

Supplementary Material (ESI) for Chemical Communications

“Nanocatalyst \cup reagent-on-a-polymer film”: A new polymer-supported system for (electro-)catalytic reactions

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Experimental for the preparation of PEDOT support and loading of metal nanocatalyst

Good quality PEDOT-ClO₄ films were deposited on a clean glassy carbon electrode by potential cycling of GC electrode in acetonitrile solutions of EDOT monomer and Bu₄NClO₄ in a range between -0.8 and 1.5 V *vs* Ag wire reference in a solution containing 0.025 M EDOT monomer and 0.025 tetrabutylammonium perchlorate in acetonitrile at a scan rate of 0.05 Vs⁻¹. Loading of metal nanoparticles (Pt, Au) on PEDOT matrix was achieved by chemical reduction by CNBH₃⁻ ion doped film. First, the PEDOT film was dipped into 0.1M TBACNBH₃ + acetonitrile for ion exchange process. The extent of cyanoborohydride doping in PEDOT film can be varied with different immersion time periods: 3 hrs, 6 hrs, 9 hrs, 12 hrs and 24 hrs respectively. A representative CV feature clearly indicates the extent of loading of cyanoborohydride through ion exchange process (Fig. S1). In the second step, the CNBH₃⁻ doped PEDOT film was dipped in 2 mM solution of metal precursor solutions for a few seconds and the dipped film was allowed to dry for 10-15 minutes before recording the cyclic voltammogram. The desired loading of metal nanoparticles in PEDOT matrix was achieved by varying the immersion period of CNBH₃ doped PEDOT film. Cyclic voltammograms were recorded for each loading of metal nanocatalyst on PEDOT in 0.5M H₂SO₄ at a scan rate of 50mV/s. CV patterns of metal nanoparticles encapsulated PEDOT matrix were obtained after 10 cycles in the background electrolyte (blank).

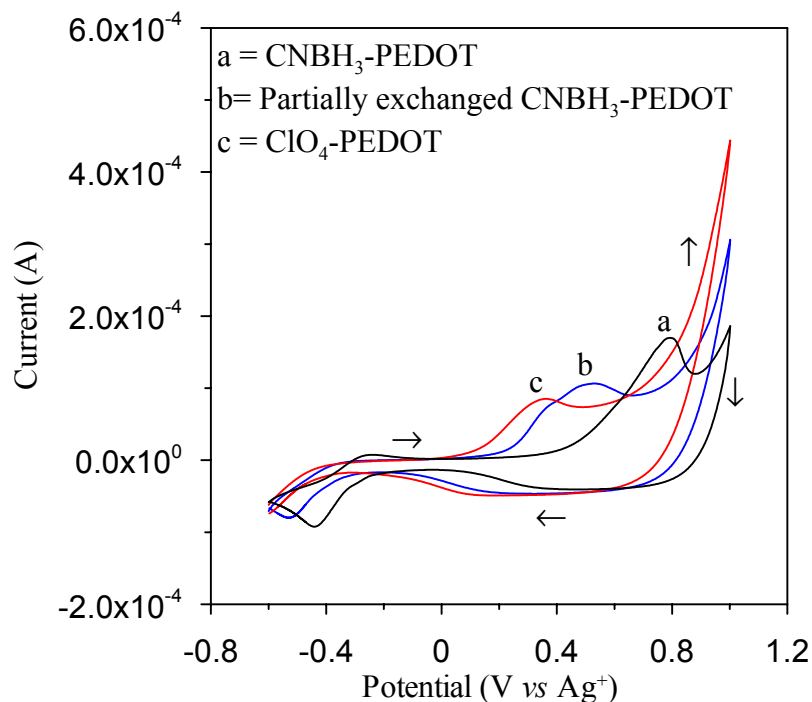


Fig. S1 Cyclic voltammograms of CNBH_3^- doped PEDOT (a), partially exchanged CNBH_3^- doped PEDOT (b), ClO_4^- doped PEDOT (c) film in acetonitrile medium at a scan rate of 50mV/s.

