Highly Efficient Electronic Sensitization of Non-oxidized Graphene Flakes on Controlled Pore-loaded WO$_3$ Nanofibers for Selective Detection of H$_2$S Molecules

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Tailoring of semiconducting metal oxide nanostructures, which possess controlled pore size and concentration, is of great value to accurately detect various volatile organic compounds in exhaled breath, which act as potential biomarkers for many health conditions. In this work, we have developed a very simple and robust route for controlling both the size and distribution of spherical pores in electrospun WO$_3$ nanofibers (NFs) via a sacrificial templating route using polystyrene colloids with different diameters (200 nm and 500 nm). A tentacle-like structure with randomly distributed pores on the surface of electrospun WO$_3$ NFs were achieved, which exhibited improved surface area as well as porosity. Porous WO$_3$ NFs with enhanced surface area exhibited high gas response ($R_{\text{air}}/R_{\text{gas}} = 43.1$ at 5 ppm) towards small and light H$_2$S molecules. In contrast, porous WO$_3$ NFs with maximized pore diameter showed a high response ($R_{\text{air}}/R_{\text{gas}} = 2.8$ at 5 ppm) towards large and heavy acetone molecules. Further enhanced sensing performance ($R_{\text{air}}/R_{\text{gas}} = 65.6$ at 5 ppm H$_2$S) was achieved by functionalizing porous WO$_3$ NFs with 0.1 wt% non-oxidized graphene (NOGR) flakes by forming a Schottky barrier ($\Delta\phi = 0.11$) at the junction between the WO$_3$ NFs ($\phi = 4.56$ eV) and NOGR flakes ($\phi = 4.67$ eV), which showed high potential for the diagnosis of halitosis.

Semiconductor metal oxides (SMOs) have attracted tremendous attention as building blocks in chemical sensors due to the distinctive resistivity changing features in a certain ambient, which stimulates many researchers to develop highly sensitive and selective sensors for applications in environmental monitoring and diagnostic analysis. An extensive amount of research has been done to develop novel synthetic processes to obtain highly porous SMO nanostructures with increased surface area, thereby leading to enhanced surface reaction sites and gas transport in sensing layers. The electrospinning approach is identified as one of the most facile and versatile routes for producing one-dimensional (1D) SMOs structures with high a surface-to-volume ratio exhibiting enhanced porosity. For example, SMO nanofibers (NFs) assisted by a hot-pressing step could generate bimodal pore distribution after the thermo-compression of metal precursor/polymer composite NFs followed by calcination. Phase separation between inorganic precursors and polymers within electrospun metal precursor/polymer composite NFs, which induces open porosity, i.e., elongated pores aligned to fiber direction, in SMO NFs after the decomposition of a polymer-rich region, leading to superior sensitivity toward analytes. In addition, polymeric nanofiber as a sacrificial template combined with physical/chemical vapor deposition of thin SMOs layers, followed by high temperature calcination, produces open tubular structures due to the thermal decomposition of inner polymeric fibers. These morphologies facilitate gas penetration through open pores and also enable an enhanced surface reaction. So far, several types of sacrificial templates such as polycrylic acid (PAA), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and mineral oil have been
adopted in the electrospinning processes to prepare the porous metal, metal oxide, polymeric and carbon NF structure with the controlled pore size and density. For example, Lee et al. and Jo et al. reported polymeric polyacrylonitrile (PAN) colloids with linked pores, which were synthesized by spherical polymethyl methacrylate (PMMA) colloid templates. In addition, Tran et al. also proposed porous carbon NFs with distributed mesopores (2–4 nm) using Nafion sacrificial templates. However, most materials are based on 1D polymers and carbons, whereas electrospun SMO NFs assisted by polymeric colloidal templates have not yet been demonstrated. In particular, the creation of bimodal-pore distribution including both mesoscopic and macroscale pores with controlled size and density has hardly been studied in SMO structures.

Besides the manipulation of surface area and porosity of SMO nanostructures, catalytic sensitization on nanostructured SMOs has been identified as an effective method to improve the sensing response as well as selectivity. Typically, noble metals, which are synthesized as nanoparticles, such as Pt, Pd, and Ag, are examples of catalytic sensitizers functionalized on an SMO. More recently, SMOs functionalized with graphene-based materials have attracted a great deal of attention for the enhanced environmental hazardous monitoring and exhaled breath analysis. We have previously demonstrated the high sensitivity and selectivity of thin graphite- and graphene oxide-loaded WO3 hemitube composites toward hydrogen sulfide (H2S) and acetone (CH3COCH3), as well as reduced graphene oxide nanosheet-loaded SnO2 NF composites for potential application in diagnosis of halitosis and diabetes. Noticeably enhanced sensing performance in graphene-functionalized SMO composites were observed, which was attributed to the sensitization effect of graphene-based materials. However, most of the work was performed using chemically modified graphene or (reduced) graphene oxide for the preparation of graphene-functionalized SMO composites. In addition, gas sensing characteristics using electrospun SMO NFs functionalized with non-oxidized graphene (NOGR) flakes have not been investigated.

