Supplementary Information

Fabrication of Cubic Zn_2SnO_4/SnO_2 Complex Hollow Structure and Their Sunlight-Driven Photocatalytic Activity

Linqiang Sun,[a] Xiao Han,[a] Zhe Jiang,[a] Tingting Ye,[a] Rong Li,[a] Xinsheng Zhao,[b] Xiguang Han*[a]

1. Experimental detail

1.1. Materials

Tin(IV) Chloride Pentahydrate ($SnCl_4 \cdot 5H_2O$), Zinc Acetate Dihydrate ($Zn(Ac)_2 \cdot 2H_2O$), Sodium Hydroxide (NaOH), Sodium Dodecyl Benzene Sulfonate (SDBS) were purchased from Sinopharm Chemical Reagent Co., Ltd.

1.2. Synthesis

1.2.1. Preparation of $ZnSn(OH)_6$ solid cubes:

In a typical synthesis, $SnCl_4 \cdot 5H_2O$ (0.35 g, 1 mmol) was added into 5 mL Ethanol under intense stirred treatment for 10 minutes to form solvent 1, and then $Zn(Ac)_2 \cdot 2H_2O$ (0.22 g, 1 mmol) and SDBS (0.35 g, 1mmol) was added into 10 ml distill water, and keep to stir for 10 minutes to form solution 2. And then solution 1 was mixed with solution 2 at room temperature. NaOH aqueous solution (5 mL, 2 M) was added into the above mixed solution under stirred for 5 min at room temperature. The white product were obtained by centrifuge and washed by deionized water and ethanol, and then the product was dried in the oven at 60 °C.

1.2.2. Preparation of single-shell $ZnSn(OH)_6$ hollow boxes: In a typical synthesis,

$ZnSn(OH)_6$ solid cubes (50 mg) were added into NaOH (5 ml, 2 M) solution, then, stirred 5 minutes at room temperature, the thickness of the shell can be controlled by changing the amount of NaOH. The white products were collected by centrifuge and washed by deionized water and ethanol, and then the product was dried in the oven at 60 ^oC for further characterization.

1.2.3. Preparation of yolk-shell $ZnSn(OH)_6$ boxes: In a typical synthesis, $ZnSn(OH)_6$ solid cubes (50 mg) as the seeds, $Zn(Ac)_2 \cdot 2H_2O$ (0.22 g, 1 mmol) and SDBS (0.35 g, 1mmol) were added into 10 mL distill water, and then stirred for 2 minutes to form solution 3, $SnCl_4 \cdot 5H_2O$ (0.35 g, 1 mmol) was added into 5 mL Ethanol under intense stirred treatment for 10 minutes to form solvent 4. And then solution 3 was mixed with solution 4 at room temperature. NaOH aqueous solution (5 mL, 2 M) was added into the above mixed solution under stirred for 5 min at room temperature. The white products were collected by centrifuge and washed by deionized water and ethanol, and then the product was dried in the oven at 60 ^oC for further characterization.

1.2.4. Preparation of double-shell $ZnSn(OH)_6$ boxes: Double-shell structure particles were also made by a similar method with yolk-shell structure but with single-shell $ZnSn(OH)_6$ hollow boxes as the seed materials.

1.2.5. Preparation of signal-shell, yolk-shell and double-shell Zn_2SnO_4/SnO_2 hybrid nanostructures: The as-prepared $ZnSn(OH)_6$ precursors (including single-shell, yolk-shell and double-shell structure) were separately loaded in a ceramic crucible and then heated to 450 °C for 4 h in air with a heating rate of 1 $°C \cdot min^{-1}$. The

products were collected by centrifuge and washed by deionized water and ethanol.

1.3. Characterization: The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Panalytical X-pert diffractometer with CuKα radiation. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (SEM, S4800), and high-resolution transmission electron microscopy (HRTEM, JEM-2100) with an acceleration voltage of 200 kV. All TEM samples were prepared from depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid. The surface areas (S) of these Zn_2SnO_4/SnO_2 hybrid nanostructures were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system.

