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] Morever, 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]

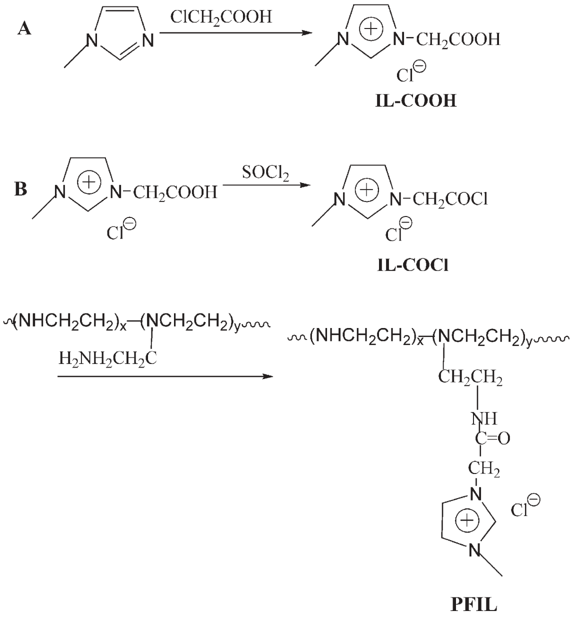
It was noted that polyelectrolytes could be easily immobilized onto many substrates through various methods such as electrophoresis,[7] layer-by-layer (LbL) assembly[8] and casting,[9] *etc.* Therefore, it would be helpful for us to immobilize ILs in a facile manner on general substrates with the aid 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.

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 immolized 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. 1*c*, 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).

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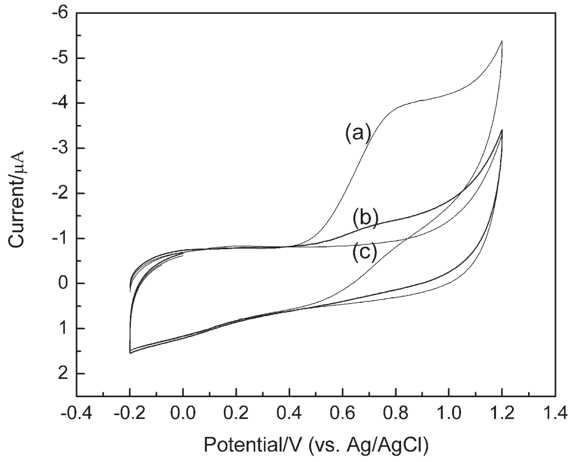

Fig. 1 Cyclic voltammograms for 0.5 mM NADH in phosphate buffer solution (0.05 M, pH = 7.4) at PFIL–Nafion (*a*), Nafion (*b*) modified GCE, and only in phosphate buffer solution (0.05 M, pH = 7.4) at PFIL–Nafion modified GCE (*c*).

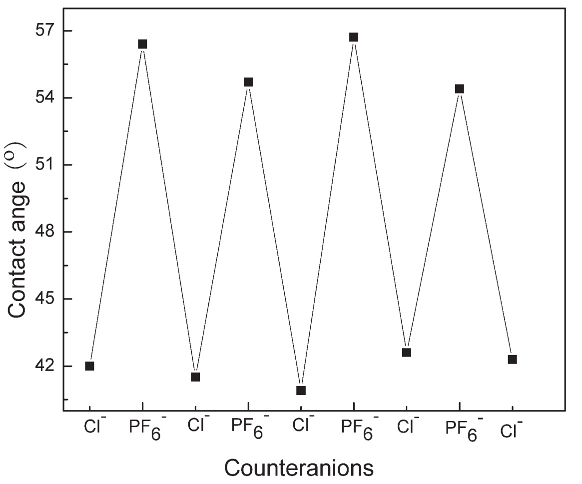

Fig. 2 Reversible change in wettability measured from PEI/PSS/PFIL multilayer on ITO by applying an electric field onto the substrate in 10 mM $NaPF_6$ or NaCl solution. Working potential: +0.3 V; time scanning: 600 s.

