

# SYNTHESIS OF CU-DOPED WO<sub>3</sub> MATERIALS WITH PHOTONIC STRUCTURES FOR GAS SENSORS

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## 1 Introduction

In 2001, Ozin investigated the chemical sensing behavior of synthetic opals and inverse opals composed of SnO<sub>2</sub> and found that the resulting tin oxide opals showed a fairly large response to carbon monoxide, which is believed to be related to the gas-sensitive necks between adjacent spheres in geometry. The effects mean that control of microstructure is necessary for command over the sensitivity to the detected gases. As a sensor material, WO<sub>3</sub> is widely used for the detection of amides and other pollutants from combustion or automotive emissions. The combination of WO<sub>3</sub> with photonic crystal structures is expected to result in an improved sensor behavior because the near-ideal microstructures of WO<sub>3</sub> can be formed, which can be used as structurally well-defined gas sensors.

## 2 Experimental

### 2.1 Materials and method

The detailed processing is described as below: the wings pretreated with 6 wt% HCl and 10 wt% NaOH were carefully dipped into 20 wt% of H<sub>3</sub>PO<sub>4</sub>0W<sub>12</sub> in ethanol solution with a certain amount of CuCl<sub>2</sub> (weight ratio W : Cu = 1 : 0.03) and kept at for 3 h, and the chitin substrates were removed by reaction with air, leaving metal oxide in the form of the butterfly wings. The resultant replicas are denoted as Cu-W-PC replica, and Cu-W replica, respectively. Pure WO<sub>3</sub> powder was prepared using the same method described above but without the presence of the butterfly wing template.

### 2.2 Characterizations

The prepared samples were examined by X-ray diffraction (XRD) on a D-max/2550 (Rigaku). Raman scattering measurements were obtained in backscattering geometry on inVia + Reflex.

Excitation was achieved with an argon-ion laser at a wavelength of 514 nm with low incident power to avoid thermal effects. Nitrogen adsorption measurements at 77 K were performed using an ASAP2020 volumetric adsorption analyzer after the samples had been outgassed for 8 h in the degas port of the adsorption apparatus. Field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX) were carried out on an FEI XL30. Transmission electron microscopy (TEM) was carried out on a JEOL 2010 microscope. Optical micrographs of the replicas were taken using a digital optical microscope VHX-600, Keyence. X-Ray photoelectron spectra (XPS) were collected on a physical electronics PHI5400 using Mg Ka radiation as the X-ray source. All the spectra were corrected with the C1s (285.0 eV) band. The gas sensing properties of the chemical WO<sub>3</sub> sensors fabricated from the Cu-W and Cu-W-PC replicas as well as the pure WO<sub>3</sub> powder were measured by using a static test system made by Hanwei Electronics Co. Ltd, Henan Province, China. The gas sensitivities to NH<sub>3</sub>, HCHO, CH<sub>3</sub>OH, acetone, H<sub>2</sub>, H<sub>2</sub>S, CO, NO<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>N were measured. A given amount of each gas was injected into the chamber and mixed by a fan for 30 s. The gas response (sensitivity) (S) is calculated using  $S = \frac{R_a}{R_g}$ , where R<sub>a</sub> and R<sub>g</sub> are the sensor resistance in air (its relative humidity is about 25%) and in the tested gases, respectively.

## 3 Results and discussion

### 3.1 Morphological and structural characterization

In an effort to convert every individual Morpho wing scale into the Cu-W-PC replicas, the sol-gel method was modified by introducing a solution of

phosphotungstic acid and  $\text{CuCl}_2$  in ethanol in order to retard the condensation of tungstic acid. After being calcined at  $430\text{ }^\circ\text{C}$  for 3 h to remove the template, the Cu-W-PC replicas were thus obtained. As shown in Fig. 1, the tile-like arrangement of the scales and the ridges decorated with nanoscale ribs were retained in the Cu-W-PC replicas (Fig. 1a). An extremely good replication of the fine detail of the original special context should appear between single quotation marks the first time they appear.

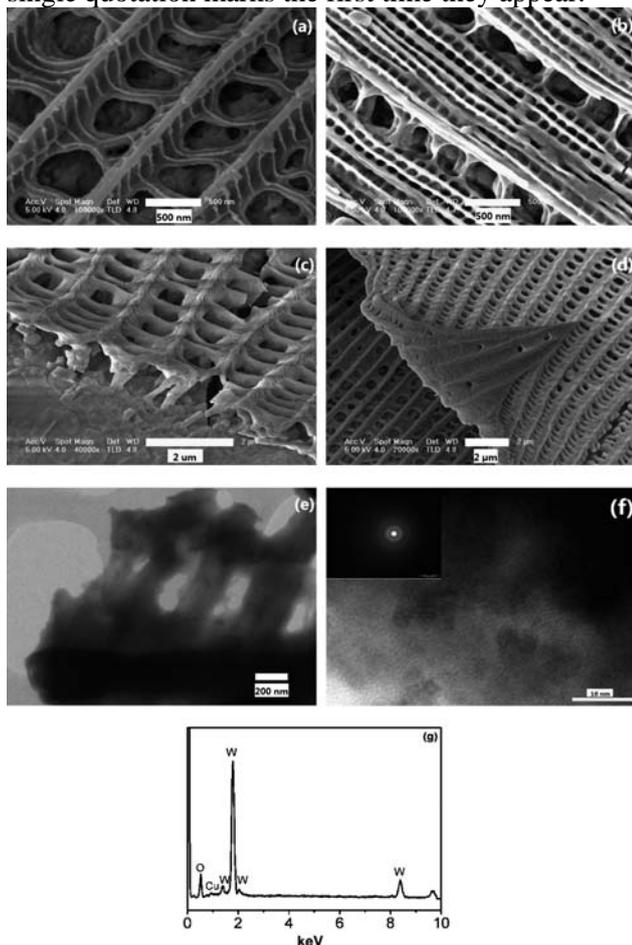


Fig. 1 Cu-W-PC replicas from a Morpho butterfly: (a), (b) FE-SEM images of the replicas, (c), (d) FE-SEM images taken on the cross section of the replica scale, (e) TEM image, (f) a high resolution TEM image. The corresponding SAED pattern is shown in (f) inset, (g) an EDX spectrum obtained from Cu-W-PC replica, revealing the presence of W, O along with Cu in the structure.

