Oriented assembly of monomicelles in beam stream enabling bimodal mesoporous metal oxide nanofibers

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ABSTRACT The assembly of monomicelles along one-dimension (1D) to construct tubular or fibrous mesostructures is greatly desired but still challenging. Herein, we have demonstrated a facile strategy to synthesize 1D bimodal mesoporous metal oxides (e.g., WO₃, WO₃/Pd, WO₃/PdCu, TiO₂, and ZrO₂) nanofibers (NFs) through assembling the organic-inorganic composite monomicelles in a beam stream generated *via* an electrospinning technique. This facile and repeatable methodology relies on the preparation of copolymer@metal-complex monomicelles in an anisotropic solution and oriented assembly of them in the beam stream by the selective evaporation of solvent. WO₃ and its derivatives are chosen as the demo, which show a uniform continuous fibrous structure with dual mesopore sizes (~4.0 and 7.6 nm) and large surface area (~93.1 m² g⁻¹). Benefitting from the unique textual structure, gas sensors made by Pd-decorated mesoporous WO₃ NFs display outstanding comprehensive sensing performance to ethylbenzene, including a high sensitivity (52.5), an ultralow detection limit (50 ppb), and fast response/recovery kinetics (11/16 s) as well as an outstanding selectivity, which render them promising for rapid environmental monitoring.

Keywords: monomicelles, dual mesoporous metal oxides, nanofibers, beam stream, ethylbenzene

INTRODUCTION

Mesoporous materials have shown immense interest in many applications owing to the excellent characteristics such as regular mesoporous structures, large surface areas, adjustable pore sizes, and abundant frameworks [1–3]. Over the past three decades, a series of significant

progress have been made for the fabrication of mesoporous materials through the “collaborative co-assembly” of amphiphilic surfactants or grafted copolymers, which realizes the effective control of them with a variety of components and tunable mesostructures [4–6]. However, most of them are three-dimensional (3D) assembled bulk mesostructures, where the internal active sites cannot be fully exposed and are not conducive to the rapid transport of guest molecules, greatly hindering their application performances [7–10].

Recently, the construction of nanostructured mesoporous materials (e.g., nanospheres, nanotubes/nanofibers (NFs), nanosheets) has become a hot topic because these structures will undoubtedly overcome the imperfections of their bulk counterparts [11–16]. Particularly, the creation of 1D mesoporous NFs has shown great potential in a broad range of applications, such as sensing, catalysis and biomedicine [17–19]. In addition to the intrinsic mesoporous properties, the 1D geometry possesses a high aspect ratio, which provides smooth pathways for the electron transfer and exhibits a robust shape to support functional units. Till now, many strategies have been demonstrated to prepare mesoporous NFs, e.g., solvothermal method [20], soft-templating route [21], and electrospinning process [22]. However, the construction of NFs with dual mesoporous structures in a facile and straightforward way is still challenging. Recently, the monomicelle-directed assembly strategy has shown great potential in creating ordered mesoporous materials with diverse morphologies and tunable mesoscopic structures [23–25]. Unlike the conventional surfactant-templated strategy using the liquid crystals as the

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pore-forming agents, the monomicelle-directed assembly strategy utilizes the composite micelles as the building units, which are flexible and changeable according to user's requirements. However, the manipulation of the assembly and growth of single micelles in 1D direction has rarely been achieved.

Electrospinning is an efficient and low-cost technology for making 1D nanostructured materials with a variety of components [26–28]. It involves the ejection of a charged jet from a polymer solution reservoir to the ground plate under the strong electrostatic field. To keep the high viscosity of the solution is essential for maintaining the jet stable and not transforming into spherical droplets, which thus leads to the formation of fiber structure. However, most of the previously reported studies have concentrated on preparing solid fibers without pores [29]. Recently, some breakthroughs have been made for the production of fibers with mesoporous structures *via* the inclusion of some pore-creating strategies, including high-volatile organic solvent-assisted, foaming-assisted, phase-separation-promoted, and amphiphilic surfactant-templated method [30–34]. However, the marriage between the facile technique of electrospinning and monomicelle assembly strategy to create NFs with dual mesoporous structures and diverse components has yet to be reported.