Here, we demonstrated for the first time, the facile manipulation of bimodal pore size and density in WO3 NFs via a spherical polystyrene (PS) colloidal templating route. In addition, remarkably improved sensing response and superior selectivity were achieved by functionalizing NOGR flakes on the controlled pore-loaded WO3 NFs. The potential use of the porous WO3 NF-NOGR composites for selective H2S detection against other interfering gases for the accurate diagnosis of halitosis is discussed.

Results

Pore Size and Pore Distribution Control in WO3 NFs. A schematic illustration for obtaining porous WO3 NFs using spherical PS colloids and the composite of NOGR-loaded porous WO3 NFs is shown in Figure 1. The nonwoven WO3 NFs can be obtained by a conventional single nozzle electrospinning of the W precursor (ammonium metatungstate hydrate)/PVP composite solution followed by high-temperature calcination. During the preparation of the electrospinning solution, insoluble PS colloids were added and dispersed homogeneously within composite electrospinning solution. After the electrospinning, the spherical PS colloids were decorated on the surface as well as embedded in the W precursor/PVP composite NFs (Figures 1a and b). The spherical PS colloids and the PVP were eliminated, and W precursor was oxidized to form WO3 NFs during the high-temperature calcination process. A distinctive morphological uniqueness indicated that the spherical pores on the surface as well as inside of the WO3 NFs were generated as a result of the decomposition of the spherical PS colloids (Figure 1c). It is advantageous that the pore size and the distribution can be controlled in WO3 NFs by using different sizes of PS colloids in the electrospinning solution, which will provide better gas-sensing performance by increasing surface area and, thus, facilitating the gas penetration path through the pores. In addition, the sensitization effect of NOGR flakes can further enhance the sensing characteristics when the porous WO3 NFs are functionalized with NOGR flakes (Figure 1d).

Microstructural and morphological observation was performed for the porous WO3 NFs synthesized by electrospinning assisted by spherical PS colloid sacrificial templates as well as for pristine WO3 NFs for comparison purposes (Figure 2). Two different sizes of spherical PS colloids having uniform diameters (i.e. average 200 nm and 500 nm) were used during the electrospinning process (Supporting Information, Figure S1). The as-spun W precursor/PVP composite NFs without PS colloid templates showed smooth surfaces (Figure 2a), whereas rough and rugged surface morphology was observed in the case of the PS colloid template assisted W precursor/PVP composite NFs with an average diameter of 1.29 ± 0.48 μm (Figures 2b and c). The spherical PS colloids with uniform size (500 nm in diameter) were well-distributed within the W precursor/PVP composite NFs (Figure 2b). In addition, two different spherical PS colloids were successfully decorated and embedded in the W precursor/PVP composite NFs (Figure 2c). After calcination in air at 500°C, polymeric components, i.e., PS colloids and PVP, were decomposed and burned out, and W precursor was crystalized into WO3 NFs. The pristine WO3 NFs showed densely packed polycrystalline microstructures exhibiting smooth surface morphology (Figure 2d) (hereafter, the pristine WO3 NFs are referred to dense WO3 NFs). However, porous WO3 NFs, obtained by spherical PS colloid templates, having diameters of 633 ± 178 nm, exhibited several pores on the surface and rugged surface morphology.

Figure 1 | Schematic illustration of synthetic process for the porous WO3 NFs: (a) Electrospinning of the spherical PS-colloid-decorated W precursor/PVP composite NFs, (b) detailed description of the spherical PS-colloid-decorated W precursor/PVP composite NFs, (c) pore size and pore distribution controlled WO3 NFs obtained after high-temperature calcination, (d) sensitizing effect of non-oxidized graphene flake functionalized porous WO3 NFs.
(Figures 2e and 2f) (hereafter, the porous WO$_3$ NFs synthesized by PS colloids having 500 nm in diameter are referred to PS (500)-WO$_3$ NFs). The PS (500)-WO$_3$ NFs exhibited a tentacle-like structure with a crater-like pore shape on the surface. A wider distribution range in pore sizes was achieved in the porous WO$_3$ NFs synthesized by the two different PS colloids (Figure 2f) (hereafter, the porous WO$_3$ NFs synthesized by two different PS colloids having diameters of 200 nm and 500 nm are referred to PS (200 & 500)-WO$_3$ NFs). To investigate the pore size and the distribution in detail, transmission electron microscopy (TEM) analysis was performed (Figures 2g-i and Figure S2 in the Supporting Information). The dense WO$_3$ NF, which was composed of closely packed small WO$_3$ grains exhibiting diameters of approximately 25 nm (Figure 2g), showed the diameter of average 767 ± 325 nm. In contrast, large spherical pores were observed with the PS (500)-WO$_3$ NFs synthesized by PS colloids having diameters of 200 nm and 500 nm are referred to PS (200 & 500)-WO$_3$ NFs (Figure 2h). In particular, larger numbers of spherical pores were interconnected with each other in the case of PS (200 & 500)-WO$_3$ NFs. It is noted that the 40–60% reduction in pore sizes were observed after calcination, compared to the original size of the PS colloids. This feature is 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. Different pore sizes could be also obtained by varying the PS colloidal sizes, i.e., 100 nm and 200 nm (Supporting Information, Figure S2). It was revealed that WO$_3$ NFs with pore sizes smaller than 50 nm were obtained by using the PS colloids having diameter of 100 nm due to the shrinkage of the PS colloids (Supporting Information, Figures S2a and b). Thus, the utilization of PS colloids with broad size distribution can lead to effective manipulation of the pore sizes. These results revealed that the pore size (from mesopore to macropore size) and the distribution in 1D metal oxide NFs can be easily controlled for a specific application by simply changing the size and the density of sacrificial colloidal templates.

