

Supplementary Material

Highly sensitive and selective nitric oxide/butanone temperature-dependent sensor based on waste biomass-derived mesoporous SnO₂ hierarchical microtubes

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Material characterization

Thermogravimetric (TG) tests of t-TSS and Sn-TSS were carried out with the TG/DTA 6300 thermal analyzer (Perkin Elmer, USA) in air atmosphere during 40~800 °C (heating rate: 10 °C·min⁻¹). IR spectra of materials were characterized by EQUINOX 55 Fourier transform infrared spectrometer (FT-IR, Bruker, Germany) during range of 4000~400 cm⁻¹. The phase and grain size of calcined product were tested using D8-Advance powder X-ray diffractometer (PXRD, Bruker, Germany) during 5~80° with radiation source of Cu-K α 1 ($\lambda = 0.15406$ nm). Mott-Schottky measurement was performed on electrochemical workstation (Princeton VersaSTAT) with a standard three-electrode configuration, where the electrolyte was Na₂SO₄ aqueous solution (0.5 M). The morphology and lattice fringes of SnO₂-6 product were characterized by S-4800 scanning electron microscope (SEM, Hitachi) and JEOL-JEM-2010 transmission electron microscope (TEM, Japan). Energy dispersive X-ray spectrometry (EDS) pattern was also determined through an attachment to the SEM. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to measure the specific surface area and pore structure of SnO₂-6 product at 77 K with TriStar 3020 nitrogen adsorption instrument (MeRSomeritics, USA). The X-ray photoelectron spectrometer (XPS, AXIS ULTRA DLD, Kratos, UK) was used to analyze the surface composition and valence state of products. The binding energy was corrected by using 284.6 eV of C 1s as reference. Electron paramagnetic resonance (EPR) spectrum was recorded using an electronic paramagnetic resonance (ER200DSRC10/12, Bruker, Germany) under 1 mW and 100 kHz. The chemical adsorption analyzer (XIANQUAN TP5080, Tianjin) was used for temperature program desorption (TPD) study. The diffuse reflectance spectrum of product was tested by Lambda 750 UV-vis spectrophotometer (Perkin Elmer, USA) with the data collection range of 200~800 nm.

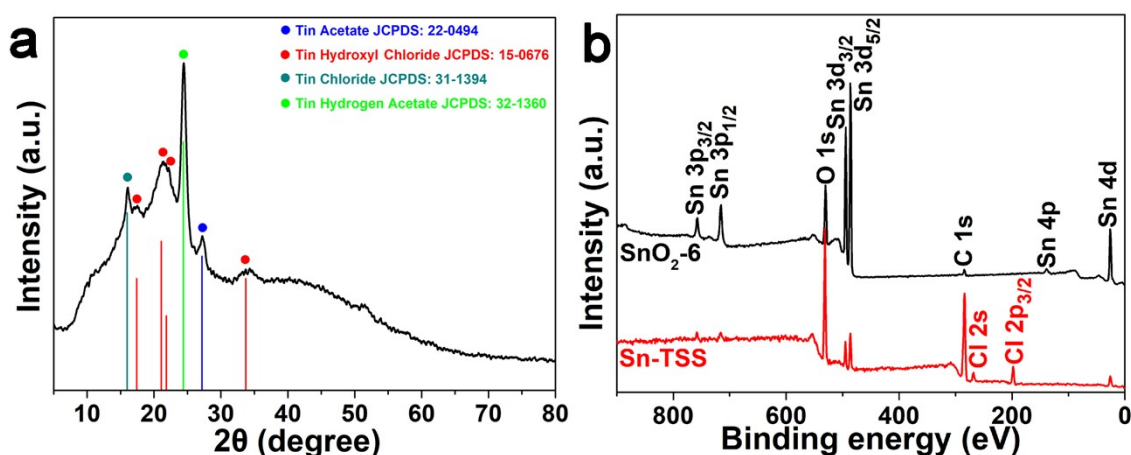


Fig. S1 (a) XRD pattern of Sn-TSS precursor; (b) Full XPS spectra of Sn-TSS precursor and SnO₂-6 product.

