

# Facile synthesis of hierarchical porous WO<sub>3</sub> nanofibers having 1D nanoneedles and their functionalization with non-oxidized graphene flakes for selective detection of acetone molecules

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## Experimental details

*Synthesis of dense WO<sub>3</sub> nanofibers (NFs):* To synthesize WO<sub>3</sub> NFs, the composite of W precursor/PVP solution was firstly prepared. 0.2 g of (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O and 0.25 g of PVP were dissolved in 1.5 g of DI water and continuously stirred at room temperature for 3 h. The electrospinning was performed with the synthesized solution at a feeding rate of 0.1 mL/min using a syringe pump and at a constant DC voltage of 15 kV between the stainless steel foil, employed as a collector, and a syringe needle (21 gauge). The collected as-spun W precursor/PVP composite NFs were calcined at 500 °C for 1 h in air ambient to obtain dense WO<sub>3</sub> NFs.

*Synthesis of porous WO<sub>3</sub> nanofibers (NFs):* Porous WO<sub>3</sub> NFs were achieved by using polystyrene (PS) colloids as sacrificial templates in electrospinning. During the preparation of electrospinning solution, 1.5 g DI water containing 2.5 wt% polystyrene (PS) latex microsphere was used instead of pure DI water with the same compositional ratio of (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O and PVP as prepared for dense WO<sub>3</sub> NFs. The electrospinning condition and the calcination temperature were maintained.

*Synthesis of hierarchical and porous WO<sub>3</sub> nanofibers (NFs):* To prepare hierarchical and porous structure of WO<sub>3</sub> NFs, heat-treatment condition was controlled with the sample of as-spun W precursor/PVP composite NFs containing PS colloid templates. The composite NFs were introduced in a horizontal quartz tube furnace and heat-treatment was performed at 700 °C for 1 h with a constant Ar flow rate of 2000 sccm, which resulted in the formation of nanoneedles on the surface of the composite NFs. Subsequently, oxidation was performed with the composite NFs at 500 °C for 1 h in air to form hierarchical and porous WO<sub>3</sub> NFs.

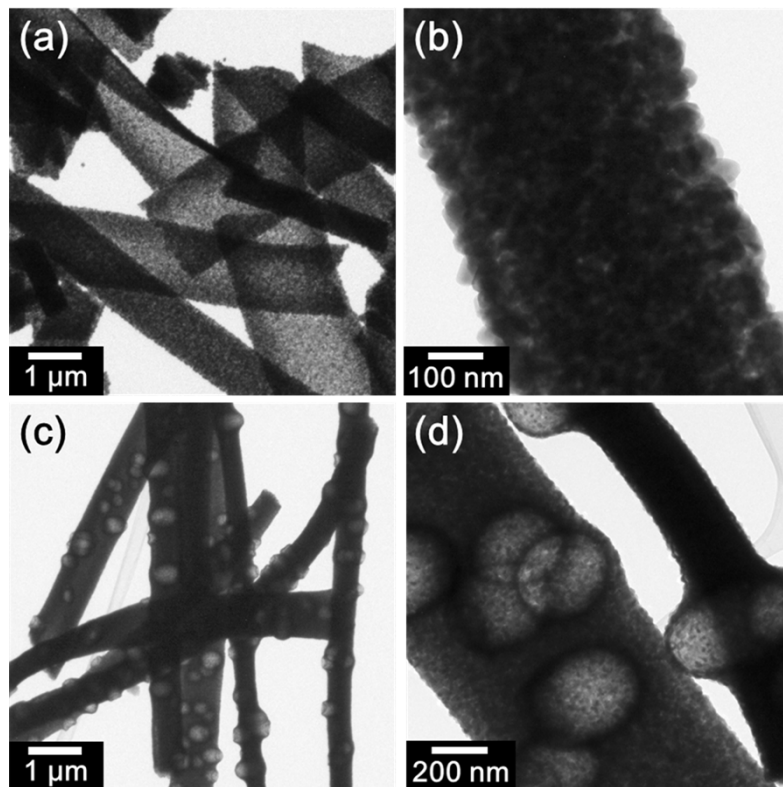
*Synthesis of non-oxidized graphene (NOGR) flakes:* The preparation of NOGR was reported in previous works.<sup>1</sup> Briefly, a ternary eutectic system (KCl (99%, Aldrich), NaCl (99%, Aldrich), and ZnCl<sub>2</sub> (99%, Aldrich)) were used to fabricate graphite intercalation compound (GIC) at 350 °C. The prepared GIC was exfoliated in a pyridine solution. For fabricating the NOGR flakes, 1-pyrenebutyric acid (20 mg, Aldrich) was added to graphene flakes (20 mg) dispersed in pyridine (40 mL, Aldrich). The mixtures were mildly sonicated for 12 h and subsequently stored at 70 °C for 24 h. The mixture was then filtered and washed with DI water using a 0.1 µm-thick Anodic filter to remove salts and residual pyridine. After drying the mixture in a furnace heated to 100 °C, the NOGR flakes (10 mg) were dispersed under sonication in 10 mL of acetone for 3 h.

