ChemComm

Cite this: Chem. Commun., 2012, 48, 1925–1927

www.rsc.org/chemcomm

COMMUNICATION

Various metal nanoparticles produced by accelerated electron beam irradiation of room-temperature ionic liquid[†]

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Received 5th October 2011, Accepted 12th December 2011 DOI: 10.1039/c2cc16183d

Various metal nanoparticles including base metal were produced by a brief accelerated electron beam irradiation of 1-alkyl-3methylimidazolium bis((trifluoromethyl)sulfonyl)amide roomtemperature ionic liquid without a stabilizing agent, which is usually employed so as to prevent aggregation.

After discovery of water- or air-stable room-temperature ionic liquids (RTILs), *e.g.*, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EtMeIm][BF₄]) and 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide ([BuMeIm][Tf₂N]), they have been investigated in various fields as one of the next-generation reaction media and liquid materials because most RTILs show attractive unique physical and chemical properties such as negligible vapor pressure, wide electrochemical window, wide handling temperature, and flame resistance.¹ Due to the interesting physicochemical properties, a great number of future technologies have been proposed by using RTILs. They have brought about new trends and directions in science and technology.²

Metal nanoparticles, which have notable features including large surface area, surface plasmon resonance, fluorescent emission *etc.*, are expected to be key materials for further development of science and technology.³ The number of articles related to metal nanoparticles continues to increase. The reaction medium for preparations using a wet process is usually aqueous solution. RTILs are just beginning to be employed in the preparation of metal nanoparticles as reaction media.⁴ It is interesting to note that RTILs work as an excellent medium for nanoparticle formation and behave as a stabilizing agent for the produced nanoparticles regardless of the types of the preparation methods such as chemical

reduction,⁵ plasma reduction,⁶ electron beam irradiation,⁷ magnetron sputtering.⁸ From a practical application standpoint of metal nanoparticle preparation in RTILs, we are keeping an eye on γ -ray and accelerated electron beam irradiation methods that can be conducted at an existing industrial plant for sterilizing medical kits in order to establish a mass production method for the metal nanoparticles in RTILs without any stabilizing and reducing agents. We have already succeeded in using this approach for preparation of Au nanoparticles.⁹ In this article, we report efforts toward preparation of various metal nanoparticles including base metal, which cannot be thermodynamically obtained in aqueous solution, by accelerated electron beam irradiation of RTIL, 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide ([R1MeIm][Tf2N]), containing metal salts. The aim of this study is to prepare various metal nanoparticles not covered with a stabilizing agent by using the accelerated electron beam irradiation method, leading to the mass production of the metal nanoparticles.

It is well-known that ionizing radiation, e.g., γ -ray and accelerated electron beam, yields strong reducing agents (solvated electrons, e_{solv}⁻, hydrogen atoms, H[•], etc.) in many solvents.¹⁰ Such generated reactive species can reduce many types of metal ions to lower valences and metal atoms. Finally metal nanoparticles are produced by the reactive species. We reported in a previous paper that similar reactions occur in RTILs by γ -ray and accelerated electron beam irradiations,⁹ although most RTILs are known to have better radiochemical stability than aqueous solution.¹¹ As shown in Fig. S1 (ESI[†]), FAB-MS experiments for RTILs before and after accelerated electron beam irradiation revealed that reactive species for reducing metal ions can be generated in [BuMeIm][Tf₂N] by the electron beam irradiation but not in tributylmethylammonium bis((trifluoromethyl)sulfonyl)amide ([Bu₃MeN][Tf₂N]) which is very stable to the ionizing radiation.¹¹ Based on these facts, in this study, we employed [R1MeIm][Tf2N] and accelerated electron beam, which can give a higher irradiation dose in a short period of time, as reaction medium and ionizing radiation, respectively, so as to produce a wide variety of metal nanoparticles including base metal.

