

Catalyst-loaded porous electrospun WO₃ nanofibers using catalyst-decorated polystyrene colloid templates for detection of biomarker molecules

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Experimental details

Synthesis of catalyst-decorated polystyrene (PS) colloids: Catalyst-decorated polystyrene (PS) colloids were synthesized by layer-by-layer (LbL) assembly. 2.5 wt% of PS latex microspheres (500 nm) dispersed in deionized (DI) water were purchased from Alfa Aesar. To accomplish LbL assembly, cationic polymer of poly(diallyldimethylammonium chloride) (PDADMAC, $M_w=200\ 000$ g/mol, Aldrich) and anionic polymer of poly(styrenesulfonate) (PSS, $M_w=70\ 000$ g/mol, Aldrich) were used. The ionic polymers of 1 wt% were dissolved including 0.5 mol of NaCl in DI water, respectively. The LbL method was started with coating multilayer of PDADMAC/PSS/PDADMAC. Firstly, the PS colloid dispersed solution of 100 μ L was mixed with cationic polymer to deposit PDADMAC. Then, the solution was washed with DI water to remove excess cationic polymers by five repeated centrifugation performed at 10 000 rpm for 10 min. Next, the anionic polymer of PSS was then deposited and washed with DI water to remove excess anionic polymer with identical centrifugation condition. The cationic polymer of PDADMAC was deposited again to form PDADMAC/PSS/PDADMAC multilayer. Finally, catalytic precursors of Pd and Pt were deposited on the surface of PS colloids to obtain catalyst-decorated PS colloid templates. Pd precursor solution was prepared by dissolving 0.01 g of K_2PdCl_4 in 2 g of DI water and mixed with PS colloid dispersed solution. The excess Pd precursor was eliminated by the repeated centrifugation and washing. Catalytic Pt-decorated PS colloid templates were synthesized by the same procedures except using Pt precursor (K_2PtCl_4) with 0.018 g instead Pd precursor by dissolving in 2 g of DI water. The obtained catalyst-decorated PS colloids were used in the electrospinning to achieve catalyst-loaded porous WO_3 nanofibers.

Synthesis of dense WO₃ nanofibers (NFs): To synthesize WO₃ NFs, the composite of W precursor/poly(vinylpyrrolidone) (PVP, M_w=1 300 000 g/mol, Aldrich) solution was firstly prepared. 0.2 g of (NH₄)₆H₂W₁₂O₄₀·xH₂O 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 WO₃ NFs.

Synthesis of porous WO₃ nanofibers (NFs): Porous WO₃ NFs were achieved by using polystyrene (PS) colloid templates without catalyst decoration in electrospinning. During the preparation of electrospinning solution, 1.5 g DI water containing 2.5 wt% polystyrene (PS) latex microsphere (500 nm) was used instead of pure DI water with the same compositional ratio of (NH₄)₆H₂W₁₂O₄₀·xH₂O and PVP as prepared for dense WO₃ NFs. The electrospinning condition and the calcination temperature were maintained.

Synthesis of catalyst-loaded porous WO₃ nanofibers (NFs): To prepare catalyst-loaded porous WO₃ NFs, catalyst-decorated PS colloid templates were introduced in electrospinning solution. During the preparation of electrospinning solution, 0.375 g of DI water containing catalyst-decorated PS colloid template was used instead of pure DI water with 0.05 g of (NH₄)₆H₂W₁₂O₄₀·xH₂O and 0.0625 g of PVP. The electrospinning condition and the calcination temperature were maintained.

Sensor fabrication: The Al₂O₃ 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 μ L of ethanol solution were prepared. Then, drop coating was performed on the substrate with 5 μ L of the dispersed solution using a micropipette.

Gas sensing characterization: The gas sensing performances were evaluated using a homemade measurement setup described elsewhere.¹ All of the sensors were stabilized at a highly humid baseline air ambient (90% RH) at least for 6 h before the measurement to simulate exhaled breath. The humidity level was calibrated by a commercialized humidity sensor (605-H1, Testo Inc.). The sensors were exposed to different analyte (toluene, acetone, carbon monoxide, ethanol, hydrogen sulfide, nitrogen monoxide, pentane, and ammonia) 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_{air} is the sensor's baseline resistance upon exposure to air and R_{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).

