

## Supporting Information

### **TiO<sub>2</sub> interpenetrating networks decorated with SnO<sub>2</sub> nanocrystals: enhanced activity of selective catalytic reduction of NO with NH<sub>3</sub>**

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## Experimental Section

**Chemicals.** All of chemicals were analytical grade and used without further purification. Ammonia aqueous solution (30 wt %), tetraethyl orthosilicate (TEOS), HCl aqueous solution (37 wt %), NaOH and SnCl<sub>4</sub> were purchased from Sinopharm Chemical Reagent Co. (China). TiCl<sub>4</sub> was purchased from Aladdin Industrial Inc. TiF<sub>4</sub> was obtained from Sigma-Aldrich Co. LLC. Deionized water was used in all experiments.

**Preparation of silica colloidal opal templates.** Silica colloidal opal templates were synthesized according to a modified Stöber method as described by G.H. Bogush<sup>1</sup> and Edward J. W. Crossland.<sup>2</sup> Typically, 6.4 mL of deionized water, 3.6 mL of ammonia aqueous solution (30 wt %) and 20 mL of TEOS were sequentially added into 150 mL of ethanol and stirred (700 rpm) for 24 h. A quasi-close-packed bead template with a translucent solid was obtained after centrifugation of the reaction solution at 7000 rpm for 5 h. The solid was sintered at 500 °C for 30 min (ramping time 4 h) for further use.

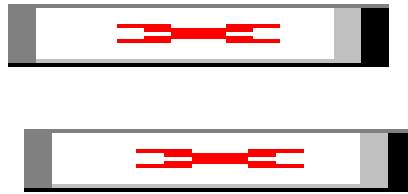
**Pre-seeding of silica opals templates.** Typically, 5 g of the sintered template was immersed in 33 mL of aqueous TiCl<sub>4</sub> (0.015 mM to 15 mM) containing 1 mL of 37 wt % HCl and held at 70 °C for 60 min. After thorough rinsing, the dried template was resintered at 500 °C for 30 min in air (ramping time 4 h).

**Synthesis of TiO<sub>2</sub> interpenetrating network architectures.** TiF<sub>4</sub> was dissolved in deionized water (200 mM) after first adjusting the pH to 2.1 by addition of 37 wt % HCl. 650 mg of the pre-treated silica template was added to 100 mL of TiF<sub>4</sub> solution in a 125 ml-volume Teflon vessel. The vessel was brought to the target reaction temperature 160 °C for the period of the reaction until the solvent evaporated to dryness and then cooling in air over approximate 1 h. The product was collected as a solid white powder, settled at the base of the vessel and rinsed with H<sub>2</sub>O by vacuum filtration on 4.5 μm paper. The silica template was selective etched in aqueous 2 M NaOH at 80 °C for 60 min in a polypropylene beaker. The remaining TiO<sub>2</sub> was collected by centrifugation (3000 r.p.m. for 60 min) and washed with H<sub>2</sub>O and ethanol.

**Synthesis of SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures.** 60 μL

of SnCl<sub>4</sub> and 1 g of as-made TiO<sub>2</sub> (Sn/Ti ratio was ~ 10 wt %) was added in 20 mL of ethanol and stirred until the solvent evaporated to dryness. The Sn-doped TiO<sub>2</sub> was sintered at 350 °C for 2h in air (ramping time 5 h).

**NH<sub>3</sub>-SCR of NO performance.** The SCR performance of the catalysts was evaluated in a fixed-bed stainless steel reactor (i.d.: 10 mm) containing 0.8 g of catalyst located inside a tube furnace. The reaction conditions were as follows: 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 5 vol. % O<sub>2</sub>, 200 ppm SO<sub>2</sub> (when used), 5 vol. % H<sub>2</sub>O (when used) and N<sub>2</sub> as the balance gas. In all tests, the total flow rate of the feed gas was 130 mL/min, which corresponded to a space velocity of approximate 10000 h<sup>-1</sup> except for investigating the effect of GHSV, which was tested ranging from 10000 to 40000 h<sup>-1</sup>. The NO conversion and N<sub>2</sub> selectivity were calculated as follows:



The concentration of NO and NO<sub>2</sub> in the inlet and outlet gases was measured using an ABB EL3020 FTIR gas analyzer. Analysis of N<sub>2</sub>O was done online by a Polytron IR N<sub>2</sub>O gas analyzer. The reaction system was kept for 1 h at each temperature to reach a steady state.

