Supporting Information for

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

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Preparation of ITO NCs and their characterization

The RTILs, the chemical structures of which are shown in Table S1, were used as received unless otherwise noted. The concentration of water contained in the RTILs as an impurity was measured with a Karl Fischer moisture titrator (Kyoto Electronics Manufacturing Co., Ltd, MKC-610).

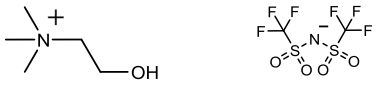
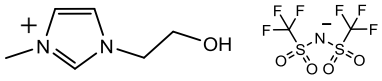
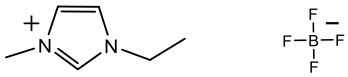
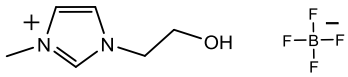
A 0.50-g portion of bulk metal, pure In or In-Sn alloy with an Sn fraction of 2.9~29 at%, was put into a test tube with a 2.0-cm^3 portion of RTIL, followed by heating at 150, 200 or 250 °C for 10 h in air with magnetic stirring (ca. 800 rpm). After cooling to room temperature, unreacted metal lumps 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 unless otherwise noted.

The shapes and sizes of obtained particles were examined using a HITACHI H-7650 transmission electron microscope (TEM) with an acceleration voltage at 100 kV. High-resolution TEM images were obtained by Cs-corrected HR-STEM (ARM-200F, JEOL Co. Ltd.) with an acceleration voltage at 200 kV. Samples for TEM measurement were prepared by dropping a small amount of the ITO NCs-dispersed acetonitrile solution onto a copper TEM grid covered with an amorphous carbon overlayer (Oken Shoji, STEM100Cu), followed by drying under vacuum.

The crystal structures of the particles were determined by measuring X-ray diffraction (XRD) patterns with a Rigaku SmartLab-3K using Cu Kα radiation. Samples for XRD measurement were prepared by centrifugation to separate nanoparticles from the ITO NCs-dispersed acetonitrile solution. The thus-obtained precipitates were loaded on a low-background Si sample holder. Chemical compositions of ITO NCs were analyzed by X-ray fluorescence spectroscopy (XRF, Rigaku, EDXL-300).

Extinction spectra of the ITO NCs dispersed in acetonitrile were acquired with an Agilent Technology 8453A spectrophotometer with a quartz cuvette having an optical path length of 0.10 mm.

Table S1. Molecular structures of RTILs used as solvents.

Abbreviation	Molecular Structure	Name
Ch-TFSA		2-hydroxyethyl-*N*,*N*,*N*-trimethylammonium bis(trifluoromethanesulfonyl)amide
TMPA-TFSA		*N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide
HyEMI-TFSA		1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide
EMI-BF4		1-ethyl-3-methylimidazolium tetrafluoroborate
HyEMI-BF4		1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate

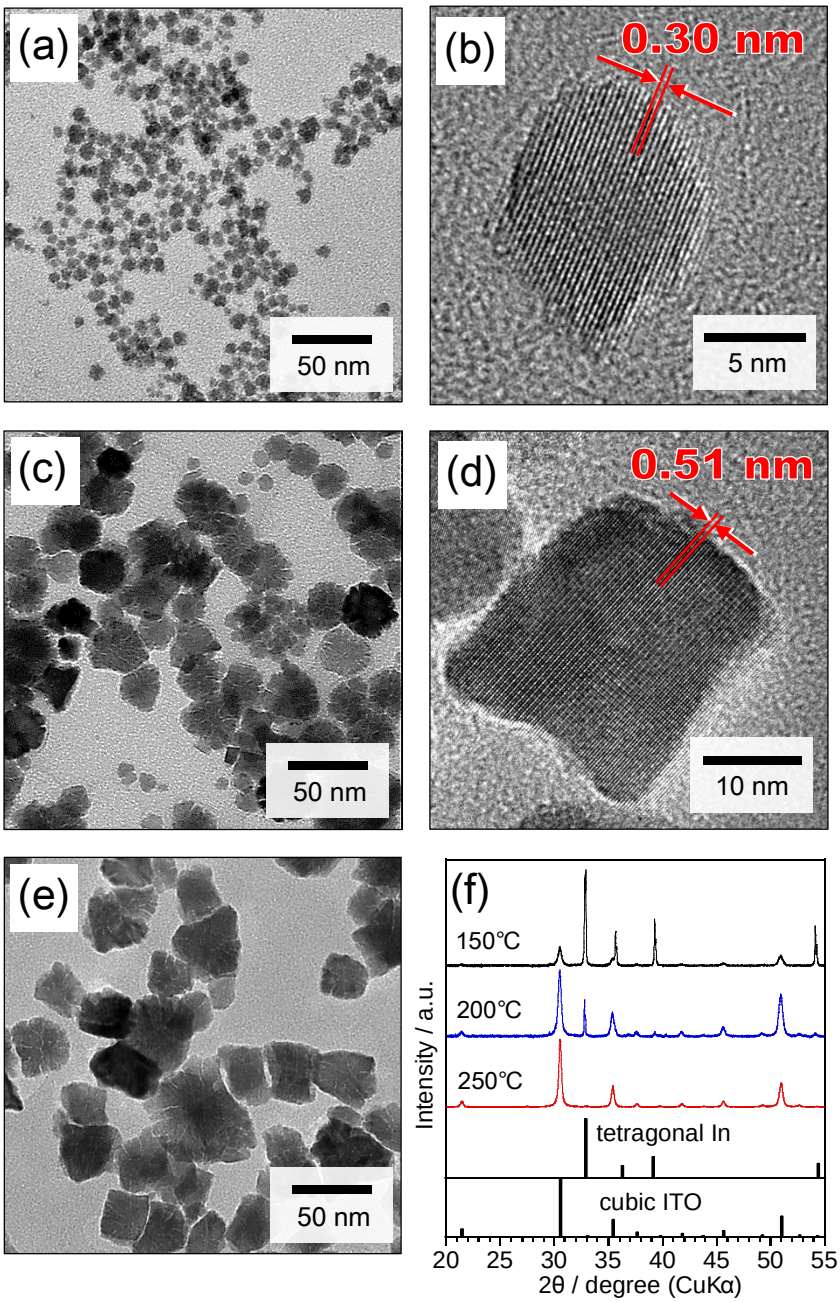


Figure S1. Large-area (a,c,e) and high-resolution (b,d) TEM images of nanoparticles prepared by heat treatment of In-Sn alloy of 10 at% Sn in Ch-TFSA at 150 (a,b), 200 (c,d), and 250 ˚C (e). The particles in panel e, obtained at 250 °C, were the same as those in Fig. 3a-c. The interplaner spacings in panel b and d were ca. 0.30 and 0.51 nm, assignable to (222) and (200) planes of the cubic crystal structure of ITO[1, 2], respectively. (f) Corresponding XRD patterns for the particles obtained by heat treatment at 150, 200, and 250 ˚C. Standard diffraction patterns of In metal and ITO ($In_{1.88}Sn_{0.12}O_3$) (PDF card# 00-005-0642 and 01-089-4598, respectively) are also shown.