1.4. Photocatalysis: The photodegradation efficiency of Rhodamine-B (RhB) in aqueous solution was measured under the Sun-light irradiation (300 W xenon lamp). All the experiments were carried out at the temperature of 25±2 °C. The initial concentration of dye is 20 μM with catalyst loading 1 mg/mL. Typically, 50 mg of Zn_2SnO_4/SnO_2 samples were dispersed in 50 mL of RhB aqueous solution (2 M) under ultrasonic to form a suspension, and the suspension was magnetically stirred for 30 min in the dark. At regular irradiation time intervals, the dispersion was sampled and centrifuged to separate the Zn_2SnO_4/SnO_2 particles. The photodegradation efficiency was monitored by measuring the absorbance of the centrifuged solutions at its maximum absorption wavelength of 554 nm with UV-vis spectroscopy (SHIMADZU, UV-2100) at room temperature.

2. Experimental results:

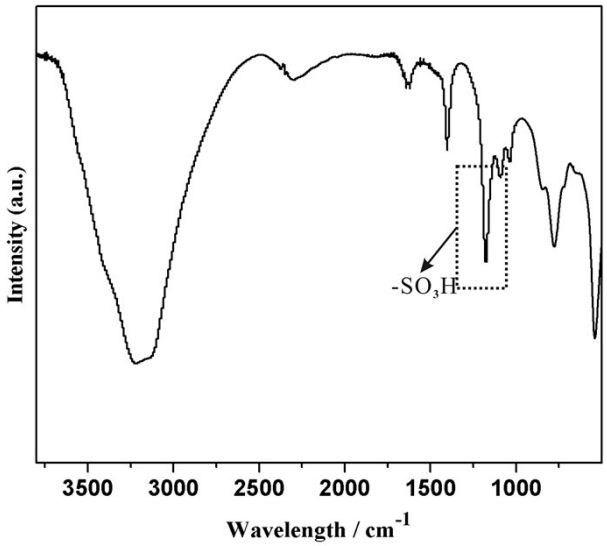

Fig. S1 FTIR spectra of the $ZnSn(OH)_6$ solid cubes。

A possible growth mechanism of cubic $ZnSn(OH)_6$ crystal in the solutions containing water and ethanol is as follow: Zn^{2+} and Sn^{4+} ions in the aqueous solution easily form $ZnSn(OH)_6$ precipitates by forming bonds with OH^- in alkaline aqueous solution. These $ZnSn(OH)_6$ precipitates grow to form larger particles. Self-aggregated particles are able to cluster together to form aggregates as well. In the presence of ionic surfactants of sodium dodecylbenzenesulfonate (SDBS), the sulfonic acid group of the surfactants preferentially adsorb on {100} planes, leading to the growth inhibition of {100} planes and final generation of the $ZnSn(OH)_6$ nanocubes.

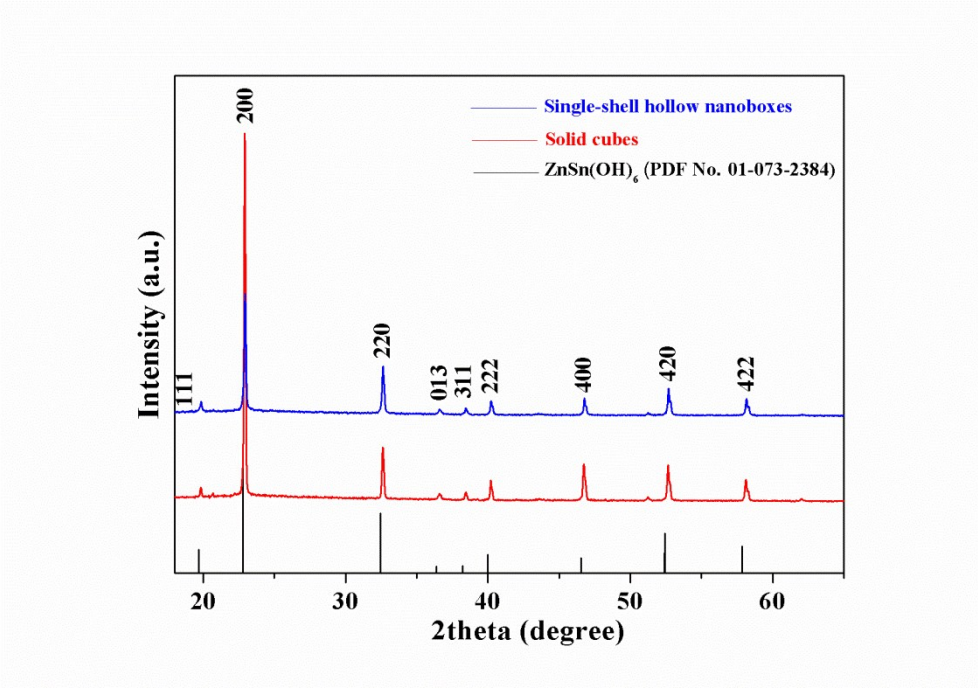

Fig. S2 XRD patterns of solid and single-shell hollow $ZnSn(OH)_6$ samples..