To evaluate the pore generation behavior during the calcination process, thermal gravimetric analysis (TGA) was performed with the samples of W precursor/PVP composite NFs and PS colloids embedded W precursor/PVP composite NFs (denoted as W precursor/PVP/PS) (Figure 3). Similar weight loss curves were observed in both samples, which showed sharp weight loss (approximately 25% loss) in the temperature range of 220–325°C and entire decomposition of organic compounds above 550°C. To confirm the decomposition temperature of the PS colloids, differential thermal gravimetric (DTG) curves of each sample were compared. The distinctive difference was observed in the temperature range of 325–390°C (red box), in which the range was considered to be the decomposition temperatures of the PS colloids. This observation is consistent with a previous study in which the PS decomposition temperatures were in the range of 200–450°C. In the case of PVP, it was reported that the decomposition occurs in the temperature range of 350–470°C. The onset decomposition temperature (350°C) of PVP was identical with our observation but a slightly higher burnout temperature was observed (550°C) (blue box), which is ascribed to the interaction between PVP and W precursor/PS colloid in the as-spun composite NFs. It was concluded that the pores can be generated by the co-decomposition of the PS colloids and the PVP during the calcination process while transforming of W precursor into WO$_3$. In addition, the spherical pore structure was attributed to the transformation of the PS colloid domains into void domains after the removal of the spherical PS colloids. The shrunk pore size can be explained by the fact that the higher decomposition temperature of PVP is attributed to the clog-
Synthesis of Porous WO₃ NFs Functionalized by Non-oxidized Graphene Flakes. Highly conducting non-oxidized graphene (NOGR) flakes exfoliated from a graphite intercalation compound (GIC) were used to enhance the overall conduction of the WO₃ NFs, and the detailed synthesis method of the flakes was reported elsewhere (see Methods Section)³¹–³³. The porous WO₃ NF-NOGR composite was achieved by simply mixing the two solutions, i.e., the porous WO₃ NF dispersed in ethanol and the NOGR flakes dispersed in acetone.

The composite of PS (500)-WO₃ NFs with 0.1 wt% NOGR flakes were investigated by TEM (Figures 4d–f). The NOGR flakes, which were prepared with 1–6 layers, were attached to the porous WO₃ NF, as shown in Figure 4d. The magnified image of Figure 4d (red solid box) revealed that the thin layer of NOGR flakes was well-decorated on the porous WO₃ NF (Figure 4e). The physical contact by anchoring the two-dimensional structure of NOGR flakes on the porous WO₃ NFs can lead to the functionalization of several WO₃ NFs (Supporting Information, Figure S4). The characteristic SAED pattern was obtained with the composite of PS (500)-WO₃ NFs with 0.1 wt% NOGR flakes, which showed the hexagonal pattern of a crystallite graphene structure³⁴ (Figure 4f).

Microstructure and Chemical Analysis of Porous WO₃ NF-NOGR Composite. The microstructure and chemical state were investigated with the dense WO₃ NFs, PS (200&500)-WO₃ NFs, and PS (500)-WO₃ NFs functionalized with 0.1 wt% NOGR flakes. X-ray diffraction (XRD) analysis revealed that several crystal planes were identified with the three samples in which the characteristic peaks of (020), (002), (200), (012), (021), (120), (022), (202), and (202) were observed (Supporting Information, Figure S5), which were partially observed in the HRTEM analysis and SAED pattern in Figures 4b and c. The crystallographic structure of WO₃ NFs was confirmed to be monoclinic crystal (JCPDS file no. 43–1035). However, the characteristic peak of NOGR flakes could not be observed in the composite of PS (500)-WO₃ NFs functionalized with 0.1 wt% NOGR flakes, which is assumed to be the detection limit of the trace of NOGR content (0.1 wt%) using the XRD.

