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### ARTICLE

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# Single-step Preparation of Two-dimensionally Organized Gold Particles via Ionic Liquid/Metal Sputter Deposition

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Sputtering of noble metals, such as Au, Ag, Pd, and Pt onto room-temperature ionic liquids (RTILs) enabled the formation of monoparticle films composed of spherical noble metal nanoparticles on the liquid surface only when the RTILs used contained hydroxyl-functionalized cations as a component. Sputter deposition of these metals under the same conditions simply produced well-dispersed metal particles without formation of any films on the solution surface when pure RTILs with non-functionalized cations were employed. Anionic species, even those containing a hydroxyl group, did not significantly affect formation of the particle film on the RTIL surface or dispersion of particles in the solution. The size of Au particles could be controlled by varying the sputtering condition regardless of the two-dimensional particle density, which was determined by the composition of RTILs used. An Au monoparticle film on the RTIL surface was easily transferred onto various solid substrates via the horizontal liftoff method without large aggregations even when the substrate surface was highly curved.

### Introduction

Assembly of size-quantized nanoparticles of metals or semiconductors has been intensively studied to enhance unique properties of nanoparticles and/or to develop collective properties induced by the electronic or optical interactions between nanoparticles for applications to plasmonic materials,<sup>1-3</sup> catalysts,<sup>4</sup> or electronic devices.<sup>5</sup> Various strategies for assembling nanoparticles into different structures have been reported.<sup>6, 7</sup> For example, selfassembly has been one of the powerful tools to spontaneously organize monodisperse particles into ordered structures by the use of interactions between particles, such as van der Waals interaction, electrostatic interaction, and hydrogen bonding.<sup>8</sup> Multi-layered films composed of metal nanoparticles as building blocks could be fabricated on solid substrates via layer-by-layer deposition,<sup>9</sup> in which the electrostatic attraction between particles was utilized to alternately immobilize particles or polymers having different charges. Microcontact printing, developed by Whiteside et al.,<sup>10</sup> was employed to easily and massively prepare sub-micrometer-scale patterned assemblies of nanoparticles with the use of elastomeric stamps and particle dispersions as an ink.<sup>11</sup> Furthermore nanoparticle ensembles have reported to exhibit tunable electronic and optical properties depending on the distance between building-block particles.<sup>12, 13</sup> Thus, Langmuir techniques,<sup>14-18</sup> based on the liquid-air interface, appear to be more advantageous for arranging nanoparticles in a two-dimensional structure, in which particle distance can be controlled by varying the compressed surface area or

surface pressure with the use of a movable barrier. It has been reported that metal-insulator transition of Ag nanoparticle films prepared on the surface of water was observed by varying the surface pressure of the Ag monoparticle layer.<sup>19</sup> Single-electron transistors could be fabricated by transferring the Au monoparticle layer from the water surface to solid substrates on which collecting electrodes were fabricated.<sup>20</sup>

Most of the nanoparticles used as building blocks have been synthesized by colloidal syntheses, in which the surfaces of the resulting nanoparticles were coated with ligand molecules, such as alkyl amines or alkyl thiols, to prevent coalescence between nanoparticles even if they have been incorporated in assemblies. On the other hand, room-temperature ionic liquid (RTILs) exhibited unique features compared with those of water or conventional organic solutions<sup>21, 22</sup> and they have attracted much attention as media for preparation of inorganic nanoparticles.<sup>23-26</sup> Recently, we have reported another simple method for the synthesis of noble metal nanoparticles by metal sputter deposition in RTILs under vacuum.<sup>27</sup> This RTIL/metal sputtering technique enabled clean preparations of pure metal nanoparticles of Ag,<sup>28</sup> Au,<sup>29</sup> Cu,<sup>30</sup> Pd,<sup>31</sup> and Pt<sup>32, 33</sup> and alloy particles of AgAu,<sup>34</sup> AuCu,<sup>35</sup> AuPt,<sup>36</sup> and AuPd.<sup>37</sup> These particles were stable and uniformly dispersed in RTILs without the use of additional stabilizing agents such as polymers or thiol compounds, so that bare surfaces of the particles were exposed to the solution, with the expectation of high catalytic activities. However, it has been difficult to isolate these particles from RTILs for the purpose of utilization as building blocks because the presence of

bare surfaces exhibited a strong tendency for nanoparticles to coalesce into larger ones.