TG and FT-IR analyses

Fig. S2a is the thermogravimetry (TG) behaviors of t-TSS and Sn-TSS samples in air atmosphere. After TSS being treated with ammonia and water, the TG curve of t-TSS in Fig. S2a exhibits consecutive thermal decomposition behaviors with final residual content being 0.0%. It indicates that the released hollow channels are more conducive to the rapid adsorption of Sn^{4+} ions into biomass template. It can be seen from the TG curve (Fig. S2a) of Sn-TSS precursor that the continuous weight losses before 550 °C separately correspond to the evaporation of adsorbed water and decomposition of TSS bio-template. The final remaining weight of 10.4% testifies successful adsorption of tin ions into t-TSS through simple impregnation method. Hence, to completely remove biomass template and well inherit its biomorphic structure, the Sn-TSS precursor was heated at 300 °C for 1 h and then calcined at 600 °C for 3 h in air. The final product was labeled as $\text{SnO}_2\text{-6}$.

The broad peak at 3445 cm^{-1} in IR spectrum of Sn-TSS (Fig. S2b) belongs to the stretching vibration of O-H groups in biomass and adsorbed water. The peaks at 2921 and 2856 cm^{-1} are assigned to alkyl C-H stretching vibrations in cellulose, and the peaks at 1729, 1651 and 1031 cm^{-1} refer to the stretching vibrations of -C=O , -CO_2^- and C-O, respectively. Thus, the presence of functional hydroxyl and carboxyl groups in biomass favors the adsorption and dispersed anchoring of tin ions. The peak at 558 cm^{-1} may refer to the $\text{Sn(OH)}_x/\text{Sn(COOH)}_x$ vibration, indicating the coordination between Sn^{4+} ions and -OH and -COOH groups in TSS template. After the Sn-TSS precursor being calcined at 600 °C, no characteristic vibration peaks of the above organic functional groups are observed in the IR spectrum of $\text{SnO}_2\text{-6}$ (Fig. S2b), indicating the completely removal of biomass template. The weak peaks around 3416 and 1635 cm^{-1} refer to the stretching vibration of surface O-H and scissoring vibration of adsorbed water, while the strong peak at 622 cm^{-1} is the characteristic Sn-O vibration of rutile SnO_2 .

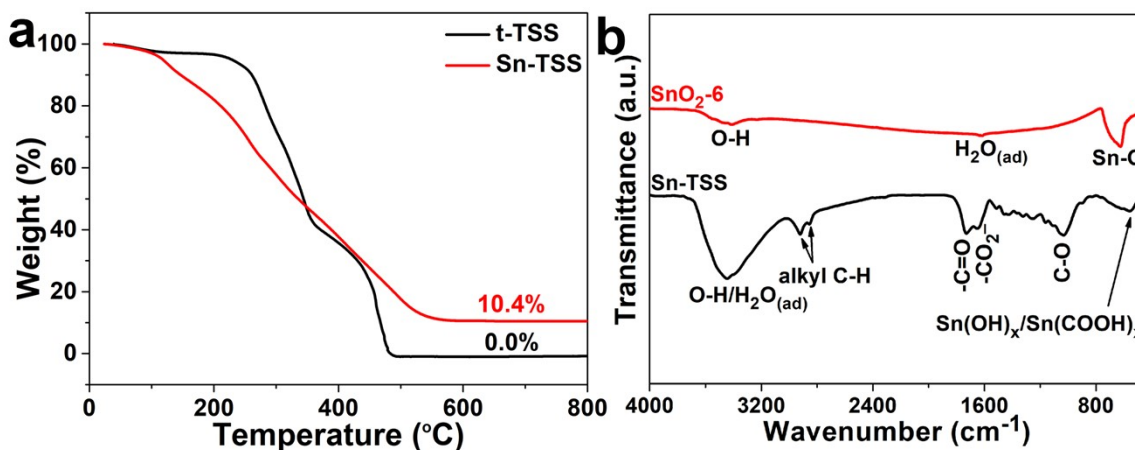


Fig. S2 (a) TG curves of t-TSS and Sn-TSS samples; (b) IR spectra of Sn-TSS precursor and $\text{SnO}_2\text{-6}$ product.

