Immobilization of ionic liquid with polyelectrolyte as carrier

Yanfei Shen [1], Yuanjian Zhang [1], Qixian Zhang [1], Li Niu [1, 2 *], Tianyan You [1 *] and Ari Ivaska [2]

[1] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, and Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun 130022, P. R. China*

[2] *Laboratory of Analytical Chemistry, Process Chemistry Centre, Åbo Akademi University, Åbo-Turku 20500, Finland*

[*] Corresponding author.
E-mail: lniu@ciac.jl.cn and youty@ciac.jl.cn
Fax: +86-431-5262425

ESI

Experimental Section

Materials

Polyethylenimine (*Mw* = 25000, PEI), poly (styrenr-4-sulfonate) (*Mw* = 70000, PSS) and $NaPF_6$ (98%) were obtained from Aldrich and used as received. β-Nicotinamide adenine dinucleotide (NADH) was obtained from Biobasic Inc. Nafion® 117 solution (~ 5% in a mixture of aliphatic alcohols and water) was from Fluka. Dialysis membranes (MWCO 10000) were from Sino-American Biotechnology Co. Other reagents were of analytical grades and used as received. All aqueous solutions were prepared with the double distilled water with a Millipore-Q system (18.2 MΩ).

Instruments

Fourier transform infrared spectroscopy (FTIR) was recorded on a Bruker Vertex 70 spectrometer (4 cm^{-1}). UV-vis-NIR spectrum of PFIL was recorded on a CARY 500 UV-vis-NIR spectrometer. ^1H NMR spectra were obtained on a Varian Unity-400 (400 MHz) NMR spectrometer with tetramethylsilane (TMS) as an internal standard in deuteriodimethyl sulfoxide (DMSO-d6). Electrospray ionization mass spectrum (ESI-MS) was obtained on a Finnigon LCQ mass spectrometer with electrospray voltage at 5.0 kV. All electrochemical measurements were carried out in a conventional three-electrode electrochemical cell with CHI 660 Electrochemical workstation (CHI Inc., USA). The working electrode was a glass carbon electrode (GCE, d = 3 mm), the auxiliary electrode was a platinum wire, and an Ag/AgCl

(saturated KCl) was used as the reference electrode. Contact angles were determined using the sessile drop technique as reported early.[1] Two parallel samples were prepared and six separate locations of each sample were measured to ensure a representative value of the contact angle.

Preparation of carboxyl-functionalized IL (IL-COOH) and PFIL

The preparation of IL-COOH and PFIL was illustrated in Scheme 1. Briefly, IL-COOH were synthesized by reflux of methylimidazole (3.3 g, 0.04 mol) and chloroacetic acid (5.7 g, 0.06 mol) in 20 ml toluene for about 24 h. [2] The resulting product was purified by recrystallization and was characterized by NMR and ESI-MS. ESI-MS (H_2O): positive ion, 141; ^1H NMR (DMSO): δ = 13.83 (s, 1H), 9.15 (s, 1H), 7.73 (s, 1H), 7.72 (s, 1H), 5.16 (s, 2H), 3.91 (s, 3H). PFIL were obtained as following procedure: a mixture of IL-COOH (0.18 g, 0.01 mol) and thionyl chloride (26.0 g, 0.22 mol) was refluxed for about 18 h. The resulting acyl chloride intermediate was obtained by removing excess thionyl chloride. PEI □0.252 g□ dissolved in *N*, *N*-dimethylformamide (DMF) was added into the excessive acyl chloride intermediate, stirred in ice water for 30 min, then stirred at 40 °C for 48 h. The product was purified in a dialysis membrane with double distilled water.

Preparation of PFIL-Nafion Modified Glass Carbon Electrode

PFIL-Nafion modified GCE was prepared by casting 2 μl aliquot of 1 mg/ml PFIL-Nafion solution (0.5% Nafion) onto the GCE. After the solvent evaporated

completely at room temperature, the PFIL-Nafion modified GCE was prepared. The Nafion-modified GCE used in the control experiment was prepared with 2 μl 0.5% Nafion in the same procedure.