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 IL[1] 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 $NaPF_6$ 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 PF_6^- solution (here, $NaPF_6$). When the film was transferred from PF_6^- 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 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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Notes and references

1 (*a*) R. D. Rogers and K. R. Seddon, Eds., *Ionic Liquids: Industrial Applications for Green Chemistry*, ACS Symposium Series 818, American Chemical Society, Washington, DC, 2002; (*b*) R. D. Rogers and K. R. Seddon, Eds., *Ionic Liquids as Green Solvents*, ACS Symposium Series 856, American Chemical Society, Washington, DC, 2003; (*c*) P. Wasserscheid and T. Welton, Eds., *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2002.

2 (*a*) K. E. Gutowski, G. A. Broker, H. D. Willauer, J. G. Huddleston, R. P. Swatloski, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*,

2003, **125**, 6632; (*b*) J. H. Li, Y. F. Shen, Y. J. Zhang and Y. Liu, *Chem. Commun.*, 2005, 360; (*c*) Y. J. Zhang, Y. F. Shen, J. H. Li, L. Niu, S. J. Dong and A. Ivaska, *Langmuir*, 2005, **21**, 4797.

3 (*a*) D. W. Kim and D. Y. Chi, *Angew. Chem., Int. Ed.*, 2004, **43**, 483; (*b*) C. P. Mehnert, *Chem. Eur. J.*, 2005, **11**, 50; (*c*) J. Huang, T. Jiang, H. X. Gao, B. X. Han, Z. M. Liu, W. Z. Wu, Y. H. Chang and G. Y. Zhao, *Angew. Chem., Int. Ed.*, 2004, **43**, 1397.

4 (*a*) B. Gadenne, P. Hesemann and J. J. E. Moreau, *Chem. Commun.*, 2004, 1768; (*b*) C. P. Mehnert, R. A. Cook, N. C. Dispenziere and M. Afeworki, *J. Am. Chem. Soc.*, 2002, **124**, 12932.

5 (*a*) B. S. Lee, Y. S. Chi, J. K. Lee, I. S. Choi, C. E. Song, S. K. Namgoong and S.-G. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 480; (*b*) Y. S. Chi, J. K. Lee, S.-G. Lee and I. S. Choi, *Langmuir*, 2004, **20**, 3024.

6 (*a*) M. H. Valkenberg, C. deCastro and W. F. Hölderich, *Green Chem.*, 2002, **4**, 88; (*b*) C. P. Mehnert, E. J. Mozeleski and R. A. Cook, *Chem. Commun.*, 2002, 3010.

7 X. Pang and I. Zhitomirsky, *Langmuir*, 2004, **20**, 2921.

8 (*a*) G. Decher, *Science*, 1997, **277**, 1232; (*b*) F. Mallwitz and A. Laschewsky, *Adv. Mater.*, 2005, **17**, 1296.

9 J. Doh and D. J. Irvine, *J. Am. Chem. Soc.*, 2004, **126**, 9170.

10 B. A. Deore and M. S. Freund, *Chem. Mater.*, 2005, **17**, 2918.

11 D. Yoo, S. S. Shiratori and M. F. Rubner, *Macromolecules*, 1998, **31**, 4309.

12 M. J. Stephenson, S. M. Holmes and R. A. W. Dryfe, *Angew. Chem., Int. Ed.*, 2005, **44**, 3075.

13 Y. Liu, L. Mu, B. H. Liu and J. L. Kong, *Chem. Eur. J.*, 2005, **11**, 2622.

14 (*a*) K. Ichimura, S.-K. Oh and M. Nakagawa, *Science*, 2000, **288**, 1624; (*b*) X. M. Wang, A. B. Kharitonov, E. Katz and I. Willner, *Chem. Commun.*, 2003, 1542; (*c*) S. Minko, M. Muller, M. Motornov, M. Nitschke, K. Grundke and M. Stamm, *J. Am. Chem. Soc.*, 2003, **125**, 3896.