Percentage of doping level in PEDOT matrix determined by Laser-Raman spectroscopy

Laser Raman spectroscopy was used to estimate the percentage doping level of PEDOT film. In this study, the oxidized PEDOT film gets de-doped by applying -0.1V for 10-15 minutes as was indicated by the color of the film to be dark blue. Re-doping process was performed by chronoamperometry in solutions containing 0.1 M $(\text{C}_4\text{H}_7)_4\text{N}^+ \text{CNBH}_3^-$ in acetonitrile at different applied potentials (0.1V, 0.3V, 0.45V, 0.55V, 1.0V, and 1.5V) for a period of 10 minutes. Before recording the spectra, the PEDOT film was dipped in acetone for a few seconds to remove any loosely bound material. *Ex-situ* Raman spectroscopy with 785 nm excitation was used to study the resonance Raman shift of the -C-C- to carbon stretching band positions in the vibrational mode, particularly symmetric $\text{C}_\alpha=\text{C}_\beta$ vibrations, due to changes in the electronic structure of PEDOT upon incorporation of dopants.

Raman spectra recorded for the de-doped PEDOT film and CNBH_3^- ion doped PEDOT film in acetonitrile at different applied potentials (0V, 0.33V, 0.55V, 1.0V and 1.5V vs pseudo reference of Ag) in the range between 200 cm^{-1} and 2000 cm^{-1} using 785 nm excitation. The symmetric stretching vibrations of $\text{C}_\alpha=\text{C}_\beta$ appeared at 1414 cm^{-1} for de-doped PEDOT film and shifted to 1445 cm^{-1} for CNBH_3^- doped PEDOT film as identified through red Laser Raman (785 nm excitation) spectroscopy. The maximum extent of CNBH_3^- doping was achieved by varying the applied potential to 1.5V. The symmetric stretching vibration intensity of $\text{C}_\alpha=\text{C}_\beta$ increases with increasing applied potentials. The doping level percentage was calculated from the ratio of integrated intensity of symmetry stretching value at 1414 cm^{-1} (de-doped PEDOT) and 1445 cm^{-1} (CNBH_3^- ion doped-PEDOT). From these intensity values, the doping level percentage was calculated using this formula $I = 0.087y - 2.279$, where I-is the natural logarithm of the ratio of intensity values of de-doped and CNBH_3^- ion doped PEDOT and y-is the percentage doping level of PEDOT. The percentage of ClO_4^- ion doped PEDOT film was found to be 42.3% and 34.47 % for CNBH_3^- ion doped film. It can be concluded that CNBH_3^- ion exchange in PEDOT proceeded successfully with change in the applied potentials (0.3 V, 0.45 V, 0.55 V and 1.0 V).

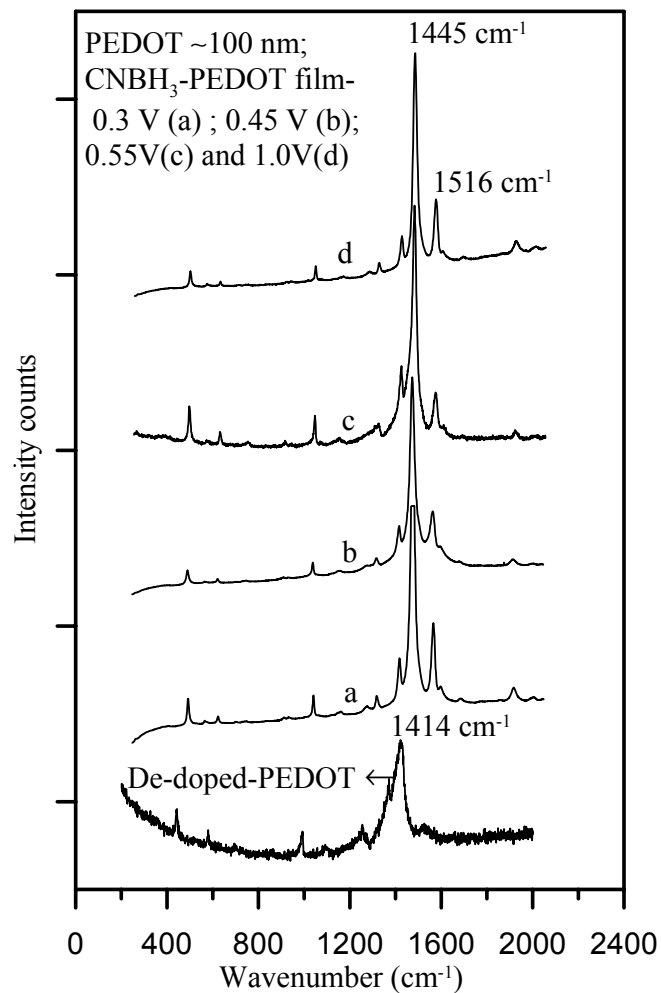


Fig. S2. Raman spectra (785 nm excitation) of de-doped PEDOT and various amounts of CNBH₃⁻ ion loaded PEDOT film in acetonitrile at different applied potentials

