

Nanoparticle Preparation in Room-Temperature Ionic Liquid under Vacuum Condition

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1. Introduction

Room-temperature ionic liquid (RTIL), which was formerly called room-temperature molten salt (RTMS) and ambient-temperature molten salt (ATMS), is just a salt but a liquid salt at room temperature. Once RTIL studies were limited because at that time the “classic” RTIL, which is composed of an anhydrous metal halide combined with a heterocyclic aromatic halide, e.g., AlCl₃-1-ethyl-3-methylimidazolium chloride ([EtMeIm]Cl) and AlCl₃-1-(1-butyl)pyridinium chloride ([BuPy]Cl), was recognized as a highly moisture sensitive solvent, especially at higher Lewis acidity; that is, the RTIL must be handled in a glove box (O₂, H₂O < 1 ppm) although it exhibits relatively low viscosity and high conductivity (Wilkes et al., 1982; Hussey & Stafford, 2001; Tsuda et al., 2007.). However, discovery of moisture-stable RTILs in 1992 took their science and technology to another level (Wilkes & Zaworotko, 1992; Cooper & O’Sullivan, 1992). Current RTIL studies in most cases use “modern” RTILs having fluoroanions such as [BF₄]⁻, [PF₆]⁻, [(CF₃SO₂)₂N]⁻ (= [Tf₂N]⁻), [CF₃SO₃]⁻ (= [TfO]⁻) and other water-stable anions including [CH₃CO₂]⁻, [N(CN)₂]⁻ etc. Now RTIL’s anomalous physicochemical properties became known in all the scientific fields and a great number of applications have been proposed so far. Especially, the application to nanoparticle preparation is one of the hot topics in the RTIL studies, since RTIL can stabilize the nanoparticles yielded in the RTIL without any stabilizing agents. In fact, the number of articles on the nanoparticle synthesis in RTIL, which is often called ionic liquid (IL), has

been steadily growing since 2001. Today the nanoparticle-related article accounts for more than 10 % of all the RTIL-related articles (Figure 1). If you need general information on the nanoparticle synthesis in RTIL, we strongly recommend that you read recent review articles (Dupont & Scholten, 2010; Torimoto et al., 2010).

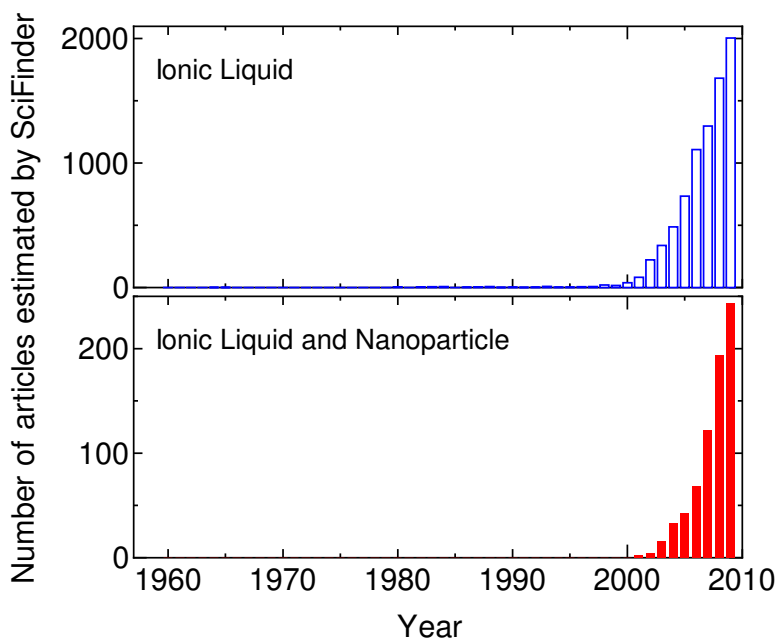


Fig. 1. Number of published articles as a function of year estimated from in-line searches using SciFinder. (top) “Ionic Liquid” and (bottom) “Ionic Liquid and Nanoparticle” were used as keywords.

The negligible vapor pressure of most RTILs at room-temperature invented a new technological concept. Only recently RTILs were beginning to be applied to vacuum technology. This must be a revolutionary incident in science history because people never would have imagined wet world in vacuum. There are many manufacturing machines and analytical instruments that require vacuum condition. Of course, they are designed under the premise that materials treated in them are dry and solid. Conventional procedures cannot be applied to a wet sample, although we occasionally get carried away with our desire to deal with it in these vacuum equipments. On the other hand, RTILs can be put in the vacuum equipments without particular care (Kuwabata et al., 2010). At this point, the numbers of researchers who exploit RTIL in vacuum equipment are quite limited. Several research groups including us have succeeded in metal nanoparticle preparation by using both RTIL and the vacuum technologies, e.g., physical vapor deposition (PVD) method (Richter et al., 2010; Prondzinski et al., 2010) and plasma deposition method (Meiss et al., 2007; Abedin et al., 2007; Baba et al., 2009; Kaneko et al., 2009; Brettholle et al., 2010).

In this chapter, we introduce our created nanoparticle preparation methods in RTIL under vacuum condition including electron beam (Imanishi et al., 2009; Tsuda et al., 2009a; Tsuda

et al., 2010a) and γ -ray radiation method (Tsuda et al., 2009a), magnetron sputtering onto IL (Hatakeyama et al., 2009; Hatakeyama et al., 2010; Kameyama et al., 2010; Khatri et al., 2008; Okazaki et al., 2008; Okazaki et al., 2009; Shishino et al., in press; Suzuki et al., 2009; Suzuki et al., in press; Torimoto et al., 2006; Tsuda et al., 2009; Tsuda et al., 2010b; Wender et al., 2010). The contents also include electrochemical applications of Pt nanoparticles produced by the methods established in our group.

