

# Various Metal Nanoparticles Produced by Accelerated Electron Beam Irradiation to Room-Temperature Ionic Liquid

Tetsuya Tsuda,<sup>\*ab</sup> Taiki Sakamoto,<sup>b</sup> Yoshitomo Nishimura,<sup>b</sup> Satoshi Seino,<sup>a</sup> Akihito Imanishi,<sup>cd</sup> and Susumu Kuwabata<sup>\*bd</sup>

<sup>a</sup> Frontier Research Base for Global Young Researchers, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: ttsuda@chem.eng.osaka-u.ac.jp

<sup>b</sup> Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: kuwabata@chem.eng.osaka-u.ac.jp

<sup>c</sup> Department of Chemistry, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

<sup>d</sup> Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

## Supporting Information

### Table of Contents

Experimental Details	2
References	5
Figs. S1-S13	6
Table S1	19

## Experimental Details

*Preparation of Room-Temperature Ionic Liquids:* The organic salts, 1-ethyl-3-methylimidazolium chloride ([EtMeIm]Cl) and 1-butyl-3-methylimidazolium chloride ([BuMeIm]Cl), were prepared by the method described in a previous article.<sup>S1</sup> The resulting salts were purified by precipitation from dry acetonitrile with dry ethyl acetate. Bis(trifluoromethane)sulfonamide lithium salt (Li[Tf<sub>2</sub>N], Aldrich, >99.95%) was used without purification. The [EtMeIm][Tf<sub>2</sub>N] and [BuMeIm][Tf<sub>2</sub>N] were prepared by mixing exactly equal molar amounts of the purified 1-alkyl-3-methylimidazolium chloride ([R<sub>1</sub>MeIm]Cl (R<sub>1</sub>: Et or Bu)) and Li[Tf<sub>2</sub>N] in ultrapure water. This solution was stirred at room temperature for 24 hrs. The resulting RTIL was then extracted with dichloromethane. The solution was washed repeatedly with reverse osmosis (RO) water until the water phase was found to contain no chloride as determined by the addition of a few drops of a silver nitrate solution. Finally the dichloromethane was removed by agitating the extraction solution under vacuum condition ( $1 \times 10^{-4}$  Torr) at 373 K for 24 hrs. The resulting [R<sub>1</sub>MeIm][Tf<sub>2</sub>N] was clear and colorless.

*Preparation of Metal Nanoparticles:* Because we revealed in previous paper that the [BuMeIm][Tf<sub>2</sub>N] can effectively yield Au nanoparticles,<sup>S2</sup> the RTIL was mostly used as a reaction medium in this investigation. But some cases we used [EtMeIm][Tf<sub>2</sub>N] to produce larger metal nanoparticles. After addition of metal salts in [BuMeIm][Tf<sub>2</sub>N] or [EtMeIm][Tf<sub>2</sub>N], sample vials containing metal salts dissolved in the RTIL (1.5 mL) were capped in a dry Ar-filled glove box with an inert gas purification system (VAC Atmospheres NEXUS II system (O<sub>2</sub>, H<sub>2</sub>O < 1ppm)). The added metal salts were Na[AuCl<sub>4</sub>] $\cdot$ 2H<sub>2</sub>O, Ag[Tf<sub>2</sub>N], Cu[Tf<sub>2</sub>N]<sub>2</sub>, C<sub>10</sub>H<sub>14</sub>NiO<sub>4</sub>, K<sub>2</sub>PdCl<sub>4</sub>, K<sub>2</sub>PtCl<sub>4</sub>, Li[Tf<sub>2</sub>N], MgCl<sub>2</sub>, Fe[Tf<sub>2</sub>N]<sub>2</sub>, Zn[Tf<sub>2</sub>N]<sub>2</sub>, [EtMeIm][Al<sub>2</sub>Cl<sub>7</sub>], and SnCl<sub>2</sub>. All metal salts with [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> and [Tf<sub>2</sub>N]<sup>-</sup> anion except Li[Tf<sub>2</sub>N] were prepared in our laboratory. Other metal salts were used as received. The ionizing radiation source was accelerated electron beam (accelerated energy: 4.8 MeV; beam current: 10 mA; irradiation dose: 6 or 20 kGy). The irradiation time was ca. 2 and 7

sec at 6 and 20 kGy irradiation, respectively. The irradiation experiments were carried out at an existing common industrial plant for sterilizing medical kits in Osaka, Japan. The dose was less than sterilization dose for usual medical instruments.

Fast atom bombardment-mass spectroscopy (FAB-MS) experiments for RTILs before and after accelerated electron beam irradiation were carried out by using a JEOL JMS-700 MStation.

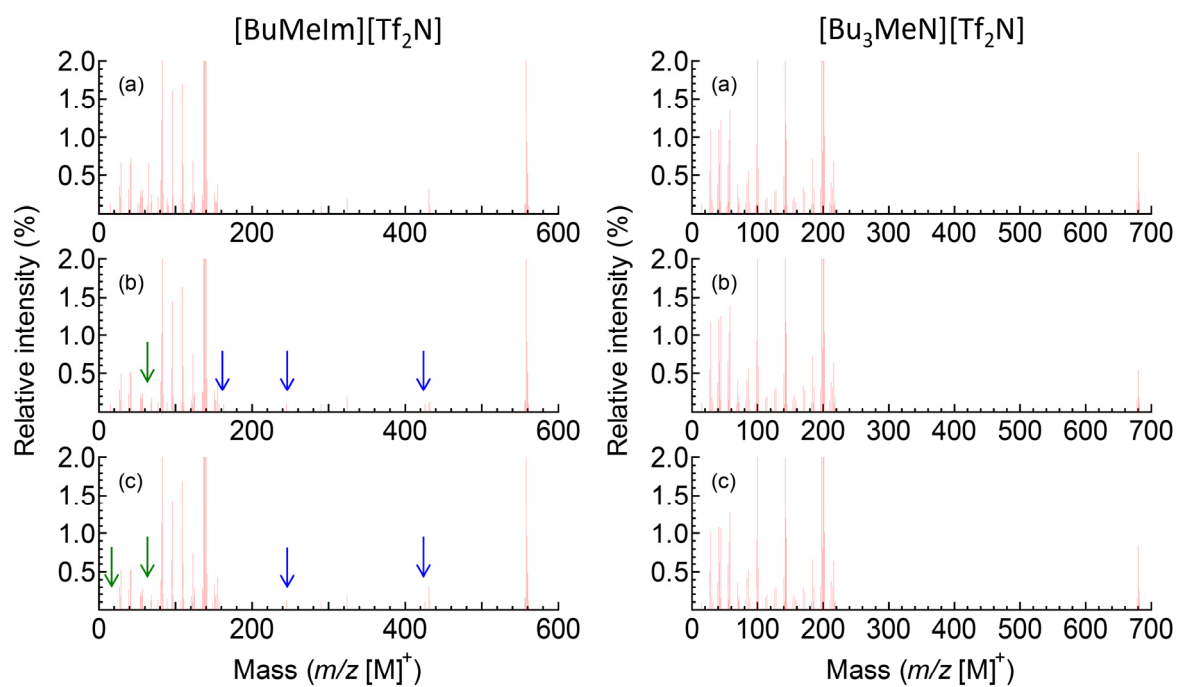
*Characterization of Metal Nanoparticles:* The UV-vis spectra of the RTIL after irradiation experiments were examined by using a Shimadzu MultiSpec-1500 spectrometer or a JASCO V-670 UV-Vis-NIR spectrometer. Morphology of the deposited metal samples was observed with a Hitachi H-7650 transmission electron microscope (TEM). Specimens for TEM observation were prepared by dropping the accelerated electron beam-irradiated RTIL onto a TEM grid ( $\phi$ 3.0 mm, copper or nickel, 400 mesh) coated with an amorphous carbon thin layer and rinsing them in dry acetonitrile and dry dichloromethane several times in order to remove excess RTIL and unreacted metal salts. The TEM grid holder was made from Al or carbon. The composition of the metal nanoparticles was analyzed with an EDAX Genesis XM2 energy dispersive X-ray spectroscopy (EDX) system mounted on the TEM.