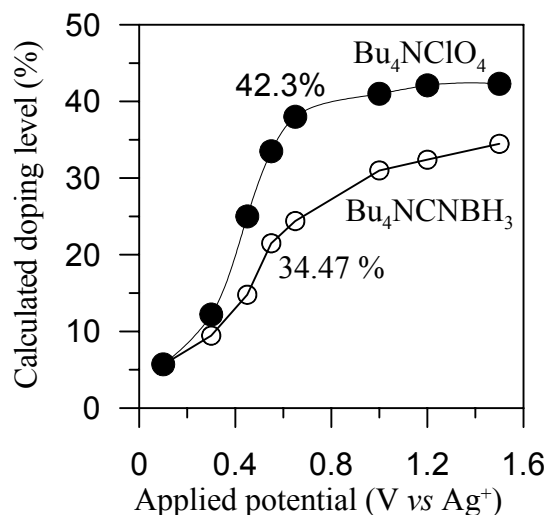


Fig. S3. Plot of the calculated doping level of the de-doped PEDOT film re-doped with ClO_4^- and CNBH_3^- ions in acetonitrile medium vs. applied potential

Conductivity measurements:

Table-1: Conductivity values of PEDOT film determined by four-probe resistivity set-up.

Sl.No	Nature of PEDOT film	Conductivity (σ) (S/cm)
1.	De-doped PEDOT containing ClO_4^- ions	44.4
2.	$\text{PEDOT}^+ \text{ClO}_4^-$ film	251.35
3.	$\text{PEDOT}^+ \text{(CNBH}_3^-)$ film	201.2

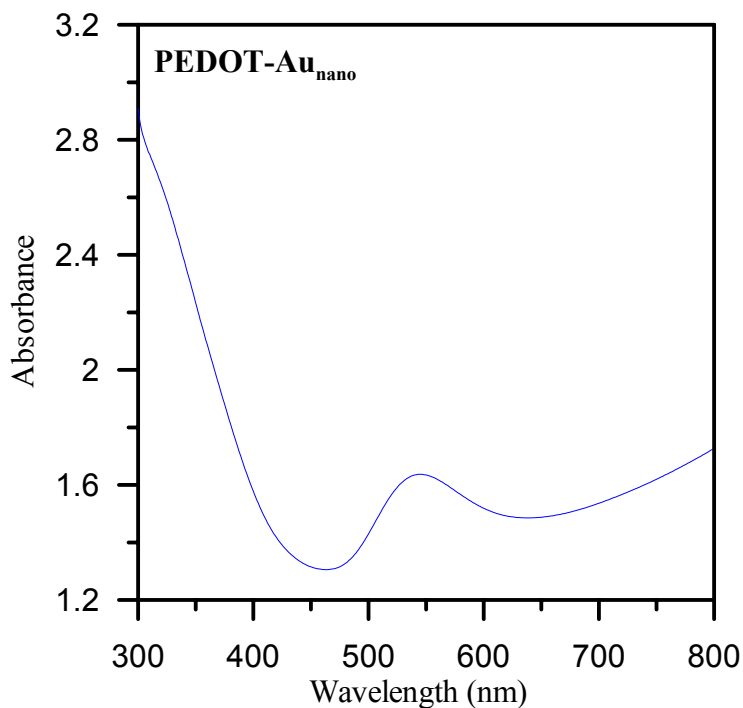


Fig. S4 UV-Visible spectrum for Au nanoparticles entrapped PEDOT film

The SPR band of PEDOT-Au_{nano} (534nm) is clearly seen in Fig. S2, but anisotropic (Triangular, pentagon, and hexagon) absorbance bands of Au_{nano} (700-900 nm) are merged with polaronic/bipoloronic transition of PEDOT support.