To confirm the chemical composition and bonding state of the PS (500)-WO₃ NFs functionalized with 0.1 wt% NOGR flakes, X-ray photoelectron spectroscopy (XPS) analysis was performed (Supporting Information, Figure S6). A survey scan of XPS spectrum confirmed the existence of three components, i.e., W, O, and C.
Figure 4 | (a) A TEM image of an extruded pore on the surface of a WO3 NF, (b) a magnified high-resolution TEM image of a crystallized WO3 NF (red dotted box in (a)), (c) selected area electron diffraction (SAED) pattern of WO3 NFs, (d) TEM image of a PS (500)-WO3 NF functionalized with a 0.1 wt% NOGR flake, (e) magnified TEM image of (d), and (f) SAED pattern of a PS (500)-WO3 NF functionalized with 0.1 wt% NOGR flakes with a TEM image of an electron beam illuminating the spot shown in the inset.

Gas-sensing Characteristics. Gas sensing characteristics were investigated with the samples of dense WO3 NFs, PS (500)-WO3 NFs, PS (200/500)-WO3 NFs, and PS(500)-WO3 NFs functionalized with 0.1 wt% NOGR flakes (referred to NOGR-loaded PS (500)-WO3 NFs) (Figure 5). The sensing performances toward hydrogen sulfide (H2S) and acetone (CH3COCH3), which are known as biomarkers in exhaled breath for the potential application in diagnosis of halitosis and diabetes, were investigated under a highly humid atmosphere (90% RH) to resemble exhaled breath. Firstly, the effects of pore size and pore distribution on the sensing performances were identified at 350 ºC with a gas concentration in the range of 1–5 ppm (Figures 5a and b). In the case of H2S sensing, PS (200/500)-WO3 NFs showed the highest response (Raif/Rgas = 43.1 at 5 ppm) compared to that of PS (200)-WO3 NFs (Raif/Rgas = 24.1 at 5 ppm), PS (500)-WO3 NFs (Raif/Rgas = 21.2 at 5 ppm) and dense WO3 NFs (Raif/Rgas = 16.4 at 5 ppm) (Figure 5a and Figure S7a in the Supporting Information). In contrast, PS (500)-WO3 NFs exhibited the highest response (Raif/Rgas = 2.8 at 5 ppm) towards acetone compared to that of dense WO3 NFs (Raif/Rgas = 2.3 at 5 ppm), PS (200/500)-WO3 NFs (Raif/Rgas = 2.0 at 5 ppm), and PS (200)-WO3 NFs (Raif/Rgas = 1.4 at 5 ppm) (Figure 5b and S7b in the Supporting Information). Secondly, the sensing performance was dramatically improved by functionalization of a small amount (0.1 wt%) of NOGR flakes. The result revealed that PS (500)-WO3 NFs functionalized with 0.1 wt% NOGR showed the highest response among the sensors toward H2S (Raif/Rgas = 65.6 at 5 ppm) and acetone (Raif/Rgas = 13.7 at 5 ppm), which are attributed to the sensitization of NOGR flakes. The sensing characteristics in the temperature range of 200–450 ºC were investigated to determine the optimum operating temperature, in which the sensors show the highest response toward H2S and acetone. It was found that the optimum sensitivity was accomplished at 300 ºC and 350 ºC for H2S and acetone, respectively (Supporting Information, Figure S8). At the limit of detection (100 ppb of H2S or acetone), the relative response (Raif/Rgas) of PS (500)-WO3 NFs functionalized with 0.1 wt% NOGR flakes is 3.9 at 300 ºC (Figure 5c) and 1.6 at 350 ºC (Supporting Information, Figure S9). The selectivity of the sensors was examined by exposing the sensor to different analytes (See Methods Section). The results showed high sensitivity to H2S (Raif/Rgas = 69.3 ± 2.5 at 5 ppm) as well as a noticeable response toward acetone (Raif/Rgas = 4.4 ± 0.6 at 5 ppm) at 300 ºC maintaining negligible responses (Raif/Rgas < 2.3) toward other interfering gases such as toluene (C6H5CH3), ethanol (C2H5OH), nitrogen monoxide (NO), ammonia (NH3), carbon monoxide (CO), and pentane (C5H12), which are known as exhaled breath components (Figure 5d).

