Supplementary Materials for

Preparation and characterization of nanocrystalline $Ti_xSn_{1-x}O_2$ solid solutions via a microwave-assisted hydrothermal synthesis process

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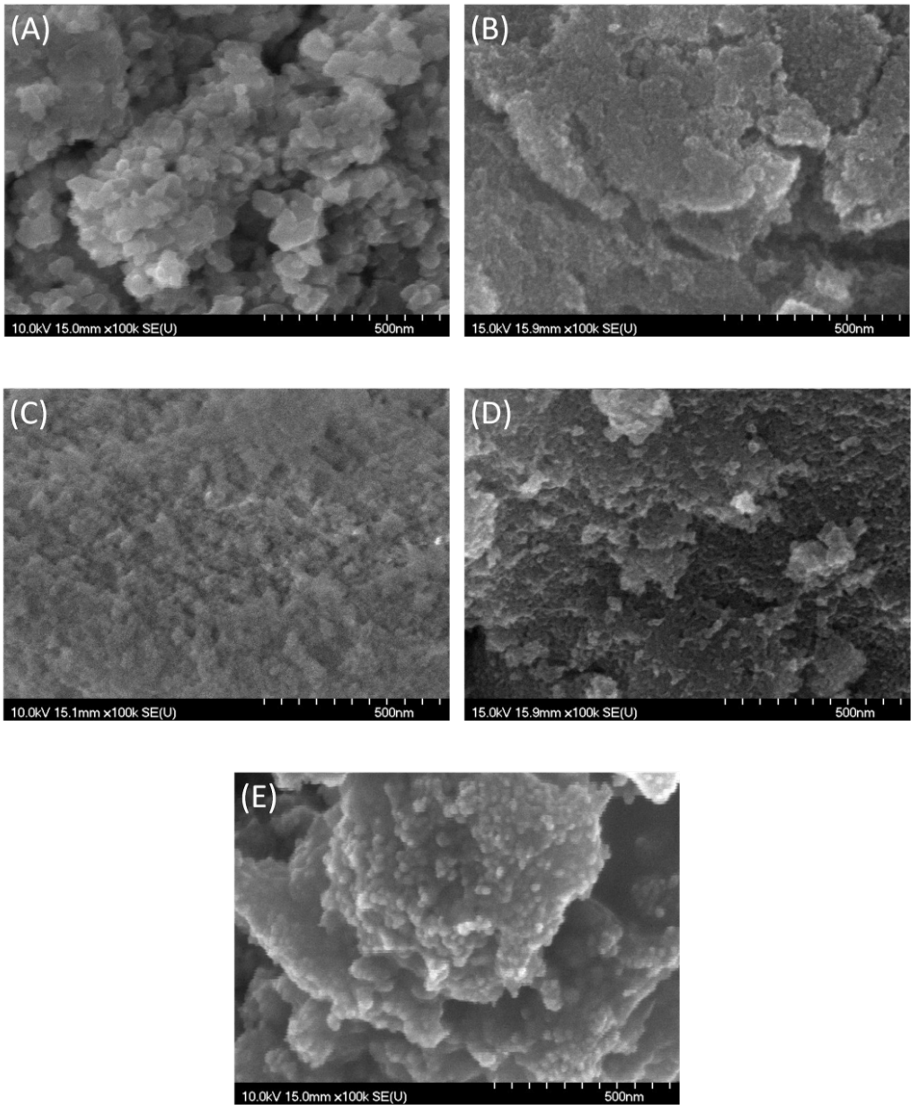
This supporting information includes the experimental details, Table S1 and Figures S1-S5.

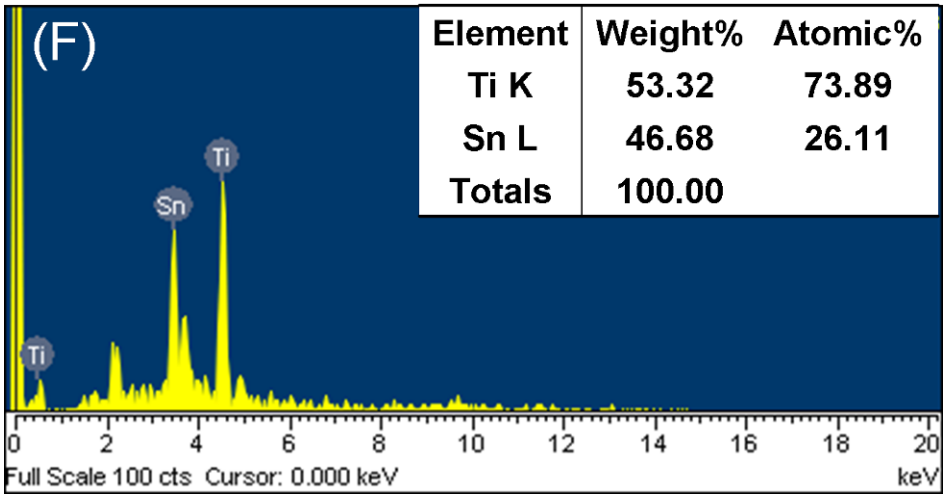
Experimental details:

The $Ti_xSn_{1-x}O_2$ solid solutions were prepared through a process of MAHS from 20-mL aqueous solutions containing stoichiometric ratio of $TiCl_3$ and $SnCl_4$ with a total metallic ion concentration = 20 mM (e.g., 10 mM $TiCl_3$ and 10 mM $SnCl_4$ for $Ti_{0.5}Sn_{0.5}O_2$). This mixed precursor solution with pH = 1.3 was stirred for 1 hr and then heated at a constant power of 100 W in a microwave reactor (Discover, CEM) from room temperature to 200 ^oC (ca. 8 min) and kept at this temperature for 10 min with an air-flow cooling. The solution was cooled to room temperature with the same cooling air-flow in ca. 5 min. The solid solution powders were obtained by means of a centrifuge, which were washed with de-ionized water several times until pH close to 7.

The crystalline structures of samples were characterized by an X-ray powder diffractometer (CuK_α, Ultima IV, Rigaku). The XRD patterns were measured at a scan rate of $1^\circ\ min^{-1}$. The microstructure, particle size distribution, and electron diffraction patterns of oxides were examined by means of a high-resolution transmission electron microscope (HR-TEM, JEM-3010, JEOL) at 200 kV. The particle size distribution of every sample was determined by the TEM images from 100 randomly-selected particles. Raman spectrograms were measured using a 3D Nanometer Scale Raman PL Micro-spectrometer (Tokyo Instruments, Inc.) with 633

nm radiation of HeNe Laser, which was focused in a circle area less than 1 μm in diameter by using a microprobe with 100-time objective. The UV-VIS diffusion reflectance spectra were measured by an UV-VIS spectrometer (Unicam UV-530) with the wavelength varied from 350 to 800 nm. The composition of solid solutions was measured using an energy-dispersive X-ray (EDX) spectroscope coupled with a field emission scanning electron microscope (FESEM, Hitachi S-4800 type I). The mean error of this EDX analysis is ca. 1.5 wt %. Dynamic light scattering (DLS; 380 ZLS, Nicomp, USA) was used to confirm the particle size distribution of all oxides. The composition of solid solutions was also confirmed using an inductively coupled plasma - atomic emission (ICP-AES; Jarrell-Ash, ICAP 9000).