FT-IR spectroscopy

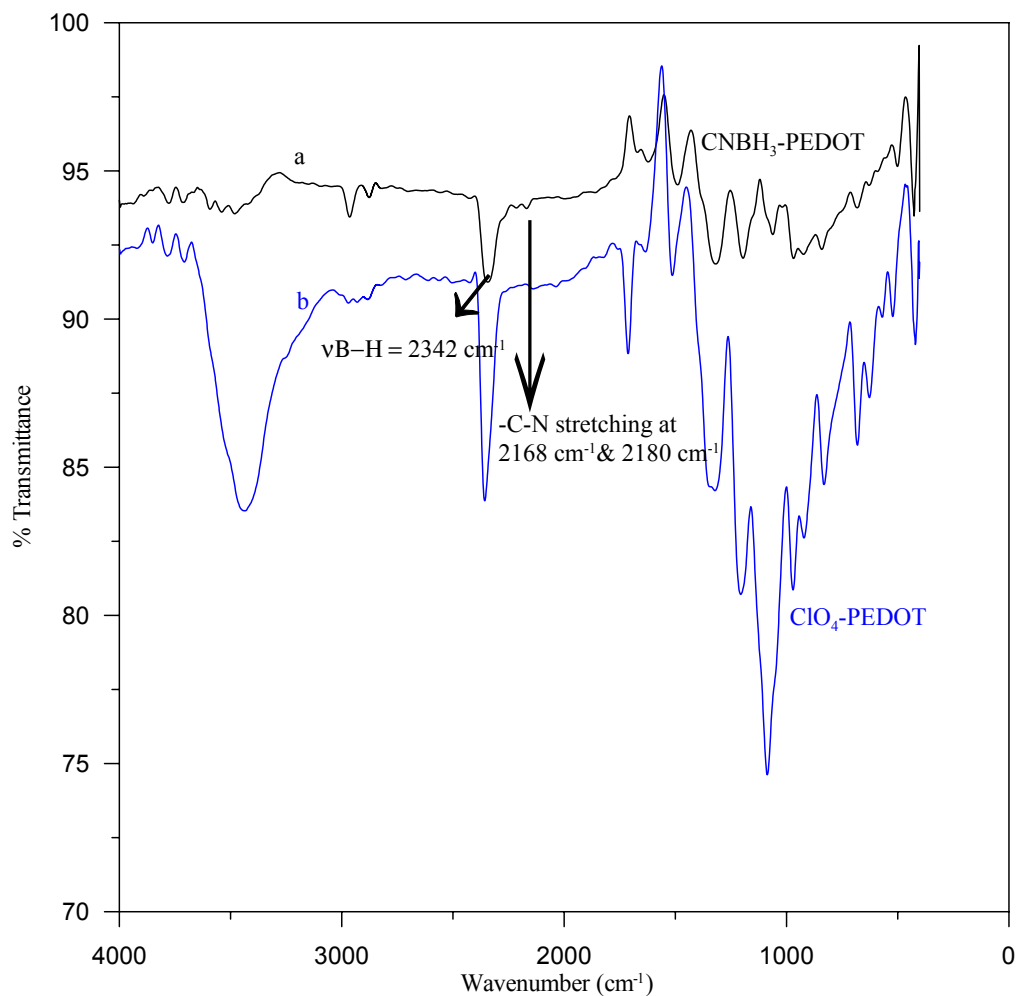


Fig. S5: FT-IR Spectra for the solid CNBH₃-PEDOT (a) and ClO₄-PEDOT (b) films

Determination of surface Area of Metal_{nano}-PEDOT films

The amount of Pt nanoparticles in PEDOT was determined by calculating the H_{upd} charge of cyclic voltammogram of Pt_{nano}-PEDOT film recorded in 0.5 M H₂SO₄ vs. MSE. Loading of Pt particles in terms of the hydrogen-upd charge in PEDOT polymer was in the range between 0.223 mC/cm² and 0.906 mC/cm².

The weight of Au nanoparticles in polymer matrix can be estimated by calculating the area of cathodic reduction peak of cyclic voltammogram recorded in 0.5M H₂SO₄ background electrolytes at a scan rate of 50 mV/s.

Table-2: Calculation of values of surface area of Pt_{nano}-PEDOT, and Au_{nano}-PEDOT films.