2. Preparation of Room-Temperature Ionic Liquid

To prepare high-purity RTIL is quite important if RTIL is employed in the vacuum equipments because the impurities in RTIL often cause unexpected troubles and reactions (Tsuda & Hussey, 2009). Several procedures are proposed to prepare high-purity RTIL so far (Wasserscheid & Welton (eds.), 2003). For your information and guidance, here we indicate our RTIL preparation methods for nanoparticle synthesis experiments.

2.1 Hydrophobic RTIL

Liquid salts with bis((trifluoromethyl)sulfonyl)amide ($[\text{Tf}_2\text{N}]$) anions, such as 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide, $[\text{EtMeIm}][\text{Tf}_2\text{N}]$, and tri-*n*-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide, $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$, show very hydrophobic nature. This feature broadened the field of application in RTIL, e.g., lubricant (Torimoto et al., 2010) and chemical extraction (Koel (ed.), 2009). The hydrophobic RTIL is prepared by mixing exactly equal molar amounts of organic salt and $\text{Li}[\text{Tf}_2\text{N}]$ in ultrapure water. The former organic salt should be purified by an appropriate method before the preparation. This solution is agitated at room temperature for 24 hours, and the resulting hydrophobic RTIL is extracted with pure dichloromethane. This solution is washed with several portions of purified water until the wash water contains no chloride as determined by the addition of a drop or two of a dilute solution of silver nitrate. If necessary, the chloride content can also be evaluated with ion chromatography. Finally, the dichloromethane is removed by evacuating the solution at 1×10^{-3} Torr for 24 h while it is heated to 373 K. The resulting RTIL is usually colorless and very dry ($\text{H}_2\text{O} < 3$ ppm) if the original organic salt is high purity. All hydrophobic RTILs can be prepared by using this same basic method. We know alumina and charcole columns work well for the purification but we do not use these columns since the usage would give very small nanoparticle contaminants. We recommend you do not use the column when you yield nanoparticles in the RTIL.

2.2 Hydrophilic RTIL

Although "classic" chloroaluminate RTIL that dangerously reacts with water especially at higher Lewis acidity is also one of hydrophilic RTILs, the preparation method is omitted here because we introduced the method in great detail in a previous literature (Tsuda et al., 2007). Common hydrophilic RTILs usually show low viscosity and high ionic conductivity compared to the hydrophobic one; that is, you should select hydrophilic RTIL for doing electrochemistry due to the electrochemical favorable properties if you do not have any reason that you use hydrophobic RTIL. The issue related to hydrophilic RTIL is the difficulty for preparation of high-purity hydrophilic RTIL more than hydrophobic one. We know there are many preparation methods for the hydrophilic RTIL. In our laboratory, the

hydrophilic RTIL synthesis is carried out as a suspension in dry dichloromethane (DCM) while the starting materials, e.g., [EtMeIm]Cl and LiBF₄, are not fully soluble in the DCM. This solution is agitated at 300 K for 24 hours, and the halide byproducts, mainly metal halide, are removed by filtration. The resulting DCM solution containing the RTIL is washed with a little ultrapure water several times to reduce halide content in the final product. Of course, using a large volume of water in the washing process directly leads to low yield of the final product since hydrophilic RTIL easily dissolve in the water phase. Finally, the DCM is removed by evacuating the solution at 1×10^{-3} Torr for 24 h while it is heated to 373 K.

3. Nanoparticle preparation in RTILs under vacuum condition

We believe that nanoparticle preparation in RTIL will contribute to development of future technology because those nanoparticles are not covered with any covalently-adsorbed stabilizing agents that often adversely affect the physicochemical properties of the nanoparticles. The stabilization mechanism is not entirely clear but it would not be an exaggeration to say that RTIL has relatively-strong interaction with the surface of the metal nanoparticles. The nanoparticles have already been prepared in RTIL using various reaction modes. Those preparation methods and characteristics of the prepared nanoparticles were painstakingly reviewed by Dupont and Scholten (Dupont & Scholten, 2010). In cases of nanoparticle preparations by chemical reduction of metal ions or metal complexes, stabilizing agent is not required in RTIL but several kinds of byproducts must be dissolved in the resulting nanoparticle-suspended RTILs. Nanoparticle preparations in RTIL under vacuum condition, which are introduced here, are groundbreaking techniques that enable synthesis of target nanoparticles without significant amount of byproduct. In this section, we present our created nanoparticle preparation method called RTIL-magnetron sputtering method.

3.1 Magnetron sputtering onto RTIL

This procedure called RTIL-magnetron sputtering method was established by our research group (Torimoto et al., 2006). Figure 2 depicts photographs of nonvolatile fluid materials after gold sputter deposition using a common magnetron sputtering equipment. Silicone-based materials (left and center) were completely covered with a gold thin film, like gold sputtering onto a solid substrate, but RTIL (right) is definitely not the case. The color of the RTIL altered from colorless to wine-colored solution after the treatment. In fact, this interesting phenomenon is caused by surface plasmon absorption of the gold nanoparticles that exist in the RTIL. In principle, all elements that can be ejected by Ar⁺ and N₂⁺ plasma bombardment are nanoparticulated by this method. Figure 3 shows a schematic illustration of this method that uses a common magnetron sputtering apparatus except for the use of RTIL as a substrate. This method has achieved the preparation of various pure metal nanoparticles, such as Au (Hatakeyama et al., 2009; Hatakeyama et al., 2010; Kameyama et al., 2010; Khatri, et al., 2008; Okazaki et al., 2009; Shishino et al., in press; Torimoto et al., 2006; Wender et al., 2010), Ag (Okazaki et al., 2008; Suzuki et al., 2009), Pt (Tsuda et al., 2009b; Tsuda et al., 2010b), In (Suzuki et al., in press) etc., possessing particle sizes less than 10 nm in diameter without any specific stabilizing agent. Small-angle X-ray scattering study revealed initial formation mechanism of the gold nanoparticles during the sputtering process onto several 1,3-dialkylimidazolium tetrafluoroborate (Hatakeyama et al., 2009). The proposed formation mechanism that is

divided into two phases, as shown in Figure 3, concluded that both surface tension and viscosity of the RTIL are important factors for the Au nanoparticle growth and its stabilization.

