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A Water-Free ITIES: Ionic Liquid/Oil Interface for Base Metal Nanostructure Formation – Zn Case

 Naoya Nishi,* Yohei Kuroyama, Naohiro Yoshida, Yuko Yokoyama, and Tetsuo Sakka^[a]

Reductive metal deposition at the interface between two immiscible electrolyte solutions (ITIES), the oil/water interface, is an attractive methodology to produce metal nanostructures. However, the metals that can be deposited are limited to noble metals; otherwise, water molecules are reduced. Herein, a method to overcome this limitation by utilizing a novel water-free ITIES between a hydrophilic ionic liquid and oil was introduced. As proof-of-concept experiments, the reductive

deposition of zinc, a base metal with a standard redox potential more negative than that of water, was successfully realized at the ionic liquid/oil interface. The morphology of the zinc nanostructures was investigated, and the reaction mechanism was discussed, in which the electron transfer and ion transfer reactions across the interface simultaneously occurred to maintain the electroneutrality of the liquids.

Introduction

The oil (O)-water (W) two-phase system has been an attractive reaction platform to prepare metal nanostructures for over a century. Faraday reported Au nanoparticle formation in the carbon disulfide-water two-phase system in the mid-19th century.^[1] Another more recent example is the Brust-Schiffrin method to prepare Au nanoparticles where the size is finely controllable with a narrow distribution.^[2,3] In the O-W two-phase system for metal nanostructure formation, metal precursors and reducing agents are dissolved in one and the other phases, respectively, and the electron transfer (ET) reaction between them can be restricted at the O/W interface in some cases.^[4] The spatial restriction aids metal nanostructures to have varied morphologies: not only nanoparticles but also nanorods,^[5] nanoplates,^[6] nanowires,^[7] and nanoshells,^[8] to name a few. This methodology for metal deposition at the O/W interface is template molecule-free; rather, the soft interface acts as a template. This methodology is also substrate-free; therefore, the formed nanostructures are easily separated from the reaction liquids and washed for purification. The liquid-liquid two-phase system for metal nanostructure formation is not limited to the O-W system; it has been extended to the ionic liquid (IL)-W two-phase system by our group^[8,9,18,10-17] and other groups,^[19-23] where a variety of metal nanostructure morphologies were attained.

Using this liquid-liquid methodology, nanostructures of various metal elements^[24] such as Au,^[23,25,26] Ag,^[27] Pt,^[28-30] Pd,^[31-33] and Cu^[34,35] have been prepared. These elements are limited to noble metals whose standard redox potentials are relatively positive. In contrast, the deposition of base metals is thermodynamically difficult because their reduction potentials are more negative than that of water and therefore the reduction of base metal ions is interfered with by the reduction of water. Thus, the presence of water limits the application of this liquid-liquid methodology to prepare base metal nanostructures.

To overcome this limitation, we prepared a liquid-liquid two-phase system that does not contain water.^[36] The two liquids are an oil and an ionic liquid (IL), 1-(3-hydroxypropyl)-3-methylimidazolium chloride (C_{30H}mimCl). The IL is hydrophilic enough to be phase-separated from the oil and even the standard ion-transfer potentials for the IL cation and anion are well separated to make the IL/O interface electrochemically polarizable. The Cl⁻ based IL can dissolve solid metal chlorides at high concentrations, forming chloro-metal complexes. As a proof-of-concept experiment, Au was deposited at the IL/O interface between C_{30H}mimCl and 1,6-dichlorohexane, with AuCl₄⁻ as the metal precursor in the IL and decamethylferrocene (DMFc) as the reducing agent in the O. The IL/O interface can be electrochemically polarizable when the IL is hydrophilic enough and the oil contains hydrophobic supporting electrolytes, as explored by a pioneering study by Couzens and Kucernak with another combination of (non Cl⁻ based) IL and oil.^[37] We were able to measure the current due to the electron transfer (ET) and ion transfer (IT) across the electrochemically polarized IL/O interface.^[36] The electrochemical measurements revealed the Au reduction mechanism at the IL/O interface; the ET between AuCl₄⁻ and DMFc, which results in Au deposition at the IL/O interface, is coupled with the IT of AuCl₄⁻ from IL to O, proceeding with the net reaction simultaneously. Although Au is a noble metal, these results suggest that the IL/O interface can be a reaction platform for the reduction of metals, including base metals.