*Electrochemical Experiments:* Electrocatalytic activities for Pt nanoparticles prepared in this investigation toward  $O_2$  reduction were examined with an ALS Model 660A potentiostat/galvanostat controlled with a desktop computer and a three-electrode cell reported in reference.<sup>S3</sup> The working electrode was a Pt-modified glassy carbon electrode (Pt-GCE), which was set at the bottom of the cell and sandwiched in between glass parts with an O-ring. A Pt mesh was used as the counter electrode. The Ag/AgCl electrode immersed in a KCl-saturated solution was employed as the reference electrode. All potential values are reported with respect to normal hydrogen electrode (NHE). The Pt-GCE was prepared by the following procedures; (i) heat treatment of the Pt-sputtered

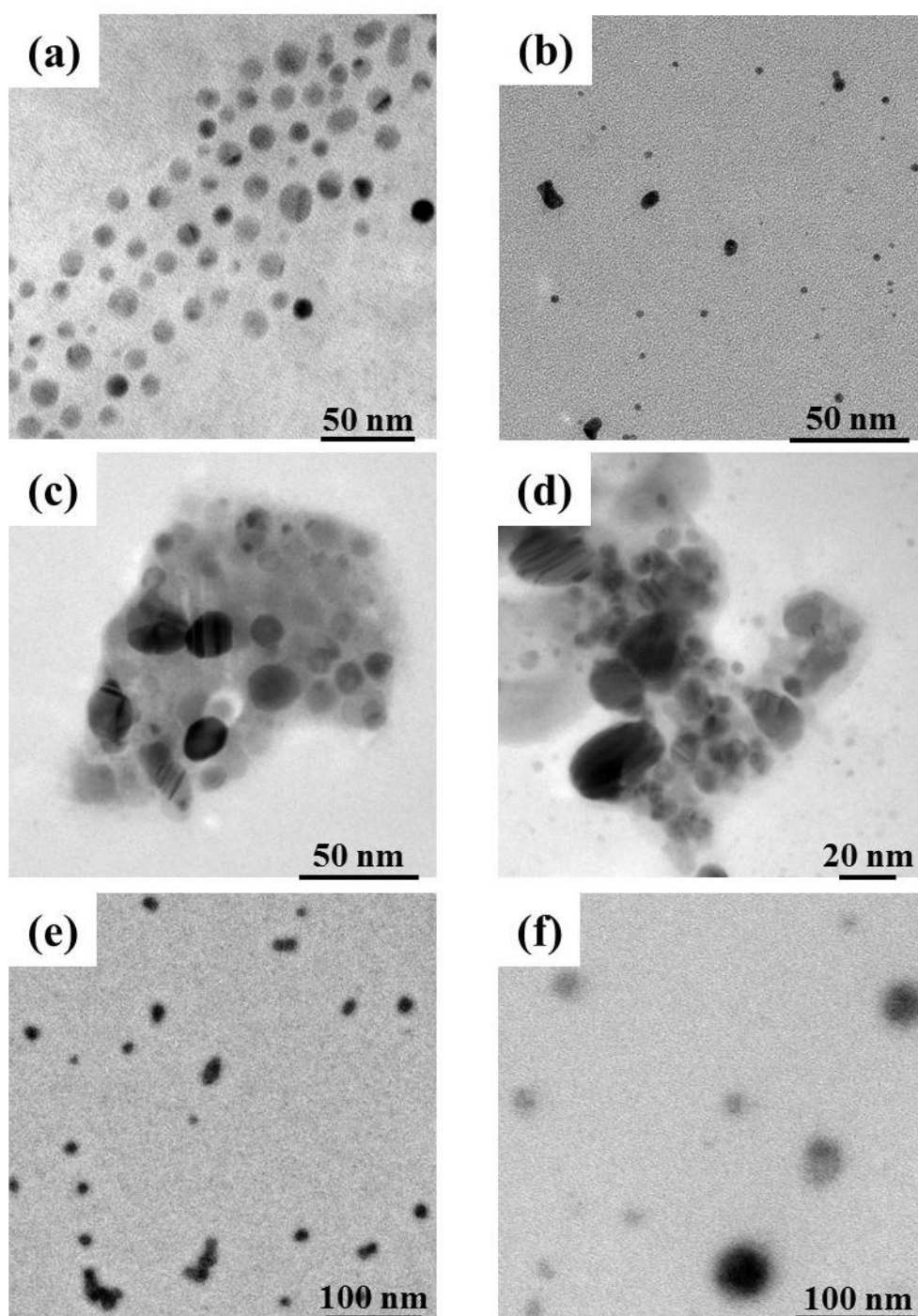
RTIL on a glassy carbon (GC) plate ( $2.5 \times 2.5$  cm) at 573 K under atmospheric conditions; (ii) rinsing the plate with dry acetonitrile; (iii) drying the resulting electrode under vacuum for 30 minutes prior to use. The heat treatment was conducted with a Koyo Thermo Systems REX-C900 electric furnace. The resulting Pt-GCE was pretreated with multiple potential scans between 0 and +1.2 V (vs. NHE) under dry N<sub>2</sub> condition before oxygen reduction experiments in 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. The 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution deaerated with oxygen gas (99.999 %) for more than 30 minutes was employed for the oxygen reduction experiments.

