Noble Metal Nanoparticles Decorated Metal Oxide Semiconducting Nanowire Arrays Interwoven into 3D Mesoporous Superstructures for Low-Temperature Gas Sensing

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ABSTRACT: Mesoporous materials have been extensively studied for various applications due to their high specific surface areas and well-interconnected uniform nanopores. Great attention has been paid to synthesizing stable functional mesoporous metal oxides for catalysis, energy storage and conversion, chemical sensing, and so forth. Heteroatom doping and surface modification of metal oxides are typical routes to improve their performance. However, it still remains challenging to directly and conveniently synthesize mesoporous metal oxides with both a specific functionalized surface and heteroatom-doped framework. Here, we report a one-step multicomponent coassembly to synthesize Pt nanoparticle-decorated Si-doped WO3 nanowires interwoven into 3D mesoporous superstructures (Pt/Si-WO3 NWIMSs) by using amphiphilic poly(ethylene oxide)-block-polystyrene (PEO-b-PS), Keggin polyoxometalates (H₄SiW₁₂O₄₀) and hydrophobic (1,5-cyclooctadiene)dimethylplatinum(II) as the as structure-directing agent, tungsten precursor and platinum source, respectively. The Pt/Si-WO₃ NWIMSs exhibit a unique mesoporous structure consisting of 3D interwoven Si-doped WO₃ nanowires with surfaces homogeneously decorated by Pt nanoparticles. Because of the highly porous structure, excellent transport of carriers in nanowires, and rich WO₃/Pt active interfaces, the semiconductor gas sensors based on Pt/Si-WO₃ NWIMSs show excellent sensing properties toward ethanol at low temperature (100 °C) with high sensitivity (S = 93 vs 50 ppm), low detection limit (0.5 ppm), fast response−recovery speed (17−7 s), excellent selectivity, and long-term stability.

INTRODUCTION

With the development of the Internet of things (IoTs), various sensors have been widely applied in many fields including industrial production, environmental monitoring, intelligent medicine, aerospace, national defense security, and space exploration. As an important kind of chemical sensor, semiconductor gas sensors based on crystalline metal oxide semiconductors (ZnO, SnO₂, WO₃, etc.) possess advantages of long-term stability, high sensitivity, ease of miniaturization, low cost, and low detection limits. The gas sensing process of semiconductor metal oxides usually involves a series of gas−solid interface interactions including the diffusion, adsorption/desorption, and catalytic reaction of gas molecules over the sensitive layers containing metal oxides, accompanying the electron transfer between gas molecules and metal oxide layers. Therefore, it is highly desired to develop sensing materials with high specific surface area, large porosity, rich active sites, and good conductivity of carriers. With these features, the sensing materials can provide rich active sites, improved diffusion, and transport of gas molecules, and thus, the interfacial reaction between target gas and sensitive materials can be dramatically enhanced, which can improve the sensitivity and lower the detection limit. Modifying metal oxides with noble metals (Au, Pt, Pd, etc.) helps to reduce the reaction barrier to enhance the catalytic activity and reaction rate of gas molecules over the metal oxide/metal interfaces, thus lowering working temperature and power consumption. Additionally, increasing attention has recently been paid to improving the selectivity of metal oxides toward specific gas molecules via various strategies, including doping metal oxides with heteroatoms (e.g., Si, N, P, S) to tune the concentration of surface adsorbed oxygen species (O⁻, O₂⁻), adjusting the polarity of the framework, and constructing multicomponent metal oxide-based sensing layers with heterophases or heterojunctions. Mesoporous metal oxides have uniform accessible nanochannels (2−50 nm), high specific surface area, large pore...
volume, and tunable chemical compositions and surface properties, which are favorable to the adsorption, diffusion, and transport of gas molecules to achieve high sensitivity, low detection limit, and fast response—recovery speed during the gas sensing process. However, limited by the classical soft-template method strongly relying on coassembly of small molecule surfactant and molecular inorganic precursors, conventional methods lead to polycrystalline metal oxide mesoporous materials with limited pore structures and monotonous chemical compositions, which is not favorable for further improving their application performances. More recently, great efforts have been devoted to enhancing the crystallization degree of mesoporous semiconductor metal oxides while maintaining their highly porous structure by using 1D nanowires as the building blocks due to their good mechanical properties and direct electronic pathways. However, the disordered stacking of nanowires by conventional methods can reduce their exposed active sites and limit their performances. Although different methods such as the Langmuir—Blodgett (LB) technique and nanotransfer printing have been applied to construct 3D nanostructures assembled from 1D nanowires, they required tedious multistep process and failed to produce metal oxide-based 3D mesoporous nanostructures. In the previous work, our group reported an interesting synthetic 3D mesoporous nanostructure consisting of multilayer cross-stacked nanowire arrays of Si-doped WO3 through the coassembly of amphiphilic block copolymers (BCPs) and silicotungstic acid. Different from a typical surfactant-directed sol–gel process in conventional synthesis, the current synthesis involves an unusual self-assembly of organic—inorganic hybrid micelles, resulting in novel topological mesoporous structures, namely, 3D orthogonally cross-stacked nanowire arrays. Furthermore, it allows for in situ doping of metal oxides with various heteroatoms such as Si and P, and it results in abundant lattice defects and surface adsorbed oxygen, which is beneficial to improving catalytic and sensing performances. This novel mesoporous material showed superior sensing performance toward acetone at 300 °C due to the highly open network of crossed nanowires that facilitates the diffusion of gas molecules and charge transport. Surface modification of metal oxides with noble metal nanoparticles (Au, Pt, Pd, etc.) is an effective method to enhance sensitivity and decrease the working temperature of the gas sensor, so as to reduce the power consumption via chemical and electronical sensitization. Based on the above consideration, design and fabrication of noble nanoparticle-decorated mesoporous materials constructed from metal oxide nanowires is a promising approach to develop high-performance gas sensors which are extremely desired for various miniaturized electronic devices.