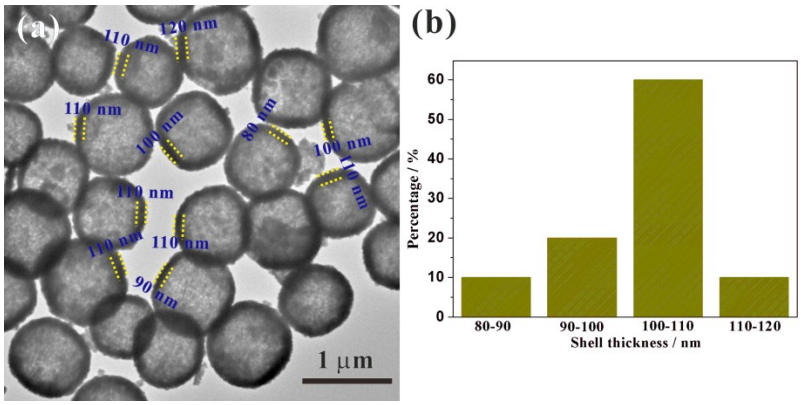

Fig. S3 (a) TEM images of single-shell $ZnSn(OH)_6$ hollow structure using 5 mL NaOH (2 mol/L), (b) the bar graph of shell thickness of $ZnSn(OH)_6$ hollow structure.

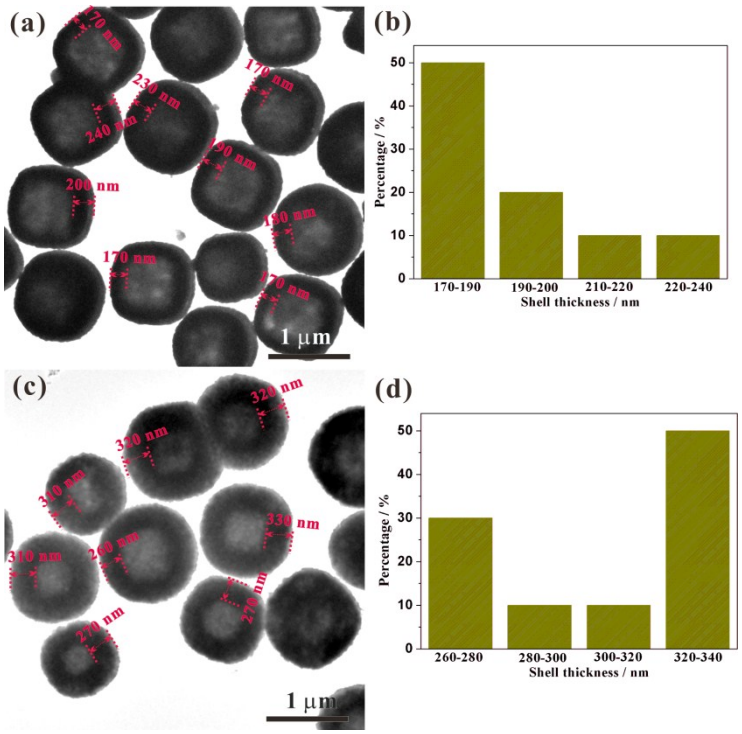

Fig. S4 TEM images of different thickness of shell $ZnSn(OH)_6$ hollow structure using different amount NaOH, (a) 5 mL, 1.5 mol/L; (c) 5 mL, 1 mol/L; (b) and (d) the bar graph of Shell thickness of $ZnSn(OH)_6$ hollow structure.

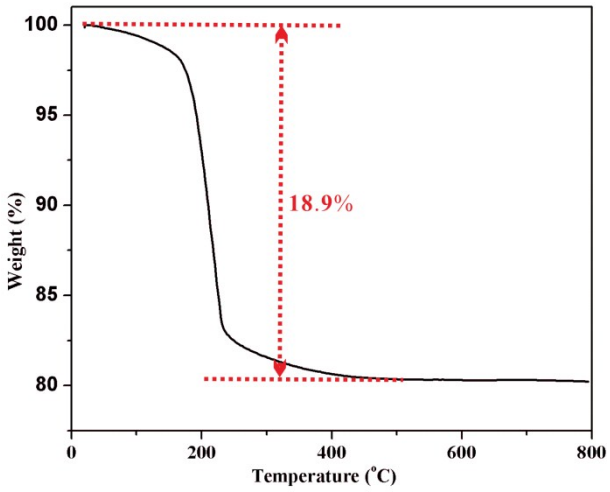

Fig. S5 TGA curves of the as-obtained single-shell $ZnSn(OH)_6$ hollow microboxes.

