Mechanochemical Synthesized Porous Organic Polmer Derived Carbon Quantum Dots/Chitosan-graphene Composit Film Electrode for Electrochemiluminescence Determination of Dopamine

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Section 1. Materials and Methods
Section 2. Synthetic Procedures
Section 3. FT-IR Spectra and 13C Solid-state NMR
Section 4. UV-absorption and Fluorescence spectra
Section 4. N2 uptake isotherm and TGA
Section 5. Powder XRD and Roman Spectrum
Section 6. XPS
Section 7 1H NMR of monomer
Section 8. Table information
Section 1. Materials and Methods

$^1$H NMR spectra of prepared monomers were recorded using an Avance Bruker DPX 400 (400 MHz) in the solvent of CDCl$_3$. Solid-state $^1$H-$^{13}$C CP/MAS NMR were collected on Bruker SB Avance III 500 MHz spectrometer. Low temperature N$_2$ adsorption-desorption measurements were conducted via Micromeritics ASAP 2020 surface area and porosimetry analyser at the temperature of 77 K. Pore size distributions curves were obtained from the adsorption isotherms by the non-local density functional theory. Total pore volumes were calculated from the uptake at a relative pressure of 0.995. And the calculated specific surface areas for N$_2$ were based on the BET model over a relative pressure (P/P$_0$) between 0.05 and 0.15. Before test, all porous polymer samples were degassed overnight under high vacuum at the temperature of 150°C to remove the solvent or the water absorbed in the porous skeleton. Thermal gravimetric analysis (TGA) were recorded using NETZSCH STA 449C analyzer from 30 to 800°C at a heating rate of 10°C min$^{-1}$ under the protection of N$_2$. The UV absorption and fluorescence spectra were recorded respectively by TU-1901 UV-spectrophotometer (Beijing, China) and F-320 fluorescence spectrophotometer (Tianjin, China). Electrochemiluminescence measurements and cyclic voltammetry curves were carried out with the MPI-A ECL analyzer (Xi'an Remex Analytical Instrument Ltd. Co., China). FTIR was recorded on KBr pellets measured from the wavelength ranged from 500 to 4500 cm$^{-1}$. Electrochemical impedance spectroscopy was performed with the VersaSTAT3 electrochemical analyzers (USA). The high transmission electron microscope (HR-TEM) was received from Tecnai G2 F20 transmission electron microscope (USA). Three electrodes system: modified glassy carbon electrodes as the working electrodes (GCE, 5 mm), a Pt wire as counter electrode and an Ag/AgCl (saturated with KCl) as reference electrode. Fourier Transform Infrared Spectroscopy (FTIR) was performed in the range of 4000 to 400 cm$^{-1}$ using Spectrum Spotlight 400. Elemental analyses for the C, H, O, and N was obtained by Elementar Vario MICRO elemental analyzer. Powder X-ray diffraction (PXRD) patterns of all the prepared samples were collected using a Rigaku-DMAX 2500 diffractometer at a rate of 5° min$^{-1}$ from 10° to 70°. Scanning electron microscopy (SEM) were gathered from SU8010
scanning electron microscope (Japan). JEOL, Tokyo, Japan at 10.0 kV. And the element mapping was also obtained from the SEM. Transmission electron microscopes (TEM) were performed on FEI model Tecnai 20 microscope and a JEOL model JSM-2100 F. The samples used both in the SEM and TEM were fabricated by drop-casting a dispersive ethanol suspension of target samples onto a copper grid. Raman spectrum was examined on a LabRAM HR at the range from the 0 to 4000 cm⁻¹. X-ray Photoelectron Spectroscopy was conducted on XPS ESCALAB 250Xi analyser.

Section 2. Synthetic Procedures

Unless specially noted, all chemicals, i. e., 1,1,2,2-tetraphenylethene (TPE, Alfa Aesar, 99%) Ferrous trichloride tetrahydrate(FeCl₃), 1,3,5-1,3,5-Benzenetricarboxylic acid (Energy Chemical, 99 %), methanol were purchased from the commercial supplier and directly used without further purification. Chitosan (CS, 95% deacetylation) and graphene (98% purity) was purchased from Aladdin Industrial Corporation (Shanghai, China). Dopamine was obtained from J&K Chemical Co., Ltd. Ammonium persulfate ((NH₄)₂S₂O₈), potassium ferricyanide (K₃[Fe(CN)₆]), potassium ferrocyanide (K₄[Fe(CN)₆]), potassium chloride (KCl), dipotassium phosphate (K₂HPO₄•3H₂O) and monopotassium phosphate (KH₂PO₄) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Double distilled water was used throughout the whole experiment.