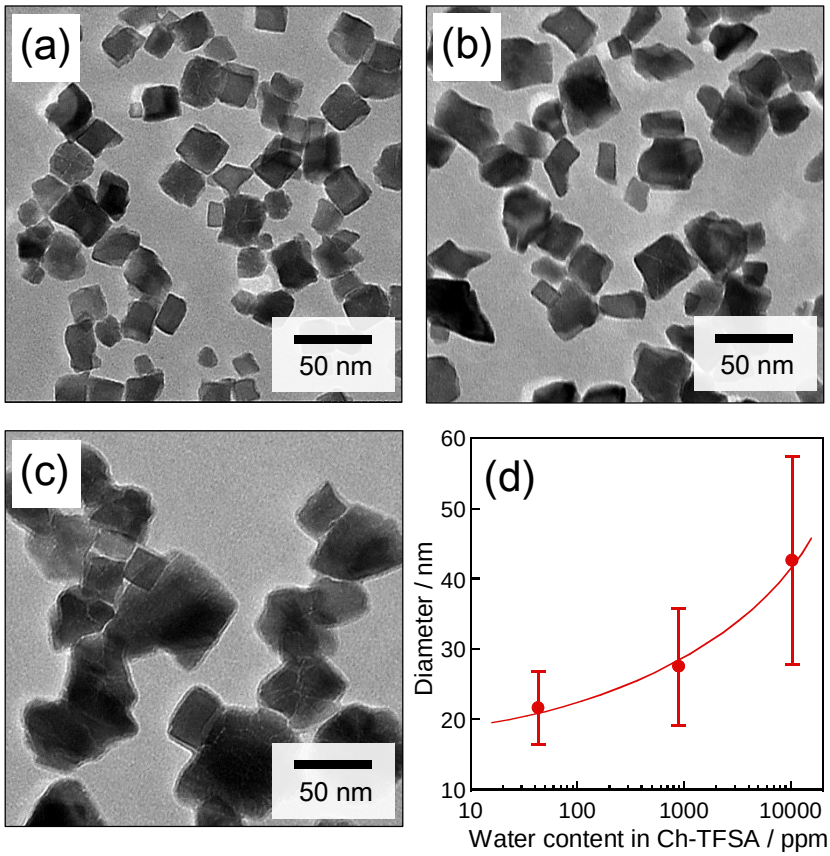


Figure S2. (a-c) TEM images of In_2O_3 NCs prepared by vigorous stirring with In metal at 250 °C for 10 h in N_2-saturated Ch-TFSA with water concentrations of (a) 43, (b) 900, and (c) 10000 ppm. (d) Relationship between average diameter of thus-obtained In_2O_3 NCs and water content in Ch-TFSA. The water content was adjusted by adding an appropriate amount of water to vacuum-dried Ch-TFSA.

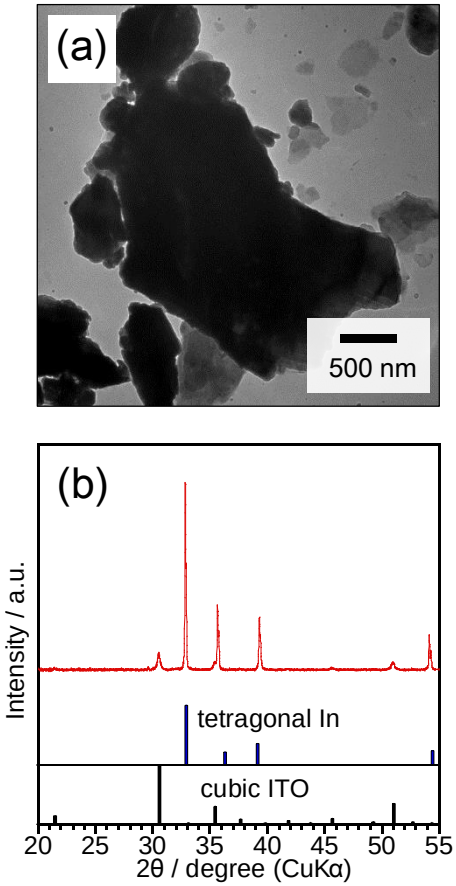


Figure S3. A TEM image (a) and XRD pattern (b) of particles obtained by heating In-Sn alloy (Sn of 10 at%) in silicone oil (AS ONE Co., Ltd, Japan, ASO-100, flashing point: 340 ˚C) at 250 ˚C for 10 h in air with magnetic stirring. The standard diffraction patterns of In metal and ITO ($In_{1.88}Sn_{0.12}O_3$) (PDF card# 00-005-0642 and 01-089-4598, respectively) are also shown.

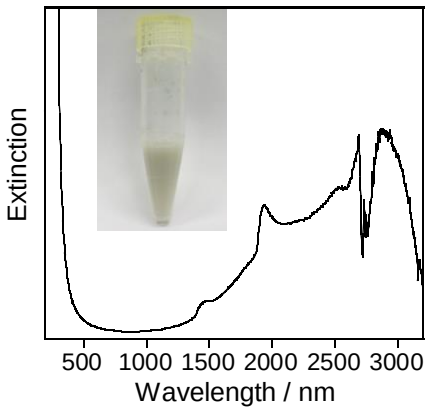


Figure S4. An extinction spectrum of ITO NCs (Sn fraction: 9.8 at%) dispersed in water. The inset shows a photograph of ITO NCs-dispersed water in a sample tube. The depression in extinction observed at around 2700 nm originated from the absorption of the quartz cell used for measurements. The peaks observed at 1450, 1900 and 2500 nm originated from the absorption of water.

References

1. J. E. Song, Y. H. Kim and Y. S. Kang, *Curr. Appl. Phys.*, 2006, **6**, 791-795.
2. T. Sasaki, Y. Endo, M. Nakaya, K. Kanie, A. Nagatomi, K. Tanoue, R. Nakamura and A. Muramatsu, *J. Mater. Chem.*, 2010, **20**, 8153-8157.