Electronic Supplementary Information for

Effects of Ga doping and hollow structure on the band-structures and photovoltaic properties of SnO_2 photoanode dye-sensitized solar cells

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The Fermi level of the photoanode in a DSSC is an important parameter because the difference between the red-ox potential in the quasi-Fermi level of the anode and the electrolyte determines the V_{oc} of the DSSCs. Flat band potentials (E_{fb}) can be obtained from the intercept on the potential axis of Mott-Schottky plots using the equation

$$\frac{1}{C^2} = (\frac{2}{A^2 e \varepsilon \varepsilon_0 N_D})(E - E_{fb} - \frac{kT}{e}),$$

where k the Boltzmann constant, T the absolute temperature, ε the dielectric constant of the SnO_2 layer, ε_0 the vacuum permittivity, e the electron charge, C represents the capacitance of the space charge region, N_D the donor density, E the applied potential, E_{fb} the flat band potential, and A is the active surface. As shown in Figure S1,the Mott-Schottky plots for the SnO_2, $Sn_{0.99}Ga_{0.01}O_2$, $Sn_{0.97}Ga_{0.03}O_2$, $Sn_{0.95}Ga_{0.05}O_2$ films at 1000Hz in the dark provided values of E_{fb} of 0.095, 0.016, -0.133, and -0.290 V (vs. SCE).

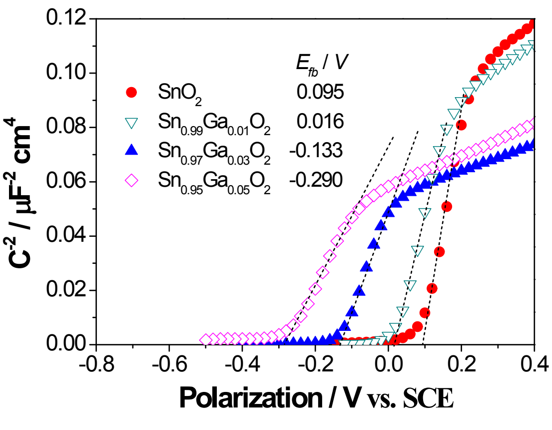

Fig. S1. Mott-Schottky plots of the SnO_2 and the Ga-doped SnO_2 films prepared on FTO substrates.

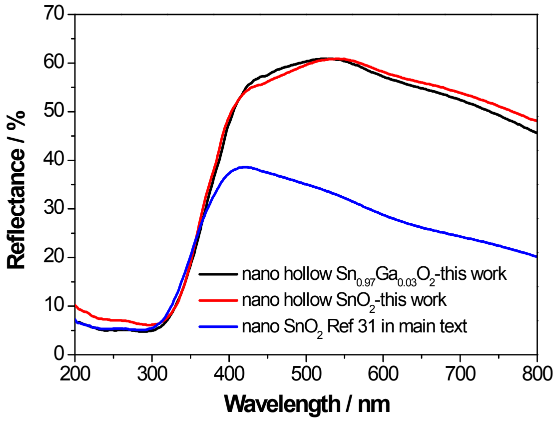

Fig. S2. Diffuse reflectance spectra of the photoelectrodes with nano SnO_2, nano hollow SnO_2 and nano hollow $Sn_{0.97}Ga_{0.03}O_2$. The reflectance of the SnO_2 and $Sn_{0.97}Ga_{0.03}O_2$ hollow sphere films are much higher than that of the SnO_2 nanocrystalline films, indicating that the particles in the hollow sphere film have a higher light scattering ability than those in the SnO_2 nanocrystalline film.

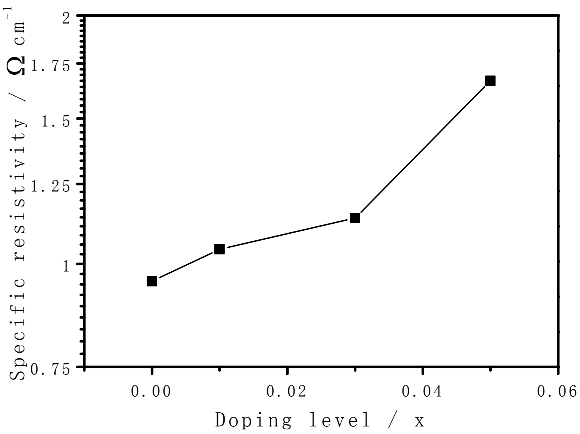

Fig. S3. Specific resistivity as a function of doping level for $Sn_{1-x}Ga_xO_2$ films.