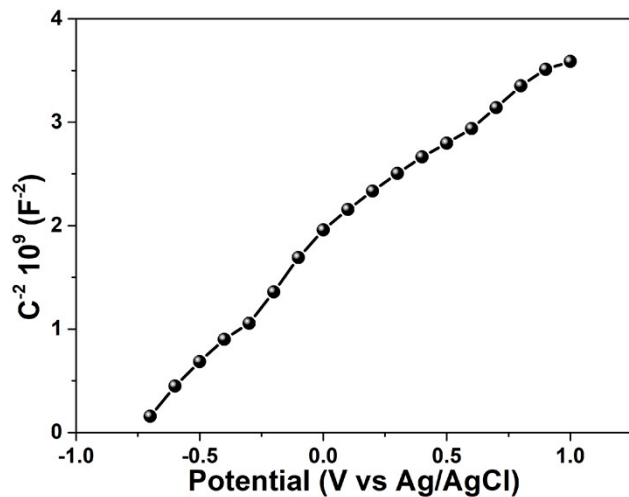


Fig. S3 Mott-Schottky plot of SnO₂-6 product.

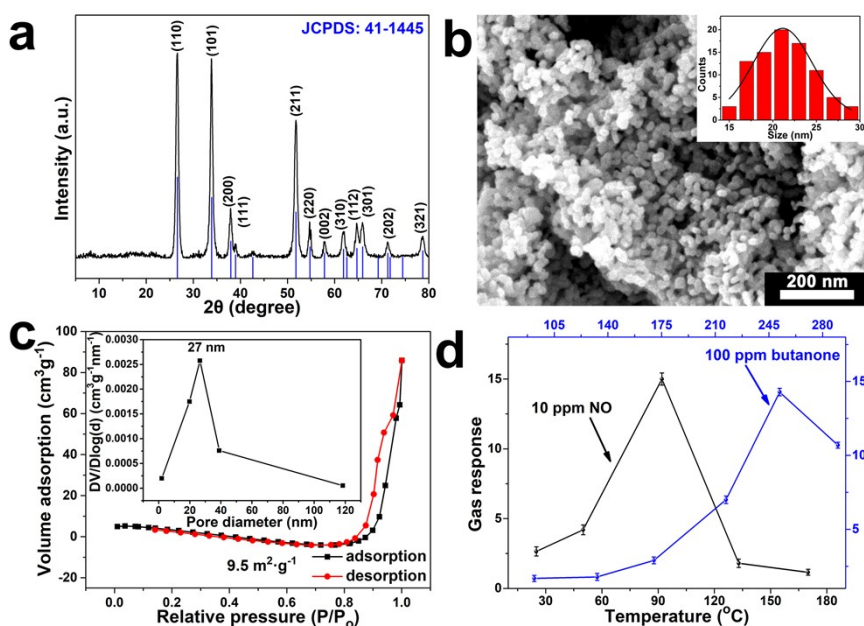


Fig. S4 (a) XRD pattern, (b) SEM image and (c) N₂ adsorption-desorption isotherms of template-free SnO₂ nanoparticles (inset: pore size distribution); (d) Temperature-dependent responses of template-free SnO₂ nanoparticles towards 10 ppm NO gas and 100 ppm butanone vapor.