Preparation of of PEI/PSS/PFIL multilayer

PEI/PSS/PFIL multilayer was prepared by alternately immersing the hydrophilic indium tin oxide (ITO)[3] in 3mg/mL solution of PEI, PSS and PFIL for 15 min. After each polyelectrolyte assembly, the ITO substrate was dipped into double distilled water three times for 1 min each time and blown dry with a nitrogen flow.

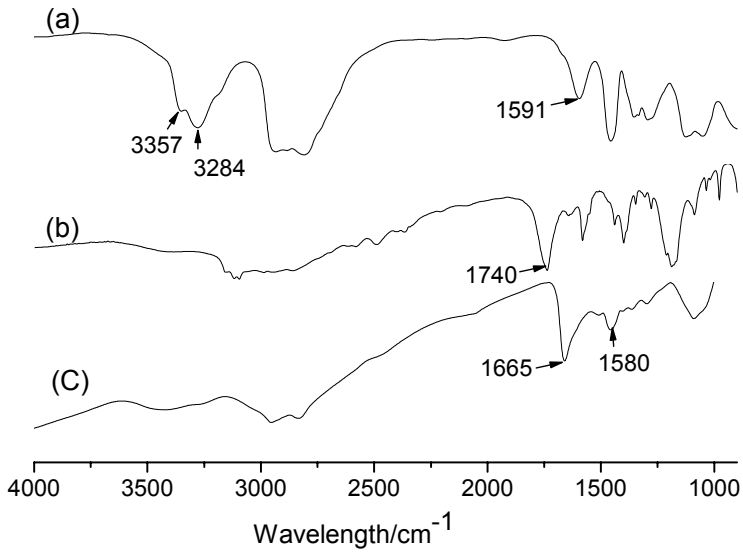

Fig. S1 FTIR spectra of PEI (a), IL-COOH (b) and PFIL (c). The bending vibration of amino groups (-NH_2) at 1591 cm^{-1} and C=O stretching mode of IL-COOH at 1740 cm^{-1} disappeared from curve a and b, respectively. Moreover, two characteristic peaks at 1665cm^{-1} and 1580 cm^{-1} assigned to the vibration of amide I and amide II in the spectrum of PFIL (curve *c*) indicated that the amino groups were entirely reacted with IL-COOH by amidation reaction.

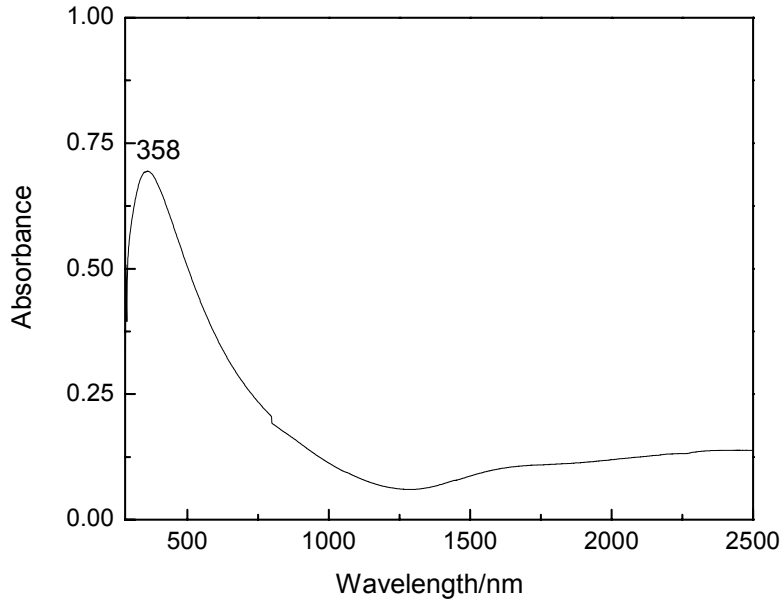

Fig. S2 UV-vis-NIR of PFIL electrodeposited onto ITO. The film of PFIL on ITO was obtained by electrophoresis at -2 V for 600 s. A strong adsorption band at 358 nm was attributed to the adsorption of imidazolium rings.[4] The result further verified the successful synthesis of PFIL, which was in agreement with FTIR data.