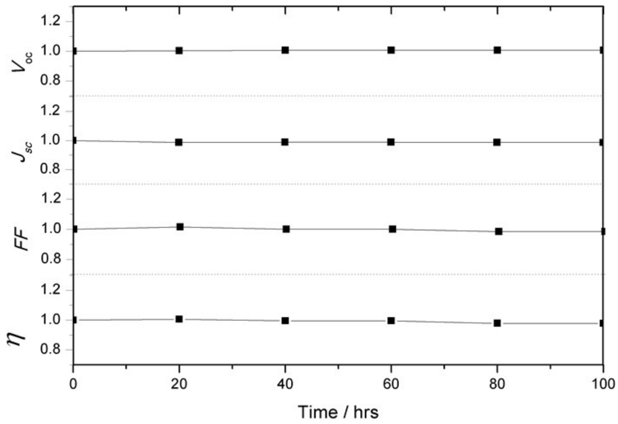

Fig. S4. Normalized device performance under constant illumination for 100h measured in air (DSSCs based on $Sn_{0.97}Ga_{0.03}O_2$/$TiCl_4$). The values plotted in **Fig. S4.** are the averages over five samples. After 100 hrs, the conversion efficiency of DSSC is maintained at about 100% to the initial one.

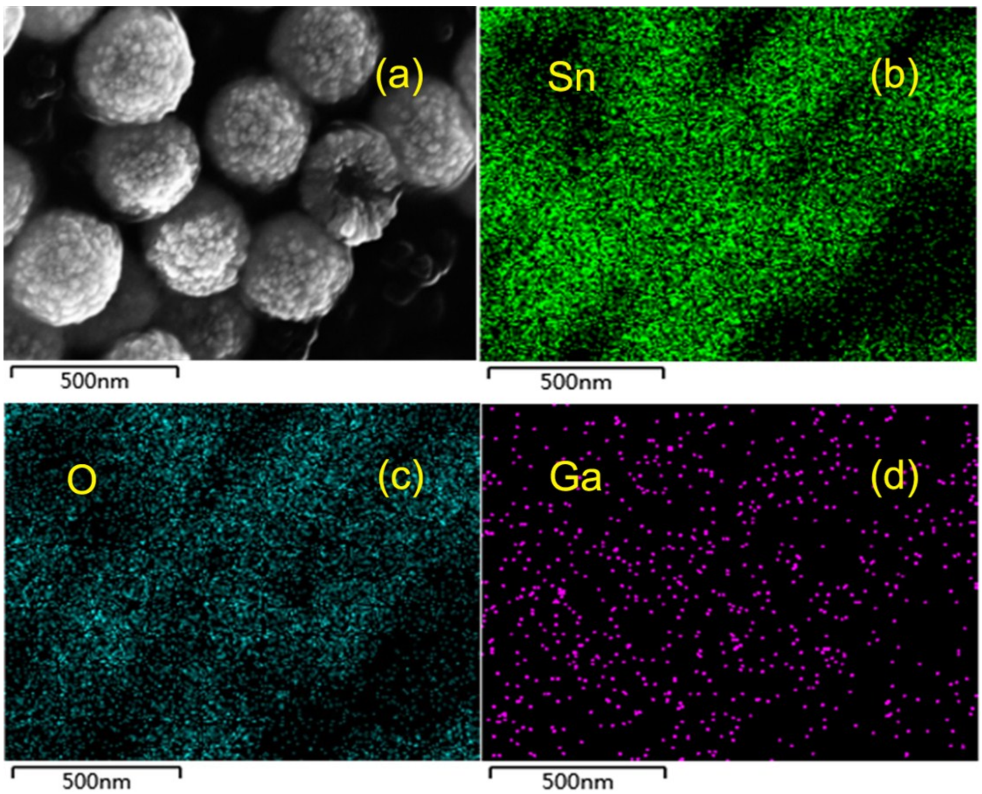

Fig. S5. (a) SEM image of the $Sn_{0.97}Ga_{0.03}O_2$ synthesized from chemicals. (b)-(d) Elemental mapping performed from the SEM image (a). The elements (Sn, O, Ga) are uniformly distributed in the sample, indicative of the high homogeneity of the $Sn_{0.97}Ga_{0.03}O_2$ particles.