**Specific reaction rate.** The pseudo-first order rate constant  $k$  (cm<sup>3</sup>g<sup>-1</sup>s<sup>-1</sup>) of the SCR reaction is calculated by Eley-Rideal mechanism. It assumed that the NH<sub>3</sub> is strongly adsorbed on the catalyst and the NO reacted from the gas phase. The equation is expressed as follows<sup>3</sup>:

$$k = \frac{V_0}{W} \ln \frac{1}{1 - X_{NO}}$$

where  $V_0$  means the total volumetric flow rate at the inlet (cm<sup>3</sup>s<sup>-1</sup>),  $W$  represents the mass of catalyst (g) and  $X_{NO}$  is the ratio of NO conversion. In this work, the catalyst amount is of 0.8 g for SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures sample, at the temperature of 175 °C, the  $V_0=9.6$  cm<sup>3</sup>s<sup>-1</sup> (GHSV=40000 h<sup>-1</sup>) and  $X_{NO}=71.2\%$ , the  $k$  is calculated to be 14.9 cm<sup>3</sup>g<sup>-1</sup>s<sup>-1</sup>. The  $k'$  of the SnO<sub>2</sub>-doped P25 is

calculated to be  $2.6 \text{ cm}^3\text{g}^{-1}\text{s}^{-1}$  with the same method.

**Characterization.** Field-emission scanning electron microscopy (FESEM) images were taken using a field-emission Hitachi S-4800 (Japan) operated at 1.0 kV. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2011 microscope (JEOL, Japan) operated at 200 kV. Samples were first dispersed in ethanol and then collected using carbon-film-covered copper grids for analysis. Mapping images were also taken by TEM to analyze the distribution of Sn and Ti. The chemical composition and valence were analyzed by an energy-dispersive X-ray spectrometer (EDX) attached to the TEM system and X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos) with a monochromatic Al  $K_\alpha$  source. The Sn/Ti ratios of catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a P-4010 ICP instrument after microwave digestion in sulfuric acid. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 X-ray diffractometer (Germany) with Ni-filtered Cu  $K_\alpha$  radiation (40 kV, 40 mA). Nitrogen adsorption-desorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (U.S.A.). Before measurements, the samples were degassed in a vacuum at 180 °C for 8 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas ( $S_{\text{BET}}$ ) using adsorption data in a relative pressure range from 0.05 to 0.2. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and size distributions were derived from the adsorption branches of isotherms, and the total pore volumes ( $V_t$ ) were estimated from the adsorbed amount at a relative pressure  $p/p_0$  of 0.995. Temperature-programmed desorption of  $\text{NH}_3$  ( $\text{NH}_3$ -TPD) was carried out in a fixed-bed quartz reactor. A typical gas flow rate of 300 mL/min and a sample mass of 0.1 g was used during the experiments. The sample underwent following experimental procedures during TPD: (1) degasification at 500 °C for 1 h in a  $\text{N}_2$  flow; (2) cooling down to 40 °C for 1 h adsorption in a  $\text{NH}_3$  flow; (3) 1 h purging by a  $\text{N}_2$  flow to remove physically adsorbed species; and (4) temperature-programmed desorption under  $\text{N}_2$  with a heating rate of 10 °C/min up to 700 °C.

## References:

- 1 G. H. BOGUSH, M. A. TRACY and C. F. Z. IV, *J. Non-Cryst Solids*, 1988, 104, 95-106.
- 2 E. J. W. Crossland, N. Noel, V. Sivaram, T. Leijtens, J. A. Alexander-Webber and H. J. Snaith, *Nature*, 2013, 495, 215-219.
- 3 S. J. Yang, C. Z. Wang, J. H. Li, N. Q. Yan, L. Ma and H. Z. Chang, *Appl. Catal. B-Environ.*, 2011, 110, 71-80.

**Table S1** Sn and Ti contents of 10 wt % SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures sample by ICP-AES analysis.

Sample*	Composition (wt. %)		Sn/Ti (atomic ratio)
	Ti	Sn	
10 wt % SnO <sub>2</sub> - decorated TiO <sub>2</sub>	52.18	4.78	0.037

\* The weight ratio of Sn/Ti is calculated to be 9.16 wt %.