Sl. No	Doping period of TBACNBH ₃ (Time in hrs)	H_{upd} charge of Pt _{nano} -PEDOT (mC/cm ²)	Surface Area of Pt _{nano} -PEDOT (cm ²)	Charge of cathodic reduction peak of Au _{nano} -PEDOT (mC/cm ²)	Surface area of Au _{nano} -PEDOT (cm ²)
1	3	0.223	1.06	14.41 x 10 ⁻³	35.15 x 10 ⁻³
2	6	0.346	1.65	23.80 x 10 ⁻³	58.05 x 10 ⁻³
3	9	0.597	2.84	31.81 x 10 ⁻³	77.59 x 10 ⁻³
4	12	0.947	4.51	43.77 x 10 ⁻³	106.76 x 10 ⁻³
5	18	0.906	4.32	39.81 x 10 ⁻³	97.1 x 10 ⁻³

$$\text{Surface area, } A_{\text{Pt}} = Q_{H_{\text{upd}}} \text{ of Pt}_{\text{nano}}\text{-PEDOT} / 0.210 \text{ mC/cm}^2$$

$$\text{Surface area, } A_{\text{Au}} = Q_{\text{cathodic reduction peak of Au}_{\text{nano}}\text{-PEDOT}} / 0.410 \text{ mC/cm}^2$$

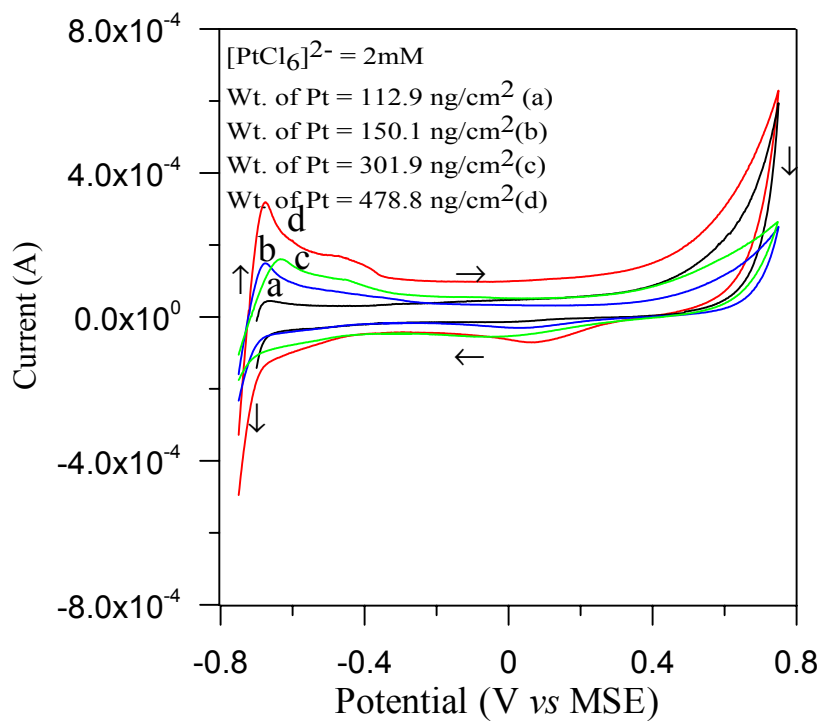


Fig.S6. Cyclic voltammograms representing different loading levels of Pt nanocatalyst on PEDOT film using various doping periods of CNBH_3^- ion in the PEDOT matrix. (Doping period a = 3 hrs , b = 6 hrs , c = 9 hrs and d = 12 hrs)

Fig.S7: Electrocatalytic oxidation of formic acid using Pt_{nano}-PEDOT film in 0.5 M H₂SO₄

