown for Ag@P-CA to illustrate typical error estimated at low, medium, and higher dye concentration.

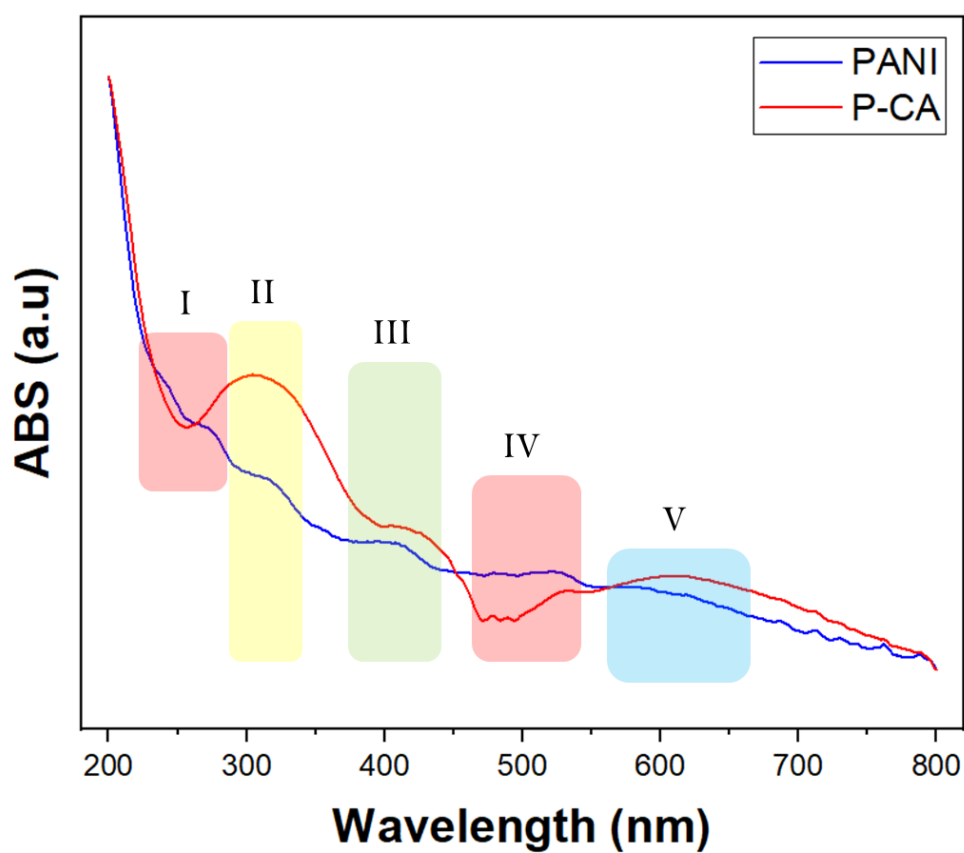


Figure S3. Solid-state UV-Vis spectra of modified PANI-based composites and the precursors (chitosan, PANI). The highlighted areas illustrate characteristic bands (I, II, III, IV, and V) of the samples. The spectra are not normalized, but scaled from 0 to 1 for qualitative comparison of the respective spectra.