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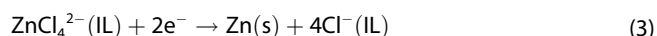
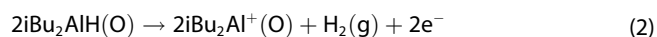
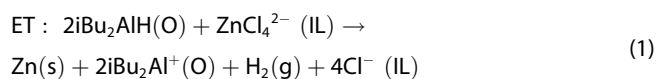
An invited contribution to the Hubert Girault Festschrift

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The present study advances the above-mentioned previous study toward the deposition of Zn, a base metal, by using the IL-O two-phase system. To the best of our knowledge, the reduction deposition of Zn has not yet been realized at the O/W interface. Mirceski et al. reported that Zn, unlike several noble metals they investigated, cannot be reductively deposited at the O/W interface.^[38] Herein, we show that Zn nanostructures are successfully formed at the water-free IL/O interface via ET and IT coupling.

Results and Discussion

We dissolved ZnCl₂ in C_{30H}mimCl to prepare a hydrophilic IL containing metal precursors. Previous studies^[39,40] by other researchers have confirmed that Zn ions exist as ZnCl₄²⁻ in Cl⁻ based ILs from $x = (n_{\text{ZnCl}_2} / (n_{\text{ZnCl}_2} + n_{\text{IL}})) = 0$ to 0.33, which is the highest x value we investigated. The O used was a toluene solution of 1 M iBu₂AlH, which is a hydrophobic reducing agent. Immediately after the contact of the two liquids, ZnCl₄²⁻-containing IL and iBu₂AlH-containing O, gas evolved from the IL/O interface (see the movie in Supporting Information). The evolved gas was identified as H₂ by using a gas detector tube. Simultaneously with the gas evolution, silver-colour deposits started to appear at the IL/O interface, which were found to be Zn metal confirmed using EDX (Figure S1) measurements. The ET reaction producing H₂ gas and Zn metal at the IL/O interface can be written as in the following reaction [Eq. (1)], for which the two half reactions for the ET are shown [Eqs. (2),(3)]:



It should be noted that iBu₂Al⁺, written on the right side of the oxidation reaction of iBu₂AlH in Equation (2), is not a final product due to its strong Lewis acidity but an intermediate reactive species that is consumed in other reactions, as discussed below.

Although Zn was deposited at the IL/O interface, the O bulk gradually became turbid and black as the two-phase system was left for several hours. EDX measurements confirmed that the deposits in the O bulk were also Zn metal, indicating that Zn species were transferred from the IL to O, and then reduced by iBu₂AlH in the O bulk. The Zn deposits produced at the IL/O interface and O bulk were observed using SEM, as shown in Figure 1. The morphologies of the two deposits were quite different; those formed at the IL/O interface (Figure 1a) showed assemblies of short one-dimensional (1D) nanostructures with a diameter of 200 nm and a length of 1–3 μm, whereas the bulk ones (Figure 1b) were featureless aggregates. This short 1D nanostructure for the former is similar to Au nanostructures formed at the IL/O interface.^[36] We also previously found that long metal nanofibers are formed at the IL/W interface for

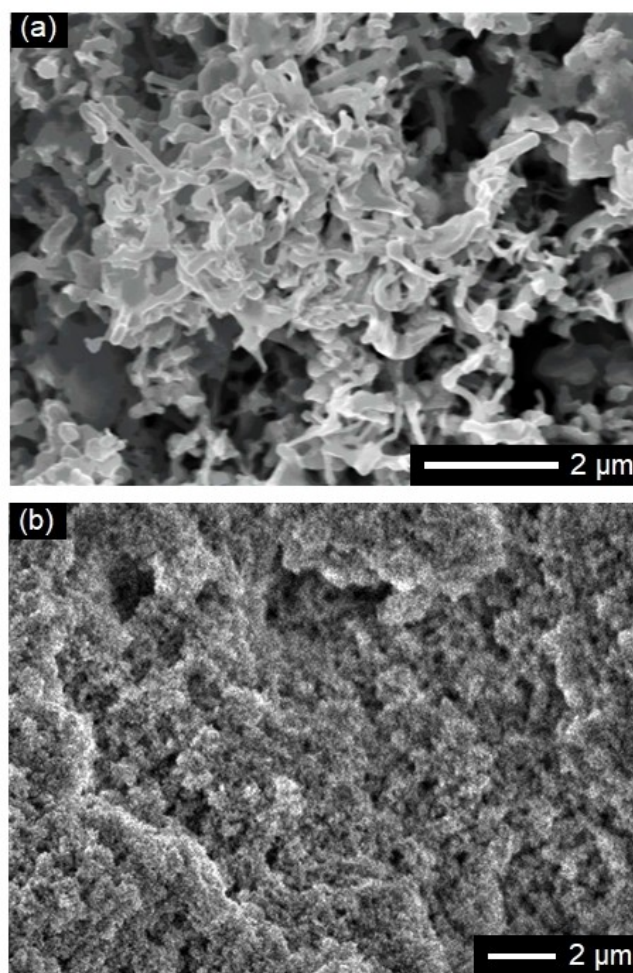
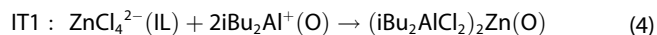


Figure 1. SEM images for Zn metal deposited via ET (a) and BET (b) reactions.

