Room-temperature ionic liquids as media to enhance the electrochemical stability of self-assembled monolayers of alkanethiols on gold electrodes†

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The electrochemical stability of self-assembled monolayers was greatly enhanced by using room-temperature ionic liquids as media.

Self-assembled monolayers (SAMs) of alkanethiols on gold surfaces have drawn considerable attention as model systems for probing electron transfer theories and interface structures,[1] as well as for potential technological applications including corrosion inhibition,[2] wetting,[3] molecular electronic devices,[4] chemical sensors[5] and electroanalysis[6] *etc*. In some electrochemical applications, the potential-dependent stability of the SAMs is a crucial point,[7] which is greatly affected by several factors such as solvents, electrolytes, temperature and substrates.[8] Aqueous media has little effect on the structure and stability of the SAMs, but the potential window is small.[8a] Although organic solvents allow one to work in a larger range of potentials than aqueous media, most of them solvate SAMs and disrupt the SAM structure,[9] hence the SAMs are stable only in a limited range of potentials.[9] In some cases, electrolyte ions could adsorb on the electrode and displace the adsorbed thiol, resulting in desorption of the SAMs.[8a] Therefore, to select proper solution environments for the SAMs to obtain high stability in a wide range of potentials is of significant importance.[9]

Here, we describe, for the first time, a novel medium for SAMs, room-temperature ionic liquids (RTILs). RTILs have been proposed as "green" alternatives to conventional organic solvents in a range of synthesis, catalysis, electrochemistry and liquid-liquid extractions[10] because of their special chemical and physical properties.[11] Particularly, they have relatively large potential windows and high conductivity, and allow studies to be undertaken without requiring added supporting electrolyte in the area of electrochemistry.[12] Here, the potential-dependent stability of octadodecanethiol ($C_{18}SH$) SAMs on gold electrodes in 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$), RTILs, and other aqueous and organic electrolyte solutions was investigated by electrochemical methods, such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy. It was found that the SAMs in $BMIMPF_6$ were stable in a much wider potential window.

The oxidative and reductive desorption behaviors of $C_{18}SH$ SAMs on Au were investigated by cyclic voltammetry. Fig. 1(A) and (B) shows the CVs of gold electrodes modified with $C_{18}SH$ in CH_2Cl_2 containing 0.1 M tetra-*n*-octylammonium bromide (TOAB) (denoted as TOAB/CH_2Cl_2), 0.5 M KCl/H_2O, 0.5 M KOH/H_2O and $BMIMPF_6$ in various potential scan limits. Due to desorption occurring when scanning both positive and negative regions, the experiments were done separately in each region. In the positive potential region (Fig. 1(A)), an oxidative current peak for the SAMs in $BMIMPF_6$ was observed at the most positive potential compared to that in other three electrolyte solutions.[13a] In the negative region (Fig. 1(B)), no thiolate reductive desorption wave was observed in KCl/H_2O and KOH/H_2O, while for water, reduction occurred first at *ca.* -1.2 V; and a thiolate reductive desorption wave was observed at -1.2 V in TOAB/CH_2Cl_2;[8a] in the case of the SAMs in $BMIMPF_6$, thiolate reduction occurred at -1.7 V, and the peak current was much smaller than that in TOAB/CH_2Cl_2, indicating a slower electrochemical process. These results showed that the stable potential window of SAMs in $BMIMPF_6$ was about twice as large as that in conventional aqueous or organic solutions. Besides, the background currents in RTILs were much smaller than others in both cases. Because aqueous solutions could only provide a relatively narrow potential window due to water reduction and oxidation, as reported previously,[8a] in the following text, the potential-dependent stability of the SAMs was further compared only in $BMIMPF_6$ and TOAB/CH_2Cl_2.