For the TGA curve of the $ZnSn(OH)_6$, an obvious weight loss of 18.9% occurred at around 450 °C. The theoretical weight loss value of $ZnSn(OH)_6$ to Zn_2SnO_4/SnO_2 is 18.9%.

The whole process of chemical reaction are as follows:

$ZnSn(OH)_6$ solid cubes: $Zn^{2+}(aq)+Sn^{4+}(aq)+6OH^-(aq)=ZnSn(OH)_6$;

$ZnSn(OH)_6$ single-shell microboxes: $ZnSn(OH)_6+4OH^-(aq)=Zn(OH)_4^{2-}+Sn(OH)_6^{2-}$;

Zn_2SnO_4/SnO_2: $2ZnSn(OH)_6=Zn_2SnO_4+SnO_2+6H_2O$ (450℃)

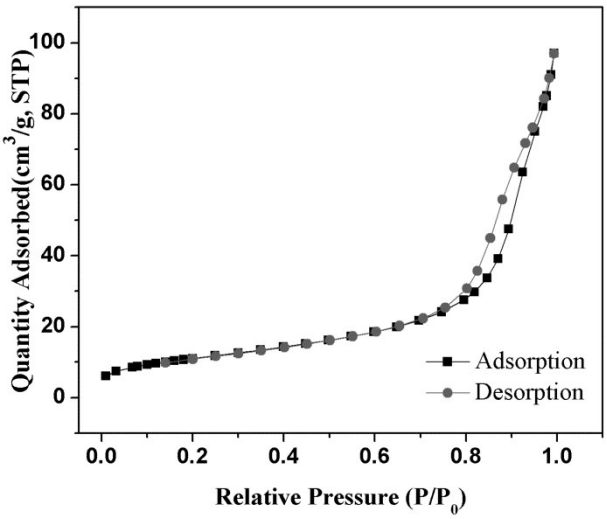

Fig. S6 The N_2 adsorption-desorption isotherms of single-shell Zn_2SnO_4/SnO_2 hollow microboxes.

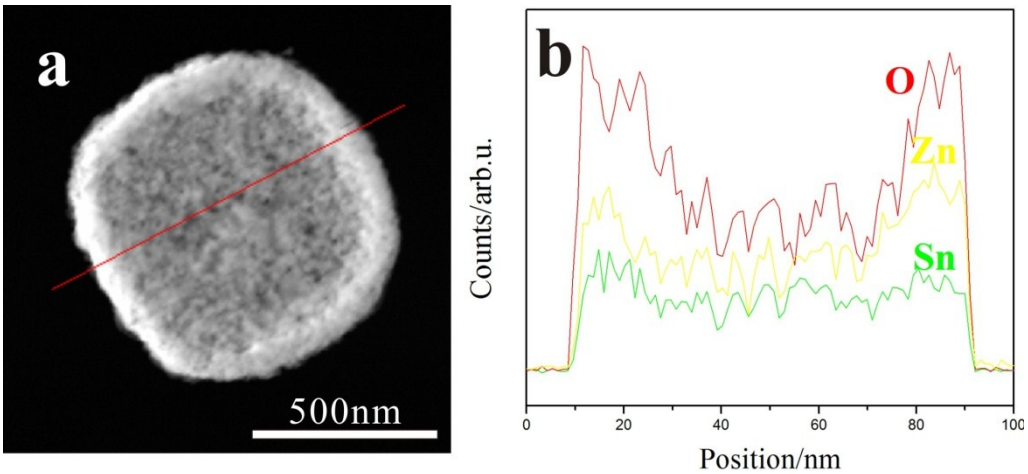

Fig. S7 The cross-sectional EDX elemental line scans of a single-shell ZTO/SnO_2 hollow microbox.

