

Supplementary Information

Facile spray reaction synthesis and characterization of hierarchically porous SnO₂ microspheres for enhanced dye-sensitized solar cell

Hui Zhang,^{*a} Rong Wu,^a Hong Xu,^a Fan Li,^{*b} Shuo Wang,^a Jinshu Wang,^{*c} and Tingting Zhang^{a†}

^a School of Science, Beijing Jiaotong University, Beijing 100044, PR China. E-mail: hzhang1@bjtu.edu.cn

^b College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, PR China. E-mail: vanadiumli@bjut.edu.cn

^c College of Materials, Beijing University of Technology, Beijing 100124, PR China. E-mail: wangjsh@bjut.edu.cn

Table of contents

1	Figure S1.	Schematic set-up for spray reaction process.
	Figure S2.	Representative EDX spectrum (right) of synthesized SnO ₂ spheres (left).
	Figure S3.	Rietveld-refined XRD patterns of SnO ₂ porous spheres calcined at 500-800 °C: — Experimental pattern, □ Refined pattern, difference pattern, —(h k l) lines.
	Figure S4.	BET plots of SnO ₂ porous spheres calcined at 600-800 °C.
	Figure S5.	The fitting results of O1s XPS spectra measured for SnO ₂ spheres annealed at 500-700 °C.
	Figure S6.	UV-Vis absorption spectra of 600 °C SnO ₂ spheres.
	Figure S7.	Histogram for the contributions to current density of dye loading and light scattering capability.
	Figure S8.	I-V curves for cells with different anode thickness using SnO ₂ microspheres heated at 600 °C as scattering layer.
	Table S1.	Assignment of the bands in FTIR spectra of N719, N719-P25, and N719-S500.
Table S2.	Summary of $\Delta\nu$ values for carboxylate/carboxylic acid group-SnO ₂ /TiO ₂ system compounds.	
2	E_g^{eff} calculation	Calculation for the SnO ₂ effective band gap energy

1. Figures and tables

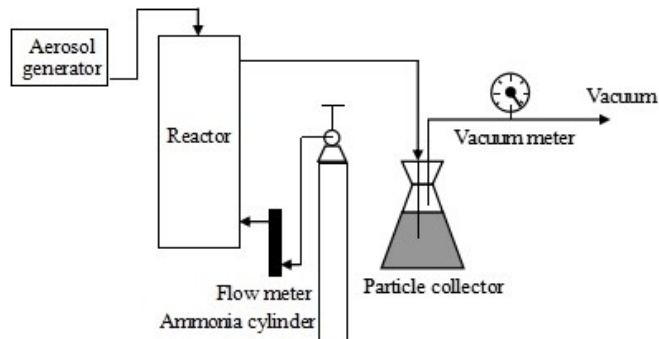


Figure S1. Schematic set-up for spray reaction process.

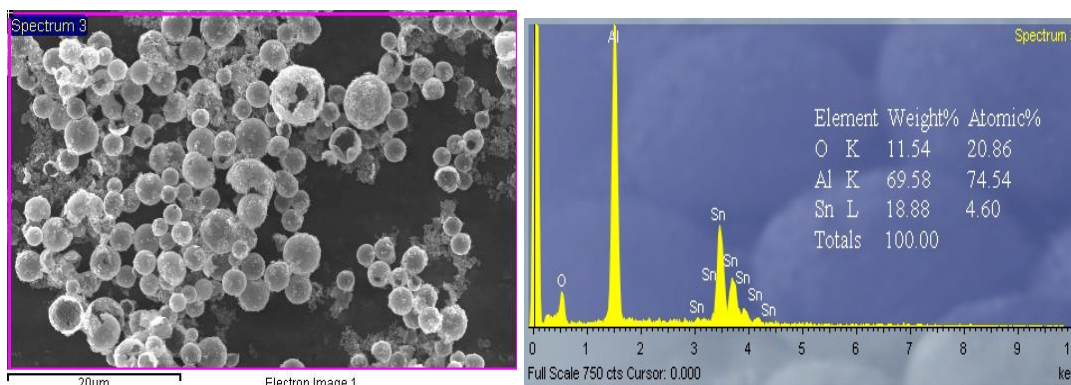


Figure S2. Representative EDX spectrum (right) of synthesized SnO₂ spheres (left).