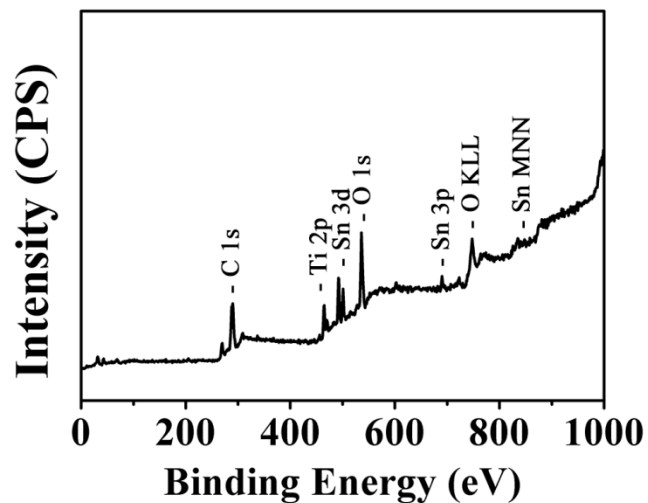
**Table S2.** The acidic sites of 10 wt % SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures sample by NH<sub>3</sub>-TPD.

Sample	Peak Number	Temperature at Maximum (°C)	Quantity (mmol/g)
10 wt % SnO <sub>2</sub> - decorated TiO <sub>2</sub>	1	382.7	1.03
	2	643.6	3.82
10 wt % SnO <sub>2</sub> - doped P25	1	342.2	0.019
	2	526.5	0.032

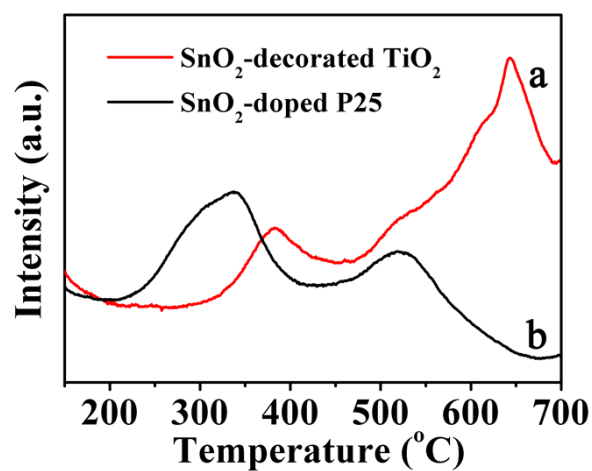
**Table S3** S<sub>BET</sub> values of TiO<sub>2</sub> interpenetrating network architectures and 10 wt % SnO<sub>2</sub>-decorated TiO<sub>2</sub> pre-seeding with various TiCl<sub>4</sub> concentrations compared with commercial TiO<sub>2</sub> (P25).

TiCl <sub>4</sub> concentration (mM)		15	1	0.2	0.015	P25
S <sub>BET</sub>	TiO <sub>2</sub>	120.2	116.0	82.9	60.3	~ 50
(m <sup>2</sup> g <sup>-1</sup> )*	Sn-decorated TiO <sub>2</sub>	78.6	71.3	48.0	36.7	23.7

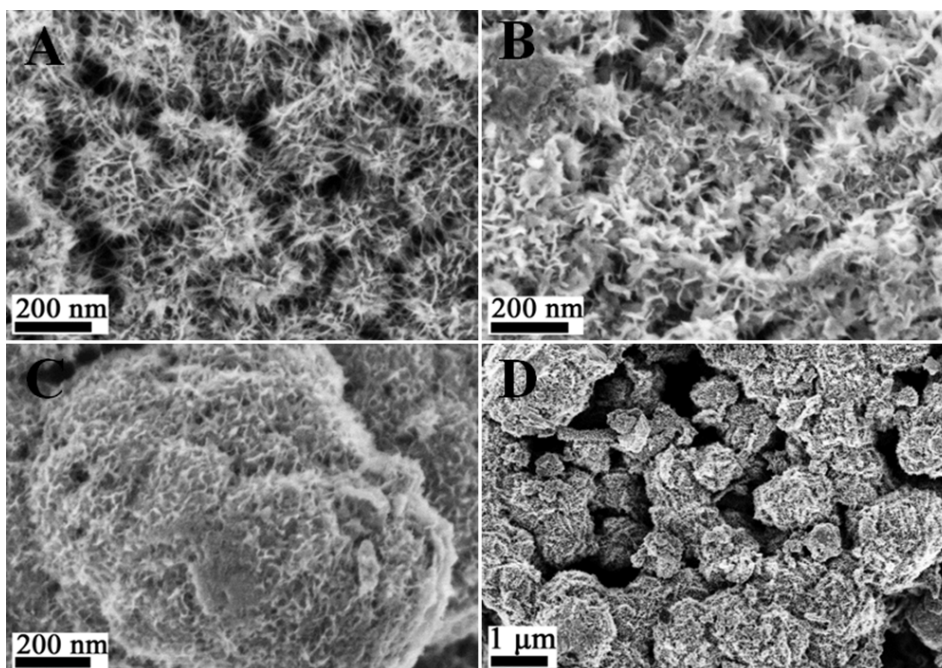
\* Surface area calculated by BET method at relative pressure of  $p/p_0 = 0.05 - 0.2$