Discussion

To understand the sensing mechanism depending on the pore size and pore distribution, the base resistance, Brunauer-Emmett-Teller (BET) surface area, and average pore diameters were measured (Figure 6). The base resistances of all the sensors were confirmed, which are closely related with the packing density of the sensing materials. Similar base resistances were observed with dense WO3 NFs (15.57 MΩ), PS (500)-WO3 NFs (10.22 MΩ), and PS (200/500)-WO3 NFs (16.31 MΩ) at an operating temperature of 350 ºC, which implies that the three sensors have similar packing densities (Figure 6a). The BET surface area and average pore diameter were measured by a surface area analyzer using N2 vapor. Although dramatic changes were not observed in the BET surface area and average pore diameter, the PS (200/500)-WO3 NFs exhibited the highest BET surface area (19.22 m²/g) while possessing the...
lowest average pore diameter (7.98 nm) among the three samples (Figure 6b). In the case of PS (500)-WO3 NFs, the highest average pore diameter was observed (8.96 nm) with a moderate BET surface area (18.60 m²/g). The dense WO3 NFs showed the lowest BET surface area (17 m²/g) with a moderate average pore diameter of 8.25 nm. It can be explained that the BET surface area was increased by the pore formation on the surface of WO3 NFs, in which a higher increase in BET surface area was achieved with the mixture of two different PS colloids (i.e., 200 nm and 500 nm in diameter) than the use of single PS colloids (i.e., 500 nm in diameter). The pore distribution analysis in a mesoscale range of 2–15 nm revealed that both PS (500)-WO3 NFs and PS (200&500)-WO3 NFs exhibited higher pore volume compared to the dense WO3 NFs (Figure 6c). The higher average pore diameter of the dense WO3 NFs than the PS (200&500)-WO3 NFs was mainly assumed to be the increased density of pores at the surface of the WO3 NFs and the formation of the dense WO3 layer around pores. However, the pore sizes created by the removal of PS colloids must be larger than 30 nm. Therefore, we investigated the macroscale (>50 nm) pore distribution in the range of 50–5000 nm using a porosimeter using Hg (Figure 6d). The result revealed that the higher pore density was observed with the PS (500)-WO3 NFs and PS (200&500)-WO3 NFs compared to the dense WO3 NFs. Similar pore diameters of 678 nm and 677 nm were measured with PS (500)-WO3 NFs and PS (200&500)-WO3 NFs, respectively, which were noticeably larger than that (433 nm) of dense PS-WO3 NFs. Macroscale pores (433 nm), formed in dense PS-WO3 NFs, are originated from voids between the WO3 NFs. In the case of PS (200&500)-WO3 NFs, linked pores, which might be formed by interconnection between pores formed by PS colloids having different diameters of 200 nm and 500 nm, can contribute to the counting of larger pore sizes. This feature can lead to comparable average pore sizes (677 nm) of PS (200&500)-WO3 NFs as compared to that (678 nm) of PS (500)-WO3 NFs by compensating the small pore sizes formed by discrete PS colloids having diameter of 200 nm. However, pore density of PS (200&500)-WO3 NFs is higher than that of the PS (500)-WO3 NFs, which is ascribed to the increase in pore density at the surface of the WO3 NFs by forming linked pores formed by PS colloids having different diameters of 200 nm and 500 nm. The gas sensing characteristics, therefore, can be interpreted to mean that the larger the BET surface, i.e., PS (200&500)-WO3 NFs, the higher the H2S sensing performance (Figure 5a), which is attributed to the fact that the small and light molecule of H2S can penetrate deep into the sensing layers, thereby enhancing the surface reaction between H2S and chemisorbed oxygen species (O2, O2, and O2–). In contrast, large and heavy molecules such as acetone cannot penetrate deep into the sensing layer, which resulted in less of a surface reaction, leading to the lowest acetone response (Figure 5b) to the PS (200&500)-WO3 NFs having relatively small pore diameter (average 7.98 nm). For this reason, the highest acetone sensing performance was achieved with the PS (500)-WO3 NFs with an increased pore diameter on the mesoscale (2–50 nm) as well as the macroscale (>50 nm) dimensions, in which the response is controlled by the acetone diffusion into the sensing layers and corresponding surface reaction. This observation is consistent with a previous report using SnO2 nanoparticle for sensing different analytes.43,44 We expect further improvement of gas response via the optimization of pore size.

Figure 5 | Gas sensing characteristics of dense WO3 NFs, PS (500)-WO3 NFs, PS (200&500)-WO3 NFs, and PS (500)-WO3 NFs functionalized with 0.1 wt% NOGR flakes in the gas concentration in the range of 1–5 ppm at 350 °C toward (a) H2S and (b) acetone. (c) Limit of detection of the PS (500)-WO3 NFs functionalized with 0.1 wt% NOGR flakes toward H2S down to 100 ppb at 300 °C. (d) Selective H2S detection characteristic of the PS (500)-WO3 NFs functionalized with 0.1 wt% NOGR flakes with respect to the interfering analytes at 300 °C.
and distribution by using PS colloids with various sizes and concentrations.

