

Immobilization of ionic liquid with polyelectrolyte as carrier†

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An all-purpose approach to immobilize ionic liquids onto solid supports is proposed by chemical grafting on a polyelectrolyte carrier.

Due to their unique chemical and physical properties and the facile tunability of their physicochemical properties,^{1,2} there is intense interest in ionic liquids (ILs) across disciplines. On the basis of economic criteria, the ease of separation and recyclable utilization,^{3,4} the immobilization of ILs on solid supports is highly desirable. Moreau and Mehnert have proposed the concept of supported ILs catalysis and designed silica-supported ILs.⁴ Moreover, the immobilization of ILs would bring new applications.⁵ The immobilization process aims to transfer the desired properties of ILs to the solid supports and it was reported that ILs can be bound to a surface either by covalent bonds or noncovalent bonds between the ILs and the surface.⁶

It was noted that polyelectrolytes could be easily immobilized onto many substrates through various methods such as electrophoresis,⁷ layer-by-layer (LbL) assembly⁸ and casting,⁹ etc. Therefore, it would be helpful for us to immobilize ILs in a facile manner on general substrates with the aid of a polyelectrolyte as carrier.

In this communication, a polyelectrolyte-functionalized IL (PFIL) was prepared by covalent attachment of an IL onto a polyelectrolyte. Our preliminary results indicated that the immobilized PFIL exhibited direct electrocatalytic activity towards the oxidation of β -nicotinamide adenine dinucleotide (NADH). In addition, *via* LbL assembly of a PFIL, an electrochemically controlled tunable surface was also constructed. Such PFIL design provides more general approaches to immobilize ILs on solid supports, and this would be very significant for chemical industrial processes.

In order to anchor an IL onto the polyelectrolyte, a carboxyl terminated ionic liquid (IL-COOH) was synthesized, which was characterized by NMR and ESI-MS (see ESI). Then IL-COOH was grafted covalently onto a polyelectrolyte with amine terminal groups, polyethylenimine (PEI), *via* an amidation reaction (Scheme 1). The amine groups on the PEI chains were reacted completely with IL-COOH, which was verified by FTIR (Fig. S1) and UV-vis-NIR (Fig. S2) measurements.

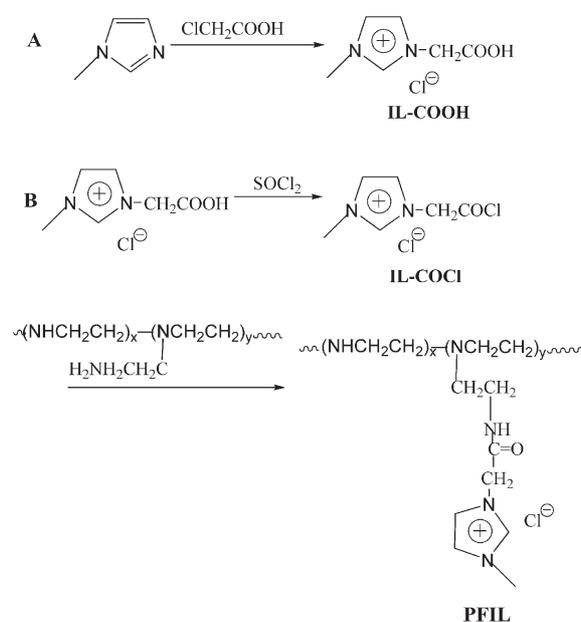
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To date, difficulties in effective immobilization of generic ILs on the electrode substrate have greatly hindered research on the electrocatalysis of ILs. However, in this development of a PFIL, the IL could be easily immobilized simply by casting the PFIL directly on the substrate (see ESI). The electrocatalytic activity of IL toward the oxidation of NADH is reported for the first time.

Fig. 1 compares the voltammetric responses for 0.5 mM NADH at PFIL–Nafion (curve *a*) and Nafion (curve *b*) modified glass carbon electrode (GCE) in phosphate buffer solution (0.05 M, pH = 7.4), along with the PFIL–Nafion modified GCE in phosphate buffer solution without the addition of NADH (curve *c*). It was noted that the same charging currents in the three curves indicated a similar active electrode area on both PFIL–Nafion and Nafion modified GCE. As shown in Fig. 1c, there was no oxidation current obtained on the PFIL–Nafion GCE in phosphate buffer solution. Upon addition of NADH to this phosphate buffer solution, an obvious growth in oxidation current was observed (curve *a*), indicating that the oxidation currents originated from the oxidation of NADH in the solution. However, such an oxidation current cannot be found at the Nafion-modified GCE in the same phosphate buffer solution containing 0.5 mM NADH (curve *b*). From the distinctive difference of oxidation current between curve *a* and *b* in Fig. 1, it was concluded that the catalysis towards NADH can be mainly ascribed to the PFIL component. The steady state chronoamperometric response of the



Scheme 1 Preparation of the carboxyl-functionalized IL (IL-COOH) (A) and PFIL (B).