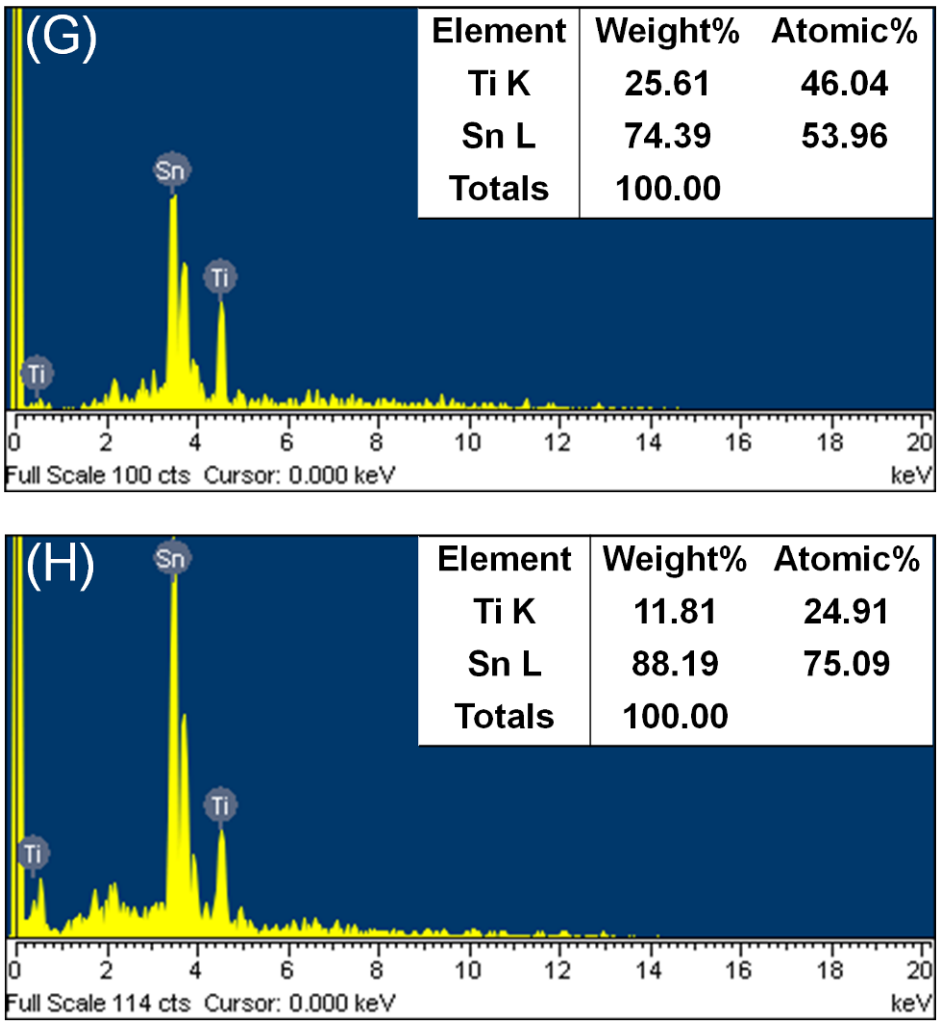


Figure S1 SEM images of (A) TiO_2, (B) $Ti_{0.75}Sn_{0.25}O_2$, (C) $Ti_{0.5}Sn_{0.5}O_2$, (D) $Ti_{0.25}Sn_{0.75}O_2$, (E) SnO_2 with annealing in air at 800 ^oC. The EDX results of (F) $Ti_{0.75}Sn_{0.25}O_2$, (G) $Ti_{0.5}Sn_{0.5}O_2$, and (H) $Ti_{0.25}Sn_{0.75}O_2$.

Electronic Supplementary Material (ESI) for CrystEngComm

Table S1 Composition of $Ti_xSn_{1-x}O_2$ solid solutions measured from EDX and ICP analyses.

Sample	Composition	
	EDX	ICP
$Ti_{0.75}Sn_{0.25}O_2$	$Ti_{0.74}Sn_{0.26}O_2$	$Ti_{0.66}Sn_{0.34}O_2$
$Ti_{0.5}Sn_{0.5}O_2$	$Ti_{0.46}Sn_{0.54}O_2$	$Ti_{0.53}Sn_{0.47}O_2$
$Ti_{0.25}Sn_{0.75}O_2$	$Ti_{0.25}Sn_{0.75}O_2$	$Ti_{0.26}Sn_{0.74}O_2$

According to Table S1, the composition of all solid solutions is generally close to their corresponding precursor composition with the exception of the ICP result for $Ti_{0.75}Sn_{0.25}O_2$. This phenomenon is attributabe to the excellent chemical stability and a larger size of $Ti_{0.75}Sn_{0.25}O_2$; thus, the repeated digestion may lead to the partial leaching of Sn^{4+} species from the solid solution. This statement is consistent with the difficult digestion and partial dissolution of this Ti-rich solid solution.