## References

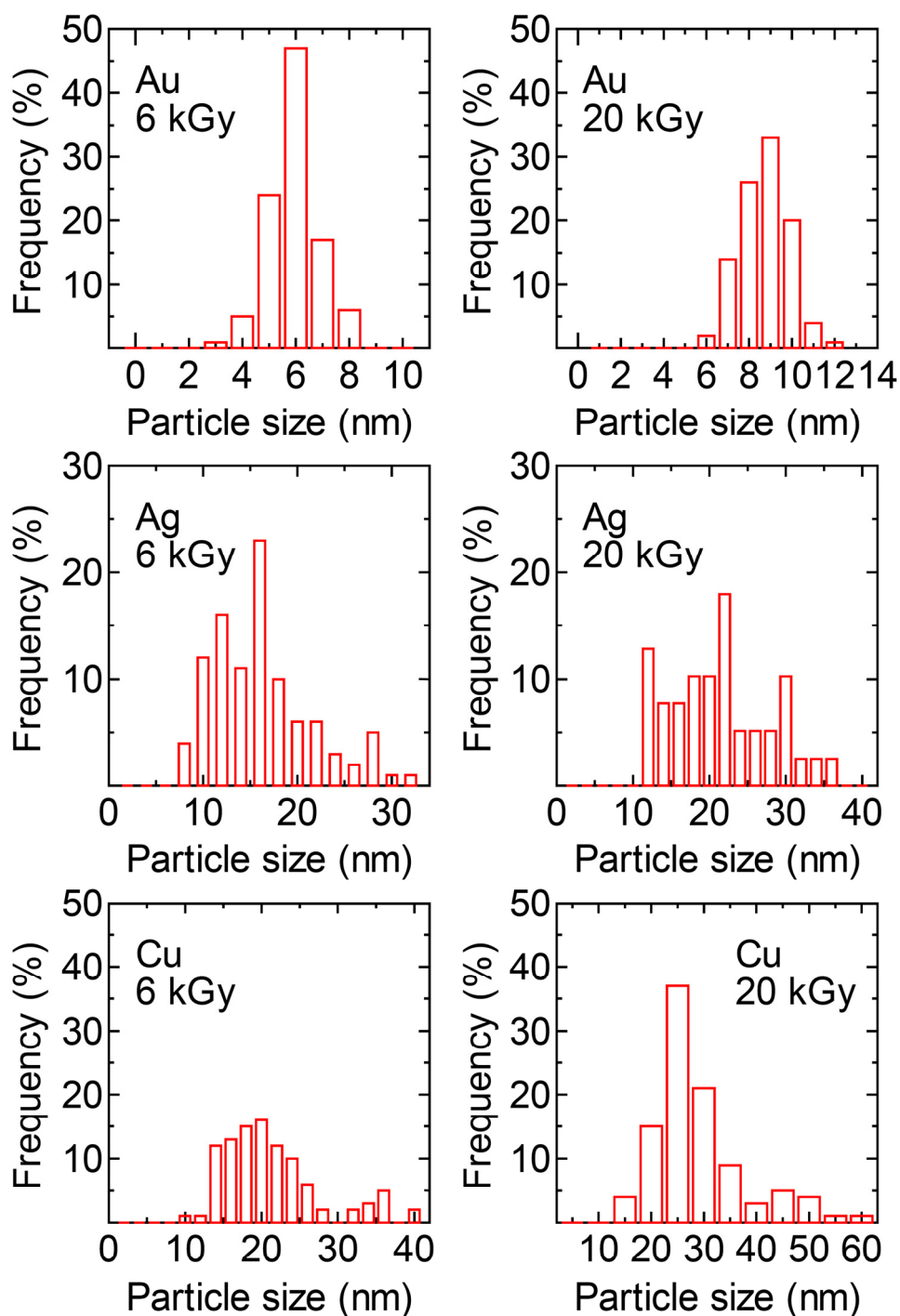
- S1 T. Tsuda and C. L. Hussey, in *Modern Aspects of Electrochemistry Vol. 45*, ed. R. E. White, Springer, New York, 2009, ch. 2, pp. 63-174.
- S2 A. Imanishi, M. Tamura and S. Kuwabata, *Chem. Commun.*, 2009, 1775; T. Tsuda, S. Seino and S. Kuwabata, *Chem. Commun.*, 2009, 6792.
- S3 T. Tsuda, K. Yoshii, T. Torimoto and S. Kuwabata, *J. Power Sources*, 2010, **195**, 5980.



**Fig. S1** Fast atom bombardment (FAB)-mass spectra of [BuMeIm][Tf<sub>2</sub>N] and tributylmethylammonium bis((trifluoromethyl)sulfonyl)amide ([Bu<sub>3</sub>MeN][Tf<sub>2</sub>N]) before and after accelerated electron beam irradiation. The irradiation dose was (a) 0, (b) 6, and (c) 20 kGy. The green and blue arrows show disappeared and appeared intensities after the irradiation, respectively. The [Bu<sub>3</sub>MeN][Tf<sub>2</sub>N] was prepared by the method described in Ref. S1.

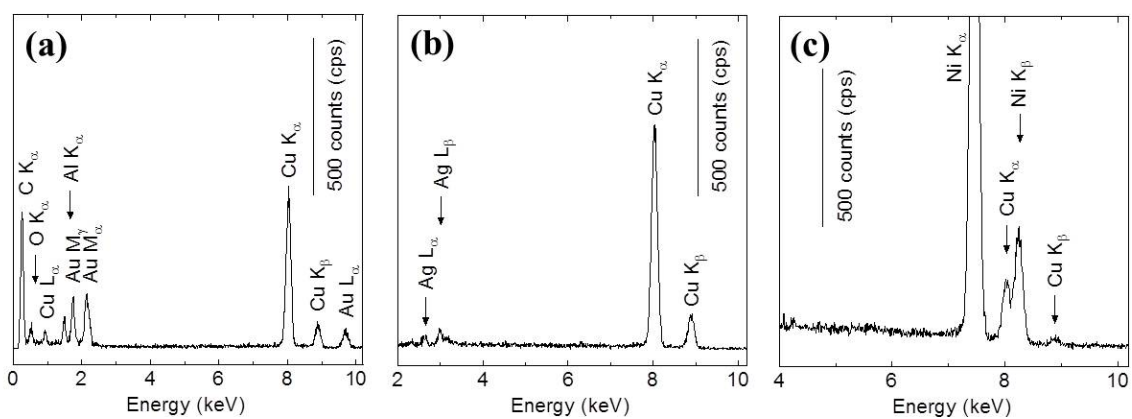


**Fig. S2** TEM images of (a, b) Au, (c, d) Ag, and (e, f) Cu nanoparticles prepared by accelerated electron beam irradiation in [BuMeIm][Tf<sub>2</sub>N] containing 5 mmol L<sup>-1</sup> metal salts. The irradiation dose was (a, c, e) 6 or (b, d, f) 20 kGy. The metal salts were NaAuCl<sub>4</sub>·2H<sub>2</sub>O, Ag[Tf<sub>2</sub>N], and Cu[Tf<sub>2</sub>N]<sub>2</sub>.