In this study, we developed a novel strategy to prepare a monoparticle film on the RTIL surface via RTIL/metal sputtering. Sputter deposition of Au onto RTILs having hydroxyl groups in cations produced thin films on their surfaces. The thus-obtained films were Au monoparticle films and could be transferred onto solid substrates, with the size of Au particles and their two-dimensional density being independently controlled. As related subjects, continuous films with relatively large thickness have been successfully prepared by metal sputtering onto various kinds of liquids. Uniform films composed of a binary Ag/Cr layer<sup>38</sup> or thick Si layer<sup>39</sup> were fabricated on RTILs by sputter deposition of corresponding metals. The surface of conventional viscous liquids such as silicone  $oils^{40-42}$  and vegetable  $oils^{43}$  could also be employed for the preparations of continuous metal films or island-like metal aggregates via metal sputtering. However, to the best of our knowledge, there has no study on two-dimensionally assembled metal particles having a desired size on the RTIL surface.

### Experimental

### Materials

RTILs used were 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (HyEMI-BF4) (Ionic Liquids Technologies Inc.), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF4) (Kanto Chemical Co., Inc.), 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF4) (Kanto Chemical Co., Inc.), 1-octyl-3methylimidazolium tetrafluoroborate (OMI-BF4) (Merck Co., Inc.), 1-(2-hydroxyethyl)-3-methylimidazolium

bis(trifluoromethanesulfonyl)amide (HvEMI-TFSA) (Solvionic Co.), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (EMI-TFSA) (Kanto Chemical Co., Inc.), N,N,N-trimethyl-Npropylammonium bis(trifluoromethanesulfonyl)amide (TMPA-TFSA) (Kanto Chemical Co., Inc.), 2-hydroxyethyl-N,N,Ntrimethylammonium bis(trifluoromethanesulfonyl)amide (Ch-TFSA) Technologies 1-(4-sulfobutyl)-3-(Ionic Liquids Inc.), methylimidazolium bis(trifluoromethanesulfonyl)amide (SBMI-TFSA) (Solvionic Co.), 1-ethyl-3-methylimidazolium ethylsulfate (EMI-EtSO4) (Merck Co., Inc.), 1-ethyl-3-methylimidazolium Co.), acetate (EMI-Ac) (Sigma-Aldrich 1-butvl-3methylimidazolium thiocyanate (BMI-SCN) (Fluka Co.), 1-butyl-3methylimidazolium (L)-lactate (BMI-lactate) (Acros Organics), and (2-hydroxyethyl)ammonium formate (HyEA-formate) (Ionic Liquids Technologies Inc.), the chemical structures of which are shown in Table S1. The RTILs were dried at 393 K for 3 h with vigorous stirring under a vacuum condition before use. Monodisperse polystyrene (PS) beads of 10 µm in diameter suspended in an aqueous solution (content of PS: 2.5 wt%) were purchased from Funakoshi Co., Ltd. Acetonitrile supplied by Kishida Reagents Chemicals was used as received.

#### Preparation of an Au monoparticle film on the RTIL surface and its immobilization on solid substrates

An 80 mm<sup>3</sup> portion of dried RTIL was spread on a glass plate of 4  $cm^2$  in area that was horizontally set in a sputter coater (JEOL, JFC-1300). The surface of the RTIL was located at a distance of 35 mm from the Au target (99.99% in purity, diameter: 5 cm). Sputter deposition of Au on the RTIL was carried out for 30, 70, 150, 300, 600, or 1200 s with a discharge current of 10 mA under an Ar pressure of ca. 20 Pa at room temperature. The thus-obtained

monoparticle film on RTIL was transferred onto the flat surface of a solid substrate, such as a quartz glass plate, highly oriented pyrolytic graphite (HOPG) or silicon wafer, by a horizontal liftoff procedure in which the surface of the solid substrate was brought down parallel to the RTIL surface and lightly touched the film formed on the solution surface. Each of the thus-obtained Au film-immobilized substrates was rinsed with an adequate amount of acetonitrile for removing the excess amount of RTIL from its surface.