In this study, a facile and controllable multicomponent coassembly method was developed to synthesize Pt nanoparticle (NP)-decorated Si-doped WO3 nanowire arrays interwoven into mesoporous superstructures (Pt/Si-WO3 NWIMSs). The synthesis was conveniently accomplished by the coassembly of amphiphilic diblock copolymer poly-(ethylene oxide)-b-poly(styrene) (PEO-b-PS, the structure-directing agent), Keggin-type polyoxometalate (POM) silicotungstic acid (H3SiW12O40), and (1,5-cyclooctadiene) dimethylplatinum(II) (Pt(cod)(Me)2) into cylindrical composite micelles and their 3D cross-packing into ordered mesostructure. Step 2: thermal treatments at 500 °C in N2 and 350 °C in air to convert the mesostructured composite into Pt/Si-WO3 NWIMSs.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of the Pt/Si-WO3 NWIMSs.** The synthesis of Pt NPs decorated Si-doped WO3 nanowire interwoven into 3D mesoporous superstructures (Pt/Si-WO3 NWIMSs) was achieved by multicomponent coassembly processes (Figure 1). First, the amphiphilic PEO-b-PS copolymers could interact with silicotungstic acid (H3SiW12O40) directly in a THF solution, forming uniform spherical micelles with a hydrophobic PS block core and a hydrophilic PEO/H3SiW12O40 shell via the electrostatic attraction (S’I) between the protonated PEO (PEO-H+) and the polyanions (SiW12O40–). This S’I interaction further increased the hydrophilicity difference between the PS and PEO segments, and the organic platinum source (1,5-cyclooctadiene) dimethylplatinum(II) (Pt(cod)(Me)2) was preferentially allocated in the PS block due to the hydrophobic–hydrophilic interactions. When the PEO-b-PS/H3SiW12O40/Pt(cod)(Me)2 hybrid colloidal solution was cast on the PS and PEO segments, and the organic platinum source (1,5-cyclooctadiene) dimethylplatinum(II) (Pt(cod)(Me)2) hybrid colloidal solution was cast on the hydrophilic substrate (silicon or glass) to evaporate THF, the uniform spherical micelles gradually self-assembled and fused into cylindrical micelles of about 20.0 nm in diameter (Figure 2a), which further orthogonally and closely stacked into three-dimensionally ordered mesostructure in a layer-by-layer manner (Figure 2b). The cylindrical composite micelles were arranged in parallel within each layer but crossed between adjacent layers. The orthogonal arrangement of cylindrical micelles helped to widen the distance between the micelles and reduced the electrostatic repulsion force, and therefore, a unique 3D crossed structure was formed during THF evaporation, by the strong electrostatic repulsion between cylindrical micelles with negatively charged surfaces. In the next step of thermal treatment of the mesostructured nanocomposite, the organic structure-directing agent PEO-b-
PS was decomposed; meanwhile, H₄SiW₁₂O₄₀ could be in situ decomposed into Si-doped WO₃, and Pt(cod)(Me)₂ was pyrolyzed and reduced into Pt nanoparticles. During the calcination treatment, the aggregated H₄SiW₁₂O₄₀ clusters tended to migrate to the voids of neighboring cylindrical micelles in the same layer and were further in situ transformed into nanowires via an Ostwald ripening-like process (Figure S1), leaving behind a uniform gap between nanowires in the same layer. Such a structure transformation leads to the formation of multilayer crossed tungsten oxide nanowire arrays decorated with uniform Pt NPs. Compared to conventional synthesis of porous metal oxides with a mesostructure using metal salts (e.g., metal chlorides) as inorganic precursors, this multicomponent coassembly method is convenient and tolerant to synthesis conditions (e.g., humidity), which is very beneficial to fabricating noble metal NP-functionalized mesoporous metal oxide semiconductor materials.