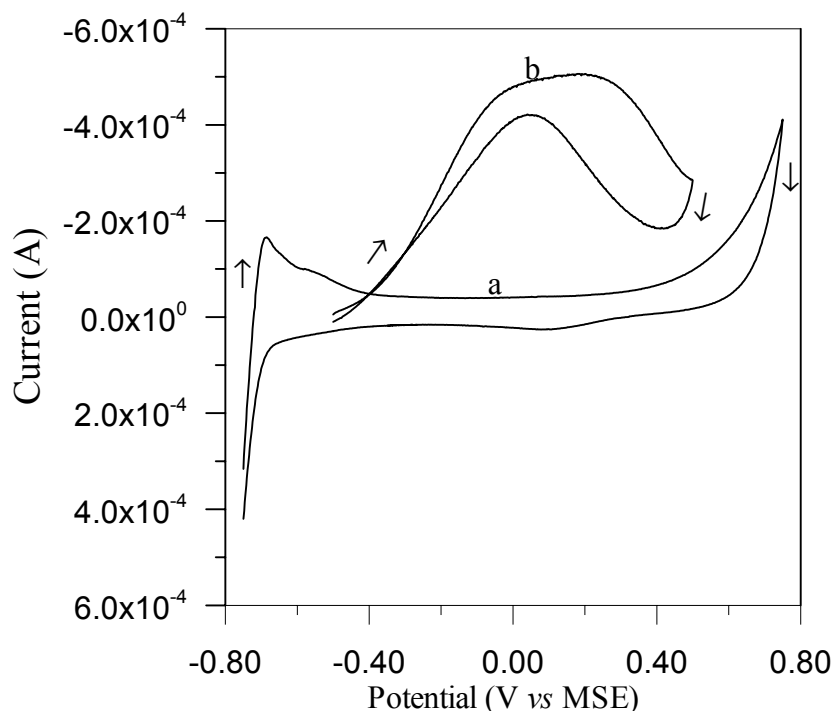


Fig. S7 Cyclic voltammogram of ($Q = 0.947 \text{ mC}\cdot\text{cm}^{-2}$) Pt nanoparticles loaded PEDOT film on glassy carbon electrode in 0.5 M H₂SO₄ at a scan rate of 50mV/s a) without formic acid; b) with 0.5 M formic acid

Electrocatalytic oxidation of NaBH₄ on Pt_{nano}-PEDOT and Au_{nano}-PEDOT films

The metal nanoparticles loaded PEDOT film was tested for borohydride oxidation as discussed below. Fig. S8(A-B) shows the CV pattern of Pt, Au nanoparticles loaded PEDOT for the electro-oxidation of 0.05 M NaBH₄ oxidation in 2M NaOH at a scan rate of 50 mV/s. Two broad oxidation peaks (0.175V, and 0.6V) were observed in the forward scan and one sharp anodic peak at 0.4V was observed in the reverse scan. In Au_{nano}-PEDOT matrix, there is no hydrolysis reaction occurring for BH₄⁻ oxidation due to high hydrogen overpotential on the Au surface. Only electro-oxidation of BH₄⁻ takes place on Au_{nano} loaded PEDOT film. Therefore, two broad peaks are observed corresponding to two electron oxidation in the forward scan and in the reverse scan a sharp peak was seen for 6e⁻ oxidation at 0.4V.

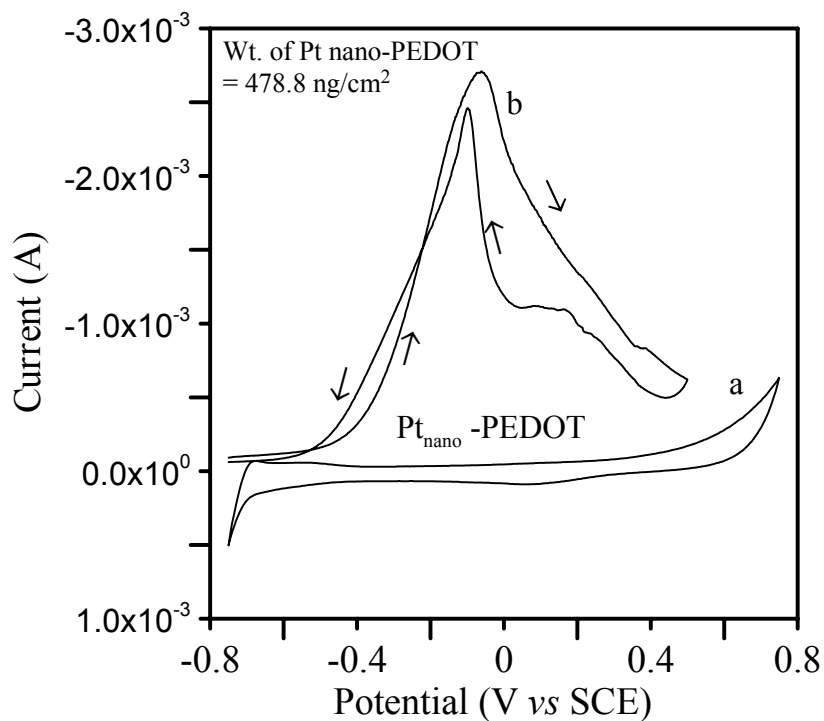


Fig. S8A: Cyclic voltammogram of borohydride oxidation: 2M NaOH (a); 2M NaOH + 0.05 M NaBH₄ on Pt_{nano}-PEDOT (b) at a scan rate of 50mV/s