# Immobilization of the Au monoparticle film on a PS bead array surface

PS beads in an aqueous solution were isolated by centrifugation and then dispersed again in 1 cm<sup>3</sup> of ethanol. A 34 mm<sup>3</sup> portion of the thus-obtained suspension containing PS beads  $(4.6 \times 10^7 \text{ particles/cm}^3)$  was spread on a 4 cm<sup>2</sup> area of an indium tin oxide (ITO) substrate, followed by drying in air at room temperature. The PS beads-immobilized ITO substrate was horizontally attached to an Au monoparticle film on RTIL that had been deposited by Au sputtering for 300 s followed by washing with acetonitrile to remove the excess amount of RTIL adsorbed.

### Characterization

Extinction spectra of Au films transferred onto quartz plates were obtained with an Agilent Technology 8453A spectrophotometer. A transmission electron microscope (TEM; HITACHI H-7650) with an acceleration voltage at 100 kV was used for measurements of the size and density of Au particles in the films. The sample for TEM measurements was prepared by transferring the Au monoparticle film on the RTIL onto a copper TEM grid covered with amorphous carbon overlayers (Oken Shoji, STEM100Cu). The excess amount of RTIL on the TEM grid was removed by washing with acetonitrile, followed by drying under vacuum. For observation of nanoparticles dispersed in RTILs, TEM samples were prepared by dropping a particle containing RTIL solution onto a TEM grid, followed by washing with acetonitrile. The surface morphology of the Au monoparticle film transferred onto HOPG was observed by using an atomic force microscope (AFM) (Veeco Instruments Inc., NanoScope IIIa) in air. Scanning electron microscopy (SEM) was carried out for the Au monoparticle film transferred onto PS beads with a Hitachi S1500 SEM. High-resolution SEM images were obtained with a JEOL JSM-7500F FE-SEM equipped with an EDX analyser (JEOL, JED-2300F). The Fourier transform infrared (FT-IR) spectrum of an Au monoparticle film immobilized on a silicon wafer was measured by a JASCO FT/IR-6100 spectrometer.

### **Results and discussion**

It was reported in our previous papers<sup>27, 34</sup> that sputter deposition of Au onto RTILs, such as EMI-BF4, BMI-PF6 and TMPA-TFSA, produced nanoparticles uniformly dispersed in the solution. However, sputter deposition of Au onto HyEMI-BF4, cation of which is functionalised with hydroxyl group, produced an Au particle film on the surface but not nanoparticles uniformly dispersed in the solution. Figure 1a shows a photograph of a film prepared by Au sputter deposition for 300 s. The Au film showing a blue colour was uniformly deposited on the whole surface of HyEMI-BF4 without formation of cracks or defects. Some cracks in the film could be made by slightly shaking the RTIL solution spread on the glass plate. The thus-obtained Au film could be transferred onto a quartz glass substrate by a horizontal liftoff method as shown in Fig.

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1b, and the RTIL solution underneath the film was observed to be colourless. This indicated that Au sputter deposition onto HyEMI-BF4 produced an Au film on the solution surface without dispersing any Au particles in the bulk solution phase, being different from the case of EMI-BF4 where Au particles uniformly dispersed in the solution phase were only observed after the sputter deposition and then the extinction spectrum of the Au particle-dispersed EMI-BF4 indicated a weak peak at 510 nm assigned to the localized surface plasmon resonance (LSPR) peak as shown in Fig. S1. Figure 1c shows the extinction spectra of Au films transferred onto quartz glass substrates from the surface of HyEMI-BF4. Each film exhibited a peak at around 550 nm, which was assignable to the LSPR peak of spherical Au nanoparticles. With an increase in the sputtering time of Au from 30 to 600 s, the intensity of the LSPR peak increased along with a slight red shift of peak wavelength from 532 to 558 nm. This suggested that the films on the HyEMI-BF4 surface were composed of Au nanoparticles and that the amount of Au deposited could be controlled by the sputtering time.

Figure 2 shows TEM images of Au films transferred onto TEM grids. Au sputter deposition for 300 s or less made a monoparticle film consisting of spherical Au nanoparticles, which became larger with an increase in sputtering time. The average size of Au nanoparticles and their two-dimensional density, estimated from TEM images, are shown in Figure 3. The size of Au particles increased from 2.7 to 5.1 nm with increase in sputtering time from 30 to 300 s, while the two-dimensional particle density remained almost constant at ca.  $4.2 \times 10^{12}$  particles cm<sup>-2</sup>. These results indicated that the sputtering time for Au deposition determined the size of Au particles trapped on the HyEMI-BF4 surface without changing their density, probably because small Au particles as nuclei were formed on the HyEMI-BF4 surface in the initial stage of



**Figure 1** (a) A top view photograph of an Au film deposited on the HyEMI-BF4 solution surface via RTIL/metal sputtering. The sputtering time of Au was 300 s. (b) A photograph of transfer of half of the Au film deposited on HyEMI-BF4 onto a glass plate by a horizontal liftoff method. (c) Extinction spectra of Au films transferred onto quartz glass plates. The sputtering time in the unit of seconds, used for Au deposition, is shown in the figure.