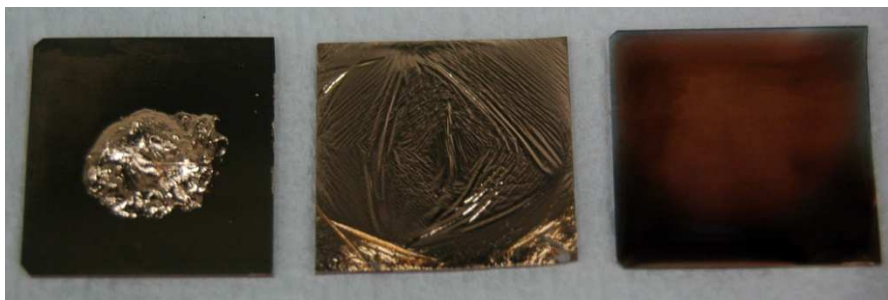


Fig. 2. Photographs of nonvolatile fluid materials placed on glass plates after gold sputter deposition using a common magnetron sputtering equipment. (left) silicone grease (center) silicone oil (right) $[\text{Me}_3\text{PrN}][\text{Tf}_2\text{N}]$. The sputtering time was 300 sec.

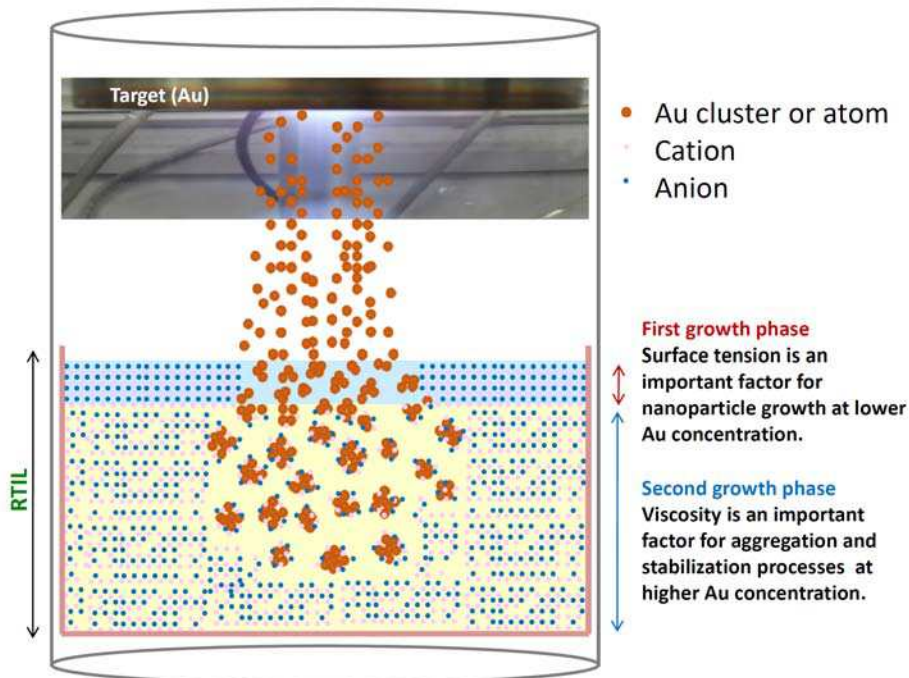


Fig. 3. Schematic illustration of Au nanoparticle formation mechanism during Au sputtering onto RTIL.

Figure 4 shows TEM images of Pt nanoparticles prepared by the RTIL-sputtering method under N_2 or Ar atmosphere. In both cases, Pt nanoparticles dispersing in the $[\text{Me}_3\text{PrN}][\text{Tf}_2\text{N}]$ were synthesized by the RTIL-sputtering method. Although any lattice fringe was not recognized in the particles, EDX, XRF, and ICP-OES analyses identified the observed

particles as Pt particles in the $[\text{Me}_3\text{PrN}][\text{Tf}_2\text{N}]$. The mean particle size strongly depended on gaseous species; the Pt particles prepared in Ar and N_2 possessed the mean diameter of 2.2 nm (Standard Deviation (SD): 0.36) and 3.3 nm (SD: 0.60), respectively. It is likely that bombardment of N_2^+ ions ejects larger Pt clusters than the case of Ar^+ ions although the details are unknown at this moment. These Pt nanoparticles were stable without aggregation more than 6 weeks at room temperature while a stabilizing agent was never added to the RTIL. This simple process can reproducibly yield Pt nanoparticles. Figure 5 depicts TEM images of Pt nanoparticles obtained by the Pt sputtering onto $[\text{Me}_3\text{PrN}][\text{Tf}_2\text{N}]$

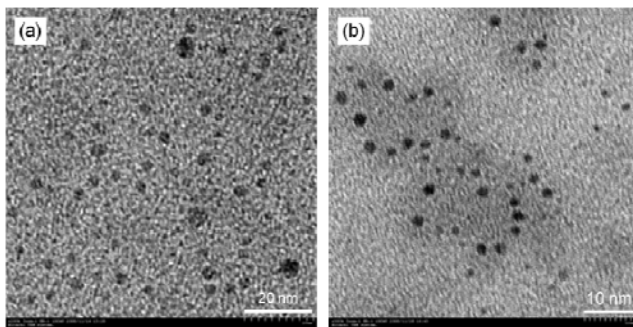


Fig. 4. TEM images of Pt nanoparticles synthesized by the RTIL-sputtering method under (a) N_2 and (b) Ar atmosphere. The sputtering time and current were 300 sec and 40 mA, respectively. The RTIL was $[\text{Me}_3\text{PrN}][\text{Tf}_2\text{N}]$.