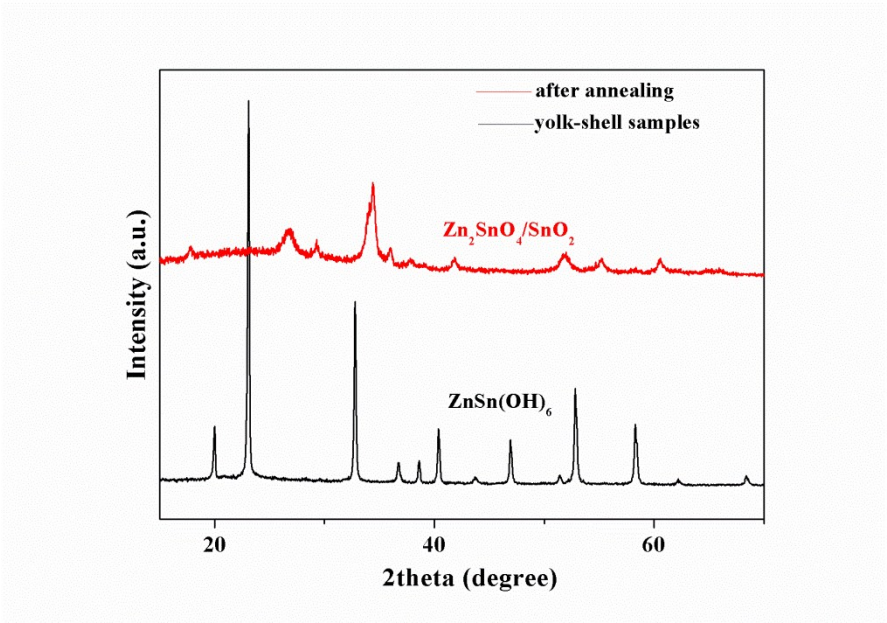

Fig. S8 XRD patterns of yolk-shell structure before and after annealing.

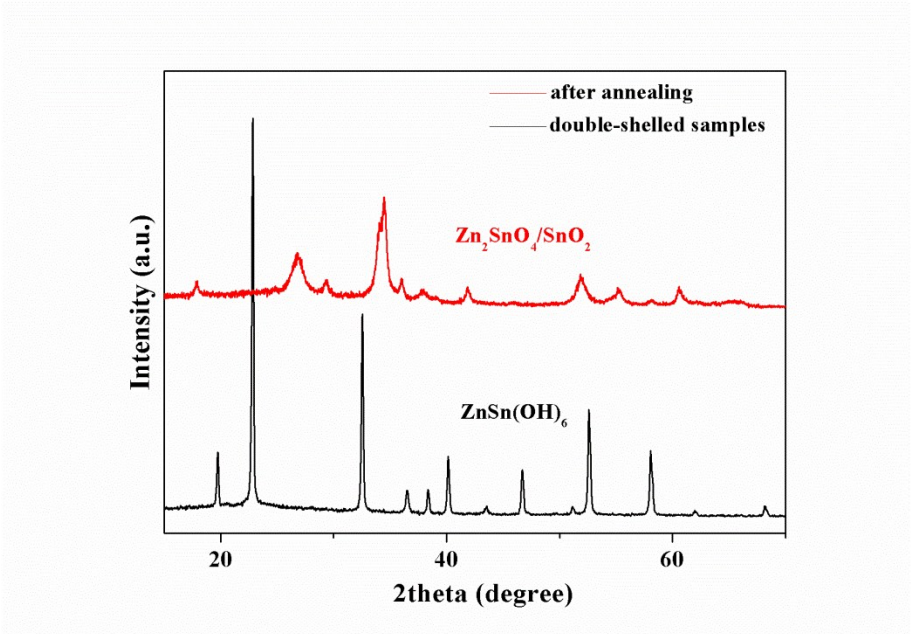

Fig. S9 XRD patterns of double-shell structure before and after annealing.