Herein, we have demonstrated a straightforward route to create metal oxide NFs with bimodal pore size distribution (PSD) *via* the oriented assembly of monomicelles in the electrospinning-generated beam stream. WO_3 and WO_3 -based composites are selected as the examples to show the versatility of our approach. The key in the synthesis is the preparation of copolymer/ W^{6+} - (polyvinyl pyrrolidone) complex composite micelles and controlled assembly of them in the charged jet. The resultant mesoporous WO_3 NFs possess well-defined 1D geometry with dual mesopores (~ 4.0 and 7.6 nm) and a large surface area ($\sim 93.1 \text{ m}^2 \text{ g}^{-1}$). In addition, this methodology can be generalized to fabricate other types of metal oxides (e.g., TiO_2 , ZrO_2) and nanoparticle-functionalized WO_3 NFs through making different types of composite single micelles. The dual mesostructures are very important in promoting the diffusion of host/guest molecules and could provide abundant interfaces for the interactions of gas molecules and support. As a result, an ethylbenzene (EB) sensor derived from the Pd-decorated m- WO_3 NFs exhibits a superior comprehensive activity, including fast response and recovery kinetics, a low concentration detection limit and an excellent selectivity. This study demonstrates a versatile strategy to fabricate mesoporous NFs with bimodal PSD and diverse compo-

nents, suggesting a great application potential in many fields.

EXPERIMENTAL SECTION

Preparation of mesoporous WO_3 NFs

The template poly(ethylene oxide)-*b*-styrene (PEO-*b*-PS) with a chemical formula of PEO_{117} -*b*- PS_{198} (molecular weight (M_n) = $25,850 \text{ g mol}^{-1}$, polydispersity index (PDI) = 1.09) was fabricated through an atom transfer radical polymerization (ATRP) method reported previously [35]. Prior to the electrospinning process, the single micelle precursor solution was first prepared. In a typical synthesis, PEO-*b*-PS (0.3 g) and polyvinylpyrrolidone (PVP, 0.2 g) were added consecutively to a mixed solvent of *N,N*-dimethylformamide (DMF) and absolute ethanol (the volume ratio is 2.6:2.4) and mixed for 10 min to form a clear solution. Then, WCl_6 (1.2 g) was added to the solution and stirred until the color of the solution turned green. The precursor solution was subsequently transferred into a plastic syringe (5 mL), after which the high voltage (20 kV, DC) was applied between the syringe needle and the roller coated with silicone paper at a fixed distance of 15 cm. The electrospinning process was carried out at room conditions. Then, the obtained membranes were thermally treated at 75°C for 6 h to solidify the framework. Then, the fiber membrane was annealed at 350°C for 2 h under N_2 to obtain mesoporous C/ WO_3 NFs. Finally, the mesoporous WO_3 NFs were obtained by annealing C/ WO_3 NFs at 450°C in air to burn out the carbon framework.

The dual mesoporous $\text{TiO}_2/\text{ZrO}_2$ NFs were fabricated through the same method by replacing the tungsten hexachloride with tetrabutyl titanate and zirconium(IV) chloride, respectively. The nanoparticle-functionalized WO_3 NFs were prepared by adding a certain amount of PdCl_2 and CuCl_2 in the micelle precursor solution, followed by the same electrospinning condition with that for WO_3 NFs.