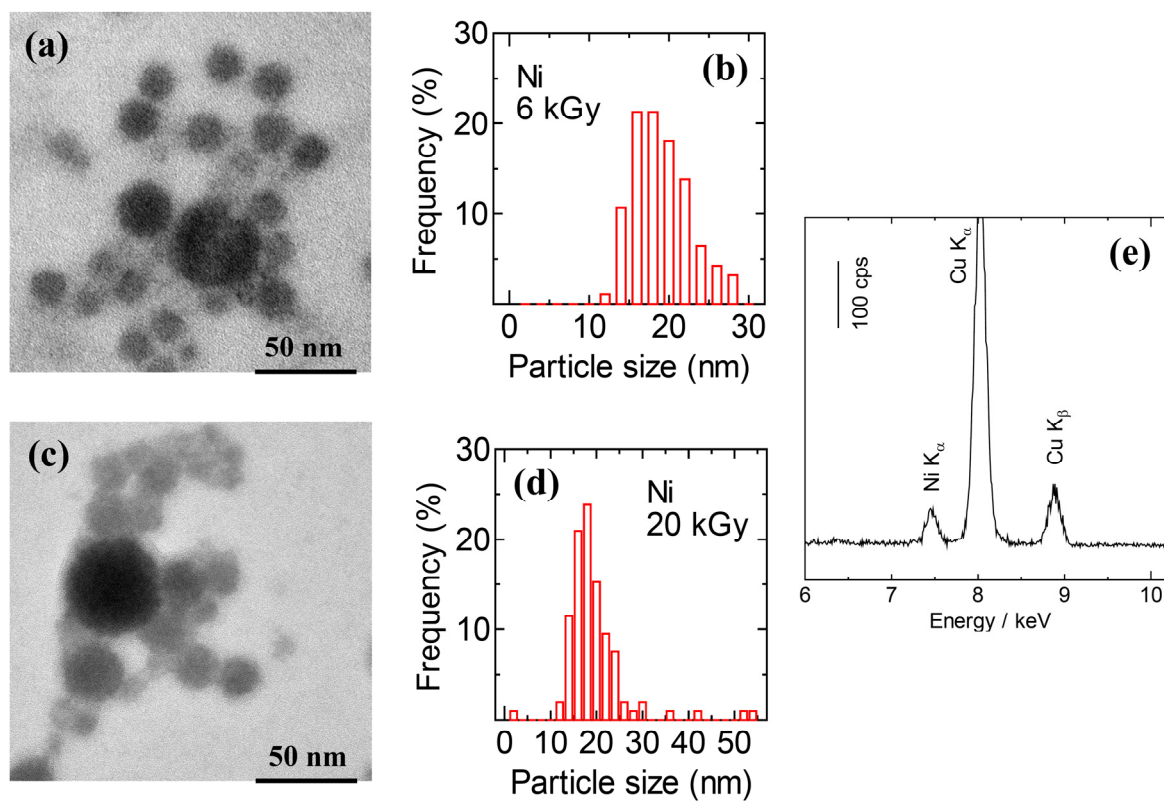


**Fig. S3** Particle size distributions of Au, Ag, and Cu nanoparticles prepared by accelerated electron beam irradiation in [BuMeIm][Tf<sub>2</sub>N] containing 5 mmol L<sup>-1</sup> metal salts. The particle sizes were estimated from TEM observation. The irradiation dose was 6 or 20 kGy. The metal salts were NaAuCl<sub>4</sub>·2H<sub>2</sub>O, Ag[Tf<sub>2</sub>N], and Cu[Tf<sub>2</sub>N]<sub>2</sub>.