To explain the significant improvement in sensing performance of the NOGR-loaded WO₃ NFs, we measured the energy band alignment between WO₃ NFs and NOGR flakes using ultraviolet photoelectron spectroscopy (UPS) analysis (Figure 7). The UPS spectrum of PS (500)-WO₃ NFs exhibited a cut-off energy (E_{cut-off}) of 16.64 eV (Figure 7a) and a HOMO energy (E_{HOMO}) of 1.46 eV (in the inset of Figure 7a), indicating that the work function and the electron affinity of the PS (500)-WO₃ NFs are 4.56 eV and 3.22 eV, respectively. The work function of the NOGR flakes was measured using UPS as well, which showed 4.67 eV (Supporting Information, Figure S10); thus, electron transfer from the low work function of PS (500)-WO₃ NFs to the high work function of NOGR flakes can be accomplished by forming a Schottky barrier of 0.11 eV between the junction of NOGR flakes and PS (500)-WO₃ NFs (Figure 7b). Therefore, the improved sensing properties were achieved by the modulating electrons in the WO₃ NFs sensitized by NOGR flakes. The functionalization of NOGR derives the lower electron concentration at the surface of WO₃ NFs in air, which results in the large conductivity changes upon the exposure of reducing gases such as H₂S and acetone.

Nevertheless, the base resistance of the PS (500)-WO₃ NFs functionalized with 0.1 wt% NOGR at 350 °C was lower than that of single phase WO₃ NFs (Figure 6a). In addition, I–V characteristics showed lower resistance of PS (500)-WO₃ NFs functionalized by NOGR flakes as compared to PS (500)-WO₃ NFs (Supporting Information, Figure S11). This is attributed to the high electrical conductivity through the NOGR flakes, facilitating charge carrier transport. In addition to the electronic sensitization of NOGR flakes, facile surface reaction process of H₂S with chemisorbed oxygen species, i.e., H₂S (gas) + 3O⁻ (chemisorbed) → SO₂ + H₂O + 3e⁻, generates highly H₂S selective detection.

In this work, facile manipulation of pore size and pore distribution in electrospun WO₃ NFs was firstly demonstrated via a polymeric templating route using different sizes of spherical PS colloids (i.e., 200 nm and 500 nm in diameter) as sacrificial templates. During high-temperature calcination step, the co-decomposition of the polymeric components, i.e., PS colloids and PVP, results in the formation of pores by converting the polymeric domains into void domains. In addition, the microstructural and morphological evaluation indicated that different pore structures such as linked, closed, and open pores were observed due to the random distribution of PS colloids in the WO₃ NFs. The gas sensing characteristics revealed that the PS (200&500)-WO₃ NFs showed a significantly enhanced H₂S response due to the increased BET surface area by an effective surface reaction of the small and light H₂S molecules penetrating through the small pores. In contrast, PS (500)-WO₃ NFs were sensitive to acetone due to the facile penetration of the large and heavy acetone molecules through the enlarged pores. The synthesized porous WO₃ NFs obtained by PS colloid templates were further integrated with NOGR flakes for the enhanced sensing characteristics. The NOGR
PS (500)-WO₃ NFs with a magnified image in the inset, and (b) schematic illustration of the bend structure of the NOGR and the PS (500)-WO₃ NFs.

Figure 7 | (a) Ultraviolet photoelectron spectroscopy (UPS) spectrum of PS (500)-WO₃ NFs with a magnified image in the inset, and (b) schematic illustration of the bend structure of the NOGR and the PS (500)-WO₃ NFs and electron transport characteristic when the electrical junction is formed.

(0.1 wt%)-loaded PS (500)-WO₃ NFs were highly sensitive to H₂S with a detection limit of 100 ppb (R_air/R_gas = 3.9) as well as superior selectivity maintaining minor response (R_air/R_gas < 2) to interfering analytes by the electrical sensitization of NOGR. This work verified the effective pore size and pore distribution control method in SMO nanofiber structure as well as the potential use of NOGR flakes without using noble metallic catalysts, which can optimize the sensing characteristics for potential application in diagnosis of halitosis.

Methods

Materials: Ammonium metatungstate hydrate [(NH₄)₆H₂W₁₂O₄₀·xH₂O] and polyvinylpyrrolidone (PVP; M₉ = 1,300,000) were purchased from Sigma-Aldrich. The mixtures were mildly sonicated for 12 hours and subsequently stored at 4°C for 24 hours. 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 hours.

Preparation of NOGR flakes-loaded porous WO₃ NFs composite. The composite of NOGR flakes-loaded porous WO₃ NFs were obtained by mixing the two dispersed solutions of the NOGR and the WO₃ NFs. For the WO₃ NF solution, 1 mg of PS (500)-WO₃ NFs was dissolved in 100 μL of ethanol. The contents of NOGR flakes in the composite with PS (500)-WO₃ NFs were maintained to be 0.1 wt% to characterize the sensing performance.

Gas sensing characterization. The gas sensing characteristics were evaluated using a measurement setup described elsewhere. All of the sensors were stabilized at a highly humid baseline air ambient (90% RH) before the measurement to simulate exhaled breath. The sensors were exposed to different analyte (hydrogen sulfide, nitrogen monoxide, acetone, ammonia, toluene, carbon monoxide, pentane, and ethanol) 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 clean the sensors. The resistance changes were measured using a data acquisition system (34972A, Agilent) and the relative response (R_air/R_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).