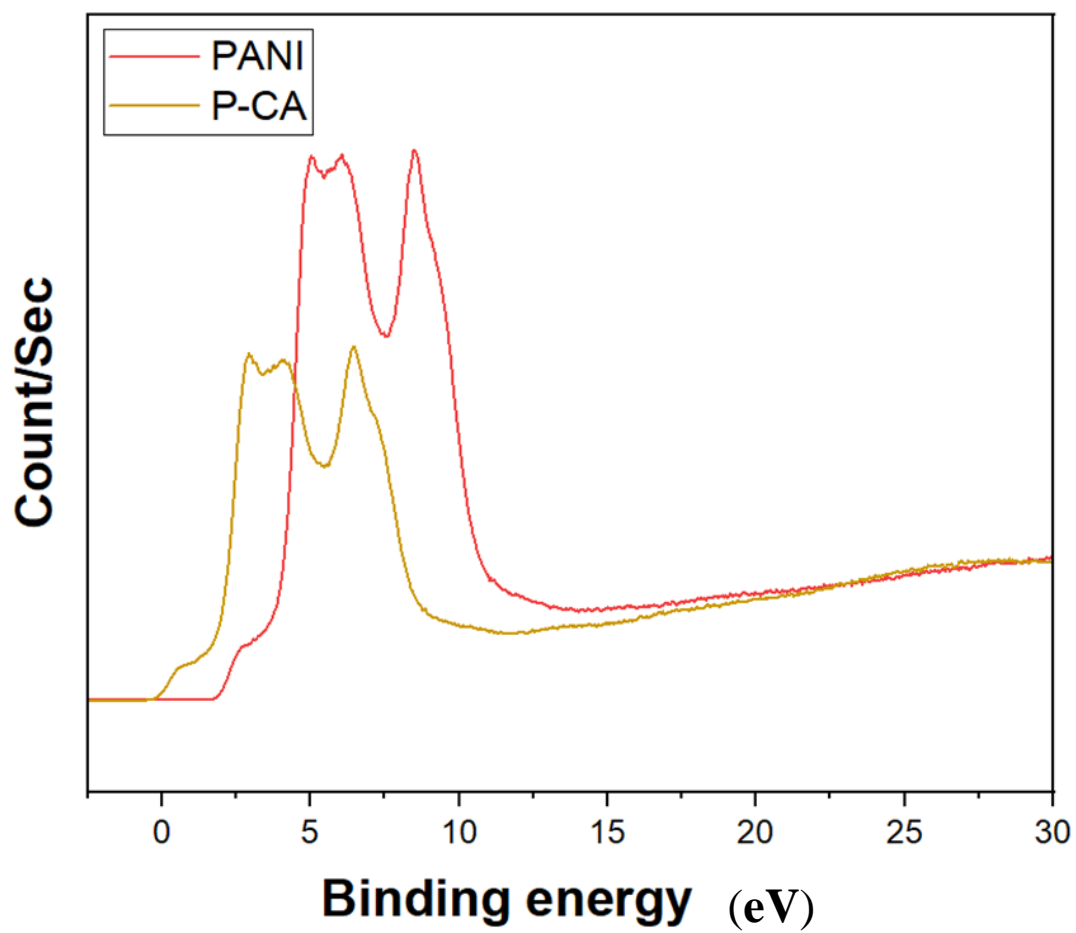


Figure S4. Valence band XPS of modified PANI-based composites. The XPS was calibrated to the C 1s spectrum at 284.8 eV, where the X-axis represents the binding energy (eV).

