

## **Structure Evolution from Prussian-Blue Nanocube to Hollow Nanocage Composites via Sodium Tungstate Etching**

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## 1. Experimental section

**1.1. Materials:** Polyvinylpyrrolidone (PVP, K30, MW  $\approx$  40 000),  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  were purchased from Aladdin Industrial Corporation.  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , HCl and ethanol were obtained from Sino-Pharm Chemical Reagent Co. Ltd. Dimethyl trisulfide were obtained from Aladdin Industrial Corporation.

**1.2. Synthesis of Prussian Blue Microcubes:** Prussian blue nanocubes were prepared according to the previous literature.<sup>1</sup> In a typical procedure, 3.8 g of PVP was dissolved in 50 ml of HCl solution (0.1 M) under magnetic stirring to form a clear solution. 0.11 g of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  was added to the clear solution. The mixture was stirred for 60 min and was then heated at 80 °C for 24 h. The obtained blue product  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  microcubes were centrifugated and washed alternately with deionized water and ethanol.

**1.3. Synthesis of  $\text{Fe}(\text{OH})_3/\text{WO}_{3-x} \cdot y\text{H}_2\text{O}$  hollow nanocages:** The  $\text{Fe}(\text{OH})_3/\text{WO}_{3-x} \cdot y\text{H}_2\text{O}$  hollow nanocages were obtained by reacting PB nanocubes with  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  at 50 °C. The reaction time was varied from 25 min to 70 min at a step of 5 min. Typically, 0.01 g of PB nanocubes was dissolved in 10 ml of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  solution (1 M) while stirring, which led to the formation of a blue solution. After the reaction, the  $\text{Fe}(\text{OH})_3/\text{WO}_{3-x} \cdot y\text{H}_2\text{O}$  hollow nanocages were collected by centrifugation and washed with deionized water, which was followed by drying in an oven at 80 °C. The  $\text{Fe}(\text{OH})_3/\text{WO}_{3-x} \cdot y\text{H}_2\text{O}$  hollow nanocages obtained at an initial reaction times of 25, 30, 35, 40, 45, 50, 55, 60, 65, and 70 min were designated as samples P1 to P10, respectively, which all had different shell thicknesses. Hollow  $\text{Fe}_2\text{O}_3/\text{W}_{18}\text{O}_{49}$  composites nanocages, which were denoted as FW, were obtained by annealing  $\text{Fe}(\text{OH})_3/\text{WO}_{3-x} \cdot y\text{H}_2\text{O}$  hollow nanocages (P7) precursor at 550 °C in air for 6 h, the heating rate used was 0.5 °C min<sup>-1</sup>.

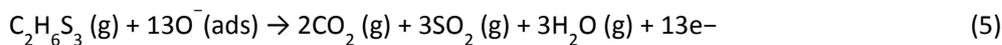
**1.4. Characterization:** X-ray diffraction (XRD) patterns were measured using a Philips X'Pert diffractometer with Cu K $\alpha$ 1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in a  $2\theta$  range from 10° to 70°. Field-emission scanning electron microscopy (FESEM, FEI Sirion 200) was used to study the morphology of the prepared samples. Transmission electron microscopy

(TEM) images were obtained using a JEOL JEM-2100F transmission electron microscope with a 200kV accelerating voltage. Fourier transform infrared (FT-IR) spectra were measured by KBr disk on the FT-IR Bruker Tensor 27.

**1.5. Gas sensing measurements:** To evaluate the gas performance of the sensors, the homogeneous suspension in ethanol of  $\text{Fe}(\text{OH})_3/\text{WO}_{3-x}\cdot\text{yH}_2\text{O}$  hollow nanocages was coated onto the surface of a ceramic gas sensor of a size  $3 \times 3$  mm with a gold electrode and a heating electrode and then heated at a heating rate of  $0.5$  °C/min to  $550$  °C and annealed at this temperature for  $6$  h to form a thick  $\text{Fe}_2\text{O}_3/\text{W}_{18}\text{O}_{49}$  film. The measurement process used for assessing the performance of the sensor was the same as that reported in previous studies.<sup>2</sup> The response value of the gas sensor was defined as the resistance ratio between the air ( $R_a$ ) and the test gas ( $R_g$ ). The times elapsed for the sensor's resistance to reach 90% of the maximum resistance change when exposed to the test gas and air were defined as the response and recovery times, respectively.