Characterization

The small-angle X-ray scattering (SAXS) analysis was performed on a Nanostar U small-angle X-ray scattering equipment (Bruker, Germany) using Cu K α radiation (40 kV, 35 mA). Scanning electron microscopy (SEM) images were obtained on a TESCAN MAIA3 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images were taken at a JEM-2100 F with an accelerating voltage of 200 kV. A Rigaku D/Max-2550 PC diffractometer (Tokyo, Japan) was used to

collect the X-ray diffraction (XRD) data at a 2θ range from 10° to 90° . The nitrogen sorption isotherms were examined using the Micromeritics Tristar 3020 analyzer made by USA. First, a degassing process was applied to pre-treat the samples at 180°C for 6 h under a vacuum condition to remove water. Then, the surface area was calculated using the adsorption data at $P/P_0 = 0.02\text{--}0.20$ based on the Brunauer-Emmett-Teller (BET) method. Barrett-Joyne-Halenda (BJH) model was applied to derive the PSD curve from the adsorption branch. The total pore volume (V_{total}) was estimated from the adsorbed amount at $P/P_0 = 0.995$. Thermogravimetric (TG) analysis was carried out on TG 209F1 in air from 50 to 900°C at a ramping rate of $10^\circ\text{C min}^{-1}$. A PHI 5000C ESCA system with a dual X-ray source was utilized to obtain the X-ray photoelectron spectroscopy (XPS) pattern. $^1\text{H-NMR}$ spectra were recorded on an AVANCE3hd 600 MHz full digital NMR spectrometer with tetramethylsilane as the internal standard and CDCl_3 as the solvent. The gel permeation chromatography (GPC) result was obtained on a BI-MWA type chromatographer with a refractive index detector using THF as the mobile phase.

Fabrication of mesoporous WO_3 NF-based sensors

Fig. S1 displays the scheme for preparing the sensor. First, the paste was prepared by dispersing a certain amount of mesoporous materials in ethanol with grounding, which was then deposited on the ceramic tube printed with the Au electrodes. The obtained tube was dried at 25°C for 24 h, and then annealed at 350°C for 2 h. The temperature of the tube during the test was controlled by using a Ni-Cr alloy coil as a heater. Finally, the welded sensor was maintained at 250°C for 7 days to improve the long-term stability. The gas response was obtained through a stationary-state gas distribution method. A load resistor was linked with the gas sensor for measuring the gas response in electric circuit (Fig. S1b), which was reflected by the voltage.

RESULTS AND DISCUSSION

The PEO-*b*-PS template was synthesized by using PEO_{114} as the starting hydrophilic block *via* an ATRP method (Fig. S2a). According to the $^1\text{H-NMR}$ spectrum, the average molecular weights of PEO-Br and PEO-*b*-PS are 5300 and $25,850\text{ g mol}^{-1}$, respectively (Fig. S2b and c). The chemical formula of the PEO-*b*-PS can be determined as $\text{PEO}_{114}\text{-}b\text{-PS}_{198}$. The PDI of $\text{PEO}_{114}\text{-}b\text{-PS}_{198}$ derived from the GPC analysis (Fig. S2d) is ~ 1.09 , suggesting a narrow molecular-weight distribution, which is favorable for the subsequent construction of an ordered