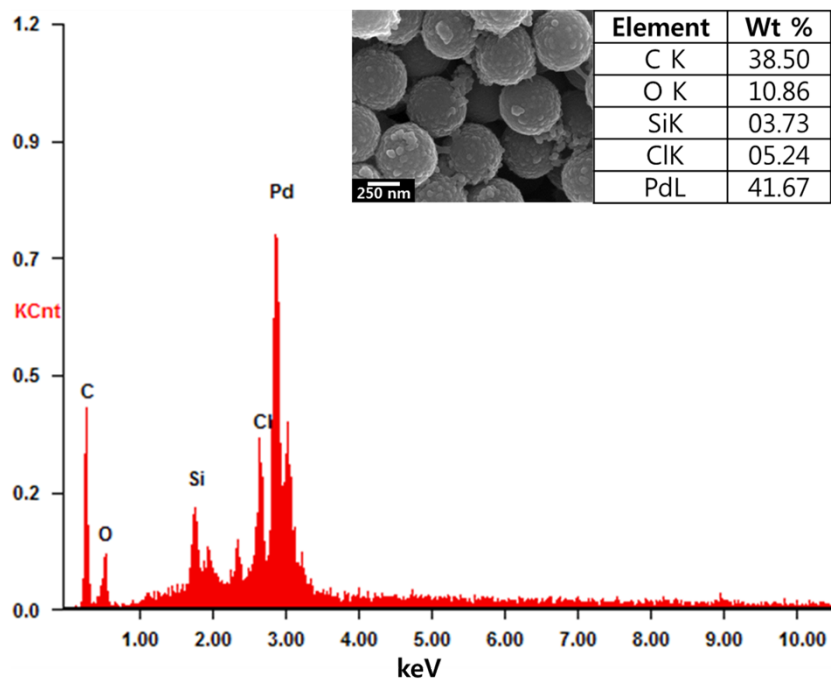


Fig. S1 Energy-dispersive X-ray spectroscopy (EDS) analysis of Pd precursor (K_2PdCl_4)-decorated PS colloid templates.

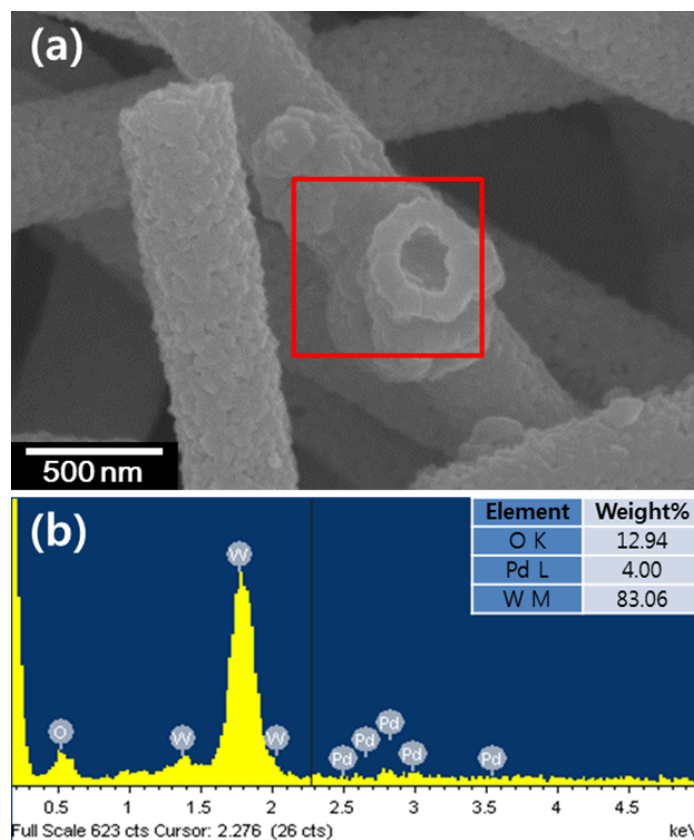


Fig. S2 (a) SEM image of Pd-loaded porous WO₃ NFs synthesized by Pd-decorated PS colloid templating route in electrospinning. (b) Energy-dispersive X-ray spectroscopy (EDS) analysis of Pd-loaded porous WO₃ NFs at pore site (red solid box).

