Hydrophobic ionic liquids/water interfacial phase transfer induced by direct current electric field

NIU Dongxiao¹ CHEN Jiajia¹ WANG Wei² YANG Xinju^{2,*} HU Jun^{1,*}

¹Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

²State Key Laboratory of Surface Physics, Fudan University, Shanghai 200433, China

Abstract To investigate the affect of direct current electric field (DCEF) on the interfacial phase, in this paper, a hydrophobic ionic liquid (HIL)/water as liquid–liquid two-phase binary system is established by using the deioned water and l-butyl-3-methyl imidazolium hexafluorophosphate, and the topographies of the HIL nanodroplets and nanolayers in ambient water are observed by atomic force microscope (AFM). The results show the AFM exerting the DCEF can enhance the intersolubility of the HIL/water binary system and induce their interfacial phase transfer. **Key words** Hydrophobic ionic liquid, l-butyl-3-methylimidazolium hexa-fluorophosphates, Atomic force microscope,

Interfacial phase transfer, Direct current electric field.

1 Introduction

Ionic liquids (ILs) are attractive candidates for clean energy^[1–3], rare metal purification^[4], pollution-free chemical synthesis^[3,5–9], nano-fabrication^[10], soft organic electric polymer devices as conductive liquid crystal^[11,12], because of their near zero vapor pressure, non-flammability, distinctive conductivity, chemical and thermal stability. ILs have a potential application of special bio-catalysis^[13,14], too. ILs in different conditions have been explored, such as temperature^[15], electric field^[16–18], light^[19], pressure^[20], magnetic field ^[21], pH^[22,23], and specific molecular recognition ^[24].

Because the ILs are hydrophilic or hydrophobic, the water/ILs intersolubility is relevant with the molecule networks^[25], and their interfacial phase is alternate under a spatial electric field^[26,27]. Some authors focused on electric field effect on ILs/ water intermiscibility in binary system, using a hydrophobic ionic liquid (HIL). Niall *et al.*^[28] reported that the gap between positive/negative poles was of micrometer level at the effective electric field strength of 1–2.5 V/ nm, but the voltage applied was up to several hundred volts. Mani Paneru *et al.*^[29] observed DC voltage of

over 100 V, affected the surface tension of ILs micron droplets in water, but this was far beyond the ILs electrochemistry windows of 5–6 $V^{[30]}$, and caused some inscrutable electrode reactions. Therefore, a nanometer gap and several volts are more feasible and credible for the high electric field strength.

In this paper, to investigate nanoscale electric field effect on HIL/water intersolubility, we use an atomic force microscope (AFM) tip holder to form a DC electric field (DCEF) between the tip and the substrate. The tip-sample distance can be adjusted between 0–10 nm, and the DCEF strength is mainly decided by the tip bias and average height of the sample surface. The results show that the DCEF of 0.3 V/nm is achieved by the 3-V tip bias inside the 10-nm high nanodroplets, and the HIL/water interfacial phase is transferred by increasing the intersolubility during AFM imaging.

2 **Experimental**

2.1 The sample preration

The hydrophobic ionic liquid, l-butyl-3-methyl imidazolium hexa-fluorophosphates, BMIM(PF₆), of

Received date: 2011-03-25

Supported by the National Basic Research Program of China (973 Program No. 2007CB936000), the National Natural Science Foundation of China (No.10874198, 90923002, 21073222 and 10975175, No. 10874030), and the Chinese Academy of Sciences (No. KJCX2-EW-N03)

^{*} Corresponding author. E-mail address: xjyang@fudan.edu.cn; hujun@sinap.ac.cn

99% purity, synthesized by Greenchem Industries Co. Ltd., was dissolved into methanol (HPLC grade, 99.8%, Sigma) to become solutions of 0.05 wt%–0.5 wt%. The 5- μ L droplet was coated on the newlycleaved surface of highly oriented pyrolytic graphite (HOPG, 1 cm × 1 cm) by 10-s spinning at 5000 rpm. Also, the droplets were fabricated into the nanolayers as reported by Liu *et al.*^[31]. The water in bulk resistance of >18.2 MΩ was from Sigma, USA.

