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Single-step Preparation of Indium Tin Oxide Nanocrystals Dispersed in Ionic Liquids via Oxidation of Molten In-Sn Alloy

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Oxidation of molten In-Sn alloy was carried out in ionic liquids by heat treatment with vigorous stirring, resulting in the formation of indium tin oxide (ITO) nanocrystals. The ITO nanocrystals exhibited a plasmon peak, the peak wavelength of which was blue-shifted with an increase in the Sn fraction in ITO.

Metal oxide nanocrystals (NCs) prepared by solution phase syntheses have been attracting increasing attention due to their applicability to wet processing, such as ink-jet printing or spin coating, for electrically conductive films and optically transparent electrodes, which are essential for the fabrication of solid state electronic devices. Among the various kinds of metal oxide NCs developed for this purpose, indium tin oxide (ITO) NCs have been important materials because of their high levels of electric conductivity and chemical stability and their unique optical properties induced by their localized surface plasmon resonance (LSPR) in the near-infrared region.[1-4] Many strategies have been developed for preparing well-dispersed ITO NCs in solutions, such as the sol-gel technique,[5] solvothermal synthesis[6] and co-precipitation method,[7] but in most cases, a high level of skill is required for precise control of the size and shape of obtained NCs.

On the other hand, mechanical pulverization of molten metals has been developed for facile preparation of spherical metal particles in the size range from tens to hundreds of nanometers. Metals with low melting points, such as gallium (melting point (m.p.): 29.8 °C), indium (m.p.: 156.2 °C), tin (m.p.: 231.9 °C) and bismuth (m.p.: 271.3 °C) or their alloys, could be melted in solutions, such as water, chloroform, alcohol and silicone oil, by heating usually at temperatures higher than their melting points, followed by pulverizing with ultrasonication or mechanical stirring.[8-13] The resulting metal

nanoparticles were also useful as precursors for the preparation of nanostructured materials. For example, Sada et al. reported that galvanic replacement reaction of Ga nanoparticles with noble metal ions produced corresponding spherical metal nanoparticles of Au, Ag, and Pd with sizes of ca. 20 nm.[10] Gedanken et al. reported that rod-shaped GaO(OH) particles of sub-micrometer size were formed by ultrasonic irradiation of molten Ga in O_2-dissolved water.[13] Nanoparticles composed of Ga- or In-based metal alloys are expected to be good precursors for direct preparation of corresponding metal oxide NCs well dispersed in solutions. However, since a thin metal oxide layer acting as a blocking layer is easily formed on the alloy surface to prevent further oxidation, such attempts have not been successful, except for a recent study on preparation of rod-shaped GaO(OH) particles in water by Gedanken et al.

Room temperature ionic liquids (RTILs) are useful media for the preparation and stabilization of metal[14-18] and metal oxide[19, 20] nanoparticles because they have unique properties, such as extremely low vapor pressure, high thermal stability, incombustibility, and capabilities to dissolve many kinds of compounds and to uniformly disperse solid nanoparticles composed of various materials,[21] being different from conventional solvents. For example, we have reported that sputter deposition of noble metals such as Au,[22] Ag,[23] and Pt[24] into RTILs under a reduced pressure produced corresponding ultrafine metal nanoparticles of several nanometers in size, which were uniformly dispersed in RTILs in the absence of additional surfactant molecules. Furthermore, the thus-obtained nanoparticles were immobilized onto various solid substrates by heat treatment of nanoparticle-dispersed RTILs at relatively high temperatures of 150~300 °C.[24] These unique features of RTILs also enable treatment of molten metals in RTILs at relatively high temperatures in the presence of O_2. In this paper, we report the preparation of well-dispersed metal oxide NCs, such as In_2O_3 and ITO, by direct oxidation of corresponding molten metals or alloys in RTILs.

