

## Supporting Information Available

# Bioinspired Hierarchical Tin Oxide Scaffolds for Enhanced Gas Sensing Properties

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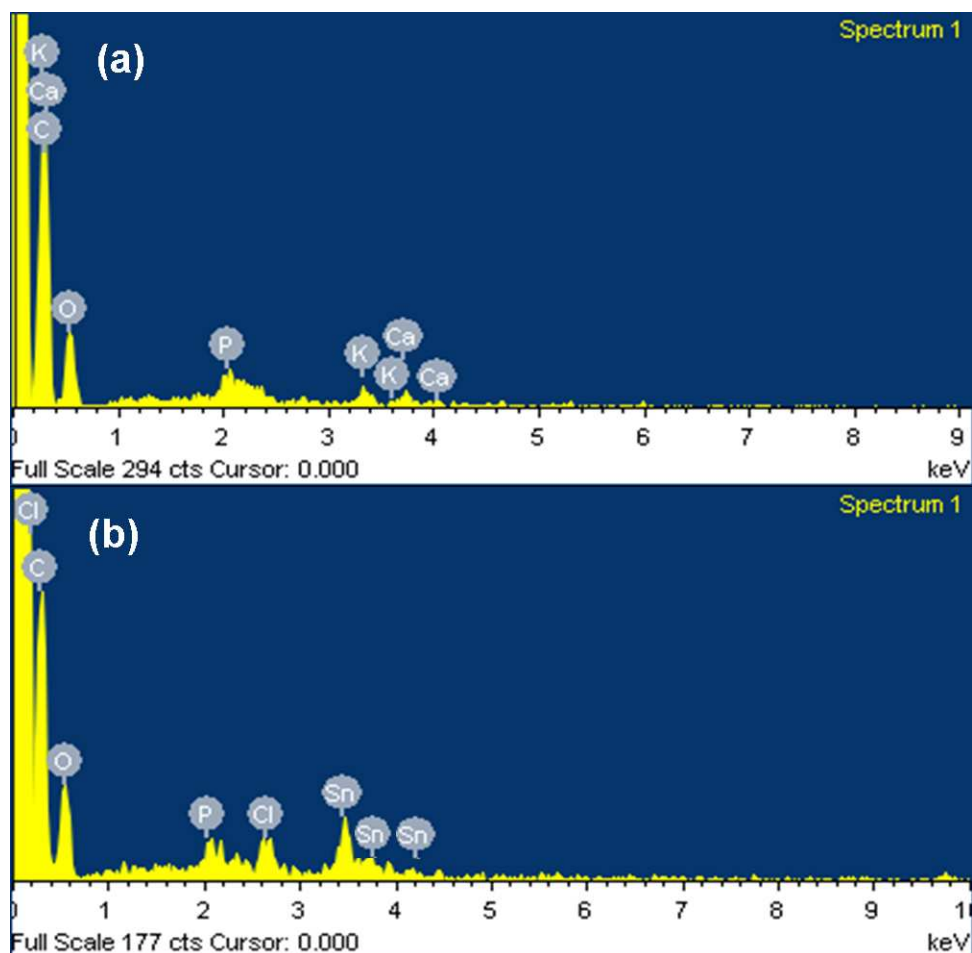
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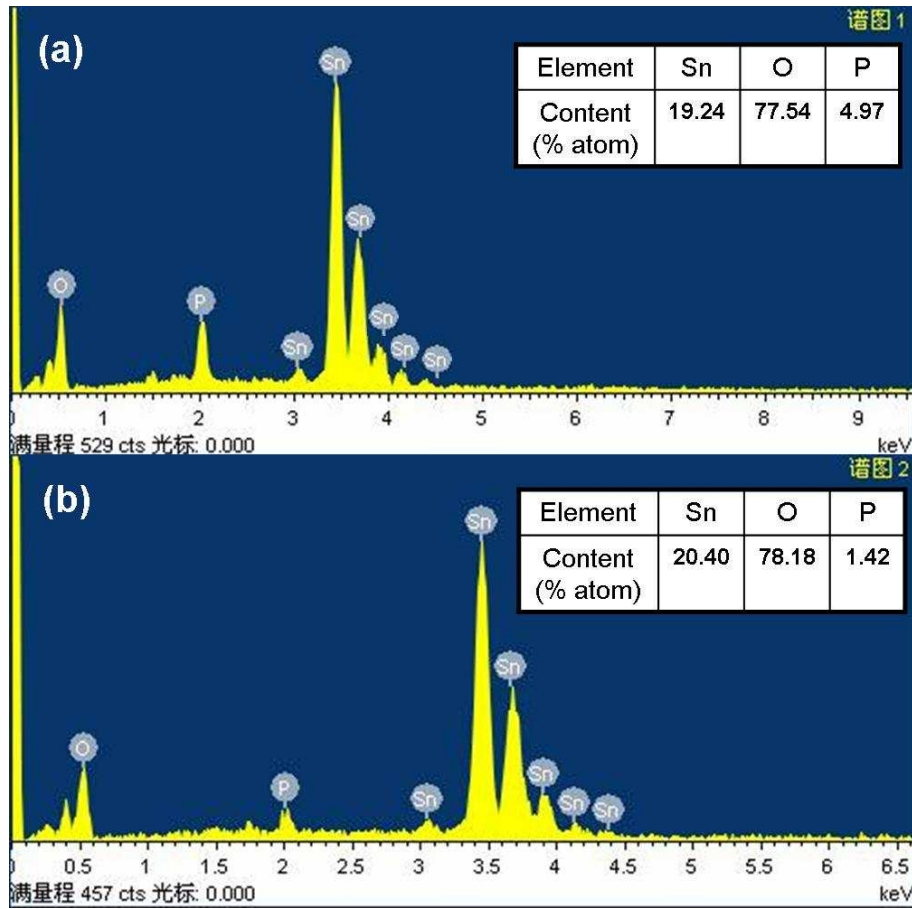
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**Figure S1.** EDX spectra of (a) natural pollen grains and (b) the hybrids after the first soakage