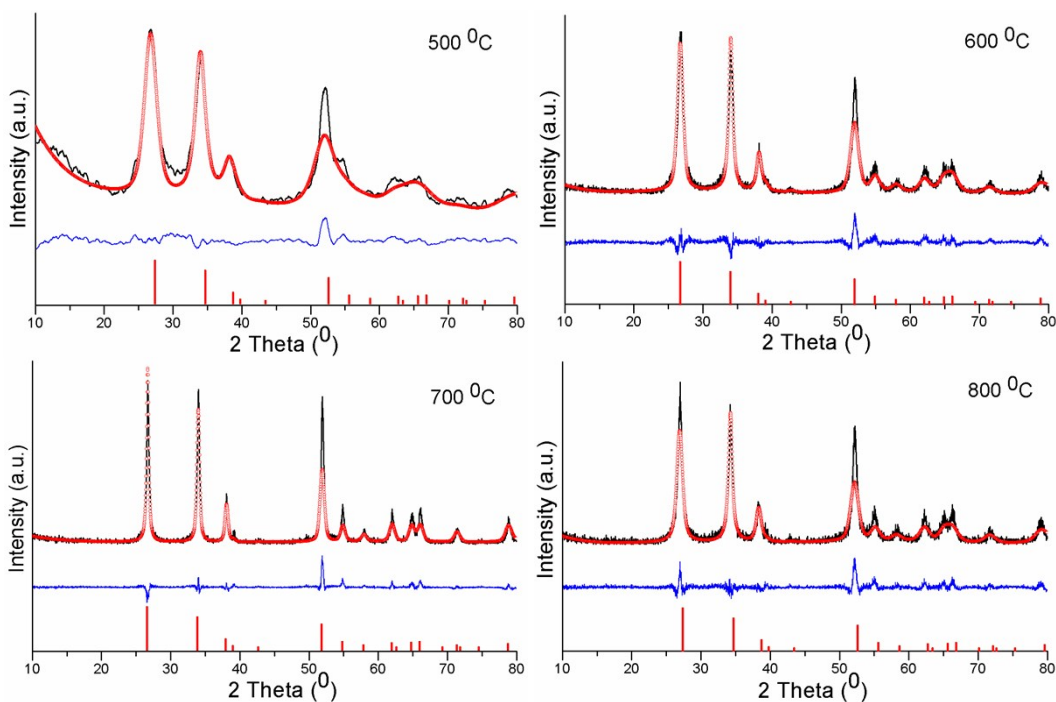


Figure S3. Rietveld-refined XRD patterns of SnO₂ porous spheres calcined at 500-800 °C: —Experimental pattern, — Refined pattern, — difference pattern, | (h k l) lines.