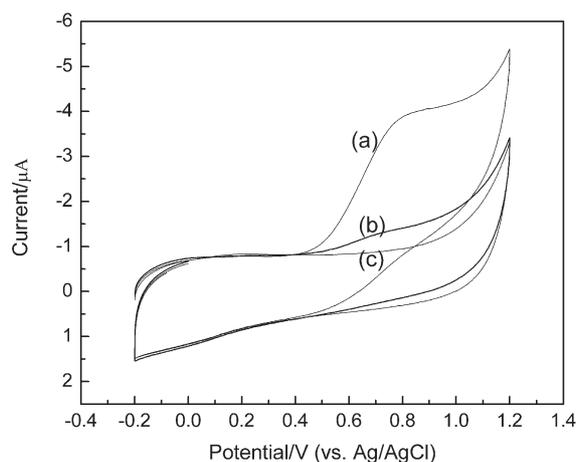


Fig. 1 Cyclic voltammograms for 0.5 mM NADH in phosphate buffer solution (0.05 M, pH = 7.4) at PFIL-Nafion (a), Nafion (b) modified GCE, and only in phosphate buffer solution (0.05 M, pH = 7.4) at PFIL-Nafion modified GCE (c).

PFIL-Nafion modified GCE to successive addition of 5 μM NADH can also be easily obtained (Fig. S3).

The electrocatalytic activity of PFIL towards the oxidation of NADH revealed more efficient electron transfer and ion transport in PFIL-Nafion film than in Nafion film. The possible processes during the electrocatalytic oxidation of NADH at such a PFIL substrate can be considered as: firstly, there is π - π stacking interaction between the imidazolium ions of PFIL and NADH (Fig. S4),¹⁰ then the PFIL on the electrode affords a platform to enrich NADH from solution; secondly, the high conductivity of IL¹ in the PFIL-Nafion film improves the charge and ion transport, which facilitates the oxidation of NADH.

PFIL could also be immobilized onto solid supports through LbL assembly, in which the facile tunable wettability of IL was retained. It is well known that the wettability of dialkylimidazolium salts can be modulated by exchanging their counteranions,^{5a} and the sequentially adsorbed polyelectrolyte layers can be used to systematically alter the wettability of the substrate surface by simply changing the outermost polyelectrolyte layer.¹¹ To get LbL assembly presenting imidazolium ions at the outermost layer, the polyelectrolytes of PEI, PSS and PFIL were sequentially assembled onto hydrophilic ITO (PEI/PSS/PFIL multilayer, see ESI). According to a previous report, several hours are needed to completely exchange counteranions of the imidazolium salts between the electrolyte solution and the film due to the slow ion diffusion process.^{5a} It was found that a fast exchange of counteranions could be obtained by applying an electric field on the substrate. A small positive potential (+0.3 V) was applied to PEI/PSS/PFIL modified ITO in 10 mM NaPF₆ solution for 600 s. A typical time-dependent current response is shown in Fig. S5. The resulting current was essentially caused by the exchange of counteranions between the interface and solution.¹² As shown in Fig. 2, the contact angle of the film increased *ca.* 15° after applying an electric field to the film in PF₆⁻ solution (here, NaPF₆). When the film was transferred from PF₆⁻ into Cl⁻ (here, NaCl) solution again under the same electric field, the contact angle of the film could be restored to its previous state with *ca.* 15° decreases. The change in wettability could be repeated reversibly. The reversible

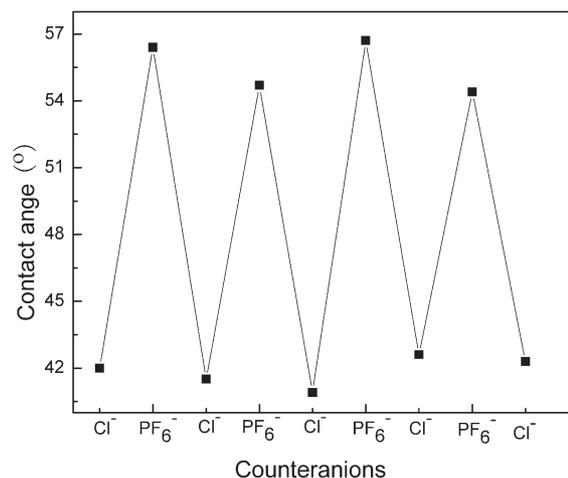


Fig. 2 Reversible change in wettability measured from PEI/PSS/PFIL multilayer on ITO by applying an electric field onto the substrate in 10 mM NaPF₆ or NaCl solution. Working potential: +0.3 V; time scanning: 600 s.