**Figure 2** TEM images of Au particle layers prepared by Au sputtering for different times. Au sputtering was carried out with a discharge current of 10 mA for 30 (a,b), 70 (c,d), 300 (e,f) and 600 s (g,h). The images in panels b, d, f, and h are magnified ones of panels a, c, e, and g, respectively. The bars in the images represent a length of 20 nm.

Au sputter deposition and then prolonged Au sputtering caused predominant crystal growth on these particles without formation of additional nuclei. The size of Au nanoparticles, giving a hexagonally close-packed monoparticle film with a particle density of  $4.2 \times 10^{12}$ particles cm<sup>-2</sup>, was estimated to be ca. 5.2 nm. This value agreed well with the particle size, 5.1 nm, observed with 300-s sputter deposition, indicating that a monoparticle film of close-packed Au particles could be prepared by sputter deposition of Au for 300 s under the present conditions. It is notable that the discharge current employed for sputtering target materials could also influence the size of resulting particles deposited on the RTIL surface: change in the sputtering current from 10 to 40 mA increased the amount of Au deposited on the HyEMI-BF4 surface even when the sputtering time was constant at 30 s, resulting in an increase in Au particle size in the monoparticle film from 2.7 to 4.7 nm (Fig. S2). It was worth noting that prolonged sputtering of Au onto HyEMI-BF4 for more



**Figure 3** (a) Average size of Au particles and (b) their twodimensional density in a monoparticle film prepared by Au sputtering onto the HyEMI-BF4 surface for various sputtering times. Error bars in panel a represent the standard deviations of particles.

than 600 s produced a multilayer film of Au nanoparticles as shown in Fig. 2 g and h. Since clear images of individual particles in the film were difficult to obtain because of the superimposition of the images of particles in Fig. 2h, the obtained films were pulverized by sonication in acetonitrile for 30 min, followed by TEM measurements to investigate the size and shape of particles. As shown in Fig. S3 a and b, most particles in the films were directly connected or coalesced with each other to form large aggregates. The average size of spherical Au particles in the multilayer films increased to 6.1 and 6.4 nm after the sputter deposition for 600 and 1200 s, respectively, being much larger than that obtained with 300-s sputter deposition, 5.1 nm (Fig. 3a). The results indicated that the Au particles on the HyEMI-BF4 surface became enlarged with an increase in the sputtering time, even when their particle size exceeded the appropriate value for the formation of hexagonally close-packed monoparticle layer in the present condition, ca. 5.2 nm, as aforementioned. This situation could induce the collapse of the monoparticle layer on the HvEMI-BF4 surface, resulting in that the particles on the solution surface formed multilayer films composed of large aggregates as illustrated in Fig. S3c.

Figure 4a shows a typical AFM image of a monoparticle film prepared by Au sputtering for 300 s that was transferred onto an HOPG substrate from the HyEMI-BF4 solution surface. Spherical Au nanoparticles were densely immobilized on the HOPG surface without formation of large aggregations. The HOPG surface could be slightly recognized through the spaces between immobilized particles. The average height of the immobilized particles from the HOPG surface was determined to ca. 5.7 nm by the cross-sectional profile of the AFM image (Fig. 4b), being comparable to the average size of Au particles determined by TEM measurement, 5.1 nm. This indicated that the Au film transferred onto the HOPG substrate from the HyEMI-BF4 solution was a monoparticle film. The FT-IR spectrum of Au particle films transferred onto Si substrates (Fig. S4) showed absorption bands at 3125 and 3164 cm<sup>-1</sup>, which were assigned to antisymmetric and symmetric stretching modes of HC-



**Figure 4** (a) A typical AFM image of an Au monoparticle film transferred onto the HOPG surface. The Au monoparticle film used was prepared by sputtering Au onto HyEMI-BF4 for 300s. (b) Height profile along with a line AB in the AFM image of panel a.