2.2 The DCEF of tip/substrate and AFM imaging

As shown schematically in Fig.1, the HIL nanodroplets and nanolayers in ambient water was imaged with the AFM (Nanoscope multimode V, Veeco/Digital Instrument, USA) operating in tapping mode, and collected at 25°C and humidity of 30±1%. The tip with a Pt/Ir-coated end provides a metallic electrical path from the cantilever die to the apex (SCM-PIT, Veeco/ Digital Instrument, USA). An additional connecting line was welded on the tip holder, so as to apply a positive voltage between the tip and HOPG substrate. To protect the metal tip coated from electrochemical corrosion, a negative voltage was applied to the HOPG substrate. The water /HIL interfacial phase transfer, which was affected by the DCEF between the AFM tip and HOPG substrate, was observed by contrasting the AFM scanning images at tip bias.

3 **Results and Discussion**

The HIL nanodroplets of about 10-nm average height and 5 μ m × 5 μ m size in ambient water were imaged,

and a random area of 2 μ m ×2 μ m is zoomed and scanned at +2-V tip bias (Fig.2a). The lowest HIL nanodroplets disappear after tip bias (Fig.2b). All the HIL nanodroplets vanished at 3-V tip bias (Fig.2c). When repeating the 5 μ m × 5 μ m scan *in situ* at zero bias, most of the HIL nanodroplets disappeared, and seemed to affect its nearby area (Fig.2d). The results could be repeated with different HOPG substrates and conductive coating tips, indicating that the tip bias in the ranges of 0.6 to 1.5 V could affect the HIL/water intersolubility, and the HIL nanodroplets images trended to vanish at a higher tip bias. This is likely that the DCEF around the AFM tip enhanced the HIL/ water intersolubility, but simultaneously the interfacial tension decreased to the extent allowing accurate AFM detection, hence the failure of tracing the HIL nanodroplets by the AFM. The phenomenon is defined as interfacial phase transfer induced by the DCEF. Also, the tip bias in scanning process disturbed the nanodroplets when the DCEF increased the HIL/water intersolubility, and dissimilarity of the in situ image of Fig.2(d) accounts for the HIL dissolved in water.



Fig.1 Sketch map of the experimental design. The HIL topographies in ambient water was obtained by tapping-mode. The water/HIL interfacial phase transfer affected by the DCEF was observed by contrasting the AFM scanning images at tip bias.



Fig.2 AFM images of the HIL nanodroplets scanned in ambient water. The inset shows the Z-range for all the images.

The DCEF strength around the AFM tip is determined by designating or adjusting the tip voltage, and the tip-substrate distance corresponds with the HIL height during image scanning process. Fig.(3) shows that DCEF affects the HIL/water interfacial phase at different HIL heights. The HIL nanolayers on

HOPG were of about 3.2-nm height (Fig.3a), from which a typical height was selected. By scanning the selected area in situ with increasing tip bias in 0.1-V steps, the nanolayer image began to vanish at about 1-V bias. Fig.3(b) shows the image at 3 V of the tip bias. However, the nanolayer reappeared when reducing the tip bias to zero and scanning the area in situ (Fig.3c). This is different from the results of nanodroplets in

Fig.2. Because the volume of nano- layer solution is far less than that of the nanodroplet, the nanolayer image vanishes when the DCEF induced HIL/water interfacial phase transfer is appropriate. The nanolayers could not be dissolved entirely in water, even under the tapping probe tip touching or disturbing in the imaging process.



(a) Tip Bias=0

(c) The Selected Area, Tip Bias=3 V (d) The Selected Area, Tip Bias=0



The images were analyzed off-line by Veeco software. Fig.4(A) and Fig.4(B) show, respectively, the height statistic distributions of Fig.3(b) and the rectangle area marked by the arrow in Fig.3(c). They have the same characteristic peaks of substrate background, indicating that Fig.3(c) is not a false image caused by the tip bias, and AFM worked properly, though the HIL nanolayer image is out of sight.



Fig.4 Height statistic distributions of (A) Fig.3(b) and (B) the rectangle area in Fig.3(c) by off-line image analysis.