change in wettability should be attributed to the corresponding exchange of counteranions of imidazolium salts at the outermost layer.^{5a} It is conceivable that the application of an electric field to the films may promote the ion-exchange equilibrium and drive the ions easily from the solution to the film. The successful modulation of surface wettability presented here would find promising applications in both fundamental and technological advances.^{13,14}

In summary, the facile immobilization of an ionic liquid (IL) by using a polyelectrolyte as carrier (PFIL) was achieved. Such immobilization could be applied to any substrate, of any size and shape, which would bring new applications of ILs. And the immobilized PFIL exhibited direct electrocatalysis activity towards the oxidation of NADH, which has never been reported before for the electrocatalysis of ILs. In addition, *via* LbL assembly of PFIL, a surface with electrochemically controlled wettability was also constructed. This practical advantage of the PFIL material is technically attractive in chemical industrial processes, and suggests a significant future for the application of ILs in surface chemistry or in catalytic chemistry.

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ESI

Experimental Section

Materials

Polyethylenimine ($M_w = 25000$, PEI), poly (styrenr-4-sulfonate) ($M_w = 70000$, 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 M Ω).

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 (H₂O): 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 μ l 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 μ l 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.

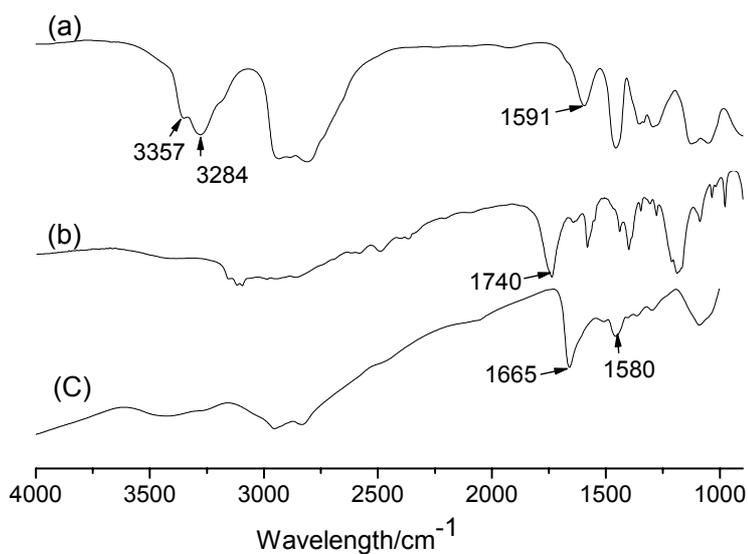


Fig. S1 FTIR spectra of PEI (a), IL-COOH (b) and PFIL (c). The bending vibration of amino groups (-NH_2) at 1591 cm^{-1} and C=O stretching mode of IL-COOH at 1740 cm^{-1} disappeared from curve a and b, respectively. Moreover, two characteristic peaks at 1665 cm^{-1} and 1580 cm^{-1} assigned to the 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.

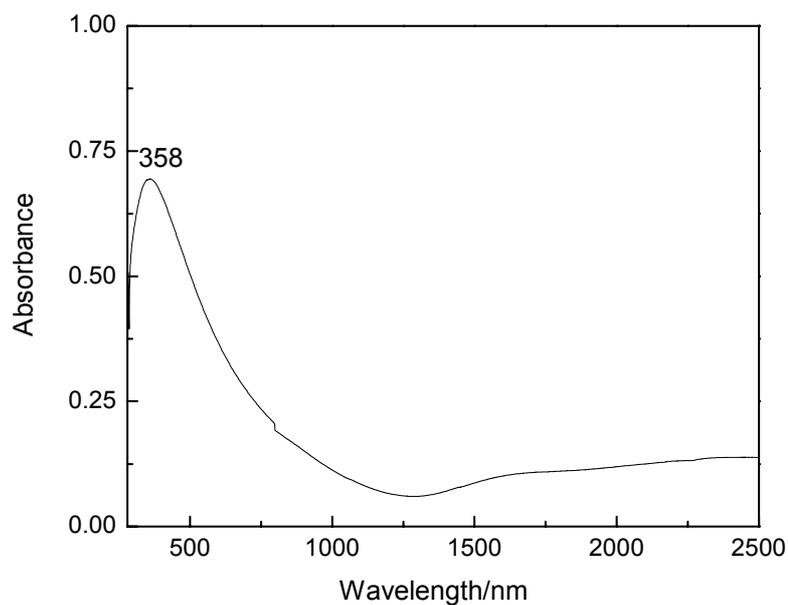


Fig. S2 UV-vis-NIR of PFIL electrodeposited onto ITO. The film of PFIL on ITO was obtained by electrophoresis at -2 V for 600 s. A strong adsorption band at 358 nm was attributed to the adsorption of imidazolium rings.^[4] The result further verified the successful synthesis of PFIL, which was in agreement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