*Synthesis of non-oxidized graphene (NOGR) flake-loaded H-WO<sub>3</sub> NFs composite:* The synthesized hierarchical and porous WO<sub>3</sub> (H-WO<sub>3</sub>) NFs were functionalized with non-oxidized graphene flakes. 3 mg of H-WO<sub>3</sub> NFs were dispersed in 100 µL ethanol solution. Then, the H-WO<sub>3</sub> NF dispersed solution was mixed with NOGR dispersed solution. The content of NOGR flakes in the composite with H-WO<sub>3</sub> NFs was maintained at 0.1 wt%.

*Sensor fabrication:* The Al<sub>2</sub>O<sub>3</sub> substrates were prepared to characterize the sensing performances of the prepared sensing layers. The front side of the substrate has two parallel electrodes for measuring resistance changes. A microheater was patterned at the backside of the substrate to evaluate the sensing performances depending on the operating temperature. The temperature was controlled by applying DC voltage. To coat the prepared sensing materials on the substrate, dispersed solutions with 3 mg of sensing materials in 50 µL of ethanol solution were prepared. Then, drop coating was performed on the substrate with 5 µL of the dispersed solution using a micropipette.

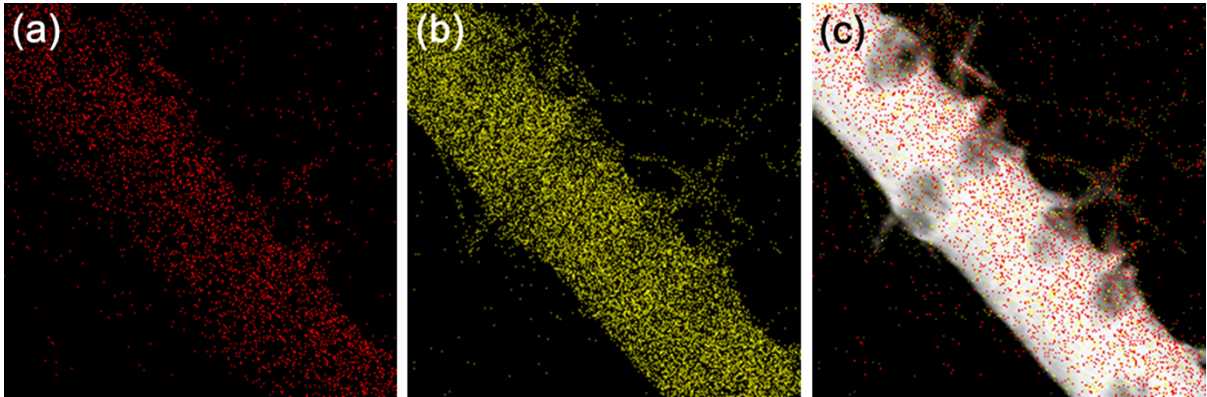
*Gas sensing characterization:* The gas sensing performances were evaluated using a homemade measurement setup described elsewhere.<sup>2</sup> All of the sensors were stabilized at a highly humid baseline air ambient (90% RH) before the measurement to simulate exhaled breath. The humidity level was calibrated by commercialized humidity sensor (605-H1, Testo Inc.). The sensors were exposed to different analytes (acetone, ethanol, nitrogen monoxide, toluene, pentane, ammonia, and carbon monoxide) concentrations ranging from 100 ppb to 5 ppm. Each analyte was exposed for a duration of 10 min followed by 10 min of exposure to air to stabilize the sensors. The resistance changes were measured using a data acquisition system (34972A, Agilent) and the relative response ( $R_{\text{air}}/R_{\text{gas}}$ ) was measured, where  $R_{\text{air}}$  is the sensor's baseline resistance upon exposure to air and  $R_{\text{gas}}$  is the resistance measured upon exposure to the different analytes. The operating temperatures were controlled by applying voltage to the microheater, which was patterned at the back side of the sensor substrate, using a DC power supply (E3647A, Agilent).