Fig. 1 shows the UV-vis spectra of the metal nanoparticles in Group 11, *i.e.*, Au, Ag, and Cu, prepared in [BuMeIm][Tf₂N] with 5 mmol L^{-1} metal salts by means of accelerated electron beam irradiation at 6 and 20 kGy. Obvious absorption, that is,

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[†] Electronic supplementary information (ESI) available: Experimental details, TEM images, UV-vis spectra, *etc.* See DOI: 10.1039/ c2cc16183d



Fig. 1 UV-vis spectra of $[BuMeIm][Tf_2N]$ with 5 mmol L⁻¹ (a) NaAuCl₄·2H₂O, (b) Ag[Tf₂N], and (c) Cu[Tf₂N]₂ after accelerated electron beam irradiation at (- -) 6 or (-) 20 kGy. Arrows show peaks of surface plasmon resonance absorption.

surface plasmon resonance absorption appeared. The absorption peak wavelength moved to higher wavelength at higher irradiation dose. In general, plasmon absorption is very sensitive to the nanoparticle size and moves to higher wavelength if the particle size becomes large.¹² In order to visually estimate the particle size and determine the composition, the resulting nanoparticles were observed with transmission electron microscope (TEM) and characterized by energy dispersive X-ray analysis (EDX). Fig. S2, S3, and S4 (ESI⁺) show typical TEM images, particle size distributions, and EDX spectra of the obtained nanoparticles, respectively. The mean diameters of the nanoparticles determined with the TEM observation are given in Table 1. Each nanoparticle had a spherical shape and became larger at the 20 kGy irradiation. Then the metal nanoparticles obtained at 20 kGy showed the plasmon absorption at higher wavelength as exhibited in Fig. 1. The increase in the particle size should have been caused by further metal deposition onto metal nanoparticles from unreacted metallic ionic species. Similarly, we also investigated preparation of metal nanoparticles in Group 10 (Ni, Pd, Pt) by the same strategy. After the irradiation, we could obtain Ni nanoparticles without difficulty (Fig. S5, ESI[†]), but measurable Pd and Pt nanoparticles were not observed in the [BuMeIm][Tf₂N] while we could confirm that very small crystals less than 1 nm exist in the RTIL. In [R1MeIm][Tf2N]based RTILs, the imidazolium cations absorbed onto metal nanoparticles cause gauche defects that increase with a decrease in alkyl chain length;¹³ that is, crystal growth of nanoparticles is enhanced in the RTILs having shorter alkyl chain like ethyl groups. Next, in order to make the Pt and Pd crystals larger, 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amide ([EtMeIm][Tf₂N]) was exploited as a reaction medium so that we can verify them visually. Fig. S6 (ESI⁺) shows typical TEM images, particle size distributions, and EDX spectra of the

 $\label{eq:table_$

			6 kGy irradiation ^a		20 kGy irradiation ^b	
Metal	Added salts	$\begin{array}{c} Concentration / \\ mmol \ L^{-1} \end{array}$	d ^c / nm	$\frac{\mathrm{SD}^d}{\mathrm{nm}}$	d ^c / nm	SD ^d / nm
Au	NaAuCl ₄ ·2H ₂ O	5	5.44	0.96	8.21	1.18
Ag	$Ag[Tf_2N]$	5	15.3	5.36	20.4	6.64
Cũ	$Cu[Tf_2N]_2$	5	20.3	6.48	26.3	8.81
Ni	$C_{10}H_{14}NiO_4$	5	18.1	3.53	19.2	11.4
Pd	K ₂ PdCl ₄	5	<1.0		< 1.0	
Pt	$K_2 PtCl_4$	5	<1.0		< 1.0	
Mg	MgCl ₂	0.5	40.7	6.53	65.6	13.6
Fe	Fe[Tf ₂ N] ₂	10	7.73	1.51	7.05	1.29
Zn	$Zn[Tf_2N]_2$	10	4.79	0.75	10.8	2.31
Al	[EtMeIm][Al ₂ Cl ₇]	4	61.0	16.4	194	124
Sn	SnCl ₂	1	43.2	5.86	52.8	7.63
FePt ^e	$Fe[Tf_2N]_2$	5	3.33	0.47	4.13	0.87
	K ₂ PtCl ₄	5				

^{*a*} The irradiation time was *ca.* 2 s. ^{*b*} The irradiation time was *ca.* 7 s. ^{*c*} Mean diameter. ^{*d*} Standard deviation. ^{*e*} The alloy phase could not be identified in this study.

Pd and Pt nanoparticles produced at 6 kGy irradiation. Mean particle sizes of the produced Pd and Pt nanoparticles were 3.51 nm (SD: 0.53 nm) and 2.13 nm (SD: 0.34 nm), respectively.

