Supporting Information

Fabrication of Ionic Liquid-Functionalized Polypyrrole Nanotubes Decorated with Platinum Nanoparticles and Their Electrocatalytic Oxidation of Methanol

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1. Chemicals

Pyrrole, ferric chloride (FeCl₃), methyl orange (MO), K₂PtCl₄, 1-vinylimidazole, sodium borohydride (NaBH₄), methanol, ethanol, methylimidazole, 2,2'-azobisisobutyronitrile(AIBN), bromoethane, 1,4-dibromobutane, dimethylformamide (DMF), polyvinylpyrrolidone (PVP, K-30) and H₂SO₄ were purchased from Sinogharm Chemical Reagent Co., Ltd. Pyrrole monomer was distilled under reduced pressure before use. 1-Vinylimidazole was made inhibitor-free by passing the liquid through a column filled with base Al₂O₃. Other chemicals were of analytical grade and used as received without further purification. Deionized water was used for all experiments.

2. Synthesis

2.1 Synthesis of PPy Nanotubes (PPyNTs)

PPyNTs was synthesized using a self-degraded template method as reported in the literature.¹ In a typical procedure, 0.243 g (1.5 mmol) of FeCl₃ was dissolved in 30 mL of 5 mM MO solution (0.15 mmol), and a flocculent precipitate appeared immediately. Pyrrole monomer (105 μ L, 1.5 mmol) was then added and the mixture was stirred at room temperature for 24 h. The formed PPy precipitate was washed with deionized water/ethanol several times until the filtrate was colourless and neutral. The produced PPyNTs was finally dried under vacuum at 60 °C for 24 h.

2.2 Synthesis of PPyNTs-(CH₂)₄Br

A mixture of PPyNTs (0.0300g), KOH powder (0.0500g), and 1,4-dibromobutane (0.1437g) was dispersed in 25.0 mL DMF and sonicated for 5 min and then held at 60 °C for 24 h under vigorous agitation. The product was filtrated and washed with deionized water and ethanol to thoroughly remove physically absorbed KOH and unreacted 1,4-dibromobutane from the surface of PPyNTs. The final products, denoted as PPyNTs-(CH₂)₄Br, were then dried in a vacuum oven at 60 °C overnight to remove the residual solvent.

2.3 Synthesis of ILs/PPyNTs

A mixture containing PPyNTs-(CH₂)₄Br (0.0250 g) and 1-methylimidazole (0.2000 g) in 25.0 mL DMF was sonicated for 5 min and then held at 60 °C for 24 h under vigorous agitation. The product was concentrated and washed with ethanol several times to thoroughly remove physically absorbed 1-methylimidazole. Then the black precipitate denoted as ILs/PPyNTs was dried in a vacuum oven at 60 °C overnight to remove the residual solvent.

2.4 Synthesis of Pt/ILs/PPyNTs Hybrids

A mixture containing 1 mg ILs/PPyNTs and 25 mg PVP was ultrasonicated in 18 mL water until the ILs/PPyNTs were well dispersed. A K₂PtCl₄ aqueous solution (1.0 mL, 30 mM) was then added and the mixture was stirred at room temperature for 3 h. Then 4.5 mL NaBH₄ (0.04 M) solution was added into the reaction mixture and further stirred at room temperature for 12 h until the Pt precursor was reduced completely. The prepared Pt/ILs/PPyNTs hybrids were centrifuged and washed thoroughly with deionized water/ethanol and then dried in vacuum.

2.5 Synthesis of Pt/PILs/PPyNTs Hybrids

PPyNTs surface-coated with poly(1-vinyl-3-ethyl imidazolium bromide) were synthesized via free radical polymerization of the IL monomer 1-vinyl-3-ethyl imidazolium bromide ([VEIM]Br) to form an ionic-liquid polymer (PIL) on the PPyNTs surface.² A mixture containing 50.0 mg PPyNTs, 200 mg

[VEIM]Br and 2,2'-azobisisobutyronitrile (AIBN, 10 mg) in 20.0 mL methanol was stirred at 80 °C for 12 h under nitrogen atmosphere. The mixture was washed with ethanol several times to thoroughly remove physically absorbed polymer and unreacted [VEIM]Br monomer from the surface of PPyNTs. The produced PILs/PPyNTs were dried in vacuum oven at 60 °C to remove the residual solvent.

Pt/PILs/PPyNTs hybrids were synthesized by following the procedure used for the preparation of Pt/ILs/PPyNTs hybrids as described above. The produced Pt/PILs/PPyNTs hybrids were centrifuged and washed with deionized water/ethanol several times and dried in vacuum.

2.6 Synthesis of Pt Nanoparticles

A mixture containing K₂PtCl₄ (1.0 mL, 30 mM), 25 mg PVP and 18 mL water was stirred for 5 min at room temperature. Then 4.5 mL NaBH₄ (0.04 M) was added into the reaction and further stirred at room temperature for 12 h until the Pt precursor was reduced completely. The solution was centrifuged and washed several times with ethanol and deionized water. The produced Pt nanoparticles were dissolved in 2.0 mL water.