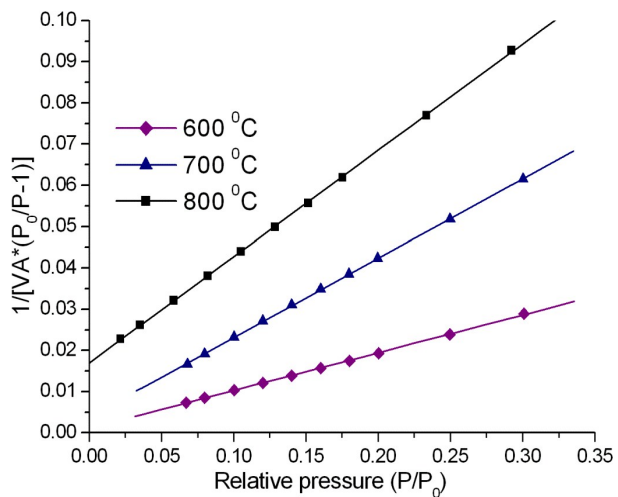
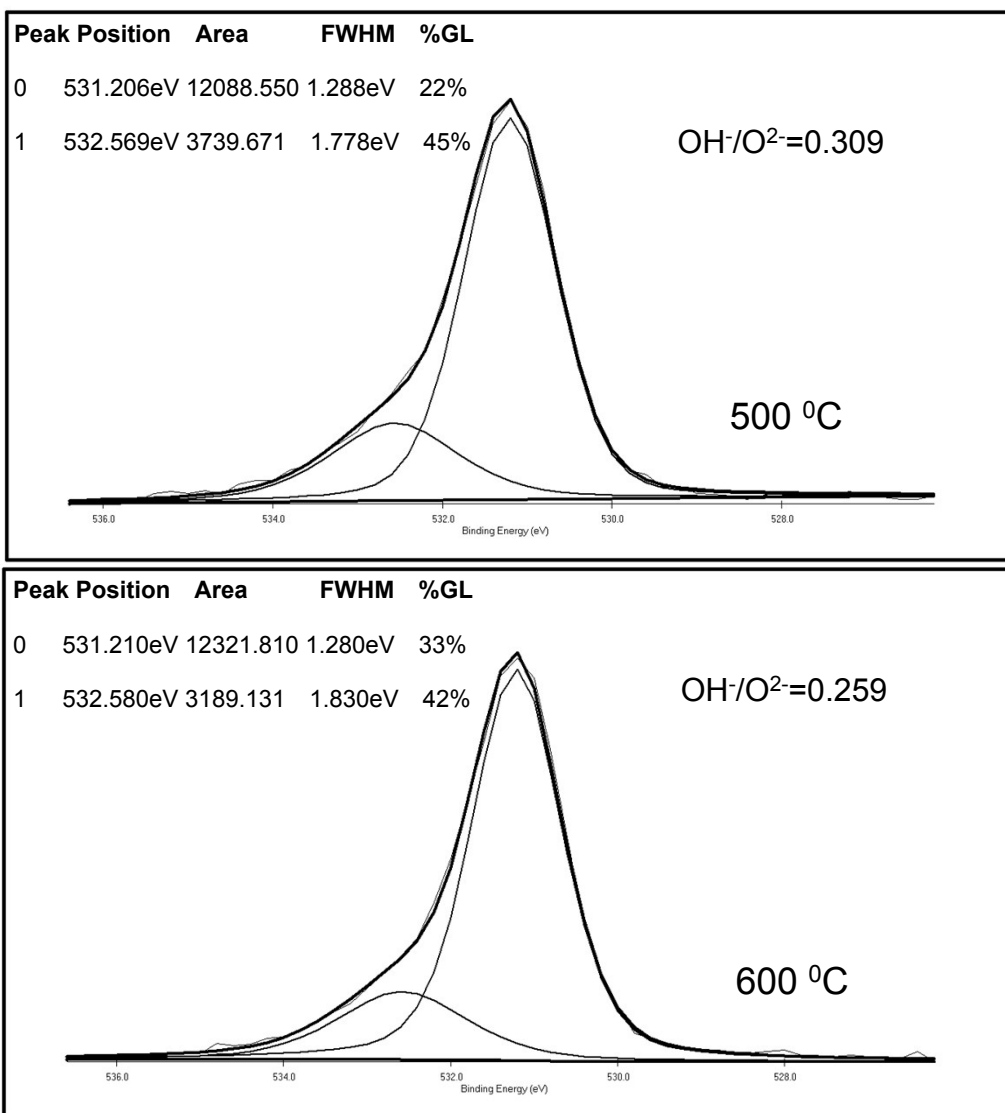


Figure S4. BET plots of SnO₂ porous spheres calcined at 600-800 °C.