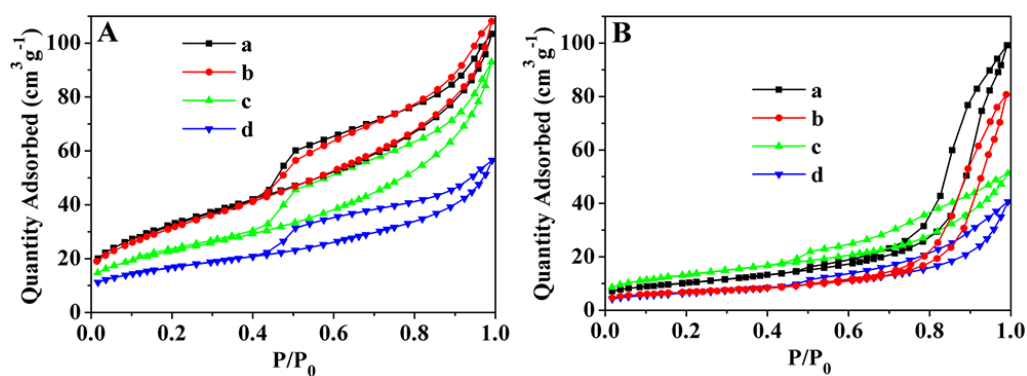
**Fig. S1** XPS survey spectrum of the 10 wt % SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures samples.



**Fig. S2** NH<sub>3</sub>-TPD profiles of the 10 wt % SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures catalysts (a) and SnO<sub>2</sub>-doped P25 (b) after calcination at 350 °C for 2h.

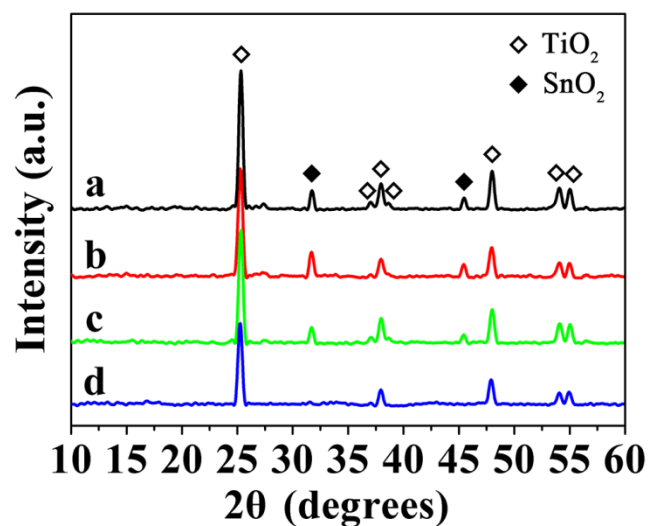


**Fig. S3** SEM images of TiO<sub>2</sub> interpenetrating network architectures and SnO<sub>2</sub>-decorated TiO<sub>2</sub> samples over arrange of crystal seeding conditions: (A) 1 mM seeded TiO<sub>2</sub>, (B) 0.2 mM seeded TiO<sub>2</sub>, (C) 0.015 mM seeded TiO<sub>2</sub>, (D) 0.015 mM seeded Sn-TiO<sub>2</sub>.



**Fig. S4** Nitrogen adsorption-desorption isotherms of the (A) TiO<sub>2</sub> interpenetrating network architectures and 10 wt % SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures with different concentration of TiCl<sub>4</sub> seeding (a) 15, (b) 1, (c) 0.2 and (d) 0.015 mM. The TiO<sub>2</sub> was synthesized for 12 h hydrothermal reaction at 160 °C.





**Fig. S5** XRD patterns of SnO<sub>2</sub>-decorated TiO<sub>2</sub> interpenetrating network architectures samples pre-seeded with various TiCl<sub>4</sub> concentrations by using SiO<sub>2</sub> opals as a template with the hydrothermal treatment at 160 °C for 12 h and doping SnO<sub>2</sub> with calcination at 350 °C: (a) 15 mM, (b) 1 mM, (c) 0.2 mM, (d) 0.015 mM TiCl<sub>4</sub>.