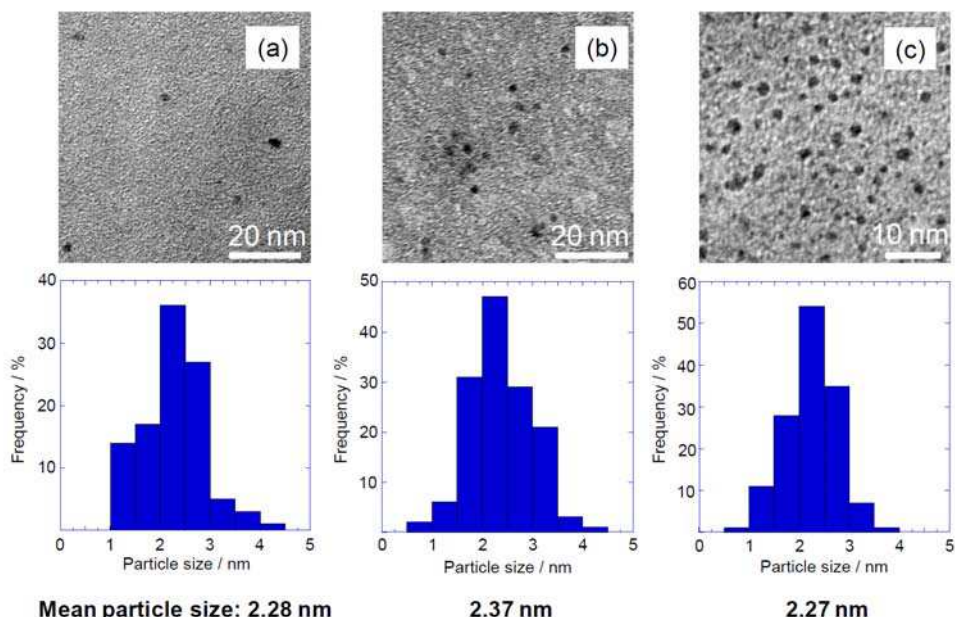


Fig. 5. TEM images and their size distribution diagrams at different sputtering time. (a) 300 sec; (b) 900 sec; (c) 1800 sec. The induced gas was Ar.

at different sputtering times and their size distribution diagrams constructed from the TEM images. The induced gas was Ar. All the Pt nanoparticles have mean particle size of ca. 2.3 ~ 2.4 nm, and the particle size was of little relevance to the sputtering time. But the Pt concentration in the sputtered RTILs linearly increased with increasing the sputtering time, suggesting that the number of Pt nanoparticles show a linear increase with the sputtering time. What is special about the Pt nanoparticles produced by the use of this method is that there is little change in the particle size even if the Pt-dispersed RTIL is heated to 373 K, but the size becomes slightly large after heat treatment exceeding 423 K. The mean particle size (ca. 3.7 ± 0.1 nm) is substantially constant value independently of the heat temperature if the heat temperature is 423 ~ 573 K. 573 K was chosen as the maximum heat temperature to avoid pyrolysis of the RTIL.

Interestingly, this technique also enables to produce alloy nanoparticles by placing different elements as a target. Figure 6 shows the first attempt to prepare Au-Ag alloy nanoparticles

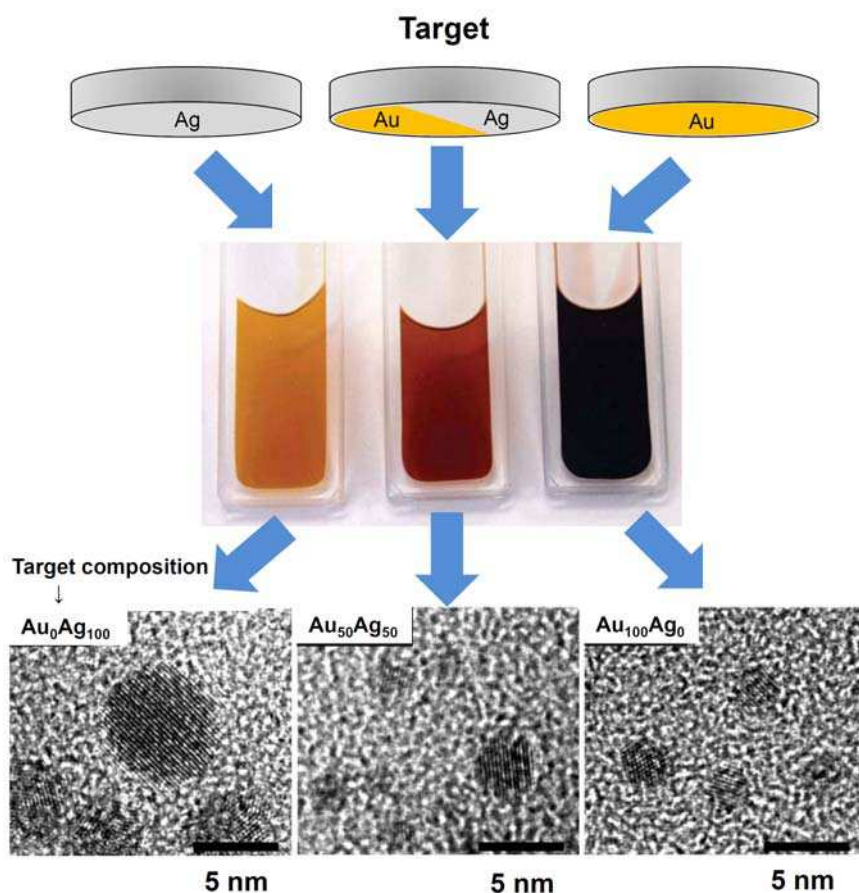


Fig. 6. Photographs of [BuMeIm][PF₆] after sputtering experiments at Au-Ag targets having different surface area ratio and TEM images of the resulting nanoparticles obtained at each Au-Ag targets.

by the sputtering method with a target having Au and Ag plates of the same area (Okazaki et al., 2008). Color of the [BuMeIm][PF₆] altered with the target composition. As recognized from TEM images, the mean particle size enlarges with an increase in the Ag area in the target. In addition to this, the chemical composition and the optical properties of the deposited alloy nanoparticles varied with the surface area ratio of Au to Ag, too. This approach will be a novel alloy nanoparticle fabrication method because of the simple process that can directly control the alloy composition by changing the ratio of the metal areas in the target.