Synthesis of trimethyl-1,3,5-benzenetricarboxylate

\[
\begin{align*}
\text{HOOC} & \quad \rightarrow \quad \text{MeOH} \\
\text{HOOC} & \quad \rightarrow \quad \text{98%H}_2\text{SO}_4 \\
\end{align*}
\]

1,3,5-Benzenetricarboxylic acid (8 g, 38 mmol) was suspended in a solution of methanol (100 mL) and sulfuric acid (2.5 mL, 98%). The suspension was refluxed for 24 hours and subsequently cooled to room temperature. A saturated solution of NaHCO₃ (100 mL, in water) was added slowly and the mixture was filtered to give trimethyl-1,3,5- benzenetricarboxylate as a colorless
solid. Yield: 98%, \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta=8.86\) ppm (s, 3H), 3.98 ppm (s, 9H). \(^{13}\)C-NMR (CDCl\(_3\), 400 MHz): \(\delta=165.43, 134.61, 131.22, 52.64\).

**Synthesis of 1,3,5-tris(hydroxymethyl)benzene**

![Chemical structure of 1,3,5-tris(hydroxymethyl)benzene](image)

Under nitrogen atmosphere, a solution of trimethyl-1,3,5-benzenetricarboxylate (8.2 g, 33 mmol) in dry THF (140 mL) was added dropwise through a pressure-equalized addition funnel to LiAlH\(_4\) (4.00 g, 107 mmol) in dry THF (45 mL) at 0°C. After complete addition, the reaction mixture was refluxed for 24 hours and then cooled to room temperature. The reaction was quenched by slow addition of water. The reaction mixture was filtered and dried in a vacuum oven for 24h at 120°C to give 1,3,5-tris(hydroxymethyl)benzene as a pale yellow solid. Yield: 75%. \(^1\)H-NMR (CD\(_3\)OD, 400 MHz): \(\delta=7.25\) ppm (s, 3H), 4.95 ppm (s, 3H), 4.60 ppm(s, 6H). \(^{13}\)C-NMR (CD\(_3\)OD, 400 MHz): \(\delta=141.61, 124.09, 63.74\).

**Synthesis of 1,3,5-Tri(bromomethyl)benzene**

![Chemical structure of 1,3,5-Tri(bromomethyl)benzene](image)

Lithium aluminum hydride (1.10 g, 29 mmol) was added to 80 mL of dry THF. Then, 1.50 g (5.81 mmol) of 1,3,5-tris(hydroxymethyl)benzene in 70 mL of dry THF was added dropwise at room temperature under vigorous stirring and an atmosphere of N\(_2\). After the dropwise addition was completed, the mixture was heated to reflux for 24h. The excess of reducing agent was destroyed by slow addition of water, and the solvent was evaporated. Then, 60 mL of a 48% HBr solution and 75 mL of toluene were added and heated to reflux for 24 h. The organic layer was separated, and the aqueous portion was extracted several
times with dichloromethane. The organic layers were combined and removed under reduced pressure. The crude material was purified through a short column of silica with petroleum ether. The solvents were evaporated under high vacuum to afford 1.65 g (4.62 mmol, 87% yield) 1,3,5-Tri(bromomethyl)benzene as a white solid. \(^1\)H NMR(CDCl\(_3\), 400 HMz): \(\delta = 7.36\) (s, 3H), 4.46 (s, 6H).

**Synthesis of TPE-HCP**

TPE-HCP was synthesised through a mechanochemical Friedel-Crafts alkylation reaction in a solvent free conditions. In brief, 1,3,5-triformylbenzene (TBM, 713.8 mg, 1.5 mmol), 1,1,2,2-tetraphenylethene (TPE, 498.7 mg, 2 mmol) and anhydrous iron (III) chloride (2.92 g, 18 mmol) were added to a 50 mL zirconium oxide milling vessel. Consequently, the vessel was milled at 500 rpm for 35 minutes. After, the resulting polymers were washed with dilute hydrochloric acid (HCl) and methanol to remove the catalysts adequately. Then the product was purified through Soxhlet extractor in methanol for 24 h in order to remove all the remaining catalyst and the unreacted monomer. Then, the obtained solid was dried at a vacuum oven at 80°C for 12 hours obtaining the TPE-HCP.

**Preparation of TB-HCP-800**

The polymer sample (TPE-HCP) was transferred into a tube furnace and heated to 800°C by 5°C/min under Ar. And the system was kept at 800°C for 2h, obtaining the final product TPE-800.