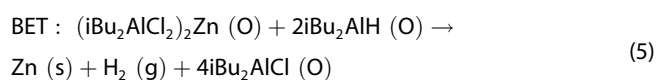
several kinds of noble metals.^[9,12,13,16] These facts imply that 1D nanostructure formation is universal for IL-related interfaces, the IL/W and the IL/O interfaces, which appear to be induced by the viscosity difference between the two liquids forming the two phases^[10] and the interfacial ionic multilayers.^[41–43]

The fact that Zn metal was deposited not only at the interface but also in the O bulk indicates that the Zn species were transferred from the IL to O during the reaction. We confirmed that solid ZnCl₂ is not soluble in the O phase (toluene solution); therefore Zn is likely to be transferred as an ionic species, with the ion transfer (IT) reaction across the IL/O interface. Actually, the ET shown in Equation (1) should be compensated for with IT so that the net reaction proceeds spontaneously. This is because ETs are charge transfer reactions that break the charge neutrality of each liquid phase. Since the ET shown in Equation (1) corresponds to the transfer of 2e⁻ from O to IL, the IT that maintains the electroneutrality should be either the IT of anion from IL to O or IT of cation from O to IL. Another clue to consider the IT is iBu₂Al⁺, the intermediate product of ET [Eqs. (1),(2)], which is a strong Lewis acid and therefore reacts with Lewis bases, i.e., the anions in the IL. Based on these considerations, we propose the following IT1

[Eq. (4)] in which the chloro complex anions of Zn are transferred from IL to O:

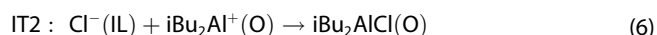


This is the facilitated ion transfer (FIT) of ZnCl_4^{2-} by iBu_2Al^+ , forming a trinuclear complex, $(\text{iBu}_2\text{AlCl}_2)_2\text{Zn}$. We do not have direct evidence for this species at this stage, however, a similar trinuclear complex, $(\text{Cl}_2\text{AlCl}_2)_2\text{Zn}$, has been identified in a molten mixture of $\text{ZnCl}_2\text{-AlCl}_3$ ^[44,45] and also in the gas phase above the mixture melt.^[46] The four *i*Bu (isobutyl) moieties in $(\text{iBu}_2\text{AlCl}_2)_2\text{Zn}$ are expected to render the complex hydrophobic enough to be dissolved in toluene. The formed complex is likely to react with iBu_2AlH , which is a bulk electron transfer (BET) reaction [Eq. (5)] in the O bulk.

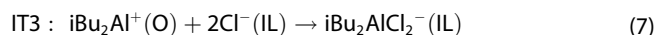


We note that the BET is a slow reaction; we observed the increase in Zn deposits even after we separated the O phase from the two-phase system after 24 h of reaction.

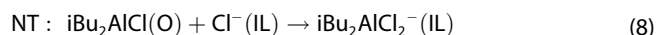
In addition to IT1, other ITs may also occur. For example, the other anionic species (Lewis base) in the IL, i.e., Cl^- , can be similarly facilitated to be transferred as shown in the following reaction [Eq. (6)]:



The produced iBu_2AlCl is known as a Ziegler-Natta catalyst. We confirmed that iBu_2AlCl (prepared from reagents, not from IT2) is highly soluble ($> 1 \text{ M}$) in toluene (O phase), implying that the standard potential for the IT2 is relatively positive. This leads to the coupling of the ET and IT.^[47] Another possible IT is the cation transfer from O to IL as



In contrast to IT2, this IT3 [Eq. (7)] is the FIT of iBu_2Al^+ by Cl^- . We qualitatively estimated which of the two ITs, IT2 and IT3, is more favourable via a partition experiment. By subtracting the reaction equations, IT2 [Eq. (6)] from IT3 [Eq. (7)], we obtain:



This [Eq. (8)] indicates the transfer of the neutral species, iBu_2AlCl , from O to IL facilitated by Cl^- . Because the transferred species is neutral in this reaction, the equilibrium constant for NT, K , is independent of the Galvani potential difference across the IL/O interface as shown in Equation (9) below.

$$K = a^{\text{IL}}(\text{iBu}_2\text{AlCl}_2^-) / \{a^{\text{O}}(\text{iBu}_2\text{AlCl}) a^{\text{IL}}(\text{Cl}^-)\} \sim [\text{iBu}_2\text{AlCl}_2^-]^{\text{IL}} / [\text{iBu}_2\text{AlCl}]^{\text{O}} \quad (9)$$