3.2 Future difficulties about the RTIL- magnetron sputtering method

Due to the high physicochemical stability of RTILs, above-mentioned RTIL-vacuum techniques can produce even base-metal nanoparticles that cannot be produced in conventional aqueous or organic solvents. Future challenge in this field will be how we collect the metal nanoparticles suspended in RTILs and how we develop a metal nanoparticle mass production method. Regarding the former matter, we found a facile way that is adsorption of the suspended nanoparticles on a solid substance (Kameyama et al., 2010; Okazaki et al., 2009; Tsuda et al., 2009b; Tsuda et al., 2010b). Nanoparticles are stably suspended in RTIL by the interaction with ionic species existing around the nanoparticles. Heating of the suspension on a glassy carbon plate is likely to weaken the interaction, resulting in their adsorption on the plate. As described in next section, when the glassy carbon plate, on which Pt nanoparticles were adsorbed, is used as an electrode, it exhibits high catalytic activities against electrochemical O₂ reduction due to the adsorbed Pt nanoparticles.

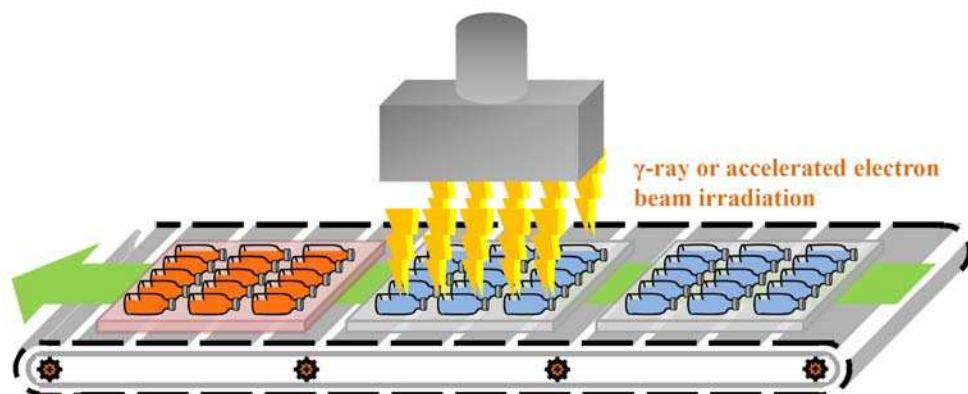


Fig. 7. Schematic illustration of an existing common γ -ray or accelerator electron beam irradiation industrial plant. The RTIL solution with metal salts is encapsulated in the glass ampoules under vacuum or Ar atmosphere condition.

A recent approach carried out at an existing common accelerator electron beam or γ -ray irradiation industrial plant for sterilizing medical kits may be a key in order to overcome the mass production issue (Tsuda et al., 2009a; Tsuda et al., 2010a). As illustrated in Fig. 7, if the glass ampoules, in which RTIL solution with metal salts are encapsulated under vacuum condition or inert gas condition, placed on the container are automatically transferred to irradiation position, metal salts should be reduced to metal state in the ampoules without

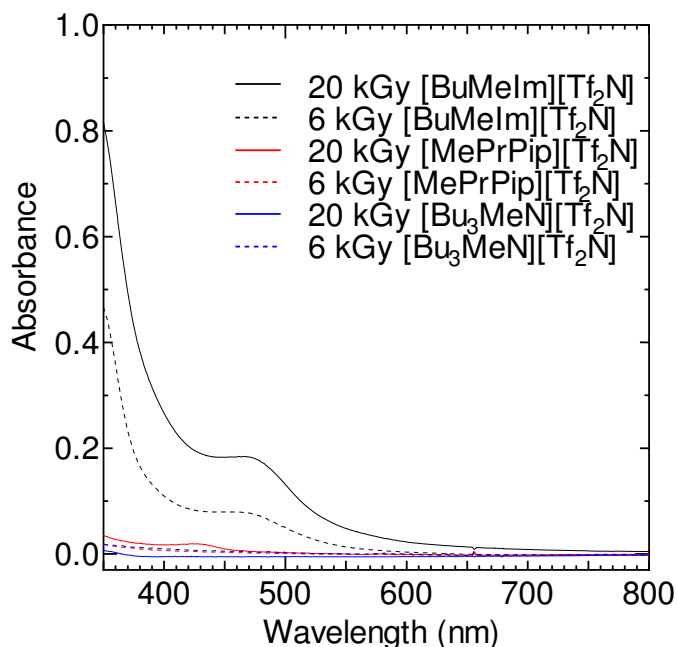
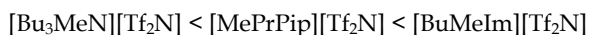


Fig. 8. UV-vis spectra of the RTILs with $0.5 \text{ mmol L}^{-1} \text{ NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ after accelerator electron beam irradiation at 20 or 6 kGy.