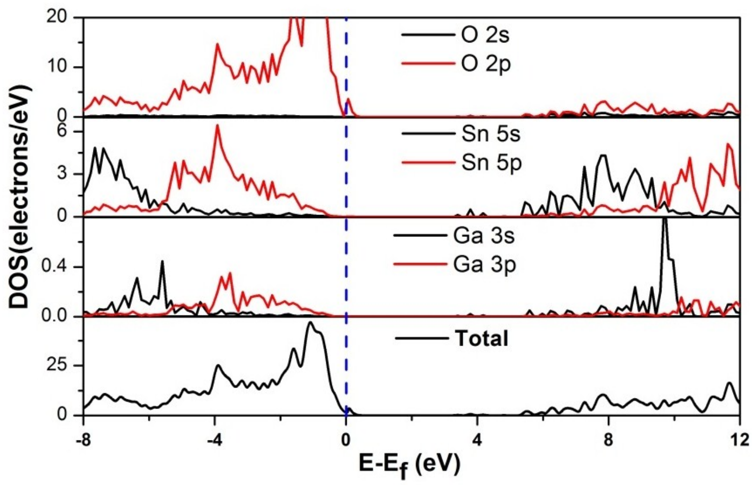

Figure S6. Calculated total and orbital resolved densities of states for the pure SnO_2 and 6.25% Ga doped SnO_2. The Fermi level is set to zero.

Table S1 The reported high values of η obtained in the DSSCs based on different SnO_2 photoanode structures.

Ref.	Morphology or structure	Diameter	Synthetic method or manufacturer	Film thickness	η (%) (no surface treatment)	η (%)(after surface treatment)[a]
1	SnO_2 nanoparticles	3-5 nm	Alfa Aesar	10 μm	1.74	MgO/7.21
2	SnO_2 nanowire	20-200nm	reactive vapor transport	25-30 μm	2.1	$TiCl_4$/4.1
3	SnO_2 hollow microspheres	1-2 μm	hydrothermal	10 μm	1.4	$TiCl_4$/5.65
4	SnO_2nanoflower	1 μm	hydrothermal	8-10 μm	3.00	$TiCl_4$/6.78
5	SnO_2 nanoparticles	15 nm	Alfa Aesar	---	1.7	$CaCO_3$/5.4
6	SnO_2nanopowder	＜100 nm	Sigma-Aldrich	8μm	3.65	MgO/6.40
7	SnO_2 nanotube	110 nm	electrospinning	13μm	0.99	$TiCl_4$/5.11
8	SnO_2 hollow nanospheres	200 nm	hydrothermal	---	0.86	$TiCl_4$/6.02
9	SnO_2octahedra	0.5-1.8 μm	sonochemical	13.2 μm	---	$TiCl_4$/6.8
10	mesoporous SnO_2 agglomerates	200-600 nm	molten salt method	8 μm	3.05	$TiCl_4$/6.23
11	SnO_2nanofibers	200 nm	---	8.7 μm	--	$TiCl_4$/4.63
Our work	**Ga-SnO_2hollow microspheres**	**11.6-15.9 nm**	**hydrothermal**	**8 μm**	**3.56**	**$TiCl_4$/7.11**

[a]surface treatment method and the corresponding photon-to-electron conversion efficiency.

Table S2. Calculated structural parameters a and c for pure SnO_2 and 6.25% Ga doped SnO_2.

	Experiment for SnO_2	Calculation for SnO_2	Calculation for $Sn_{0.9375}Ga_{0.0625}O_2$	Calculation for 6.25% Ga interstitial doping
a (Å)	4.74[b]	4.76	4.75	4.81
c (Å)	3.19[b]	3.21	3.20	3.22

[b]Phys. Rev. B. 81, 245216, 2010

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