The potential-dependent stability of the SAMs was also investigated through the method proposed by Fritsch-Faules and co-workers.[13b] The SAM modified electrode was conditioned at a given potential for a specified time in $BMIMPF_6$ and TOAB/CH_2Cl_2, and then the surface-bound molecules that survived this treatment were quantified using $K_3Fe(CN)_6$ as a redox probe.[14] Fig. 1(C) shows the surface coverage of SAMs on Au after the SAM modified electrode was conditioned at various potentials for 30 min in $BMIMPF_6$ and TOAB/CH_2Cl_2, respectively. In $BMIMPF_6$ (curve 1), the SAMs were stable in the window from -1.44 to 1.36 V. However, under similar conditions, the SAMs in TOAB/CH_2Cl_2 were stable only at potentials near 0 V (curve 2), which was consistent with the results reported by Fritsch-Faules and co-workers.[13] Although the stable potential windows obtained from this method were slightly narrower than those from CVs due to the prolonged time scale of electrochemical processes, the stable potential window in $BMIMPF_6$ was still much wider than that in TOAB/CH_2Cl_2.

The energy barrier to desorb an alkanethiolate molecule from Au should involve interaction energies of alkanethiolate–Au, alkanethiolate–alkanethiolate, solvent (and/or electrolyte ions)–alkanethiolate and solvent (and/or electrolyte ions)–Au.[15] Herein,

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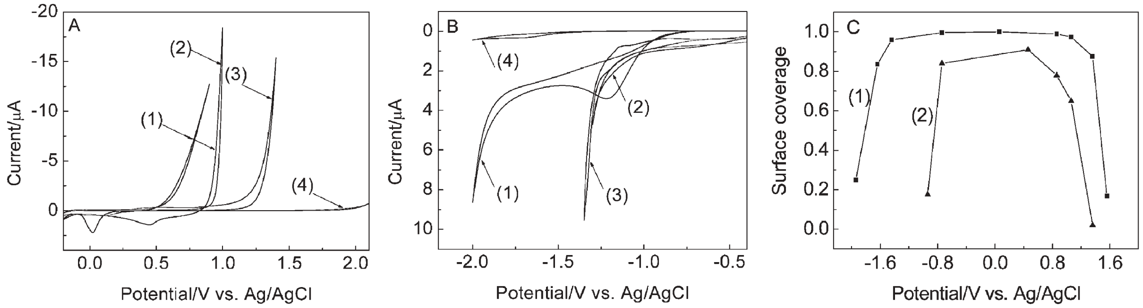

Fig. 1 Cyclic voltammograms of $C_{18}SH/Au$ SAMs in positive (A) and negative (B) potential regions in 0.1 M $TOAB/CH_2Cl_2$ (1), 0.5 M KCl/H_2O (2), 0.5 M KOH/H_2O (3) and $BMIMPF_6$ (4). Scan rate, 100 mV s^{-1}. (C) Surface coverage of $C_{18}SH$ SAMs on Au after being conditioned at different potentials in BMIMPF6 (1) and $TOAB/CH_2Cl_2$ (2) for 30 min.

the different stability of the SAMs in $TOAB/CH_2Cl_2$ and $BMIMPF_6$ is likely due to the different interaction ability of the solvent (and/or electrolyte ions)–alkanethiolate, and solvent (and/or electrolyte ions)–Au. The stronger interaction would lead to the easier penetration of solvent (and/or electrolyte ions) into the SAMs. If solvent (and/or electrolyte ions) penetrated into the monolayer, the surface order would be disrupted to accommodate these extra materials within the monolayers.[2a] To examine the different interaction abilities, we investigated the ionic permeability of the SAMs by electrochemical impedance spectroscopy in the absence of redox active species (Fig. 2), as proposed by Boubour and Lennox.[16] In $BMIMPF_6$, the effect of the applied dc potential (E_{dc}) on the SAMs permeability was investigated from 0 to -1.3 V in 0.1 V steps and three representative curves are shown in Fig. 2(A). The time scale of each experiment was about 30 min. From 0 to -0.8 V, the Nyquist plots remained straight lines and almost overlapped at all potentials, whose equivalent circuit involved a solution resistance (R_s) in series with a constant phase element (CPE) (I in Fig. S2, ESI†).[9] In this potential range, the SAMs behaved as ionic insulators. When the potential became more negative ($E_{dc} < -0.8$ V), significant curvature of these plots was observed and the SAMs became permeable to solvent (and/or electrolyte ions), so that the resistance of the SAMs (R_{ct}) should be included in the circuit to account for the permeability (II in Fig. S2, ESI†). Thus, the critical potential (V_c) value for the SAMs in $BMIMPF_6$ was -0.8 V. With the same procedure, similar behaviors were also observed in $TOAB/CH_2Cl_2$ from 0 to -0.7 V, and the V_c value was -0.5 V (Fig. 2(B)). The V_c value in $BMIMPF_6$ was more negative than that in $TOAB/CH_2Cl_2$. From the fitting results (Table S1, ESI†), it could be concluded that the capacitance increase and the resistance decrease in $BMIMPF_6$ were less sensitive to the decreased potential than those in $TOAB/CH_2Cl_2$ at potentials more cathodic than their respective V_c. All these results demonstrated that the energy barrier of the SAMs desorption in $BMIMPF_6$ was higher, and higher driving force was needed for $BMIMPF_6$ to penetrate the SAMs.