mesoporous structure [36,37]. The WO_3 NFs with dual mesoporous structures (m- WO_3 NFs) were constructed through the oriented assembly of monomicelles in the electrospinning-generated beam stream by using PEO-*b*-PS as a template, WCl_6 as a tungsten source, and PVP as both thickening and complexing agent in the DMF/ethanol system, followed by a successive calcination process in N_2 and air atmosphere (Fig. S3). The SEM images unambiguously demonstrate that the m- WO_3 NFs possess a long, continuous and straight fibrous shape with a diameter of $\sim 420\text{ nm}$ (Fig. 1a and b). The high-resolution SEM (HRSEM) image (Fig. 1b inset and c) indicates that the NFs possess two types of mesopore channels with one type patterned on the surface ($\sim 3.8\text{ nm}$) and the other aligned along the fiber direction ($\sim 7.8\text{ nm}$). TEM image (Fig. 1d) further confirms that m- WO_3 NFs are fibrous in shape with a uniform diameter ($\sim 420\text{ nm}$), exhibiting a large number of mesopores. The cracked pieces from NFs (Fig. 1e) also suggest that the mesoporous structures along the NF direction are relatively ordered and show a 2D hexagonal channel structures. High-resolution TEM (HRTEM) image of the mesoporous WO_3 NFs reveals that the pore walls consist of highly crystallized WO_3 with clear lattice fringes of $\sim 0.435\text{ nm}$, in reflection of (111) plane of WO_3 (Fig. 1f). In addition, the grain size of the WO_3 was measured to be $\sim 8.2\text{ nm}$. The selected area electronic diffraction (SAED) pattern shows three diffraction rings and numerous spots, implying a polycrystalline feature of WO_3 (Fig. 1f inset). Furthermore, the scanning TEM (STEM) image further proves that two different kinds of pores exist in the NF, corresponding well with the SEM images (Fig. 1g). The corresponding elemental mappings of m- WO_3 NFs show the uniform distribution of W and O atoms throughout the entire NFs (Fig. 1h and i).

The SAXS pattern (Fig. S4) of the m- WO_3 NFs exhibits two well-resolved (200) and (210) scattering peaks, indicating the formation of 2D hexagonal mesostructure with $p6mm$ space group [38], which matches well with the SEM and TEM results. The XRD pattern of the m- WO_3 NFs (Fig. 2a) shows several well-resolved diffraction peaks, which can be indexed as the orthorhombic phase of WO_3 (PDF #97-005-0728) [39]. No additional diffraction peaks are observed, suggesting the high purity of crystalline WO_3 . According to the Scherrer equation, the size of WO_3 nanocrystals in the NFs was calculated to be $\sim 7.8\text{ nm}$, similar to the observation in HRTEM image. Nitrogen sorption isotherms of m- WO_3 NFs display a type IV curve with H1-type hysteresis loop, which is typical for materials with uniform mesopores (Fig. 2b). The

Figure 1 SEM images of m-WO₃ NFs (a–c). Inset in (b) shows the HRSEM image of m-WO₃ NFs; TEM (d, e) and HRTEM (f) images of m-WO₃ NFs. Inset in (f) shows the diffraction pattern; STEM image of m-WO₃ NFs (g) and the corresponding EDX maps of (h) W and (i) O.

BET surface area and pore volume of the NFs are measured to be $93.1 \text{ m}^2 \text{ g}^{-1}$ and $0.13 \text{ cm}^3 \text{ g}^{-1}$, respectively. The PSD derived from adsorption branch using the BJH method shows two sharp peaks centered at ~ 4.0 and 7.6 nm , respectively, suggesting the formation of dual mesoporous structure. Three peaks related to W 4f, W 4d and O 1s are detected in the XPS spectra, suggesting the formation of WO₃ (Fig. S5). The W 4f XPS spectrum of m-WO₃ NFs can be split into two peaks at 35.8 and 37.9 eV, respectively, assigned to $\text{W}^{6+} 4\text{f}_{7/2}$ and $\text{W}^{6+} 4\text{f}_{5/2}$ (Fig. 2c). The high-resolution O 1s spectrum (Fig. 2d) reveals the presence of two kinds of oxygen species: surface adsorbed O^- and lattice O_2^- respectively.

To obtain the formation mechanism of bimodal mesoporous NFs in the beam stream, the structures of samples synthesized without PEO-*b*-PS and with different amounts of PVP were also investigated. In the absence of PEO-*b*-PS, WO₃ NFs with only one type of mesopores on the surface of NFs were obtained. The SEM image from the side view of the NFs shows a nonporous structure along the NF direction, which forms a clear contrast to

the sample obtained in the presence of PEO-*b*-PS (Fig. S6). In addition, the PSD curve displays only one clear peak centered at $\sim 4.0 \text{ nm}$ (Fig. S7), further indicating that the PEO-*b*-PS plays an important role in the formation of secondary mesopores. Furthermore, the morphology of the NFs can be controlled by tuning the amount of PVP (Fig. S8). When the amount of PVP is less than 0.1 g, the beam stream is not able to be formed due to the low viscosity of the solution. As the amount of PVP rises, both the diameter of the NFs and the density of the mesopores on the NF surface increase. These results suggest that the PVP molecules not only act as a thickening agent to increase the viscosity of the stock solution, but also are responsible for the formation of primary mesopores on the surface originating from the phase separation of PVP.

