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Coaxial electrospinning of WO$_3$ nanotubes functionalized with bio-inspired Pd catalyst and their superior hydrogen sensing performance

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Macroporous WO$_3$ nanotubes (NTs) functionalized with nanoscale catalysts were fabricated using coaxial electrospinning combined with sacrificial templating and protein-encapsulated catalyst. The macroporous thin-walled nanotubular structures were obtained by introducing colloidal polystyrene (PS) particles to a shell solution of W precursor and poly(vinylpyrrolidone). After coaxial electrospinning with a core liquid of mineral oil and subsequent calcination, open pores with an average diameter of 173 nm were formed on the surface of WO$_3$ NTs due to decomposition of the PS colloids.

In addition, catalytic Pd nanoparticles (NPs) were synthesized using bio-inspired protein cages, i.e., apoferritin, and uniformly dispersed within the shell solution and subsequently on the WO$_3$ NTs. The resulting Pd-functionalized macroporous WO$_3$ NTs were demonstrated to be high performance hydrogen (H$_2$) sensors. In particular, Pd-functionalized macroporous WO$_3$ NTs exhibited a very high H$_2$ response (R_H2/R_air) of 17.6 at 500 ppm with short response time. Furthermore, the NTs were shown to be highly selective for H$_2$ compared to other gases such as carbon monoxide (CO), ammonia (NH$_3$), and methane (CH$_4$). The results demonstrate a new synthetic method to prepare highly porous nanotubular structure with well-dispersed nanoscale catalysts, which can provide improved microstructures for chemical sensing.

1 Introduction

Hydrogen (H$_2$) has been regarded as a next generation fuel energy considering its abundance and high heat of combustion (142 kJ/g).\(^1,2\) In addition, burning of hydrogen produces only water, without harmful by-products, enabling environmentally friendly energy generation.\(^3,4\) However, there are several potential risks to be addressed prior to commercial use, such as the wide range of flammable concentration (4–75%), low ignition energy (0.02 mJ), high diffusion coefficient (0.6 cm$^2$/s), and large flame propagation velocity.\(^5,6\) Moreover, hydrogen gas is colourless, odourless, and tasteless, which leads to difficulty in detection.\(^7\) For these reasons, a highly sensitive hydrogen detector is required for safe storage and monitoring of hydrogen leakage.\(^8\)

Semiconductor metal oxides (SMOs) have been studied promising gas sensors, considering their low cost, fast response, stability, and high reactivity toward analyte gases.\(^9\) Recently, advances in nanostructure synthetic methods have promoted the development of highly sensitive and selective gas sensors having large surface area and porosity.\(^10,11\) Among the various approaches, electrospinning is a facile and versatile method to obtain one-dimensional (1D) SMO nanostructures with large surface-to-volume ratio and high porosity, adequate for high performance hydrogen sensors.\(^12,13\) A templating route combined with electrospinning has been suggested as a powerful strategy to obtain porous nanostructures.\(^14\) For example, hollow nanotubular structures were demonstrated using electrospin polymeric composite nanofibers (NFs) by coating a thin inorganic layer, such as Al$_2$O$_3$,\(^15\) NiO,\(^16\) WO$_3$,\(^17,18\) and ZnO,\(^19\) and subsequent high-temperature calcination to decompose the inner polymeric component and crystallize the outer inorganic layer. In addition, polymeric colloids were introduced into the electrospinning solution to form pores on SMO NFs.\(^20,22\) It was shown that pore diameter and distribution on the SMO surface can be controlled by introducing different sizes of the colloid templates.

Coaxial (or two-fluid) electrospinning has been proposed as an effective method to fabricate hollow nanotubular structure that eliminates the additional synthesis processes such as coating of inorganic layer on the sacrificial templates.\(^13,23–26\) A variety of inorganic nanotubes (NTs) were obtained using coaxial electrospinning, including TiO$_2$,\(^27,28\) α-Fe$_2$O$_3$,\(^29\) and SnO$_2$\(^30\) for specific applications. However, to the best of our knowledge, coaxial electrospinning combined with sacrificial templating to synthesize macroporous SMO NTs has not yet been demonstrated. The macroporous SMO NTs are advantageous, considering that gas molecules can more
49 48 47 46 44 43 41 36 30 28 26 25 24 22 19 18 17 16 14 13 11 10 9 6 5 4 3 2

**Experimental section**

**Materials**
- Ammonium metatungstate hydrate [(NH₄)₂H₂W₁₂O₄₀·xH₂O]
- polyvinylpyrrolidone (PVP, Mₜₜ = 1,300,000 g/mol), potassium tetrachloroplatinate(II) (K₂PtCl₄), sodium borohydride (NaBH₄), heavy mineral oil, and 0.2 µm filtered apoferritin from equine spleen were purchased from Sigma-Aldrich (St. Louis, USA). Polystyrene (PS) latex microspheres with an average diameter of 200 nm dispersed at 2.5 wt% in water were purchased from Alfa Aesar (Ward Hill, USA). All chemicals were used without further purification.