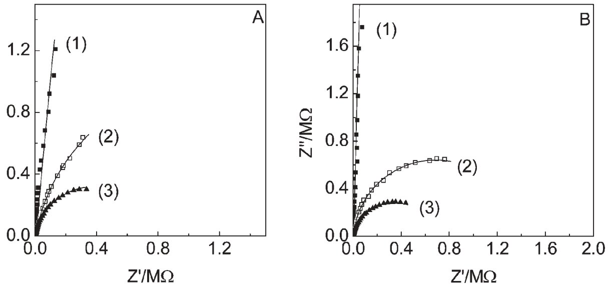

Fig. 2 (A) Nyquist plots of $C_{18}SH/Au$ SAMs in $BMIMPF_6$ at $E_{dc} = 0$ to -0.8 V (1), $E_{dc} = -1.0$ V (2) and -1.3 V (3). (B) Nyquist plots of $C_{18}SH/Au$ SAMs in 0.1 M $TOAB/CH_2Cl_2$ at $E_{dc} = 0$ V to -0.5 V (1), $E_{dc} = -0.6$ V (2) and -0.7 V (3).

We hypothesized that the penetration of solvent (and/or electrolyte ions) into the SAMs and access to the Au substrate relied on specific paths in the SAMs. The large ions of $BMIMPF_6$[17] may have few paths available to them, and thus they penetrate slowly into the SAMs to access the Au substrate. In addition to size, the high viscosity of $BMIMPF_6$[10c] may also limit penetration into the SAMs.[18] However, in organic solutions, some organic solvent molecules may solvate the thiol chain and some electrolyte ions could adsorb on the Au substrate and displace the thiol.[17] Therefore, the interaction between the solvent (and/or electrolyte ions) of organic solutions and the SAMs is much stronger, and hence the penetration of the solvent molecules (and/or electrolyte ions) also becomes easier. Further investigation on the relationship between the monolayer chain length and the monolayer stability (Fig. S3, ESI†) showed that the monolayer stability increased with the thickness of the monolayer. It supported the hypothesis that the high stability of SAMs was due to the retarded penetration of large BMIM and PF_6 ions into the monolayers. Therefore, a higher driving force was needed for $BMIMPF_6$ to penetrate into the SAMs and access to the Au substrate, *i.e.*, the electrochemical desorption potentials of the SAMs in $BMIMPF_6$ were much higher than that in conventional organic solutions.

In conclusion, this work describes, for the first time, a new type of "green" medium, RTILs, for SAMs, and demonstrated that the electrochemical stability of the SAMs was greatly enhanced by using the RTIL $BMIMPF_6$, as medium. The high electrochemical stability could be attributed to the unique properties of RTILs such as high viscosity and the large ion sizes. The results represent a significant advance toward the electrochemical applications of SAMs, such as electron-transfer studies, electroanalysis and chemical sensors, to be undertaken in a large potential range, which was previously limited in a narrow potential region.

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