Field-emission scanning electronic microscopy (FESEM) characterization showed that the obtained Pt/Si-WO₃ NWIMSSs (containing 1 wt % Pt; see Experimental Section) possessed well-defined 3D ordered mesoporous nanostructure consisting of orthogonally cross-stacked nanowires over a large area (Figure 2c), and the nanowires had a mean diameter of about 15 nm. Due to the uniform gap of about 20 nm between the interwoven nanowires, the Pt/Si-WO₃ NWIMSSs exhibited uniform mesopores of about 28 nm in the orthogonally stacked structure, and tiny Pt NPs homogeneously decorating the nanowires could be clearly observed in the surface of nanowires from the FESEM images (Figures 2d,e, and S2–3). Transmission electron microscopy (TEM) observation revealed a woodpile-like mesoporous structure of the Pt/Si-WO₃ NWIMSSs, and the nanowires were “welded” at the crossing point, indicative of stable mesostructure (Figure 2f). Moreover, the nanowires showed a well-crystallized framework with a polycrystalline feature as revealed by the spotty rings of the selected area electron diffraction (SAED) patterns (Figure 2f, inset), and the Pt NPs with a mean size of about 2.8 nm (counted from 30 particles) were homogeneously distributed on the surface of the crystalline WO₃ nanowires (Figure 2g and the inset). TEM image with high magnification clearly showed the lattice fringes of Pt (0.224 nm) and WO₃ (0.387 nm), which could be ascribed to the (111) lattice plane of Pt and (001) lattice plane of orthorhombic WO₃ (JCPDS. 20-1324), respectively (Figure 2h). As indicated in our previous work, during thermal treatment of the closely packed organic–inorganic hybrid cylindrical micelles, the PEO-b-PS gradually decomposed and the silicotungstic acid migrated to the one-dimensional voids of the neighboring cylindrical micelles where the tungsten precursor was in situ converted into tungsten oxide nanowires. Moreover, accompanying the formation of tungsten oxide nanowires, the Pt precursor initially incorporated in the organic phase (i.e., the core of micelles) via hydrophobic–hydrophobic interaction was released during thermal treatment and in situ decomposed into Pt NPs around the WO₃ phase. The resultant Pt NPs were uniformly distributed on the surface of WO₃ nanowires. The
fully exposed noble metal–metal oxide interfaces provided a large number of reactive sites, making them ideal candidates for applications such as heterogeneous catalysis and gas sensing. The energy-dispersive spectrometric (EDS) analysis showed that the Si, W, O, and Pt elements were homogeneously distributed throughout the Pt/Si-WO₃ NWIMSs (Figures 2i and S5–6), indicating that the tungsten oxide nanowires were uniformly doped by Si and modified by Pt NPs on the surface.

Following the multicomponent coassembly method, a series of Pt/Si-WO₃ NWIMSs samples with different Pt contents (0, 0.2, 0.5, 1.0, 2.0, and 4.0 wt %) could be synthesized (Figures S7–11). Without the addition of Pt source, the obtained materials possess a 3D mesoporous framework similarly to the typical Pt/Si-WO₃ NWIMSs (Figure S7a), where uniform tungsten oxide nanowires were interwoven into a 3D woodpile-like porous structure. This nondecorated 3D Si-WO₃ nanowire interwoven mesostructure has a relatively smooth surface as compared to Pt/Si-WO₃ NWIMSs. All the samples have similar Pt NP decorated 3D mesoporous structures with multilayers made of orthogonally cross-stacked nanowire arrays. With the increase of content of Pt(cod)(Me)₂ in the initial precursor solution, Pt NPs decorating the interwoven WO₃ nanowires could be seen more clearly under SEM (Figure S7a–f) and the size becomes larger from 1.5 to 5.2 nm, as shown in the TEM characterizations (Figure S8). For all these samples, their mesoscopic structures remain similar, indicating that the addition of small amounts of hydrophobic Pt(cod)(Me)₂ has little interference on the BCPs-POMs assembly process. The small-angle X-ray scattering (SAXS) patterns of the typical 1 wt % Pt/Si-WO₃ NWIMSs sample and the resultant Pt/Si-WO₃ NWIMSs samples (Figure S7g and Figure 3b) showed three scattering peaks at 0.025, 0.052, and 0.083 Å⁻¹ \((q_1;q_2;q_3 \approx 1:2:3)\), corresponding to the crystal face of 100, 200, and 300, respectively, indicating a quasi-lamellar structure with a \(d\) value of 25.1 nm \((d = 2\pi/q = 25.1)\). The powder X-ray diffraction (PXRD) pattern of Pt/Si-WO₃ shows diffraction peaks at 23.6°, 33.5°, 41.3°, 48.2°, 54.3°, and 60.0° (Figure 3a), corresponding to the orthorhombic tungsten oxide JCPDS 20-1324. These results suggest a highly crystallized framework of Pt/Si-WO₃. The intensities of the diffraction peaks become weaker as the Pt loading content increases (Figure S7h), probably due to the increasing amount of lattice defects caused by Pt²⁺ doping. This could be further confirmed by X-ray photoelectron spectroscopy (XPS) analysis of the 1 wt % Pt/Si-WO₃ sample (Figure 3i), in which both Pt²⁺ and Pt⁰ species could be observed in the Pt 4f peak profile. The Raman spectra (Figures S7i and 3c) show that the intensities of scattering peaks of the 0.2 wt % Pt/Si-WO₃ NWIMSs were much weaker than the undecorated Si-WO₃ sample, further confirming the effect of Pt²⁺ doping. Compared to the unloaded Si-WO₃ sample, the scattering peaks of 1 wt %
Pt/Si-WO3, moved from 267, 682, and 799 cm⁻¹ to 288, 685, and 799 cm⁻¹, respectively, due to the doping of Pt²⁺ and Pt⁴⁺ species. Interestingly, among the Pt/Si-WO3 samples, the Raman scattering signals first become stronger and then weaker with the Pt content increasing from 0.2 to 4.0 wt %, and reach the maximum at 1.0 wt %. This phenomenon may be caused by surface enhanced Raman scattering (SERS) effect of the uniform Pt NPs decorating the 3D frameworks.²⁴,²⁵ The Pt nanoparticles are too small and dispersive at low content, while they grow larger and aggregating at high content and exhibit the optimum SERS effect at content of 1.0 wt % with suitable particle size and dispersion.