contamination derived from air. This would be one way to churn out metal nanoparticles because the industrial plant can irradiate 200 glass ampoules \times 100 mL at a time. The irradiation time of accelerated electron beam and γ -ray are 7 sec and 3 hrs, respectively, if the irradiation dose is 20 kGy. These electron beam (Imanishi et al., 2009; Tsuda et al., 2009a; Tsuda et al., 2010a) and γ -ray irradiation (Tsuda et al., 2009a) methods exploit solvated electrons and/or radicals yielded during the beam irradiation to the RTIL containing metal salts so as to synthesize metal nanoparticles. *Note that primary electron beam and γ -ray themselves cannot directly contribute to nanoparticle preparation because of their considerably strong energy!* In other words, no solvated electrons and no radicals would result in no nanoparticles. It has been already verified through the experiments using several $[\text{Tf}_2\text{N}]$ -based RTILs. As a typical example, variation in UV-vis spectra of the RTILs with $0.5 \text{ mmol L}^{-1} \text{ NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ after accelerator electron beam irradiation is shown in Fig. 8 (Tsuda et al., 2009a). The accelerator electron beam irradiation of 20 kGy to $[\text{BuMeIm}][\text{Tf}_2\text{N}]$ and $[\text{MePrPip}][\text{Tf}_2\text{N}]$ resulted in appearance of broad absorption peak, which is attributable to plasmon absorption of Au nanoparticles, whereas irradiation to $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$ caused almost no spectrum change. In case of electron beam irradiation at 6 kGy, only $[\text{BuMeIm}][\text{Tf}_2\text{N}]$ showed spectral change. These results indicate that Au nanoparticle generation in the RTILs become easier in the following order:



Our recent results on mass spectrometry measurements for the RTILs also support this order. Considering the fact that $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$ is more radiochemically-stable than

[BuMeIm][Tf₂N] (Bossé et al., 2008; Behar et al., 2001; Grodkowski et al., 2002; Shkrob et al., 2009), it is highly likely that radiochemically-unstable RTIL tends to generate Au nanoparticles. TEM observation revealed that the Au nanoparticles prepared in the experiments using the [BuMeIm][Tf₂N] solution had mean particle size of 26.4 nm at 20 kGy irradiation and 7.6 nm at 6 kGy. We have succeeded in many types of nanoparticle preparation by using this method, e.g., Cu, Pt, etc. (Tsuda et al., 2010a).

4. Application of metal nanoparticle prepared in RTILs under vacuum condition

In contrast to a simple one-electron oxygen reduction reaction (ORR) in RTIL (Tsuda & Hussey, 2009), it is well-known that the ORR occurs with several reaction paths in aqueous solution. However, Pt catalysts induce the ORR with the four electron reduction that is formulated as:



This reaction is the key to put almost all fuel cell systems to practical use. Very recently we have reported that a Pt-supported glassy carbon electrode (Pt-GCE), which was obtained by heat treatment of the RTIL with Pt nanoparticles that were prepared by the RTIL-magnetron sputtering method spreaded on a glassy carbon (GC), shows a favorable catalytic activity for oxygen reduction reaction (ORR) in 0.5 M H₂SO₄ aqueous solution (Tsuda et al., 2009b). Also we revealed that important information on the surface condition of Pt nanoparticles on the Pt-GCE and on the catalytic ability of the Pt nanoparticles per unit area. The former was examined with infrared reflection absorption spectroscopy, and the latter was determined by a common electrochemical method. Figure 9a and b indicate infrared reflection spectra for pure [Me₃PrN][Tf₂N] and Pt-GCE rinsed with 1.67 M KOH *iso*-propanolic solution. After rinsing the Pt-GCE, there was no peak related to the RTIL, i.e., bare Pt surface appeared.

In order to determine active surface area of the Pt nanoparticles on the Pt-GCE, carbon monoxide, CO, stripping voltammetry was conducted. Steady state cyclic voltammograms recorded at CO-absorbed Pt-GCEs are shown in Fig. 10a-c. These Pt-GCEs were prepared by heat treatment temperature of 473, 523, and 573 K. At first cycle, in all figures, an obvious oxidation wave corresponding to CO stripping appears at 0.8 ~ 0.9 V, and the wave completely disappears at second cycle. The CO stripping wave becomes large with increasing the heat treatment temperature for the Pt-supported process. The Pt areas at the treatment temperature of 473, 523, and 573 K were 0.031, 0.100, and 0.200 cm²-Pt, respectively. Catalytic activity of these Pt-GCEs was examined by cyclic voltammetry in O₂-saturated 0.5 mol L⁻¹ H₂SO₄ aqueous solution. The observed current densities were based on the active surface area of the Pt nanoparticles. In each case, a distinct reduction wave for ORR appeared (Fig. 11). What is interesting is that the catalytic activity per unit area was enhanced at lower heat treatment temperature. In fact, we expected an opposite result; that is, the catalytic activity per unit area increases as the Pt-supported temperature increases because our previous result was that the reduction current for ORR increased at higher heat treatment temperature (Tsuda et al., 2009b). To understand this unexpected result precisely, surface morphology of these electrodes was observed by SEM. Figure 12 exhibits typical SEM images at various Pt-supported temperatures. Here, bright moiety should be Pt since

Pt nanoparticles can release more secondary electrons than the GC substrate. SEM images obviously whiten as the Pt-supported temperature increases, i.e., amount of deposited Pt