The energy dispersive X-ray (EDX) spectroscopy reveals that natural pollen grains are mainly composed of elements C, P, K, and Ca. Element P and elements K and Ca are well-known major and minor elements in biospecies, respectively, which should derive from  $\text{PO}_4^{3-}$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ . After the first soakage in  $\text{SnCl}_4$  ethanol solution, the spectra of pollen hybrids reveals that K and Ca element are absent in the hybrids, being replaced by Sn( $\text{Sn}^{4+}$ ) and Cl( $\text{Cl}^-$ ) elements. This composition change should be caused by two process: i)  $\text{Sn}^{4+}$  ions substitute  $\text{K}^+$  and  $\text{Ca}^{2+}$  ions, and ii)  $\text{Sn}^{4+}$  ions and  $\text{Cl}^-$  anions directly bind on the active functional groups of the pollen coats.



**Figure S2.** EDX spectra of the SnO<sub>2</sub> sinters (a) without and (b) with the second soakage, inset showing the corresponding content of each element.

In the present synthetic process, the P element cannot be removed even by the final calcinations treatment. Supposing that the quantity of P element is constant, the relative amount of Sn-precursors that were introduced in the second soakage can be calculated. We denote the P quantity as “p” and the SnO<sub>2</sub> quantity derived from the first soakage as “s”. We also assume SnO<sub>2</sub> quantity derived from the second soakage is X times of “s”, denoted as “Xs”. Thus, for SnO<sub>2</sub> sinter without the second soakage:

$$\frac{P}{s + p} = 4.97\% \quad (1)$$

For SnO<sub>2</sub> sinter with the second soakage:

$$\frac{p}{(x+1)s+p} = 1.42\% \quad (2)$$

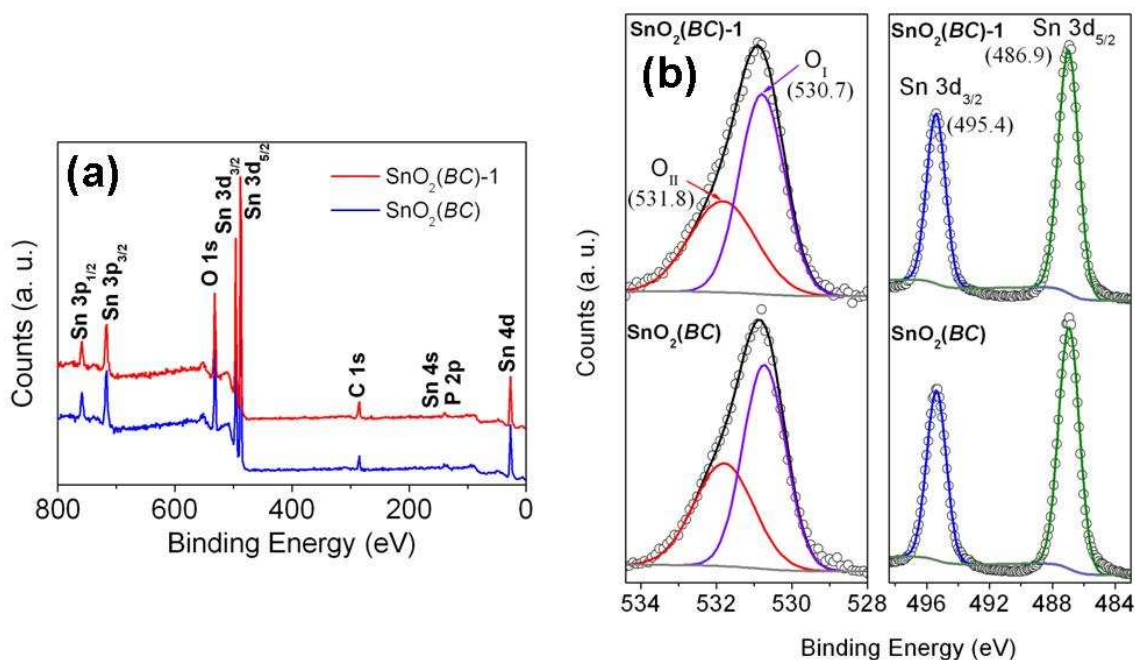
Based on eq. (1) and (2),

$$\frac{p}{(x+1)s+p} = 1.42\% > \frac{p}{(x+1)(s+p)} = \frac{1}{x+1} \times 4.97\% \quad (3)$$

Thus

$$x > \frac{4.97\%}{1.42\%} - 1 = 2.5 \quad (4)$$

This result shows that SnO<sub>2</sub> quantity derived from the second soakage is more than 2.5 times of that derived from the first soakage. The large quantity suggests that the second