The XPS spectra of 1 wt % Pt/Si-WO3 NWIMSs sample show the core level peak regions of O 1s, W 4f, Si 2p, and Pt 4f (Figure 3f–i). The peak-differentiation-imitating analysis of the O 1 s peak indicates the presence of large amount (20.4%) of adsorbed oxygen species (O⁺, O₂⁺) due to the formation of numerous oxygen vacancies by the Si and Pt doping in the crystal lattice of WO3.⁴⁵,⁵⁶−⁵⁸ The splitting of the Pt 4f peak reveals that, except for zero-valence Pt (43.5%), there are large amounts of Pt⁵⁺ (19.8%) and Pt⁶⁺ (36.7%) species formed by the one-step synthesis method, allowing for in situ doping Pt atoms in the crystal lattice of WO3. Meanwhile, some of metallic Pt species on the surface of the Si-WO3 nanowires might be oxidized into PtO₂ after calcination in air.³⁹,⁶⁰ The sensing materials with rich surface-adsorbed oxygen species were favorable for oxidation reactions of reducing gas molecules, thus improving the catalytic efficiency and the sensing response. The W 4f peak revealed the existence of a high content of W⁵⁺ species (30.6%), which was higher than that of the undecorated Si-WO3 NWIMSs (24.5%) (Figure S12). The above results further confirmed the existence and the doping effect of Pt⁵⁺ and Pt⁶⁺.

Nitrogen adsorption−desorption isotherms of 1 wt % Pt/Si-WO3 NWIMSs exhibit an open IV curve with an H3-type hysteresis loop, indicating an open porous structure (Figure 3d). The pore size distribution derived from the adsorption branch using the Barrett−Joyner−Halenda (BJH) method shows that the Pt/Si-WO3 NWIMSs have mesopores of about 27.8 nm (Figure 3e) formed by the multilayered cross-packaging of nanowires. This pore size is close to the theoretical length \((D = 28.3 \text{ nm})\) of a diagonal line in the four crossed neighboring nanowires calculated by the equation \(D = \sqrt{2} \times \text{spacing} \sim (20.0 \text{ nm})\), where the spacing value is estimated from the SEM image (Figure 2c). The Brunauer−Emmett−Teller (BET) surface area and pore volume are 46.8 m²/g and 0.085 cm³/g, respectively, which are noticeably high for metal oxides considering the high density of tungsten oxide (7.16 g/cm³). Comparatively, the nondecorated 3D Si-WO3 nanowire interwoven mesostructure (Figure S7a) has a pore size of 28.4 nm and lower BET surface area of 40.6 m²/g, indicating that the introduction of an organic noble metal precursor in the coassembly process has little influence on the porous structure.

It is worth noting that the choice of hydrophobic platinum source is very important to the formation of Pt/Si-WO3 NWIMSs with well-defined mesoporous structure and highly dispersive Pt nanoparticles (Figure 4). When hydrophilic chloroplatinic acid \((H_2PtCl_6\cdot6H_2O)\) was used, the material obtained via the same multicomponent coassembly was found to consist of aggregated Pt nanoparticles and disordered Si-WO3 nanowires (Figure S13a). It indicates a macroscopic phase separation between the Pt and WO3, possibly due to the electrostatic repulsion between PtCl₆⁻ and SiW₁₂O₄₀⁻ species. On the contrary, other hydrophobic and electrically neutral source, such as \(Pt(cod)(Me)₂\), could interact with PS segment via hydrophobic−hydrophobic interactions without interference within the inorganic−organic coassembly, resulting in an ordered mesostructure of Si-WO3 NWs with highly dispersed Pt NPs (Figure S13c). The above results further confirm that such a multicomponent coassembly is a reliable and reproducible approach to generally synthesize functional mesostructured metal oxide nanowire materials.