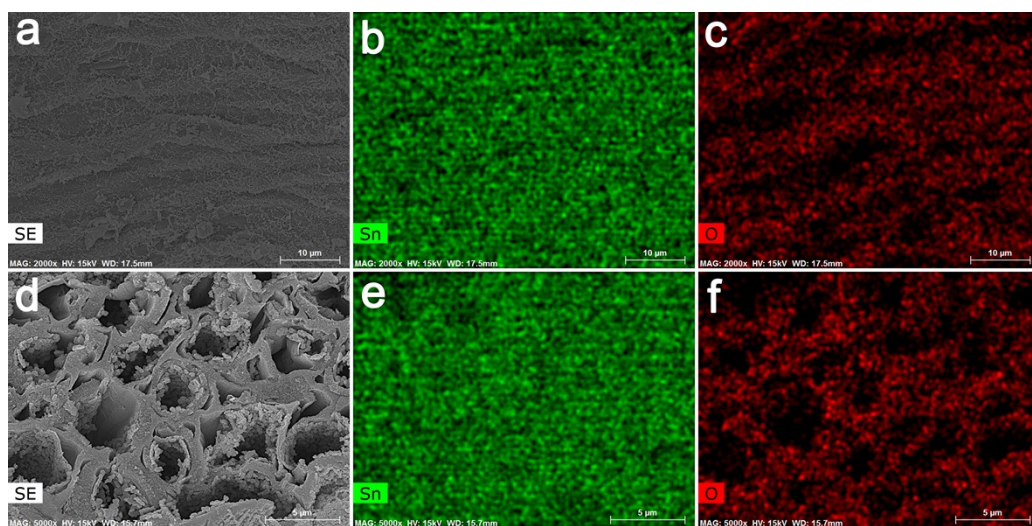
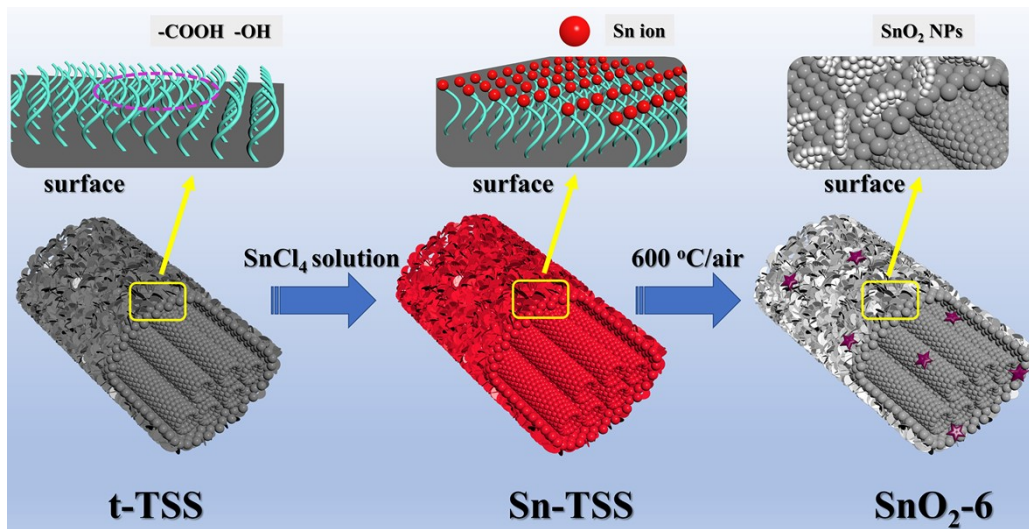


Fig. S5 EDS mapping of SnO₂-6: (a-c) surface of nanosheet-coated microtubes; (d-f) cross section.



Scheme S1 Proposed process for the formation of SnO₂-6 hierarchical microtubes.