**Synthesis of nanocatalyst particles encapsulated by protein cages**
- To synthesize well-dispersed and nanoscale catalyst particles, we employed bio-inspired protein cages, i.e., apoferritin, that consist of a 24-subunit protein complex that exhibits a hollow spherical structure (Fig. 1a). These protein cages can encapsulate metal ions, and the subsequent reduction process can produce protein-encapsulated metallic NPs. Firstly, 1 M NaOH solution was mixed with 0.1 M Pd precursor (K₂PdCl₄) aqueous solution to add the apoferritin solution and gently stirred at 100 rpm using a magnetic bar to penetrate Pd²⁺ ions into the inner cavity of apoferritin. After stirring for 1 h, a reducing agent of NaBH₄ (1 M) was rapidly injected into the solution to form metallic Pd NPs encapsulated by apoferritin (hereafter, apoferritin-encapsulated Pd NPs are referred as AF-Pd NPs). Finally, the prepared AF-Pd NPs were centrifuged at 12,000 rpm for 10 min to remove the remaining Pd²⁺, and subsequently re-dispersed in DI water.

**Synthesis of Pd-loaded macroporous WO₃ NTs**
- Hollow WO₃ nanotubular structure was synthesized by the coaxial electrospinning approach as illustrated in Fig. 2a. Different electrospinning solutions were emitted through the coaxial nozzle (SKU BCN-0802, Inovenso™) having different diameters, i.e., core diameter of 0.8 mm and shell diameter of 1.6 mm, with concentric configuration. Mineral oil was utilized as a core electrospinning solution due to its easy vaporization at high-temperature. For the shell solution, 0.2 g of ammonium metatungstate hydrate and 0.25 g of PVP were dissolved in 1.5 g of DI water containing 2.5 wt% PS colloids and continuously stirred at room temperature for 3 h. For catalyst functionalization, the prepared AF-Pd NPs were separately introduced into the shell electrospinning solution with the concentrations of 0.1 wt%.

The resulting solutions were electrospun at feeding rates of 10 µL/min of mineral oil for the core and 30–100 µL/min of composite solution for the shell, using syringe pumps. A constant DC voltage of 30 kV was applied between the coaxial nozzle and aluminum foil, employed as collector. The distance between the nozzle and the collector was 15 cm. The as-spun core/shell composite NFs were obtained after coaxial electrospinning (Fig. 2b). The shell layer comprised apoferritin-encapsulated catalytic NPs and W precursor/PVP composite decorated with PS colloids. For the core fluid, mineral oil was used. The as-spun core/shell composite NFs were calcined at 600 °C for 1 h in ambient air to obtain catalyst-loaded macroporous WO₃ NTs having multiple, approximately circular pores on the thin wall of NTs (Fig. 2c). Dense WO₃ NTs without PS colloid templates and pristine macroporous WO₃ NTs without catalyst functionalization were synthesized as well, for comparison.

**Characterization of H₂ sensing performances**
- All of the sensors were stabilized in air for 24 h as baseline before the measurement. The sensors were exposed to different analytes (hydrogen, carbon monoxide, ammonia, and methane) with concentrations ranging from 10 ppm to 500 ppm. Each analyte was exposed for 10 min, followed by 10 min of exposure to air to recover the initial baseline values. The resistance changes were measured using a data acquisition system (34970A, Hewlett-Packard), and the sensors were characterized by their relative response (R_rel/R_bas), where R_bas is the baseline resistance of the sensor upon exposure to air and R_rel is the resistance measured upon exposure to a particular...
analyte. The operating temperatures of the sensors were controlled to be 450 °C in a furnace tube.