3. Characterization

Transmission infrared spectra were recorded on a Nicolet 5200 Fourier transform infrared (FTIR) in the transmission mode. Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectroscopy were taken on a FEI-quanta 200F scanning electron microscope with acceleration voltage of 20 kV. A TecnaiG 220 transmission electron microscopy (TEM) was used to determine the microstructure of samples. The samples were prepared by placing a drop of diluted latex onto a piece of copper EM grid and dried at room temperature. X-ray Photoelectron Spectroscopy (XPS) were obtained by using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg Ka X-ray (hv = 1283.3eV). The composition of the samples was determined by inductively coupled plasma-mass spectroscopy (ICP-MS, Varian 710-ES). The powder XRD pattern was recorded on a Rigaku D/max 2500 X-ray diffractometer with parallel Cu Ka radiation (λ =1.54178 Å). The samples were dried under vacuum at 50 °C and then be placed on a glass slide. The electrochemical impedance measurements were carried out with an IM6e potentiostat (Zahner Elektrik Company, Germany). The interfacial charge-transfer resistance of samples was determined by using electrochemical impedance spectroscopy (EIS) in the frequency range between 0.1 Hz and 1 MHz with a perturbation signal of 5 mV. CV experiments were performed using a conventional three-electrode cell.

Electrocatalytic measurements were performed on a CHI842B (Chenhua Instrument Company of Shanghai, China) with conventional three-electrode glass cell. A modified glassy carbon (GC) electrode with a diameter of 3 mm and platinum foil were used as working and counter electrode, respectively. A saturated calomel electrode (SCE) was used as the reference electrode. The GC electrode was prepared as follows: prior to the surface coating, the GC electrode was polished carefully with 0.5 μ m and then with 0.05 μ m alumina powder, and followed by sonication in 1:1 nitric acid/water (v/v), acetone and in doubly distilled water successively. The surface of GC electrodes was allowed to dry under nitrogen atmosphere.

The Pt/ILs/PPyNTs, Pt/PILs/PPyNTs hybrids or Pt NPs were ultrasonically dispersed in water to form a homogeneous dispersion (1 mg/mL). The surface of GC electrode was coated with 5 μ L of catalyst solution and then dried in air. The surface of modified GC electrode was further coated with 5 μ L of Nafion ethanol solution (0.2 wt %) and then dried in air before the electrochemical experiments. The loading Pt amount was 19.81, 44.59, and 410.47 μ g/cm⁻² for Pt/ILs/PPyNTs, Pt/PILs/PPyNTs hybrids and pure Pt NPs, respectively. For the determination of interfacial charge-transfer resistance using EIS, 5 μ L of PPyNTs, PPyNTs-(CH₂)₄Br, and ILs/PPyNTs solution (1 mg/mL) was coated on the surface of GC electrodes and dried in air before the measurements. All the experiments were carried out at ambient temperature and the potentials in this work were in respect to SCE.

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4. FTIR spectra



Figure S1. FTIR spectra of PPyNTs (red), PPyNTs-(CH₂)₄Br (purple) and ILs/PPyNTs (green).

5. EIS Analysis



Figure S2. EIS plots of PPyNTs, PPyNTs-(CH₂)₄Br and ILs/PPyNTs in 0.1 M KCl solution containing 2.5 mM K₃Fe(CN)₆ and 2.5 mM K₄Fe(CN)₆.

The change of interfacial charge-transfer resistance (Rct) resulting from changes of electrocatalytic activity can be monitored by EIS. Figure S2 shows the Nyquist plots of PPyNTs, PPyNTs-(CH₂)₄Br and ILs/PPyNTs modified GC electrodes in a frequency range of 0.1 Hz to 100 kHz and AC amplitude of 0.005 V. The spectra are typically presented in the form of a Nyquist plot, where Z is the real and -Z' is the imaginary part of impedance. An ideal Nyquist plot reveals the semicircle (with the diameter, corresponding to the charge transfer resistance, *R*ct, produced by redox reactions at the interface with the

electrode) followed by a diagonal straight line (corresponding to the impedance of the current due to diffusion from the solution to the interface).³ As seen from Figure S3, the diameter of the impedance arc (DIA) decreases in the order of PPyNTs-(CH₂)₄Br, ILs/PPyNTs and PPyNTs, indicating that Rct is much smaller on ILs/PPyNTs than PPyNTs-(CH₂)₄Br.

6. XRD Patterns of Pt/ILs/PPyNTs Hybrids



Figure S3. XRD patterns of ILs/Pt/PPyNTs hybrids

XRD was further used to determine the metal size of Pt NPs on the surface of ILs/PPyNTs. Figure S3 shows the XRD patterns of Pt NPs deposited on ILs/PPyNTs. The average size of Pt NPs was calculated based on the half-peak width of Pt (220), using Scherrer's equation: $d = 0.9 \lambda/\beta \cos\theta_{max}$. Where d is the average size of the Pt NPs, λ is the X-ray wavelength (Cu K $\alpha \lambda = 1.54178$ Å), θ_{max} is the diffraction angle at the peak position and β is the full width at half-maximum in radians.