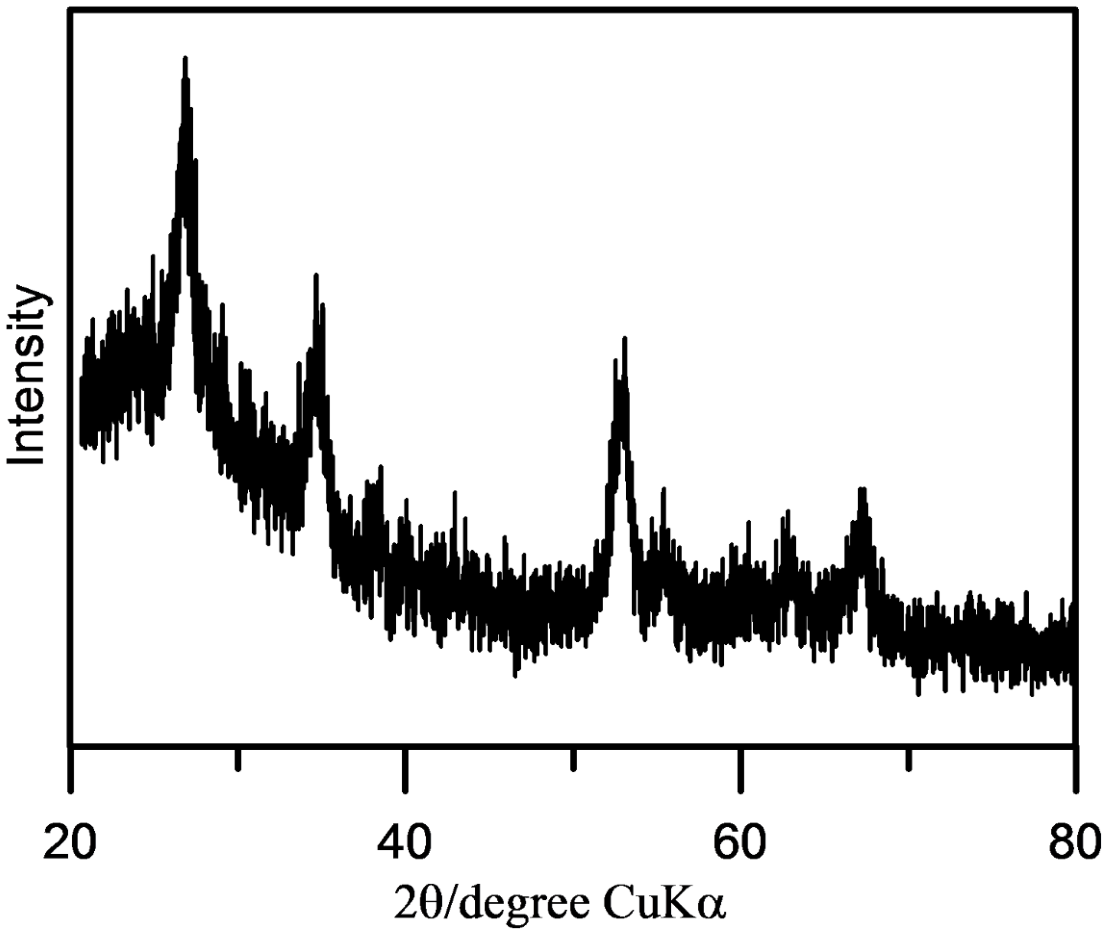
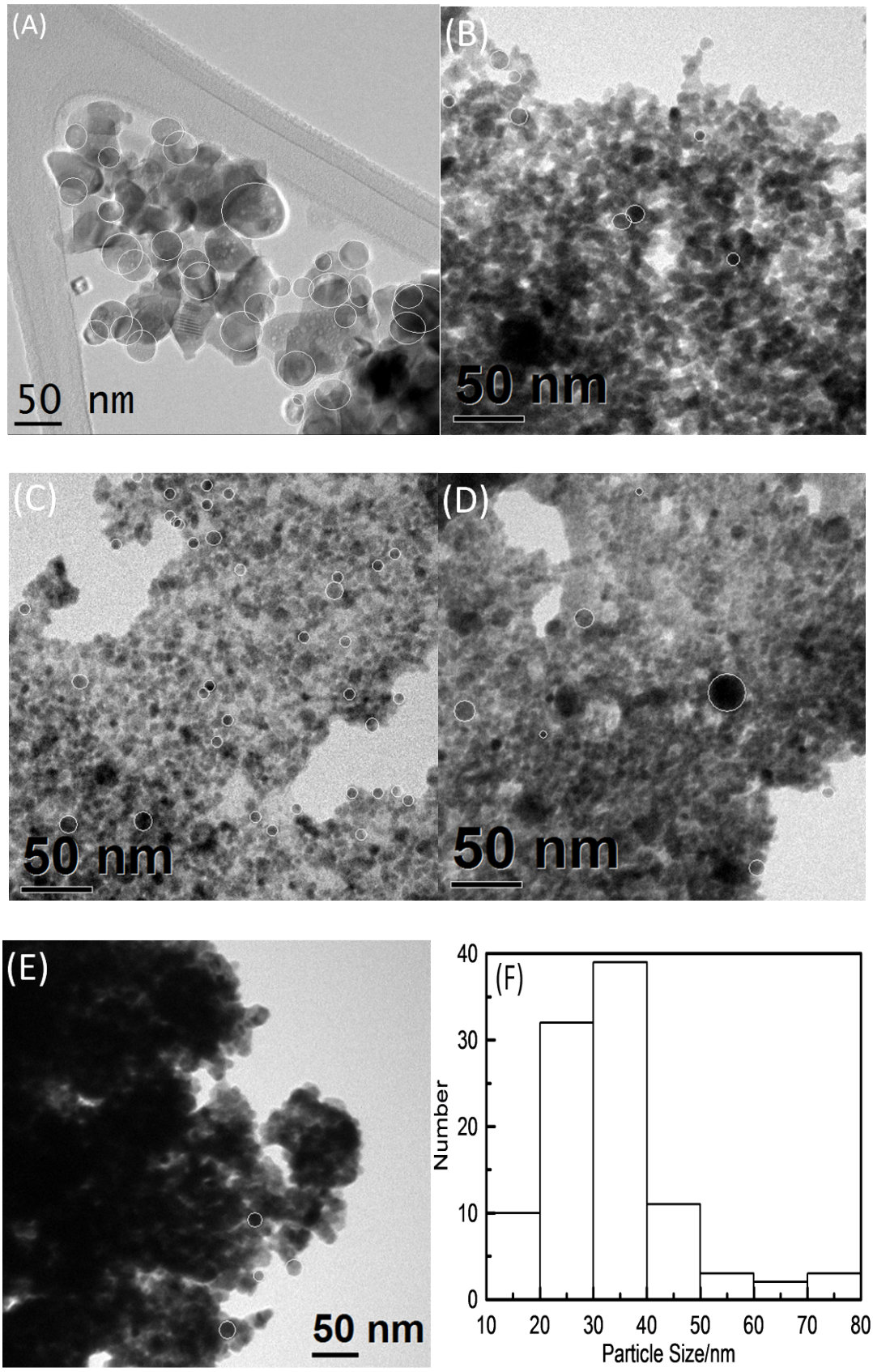