It is very difficult to produce base-metal nanoparticles by using conventional methods such as vapor-phase synthesis,¹⁴ laser ablation method,15 mechanical milling/alloying process,16 and chemical reduction reaction in organic solvents.¹⁷ because base-metal nanoparticles have a highly-reactive nature that brings about unfavorable reactions with moisture, oxygen, and solvent. Our approach can be completed in an airtight container without any contamination and most RTILs show high physicochemical stability to base metal. If we can produce base-metal nanoparticles by this approach, it will greatly contribute to development of nanomaterials science. Herein, base-metal nanoparticles were prepared in [BuMeIm][Tf2N] RTIL. After the accelerated electron beam irradiation of the RTILs containing base-metal salts, we verified existence of base-metal nanoparticles in the RTIL with TEM observation. Typical TEM images of the nanoparticles yielded at 6 kGy and 20 kGy irradiation are depicted in Fig. 2 and Fig. S7 (ESI[†]), respectively. The particle size distributions were estimated from TEM observation of the resulting nanoparticles (Fig. S8 and S9, ESI[†]), and the characterization was conducted by the EDX analysis of the nanoparticles (Fig. S10, ESI⁺). The mean diameters of the nanoparticles are given in Table 1. Similar to the noble metal nanoparticles, their particle size showed a tendency to become large at an irradiation dose of 20 kGy except that Fe nanoparticles maintained a roughly constant particle size.

It is noteworthy that all the metal nanoparticles prepared in this investigation were very stable without a stabilizing additive for more than three months. It is highly likely that RTIL itself works as a stabilizing agent for the nanoparticles.⁴ In some cases RTIL gives functionality to the nanoparticles.¹⁸ The features will be an advantage to using RTILs as reaction media for nanoparticle preparation. We examined a catalytic activity for electrochemical oxygen reduction reaction (ORR) of the Pt nanoparticles prepared in this investigation. Pt nanoparticle-modified glassy carbon electrode (Pt-GCE) was fabricated using the preparation method



Fig. 2 TEM images of (a) Mg, (b) Fe, (c) Zn, (d) Al, (e) Sn, and (f) FePt nanoparticles prepared by accelerated electron beam irradiation at 6 kGy in [BuMeIm][Tf₂N]. The concentration of the metal salts added to the RTIL is shown in Table 1.

given in the ESI.[†] We found that the Pt nanoparticles become large upon heating the accelerated electron beam-irradiated 5 mmol L⁻¹ K₂PtCl₄ RTIL solutions at 573 K for 30 min (Fig. S11 and S12, ESI[†]). Variation in the Pt nanoparticle size after the process is summarized in Table S1 (ESI[†]). Catalytic activity for electrochemical ORR of the Pt-GCE was estimated by cyclic voltammograms recorded in O₂-saturated 0.5 mol L⁻¹ H₂SO₄ aqueous solution. As shown in Fig. S13 (ESI[†]), there is no wave for ORR in the voltammogram recorded at a bare GC electrode, but if the Pt-GCE was employed, current increment for electrochemical ORR initiated at *ca.* +0.93 V *vs.* NHE and a distinct redox couple for H⁺/H₂ reaction appeared at *ca.* 0 V due to the Pt nanoparticles modified on the GCE. The Pt-GCE prepared in this work exhibited a favorable electrocatalytic activity to ORR as an electrode catalyst for PEM fuel cell.

In conclusion, a wide variety of metal nanoparticles were obtained by the accelerated electron beam irradiation of the $[R_1MeIm][Tf_2N]$ RTIL without a stabilizing agent. Even base-metal nanoparticles were produced without any difficulties, although the nanoparticles may not be sufficiently characterized because of their instability in air. In addition to this, Pt nanoparticles prepared in this investigation showed a favorable catalytic activity for electrochemical ORR. The most important thing is that this study was carried out at an existing common industrial

plant for sterilizing medical kits with future mass production of metal nanoparticles prepared in RTIL in mind. The industrial plant can irradiate 200 vials \times 100 mL with the accelerated electron beam at a time and the process can be completed within 10 s.

Part of this research was supported by Grant-in-Aid for Scientific Research on Innovative Areas (Area No. 2206), Grant No. 23107518, from Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) and General Sekiyu R&D Encouragement Assistance Foundation.

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