3 Results and discussion

Morphological and structural evaluation

The microstructures of the protein-encapsulated catalytic Pd NPs were examined using TEM (Fig. 1b and c). It was clearly observed that well-dispersed NPs were synthesized within the protein cages. The good dispersion can be explained by electrostatic repulsion between the protein templates due to surface charge, which prevented agglomeration between the NPs. In addition, the overall size of the protein cage was 12–13 nm, whereas the inner cavity size was 7–8 nm. The inner cavity size limited the size of the nanoscale particles to diameters less than 8 nm. As confirmed by TEM analysis, the synthesized AF-Pd NPs showed average diameters of 2 nm (Fig. 1b). Moreover, the Pd NPs were found to be crystalline with the crystal planes of Pd (111), corresponding to interplanar distances of 2.26, in evidence (Fig. 1c).

The AF-Pd NPs were dispersed in the shell electrosprinning solutions for the catalytic functionalization. Core/shell composite NFs were synthesized using PS colloid templates and apoferritin-encapsulated catalytic NPs were achieved after the electrospinning (Fig. 2b). Polymeric components, mineral oil, and protein cages were decomposed during subsequent calcination of the as-spun core/shell composite NFs, while forming WO₃ NTs by oxidation of the W precursor (Fig. 2c). SEM observation revealed the rugged surface morphology of the as-spun core/shell composite NFs due to the decoration of PS colloids on the surface (Fig. 2d). Different microstructures were obtained after calcination at 600 °C, depending on the feeding rate of shell solution (fₛ) with the fixed core solution feeding rate (fₖ=10 µL/min) (Supporting Information, Fig. S1). When the shell feeding rate was slow, i.e., fₛ=30 µL/min, a perfect tubular structure was achieved (Fig. 2e). The average diameter was 173 nm (Supporting Information, Fig. S2). The decreased average pore diameter, comparing with the original diameter (i.e., 200 nm) of the PS colloid was mainly attributed to the shrinkage of the spherical PS colloids during the thermal decomposition and the migration of W precursor in the early stage of heat treatment. The microstructures of the catalytic Pd-loaded macroscopic WO₃ NTs were investigated (Fig. 2f). The surficial morphologies of the Pd-loaded macroscopic WO₃ NTs were maintained, with only minor differences when compared to the pristine macroscopic WO₃ NTs. In addition, close observation of Pd-loaded macroporous WO₃ NTs exhibited approximately circular pores on the surface (Fig. 2g). High-resolution TEM (HR-TEM) observation of Pd-loaded macroporous WO₃ NTs revealed the polycrystalline WO₃ structures with crystal planes of (020) and (202), which corresponds to inter-planar distances of 3.77 Å and 2.23 Å (Fig. 2h). Selected area electron diffraction (SAED) patterns of Pd-loaded macroporous WO₃ NTs presented WO₃(020), WO₃(112), and WO₃(202) crystal planes, with inter-planar distances of 3.77 Å, 3.12 Å, and 2.62 Å, respectively, which are partially investigated in HR-TEM analysis (in the inset of Fig. 2h). However, crystal planes and SAED pattern of Pd NPs were not clearly observed due to the low content of Pd in WO₃ NTs. To confirm the Pd component and the distribution, energy dispersive X-ray spectroscopy (EDS) analysis was carried out. The result clearly revealed uniform distribution of Pd over the WO₃ NTs (Fig. 2i). In addition, a scanning TEM image also showed the hollow structure of Pd-loaded macroporous WO₃ NTs (Fig. 2i). To further confirm the chemical state of Pd, X-ray photoelectron spectroscopy (XPS) analysis was performed (Fig. S3). Even though the intensities of Pd peaks were very weak due to the low concentration of Pd in the WO₃ NTs, high-resolution XPS peaks at the vicinity of Pd 3d are mainly originated by the oxidized state of Pd, i.e., Pd²⁺(PdO) with binding energies of 336.9 eV and 342.2 eV for 3d₃/₂ and 3d₅/₂, respectively.
Hydrogen molecule sensing characterization