soakage is great beneficial for the faithful structure maintaining.



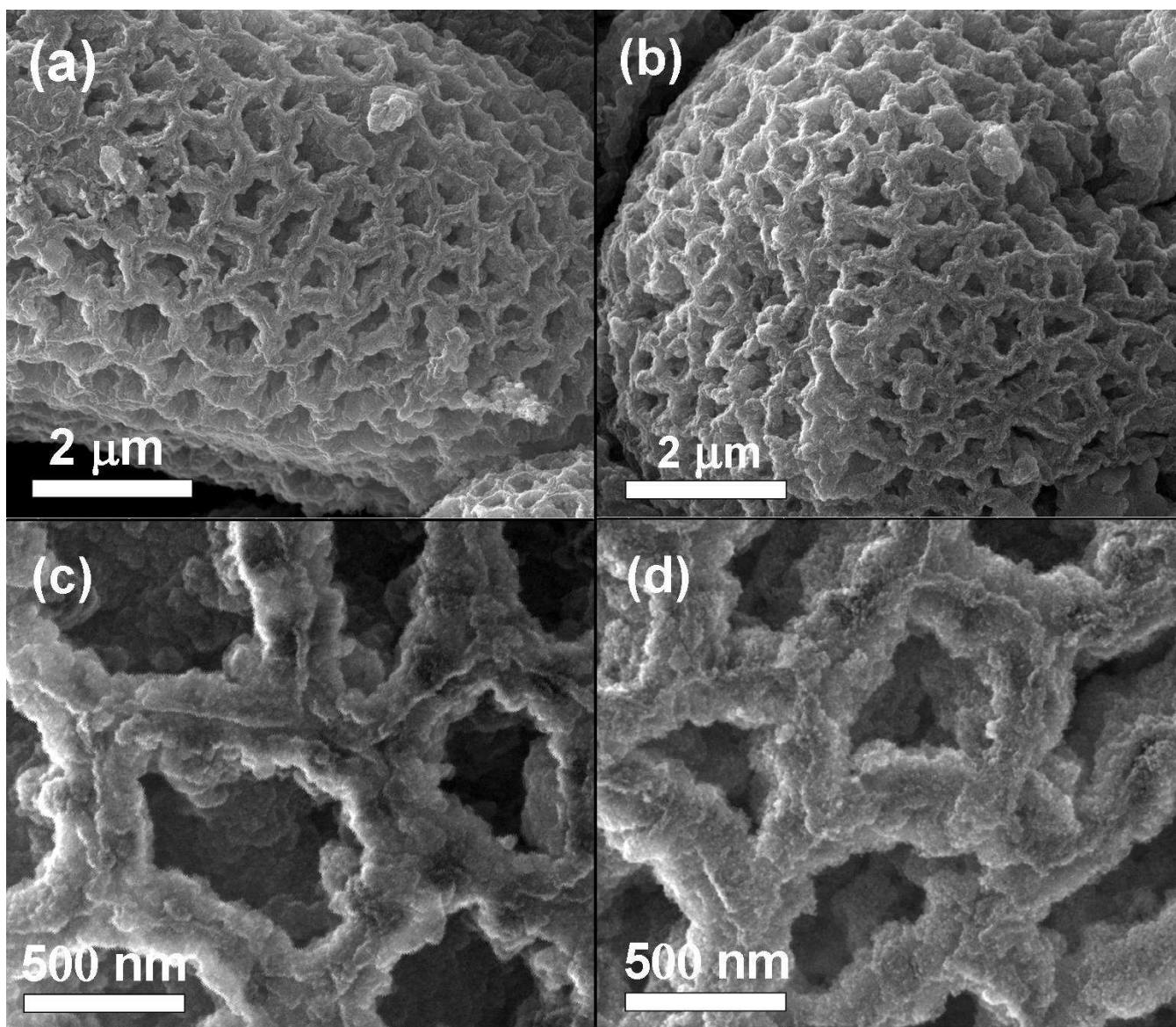
**Figure S3.** (a) Full-range XPS spectra of  $\text{SnO}_2(\text{BC})$  and  $\text{SnO}_2(\text{BC})\text{-1}$  measured within a range of binding energy of 0-800 eV, (b) high resolution XPS spectra of  $\text{SnO}_2(\text{BC})$  and  $\text{SnO}_2(\text{BC})\text{-1}$  at binding energies corresponding to O 1s and Sn 3d, respectively.