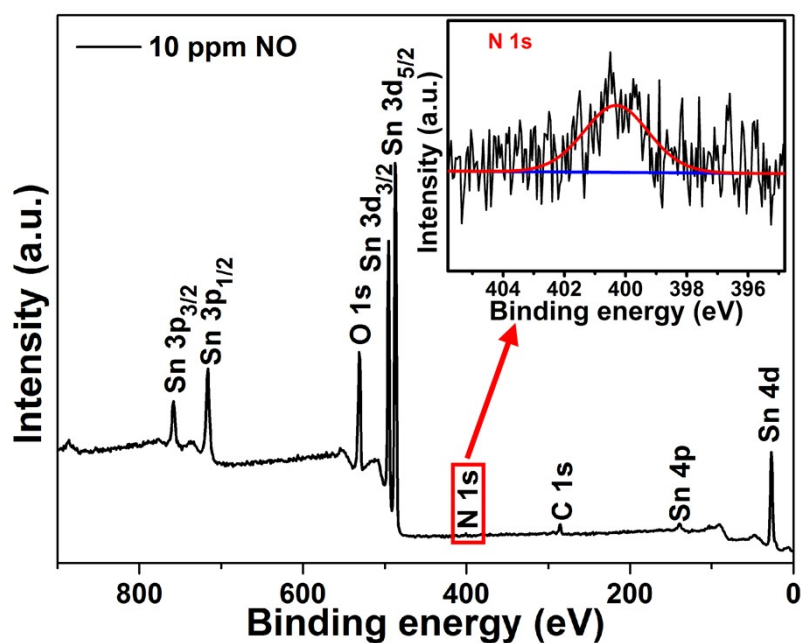


Fig. S6 Full XPS spectrum of SnO₂-6 sensor after contacting with 10 ppm NO gas at 92 °C

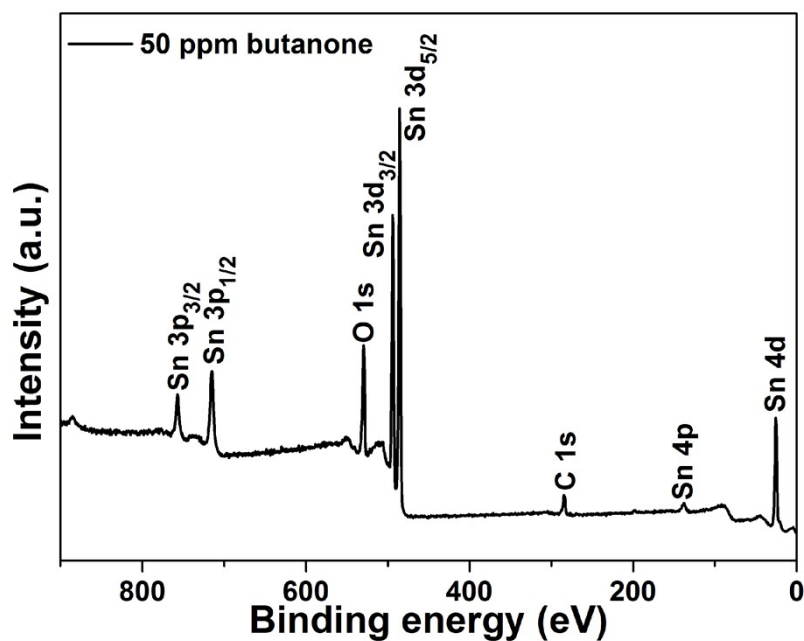


Fig. S7 Full XPS spectrum of SnO₂-6 sensor after contacting with 50 ppm butanone vapor at 217 °C.

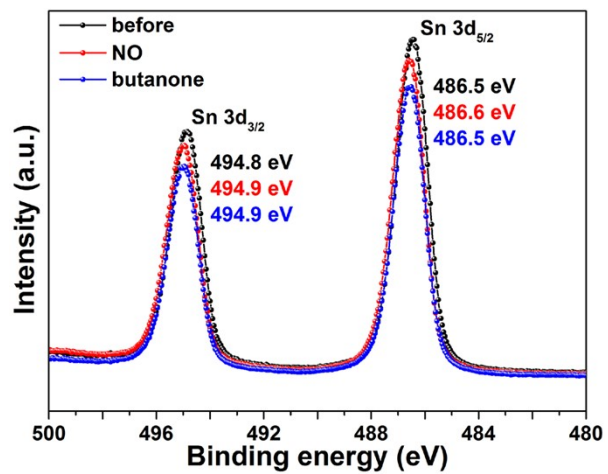


Fig. S8 High-resolution Sn 3d XPS spectra before and after contacting with 10 ppm NO gas or 50 ppm butanone vapor at 92 or 217 °C.