RTILs of 2-hydroxyethyl-*N,N,N*-trimethylammonium bis(trifluoromethanesulfonyl)amide (Ch-TFSA; water conc.: 900

ppm), N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA-TFSA; water conc.: 710 ppm), 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (HyEMI-TFSA; water conc.: 670 ppm), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF4; water conc.: 730 ppm) and 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (HyEMI-BF4; water conc.: 1400 ppm), the chemical structures of which are shown in Table S1, were used as received unless otherwise noted. A 0.50-g portion of bulk metal, pure In or In-Sn alloy with an Sn fraction of 2.9~29 at%, was put into a test tube with a 2.0-cm^3 portion of RTIL, followed by heating at 150, 200 or 250 °C for 10 h in air with magnetic stirring (ca. 800 rpm). After cooling to room temperature, unreacted metal lumps were removed from the mixture solution by decantation, and then the supernatant was subjected to centrifugation to separate nanoparticles. The thus-obtained precipitates were rinsed with acetonitrile several times, followed by dispersing again in acetonitrile for measurements. Experimental details are shown in the Supporting Information.

Magnetic stirring of In metal in hydroxyl-functionalized RTILs at 250 °C in air produced uniformly dispersed NCs as shown in Figure 1. The average sizes of NCs formed in Ch-TFSA, HyEMI-TFSA, and HyEMI-BF4 were 38, 21 and 28 nm, respectively. In contrast, non-functionalized RTILs, TMPA-TFSA and EMI-BF4, gave largely aggregated NCs with primary particle sizes of 20~50 nm. XRD patterns of thus-obtained NCs
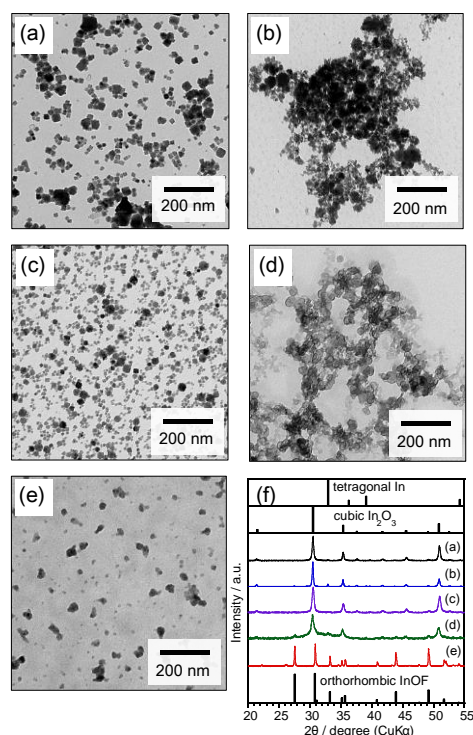
(Fig. 1f) were assignable to cubic In$_2$O$_3$, except for the case of using HyEMI-BF4. These results indicated that direct oxidation of molten In metal in RTILs produced In$_2$O$_3$ NCs, which were uniformly dispersed in hydroxyl-functionalized RTILs probably due to strong adsorption of hydroxyl groups in cationic species on the metal oxide surface. On the other hand, the NCs formed in HyEMI-BF4 exhibited an XRD pattern assigned to an orthorhombic InOF crystal structure. It is well known that BF$_4^-$ anion is apt to be hydrolyzed to BO$_3^{2-}$ and F$^-$ anions in the presence of a sufficient amount of water.[25] The concentration of water in HyEMI-BF4 was about two-times larger than the concentrations in other RTILs, resulting in a larger amount of F$^-$ anions released in HyEMI-BF4.