We further demonstrate the versatility of this strategy by preparing other metal oxides (e.g., TiO₂ and ZrO₂) using different micellar solutions. XRD, SEM and TEM images confirm the successful formation of TiO₂ and ZrO₂ NFs with dual mesoporous structures (Figs S9 and

Figure 2 (a) XRD pattern of m-WO₃ NFs. (b) The nitrogen adsorption-desorption isotherms and the corresponding pore-size distribution curve of m-WO₃ NFs. (c) High-resolution W 4f and (d) O 1s XPS spectra of m-WO₃ NFs.

S10). More interestingly, this strategy is also feasible for the direct incorporation of functional nanoparticles (e.g., Pd, PdCu) into the mesoporous framework of m-WO₃ NFs. SEM and TEM images of Pd nanoparticles (2 wt%)-decorated m-WO₃ (m-WO₃/Pd) NFs clearly show that Pd nanoparticles with a diameter of ~3 nm are homogeneously anchored on the surface of the m-WO₃ NFs (Fig. 3a–d). In addition, the dual mesoporous structures are clearly observed in the whole NFs from the TEM and STEM images (Fig. 3c and e). The corresponding elemental maps of W, O, and Pd further confirm that these elements are uniformly distributed to construct the fibrous structure. In addition, the loading amount of Pd can be easily adjusted by changing the addition amount of Pd precursors in the micelle solution. XRD pattern of m-WO₃/Pd (Fig. S11) clearly shows that increasing the dose of Pd results in the appearance of Pd diffraction peak (PDF#46-1043) but has little effect on the morphology change of NFs (Fig. S12). It is also worth noting that the addition of more functional elements (e.g., Cu) would not change the morphology and mesostructures of the WO₃ NFs (Fig. 3f–i). These results indicate that the formation of bimodal mesoporous metal oxides by this oriented assembly strategy in beam stream is general and feasible for functionalization, which is independent of the com-

positions.

On the basis of the above observations, the oriented assembly process of monomicelles in the beam stream was proposed for the construction of bimodal mesoporous metal oxide NFs. At first, the PEO-*b*-PS molecules were organized to generate spherical micelles with the PS blocks as the inner core and the PEO blocks as the shell resulting from the anisotropy in solution [40,41]. In this study, the PVP acts not only as a thickening agent, but also a chelating agent. It can interact with W⁶⁺ to form a metal-complex [42–44], which can further bind with the PEO shell to form the composite PEO-*b*-PS@W-PVP micelles by hydrogen bonding interaction or electrostatic interaction. This also explains the easy incorporation of other functional metal elements without disturbing the formation of mesostructures. The TEM image clearly reveals the formation of uniform spherical single micelles with a diameter of ~12 nm (Fig. 4a). After the application of high voltage, the electrostatic field between the needle and the collectors forms and deforms the precursor solution in the needle tube, generating overhanging conical droplets at the nozzle. When the charge repulsion of droplet exceeds its surface tension, the jets are ejected at a high velocity from the surface of the droplet. These jets are subjected to a high-speed stretching of electric field

Figure 3 SEM (a, b), TEM (c), and HRTEM (d) of m-WO₃/Pd NFs; (e) STEM image and corresponding elemental maps of W, O, and Pd of m-WO₃/Pd NFs. TEM (f, g) and HRTEM (h) of m-WO₃/PdCu NFs; (i) STEM image and corresponding elemental maps of W, O, Pd, and Cu of m-WO₃/PdCu NFs.