Figure S2 The XRD pattern of $Ti_{0.5}Sn_{0.5}O_2$ with annealing in air at 800 ^{o}C.

The average crystal size of this solid solution is about 7.6 nm. The XRD pattern shows a stable solid solution.



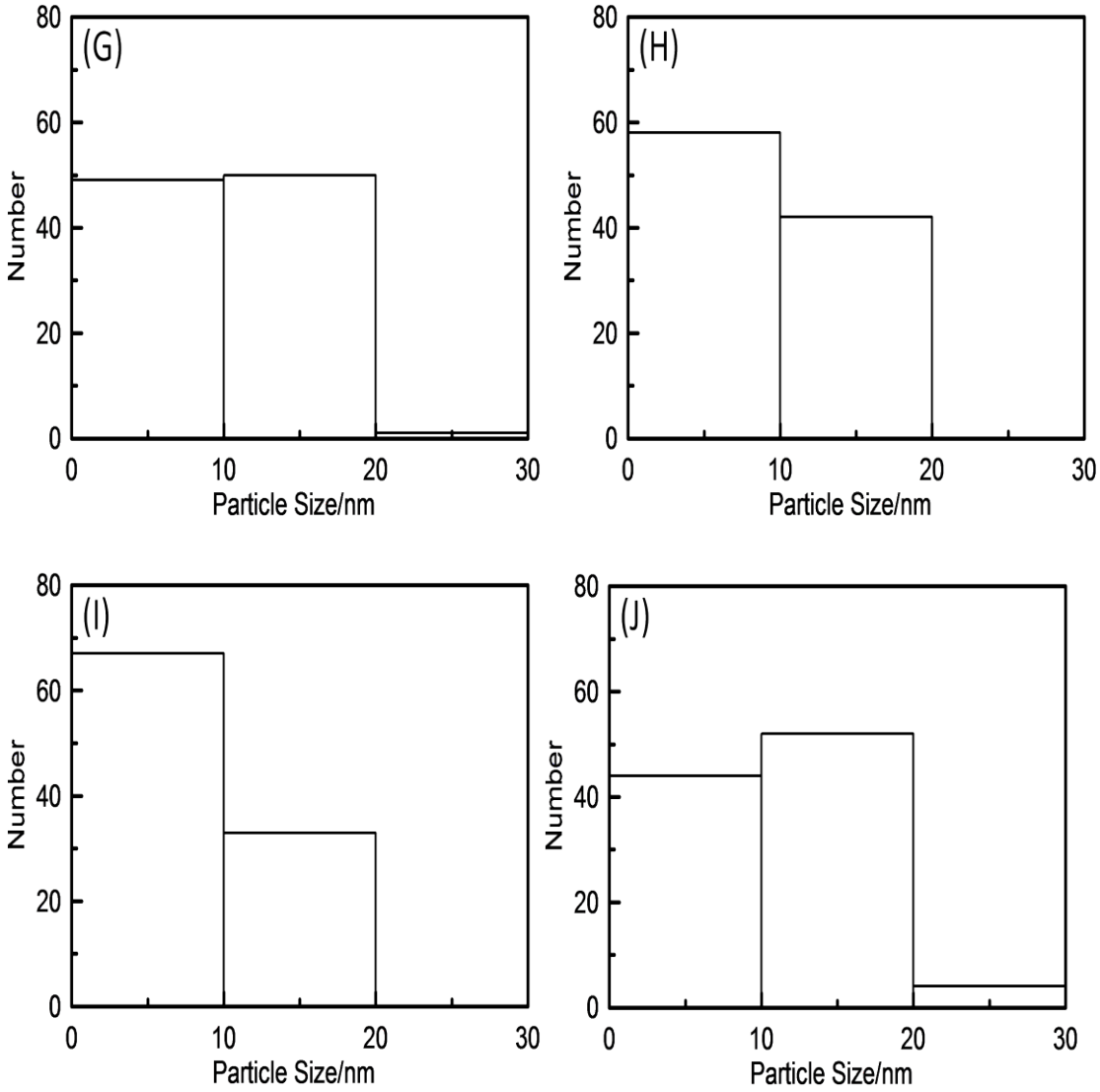
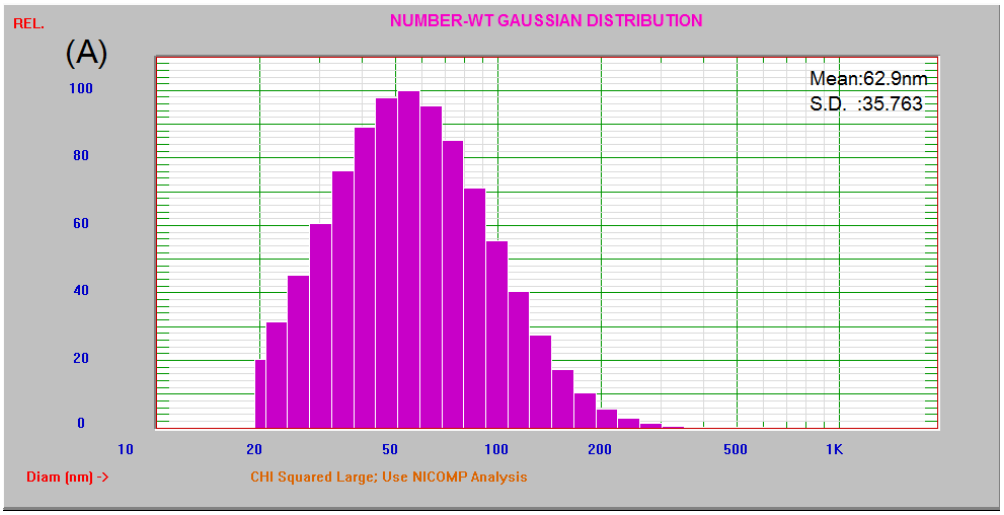
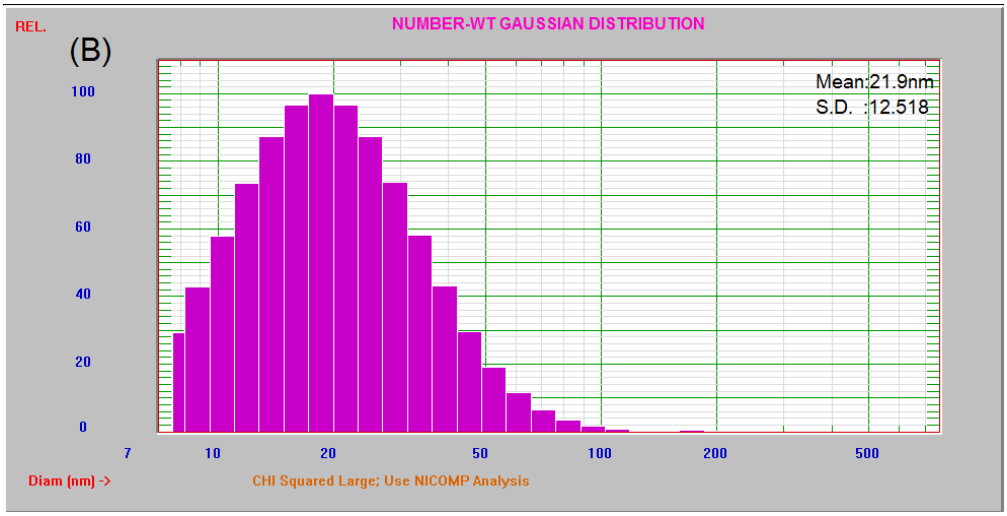
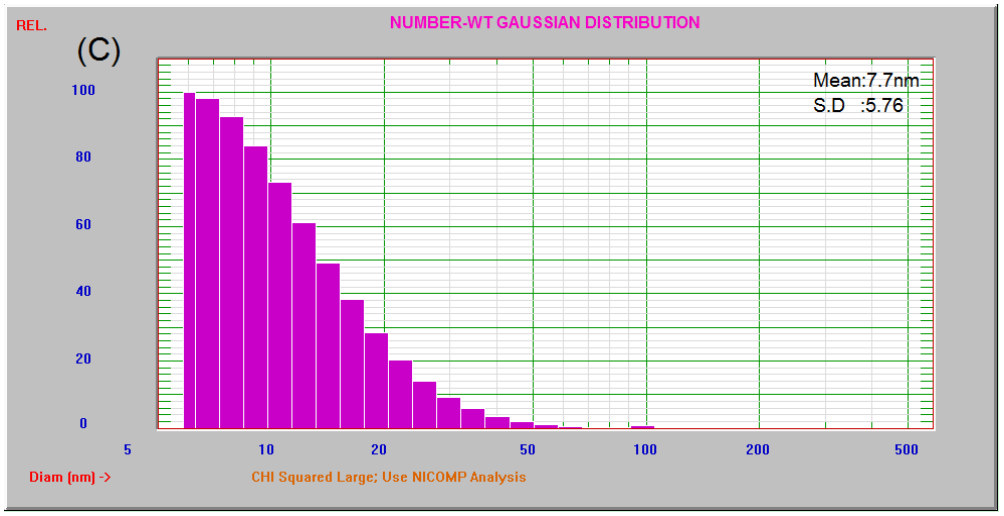