**Preparation of TPE-800 derived CQDs**

The carbon quantum dots was synthesized according to the previous reported literature. In short, to a 500 mL round bottom flask containing 100 mL 6 M HNO\(_3\), TPE-800 was added, then the mixture was refluxed for 24 hours at 120°C. In the meanwhile, the mixture solution turned to brown. Then the pH of the suspension was adjusted to close to the neutral (pH=7) by 6 M NaOH. The crude product was separated by centrifugation at 10000 rpm for half an hour. Then, the supernatant was dialyzed for 48 hours with a 1000D dialysis bag. Ultimately, a condensed carbon quantum dots solution in light yellow colour was obtained. The CQDs solution was stored in the dark at 4°C .
**Fabrication of modified electrode**

The glassy carbon electrode was initially polished by Al₂O₃ (0.05 µm) and washed thoroughly with distilled water. Then the electrode was dried with pure N₂. In a ultrasonic bath, the concentrated carbon quantum dots solution was dispersed in the same volume of chitosan-graphene collosol for 60 min. And the carbon quantum dots doped chitosan-graphene composite sol was obtained. Subsequently composite sol (10 µL) was dropped on the surface of electrode and dried at ambient temperature. The electrode was stored in a refrigerator.

**Section 3. FT-IR Spectra and ¹³C Solid-state NMR**

![FT-IR Spectra and solid state ¹³C NMR](image)

**Figure S1.** Infrared spectra and solid state ¹³C NMR of as-synthesized materials. a) FTIR of TPE-HCP; b) FTIR of TPE-HCP derived porous carbon TPE-800; c) FTIR of CQDs; d) Solid state ¹³C NMR of TPE-HCP.

**Section 4. UV-absorption and Fluorescence spectra**

![UV-absorption and Fluorescence spectra](image)
**Figure S2.** Property characterization of as-synthesized carbon quantum dots: a) UV-absorption curve of synthesized carbon quantum dots; b) Fluorescence spectra of prepared carbon quantum dots.

**Section 4. N₂ uptake isotherm and TGA**

![Figure S3.](image)

**Figure S3.** Pore feature of prepared polymer and corresponding porous carbon. a) N₂ sorption isotherms of TPE-HCP and TPE-800 at 77 K; b) Pore width distribution curve of TPE-HCP and TPE-800; c) TG of TPE-HCP.

**Section 5. Powder XRD and Roman Spectrum**

![Figure S4.](image)

**Figure S4.** a) Powder XRD and of prepared polymer and corresponding porous carbon; b) Roman spectrum of TPE-800 and CQDs.

**Section 6. XPS**

![Figure S5.](image)

**Figure S5.** XPS of TPE-800. a) XPS of survey spectrum of TPE-800; b) C1s spectrum of TPE-800; c) High-resolution XPS of O 1s for TPE-800.
Section 7 $^1$H NMR of monomer

**Figure S6.** $^1$H NMR of trimethyl-1,3,5-benzenetricarboxylate

**Figure S7.** $^1$H NMR of 1,3,5-tris(hydroxymethyl)benzene
Section 8. Table information

Table S1. Porosity Parameters of prepared polymer and derived porous carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area: (m² g⁻¹)</th>
<th>Langmuir Surface Area (m² g⁻¹)</th>
<th>V total (cm³ g⁻¹)</th>
<th>V micro (cm³ g⁻¹)</th>
<th>Pore width distribution (nm)</th>
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</thead>
<tbody>
<tr>
<td>TPE-HCP</td>
<td>158.4</td>
<td>766.0</td>
<td>0.353</td>
<td>0.295</td>
<td>1.89/3.99/5.13</td>
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<tr>
<td>TPE-800</td>
<td>389</td>
<td>748.8</td>
<td>0.358</td>
<td>0.276</td>
<td>1.59/2.68/4.03</td>
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</table>

Tab S2. Performance comparison of representative literatures for the DA detection in various methods.

<table>
<thead>
<tr>
<th>Analytical methods</th>
<th>Detection limit</th>
<th>Linear range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPLC</td>
<td>0.08 μg/L</td>
<td>2 - 10000 μg/L</td>
<td>S1</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>5.5 nM</td>
<td>10 nM - 5.0 μM</td>
<td>S2</td>
</tr>
<tr>
<td>Colorimetry</td>
<td>0.031 μM</td>
<td>0.1-7.5 μM</td>
<td>S3</td>
</tr>
<tr>
<td>Electrochemistry</td>
<td>0.02 μM</td>
<td>0.1- 100 μM</td>
<td>S4</td>
</tr>
<tr>
<td>Electrochemistry</td>
<td>0.33 μM</td>
<td>1-150 μM</td>
<td>S5</td>
</tr>
<tr>
<td>ECL</td>
<td>26 pM</td>
<td>50 pM - 10 nM</td>
<td>S6</td>
</tr>
<tr>
<td>ECL</td>
<td>355 nM</td>
<td>0.5 - 100 μM</td>
<td>S7</td>
</tr>
<tr>
<td>ECL</td>
<td>0.028 μM</td>
<td>0.06 - 1.6 μM</td>
<td>In this work</td>
</tr>
</tbody>
</table>

HPLC: high performance liquid chromatography. ECL: Electrochemiluminescence.
Section 9. Supporting References