forces and rapid evaporation of mixed solvents over a short distance. The TEM images of the samples collected from the beam stream clearly show that several spherical composite micelles are packed together and tend to fuse into cylindrical composite micelles (Fig. 4b). This could be due to the increase of concentration of single micelles after the evaporation of the solvent [45,46]. Along with the complete evaporation of mixed solvents, the as-spun inorganic-organic NFs are obtained after the jets deposit on the receiver plate. SEM image depicts that the cylindrical core-shell composite micelles are stacked together to shape into regular mesostructures with a diameter of ~500 nm (Fig. 4c). Subsequently, the calcination of the as-spun W⁶⁺-PVP@PEO-*b*-PS NFs in N₂ atmosphere could lead to the carbonization of PEO-*b*-PS and PVP to form carbon-supported WO₃ (m-C/WO₃) NFs, exhibiting a long and continuous fibrous structure with a diameter of ~420 nm and uniform mesopores on

the entire NFs (Fig. 4d). The sharp reduction of the diameter of NFs indicates the thermal shrinkage during the calcination process. Direct calcination in air can result in the complete removal of PEO-*b*-PS and PVP at a very low temperature (as revealed from the TGA curve, Fig. S13), which is not favorable for the formation of ordered mesoporous structure. In this work, the carbon framework is essential for supporting the WO₃ skeleton and preventing it from collapse, acting like a “reinforced-concrete” structure [47,48].

Encouraged by the unique bimodal mesoporous nanofibrous structures, the gas sensors by using m-WO₃/Pd NFs as the raw materials were fabricated to examine their application potential in EB sensing. EB, as one type of volatile organic compounds, is widely applied as the organic solvent in painting, leather making and plastics. However, the accidental leakage or careless release of EB to the environment could cause severe problems because

Figure 4 TEM images of composite PEO-*b*-PS@W⁶⁺-PVP single micelles in the stock solution (a), and composite PEO-*b*-PS@W-PVP single micelles in the beam stream (b); SEM images of the (c) as-spun organic-inorganic fibers and (d) mesoporous C/WO₃ fibers after carbonization in N₂ atmosphere. Inset in (d) is the enlarged SEM image of mesoporous C/WO₃ fibers, showing that uniform mesopores are patterned on the fiber surface; (e) schematically illustration for the formation mechanism of bimodal mesoporous WO₃ NFs: Stage 1, the oriented assembly of monomicelles in the beam stream under the evaporation of solvent; Stage 2, with the complete evaporation of solvent at the collector, the micelles are packed into ordered mesostructures; Stage 3, the carbonization of the as-spun fiber to form m-C/WO₃ NFs.

it possesses a strong carcinogenicity to human beings [49–51]. Therefore, increasing attention has been attracted for the development of gas sensors in manufacturing industries and human life for the detection of EB. Here, the sensors based on m-WO₃ NFs and bulk m-WO₃ (mesoporous WO₃ prepared using evaporation-induced self-assembly process) were also prepared, respectively, as the control experiments. The effect of operating temperature on the sensing performance of all types of sensors was first examined in a temperature range of 160 to 320°C (Fig. 5a). The responses for both m-WO₃/Pd- and m-WO₃-NFs-derived sensors increase with rising operating temperature, and reach the maximum at 240°C;

whereafter, the responses decrease. The optimal operating temperature for bulk m-WO₃ is ~280°C, higher than that of fibrous structure. Moreover, the m-WO₃/Pd NFs-based sensor shows the maximum response of ~50 in the tested temperature range, which is 3.8 and 7.1 as large as that of m-WO₃ NFs (~13) and bulk m-WO₃ (~7), respectively. This result suggests that both the presence of Pd nanoparticles and keeping the NF structure are advantageous to enhancing the sensing performance of WO₃ toward EB.