The nanolayer heights are of 0.3 to 1.2 nm. In Fig.5(a), a typical height is 0.73-nm, which is two times larger than the theoretically estimated height of a single nanolayer (0.36–0.37 nm)^[32]. The AFM image in Fig.5(b) was recorded by disabling it at the slow axis (arrowed in Fig.5a) and increasing the tip bias to 4 V in 50-mV steps, and the image in Fig.5(c) was recorded by decreasing the bias to zero. The false image lines in Figs.5(b) and 5(c) were caused by the tip bias jumping. Although they can be erased by the off-line software, this was not performed so as to record the tip bias change distinctly. The DCEF strength around the tip was larger in the lower nanolayer at the same tip bias, but at an abnormally large tip bias of 4 V (it was 1 V in Fig.3), the HIL/water phase transfer would occur. This is likely related with the HOPG surface potential because the HIL epitaxial nanolayers in Fig.5(a) were confined by the HOPG surface, and its surface potential was amplified by the HOPG. Fig.5(d) shows that the tip bias changed the HIL nanolayers and the change might be caused by HIL dissolving and a reversible process.

Figure 6 shows the imaging results with even larger changes in experimental conditions. The HIL nanolayers (Fig.6a) was applied with a 4-V tip bias, most of the morphology information was gone (Fig.6b). By reducing the bias to zero, the HIL nanodroplets were separated (Fig.6c), indicating the nanodroplets dissolved in water were precipitated again. The AFM experiment was performed in air ambient. The HIL nanodroplets and nanolayers could be observed in ambient air with tapping mode (Fig.6d),

and steadily imaged up to +8-V tip bias (Fig.6e). These confirm that the phenomena observed above are

not because of the tip force but DCEF-induced water /HIL interfacial phase transfer.



Fig.5 The confined HIL nanolayer images of 3 μ m ×3 μ m in ambient water. (a) tip bias=0, (b) disabling at the slow axis line arrowed in Fig.(a) and increasing the bias to 4 V in 50-mV step, (c) decreasing the tip bias to zero, (d) in situ image of (a) at zero tip bias after scanning (b) and (c). Z-range for all the images is indicated by the insert.



Fig.6 In situ AFM images of the nanolayers in ambient water at (a) tip bias-0, (b) tip bias=4 V, and (c) in reducing tip bias to zero, and in ambient air at (d) tip bias-0 and (e) tip bias=8 V. Z-rang is 3 nm from (a) to (c), and 10 nm for (d) and (e).

However, there are still three issues to be further discussed.

Firstly, increasing the tip-sample voltage spontaneously increases the tip-sample electrostatic force. As a long-range force, the electrostatic force will magnify the tapping amplitude, but the tip-sample force is defined and fixed by the amplitude setting of the AFM. On applying the tip bias, the tip-sample force has a sudden increase, whereas the AFM will promote the scanning height at the next scan line to keep the amplitude setting. In Figs.5(b) and 5(c), the false scanning lines correspond to the tip bias changes. Consequently we exclude the possible effect caused by electric force of tip-sample status. To confirm this, the AFM experiment in air ambient was performed. The HIL nanodroplets could be steadily imaged at 8-V tip (Fig.6d and Fig.6e). In another experiment, we merely enhanced the amplitude with a zero tip bias and no HIL nanodroplets disappeared in the imaging process.

Secondly, the DCEF can lead to HILs electric wetting on the electrode surface ^[29,32]. With a positive pole, HILs may be adsorbed to the probe tip surface. If that happens, an HIL-coated tip will replace the metal

coated-tip to detect water/HIL interface, the tip will ignore the water/HIL boundary and the HILs will likely to disappear in the AFM imaging, just as Nainaparampil *et al.*^[16] reported. However, comparing Fig.3(d) with Fig.3(a), the HIL disappearing in Fig.3(c) is primarily relevant to tip bias.

Finally, we had been worrying about the complex electrochemical reaction around the AFM probe tip, but it is easier for the water to be electrolyzed than HILs, and as an equal-potential conductive compound, the cantilever and the probe base, with bigger surface areas, are more likely to release the electrochemistry energy preferentially. In our experiment, electrolytic bubbles gathering were seen at the edge of probe base, but no bubbles were seen nearby the tip in a long time scanning at 3-V bias.