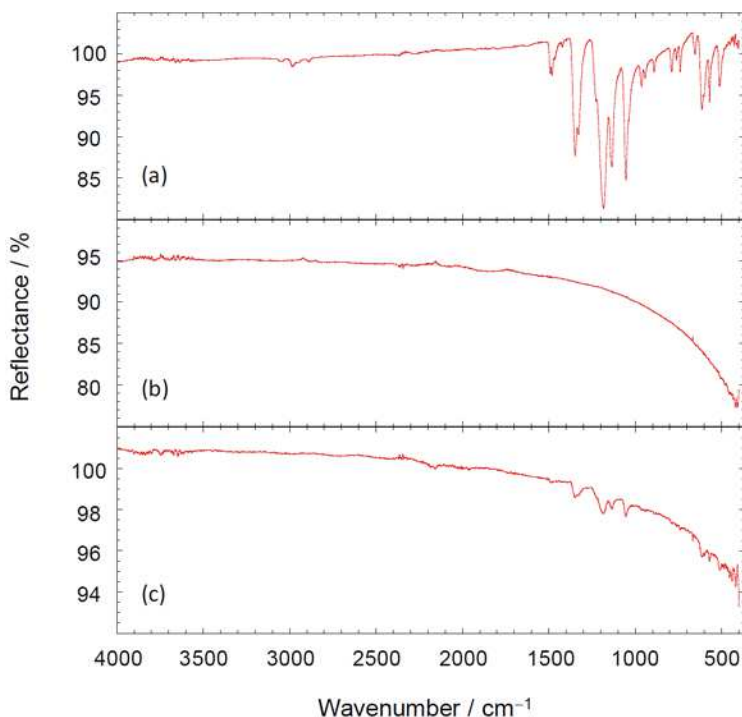


Fig. 9. Reflective FT-IR spectra of Pt-GCE prepared at 573 K. (a) $[\text{MePrN}][\text{Tf}_2\text{N}]$ on GC without heat treatment; (b) Pt-GCE rinsed with KOH iso-propanolic solution and nitric acid; (c) Pt-GCE rinsed with acetonitrile. The Pt nanoparticles were prepared by RTIL-magnetron sputtering method.

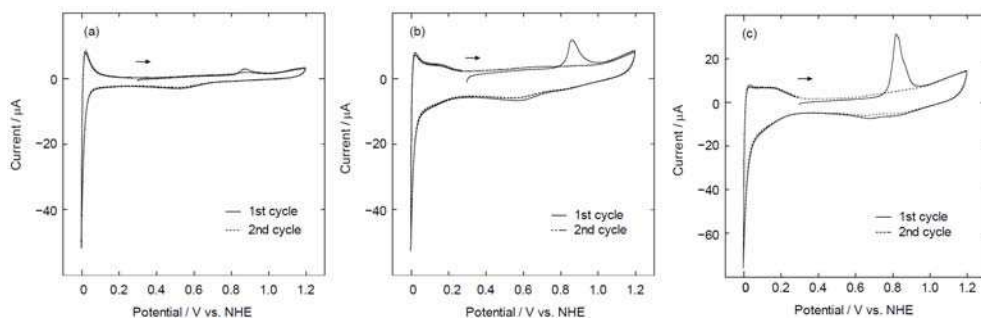


Fig. 10. Cyclic voltammograms recorded at Pt-GCEs, on which CO monolayer was absorbed. The heat temperatures for the Pt-GCE preparation were (a) 473 K, (b) 523 K, and (c) 573 K. The electrolyte was 0.5 M H_2SO_4 aqueous solution at 298 K. The scan rate was 10 mV s^{-1} . The Pt nanoparticles were prepared by RTIL-magnetron sputtering method.

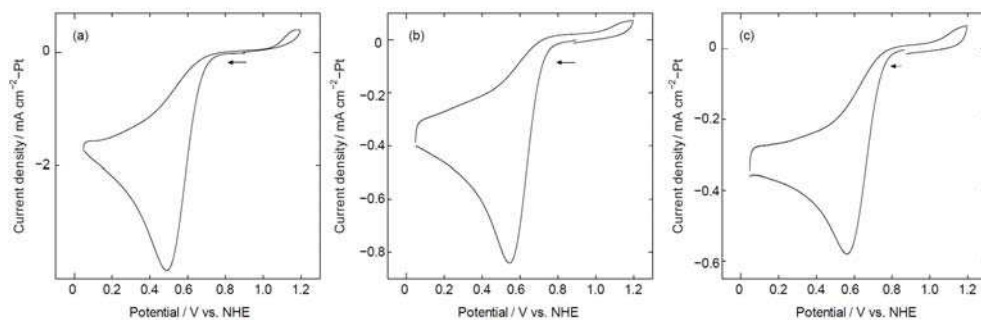


Fig. 11. Cyclic voltammograms recorded at Pt-GCEs in O_2 -saturated 0.5 M H_2SO_4 aqueous solution at 298 K. The heat temperatures for the Pt-GCE preparation were (a) 473 K, (b) 523 K, and (c) 573 K. The scan rate was 10 mV s^{-1} . The Pt nanoparticles were prepared by RTIL-magnetron sputtering method.

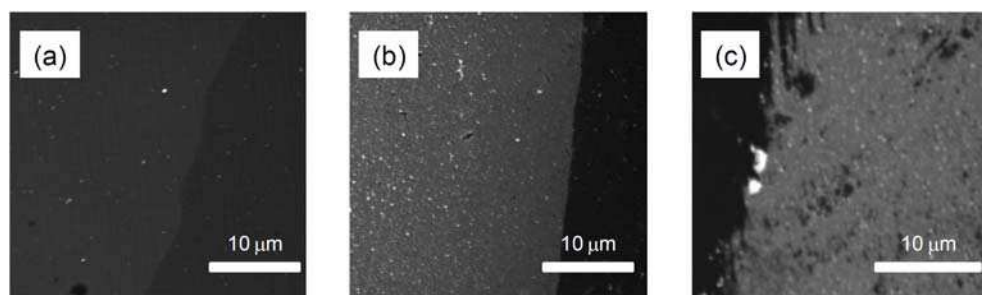


Fig. 12. SEM images of Pt-GCEs prepared at (a) 473 K, (b) 523 K, and (c) 573 K. The Pt-GCEs were rinsed with KOH iso-propanolic solution and nitric acid.

nanoparticles increases with the temperature. Therefore, increment in apparent reduction current for ORR should be caused by increase in Pt nanoparticles supported on the GC. However, as shown in Fig. 11, the catalytic activity per unit area for the ORR becomes small at higher Pt-embedded temperature. It is highly likely that effective Pt surface area decreases if the Pt-supported temperature increases because a dense Pt nanoparticle layer is formed on GC at higher temperature (Fig. 12).