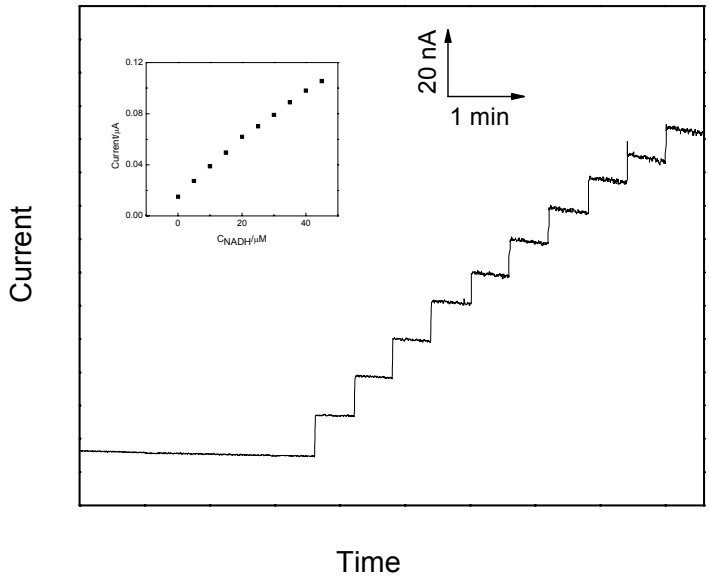

Fig. S3 Chronoamperometric curve of the steady state response at PFIL-Nafion modified glass carbon electrode in phosphate buffer solution (0.05 M, pH = 7.4) on increasing the concertration of NADH in 5 μM steps. Working potential: +0.75 V. Insert: the calibration curve for NADH at PFIL-Nafion modified GCE.

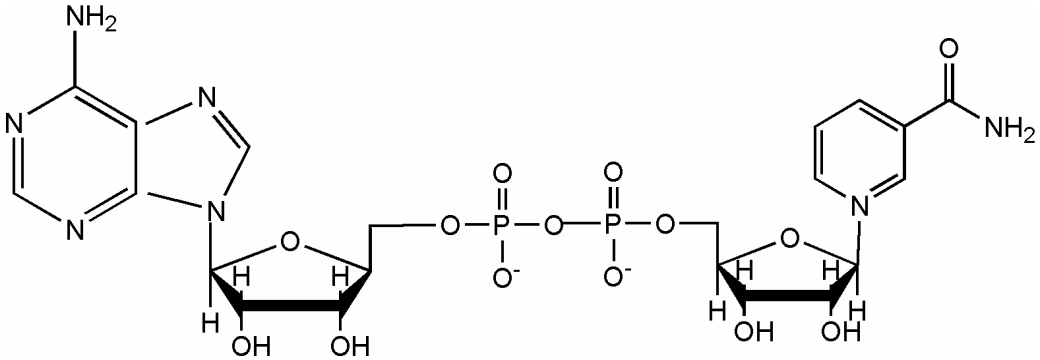

Fig. S4 Structure of NADH.

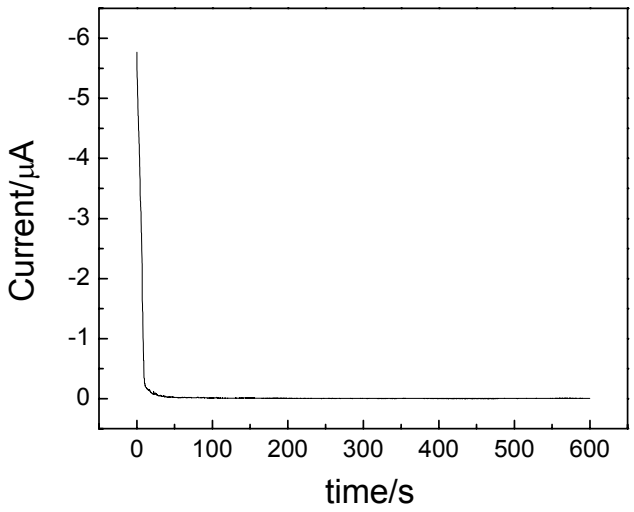

Fig. S5 Chronoamperometric response of PEI/PSS/PFIL multilayer on ITO in 10 mM $NaPF_6$ or NaCl. The potential was held at 0.3V for 600 s.

References

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