CH in the imidazolium ring of the HyEMI cation, respectively.<sup>44</sup> A broad band at ca. 3500 cm<sup>-1</sup> originating from the hydroxyl group in the HyEMI cation was also observed. Thus, it was thought that RTIL species were adsorbed on Au particle surfaces to prevent coalescence between particles in the immobilized films even after washing with acetonitrile several times.

It was reported in our previous paper<sup>45</sup> that the surface tension and viscosity of RTIL greatly influenced the size of metal nanoparticles formed in the RTIL solutions; RTILs with higher surface tension and larger viscosity tended to generate larger particles, probably because the sputtered metal atoms and/or clusters remain for a longer time on the surface of the RTIL with a higher surface tension and then metal nanoparticles more slowly diffuse into the bulk RTIL of larger viscosity. Therefore, it is expected that the formation of a metal particle film on the RTIL surface is also greatly influenced by the degree of viscosity or surface tension of the RTIL. We carried out Au sputter deposition onto various kinds of RTILs having different degrees of surface tension or viscosity.<sup>46-60</sup> The results are summarized in Table 1. Au particle films were formed only in the case of sputter deposition of Au being carried out onto RTILs containing cations having hydroxyl groups, HyEMI-BF4, HyEMI-TFSA, Ch-TFSA, or HyEA-formate. The average sizes of Au nanoparticles comprising the films were ca. 4~5 nm regardless of the kind of RTIL used. On the other hand, Au sputtering onto RTILs having non-functionalized or sulfonate-functionalized cations predominantly produced Au particles of ca. 2~3 nm in diameter that were uniformly dispersed in the bulk solution, and then no particle films were observed on the liquid surfaces under the present sputtering conditions even in the cases of using RTILs with large viscosity, such as OMI-BF4 and EMI-EtSO4, or using RTILS of EMI-BF4 and BMI-SCN with relatively large surface tension. It should also be noted that no Au particle film was formed when

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Table 1 Physical properties of several RTILs and average sizes of Au particles formed in RTILs and on their surfaces. Au sputtering was carried out for 300 s onto each RTIL.

RTIL	Functional group of cation	Functional group of anion	Viscosity (mPa s)	Surface tension (mN m <sup>-1</sup> )	Au particle size in the solution (nm)	Au particle size in the monoparticle film (nm)
HyEMI-BF4	-OH	$BF_4$	70.9 <sup>46</sup>	64.7 <sup>47</sup>	n.d.	$5.1 \pm 0.7$
EMI-BF4	alkyl	$BF_4$	38 <sup>48</sup>	54.4 48	$2.9 \pm 0.8$	n.d.
BMI-BF4	alkyl	$BF_4$	114 49	44.0 49	$2.5 \pm 0.6$	n.d.
OMI-BF4	alkyl	$BF_4$	440 50	32.3 51	$2.4 \pm 0.8$	n.d.
HyEMI-TFSA	-OH	$[(CF_3SO_2)_2N]^-$	91 <sup>49</sup>	34 49	n.d.	$4.3 \pm 0.8$
EMI-TFSA	alkyl	$[(CF_3SO_2)_2N]^-$	33 52	35.71 53	$2.9 \pm 0.6$	n.d.
TMPA-TFSA	alkyl	$[(CF_3SO_2)_2N]^-$	59.6 <sup>54</sup>	35.0 54	$2.2 \pm 0.4$	n.d.
Ch-TFSA	-OH	$[(CF_3SO_2)_2N]^-$	118.5 55	-	n.d.	$5.5 \pm 1.1$
SBMI-TFSA	-SO <sub>3</sub> H	$[(CF_3SO_2)_2N]^-$	_	-	$2.2 \pm 0.6$	n.d.
EMI-EtSO4	alkyl	-SO <sub>4</sub> -	125.4 56	45.43 53	$2.5 \pm 0.6$	n.d.
EMI-Ac	alkyl	-COOH	91 <sup>50</sup>	37.8 57	$3.8 \pm 1.3$	n.d.
BMI-SCN	alkyl	SCN-	51.74 58	46.9 51	$2.8 \pm 0.7$	n.d.
BMI-lactate	alkyl	-ОН, -СООН	_	-	$3.0 \pm 0.7$	n.d.
HyEA-formate	-OH, -NH <sub>3</sub> <sup>+</sup>	-COOH	105 59	70.3 60	n.d.	$5.2 \pm 1.3$

n.d. : not detected

anionic species were functionalized with hydroxyl or carboxyl groups.