A simple partition experiment was performed, in which a toluene solution of iBu_2AlCl was made in contact with neat

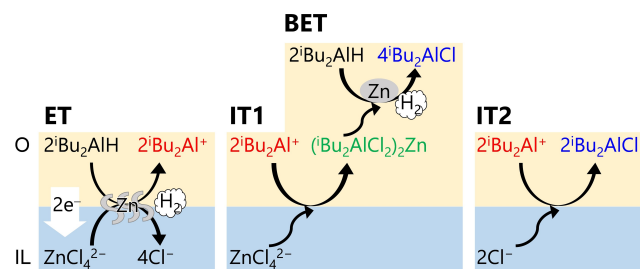


Figure 2. Plausible reaction mechanism for the Zn deposition at the IL/O interface and the O bulk, composed of the electron transfer (ET) and ion transfer (IT1 and IT2) across the IL/O interface, and bulk electron transfer (BET) reactions.

$\text{C}_{30\text{H}}\text{mimCl}$, and the partition of iBu_2AlCl was investigated (see Experimental for details). The experiment estimated that the K value is $\sim 10^{-4}$ at most, which corresponds to the relation that IT2 is significantly favourable than IT3. On the other hand, IT2 is comparable to IT1 and the preference depends on the mole fraction of ZnCl_2 , x . Figure S2 shows the photographs during the reactions at $x=0.25$ and 0.33 ; at $x=0.33$, IT1 was dominant whereas at $x=0.25$, the deposited Zn amounts at the IL/O interface and O bulk appear comparable.

Based on the above experiments and discussion, Figure 2 shows a plausible mechanism for Zn deposition at the IL/O interface. The ET reaction produces Zn metal and H_2 gas at the interface. The ET reaction is coupled with IT1 and IT2, both of which consume iBu_2Al^+ formed by the ET. IT1 transfers Zn species from the IL to O, and the BET reaction produces Zn metal and H_2 gas also in the O bulk.

Conclusion

A base metal, Zn, was successfully deposited at the IL/O interface, which is a new interface between two immiscible electrolyte solutions (ITIES), owing to its water-free nature. Zn deposition also occurred in the O bulk, which was triggered by the ion transfer of Zn species from the IL to O. A plausible reaction mechanism was presented herein, however, electrochemical measurements of this system can reveal further reaction details. This IL/O methodology could be applied to other base metals whose standard redox potentials are moderately negative such as Ni and Co and could also be applied to further negative ones such as Al and Mg if both a reducing agent in O and a metal complex in IL is designed. The experiments on these points are currently in progress in our laboratory.

Experimental Section

1-(3-hydroxypropyl)-3-methylimidazolium chloride ($\text{C}_{30\text{H}}\text{mimCl}$), a Cl^- based hydrophilic IL with a water content of $\sim 1000 \text{ ppm}$, was synthesized as previously reported.^[36] ZnCl_2 was dissolved in $\text{C}_{30\text{H}}\text{mimCl}$ at a mole fraction, x ($= n_{\text{ZnCl}_2} / (n_{\text{ZnCl}_2} + n_{\text{IL}}) = 0.25$ unless otherwise specified. As the O phase, a toluene solution of 1 M

diisobutylaluminium hydride (iBu₂AlH) was used. iBu₂AlH, a reducing agent frequently used in organic chemistry, is lipophilic because it is neutral and contains two isobutyl moieties. The two liquids, handled in a glove box filled with N₂, were made contact in a test tube. The IL and O are the lower and upper phases, respectively. The liquid-liquid two-phase system was kept still for 24 h at room temperature to complete the reaction. The deposits that appeared at the IL/O interface and in the O bulk were separated from each other and from the remaining liquids by repeated centrifugation and washing with toluene, dichloromethane, and methanol, all of which were water-free grade reagents (water content: ~10 ppm). For the SEM/EDX analysis, the deposits were placed on an Al sheet attached to an SEM sample stage, and the SEM and EDX images were taken with SU8200 (Hitachi) equipped with EMAX Evolution X-Max (Horiba). For the iBu₂AlCl partition experiment, the two-phase system of a toluene solution of 1 M iBu₂AlCl and C_{30H}mimCl (x=0) was equilibrated at room temperature for 24 h, and then the IL was separated and diluted with water to quantify possible Al(OH)₃ precipitates. In fact, no precipitation was observed, indicating that the Al concentration in the neutral aqueous solution was below the solubility of Al(OH)₃.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: electroless deposition · ionic liquids · ITIES · liquid/liquid interface · zinc

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