4 Conclusions

The liquid phase AFM tip holder is remoulded to form the DCEF around probe tip in ambient water, and is used to observe the HIL nanodroplets and nanolayers on HOPG substrate. At proper tip bias, the HIL vanishes in AFM imaging, because the intension of DCEF induces the IL/water interfacial phase transfer. All the AFM images are obtained with a minute tip-sample force, and the HIL/water interfacial electric properties are detected in nanoscale. In our further studies, the interfacial tension will be estimated qualitatively and quantitatively from the accurate tip shape, cantilever elastic constant, and other parameters of the AFM.

References

- 1 Ito S, Zakeeruddin S M, Comte P, *et al.* Nat Photonics, 2008, **2:** 693–698.
- 2 Aricò A S, Bruce P, Scrosati B, Tarascon J M, Van Schalkwijk W. Nat Mater, 2005, **4:** 366–377.
- 3 Wu B, Reddy R, Rogers R. Sol Eng, 2001, 445–452.
- 4 Wu B, Reddy R G, Rogers R D. Light Metals, 2001, 26: 237–243.
- 5 Welton T. Chem Rev, 1999, **99:** 2071–2084.
- 6 Koel M. Crit Rev Anal Chem, 2005, **35**: 177–192.
- 7 Anderson J L, Armstrong D W, Wei G T. Anal Chem, 2006, 78: 2892–2902.
- 8 Hayes R, Warr G G, Atkin R. Phys Chem Chem Phys, 2010, 12: 1709–1723.
- 9 Parvulescu V, Hardacre C. Chem Rev, 2007, 107: 2615– 2665.
- 10 Soejima T, Kimizuka N. Chem Lett, 2005, 34:1234–1235.
- 11 Pandey S. Anal Chim Acta, 2006, **556:** 38–45.
- Kaur D, Yamada K, Park J, et al. J Phys Chem B, 2009, 113: 5381–5390.
- 13 Moniruzzaman M, Kamiya N, Nakashima K, et al. Green Chem, 2008, 10: 497–500.
- 14 Sheldon R A, Van Rantwijk F, Lau R M. Abstr Pap Am Chem S, 2002, **224:** 626.
- 15 Baker S N, Baker G A, Bright F V. Green Chem, 2002, 4:

165-169.

- 16 Nainaparampil J J, Phillips B S, Eapen K C, et al. Nanotechnol, 2005, 16: 2474–2481.
- Tomer R, Dimitrijevic D, Florence A T. J Control Release, 1995, 33: 405–413.
- 18 Murdan S. J Control Release, 2003, 92:1–17.
- Harrington B A, Mullen R L, Kenney M E. Macromol, 1986, 19: 2888–2890.
- 20 Lee K K, Cussler E L, Marchetti M, *et al.* Chem Eng Sci, 1990, **45:** 766–767.
- 21 Filipcsei G, Csetneki I, Szilagyi A, *et al.* Adv Polym Sci, 2007, **206**: 137–189.
- 22 Diez-Pena E, Quijada-Garrido I, Barrales-Rienda J M. Polym, 2002, **43**: 4341–4348.
- 23 Mohan Y M, Murthy P S K, Raju K M. React Funct Polym, 2005, **63:**11–26.
- 24 Miyata T, Asami N, Uragami T. Nat, 1999, **399:** 766–769.
- Susilo R, Alavi S, Lang S, *et al.* The J Phys Chem C, 2008,
 112: 9106–9113.
- 26 Kuwajima S, Warshel A. J Phys Chem, 1990, 94: 460– 466.
- Padua A A H, Costa Gomes M F, Canongia Lopes J N A. Acc Chem Res, 2007, 40: 1087–1096.
- 28 English N J, Mooney D A. J Phys Chem B, 2009, 113: 10128–10134.
- Paneru M, Priest C, Sedev R, *et al.* J Am Chem Soc, 2010,
 132: 8301–8308.
- 30 Buzzeo M C, Hardacre C, Compton R G. Chem Phys Chem, 2006, 7: 176–180.
- 31 Liu Y, Zhang Y, Wu G, et al. J Am Chem Soc, 2006, 128: 7456–7457.
- 32 Millefiorini S, Tkaczyk A H, Sedev R, *et al.* J Am Chem Soc, 2006, **128**: 3098–3101.