Dupont et al. suggested that the surface composition of IL also affected the size of metal particles dispersed in the RTIL solution, because nucleation and subsequent nanoparticle growth occurred on the RTIL surface with RTIL/metal sputtering.61, 62 In fact, they succeeded in the preparation of disk-like Au particles by sputter deposition of Au on RTIL composed of a nitrile-functionalized imidazolium cation, in which strong interaction was exerted between sputtered Au species and nitrile groups protruding from the solution surface to the vacuum. Also they have found that RTILs having specific functional groups in cations could modulate the diffusivity of Au atoms sputter-deposited in the solutions depending on the interaction between RTILs and Au: small Au nanoparticles modified with RTIL having thiol or nitrile groups in cations tended to be located near the RTIL surface but larger particles were dispersed into the bulk solution phase, while the sputter-deposited Au species on RTIL having carboxyl group in cations could not penetrate into the bulk solution because of strong interaction between carboxyl groups and Au species, resulting in the formation of thin films on the RTIL surface.<sup>63</sup> Recently, it has been revealed by XPS analyses and theoretical simulation that the hydroxyl group at the end of the alkyl chain in imidazolium cation formed the topmost surface of the solution phase at the vacuum/HyEMI-BF4 interface.64, 65 Furthermore, alcohol molecules have made relatively strong adsorption on the bare Au surface via deprotonation of hydroxyl groups, resulting in alkoxide being adsorbed on the Au surface.<sup>66, 67</sup> As related subjects, vacuum vapour deposition of metals on functionalized alkanethiol self-assembled monolayers (SAMs) has been intensively studied to understand the interaction of metals with thin organic films.68-70 It was reported for -OH and -COOH terminated SAMs that metal atoms deposited at the vacuum/SAM interface caused the formation of metal islands on the SAM surface when metal atoms could strongly interact with terminal functional groups, while in the case of weak interaction between metal atoms and non-functionalized SAMs, deposited atoms could penetrate



**Figure 5** Schematic illustration of the formation mechanisms (a) for an Au monoparticle film on the surface of HyEMI-BF4 and (c) for Au particles uniformly dispersed in the EMI-BF4 solution phase. Panel b shows the mechanism for Au particle formation in the case of a mixture solution of HyEMI-BF4 and EMI-BF4 with an HyEMI-BF4 fraction of 60%.



**Figure 6** TEM images of Au monoparticle films prepared on RTIL mixture surfaces with Au sputter deposition for 300s. The contents of HyEMI-BF4 in the mixture solution were (a) 100, (b) 90, (c) 75, (d) 60, (e) 50, and (f) 0 vol%. The bars in the pictures represent a length of 20 nm.

through SAM layer, resulting in the formation of buried metal layers on the Au substrate surface.

Therefore, considering the difference in the molecular structures of HyEMI-BF4 and EMI-BF4, metal particle layers on the RTIL surface might be induced by stronger adsorption of the hydroxyl group than that of the ethyl group of imidazolium cation in RTIL. Figure 5a shows a proposed mechanism of Au particle film formation on HyEMI-BF4. First, the sputtered species of Au atoms



**Figure 7** Extinction spectra of monoparticle films prepared on RTIL mixture surfaces with Au sputter deposition for 300 s. The numbers in the figure represent the fractions of HyEMI-BF4 in the mixture solution.



**Figure 8** (a) Average size of Au particles in the films on the solution surface (solid circles) and average size of particles uniformly dispersed in the solution phase (open circles) as a function of the fraction of HyEMI-BF4 in the RTIL mixture solution. (b) Relationship between two-dimensional particle density in an Au monoparticle film and the fraction of HyEMI-BF4.