The response and recovery kinetics of the sensors toward different concentrations of EB (50 ppb to 50 ppm) were investigated at 240°C (Fig. 5b and c). With in-

Figure 5 (a) The response of sensors based on different types of materials to 50 ppm EB at different temperatures (160–320°C); (b) response-recovery curves of various sensors to EB at different concentrations at 240°C; (c) the relationship between the response and the concentration of EB gases; (d) dynamic response-recovery curve of m-WO₃/Pd NFs sensors to 50 ppm of EB; (e) repeating response and recovery curves to 1 ppm of EB; (f) the responses of sensors based on m-WO₃ and m-WO₃/Pd NFs to different gases at 50 ppm.

creasing EB concentration in the tested chamber, all sensors display continuously increasing responses. Even at low concentrations of 5, 50, 100, 200 and 500 ppb, the responses for m-WO₃/Pd NFs-based sensor can reach 2.3, 3.6, 4.2, 5.0 and 8.6, respectively. Particularly, the lowest detectable limit can reach 5 ppb (Fig. 5c). As gas is off, the response can be immediately restored to its initial value, indicating the excellent response and recovery kinetics of m-WO₃/Pd. As a contrast, the sensors based on m-WO₃ NFs and bulk-WO₃ were also examined. At low concentrations of EB (<500 ppb), both of these two sensors exhibit negligible responses, suggesting the superiority of Pd loading. With the rise of EB concentration, the responses for both sensors slightly increase and the increment of the m-WO₃ NFs-based sensor is larger than that of the bulk-WO₃-based one. Given that the performance of a sensor is related to the surface adsorption and diffusion of gasses, the high specific surface area of the NF structure ensured more adsorption sites and the dual mesoporous structure enabled a fast mass diffusion, thus increasing the sensing performance of m-WO₃ NFs [52–54].

The response/recovery times are important parameters for examining the sensing performance of gas sensors. The response and recovery times of m-WO₃/Pd NFs-based sensor are estimated to be ~11 and 16 s, respec-

tively (Fig. 5d). The fast response-recovery kinetics of the sensor is due to the unique dual mesoporous structure, which can not only promote the fast diffusion of EB molecules throughout the entire pore systems (i.e. pathways), but also produce enormous interfaces for the gas-solid interaction [55]. The reversible cycles of the response curves indicate that both the m-WO₃/Pd and m-WO₃ NFs exhibit stable and reliable operation of EB sensing (Fig. 5e). The selectivities of the fabricated gas sensors were also investigated at 240°C by adding several interfering gases such as xylol, toluene, methanol, formaldehyde, ammonia, ethanol, and EB (Fig. 5f). The sensing performance of m-WO₃/Pd NFs toward EB was measured to be ~4 times larger than those toward other interfering gases, suggesting that m-WO₃/Pd NFs possess a superior selectivity. Moreover, the difference for the m-WO₃/Pd NFs-based sensor is larger than that for the m-WO₃ NFs-based sensor, indicating that Pd nanoparticles could greatly improve the sensitivity of m-WO₃ NFs toward EB.

More importantly, the m-WO₃/Pd NFs-based EB sensor exhibits much better comprehensive performance than previously reported EB sensors, such as low operating temperature, high sensitivity, fast response-recovery and low limit of detection (Table S1). This can be attributed to the unusual textual structures of m-WO₃/Pd