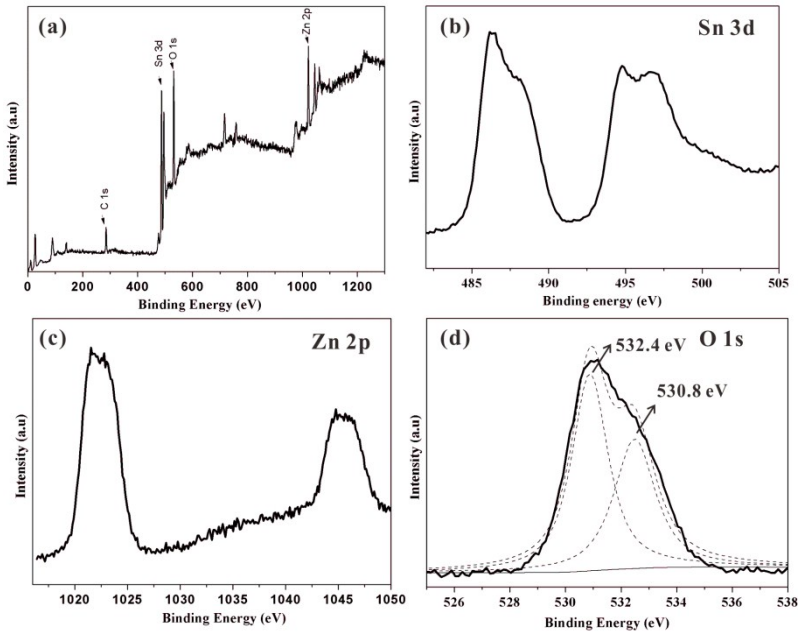

Fig. S10 XPS spectra of double-shell structure of Zn_2SnO_4/SnO_2 samples, survey (a), and high resolution spectra of Sn 3d (b) , Zn 2p (c), O 1s (d).

As shown from the survey spectra in Fig. S10, element Zn, Sn, O coexisted in the samples. The Sn 3d and Zn 2p spectrums (Fig. S10 b-c) confirms of the presence of Zn and Sn elements in the products. Meanwhile, O 1s spectra of the samples were also recorded (Fig. S10 d). The broad peak of O 1s can be fitted to two peaks at binding energies of 530.8 eV and 532.4 eV respectively by using Gaussian fitting method. The dominant peak at 530.8 eV is characteristics of oxygen in metal oxide such as Sn-O-Zn, and other peaks at around 532.4 eV is assigned to other oxygen components such as OH, H_2O adsorbed on the surface of Zn_2SnO_4/SnO_2. The results of XPS are consistent with XRD results.

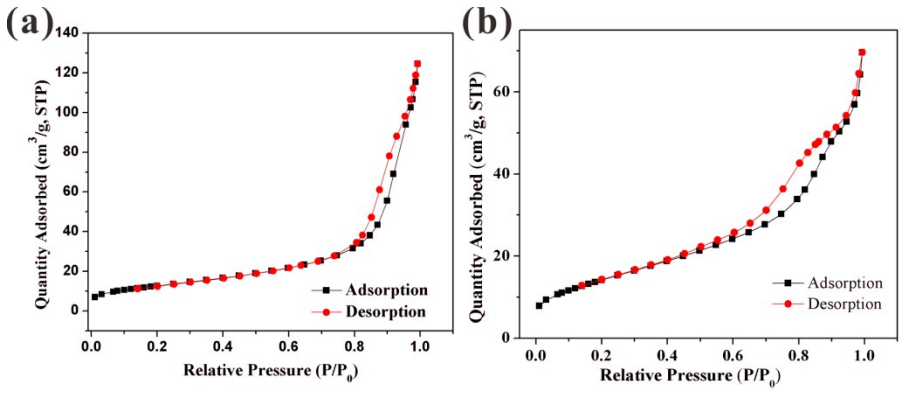

Fig. S11 The N_2 adsorption-desorption isotherms (a) yolk-shell structure, (b) double-shell structure.

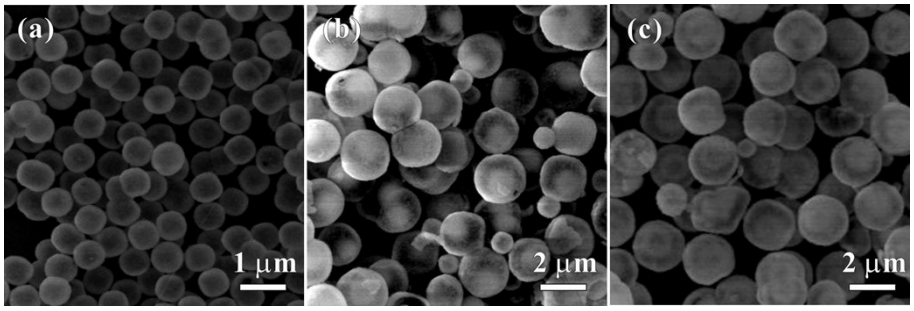

Fig. S12 SEM images of different structures Zn_2SnO_4/SnO_2 samples after photocatalytic measurement, (a) single-shell boxes, (b) yolk-shell structure, (c) double-shell structure.