**Generality of the Coassembly Strategy.** Polyoxometalates (POMs) are a class of metal−oxygen clusters with subnanometer size (0.5−6 nm), rich chemical compositions, diverse topological structures, and abundant surface charges.⁴¹−⁶⁵ Coassembly of block copolymers and polyoxometalates is a promising strategy to construct transition metal oxides with unconventional architectures, porous nanostruc-
tures, and diverse chemical compositions. Thus, following the same synthesis process, a variety of noble metal nanoparticle-decorated heteroatom-doped metal oxide nanowires interwoven into 3D mesoporous superstructures, such as silicon-doped molybdenum oxide (Si-MoO₃), phosphorous-doped molybdenum oxide (P-MoO₃), and phosphorous-doped tungsten oxide (P-WO₃), decorated with Pt NPs could be readily synthesized through this one-step multicomponent coassembly method, by using different kinds of Keggin-type polyoxometalates such as silicomolybdic acid (H₄SiMo₁₂O₄₀), phosphomolybdic acid (H₃PMo₁₂O₄₀), and phosphotungstic acid (H₃PW₁₂O₄₀) as inorganic precursors, respectively. SEM (Figure 5) and XRD characterizations (Figure S14) show that all the obtained materials possess mesoporous structure made of 3D cross-stacked nanowires and uniform element distributions, and the nanowires were homogeneously doped by corresponding nonmetallic atom (Si, P). As a result, all the obtained heteroatom-doped metal oxide nanowire-based mesostructures with highly dispersed metal NPs possess high specific surface area, highly crystallized semiconducting framework, and abundant oxygen vacancies generated by heteroatom doping, as well as rich noble metal−metal oxide catalytic interfaces. Such outstanding features are favorable for the adsorption of guest molecules and the rapid transfer of electrons in various application fields such as heterogeneous catalysis, energy storage and conversion, and low-temperature gas sensing.

**Gas Sensing Performance of the Pt/Si-WO₃ NWIMSs.** Considering the aforementioned advantages of the Pt NP-decorated heteroatom-doped metal oxide nanowire interwoven into mesoporous superstructures, side-heated gas sensors were fabricated using the Pt/Si-WO₃ NWIMSs as the sensitive materials to evaluate their gas sensing performances (Figure 6a and S15). As a typical n-type semiconductor, the electrons behave as carriers in WO₃. The oxygen molecules adsorbed on tungsten oxide could be activated to O₂⁻ species, such as O₂⁻ and O³⁻, by extracting electrons from the electron conduction layer (ECL) of WO₃, and it causes an increase of resistance due to the formation of an electron depletion layer (EDL) in the surface region of WO₃. When the sensor is exposed to...
reducing gases such as ethanol, ethanol molecules are oxidized by the adsorbed oxygen species and release the trapped electrons back to the electron conduction layer. As a result, a decreased resistance of sensing signal is output by the sensor (Figure S16). Usually, the sensing activity is strongly affected by working temperatures, and the sensing response first rises and then goes down with the rise of the temperature for most semiconducting materials. This phenomenon is mainly attributed to the competition between the increase of surface reaction rates and the decrease in the number of active sites for the adsorption of gas molecules at high temperatures. First, in order to obtain the optimal working temperature, the sensors based on Si-WO3 NWIMSs with different Pt content (0−4 wt %) were tested toward 50 ppm ethanol at temperatures in the range of 50−350 °C (Figure 6b). For the undecorated Si-WO3 NWIMSs sample, the sensing response first rises and then goes down with the rise of the working temperature, reaching its maximum (S = 21) at 250 °C. Meanwhile, the sensing responses for all Pt/Si-WO3 NWIMSs samples show similar trends, and their sensitivity reaches a respective maximum value at 100 °C, and the 1 wt % Pt/Si-WO3 NWIMSs showed the highest sensing response (S = 93). Thus, the working temperature was selected as 100 °C for subsequent tests (Figure 6c). The sensing performance degrades at higher Pt loading due to the aggregation and growth of Pt nanoparticles and the reduction of catalytic active sites. Then, the sensors were tested with increase of the concentration of ethanol from 0.5 to 500 ppm, and the response of 1 wt % Pt/Si-WO3 NWIMSs increased from 1.8 to 611. The high sensitivity to ethanol could be partially attributed to high concentration of adsorbed oxygen species (O−, O2−) on the surface of WO3, which is beneficial for oxidizing reactions with reducing gases like ethanol, thus enabling more electronic transfer and high sensing response. The adsorbed oxygen species is related to high concentration of lattice oxygen vacancies in WO3, which originated from codoping of Si and Pt2+ in crystal lattice of WO3. Figures 6e and S17 show the dynamic response−recovery curves with the increase of concentration; the response of Pt/Si-WO3 sample was much higher than undecorated Si-WO3. For example, the sensor response to 50 ppm ethanol was 93 and 4.8 for 1 wt % Pt/Si-WO3 and Si-WO3 NWIMSs, respectively, due to the catalytic activations of Pt NPs at low temperatures. For a gas sensor, the cycling stability is also essential, the sensor was tested toward 50 ppm ethanol for 11 cycles, and the response−recovery curves and sensing responses were both well retained (Figures 6h and S18). The response and recovery time was 17 and 7 s, respectively to 50 ppm ethanol (Figure 6f), indicating a fast adsorption−desorption dynamics of ethanol molecules on the surface of tungsten oxides, owing to the highly open and 