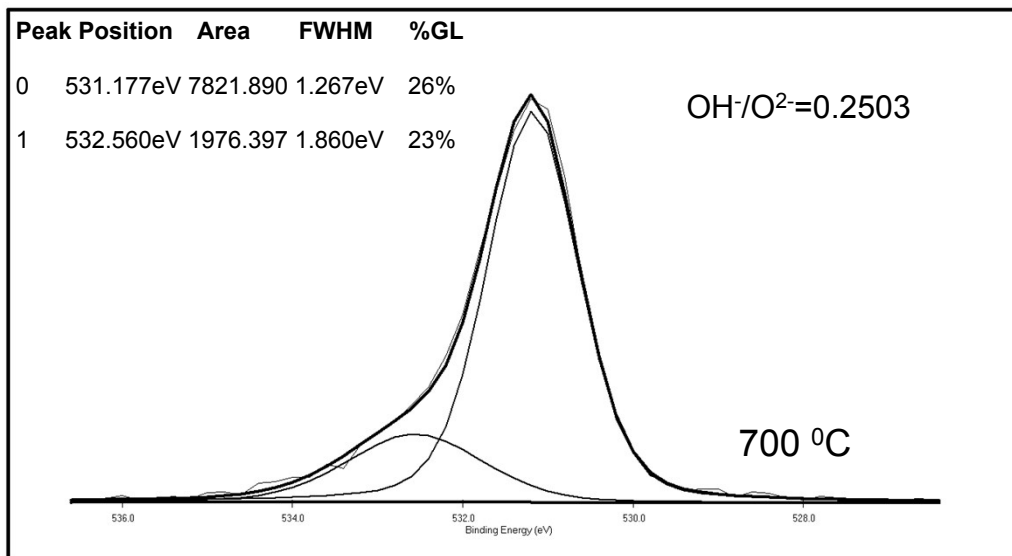


Figure S5. The fitting results of O1s XPS spectra measured for SnO₂ spheres annealed at 500-700 °C.

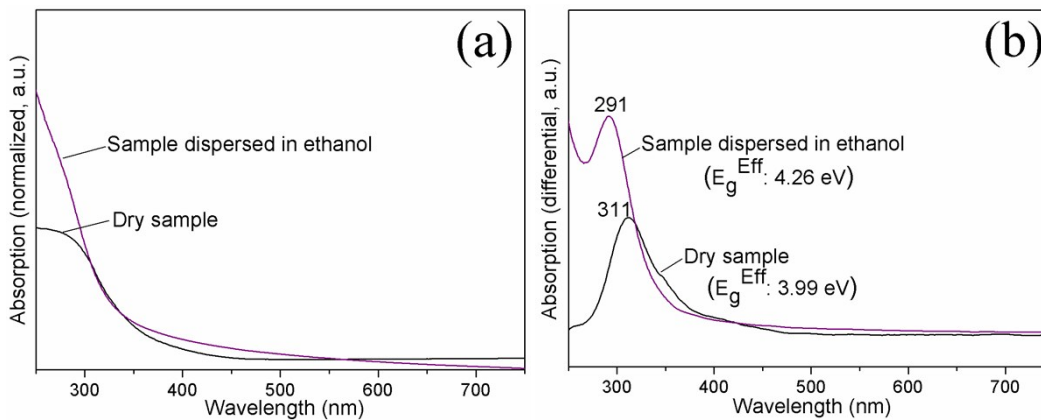


Figure S6. (a) UV-Vis absorption spectra and corresponding differential absorption spectra of the dry 600 °C SnO₂ spheres and the 600 °C SnO₂ spheres dispersed in ethanol.