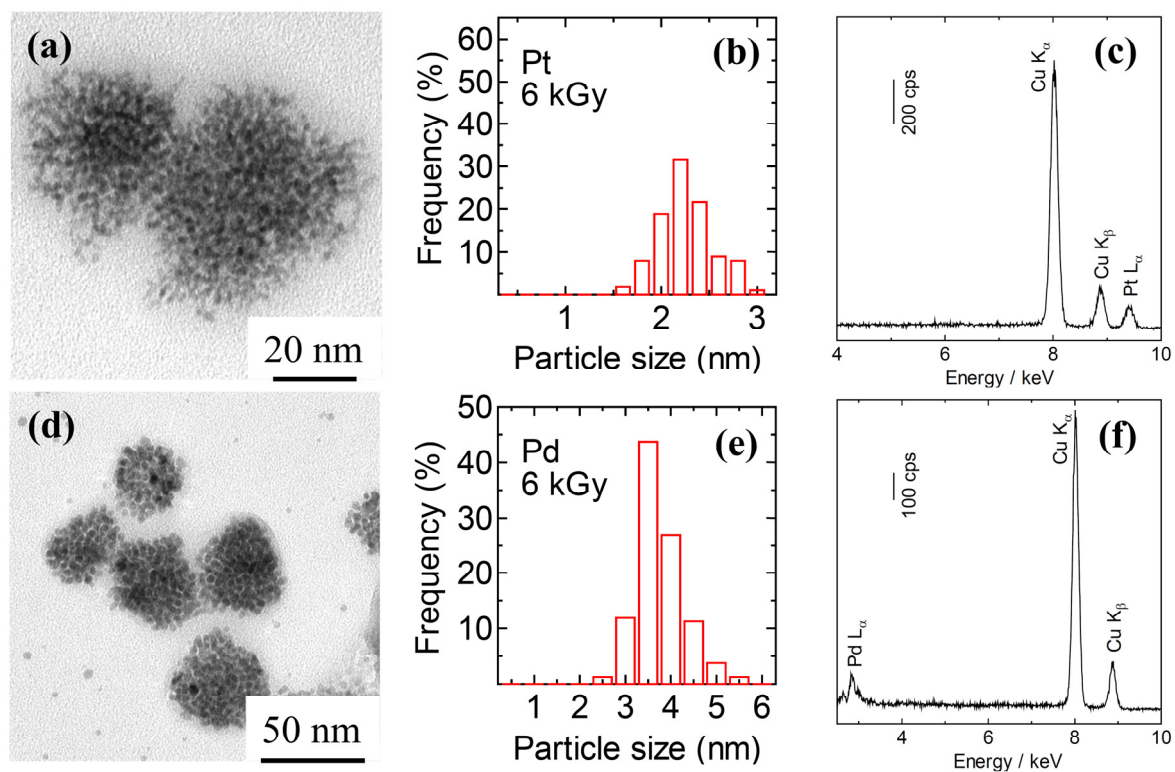




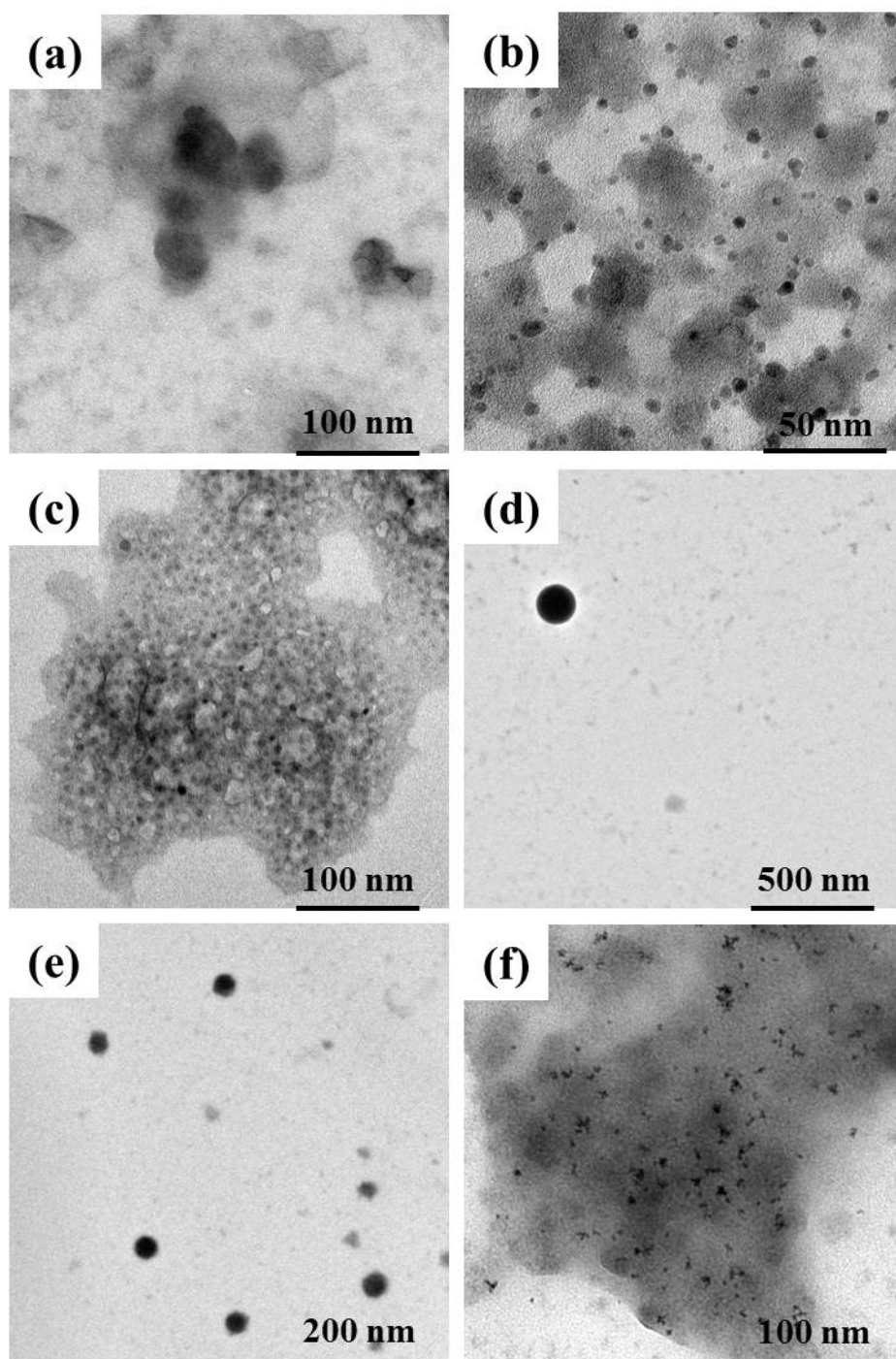
**Fig. S4** Typical EDX spectra of (a) Au, (b) Ag, and (c) Cu nanoparticles prepared by accelerated electron beam irradiation in [BuMeIm][Tf<sub>2</sub>N]. The spectra for Cu and Ni shown in (a, b) and (c), respectively, were attributed to TEM grid materials.



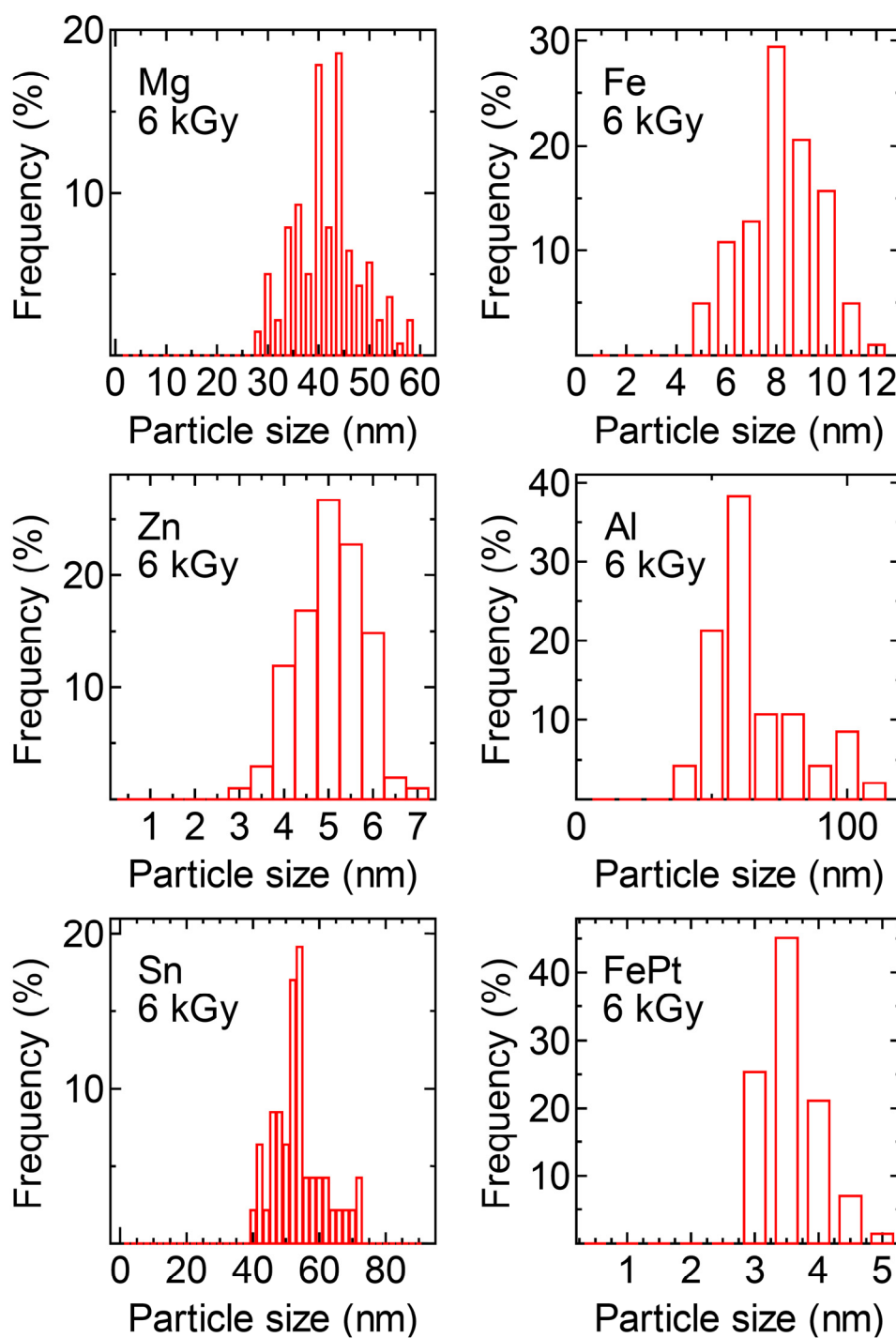
**Fig. S5** (a, c) TEM images, (b, d) particle size distributions, and (e) EDX spectra of Ni nanoparticles prepared by accelerator electron beam irradiation in [BuMeIm][Tf<sub>2</sub>N] containing 5 mmol L<sup>-1</sup> C<sub>10</sub>H<sub>14</sub>NiO<sub>4</sub>. The particle sizes were estimated from the TEM images. The irradiation dose was (a, b) 6 and (c, d, e) 20 kGy. The EDX spectra for Cu were attributed to Cu TEM grids.