Peaks at binding energies corresponding to O, Sn, and C are clearly observed in the full-range XPS spectra in Figure S3a. The small C peak at 284.6 eV is most likely due to surface contamination or adsorbed carbonaceous species, and is used to correct the relative peak shifts caused by electrostatic charge-up. Feeble peak corresponding to P element should be derived from the residue of natural pollen grains. More detailed information on the chemical state of these elements is obtained from the high resolution XPS spectra of the Sn 3d and O 1s in Figure S3b. The peaks of Sn  $3d_{3/2}$  and Sn  $3d_{5/2}$  at 495.4 and 486.9 eV show a good symmetry and should be assigned to the lattice tin (Sn(IV) oxidation state) in tin oxide.<sup>1,2</sup> The peak separation of 8.5 eV between these two peaks is in agreement with the standard spectrum of  $\text{SnO}_2$ . The O 1s peaks are much asymmetric, with a shoulder on the high binding energy (BE) side. The peaks can be deconvoluted into two contributions, which suggest the coexistence of different chemical environments. The major component at 530.7 eV is typical for the  $\text{SnO}_2$  cassiterite network, whereas the second minor band at higher BE (531.8 eV) is mainly related to the presence of

Sn-OH species and/or to some surface hydration.<sup>1</sup>

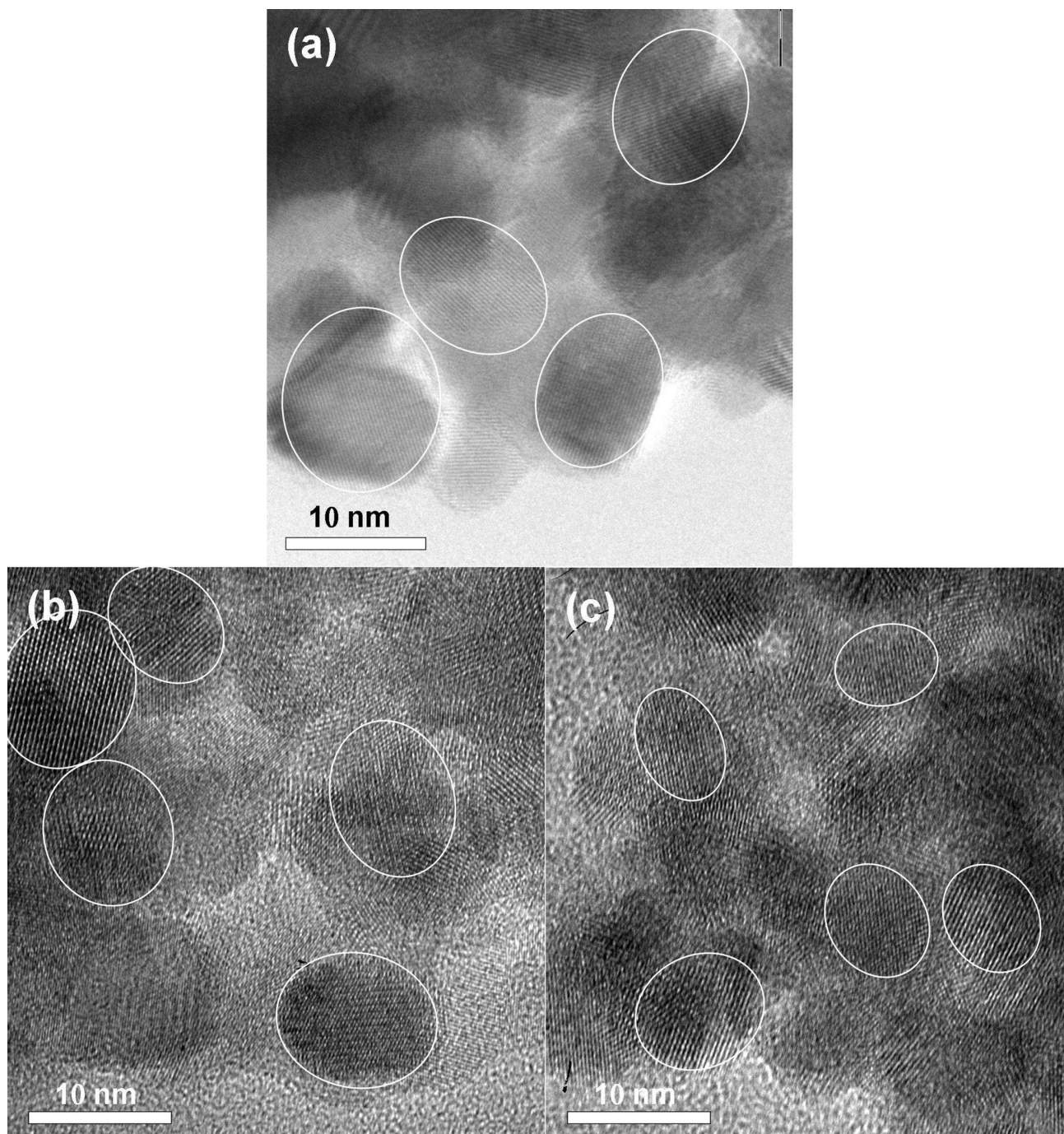
(1) D'Arienzo, M.; Armelao, L.; Cacciamani, A.; Mari, C. M.; Polizzi, S.; Ruffo, R.; Scotti, R.; Testino, A.; Wahba, L.; Morazzoni, F. *Chem. Mater.* **2010**, 22, 4083-4089.

(2) Wang, Y.; Ma, C.; Sun, X.; Li, H. *Nanotechnology* **2002**, 13, 565.



**Figure S4.** (a) FESEM images of (a, c)  $\text{SnO}_2(\text{BC})$  and (b, d)  $\text{SnO}_2(\text{BC})$ -1

FESEM images in Figure S4 shows that both the  $\text{SnO}_2(\text{BC})$  and  $\text{SnO}_2(\text{BC})$ -1 retain the scaffolds of microreactors. The scaffolds' surface of  $\text{SnO}_2(\text{BC})$ -1 is coarser than that of  $\text{SnO}_2(\text{BC})$ , which indicates the particles aggregation is more serious.



**Figure S5.** (a) TEM images of (a) R-SnO<sub>2</sub>, (b) SnO<sub>2</sub>(BC)-1 and (c) SnO<sub>2</sub>(BC), the average grain sizes are estimated to be about 10.5, 9.6 and 7.3 nm, respectively.

The average grains size of SnO<sub>2</sub>(BC)-1 is about 9.6 nm, which is almost the same as that of R-SnO<sub>2</sub> (10.5 nm) and larger than that of SnO<sub>2</sub>(BC) (7.3 nm).