or clusters, which are ejected from the Au metal target plate by bombardment with energetic Ar<sup>+</sup> ions, are trapped at the RTIL surface via strong adsorption with hydroxyl groups protruding toward the vacuum from the RTIL surface, resulting in nucleation at the RTIL interface. The thus-formed nuclei remain on the solution surface and are not diffused into bulk solution phase owing to strong adsorption of the hydroxyl groups on Au nuclei. Consequently, the continuous supply of sputtered Au species can induce crystal growth of these nuclei on the RTIL surface, the degree being dependent on the time used for Au sputter deposition. It should be noted that the particle surface of Au in monoparticle layers was probably covered with adsorption layer of HyEMI-BF4 to stabilize individual nanoparticles as suggested by the FT-IR spectrum of Fig. S4, which is omitted in the schematic illustration of Fig. 5, and then washing Au particle films transferred on the substrates with acetonitrile for several times did not cause coalescence or large aggregation of particles at all, as shown in Figs. 2 and 4. On the other hand, EMI-BF4 only contains non-functionalized cations having a weaker adsorbability on the Au surface. Even if nanoparticles are formed on the surface of RTIL or in the solution phase adjacent to the surface, they can diffuse into the bulk solution phase, probably being dependent on the surface tension and viscosity of RTIL (Fig. 5c). These properties of RTILs may determine the time during which sputtered Au species remain on the RTIL surface or in the solution phase adjacent to the surface as suggested in our previous paper.<sup>45</sup>

This mechanism was also supported by the sputter deposition of Au onto the mixture of HyEMI-BF4 and EMI-BF4 RTILs. Although Au sputtering onto EMI-BF4 produced uniformly dispersed Au nanoparticles in the bulk solution, the addition of HyEMI-BF4 to EMI-BF4 resulted in the production of Au nanoparticle films depending on the fraction of HyEMI-BF4 in the mixture solution. Figure 6 shows TEM images of Au particle films transferred onto TEM grids from the surfaces of mixture solutions. No films composed of Au particles were observed on the mixture Journal Name



**Figure 9** Extinction spectra of monoparticle films of Ag, Pd, and Pt. The films were transferred onto quartz glass plates from the HyEMI-BF4 surface. The films of Ag and Pd were prepared by sputter deposition of corresponding metals with discharge current of 10 mA, while the Pt film was prepared by Pt sputtering with current of 40 mA. The sputtering time for each case was 300 s.

solutions with an HyEMI-BF4 fraction of 50 vol% or less as shown in Figs. 6 e and f, though some Au particles of ca. 2.7 nm in diameter that were uniformly dispersed in the bulk solution were observed to be attached to the carbon overlayer of TEM grids. On the other hand, sputtering Au onto the RTIL mixture containing an HyEMI-BF4 fraction equal to or higher than 60 vol% resulted in the production of Au particle films on the solution surface (Figs. 6a-d). The two-dimensional density of Au particles in the films became smaller when they were deposited on the mixture solution containing a lower fraction of HyEMI-BF4. Figure 7 shows the extinction spectra of Au nanoparticle films transferred onto quartz substrates. The LSPR peak was observed at around 550 nm in each film and its intensity was attenuated with a decrease in the HyEMI-BF4 fraction due to the change in two-dimensional particle density.

The sizes of Au particles in the film and those dispersed in the solution phase were determined from TEM images as a function of the composition of the RTIL mixture as well as the two-dimensional particle density in the films. Although sputter deposition of Au on a mixture solution with an HyEMI-BF4 fraction of 60 vol% produced both Au particle films on the solution surface and Au nanoparticles uniformly dispersed in the solution phase, selective formation of Au films was observed on the surface of mixture solutions containing an HyEMI-BF4 fraction of more than 75 vol% with Au sputtering and then uniformly dispersed Au particles were only formed in the case of using mixture solutions with an HyEMI-BF4 faction less than 50 vol%. Figure 8a show the average diameter of Au particles in the film or in the solution phase as a function of the composition of the RTIL mixture solution. The size of Au particles incorporated in the film on the solution was almost constant at ca. 5.4 nm regardless of the faction of HvEMI-BF4 in the solution. In contrast, the average size of Au particles dispersed in the solution phase slightly decreased from 4.1 to 2.9 nm with a decrease in the HyEMI-BF4 fraction from 60% to 50%. It is notable that Au particles in the solution containing 60 vol% HyEMI-BF4 were smaller than those in the film on the solution surface even though both the monoparticle film on the surface and particles dispersed in the solution were prepared by Au sputtering onto this mixture solution, indicating that the Au particles dispersed in the solution phase did not originate from particles comprising the monoparticle film on the surface. Therefore, we



Figure 10 (a) SEM secondary-electron image of an Au monoparticle film transferred onto a PS bead (size: 10  $\mu$ m) array. Arrows in panel a show the boundary between the bare PS bead array and the Au film-covered one. (b) A high magnification secondary-electron image of panel a obtained with an FE-SEM. (c) An SEM backscattered-electron image of PS beads scratched off from the Au-coated PS bead array shown in panel a. The Au monoparticle film used was prepared by sputtering Au onto HyEMI-BF4 for 300 s.