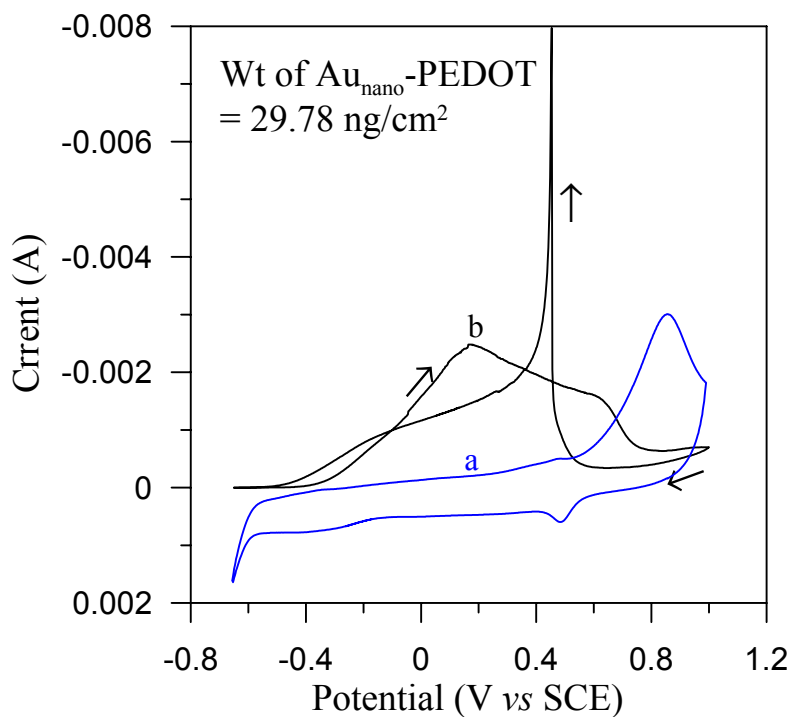


Fig. S8B. Cyclic voltammogram of borohydride oxidation: 2M NaOH (a); NaOH + 0.05 M NaBH₄ on Au_{nano}-PEDOT (b) at a scan rate of 50 mV/s.

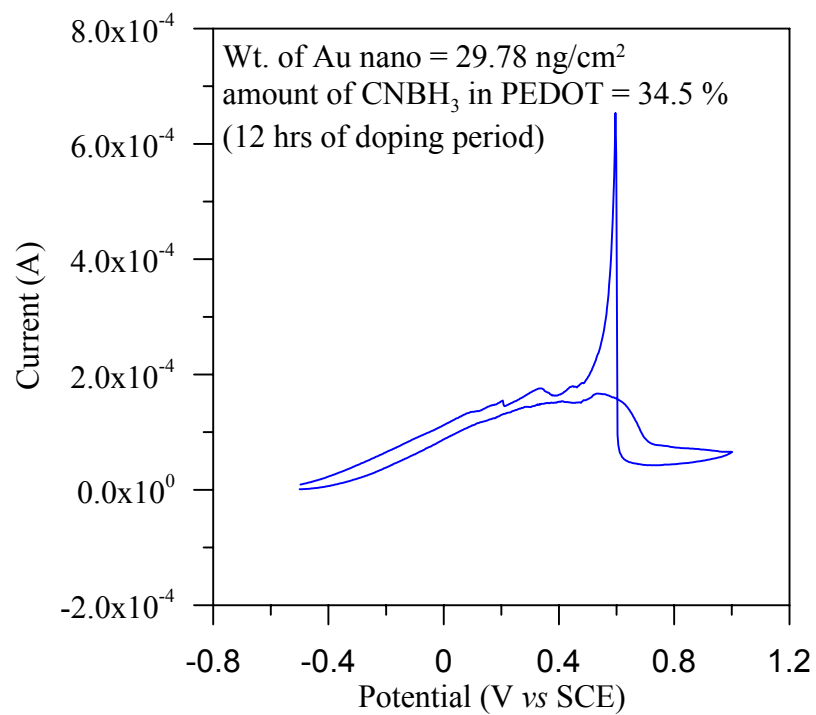


Fig. S9. Cyclic voltammogram for oxidation of CNBH₃ contained in the Au_{nano}/CNBH₃-PEDOT film recorded in 2M NaOH solution.