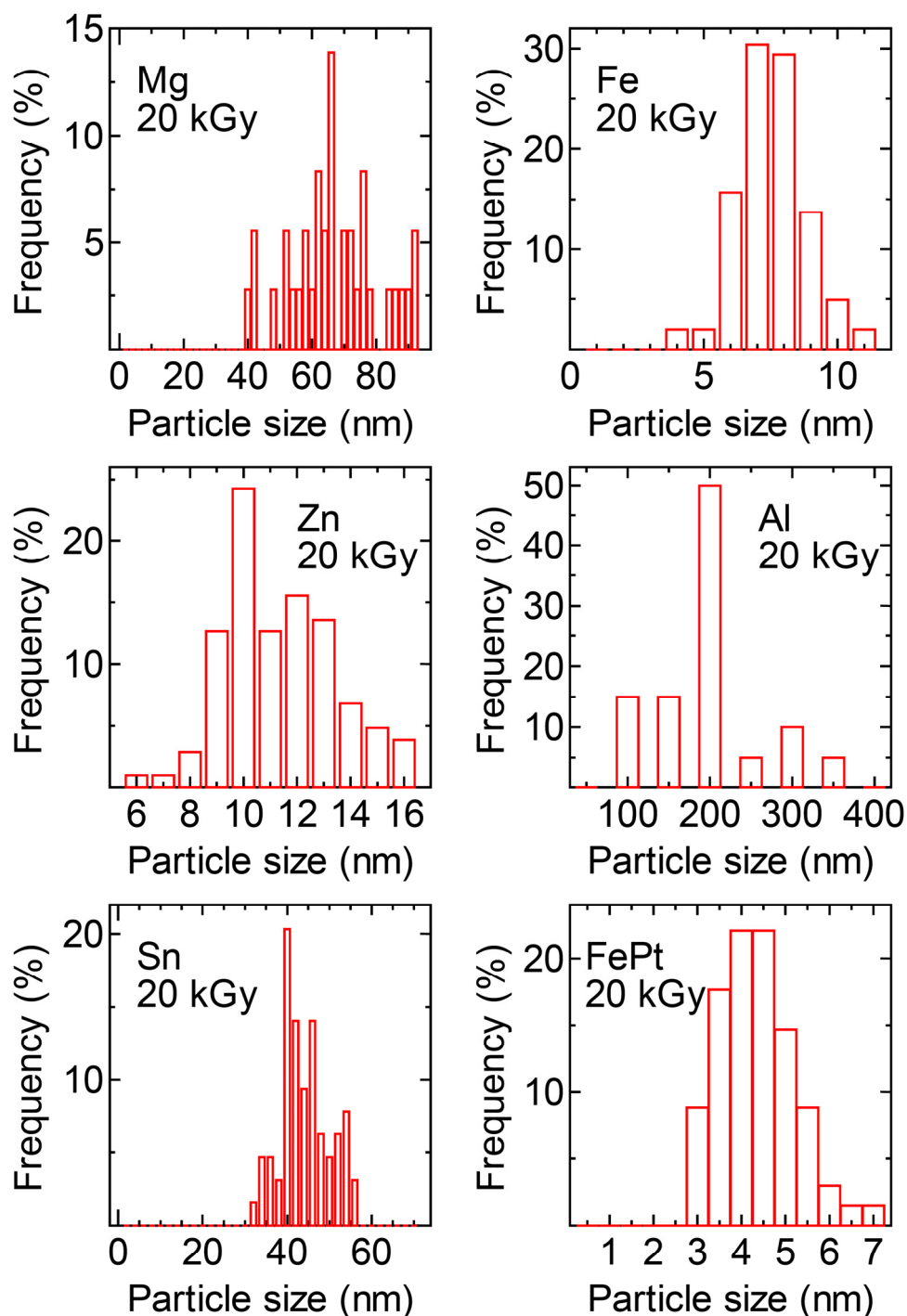
**Fig. S6** (a, d) TEM images and (b, e) particle size distributions, and (c, f) EDX spectra of Pt and Pd nanoparticles prepared by accelerated electron beam irradiation at 6 kGy in [EtMeIm][Tf<sub>2</sub>N] containing 5 mmol L<sup>-1</sup> K<sub>2</sub>PtCl<sub>4</sub> and K<sub>2</sub>PdCl<sub>4</sub>, respectively. The spectra for Cu were attributed to Cu TEM grid.