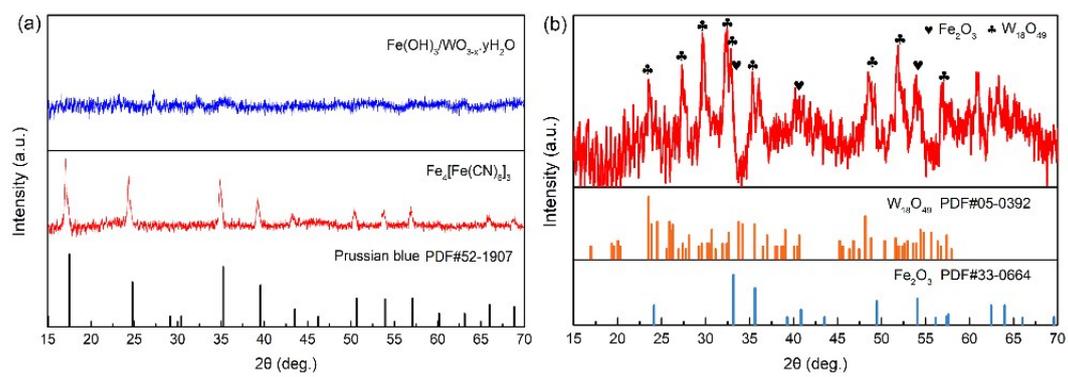
## 2. Discussion of gas sensing mechanism

Traditional oxygen depletion theory-based mechanisms can be used to account for the interaction of gas molecules with gas sensing materials. When the sensing materials are exposed to air, the oxygen absorption ( $\text{O}_2^-$ ,  $\text{O}^-$  or  $\text{O}^{2-}$ ) will be occurred.<sup>3-5</sup> When the test gas  $\text{CH}_3\text{SSSCH}_3$  is contacted with the sensing materials, the reductive gas  $\text{CH}_3\text{SSSCH}_3$  will react with oxygen ions absorbed on the material surface, finally turned into  $\text{SO}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The chemical reaction formulas are as follows:



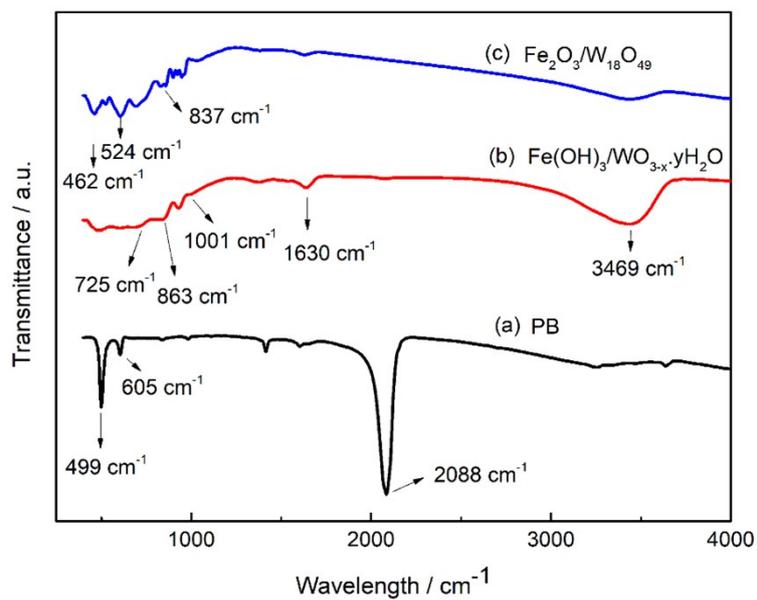


**Figure. S1**



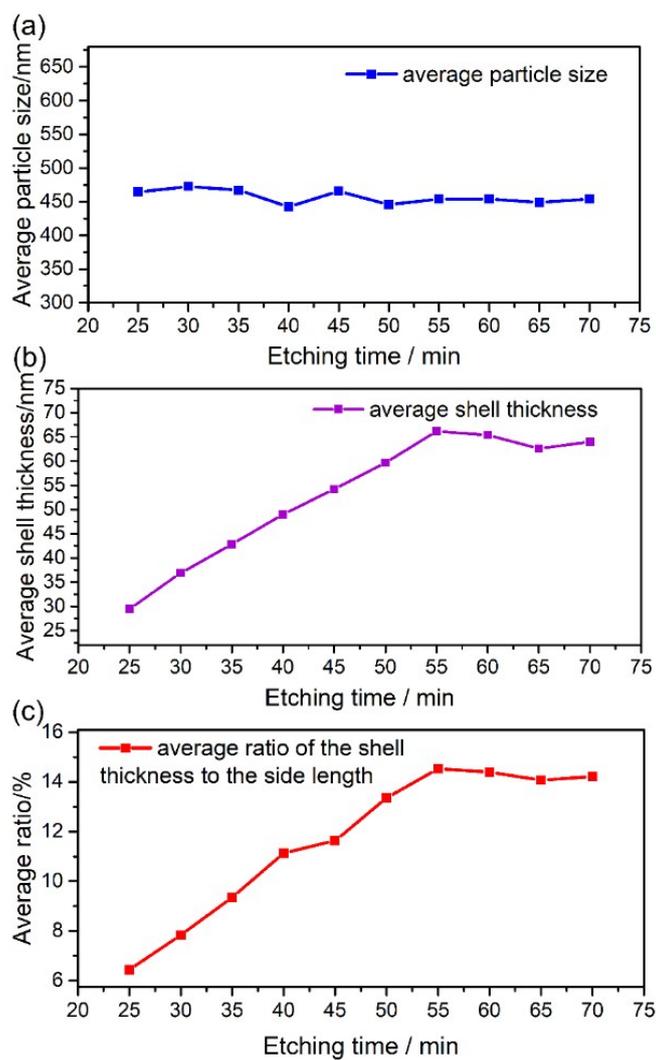
**Fig. S1 (a)** XRD patterns of the PB cubes,  $\text{Fe}(\text{OH})_3/\text{WO}_{3-x}\cdot y\text{H}_2\text{O}$  (P7) and (b) FW nanocages.