The average size of Pt NPs for Pt/ILs/PPyNTs is calculated to be 2.9 nm. The reason for choosing the Pt (220) peak but not others is that the Pt (111) peak is interfered with by the neighbouring Pt (200) due to its closeness.⁴



Figure S4. XPS patterns (A, B) of ILs/PPyNTs. A: C1s; B: N1s; XPS pattern (C) of PPyNTs/IL/Pt hybrid nanostructure, and EDX pattern (D) of Pt/ILs/PPyNTs hybrids.

8. TEM Images



Figure S5. TEM images of Pt/PPyNTs. Reaction conditions: 1 mg PPyNTs, 1.5 mL K₂PtCl₄ (30 mM), 25 mg PVP, 6.75 mL NaBH₄ (40 mM) in 18 mL water.

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Figure S6. TEM images of Pt/PILs/PPyNTs hybrid nanostructure. Reaction conditions: 1 mg PILs functionalized PPyNTs, 1.0 mL K₂PtCl₄ (30 mM), 25 mg PVP, 4.5 mL NaBH₄ (40 mM) and 18 mL water.



Figure S7. TEM images of Pt/ILs/PPyNTs hybrids. Reaction conditions: 1 mg ILs/PPyNTs, 0.5 mL K₂PtCl₄ (30 mM), 25 mg PVP, 2.3 mL NaBH₄ (40 mM) in 18 mL water.



Figure S8 TEM images of Pt/ILs/PPyNTs hybrids. Reaction conditions: 1 mg ILs/PPyNTs, 0.7 mL K₂PtCl₄ (30 mM), 25mg PVP, 3.2 mL NaBH₄ (40 mM) in 18 mL water.



Figure S9. TEM images of Pt/ILs/PPyNTs hybrids. Reaction conditions: 1 mg ILs/PPyNTs, 1.0 mL K₂PtCl₄ (30 mM), 25mg PVP, 4.5 mL NaBH₄ (40 mM) in 18 mL water.



Figure S10. TEM images of synthesized Pt NPs. Reaction conditions: 1.0 mL K₂PtCl₄ (30 mM), 4.5 mL NaBH₄ (40 mM), 25 mg PVP and 18 mL water.

9. ECSA Analysis



Figure S11. CV of Pt/ILs/PPyNTs, Pt/PILs/PPyNTs hybrids and pure Pt NPs modified electrodes in N₂-saturated 0.5M H₂SO₄ at a scan rate of 50 mV.s⁻¹.

By using hydrogen adsorption-desorption method in conjunction with cyclic voltammetry, the ECSA of Pt/ILs/PPyNTs, Pt/PILs/PPyNTs hybrids, and Pt NPs were measured. Figure S9 shows the cyclic voltammograms of the catalysts in nitrogen-saturated 0.5 M H_2SO_4 solution at a scan rate of 50 mV s⁻¹. The ECSA value can be measured by integrating Coulombic charge for hydrogen adsorption-desorption from the cyclic voltammograms shown in Figure S9 according to the following equation:⁵

$$ECSA = \frac{Q_H}{0.21 \times L_{P_t}}$$

where Q_H (mC.cm⁻²) represents the mean value between the amounts of charge exchanged during the electro-adsorption and desorption of H₂ on Pt sites, L_{Pt} is the Pt loading (mg/cm²) on the GC electrode and 0.21 (mC.cm⁻²) represents the charge required to oxidize a monolayer of H₂ on Pt. The loading mass of Pt nanoparticles on the GC of Pt/ILs/PPyNTs, Pt/PILs/PPyNTs and pure Pt NPs were determined by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). From Figure S6, the ECSA values of three catalysts (Pt/ILs/PPyNTs, Pt/PILs/PPyNTs hybrids and Pt NPs) were calculated and summarized in Table S1.

catalyst	$L_{Pt}(\mu g.cm^{-2})$	$Q_{\rm H}({\rm mC.cm}^{-2})$	$ECSA[m^2/gPt]$
Pt/ILs/PPyNTs	19.81	2.87	68.88
Pt/PILs/PPyNTs	44.59	5.39	57.56
Pt NPs	410.47	3.70	4.29

Table S1. Hydrogen adsorption and desorption charges and the electrochemical surface area (ECSA) of different catalysts

Reference:

- [1] X. M. Yang, Z. X. Zhu, T. Y. Dai, Y. Lu, Macromol. Rapid Commun. 2005, 26, 1736.
- [2] C. H. Xiao, X. C. Chu, B. H. Wu, H. L. Pang, X. H. Zhang, J. H. Chen, Talanta 2010, 80, 1719.
- [3] A. Bogomolova, E. Komarova, K. Reber, T. Gerasimov, O. Yavuz, S. Bhatt, M. Aldissi, Anal. Chem. 2009, 81, 3944.
- [4] S. Y. Wang, S. P. Jiang, X. Wang, *Nanotechnology* 2008, 19, 1.
- [5] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, J. Power Sources 2002, 105, 13.