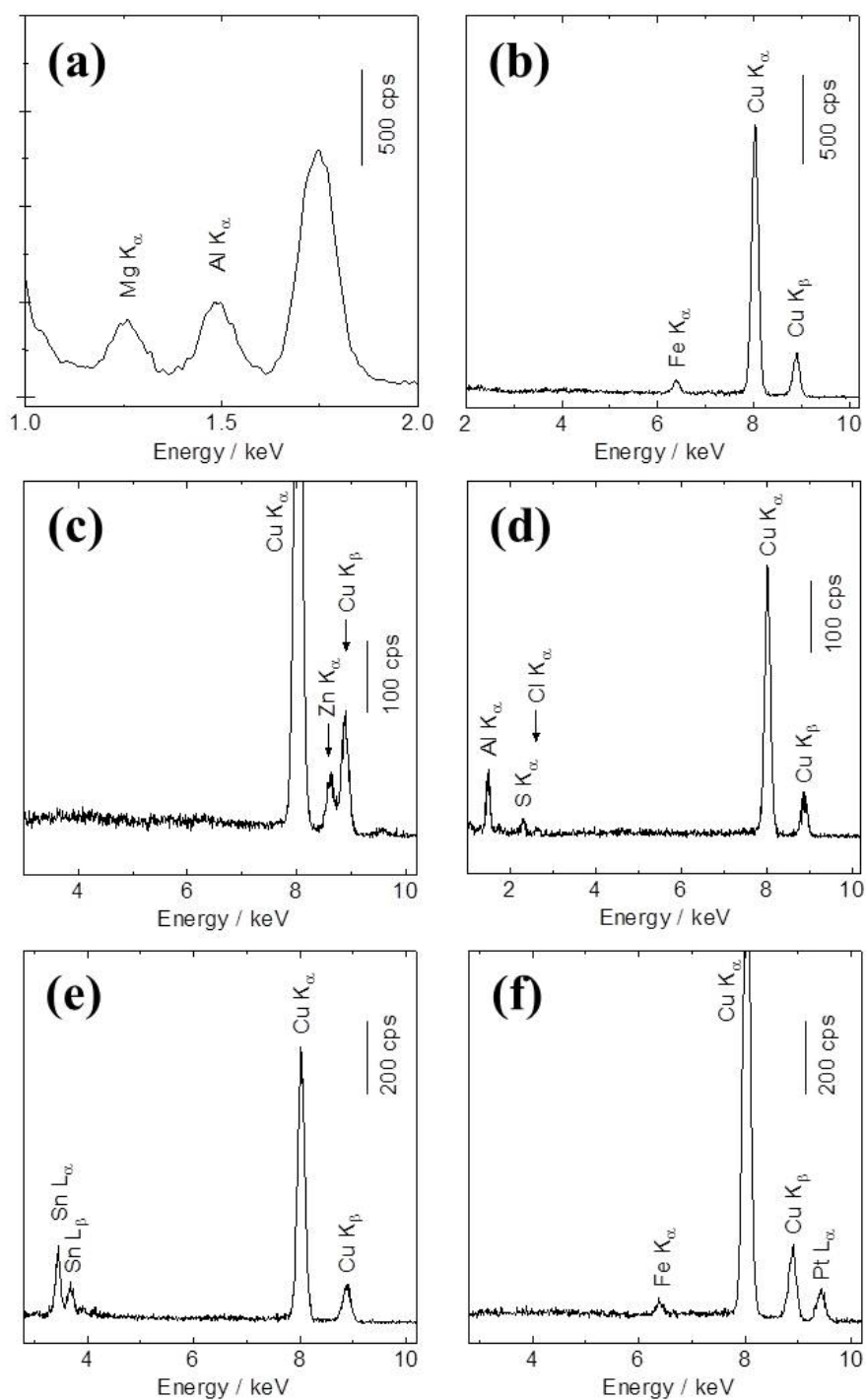
**Fig. S7** TEM images of (a) Mg, (b) Fe, (c) Zn, (d) Al, (e) Sn, and (f) FePt nanoparticles prepared by accelerated electron beam irradiation at 20 kGy in [BuMeIm][Tf<sub>2</sub>N]. The concentration of the metal salts added to the RTIL is given in Table 1.



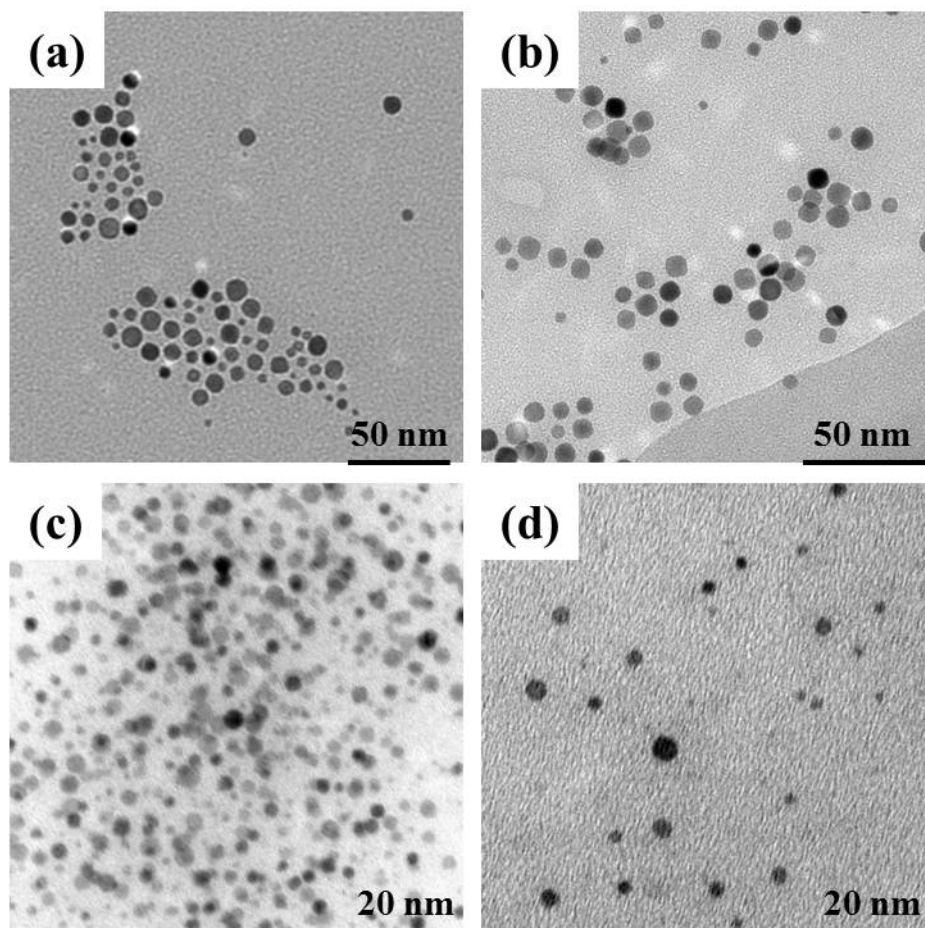
**Fig. S8** Particle size distributions of Mg, Fe, Zn, Al, Sn, and FePt nanoparticles prepared in this investigation. The particle sizes were estimated from the TEM images. The irradiation dose was 6 kGy. The detailed experimental conditions were given in Table 1.



**Fig. S9** Particle size distributions of Mg, Fe, Zn, Al, Sn, and FePt nanoparticles prepared in this investigation. The particle sizes were estimated from the TEM images. The irradiation dose was 20 kGy. The detailed experimental conditions were given in Table 1.