Ternary metal oxide NCs could be obtained when binary alloys of In-Sn were vigorously stirred in Ch-TFSA at 250 °C. Figure 2a shows the XRD patterns of NCs prepared by heating molten In-Sn alloy of 29 at% Sn for different reaction times. XRD peaks originating from the ITO crystal were observed regardless of heating time. However, at the initial stage of the reaction, XRD patterns also exhibited peaks assignable to tetragonal In and Sn metals, the peak intensities being rapidly reduced with prolongation of heating time and being null after 4 h of heating. The particle size determined by TEM measurements (not shown) increased from 16 to 38 nm with an increase in heating time. The yield of ITO particle formation, calculated as the In utilization, was in rough proportion to the heating time and finally reached ca. 30% at 10 h. Figure 2b
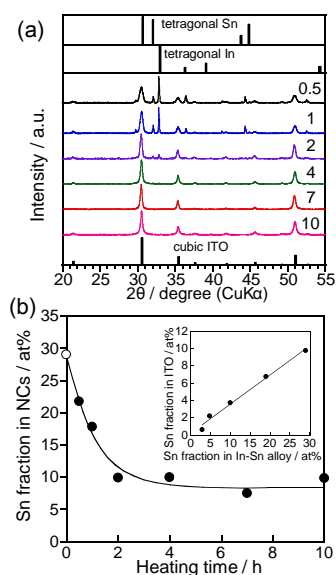

Figure 1. TEM images of NCs prepared by vigorous stirring of molten In metal in RTILs at 250 °C for 10 h. The RTILs used were (a) Ch-TFSA, (b) TMPA-TFSA, (c) HyEMI-TFSA, (d) EMI-BF4, and (e) HyEMI-BF4. (f) XRD patterns of the obtained NCs corresponding to panels a-e. Standard diffraction patterns of In metal, In$_2$O$_3$ and InOF (PDF card# 00-005-0642, 00-006-0416 and 01-070-1294, respectively) are also shown.

Figure 2. (a) XRD patterns of NCs prepared by reacting molten In-Sn alloy of 29 at% Sn in Ch-TFSA at 250 °C in air for different reaction times. Each number in the figure is the heating time in hours. Standard diffraction patterns of Sn metal, In metal, and ITO (In$_{1.88}$Sn$_{0.12}$O$_3$) (PDF card# 00-004-0673, 00-005-0642 and 01-089-4598, respectively) are also shown. (b) Dependence of the Sn fraction in total metal atoms in the NCs on heat treatment time at 250 °C in Ch-TFSA. The Sn fraction in In-Sn used as a precursor is indicated in the figure as an open circle. (Inset) Relationship between the Sn fraction in ITO NCs and that in In-Sn alloys used as a precursor. Heating was carried out at 250 °C in Ch-TFSA for 10 h.

shows the change in the Sn fraction in total metal atoms contained in NCs with prolongation of heating time. The Sn fraction in the particles decreased to a plateau of ca. 9.8 at% in NCs with heating for more than 4 h. These results suggested that vigorous stirring of the mixture solution of molten In-Sn alloy and RTIL at 250 °C initially produced a dispersion of nanoparticles composed of molten In-Sn and that they were subsequently oxidized to ITO NCs, accompanied by leaching of the excess amount of Sn from the nanoparticles. Furthermore, as shown in the inset of Figure 2b, the Sn fraction in ITO NCs could be freely controlled from 0.65 to 9.8 at% by changing the composition of the In-Sn alloy from 2.9 to 29 at% Sn. The largest Sn fraction in ITO NCs was 9.8 at%, which was similar to the threshold value of Sn doping into bulk ITO crystals, 6-8 at%,[26] probably because of their large particle size, ca. 40 nm.

Figure 3a shows a TEM image of ITO NCs containing 3.8 at% Sn, which were prepared by heat treatment of molten In-Sn alloy of 10 at% Sn in Ch-TFSA at 250 °C for 10 h. Well-dispersed particles with rectangular or polygonal shapes were observed, and their average size was determined to 38 nm, being in rough agreement with the crystallite size estimated from the XRD peak, 31 nm. High-resolution TEM images (Fig. 3b and c) of an ITO NC exhibited clear lattice fringes throughout the particle without showing a grain boundary, the interplaner spacing of which was ca. 0.52 nm assigned to (200) planes of the cubic crystal structure of ITO.[27] These results suggested that each particle obtained by heat treatment at 250 °C was composed of a single crystal of ITO. It should be noted that lowering the heat treatment temperature from 250 to 150 °C

caused a decrease in the average particle size from 38 to 12 nm as shown in Fig. S1. The corresponding high-resolution TEM images confirmed a single crystalline nature of thus-formed ITO NCs. However, reactions at lower temperatures could not completely oxidize preformed metal alloy nanoparticles, with NCs prepared by heating at temperatures lower than 200 °C showing larger XRD peaks assignable to tetragonal In crystal in addition to those of ITO crystal (Fig. S1f).