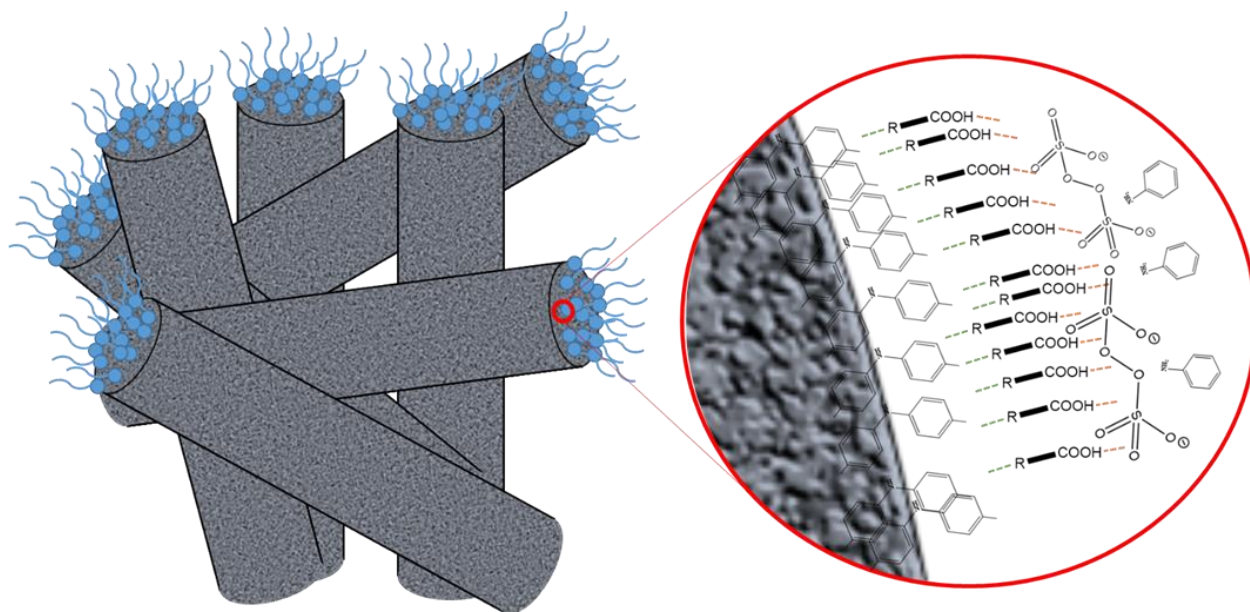


Figure S5. The micellar role of organic acids (denoted in blue) in the polymerization of aniline (located at the grey interface region). R represents the hydrocarbon that may possess variable functionality.

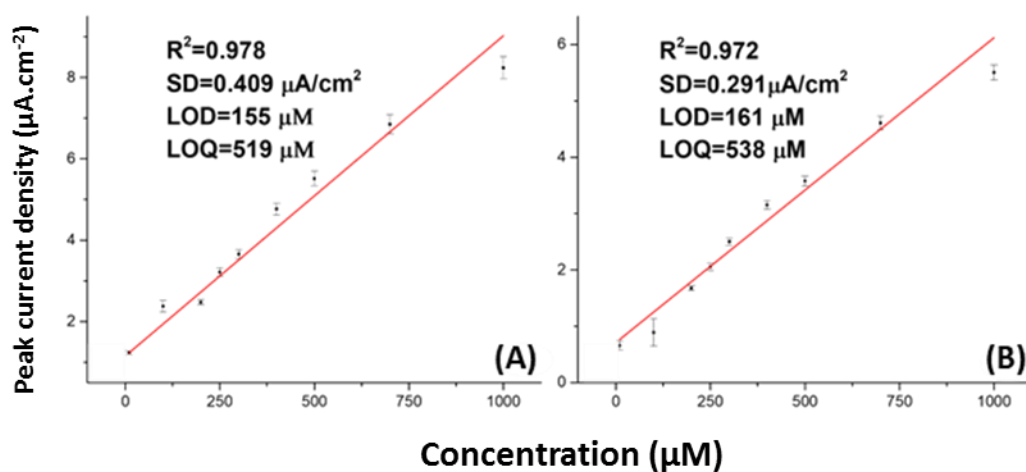


Figure S6. Calibration curves for the detection of 2-NP (A) and 4-NP (B) with Ag@P-CA modified electrode material and their electrochemical characteristic parameters (SD: standard deviation, LOD: limit of detection, LOQ: limit of quantification). The Y-axis represents current density ($\mu\text{A}\cdot\text{cm}^{-2}$), and X-axis represents concentration (μM). The CV analysis of the composites was carried out at a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$ and a potential range from -600 to 1200 mV using the three-electrode system in PBS-7 buffer solution ($\text{pH} = 7$) at 298 K .

Table S1. Recent examples of literature studies for the detection of nitrophenols.