**Figure 6.** (a) Optical image and schematic illustration of the gas sensor device. (b) Diagram of the interaction between ethanol molecules and Pt nanoparticles decorated tungsten oxide nanowires. (c) Responses to 50 ppm ethanol at different work temperatures and (d) responses to ethanol of different concentration (0.5−500 ppm) at 100 °C of Pt/Si-WO3 NWIMSs with different Pt content (wt %). (e) Dynamic response−recovery curves at different concentration (0.5−500 ppm) at 100 °C. (f) Response−recovery times to 50 ppm ethanol. (g) Responses to different gases of 50 ppm. (h) Cycle performances to 50 ppm ethanol. (i) Long-term stability of the gas sensor.
accessible mesoporous nanostructure made of 3D cross stacking of WO$_3$ nanowires and uniformly dispersed Pt NPs. In addition, to investigate the selectivity of the sensor, the 1 wt% Pt/Si-WO$_3$ NWIMSs based sensor was tested toward ten kinds of interfering gases of 50 ppm at 100 °C, including volatile organic compounds (VOCs), flammable gases, and toxic gases (Figure 6g). The responses to these gases were much lower than ethanol, and the sensing response to ethanol was at least six times that of other gases. More specifically, the response ($R_{\text{air}}/R_{\text{gas}}$) was 2.7, 12, 14, 11, 5.5, 2.3, 7.6, 2.1, 1.1, and 2.8 to acetone, formaldehyde, toluene, methanol, benzene, nitrogen dioxide, carbon monoxide, nitric oxide, methane, and hydrogen, respectively, indicating an outstanding selectivity to ethanol of the Pt/Si-WO$_3$ NWIMSs based sensor.

The long-term stability of the sensor was also studied by testing its performance every week (Figure 6i). The results showed that the sensor was stable, and even after 5 weeks, the gas response ($R_{\text{air}}/R_{\text{gas}}$) to 50 ppm of ethanol was still maintained at around 90. In addition, the humidity resistance of the sensor is crucial in terms of detection of human breath. The sensing transients upon 50 ppm of ethanol under different humidity conditions (RH 25%, RH 32%, RH 48%, RH 75%, and RH 97% at 25 °C) were measured (Figure S19). Although the sensor showed the decrease of sensing response with increasing humidity, the sensing response remained substantial ($R_{\text{air}}/R_{\text{gas}} = 62.6$) even in high humidity atmosphere (RH 84%). These results demonstrated that the Pt/S-WO$_3$ NWIMSs based sensor could be used to detect ppm-level ethanol under a varied-humidity atmosphere.

Compared to previously reported ethanol sensors based on different metal oxide nanostructures, our sensor shows an obviously outstanding comprehensive sensing performance (Table S1), including lower detection limit, higher sensitivity, and lower operating temperature due to the following reasons. First, the 3D open and accessible framework and high porosity of the Pt/Si-WO$_3$ NWIMSs not only provide a large amount of activation sites for adsorption/desorption of gas molecules, but also favor the diffusion and transmission of gas molecules. In addition, the crystalline nanowires in the Pt/Si-WO$_3$ NWIMSs enable a fast transport of charge carriers (electrons) between the bulk and the surface. Finally, the catalytic sensitization of Pt nanoparticles promotes the reaction rate of ethanol with oxygen species on the surface of tungsten oxide at low working temperature. Therefore, it could be summarized that the high crystallinity, open porous structure, and sensitization of noble metal particles lead to the excellent ethanol sensing performances.

**Study on Gas Sensing Mechanism.** Furthermore, to investigate the catalytic reaction pathways during the gas sensing process, in situ Fourier transform infrared spectroscopy (in situ FTIR) was conducted to study the gas sensing mechanism (Figure S20), by monitoring the IR absorption signals in real time, with the temperature of Pt/Si-WO$_3$/KBr rising from room temperature to 200 °C in ethanol atmosphere (500 ppm). The infrared spectra at different temperatures displayed that, with the catalytic reaction of ethanol on surface of Pt/Si-WO$_3$, the absorption peak around 2970 cm$^{-1}$ disappeared gradually, which was attributed to the hydrocarbon bond (C–H) in ethanol, indicating that ethanol decomposed gradually. Meanwhile, new absorption peaks around 1868, 2306, and 2381 cm$^{-1}$ appeared gradually, which could be referred to as carbonyl (C=O) and carbon...
dioxide (CO₂), respectively. We further conducted gas chromatography–mass spectrometry (GC-MS) characterizations. As shown in Figure S21, 5000 ppm of ethanol was injected into the test chamber (1.8 L). After reaction with 1 wt % Pt/Si-WO₃ at 200 °C for 30 min, an obvious peak appeared at the position with a retention time of 1.63 min which can be identified as acetaldehyde (CH₃CHO). Therefore, it could be concluded that ethanol was first oxidized into acetaldehyde, and then into carbon dioxide and water at the surface of Pt/Si-WO₃. As a result, the electrons flowed from ethanol to Pt/Si-WO₃, leading to a dramatic decrease in its resistance. The reaction equations are as follows:

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\begin{align*}
\text{CH}_3\text{CH}_2\text{OH(ad)s} + \text{O}^-(\text{ads}) &= \text{CH}_3\text{CHO(ad)s} + \text{H}_2\text{O} + e^- \quad (1) \\
\text{CH}_3\text{CHO(ad)s} + 5\text{O}^-(\text{ads}) &= 2\text{CO}_2 + 2\text{H}_2\text{O} + 5e^- \quad (2)
\end{align*}
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Theoretical DFT Calculations. In order to study the gas sensing mechanism in depth, a theoretical calculation based on density functional theory (DFT) was conducted to explain the high sensitivity and selectivity toward ethanol of the Pt/Si-WO₃-based sensor (Figure 7). The Pt/Si-WO₃ structure was initially built and optimized serving as a dominant interface region interacting with ethanol molecules. The adsorption configurations of the (020) plane on the WO₃ of Pt/Si-WO₃ are optimized and the adsorption energies (E_ads) for ethanol were calculated to be -3.42 eV, indicating a strong adsorption capacity to ethanol molecules of Pt/Si-WO₃ (Figure 7a). In comparison, the optimized structures for the other ten coexisting gases absorbed on Pt/Si-WO₃ were also built, and the corresponding adsorption energies were calculated (Figure S22). Among all the investigated gases, E_ads for ethanol was the most negative one (-3.42 eV), while for other gases, the adsorption energies are all higher than -2.0 eV (Figure 7b). It indicates that the (020) facets of Pt/Si-WO₃ greatly benefit the adsorption and the subsequent catalysis of ethanol compared with other gases. In addition, no obvious changes in molecular structures were observed after the adsorption of gas molecules onto the Pt/Si-WO₃, and therefore, it can be proven that all the gases on the Pt/Si-WO₃ are physically adsorbed. Meanwhile, the E_ads for ethanol adsorbed on the undecorated Si-WO₃ was calculated to be -0.52 eV (Figure S23a), much higher than that of Pt/Si-WO₃, indicating that Pt functionalization is beneficial to the adsorption of ethanol. The above results are consistent with the experimental results, further confirming the ultrahigh selectivity to ethanol of the Pt/Si-WO₃. Further calculations reveal that the band gap is narrowed after ethanol absorption (Figure 7c,d), and the density of states (DOS) of the Pt/Si-WO₃+ethanol displays a new energy level in the conduction band (Figure 7e,f), due to the strong bonding adsorption of ethanol on the Pt/Si-WO₃ and electron transfer from ethanol to Pt/Si-WO₃, which resulted in a decrease in resistance. These results consistently demonstrate that the ethanol adsorption changes electronic structure and surface energy level of the Pt/Si-WO₃.

Charge density difference was further calculated to elucidate the accurate electronic transfer during ethanol sensing process. As shown in Figure 7g, the blue and yellow lobes represent the charge depletion and accumulation, respectively, due to adsorption and oxidation of ethanol molecules, and the Bader charge analysis shows that there is 0.83 e of charge transfer from ethanol to Pt/Si-WO₃, which is obviously higher than that of the undecorated Si-WO₃ (Δq = 0.64 e, Figure S23b). This result is in accordance with the DOS results and charge distribution in the 2D plane of Pt/Si-WO₃ (Figure 7h). In conclusion, the gas sensor based on the Pt/Si-WO₃ NWIMs shows ultrahigh selectivity and sensitivity toward ethanol under low working temperature, because the Pt/Si-WO₃ provides abundant active sites for ethanol adsorption and accelerates electronic transfer during gas sensing process.

Construction of Gas Sensor Module. Finally, in order to realize real-time monitoring of gas concentrations on mobile devices, a portable sensing module wirelessly connected to a smart phone was fabricated to detect ethanol in the atmosphere (Figure 8). The module was composed of a battery, a gas sensor based on our 1 wt % Pt/Si-WO₃ NWIMs, a microcontroller unit (MCU), and a wireless data communication (WDC) part (Figure 8a). Through the signal conversion systems in the device, the concentration of ethanol could be monitored in real-time through an application in the smartphone, and the concentration could be displayed directly on the screen (Figure 8b,c). Therefore, it is expected that the combination of microelectronic devices and high-performance semiconductor gas sensor enables intelligent detection of target gas, and will push forward the practical applications of advanced nanomaterials and microdevices.