**Fig. S1**



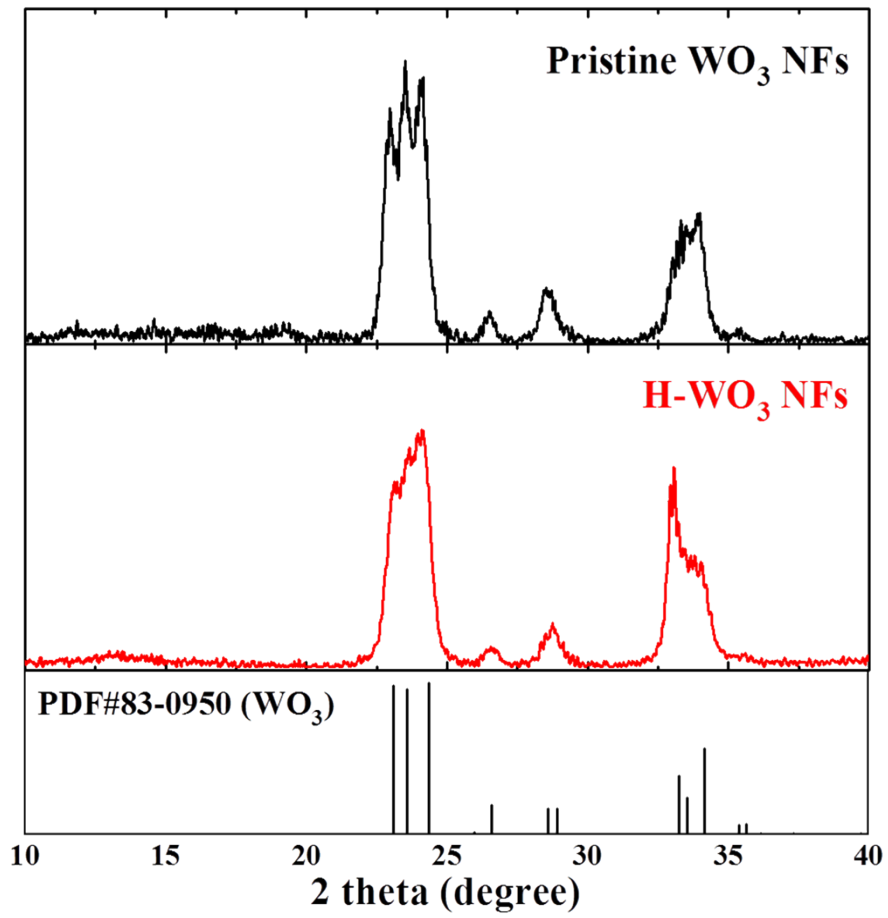
**Fig. S1** (a) TEM image of dense  $\text{WO}_3$  NFs, (b) magnified TEM image of (a), (c) TEM image of porous  $\text{WO}_3$  NFs synthesized by polystyrene colloid templates, and (d) magnified TEM image of (c).