Analyte	Detection method
4-NP [25]	fluorescent sensor
4-NP [26]	fluorescent sensor
4-NP [36]	fluorescent sensor
4-NP [37]	electrochemical sensor
4-NP [38]	fluorescent sensor
4-NP [39]	fluorescent sensor
4-NP [40]	electrochemical sensor
4-NP [41]	electrochemical sensor
4-NP [42]	electrochemical sensor
4-NP [43]	fluorescent sensor
2-NP [27]	electrochemical sensor
4-NP [28]	electrochemical sensor
4-NP [29]	electrochemical sensor
4-NP [30]	electrochemical sensor
4-NP [31]	fluorescent sensor
2-NP/4-NP [32]	electrochemical sensor
4-NP [33]	surface plasmon resonance sensor
4-NP [34]	fluorescent sensor
4-NP [35]	luminescent sensor

Table S2. Examples of recent studies on the electrochemical detection of nitrophenols.

Analyte	Detection method	Approach	Linear range (μM)	Detection limit (nM)
4-NP [37]	DPV	Reduction reaction	2.0–9.0 and 9.0–210.0	700
4-NP [40]	DPV	Reduction reaction	0.1–4.0 and 5–150	65
4-NP [41]	SWV	Reduction reaction	3–50	23
4-NP [42]	SWV	Reduction reaction	3–50	10
2-NP [27]	LSV	Reduction reaction	0.5–100	160
4-NP [28]	DPV	Reduction reaction	0.05–200	60
4-NP [29]	DPV	Reduction reaction	0.5–250	100
4-NP [30]	SWV	Reduction reaction	3–50	110
2-NP/4-NP [32]	DPV	Reduction reaction	100–370	300 (4-NP)/360 (2-NP)
4-NP [74]	DPV	Reduction reaction	2–1117	39

S1. TGA Results

Non-PANI content in Ag@PANI composites is assumed to be a mixture of PANI oligomers and the acid dopant. Since aniline as a limiting reagent was converted to PANI and its oligomers; therefore, there is a linear relationship between the content (%) of PANI and its oligomers.

In the following equations, P = PANI, O = PANI oligomers, and A = Acid dopant.

$$Non - PANI = A + O$$

$$P = 100 - O$$

S2. XRD Results

The crystalline size of Ag NPs deposited onto composites was calculated based on Debye–Scherrer equation (Equation S1).

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (S1)$$

Where D indicates the crystalline size of Ag NPs, K is a constant equal to 0.90, λ is the wavelength of the incident X-ray, β is the FWHM of the related diffraction, and θ is the Bragg angle. The instrumental broadening effect was calculated based on Equation S2 and subtracted from β_{measured} based on Equation S3.

$$\beta_{\text{instrumental}} = 0.00558 \tan^2(\theta) - 0.00901 \tan(\theta) + 0.01039 \quad (S2)$$

$$\beta_1 = \sqrt{\beta_{\text{measured}}^2 - \beta_{\text{instrumental}}^2} \quad (S3)$$

The microstrain effect was calculated based on Equation S4 and subtracted from β_1 based on Equation S5.

$$\varepsilon = \frac{\beta_{\text{measured}}}{4 \tan(\theta)} \quad (S4)$$

$$\beta = \beta_1 - \varepsilon \quad (S5)$$

S3. Dye Adsorption Results

A dye adsorption isotherm is a plot of the amount of dye adsorbed for a given weight of adsorbent (Q_e) vs the dye residual equilibrium concentration (C_e). Equation S6 gives the value of Q_e , where C_0 is the initial dye concentration, V is the volume of solution, and m is the sorbent weight.

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (S6)$$

C_0 is measured based on the linear calibration curve obtained from the Beer-Lambert law. (Equation S7) where A is the optical absorbance (unitless), ϵ is molar absorptivity ($\text{mM}^{-1}.\text{cm}^{-1}$), b is the length of the cuvette (cm), and c is the concentration of the sample (mol.L^{-1}).

$$A = \epsilon bc \quad (S7)$$

The Langmuir (Equation S8), Freundlich (Equation S9), and Sips (Equation S10) isotherm models have been used to estimate adsorption isotherms.

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (S8)$$

$$Q_e = K_F C_e^{1/n_f} \quad (S9)$$

$$Q_e = \frac{Q_m (K_S C_e)^{n_s}}{1 + (K_S C_e)^{n_s}} \quad (S10)$$