### 3.2 Sensor properties

Gas sensors were constructed with the Cu-W-PC replica and tested with  $(\text{CH}_3)_3\text{N}$  (TMA),  $\text{NH}_3$ ,

$\text{C}_2\text{H}_5\text{OH}$ , HCHO,  $\text{CH}_3\text{OH}$ , acetone,  $\text{H}_2$ , CO and  $\text{NO}_2$ . The Cu-W-PC replica sensor is very sensitive to TMA at  $290\text{ }^\circ\text{C}$ , but not sensitive to  $\text{NH}_3$ ,  $\text{C}_2\text{H}_5\text{OH}$ , HCHO,  $\text{CH}_3\text{OH}$ , acetone,  $\text{H}_2$ , CO and  $\text{NO}_2$  (Fig. 2a). The Cu-W-PC replica sensor response to TMA was evaluated in the range of 0.5–10 ppm. The response sensitivity increased with the rise of the  $(\text{CH}_3)_3\text{N}$  concentration and exhibited an extremely high sensitivity to the  $(\text{CH}_3)_3\text{N}$  gas and the sensitivities are 2.0, 3.3 and 49.6 corresponding to the concentrations of 0.5, 1, 10 ppm, respectively (Fig. 2b). From Fig. 2b, it is known that the sensitivity of pure  $\text{WO}_3$  is around 4.5 for 10 ppm, whereas the sensitivity of the Cu-W-PC replicas reaches as high as 49.6 for the same concentration. This much improved sensitivity of the Cu-W-PC replicas over the pure  $\text{WO}_3$  is probably due to the doping of Cu which occupies the atomic sites instead of interstitial sites of the  $\text{WO}_3$  lattice. The Cu doping caused negligible lattice distortion and acted as an acceptor-type impurity, thereby increasing the number of oxygen vacancies. Thus the Cu doping enhanced the interaction between the target gas and the semiconductor oxide. In the case of reducing gases, these changes are often due to the interaction of the gas with oxygen species present on the surface of metal oxides. Sensing properties can be enhanced by the addition of suitable transition metal ions that catalyse these surface reactions which have been the key research interest in using metal oxides for gas sensing applications. As a result, the response of both the Cu-W-PC and Cu-W replicas display an enhanced sensitivity to TMA compared with the pure  $\text{WO}_3$ .

It is interesting to note that the Cu-W-PC replicas sensor shows much better performance than the Cu-W replica sensor and the sensitivity of the Cu-W-PC replicas to TMA is twice that of the Cu-W replica. It is well known that increasing oxide surface area makes a great contribution to the improved sensor response. In order to get an explanation, the samples were characterized by using  $\text{N}_2$  adsorption/desorption measurements. A Brunauer–Emmett–Teller (BET) analysis showed that the Surface area of the Cu-W-PC replica was  $4.9\text{ m}^2\text{ g}^{-1}$ , similar to that of the Cu-W replica ( $4.2\text{ m}^2\text{ g}^{-1}$ ) (not shown here). Thus the better performance of the Cu-W-PC replica sensor over the Cu-W replica sensor cannot be explained by the different surface areas. However it may be explained in terms of different

geometries of these two replica sensors as described elsewhere. Ozin et al. found that periodic macroporous forms of  $\text{SnO}_2$  with opal and inverse opal structures are close to the theoretical ideal structure for a gas sensor. Thus, a similar explanation can be used here for the chemical sensing behaviors of the Cu-W-PC replicas with and without photonic structure. The actual active surface area “seen” by the gas in the Cu-W-PC replica sensors is probably higher than for the Cu-W replica sensor due to the photonic crystal structure.

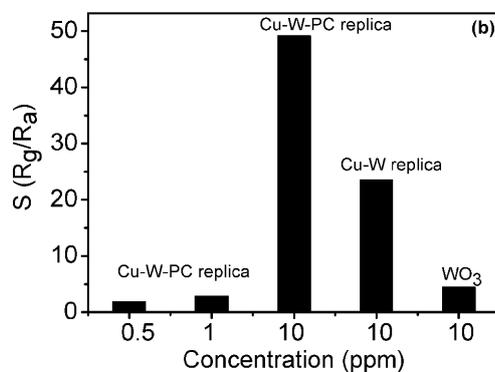
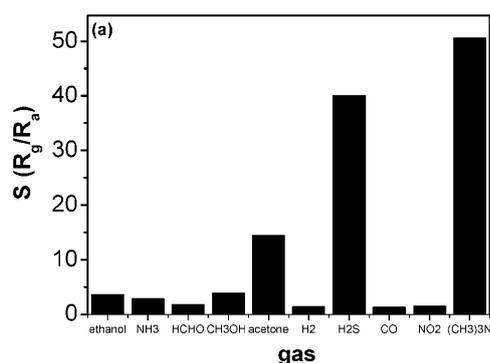


Fig. 2 (a) Sensitivity of Cu-W-PC sensors to different gases (10 ppm) at 290°C and (b) the relationship between the gas sensitivity and TMA concentration.

## References

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