1. Kim, I. D., Rothschild, A. & Tuller, H. L. Advances and new directions in gas-sensing devices. Acta Mater. 61, 974–1000 (2013).
2. Na, C. W., Woo, H. S., Kim, J. D. & Lee, J. H. Selective detection of NO₂ and C₂H₃OH using a Co₃O₄-decorated ZnO nanowire network sensor. Chem. Commun. 47, 5148–5150 (2011).
3. Peng, G. et al. Diagnosing lung cancer in exhaled breath using gold nanoparticles. Nat. Nanotechnol. 4, 669–673 (2009).
4. Yamazoe, N. Toward innovations of gas sensor technology. Sens. Actuators B 108, 2–14 (2005).
5. Lu, X. F., Wang, C. & Wei, Y. One-Dimensional Composite Nanomaterials: Synthesis by Electrospinning and Their Applications. Small 5, 2349–2370 (2009).
6. Greiner, A. & Wendorff, J. H. Electrospinning: A fascinating method for the preparation of ultrathin fibres. Angew. Chem. Int. Ed. 46, 5670–5703 (2007).
7. Kim, I. D. et al. Ultrasensitive chemiresistors based on electroposn TiO₂ nanofibers. Nano Lett. 6, 2009–2013 (2006).
8. Kim, I. D. et al. Electroposn SnO₂ nanofiber mats with thermo-compression step for gas sensing applications. J. Electroceram. 25, 159–167 (2010).
9. Shin, J. et al. Thin-Wall Asssembled SnO₂ Fibers Functionalized by Catalytic Pt Nanoparticles and their Superior Exhaled-Breath Sensing Properties for the Diagnosis of Diabetes. Adv. Funct. Mater. 23, 2357–2367 (2013).
10. Bognitzki, M. et al. Nanostructured fibers via electrospinning. Adv. Mater. 13, 70–72 (2001).
11. Choi, S. J. et al. Selective Diagnosis of Diabetes Using Pt-Functionalized WO₃ Hemitube Networks As a Sensing Layer of Acetone in Exhaled Breath. Anal. Chem. 85, 1792–1796 (2013).
12. Choi, S. H. et al. Hollow ZnO Nanofibers Fabricated Using Electroposn Polymer Templates and Their Electronic Transport Properties. ACS Nano 3, 2623–2631 (2009).
13. Horzum, N. et al. Hierarchically Structured Metal Oxide/Silica Nanofibers by Colloid Electrospinning. ACS Appl. Mater. Interfaces 4, 6338–6345 (2012).
14. Wu, H. et al. A transparent electrode based on a metal nanotrough network. Nat. Nanotechnol. 8, 421–425 (2013).
15. Li, D. & Xia, Y. N. Direct fabrication of composite and ceramic hollow nanofibers by electrospinning. Nano Lett. 4, 933–938 (2004).
16. Lee, S. et al. Preparation of macroporous carbon nanofibers with macroscopic openings in the surfaces and their applications. Nanotechnology 20, 445702 (2009).
17. Jo, E. et al. Core-Sheath Nanofibers Containing Colloidal Arrays in the Core for Programmable Multi-Agent Delivery. Adv. Mater. 21, 968–972 (2009).
18. Tadano, C. & Kaira, V. Fabrication and functionalization of porous carbon nanofibers with adjustable pore sizes as electrodes for supercapacitors. J. Power Sources 235, 289–296 (2013).
19. Yang, D. J. et al. Ultrasensitive and Highly Selective Gas Sensors Based on Electroposn SnO₂ Nanofibers Modified by Pd Loading. Adv. Funct. Mater. 20, 4258–4264 (2010).
20. Hwang, I. S. et al. Facile Control of C₂H₃OH Sensing Characteristics by Decorating Discrete Ag Nanoclusters on SnO₂ Nanowire Networks. ACS Appl. Mater. Interfaces 3, 3140–3145 (2011).
21. Zhu, Y. W. et al. Graphene and Graphene Oxide: Synthesis, Properties, and Applications. Adv. Mater. 22, 5226–5226 (2010).
23. Huang, X. et al. Graphene-Based Materials: Synthesis, Characterization, Properties, and Applications. Small 7, 1876–1902 (2011).
24. Huang, Q. W., Zeng, D. W., Li, H. Y. & Xie, C. S. Room temperature formaldehyde sensors with enhanced performance, fast response and recovery based on zinc oxide quantum dots/graphene nanocomposites. Nanoscale 4, 5651–5658 (2012).
25. Choi, S. J. et al. Fast Responding Exhaled-Breath Sensors Using WO3 Hemitubes Functionalized by Graphene-Based Electronic Sensitizers for Diagnosis of Diseases. ACS Appl. Mater. & Interfaces 6, 9061–9070 (2014).
26. Choi, S. J. et al. Selective Detection of Acetone and Hydrogen Sulfide for the Diagnosis of Diabetes and Halitosis Using SnO2 Nanofibers Functionalized with Reduced Graphene Oxide Nanosheets. ACS Appl. Mater. & Interfaces 6, 2588–2597 (2014).