Figure S3 (A-E) TEM images and (F-J) particle size distributions of (A,F) TiO_2, (B,G) $Ti_{0.75}Sn_{0.25}O_2$, (C,H) $Ti_{0.5}Sn_{0.5}O_2$, (D,I) $Ti_{0.25}Sn_{0.75}O_2$, (E,J) SnO_2 with annealing in air at 800 ^oC.







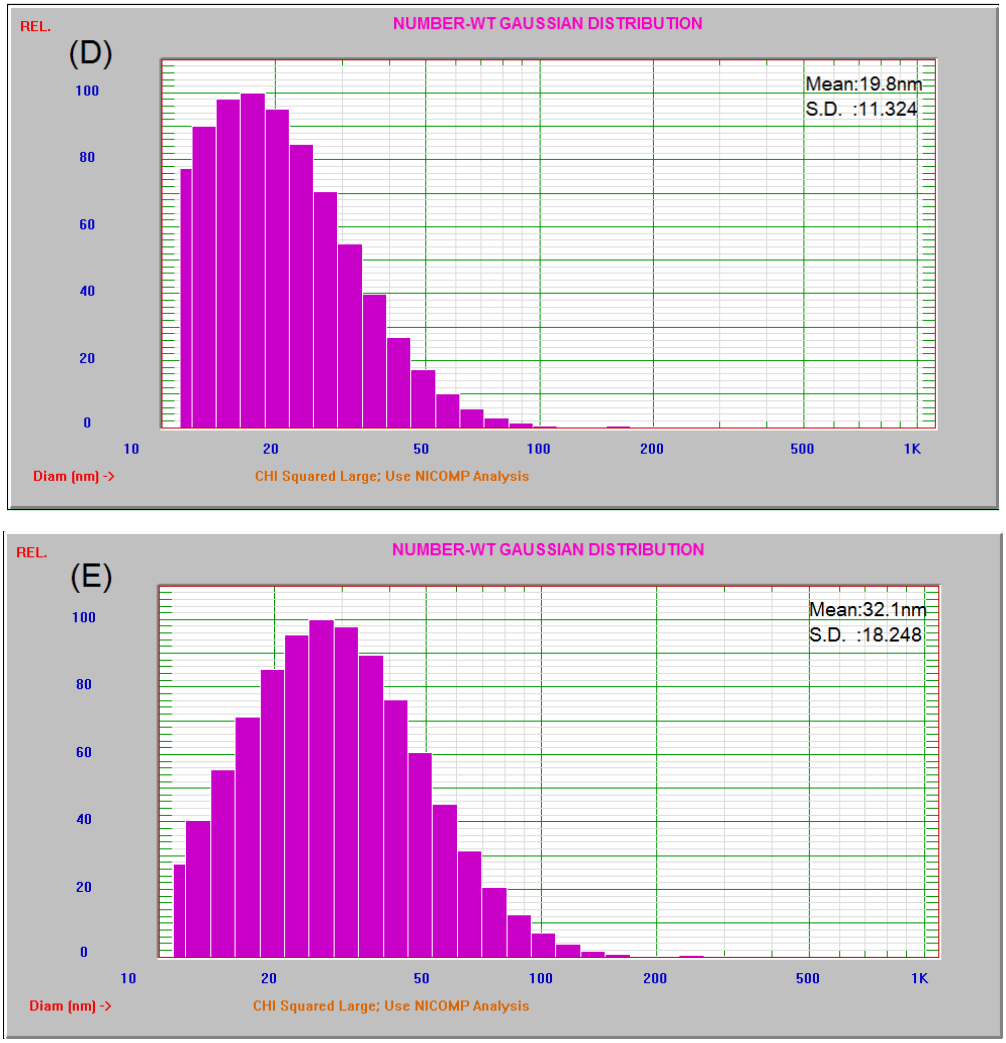


Figure S4 Particle size distributions of (A) TiO_2, (B) $Ti_{0.75}Sn_{0.25}O_2$, (C) $Ti_{0.5}Sn_{0.5}O_2$, (D) $Ti_{0.25}Sn_{0.75}O_2$, (E) SnO_2 with annealing in air at 800 ^oC.