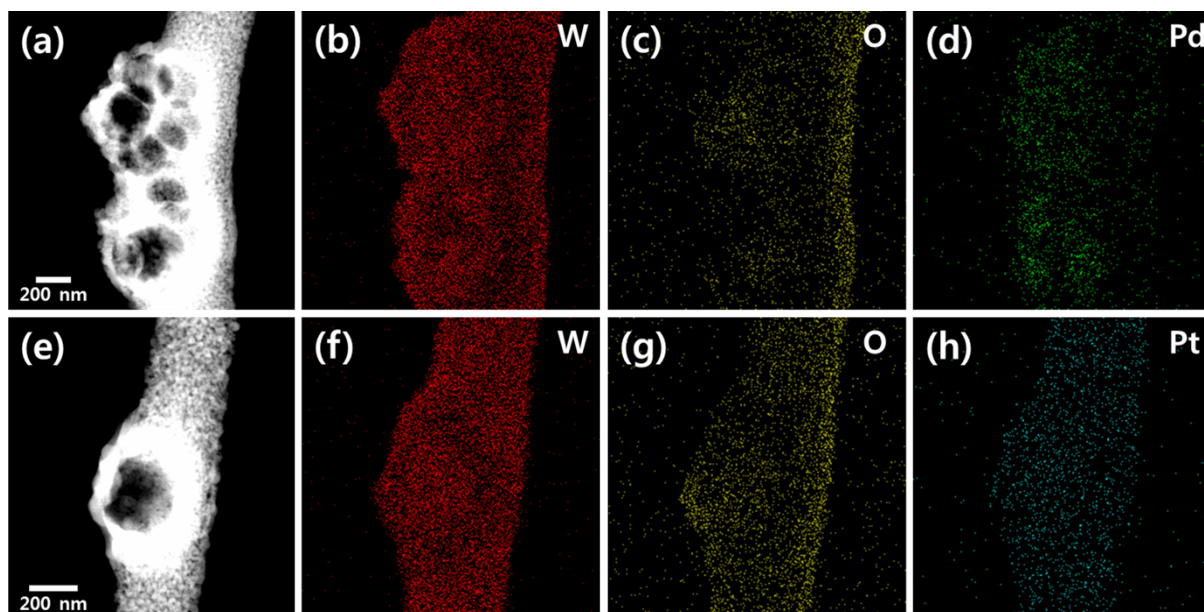


Fig. S3 Energy-dispersive X-ray spectroscopy (EDS) elemental mapping analysis of catalyst-loaded porous WO₃ NFs: (a) STEM image of Pd-loaded WO₃ NFs, elemental analysis of (b) W, (c) O, and (d) Pd. (e) STEM image of Pt-loaded WO₃ NFs, elemental analysis of (f) W, (g) O, and (h) Pt.

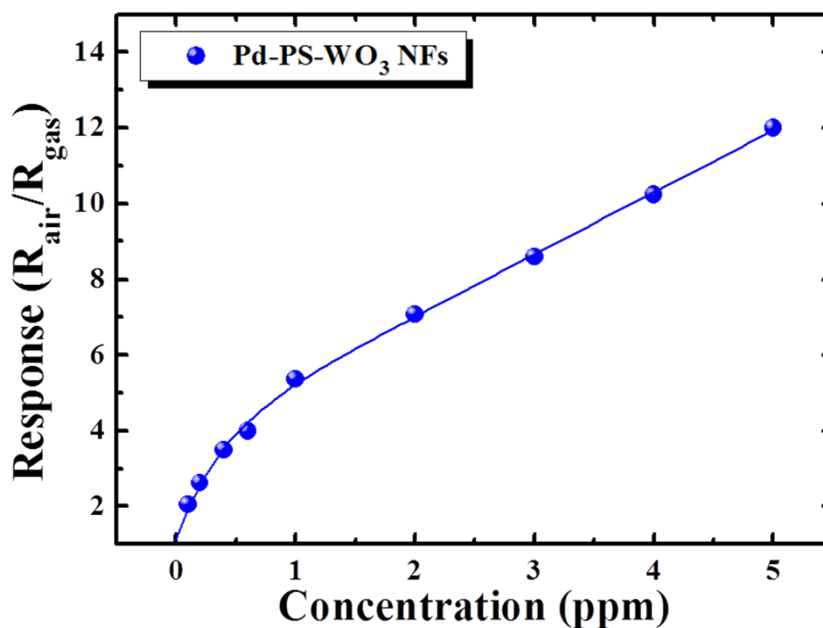


Fig. S4 Limit of detection characteristic of Pd-loaded porous WO_3 NFs toward toluene at $350\text{ }^\circ\text{C}$.