27. Yuan, W. J. et al. High-Performance NO2 Sensors Based on Chemically Modified Graphene. Adv. Mater. 25, 766–771 (2013).
28. Yuan, W. J. & Shi, G. Q. Graphene-based gas sensors. J. Mater. Chem. A 1, 10078–10091 (2013).
29. Peterson, J. D., Vyzovkin, S. & Wight, C. A. Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene). Macromol. Chem. Phys. 202, 775–784 (2001).
30. Newsome, T. E. & Olesik, S. V. Electrosprinning Silica/Polyvinylpyrrolidone Composite Nanofibers. J. Appl. Polym. Sci. 131, 4096 (2014).
31. Park, K. H. et al. Exfoliation of Non-Oxidized Graphene Flakes for Scalable Conductive Film. Nano Lett. 12, 2871–2876 (2012).
32. Ryu, W. H. et al. Bifunctional Composite Catalysts Using Co3O4 Nanofibers Immobilized on Nonoxidized Graphene Nanoflakes for High-Capacity and Long-Cycle LiFePO4 Batteries. Nano Lett. 13, 4190–4197 (2013).
33. Guo, W. M. & Chen, G. H. Fabrication of Graphene/Epoxy Resin Composites with Much Enhanced Thermal Conductivity via Ball Milling Technique. J. Appl. Polym. Sci. 131, 4056 (2014).
34. Kwon, J. et al. Simple Preparation of High-Quality Graphene Films without Oxidation Using Potassium Salts. Small 7, 864–868 (2011).
35. Hernandez, Y. et al. High-yield production of graphene by liquid-phase exfoliation of graphite. Nat. Nanotechnol. 3, 563–568 (2008).
36. Wang, G. M. et al. Hydrothermal-treated WO3 nanoflakes show enhanced photostability. Energ. Environ. Sci. 5, 6180–6187 (2012).
37. Yang, D. et al. Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy. Carbon 47, 145–152 (2009).
38. Lv, R. et al. Nitrogen-doped graphene: beyond single substitution and enhanced molecular sensing. Sci. Rep. 2, 586 (2012).
39. Tangerman, A. & Winkel, E. G. Extra-oral halitosis: an overview. J. Breath Res. 4, 017003 (2010).
40. Righettoni, M. et al. Breath acetone monitoring by portable Si:WO3 gas sensors. Anal. Chim. Acta 738, 69–75 (2012).
41. Righettoni, M., Tricoli, A. & Pratsinis, S. E. Si:WO3 Sensors for Highly Selective Detection of Acetone for Easy Diagnosis of Diabetes by Breath Analysis. Anal. Chem. 82, 3581–3587 (2010).
42. Seo, M. H. et al. Shimanoe, K. Microstructure control of TiO2 nanotubular films for improved VOC sensing. Sens Actuators B 154, 251–256 (2011).
43. Kida, T. et al. Pore and Particle Size Control of Gas Sensing Films Using SnO2 Nanoparticles Synthesized by Seed-Mediated Growth: Design of Highly Sensitive Gas Sensors. J. Phys. Chem. C 117, 17574–17582 (2013).
44. Suenatsu, K. et al. Nanoparticle Cluster Gas Sensor: Controlled Clustering of SnO2 Nanoparticles for Highly Sensitive Toluene Detection. ACS Appl. Mater. & Interfaces 6, 5319–5326 (2014).
45. Russo, P. A. et al. Room-Temperature Hydrogen Sensing with Heteronanostructures Based on Reduced Graphene Oxide and Tin Oxide. Angew. Chem. Int. Edit. 51, 11053–11057 (2012).
46. Rout, C. S., Hegde, M. & Rao, C. N. R. H2S sensors based on tungsten oxide nanostructures. Sensor Actuat B 128, 488–493 (2008).
47. Choi, S. J. et al. Facile Au catalyst loading on the inner shell of hollow SnO2 spheres using Au-decorated block copolymer sphere templates and their selective H2S sensing characteristics. Nanoscale 6, 11898–11903 (2014).

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Author contributions
S.J.C. and S.J.K. prepared the pore-loaded WO3 nanofibers using an electrospinning method. C.C. prepared the non-oxidized graphene (NOGR) flakes and analyzed their work function. S.J.C. and H.J.C. characterized the gas sensing properties of WO3 nanofiber-NOGR composite layers. M.H. and S.J.C. provided helpful advice during this research work. S.J.C. and I.D.K. analyzed the data and wrote the manuscript. I.D.K. generated the idea and designed the experiments. All authors reviewed the manuscript.

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