propose the formation mechanism of Au particles by sputtering Au onto the mixture solution composed of 60 vol% HyEMI-BF4 as shown in Fig. 5b. The number of hydroxyl groups exposed to vacuum from the mixture solution affects the degree of nucleation of Au particles to determine two-dimensional particle density in the film on RTILs, while nucleation also occurs in the solution phase adjacent to the surface, in which resulting Au particles easily diffuse into the bulk solution before crystal-growing to large particles. This was also supported by the change in two-dimensional particle density as shown in Fig. 8b. The density was simply diminished with

a decrease in the fraction of HyEMI-BF4, though the size of particles composing the monoparticle film did not change.

Nanoparticle films of different kinds of noble metals can also be prepared by sputter deposition of corresponding metals onto HyEMI-BF4 (Fig. S5). Sputter deposition of Ag or Pd for 300 s with a discharge current of 10 mA under an Ar pressure of ca. 20 Pa produced similar nanoparticle films composed of corresponding metal nanoparticles with average sizes of 28 and 3.8 nm, respectively (Fig. S5 b and d). A Pt sputtering with a discharge current of 40 mA onto HyEMI-BF4 also produced the monoparticle layer composed of Pt nanoparticles of 1.7 nm in diameter on the solution surface as shown in Fig. S5f, though the decrease of the discharge current to 10 mA did not result in the formation of recognizable films probably due to little amount of Pt deposited. Figure 9 shows the extinction spectra of thus-obtained monoparticle films. The Ag film exhibited a peak at ca. 420 nm assigned to LSPR peak of spherical Ag particles,<sup>34</sup> while the extinction spectra of Pd or Pt films had no characteristic peaks being similar to those of corresponding spherical nanoparticles dispersed in the RTIL solution.36,37

The fabrication of novel plasmonic structures or electronic devices has been intensively investigated by the immobilization of metal particles as building blocks. Thus, it is important to demonstrate that Au particles on the RTIL surface can be immobilized on substrates having micrometer-scale structures. The horizontal liftoff technique enabled transfer of the Au monoparticle film formed on the HyEMI-BF4 surface to highly curved surfaces as well as on planer surface such as glass or HOPG substrates (Figs. 1 and 4a). We chose an array of polystyrene (PS) beads with diameters of 10 µm as a micro-structured substrate. Figure 10a shows a typical SEM image of the Au monoparticle film transferred onto the PS bead array. The Au particle layer successfully covered a large area of the PS bead array, though some of the transferred film was wrinkled during the horizontal liftoff process. Figure 10b shows a high magnification image of an Au-coated PS bead. The upper hemisphere of the bead was covered by the particle film without large aggregation, though some small cracks, which were not observed in the film on the HOPG surface (Fig. 4a), appeared in the coated film. The PS beads on the glass plate were peeled off to obtain a side view image of Au-coated PS beads. Figure 10c shows an SEM image of the thus-obtained particles. In EDX analysis, the element of Au was detected only in the area of brighter contrast covering the half side of individual PS beads. These observations indicated that an Au monoparticle film could cover only the upper hemisphere of each PS bead and that the bare PS surface was exposed on the other side, resulting in the formation of a Janus-like structured PS bead.

### Conclusions

We have succeeded in single-step deposition of monoparticle films of noble metals such as Au, Ag, Pd, and Pt via RTIL/metal sputtering. Spherical particles of these materials were deposited on the surface of RTILs having hydroxyl-functionalized cations as a component. The size of Au particles on the RTIL surface was simply determined by the sputtering time and discharge current used for metal deposition, the two-dimensional particle density being independently varied with change in the composition of the RTIL mixture solution. A bare Au monoparticle film sputter-deposited on the HyEMI-BF4 surface could act as a useful precursor to uniformly wrap the uppermost surface of micrometer-scale structures. These features will be advantageous both for preparing novel nanoparticleassembled devices and for modulating their properties by surface modification of individual bare Au particles with functional molecules such as thiols. Study along this line is currently in progress.

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### TOC image



Sputter deposition of Au onto an ionic liquid with hydroxyl-functionalized cation produces uniform monoparticle film on the liquid surface. The size of nanoparticles is controlled by the sputtering condition.