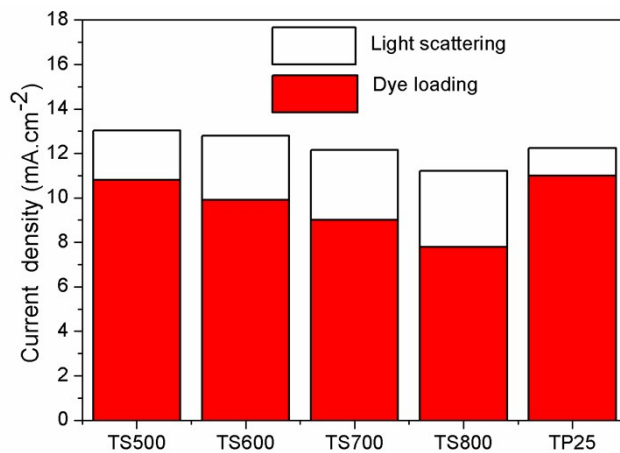


Figure S7. Histogram for the contributions to current density of dye loading and light scattering capability.

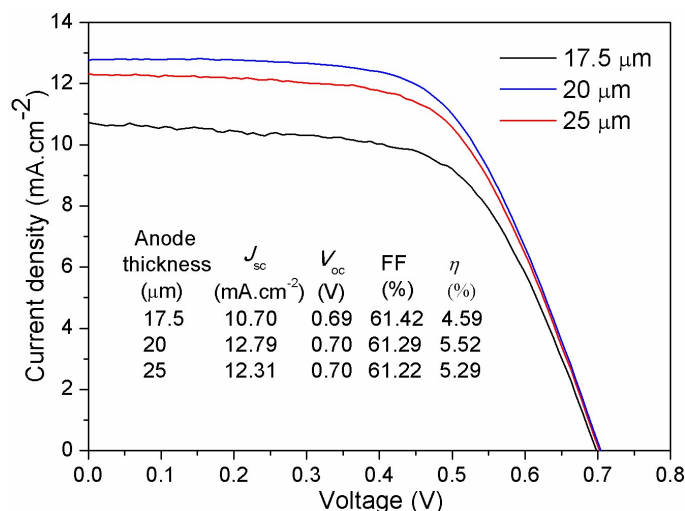


Figure S8. I-V curves for cells with different anode thickness using SnO₂ microspheres heated at 600 °C as scattering layer.

Table S1. Assignment of the Bands in FTIR Spectra of N719, N719-P25, and N719-S500.

N719 v(cm ⁻¹)	N719-S500 v(cm ⁻¹)	N719-P25 v(cm ⁻¹)	Assignment
1232	1237	1266	C-O
1373	1377	1382	COO _{-sym}
1404	1408	1430	bpy
1468	1461	1469	δ(CH ₂) in TBA
1546	1541	1560	bpy
1607	1621	1610	COO _{-asym}
1712	1713	1693	C=O
2101	—	2079	NC
2875	2874	2852	CH _{2, asym}
2933	2930	2922	CH _{2, sym}
2963	2965	2971	CH ₃

Table S2. Summary of Δv Values for Carboxylate/Carboxylic Acid Group-SnO₂/TiO₂ System Compounds.

Compound	$\nu_{asym}(\text{COO})$ (cm ⁻¹)	$\nu_{sym}(\text{COO})$ (cm ⁻¹)	Δv (cm ⁻¹)	Binding mode
N719	1607	1373	234	N/A
N719-S500	1621	1377	244	Unidentate
N719-P25	1610	1382	228	Bridging

2. Calculation for the SnO₂ effective band gap energy (E_g^{eff})

When the SnO₂ crystallite radius is near or larger than the exciton Bohr radius (2.7 nm) of bulk SnO₂, E_g^{eff} of SnO₂ crystallite can be approximately calculated by following equation.

$$E_g^{eff} \approx E_g^{bulk} + \frac{h^2 \pi^2}{2\mu R^2} \quad (1)$$

where E_g^{bulk} is the bulk band gap energy, R is the crystallite radius, h is the reduced Planck constant, μ is the effective reduced mass ($\mu \approx 0.275m_e$).