The limit of detection capability was determined by exponential plotting of measured data. Well-defined exponential plot were generated with the equation as shown below.

$$R = -2.63511 \times \exp\left(-\frac{C}{0.36417}\right) - 3.70772 \times 10^5 \times \exp\left(-\frac{C}{2.26191 \times 10^5}\right) + 3.70776 \times 10^5$$

Here, R and C represent response and concentration, respectively. The detection limit toward toluene was revealed to be 1.53 in response ($R_{\text{air}}/R_{\text{gas}}$) at 50 ppb of toluene.

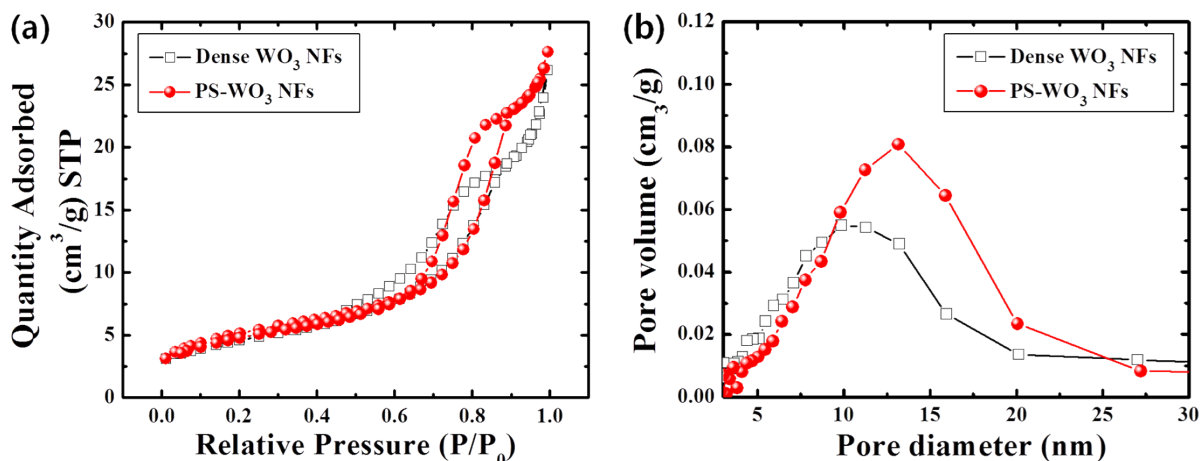


Fig. S5 (a) nitrogen adsorption and desorption isotherms and (b) average pore diameters of dense WO₃ NFs and PS WO₃ NFs.

In order to understand the improved toluene sensing performance of the PS-WO₃ NFs compared with that of the dense WO₃ NFs, the effects of the pore size and surface area were investigated through analyzing the nitrogen adsorption and desorption isotherms, Brunauer-Emmett-Teller (BET) surface areas, and average pore diameters. The nitrogen adsorption and desorption isotherms of the dense WO₃ NFs and PS-WO₃ NFs exhibited the characteristic features of Type IV isotherms with a type H3 hysteresis loop (Fig. S5a), which presents aggregated compounds of sheet-like particles that form slit-like pores.² The BET surface areas of the dense WO₃ NFs and PS-WO₃ NFs were 17.0 m²/g and 18.6 m²/g, respectively. The Barrett-Joyner-Halenda (BJH) desorption average pore diameter analyses revealed that the average pore diameters of the dense WO₃ NFs and PS-WO₃ NFs were 8.3 nm and 9.0 nm, respectively. In addition, a larger pore volume was observed in the PS-WO₃ NFs compared with that of the dense WO₃ NFs.