**Fig. S2**



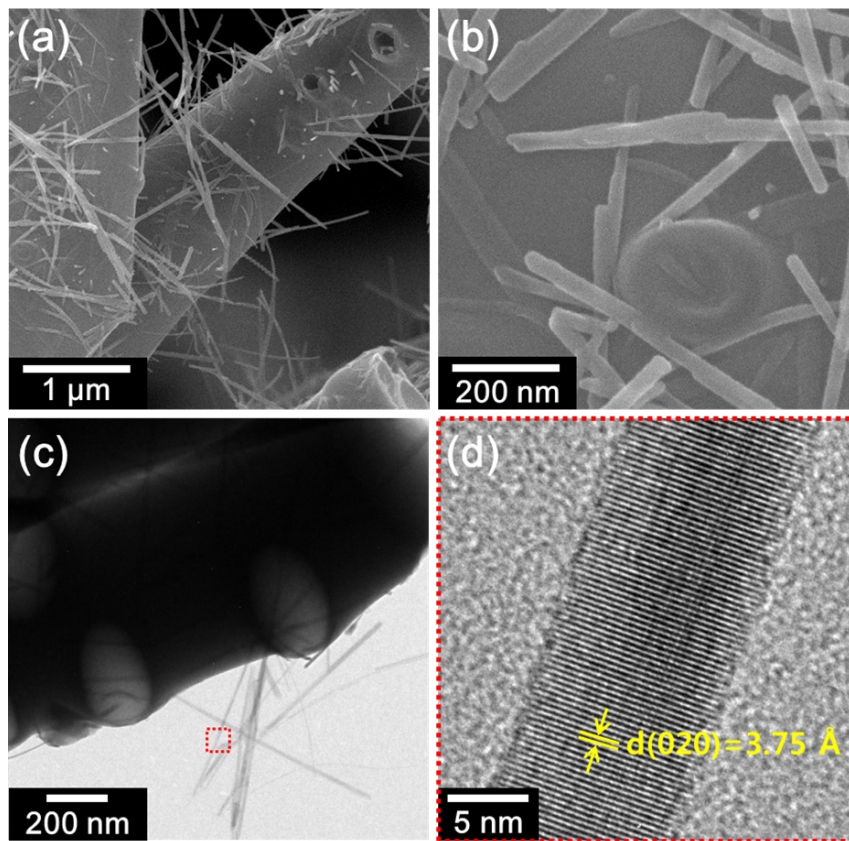
**Fig. S2** Energy-dispersive X-ray spectroscopy (EDS) elemental mapping analysis of hierarchical  $\text{WO}_3$  (H- $\text{WO}_3$ ) NFs: (a) O, (b) W, and (c) overlap elemental mapping of O and W with STEM image.

**Fig. S3**



**Fig. S3** XRD analysis of pristine WO<sub>3</sub> NFs and hierarchical and porous WO<sub>3</sub> (H-WO<sub>3</sub>) NFs.