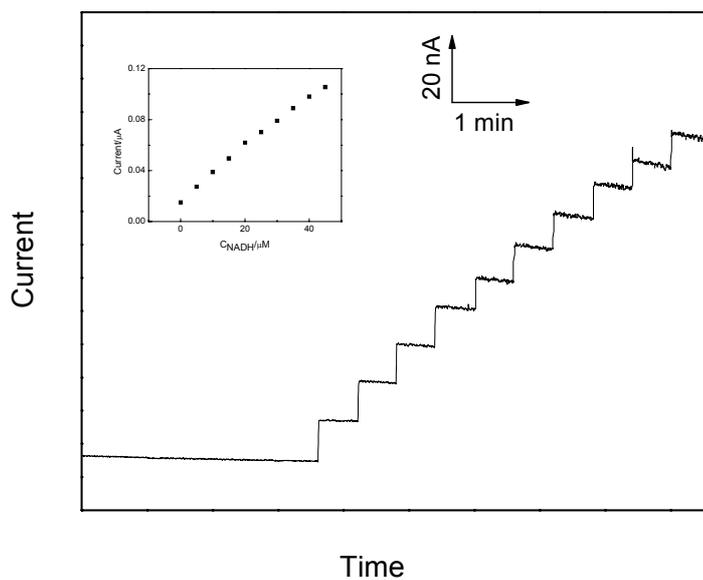


Fig. S3 Chronoamperometric curve of the steady state response at PFIL-Nafion modified glass carbon electrode in phosphate buffer solution (0.05 M, pH = 7.4) on increasing the concentration of NADH in 5 μM steps. Working potential: +0.75 V. Insert: the calibration curve for NADH at PFIL-Nafion modified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

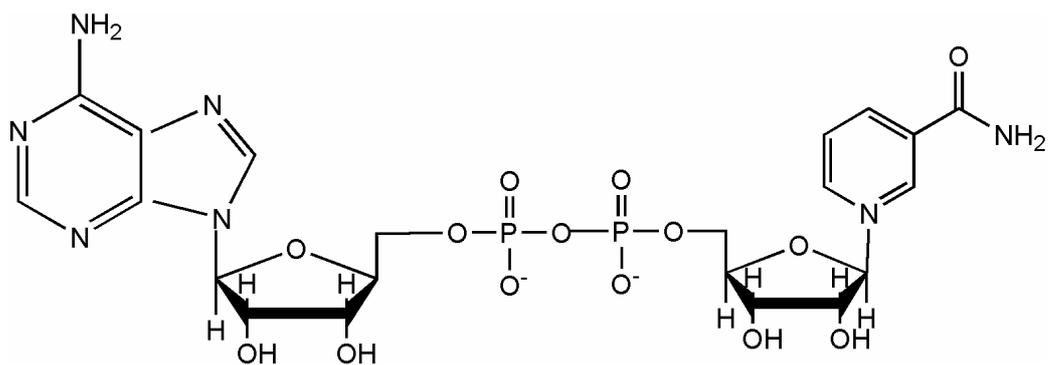


Fig. S4 Structure of NADH.

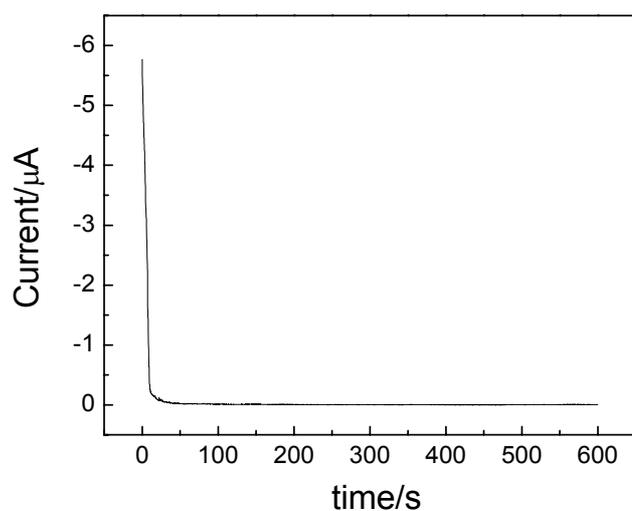


Fig. S5 Chronoamperometric response of PEI/PSS/PFIL multilayer on ITO in 10 mM NaPF₆ or NaCl. The potential was held at 0.3V for 600 s.

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