We propose the formation mechanism of ITO NCs in RTILs as shown in Fig. 3d. In-Sn alloys with the composition range used in the present study are liquid at temperatures higher than 150 °C and phase-separated from RTILs. With vigorous stirring of the mixture, an emulsion in which molten In-Sn nanoparticles are dispersed more in hydroxyl-functionalized RTIL phases can be prepared because RTIL molecules are strongly adsorbed on the nanoparticle surface through hydroxyl groups to prevent their aggregation. In contrast, molten alloy nanoparticles are relatively agglomerated in the non-functionalized RTIL phases owing to the weak adsorption of RTIL molecules. Subsequently, oxidation of In-Sn nanoparticles to ITO NCs occurs by reaction with oxygen species, such as water and O_2 molecules in the RTILs as impurities and/or OH groups in cationic species, the degree being enhanced with higher heating temperature. As suggested by this mechanism, the concentration of water in RTILs could significantly affect the size of resulting NCs. In contrast to BF_4^- anion, $TFSA^-$ anion was hardly decomposed under the present conditions, especially by the content of water in RTILs as an impurity. An Increase in the water concentration from 43 to 10000 ppm resulted in the enlargement of In_2O_3 NCs formed at 250 °C in Ch-TFSA from 21 to 42 nm (Fig. S2). Furthermore, similar heat treatment of molten In-Sn alloy in silicone oil at 250 °C in air resulted in the production of bulk particles of several micrometers in size that were composed of a mixture of In-Sn metal alloy and ITO (Fig. S3). These results indicated the importance of surface adsorption of RTIL species for both the rapid oxidation of In-Sn alloy and the stabilization of resulting nanometer-sized ITO particles. It should be noted that the ITO NCs in the present study could be readily dispersed in polar solvents, such as acetonitrile and water, without removing surface-adsorbed Ch-TFSA species (Fig. 4a and S4). This feature is remarkably different from ITO NCs prepared in conventional organic solvents, the particle surface of which was hydrophobic because of surface modification with large organic capping ligands such as oleylamine.[4, 28]

It is well known that the degree of the Sn fraction in ITO NCs is important for controlling the electric conductivity and optical property. The present technique enabled preparation of ITO NCs with sizes that were roughly constant at ca. 40 nm regardless of the Sn fraction in ITO NCs (Fig. 4b). Figure 4a shows the extinction spectra of ITO NCs with different fractions of Sn. The depression in extinction observed at around 2700 nm originated from the absorption of the quartz cell used for measurements. The ITO NCs exhibited an intense LSPR peak at around 2500 nm, the peak wavelength being blue-shifted from 2860 to 2400 nm with an increase in the Sn
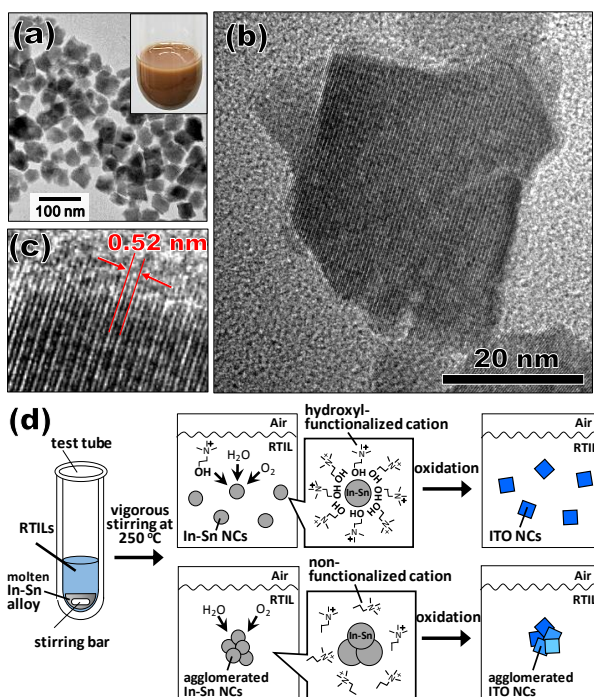