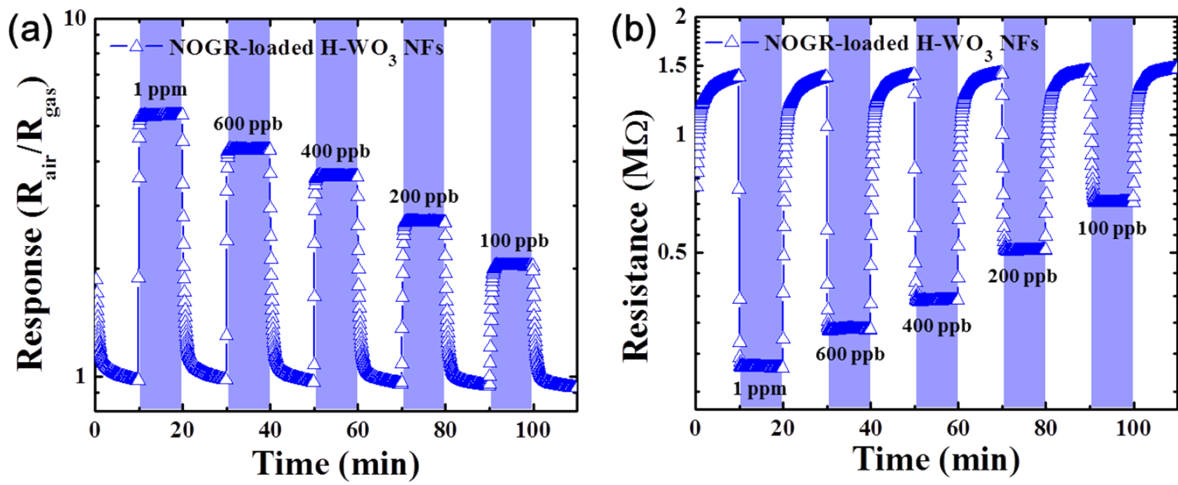
**Fig. S4**



**Fig. S4** (a) SEM image of as-spun W precursor/PVP/PS composite NFs after calcination at 700 °C for 1h in Ar ambient, (b) magnified SEM image of (a), (c) TEM image of as-spun W precursor/PVP/PS composite NFs after calcination at 700 °C for 1h in Ar ambient, and (d) magnified TEM image of  $\text{WO}_3$  nanoneedle (red dotted box) in (c).

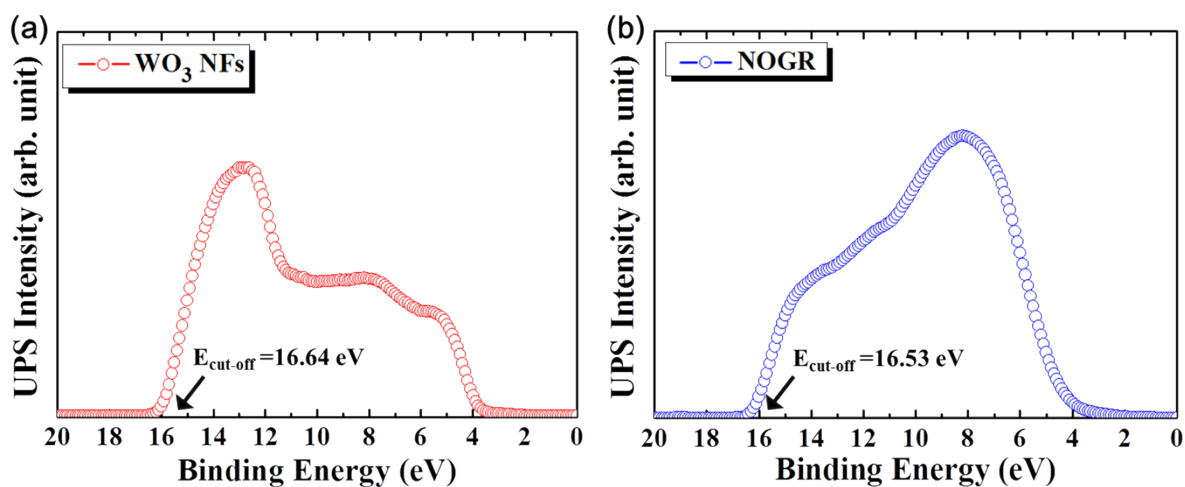


**Fig. S5**



**Fig. S5** (a) Dynamic response ( $R_{\text{air}}/R_{\text{gas}}$ ) transition and (b) resistance transition toward acetone in a concentration range of 100 ppb – 1 ppm at 350 °C.

**Fig. S6**



**Fig. S6** Ultraviolet photoelectron spectroscopy (UPS) analysis of (a) pristine WO<sub>3</sub> NFs and (b) non-oxidized graphene (NOGR) flakes for investigation of the work functions.

Ultraviolet photoelectron spectroscopy (UPS) analysis was performed to investigate the work function ( $\Phi$ ) of WO<sub>3</sub> NFs and NOGR flakes. The results revealed that the work function of WO<sub>3</sub> NFs was 4.56 eV, whereas the work function of NOGR flakes was 4.67 eV.

## References

1. K. H. Park, B. H. Kim, S. H. Song, J. Kwon, B. S. Kong, K. Kang and S. Jeon, *Nano Lett*, 2012, **12**, 2871-2876.
2. S. J. Choi, I. Lee, B. H. Jang, D. Y. Youn, W. H. Ryu, C. O. Park and I. D. Kim, *Anal Chem*, 2013, **85**, 1792-1796.