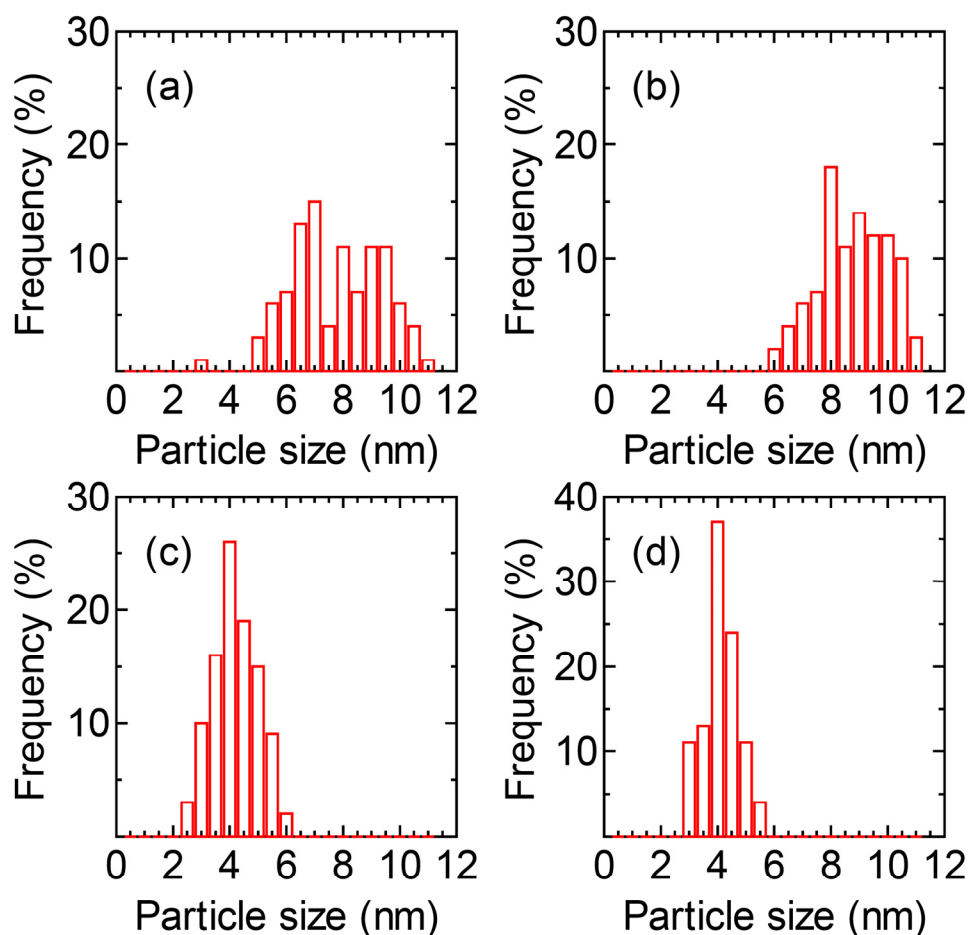


**Fig. S10** EDX spectra of (a) Mg, (b) Fe, (c) Zn, (d) Al, (e) Sn, and (f) FePt nanoparticles prepared by accelerated electron beam irradiation in [BuMeIm][Tf<sub>2</sub>N]. All the spectra for Cu were attributed to Cu TEM grid.

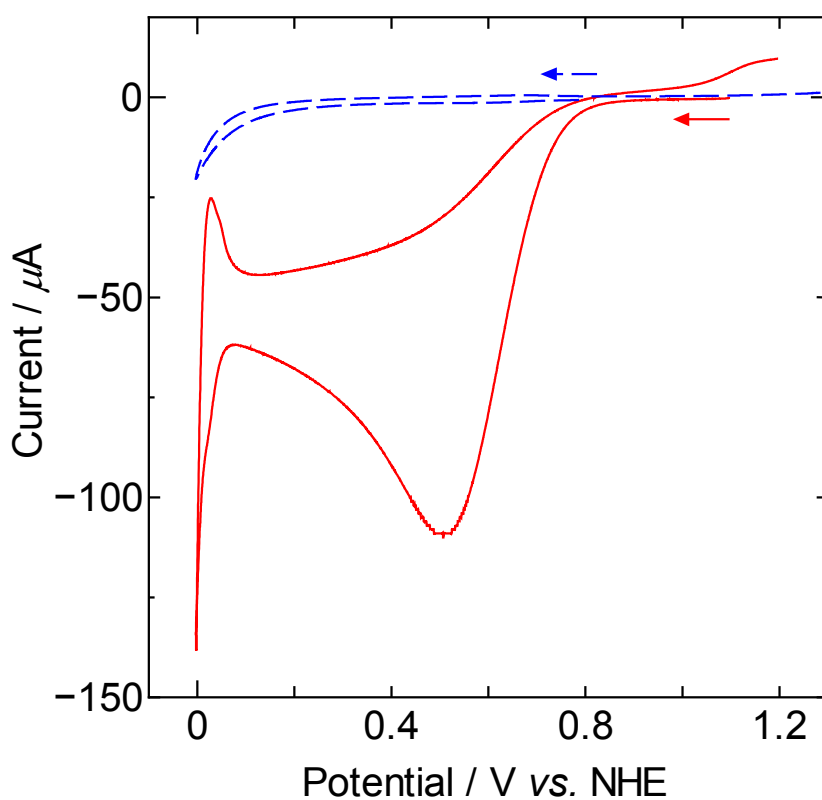


**Fig. S11** TEM images of Pt nanoparticles obtained after heating the accelerated electron beam-irradiated 5 mmol L<sup>-1</sup> K<sub>2</sub>PtCl<sub>4</sub> RTIL solutions at 573 K for 30 min. The RTILs were (a, b) [EtMeIm][Tf<sub>2</sub>N] and (c, d) [BuMeIm][Tf<sub>2</sub>N]. The irradiation dose was (a, c) 6 and (b, d) 20 kGy.





**Fig. S12** Particle size distributions of Pt nanoparticles obtained after heating the accelerated electron beam-irradiated 5 mmol L<sup>-1</sup> K<sub>2</sub>PtCl<sub>4</sub> RTIL solutions at 573 K for 30 min. The RTILs were (a, b) [EtMeIm][Tf<sub>2</sub>N] and (c, d) [BuMeIm][Tf<sub>2</sub>N]. The irradiation dose was (a, c) 6 and (b, d) 20 kGy.



**Fig. S13** Cyclic voltammograms recorded at (---) a bare GC electrode and (—) a Pt-GCE in O<sub>2</sub>-saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> aqueous solution at 298 K. The Pt-GCE preparation was conducted at 573 K. The irradiation dose for the Pt nanoparticle production was 6 kGy. The scan rates were 10 mV s<sup>-1</sup>.

**Table S1** Mean diameter of Pt nanoparticles after heating the accelerated electron beam-irradiated 5 mmol L<sup>-1</sup> K<sub>2</sub>PtCl<sub>4</sub> RTIL solutions at 573 K for 30 min

RTILs	Irradiation dose (kGy)			
	6		20	
	Mean diameter (nm)	Standard deviation (nm)	Mean diameter (nm)	Standard deviation (nm)
[EtMeIm][Tf <sub>2</sub> N]	7.53	1.56	8.55	1.29
[BuMeIm][Tf <sub>2</sub> N]	3.93	0.80	3.87	0.62