**Figure. S2**



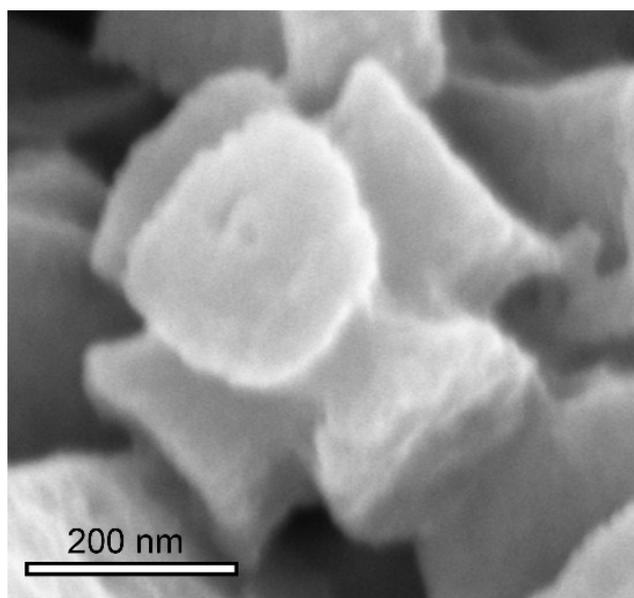
**Fig. S2** FTIR spectra of (a) PB cube, (b) Fe(OH)<sub>3</sub>/WO<sub>3-x</sub>·yH<sub>2</sub>O (P7) and (c) Fe<sub>2</sub>O<sub>3</sub>/W<sub>18</sub>O<sub>49</sub> hollow nanocages (FW cages) .

**Figure. S3**



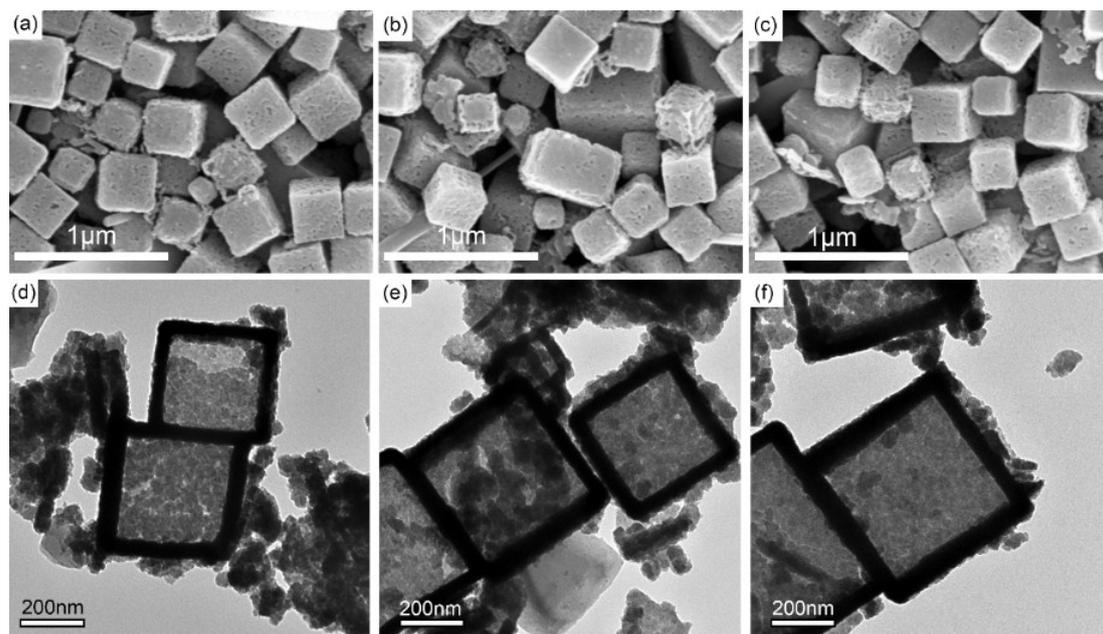
**Fig. S3** (a) The average side length of the selected samples etched within different etching time. (b) The average shell thickness of the selected samples. (c) The average ratio of the shell thickness to the side length of the selected samples.

**Figure. S4**



**Fig. S4** SEM image of the etching products P4 obtained by reacting with 1 M  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  solution at 50 °C for 40 min.

**Figure. S5**



**Fig. S5** SEM images and TEM images of the etching products (P8, P9, P10) obtained by reacting with 1 M  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  solution at 50°C for (a, d) 60 min, (b, e) 65 min and (c, f) 70 min.

## Reference

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