Several research groups point out that RTIL improves a catalytic ability for ORR (Li et al., 2009; Wang et al., 2008; Wu et al., 2009; Yu et al., 2008; Zhao et al., 2006). We have investigated ORR using a RTIL-modified Pt-GCE. The RTIL-modified Pt-GCE was prepared by rinsing Pt-GCE with dry acetonitrile, not 1.67 M KOH iso-propanolic solution. The surface state of the Pt-GCE was examined with infrared reflection absorption spectroscopy. As shown in Fig. 9c, the Pt-GCE rinsed with dry acetonitrile indicated weak absorption related to the $[Me_3FrN][Tf_2N]$ RTIL. The surface area of the RTIL-modified Pt-GCE was estimated by using CO stripping voltammetry, like an original Pt-GCE described above. Figure 13 indicates cyclic voltammograms recorded at the RTIL-modified Pt-GCE on which CO was absorbed. There is a no CO stripping wave, but is a reduction wave for hydrogen evolution. It implies that the RTIL-modified Pt-GCE is electrochemically active without CO poisoning. As expected, RTIL-modified Pt-GCE with CO poisoning reduced oxygen electrochemically (Fig. 14a). Voltammograms recorded at different initial potentials,

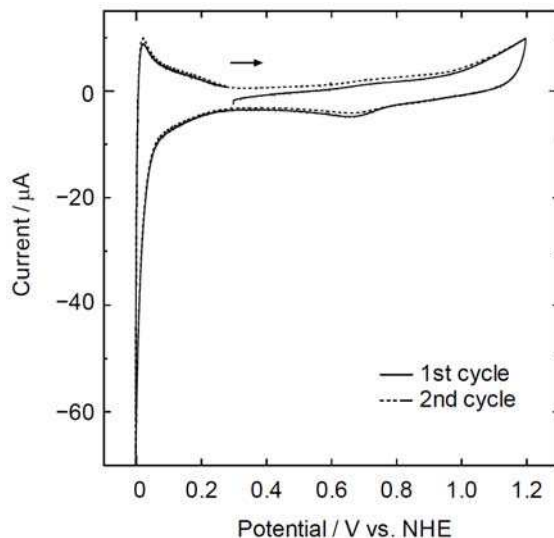


Fig. 13. Cyclic voltammograms recorded at a RTIL-modified Pt-GCE, on which CO monolayer was absorbed. The heat temperature for the Pt-GCE preparation was 573 K. The electrolyte was 0.5 M H_2SO_4 aqueous solution at 298 K. The scan rate was 10 mV s^{-1} .

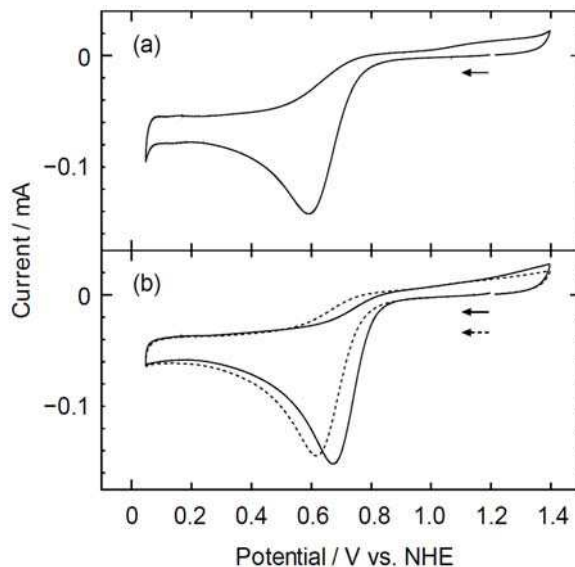


Fig. 14. Cyclic voltammograms recorded at (a) a RTIL-modified Pt-GCE with CO poisoning and (b) (—) a RTIL-modified Pt-GCE and (---) an original Pt-GCE in O_2 -saturated 0.5 M H_2SO_4 aqueous solution at 298 K. The heat temperature for the Pt-GCE preparation was 573 K. The scan rate was 10 mV s^{-1} . The Pt nanoparticles were prepared by RTIL-magnetron sputtering method.

e.g., +0.70 V, also showed a remarkably-similar oxygen reduction wave. In fact, a number of groups report an effective interaction between RTIL and metal nanoparticles (Dupont & Scholten, 2010; Torimoto et al., 2010). Probably the interaction prevents CO adsorption onto the Pt nanoparticles. Catalytic activity of the RTIL-modified Pt-GCE without CO poisoning toward ORR was investigated by cyclic voltammetry (Fig. 14b). This RTIL-modified electrode showed better catalytic ability than an original Pt-GCE. The reason is not clear but the high activity would be due to the high oxygen solubility in the RTIL (Tsuda & Hussey, 2009). Using $[\text{Me}_3\text{PrN}][\text{Tf}_2\text{N}]$ RTIL as a solvent and a material, we succeeded in fabrication of a novel electrode, which has both O_2 reduction catalytic ability and anti-CO poisoning nature.

5. Concluding remarks

RTIL is the first liquid that works well as reaction media even under vacuum condition. To apply RTIL science to the vacuum technology likely contributes to further development of science and technology, although modern vacuum technology already supports our comfortable daily lives. Especially we believe nanoparticle preparation by the use of the cutting-edge technology that combines RTIL and vacuum condition will be a future key technology in energy device and photonics material because even base metal, alloy, and semiconductor nanoparticles can be yielded by the technology without difficulty.

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Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. This book, consisting of 29 chapters gathered in 4 sections, reviews in detail and compiles information about some important physical-chemical properties of ILs and new practical approaches. This is the first book of a series of forthcoming publications on this field by this publisher. The first volume covers some aspects of synthesis, isolation, production, modification, the analysis methods and modeling to reveal the structures and properties of some room temperature ILs, as well as their new possible applications. The book will be of help to chemists, physicists, biologists, technologists and other experts in a variety of disciplines, both academic and industrial, as well as to students and PhD students. It may help to promote the progress in ILs development also.

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