Figure 3. Large-area (a) and high-resolution TEM images (b,c) of ITO NCs with 3.8 at% Sn. The NCs were obtained by heat treatment at 250 °C in Ch-TFSA for 10 h. The inset in panel a shows a photograph of ITO NCs-dispersed Ch-TFSA in a test tube. (d) Schematic illustration of the formation of ITO NCs in RTILs by heat treatment.
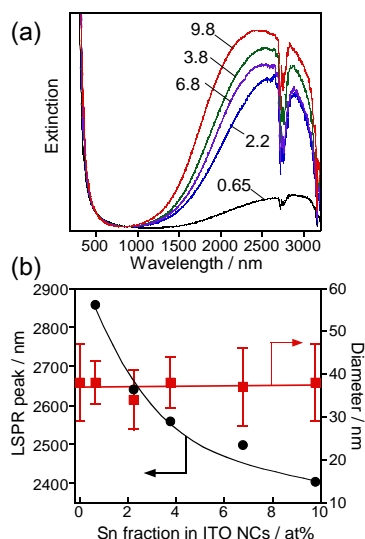
Figure 4. (a) Extinction spectra of ITO NCs with various Sn fractions uniformly dispersed in acetonitrile. ITO NCs were prepared by heat treatment at 250 °C in Ch-TFSA. The numbers in the figure represent the Sn fractions of ITO NCs in the unit of at%. (b) Plots of particle size and LSPR peak wavelength of ITO NCs as a function of Sn fraction.

fraction in ITO from 0.65 to 9.8 at% due to an increase in the charge carrier concentration in the particles (Fig. 4b). This tendency agrees well with that previously reported for ITO NCs of ca. 11 nm in diameter.[4] However, the LSPR peak wavelength of the present ITO NCs with Sn of 9.8 at% was largely red-shifted compared to that reported for ca. 11-nm-sized ITO NCs with Sn of 10 at%, 1618 nm,[4] because the LSPR peak was also remarkably dependent on the size of ITO NCs.[29]

In conclusion, we demonstrated the preparation of composition-controlled ITO NCs well dispersed in RTILs with direct oxidation of the corresponding molten In-Sn alloy, which was carried out by heat treatment at a relatively high temperature of 250 °C in air with vigorous stirring. A similar preparation process cannot be used for conventional organic solvents because of their high vapor pressure and combustibility in air. The obtained 40-nm-sized ITO NCs exhibited an LSPR in the near IR wavelength region, and their peak wavelength was tunable by the Sn fraction in ITO. Although only the preparation of ITO NCs as a multinary metal oxide is described in this paper, the use of the technique would enable novel preparation of various kinds of multinary metal oxide particles such as $AgGaO_2$, $CuInO_2$, and Zn-doped $(Ga,In)_2O_3$, which are useful for the fabrication of energy conversion systems and optoelectronic devices,[30] via direct oxidation of the corresponding Ga-based or In-based alloys in RTILs. Studies along this line are currently in progress.

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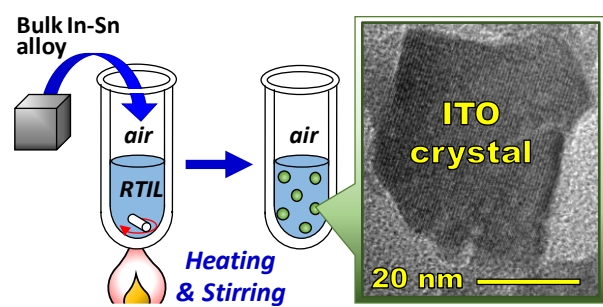
ITO nanocrystals were produced by oxidizing In-Sn alloy in an ionic liquid at 250 °C in air with vigorous stirring.