**CONCLUSIONS**

In summary, we demonstrated a one-pot multicomponent coassembly method to construct unconventional silicon-doped tungsten oxide nanowire arrays interwoven into 3D mesoporous superstructures with surface decorated by in situ formed platinum particles (Pt/Si-WO₃ NWIMs). By using inorganic polyoxometalates clusters (H₄SiW₁₂O₄₀) and organic platinum complexes (Pt(cod)(Me)₂) as hydrophilic and hydrophobic precursors, respectively, ordered mesoporous structure constructed by Pt nanoparticles decorated silicon-doped tungsten oxide nanowires 3D arrays were obtained. The 3D Pt/Si-WO₃ NWIMs possess highly ordered porous nanostructures, high specific surface areas, highly crystalline framework, and abundant surface chemisorbed oxygen species caused by homogeneous heteroatom (Si) doping, as well as large number of metal oxide-noble metal (WO₃–Pt) active interfaces, showing great potentials for applications in fields of heterogeneous catalysis, gas sensing, and energy conversions. As a proof of concept, the Pt/Si-WO₃ NWIMs-based semiconductor gas sensor exhibited high sensitivity and
selectivity toward ethanol at low working temperature (100 °C), as well as a fast response–recovery speed and good stability. In addition, the gas sensing mechanism was investigated in depth by in situ FTIR techniques and DFT calculations. Furthermore, the block copolymers–polyoxometalates (BCPs-POMs) coassembly strategy paves a new way to construct a variety of metal oxides–noble metal nanocomposites with novel 3D ordered mesoporous structures, highly crystalline features, and diverse chemical compositions, which are extremely advantageous for diffusion of guest molecules, gas–solid interfacial catalytic reactions, and transport of charge carriers in various practical applications.

### EXPERIMENTAL SECTION

**Synthesis of Pt/Si-WO₃ NWIMSs.** A typical synthesis was carried out as follows: 0.10 g of the amphiphilic diblock copolymer PEO₁₁₄-b-PS₁₅₆ (Mₑ = 16,500 g mol⁻¹, PDI = 1.05) designed through a classical atom-transfer radical polymerization (ATRP) strategy was dissolved in 3.0 mL of THF to form a homogeneous solution. Then, 1.0 mL THF solution of (1,5-cyclooctadiene) dimethylplatinum(II) (Pt(cod)(Me)₂)₅ (50 mg/mL) was added to the solution. Almost simultaneously, 0.35 g of silicotungstic acid hydrate (H₄SiW₁₂O₴₀·15H₂O, AR, Aladdin) was also dissolved in 1.0 mL of THF to form the precursor solution. After all the solid-phase components had been dissolved, they were mixed to produce a light-blue colloidal solution. After 1.0 h, this solution was cast onto glass Petri dishes to evaporate THF slowly at room temperature for 12 h, followed by a sequential thermal treatment at 100 °C for 12 h. The target Pt/Si-WO₃ film was generated through a gradient calcination treatment at 500 °C for 1 h in N₂ (heating rate, 1 °C min⁻¹ below 350 and 5 °C min⁻¹ above 350 °C) and then at 350 °C for 2 h in air (5 °C min⁻¹).

**Characterizations and Measurements.** Field emission scanning electron microscopy (FESEM) images were obtained on Zeiss Ultra 55 (Germany) operated at 3 kV and 10 μA. The dried samples were directly used for the observation without any treatment. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer. Before measurements, the samples were degassed in a vacuum at 180 °C for at least 8 h. The specific surface area and the pore size distribution were calculated by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method, respectively. The total pore volume (Vₜotal) was calculated from the adsorbed amount at P/P₀ = 0.995. Fourier-transform infrared (FTIR) spectra was collected on a Nicolet Fourier spectrophotometer using KBr pellets.

**Gas Sensing Tests.** Gas sensing measurements were carried out on a gas sensing system of MA1.0 (Xikang Nano Electronics Co. Ltd., China). The side-heated gas sensors were fabricated according to the following procedures. The powder samples (Pt/Si-WO₃ NWIMSs) were mixed and ground with ethanol to form a paste, which was then coated on an alumina tube attached with a pair of Au electrodes. After drying at 100 °C for 2 h, a Ni–Cr alloy wire was inserted into the tube as a heater. The assembled sensor was then aged at 250 °C for 12 h before measurement. Target gas, such as ethanol, was injected onto a heating plate to evaporate and mix with air in the gas chamber. The resistance of a sensor in air (Rₐ) and in target gas (Rₕ) was measured in real-time. The response of the sensor is defined as Rₕ/Rₐ. The response or recovery times was defined as the time required for the sensor to reach 90% of the variation in resistance after switching atmosphere.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssentsci.1c00912.

Supplementary synthesis and computational methods; supplementary structural characterizations (Figure S1–S14); supplementary experimental details of gas sensing (Figure S15–S23); in situ Fourier transform infrared spectroscopy; supplementary DFT calculations; and supplementary tables (Table S1) (PDF)

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Notes
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