To demonstrate the superior H₂ sensing performance of the Pd-loaded macroporous WO₃ NTs, gas sensing characteristics were evaluated using dense WO₃ NTs, macroporous WO₃ NTs, and Pd-loaded macroporous WO₃ NTs (Pd-WO₃ NTs) at different concentrations (Fig. 3b). The model response time characteristic of the Pd-WO₃ NTs showed remarkably high H₂ detection sensitivity compared to the dense WO₃ NTs. In addition, it should be noted that all the sensors showed longer response times at low H₂ concentration. The observation of longer response times with decreasing gas concentrations has been reported previously. The reaction is basically diffusion-limited at low H₂ concentration. Based on the theoretical study, the response time transition can be explained by a non-linear diffusion reaction model. In this study, the diffusion time (t) was estimated

\[ t = k \cdot x_{0}^{2} \cdot \frac{1}{D} \cdot \frac{1}{C_{0}} \] (1)

where, \( k \), \( x_{0} \), \( C_{0} \) and \( D \) are the reaction rate constant, film thickness, gas concentration, and diffusion coefficient, respectively. The constant \( r \) was found to be in the range of 0.3–1. In the present study, our sensor exhibited the constant \( r \) in the range of 0.7–0.8 as indicated by fitting of eqn (1) to the data in Fig. 3b. The model is based on the dependence of response time on gas concentration. Specifically, the response time is determined by a non-linear adsorption isotherm, which leads to a concentration-dependent response time.

Selectivity of H₂ detection with respect to other, potentially interfering gases such as carbon monoxide (CO), ammonia (NH₃), and methane (CH₄) at 500 ppm was investigated using Pd-WO₃ NTs (Fig. 3c). The results revealed that Pd-WO₃ NTs showed remarkably high H₂ response (\( R_{\text{air}}/R_{\text{gas}} = 16.3 \pm 1.1 \)) with minor responses (\( R_{\text{air}}/R_{\text{gas}}<1.6 \))
The effect of moisture on the H₂ sensing property was investigated using the porous WO₃ NTs and Pd-Porous WO₃ NTs in the concentration range of 5–20 ppm in air with high relative humidity (90% RH) at 450 °C (Fig. 3e). Under these conditions, the Pd-Porous WO₃ NTs exhibited a response of 1.26 at 20 ppm, which is a 20% improvement in response compared to that of pristine porous WO₃ NTs. However, dramatically decreased response characteristics were observed in both Pd-Porous WO₃ NTs and pristine porous WO₃ NTs under the high humidity conditions. A reduction in response of approximately 90% was observed for Pd-Porous WO₃ NTs at 10 ppm of H₂ in humid air (Fig. 3f). The relatively insensitive H₂ response of Pd-Porous WO₃ NTs in humid air is mainly attributed to the formation of hydroxyl groups (~OH) on the surface of WO₃ NTs. As a result, decreased baseline resistance was also observed with Pd-Porous WO₃ NTs in humid air (Fig. 3f).

### Hydrogen sensing mechanism

The mechanism responsible for the improved H₂ sensing performance of the Pd-Porous WO₃ NTs was investigated (Fig. 4). Changes in the dynamic resistance of the sensors with respect to changes in H₂ concentrations were evaluated by comparing the baseline resistances and resistance changes (Fig. 4a). All the sensors exhibited decreasing resistance when the sensors were exposed to H₂ gas. A well-known explanation for the decreasing resistance attributes the decrease to the elimination of chemisorbed oxygen species, i.e., O, O₂, and O₂⁻, by the reaction with H₂ on the surface of WO₃. When n-type WO₃ is stabilized in ambient air, oxygen species are chemisorbed on the surface of WO₃, withdrawing electrons from the conduction band to provide the baseline resistance. Then, upon exposure to H₂ gas, the resistance decreases as H₂ reacts with the chemisorbed oxygen species, thereby donating...
During the coaxial electrospinning, PS colloids were introduced to the electrospinning solution to serve as templates for macropores on the surface of the WO₃ NTs. Circular-shaped pores with an average diameter of 173 nm were achieved on the WO₃ NTs after subsequent calcination. The apoferritin protein cage is shown to be a powerful agent for distributing nanocatalyst uniformly on SMO sensing layers. The noble metallic Pd NPs were synthesized using apoferritin protein cages and thus distributed on the macroporous WO₃ NTs during coaxial electrospinning. The Pd-loaded macroporous WO₃ NTs exhibited very fast response times, which is mainly attributed to the catalytic effect of Pd. Particularly, Pd-loaded macroporous WO₃ NTs showed high sensitivity and selectivity toward H₂. Very high response (R₉₀/R₅₀) of 17.6 was achieved at 500 ppm of H₂. In addition, Pd-loaded macroporous WO₃ NTs revealed high H₂ selectivity with minor responses toward potential interfering gases such as CO, NH₃, and CH₄. This work provides a novel synthetic method using two-fluid electrospinning for macroporous WO₃ NTs with bio-inspired nanocatalyst for high performance chemical sensors.

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Notes and references