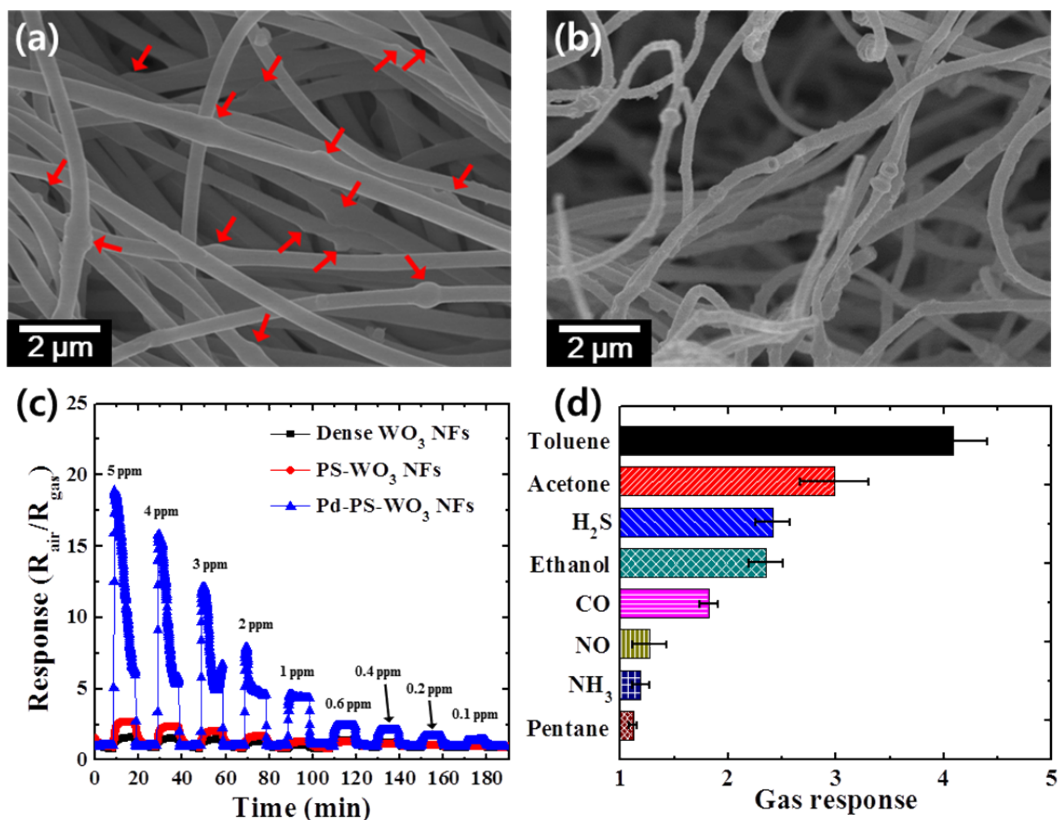


Fig. S6 (a) SEM image of as-spun Pd-decorated PS colloids embedded W precursor/PVP composite NFs and (b) Pd-loaded porous WO_3 NFs after calcination at 500 °C for 1 h in air ambient. Gas response characteristics of dense WO_3 NFs, porous WO_3 NFs (denoted as PS- WO_3 NFs), and Pd-loaded porous WO_3 NFs (denoted as Pd-PS- WO_3 NFs) at 350 °C: (c) dynamic response characteristics of the sensors toward toluene in a concentration range of 0.1 ppb–5 ppm, and (d) selective toluene response characteristic of Pd-loaded porous WO_3 NFs at the gas concentration of 1 ppm with interfering analytes.

Different content of Pd-decorated PS colloid templates can be embedded in electrospun WO_3 NFs to optimize the pore formation as well as catalytic Pd functionalization. As shown in Fig. S6a, three times higher concentration of Pd-decorated PS colloid templates (red arrows) were embedded in W precursor/PVP composite NFs. The increased open pores as well as Pd functionalization were achieved after calcination at 500 °C for 1 h (Fig. S6b). Noticeably different toluene sensing performances were observed after changing the content of Pd-decorated PS colloid templates in WO_3 NFs. Highly sensitive toluene response ($R_{air}/R_{gas} = 18.6$) were achieved at 5 ppm with detection limit of 1.4 at 100 ppb, which was mainly attributed to the catalytic effect of Pd as well as increased porosity (Fig. S6c). In addition, increased toluene selective property ($R_{air}/R_{gas} = 4.1$) was obtained with Pd-loaded porous WO_3 NFs at 1 ppm compared to the responses ($R_{air}/R_{gas} < 3$) of other interfering analytes (Fig. S6d).

Reference

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2. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniowska, *Pure Appl. Chem.* 1985, **57**, 603-619.