NFs. (1) The continuous fiber skeleton, where dual mesopores are patterned on both the surface and inside of the NF, is beneficial for the fast diffusion of gas molecules and quick transportation of electrons from both the inner and outer surfaces of the NFs to the bulk atmosphere. (2) The large surface area and abundant interfaces enabled by the dual mesoporous structure provide enormous active sites for the adsorption and desorption of O_2 and EB molecules. To further give an insight into the dual mesoporous structural effect, the sensing activity of a sensor based on mesoporous WO_3 NFs (synthesized without PEO-*b*-PS) toward different concentrations of EB was also measured (Fig. S14). It is clear that the responses of m- WO_3 synthesized without PEO-*b*-PS (with single mesopores) at all concentrations are smaller than that of m- WO_3 NFs, confirming the superiority of the dual mesoporous structure. (3) The fast response, ultralow detection limit and superior selectivity of the m- WO_3 /Pd NFs-based sensor can be attributed to the Pd sensitization. It is well known that the sensing activity of a metal oxide semiconductor relies on the change in the resistance when exposed to the target gas. The surface depletion model is usually proposed to explain the sensing mechanism of metal oxide-based sensors (Fig. S15) [56–58]. When the sensors are exposed to air, oxygen molecules can be chemisorbed on the surface of the m- WO_3 NFs, trapping electrons from the conduction band and forming adsorbed oxygen anions. Simultaneously, an electron depletion layer with a high resistance state is formed near the surface of the NFs. When the mesoporous WO_3 NFs-based sensors are exposed to EB gas, the target molecule can react with the oxygen anion and release free electrons back to the conduction band of the material, thus reducing the barrier thickness and electrical resistance. Clearly, the level of response is related to the adsorbed oxygen species and electron transfer rate. The incorporation of Pd nanoparticles in m- WO_3 NFs can not only help to accelerate the transmission of electrons between the molecules and solid surface [59,60], but also increase the amount of surface reactive oxygen groups (mainly O^- at 260°C) [61–63]. The O 1s spectra of the m- WO_3 and m- WO_3 /Pd (Fig. S16) reveal that the content of adsorbed oxygen O^- of m- WO_3 /Pd (13.2%) is higher than that of m- WO_3 (9.0%), which is mainly attributed to the spill-over effect of noble metal additives on metal oxide semiconductors [64,65].

CONCLUSIONS

In summary, we have developed a general method for the synthesis of 1D metal oxide NFs with dual mesoporous

structures by the oriented assembly of monomicelles in the electrospinning-generated beam stream. Owing to the easy functionalization of the monomicelles, this strategy shows high feasibility toward the preparation of various metal oxides (e.g., WO_3 , TiO_2 , ZrO_2) and their functional derivatives (e.g., WO_3 /Pd, WO_3 /PdCu). The obtained Pd-sensitized mesoporous WO_3 NFs were evaluated as an excellent EB sensor, showing excellent performances including a high sensitivity (52.5), an ultralow limit of detection (50 ppb), and a fast response (11 s) as well as an outstanding selectivity. The comprehensive performances are much better than that of most previously reported EB sensors, due to the combined effects of unique textual structure and Pd sensitization. This study paves a great way for the design and synthesis of bimodal mesoporous metal oxide NFs with diverse components and functions, which is highly promising for various applications.

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Supplementary information Supporting data are available in the online version of the paper.

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束流中的胶束定向组装制备双介孔金属氧化物纳米纤维

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摘要 利用胶束的一维(1D)定向组装来构建管状或纤维状的双介孔材料具有重要的科学意义,但仍面临巨大挑战.本文中,我们提出了一种简单、普适的合成策略,通过静电纺丝产生的束流限域有机-无机复合胶束使其沿着1D方向组装,从而构建一系列双介孔金属氧化物纳米纤维(如WO₃, WO₃/Pd, WO₃/PdCu, TiO₂和ZrO₂).这种方法主要依赖于共聚物@金属络合物复合胶束在各向异性溶液中的形成,然后通过溶剂的选择诱导使它们在束流中定向组装.以WO₃及其衍生物为例,所得WO₃纤维显示出均一的连续纤维结构,具有双介孔尺寸(~4.0和7.6 nm)和较大的比表面积(~93.1 m² g⁻¹).将钯修饰的介孔WO₃纳米纤维用于乙苯气体传感器,展现出了优异的综合传感性能,如高灵敏度(52.5)、超低浓度检测限(50 ppb)、快速的响应/恢复动力学(11/16 s)和优异的选择性,在环境快速监测方面显示了广阔的应用前景.