“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-ClO\(_4\) films were deposited on a clean glassy carbon electrode by potential cycling of GC electrode in acetonitrile solutions of EDOT monomer and Bu\(_4\)NCIO\(_4\) 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 CNBH\(_3^-\) ion doped film. First, the PEDOT film was dipped into 0.1M TBACNBH\(_3^+\) 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 CNBH\(_3^-\) 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 CNBH\(_3^-\) doped PEDOT film. Cyclic voltammograms were recorded for each loading of metal nanocatalyst on PEDOT in 0.5M H\(_2\)SO\(_4\) 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 (C$_4$H$_7$)$_4$N$^+$ 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 C$_\alpha$=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 actetonitrile 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 $C_\alpha=C_\beta$ 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 $C_\alpha=C_\beta$ 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 CNBH$_3^-$ 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.

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Nature of PEDOT film</th>
<th>Conductivity (σ) (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>De-doped PEDOT containing ClO$_4^-$ ions</td>
<td>44.4</td>
</tr>
<tr>
<td>2.</td>
<td>PEDOT$^+$ ClO$_4$ film</td>
<td>251.35</td>
</tr>
<tr>
<td>3.</td>
<td>PEDOT$^+$ (CNBH$_3$) film</td>
<td>201.2</td>
</tr>
</tbody>
</table>

Fig. S4 UV-Visible spectrum for Au nanoparticles entrapped PEDOT film
The SPR band of PEDOT-Au\textsubscript{nano} (534nm) is clearly seen in Fig. S2, but anisotropic (Triangular, pentagon, and hexagon) absorbance bands of Au\textsubscript{nano} (700-900 nm) are merged with polaronic/bipolaronic transition of PEDOT support.

**FT-IR spectroscopy**

![FT-IR Spectra](image)

**Fig. S5: FT-IR Spectra for the solid CNBH\textsubscript{3}-PEDOT (a) and ClO\textsubscript{4}-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 H_2SO_4 vs. MSE. Loading of Pt particles in terms of the hydrogen-upd charge in PEDOT polymer was in the range between 0.223 mC/cm^2 and 0.906 mC/cm^2.

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 H_2SO_4 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.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Doping period of TBACNBH_3 (Time in hrs)</th>
<th>H_{upd} charge of Pt_{nano}-PEDOT (mC/cm^2)</th>
<th>Surface Area of Pt_{nano}-PEDOT (cm^2)</th>
<th>Charge of cathodic reduction peak of Au_{nano}-PEDOT (mC/cm^2)</th>
<th>Surface area of Au_{nano}-PEDOT (cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0.223</td>
<td>1.06</td>
<td>14.41 x 10^{-3}</td>
<td>35.15 x 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0.346</td>
<td>1.65</td>
<td>23.80 x 10^{-3}</td>
<td>58.05 x 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.597</td>
<td>2.84</td>
<td>31.81 x 10^{-3}</td>
<td>77.59 x 10^{-3}</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>0.947</td>
<td>4.51</td>
<td>43.77 x 10^{-3}</td>
<td>106.76 x 10^{-3}</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
<td>0.906</td>
<td>4.32</td>
<td>39.81 x 10^{-3}</td>
<td>97.1 x 10^{-3}</td>
</tr>
</tbody>
</table>

Surface area, \( A_{Pt} = \frac{Q_{H_{upd}} of Pt_{nano}-PEDOT}{0.210 \text{ mC/cm}^2} \)

Surface area, \( A_{Au} = \frac{Q_{cathodic reduction peak of Au_{nano}-PEDOT}}{0.410 \text{ mC/cm}^2} \)
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\textsubscript{nano}-PEDOT film in 0.5 M H\textsubscript{2}SO\textsubscript{4}**

![Cyclic voltammogram](image)

**Fig. S7** Cyclic voltammogram of (Q = 0.947 mC.cm\textsuperscript{-2}) Pt nanoparticles loaded PEDOT film on glassy carbon electrode in 0.5 M H\textsubscript{2}SO\textsubscript{4} at a scan rate of 50mV/s  
   a) without formic acid;  
   b) with 0.5 M formic acid

**Electrocatalytic oxidation of NaBH\textsubscript{4} on Pt\textsubscript{nano}-PEDOT and Au\textsubscript{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 NaBH\textsubscript{4} 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\textsubscript{nano}-PEDOT matrix, there is no hydrolysis reaction occurring for BH\textsubscript{4}\textsuperscript{-} oxidation due to high hydrogen overpotential on the Au surface. Only electro-oxidation of BH\textsubscript{4}\textsuperscript{-} takes place on Au\textsubscript{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\textsuperscript{-} oxidation at 0.4V.
**Fig. S8A.** Cyclic voltammogram of borohydride oxidation: 2M NaOH (a); 2M NaOH + 0.05 M NaBH₄ on Pt<sub>nano</sub>-PEDOT (b) at a scan rate of 50 mV/s.

**Fig. S8B.** Cyclic voltammogram of borohydride oxidation: 2M NaOH (a); NaOH + 0.05 M NaBH₄ on Au<sub>nano</sub>-PEDOT (b) at a scan rate of 50 mV/s.
Fig. S9. Cyclic voltammogram for oxidation of CNBH$_3$ contained in the Au$_{nano}$∪CNBH$_3$-PEDOT film recorded in 2M NaOH solution.

Wt. of Au nano = 29.78 ng/cm$^2$  
amount of CNBH$_3$ in PEDOT = 34.5%  
(12 hrs of doping period)