The order of oxides with respect to decreasing the average particle size is: TiO_2 > SnO_2 > $Ti_{0.75}Sn_{0.25}O_2$ > $Ti_{0.25}Sn_{0.75}O_2$ > $Ti_{0.5}Sn_{0.5}O_2$.

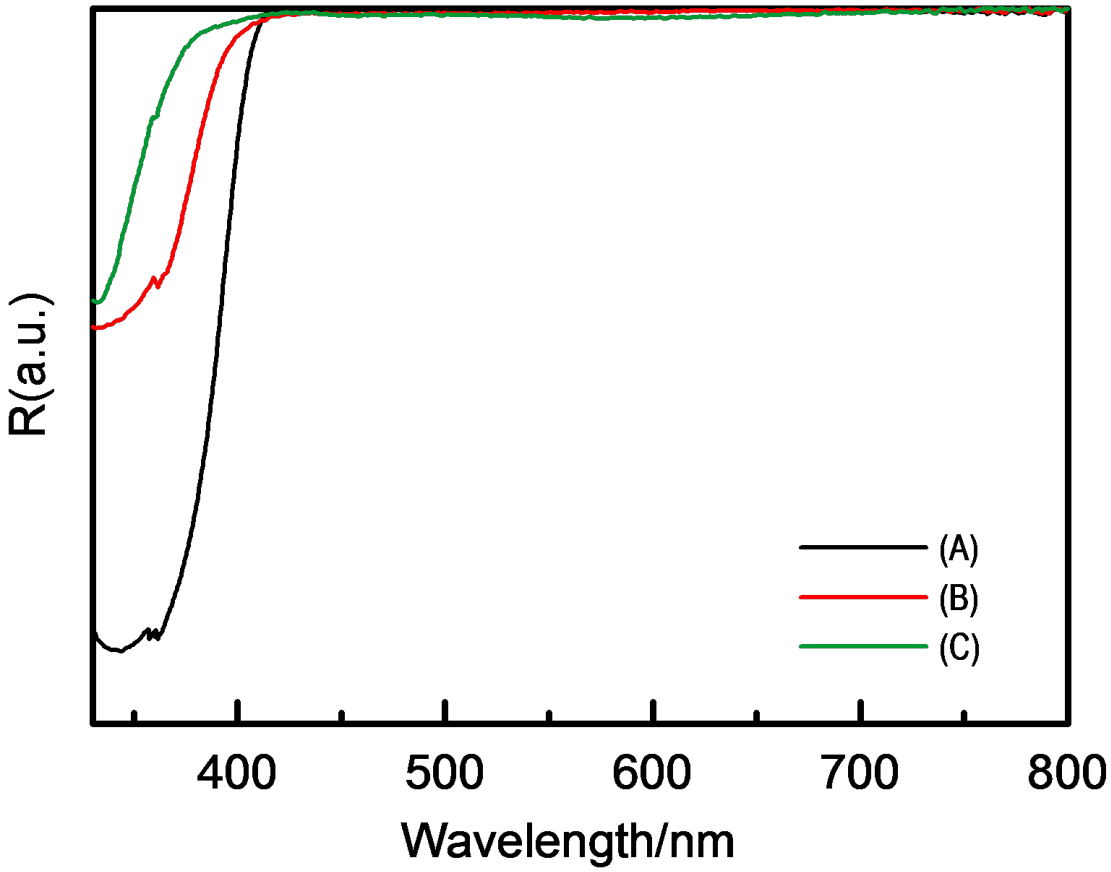


Figure S5 UV-VIS diffusion reflectance spectra of (A) TiO_2, (B) $Ti_{0.5}Sn_{0.5}O_2$, and (C) SnO_2 with annealing in air at 800 ^oC.

The spectrum of the binary oxide located between the spectra corresponding to SnO_2 and TiO_2 supports the successful formation of a $Ti_{0.5}Sn_{0.5}O_2$ solid solution.