Supporting Information

Dynamic Coassembly of Amphiphilic Block Copolymer and Polyoxometalates in Dual Solvent Systems: An Efficient Approach to Heteroatom-Doped Semiconductor Metal Oxides with Controllable Nanostructures

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**Supplementary Experiments**

1. **Characterizations and measurements.**

Field emission scanning electron microscopy (FESEM) was performed on a Zeiss Ultra 55 field-emission SEM (Germany) operated at 3 kV and 10 μA. Transmission electron microscopy (TEM) was conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. The samples for TEM measurements were first dispersed in ethanol and supported onto a carbon coated copper grid. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer. Before measurements, the samples were degassed in vacuum at 180 °C for at least 6 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 ($V_{\text{total}}$) was calculated from the adsorption volume at $P/P_0 = 0.995$. Fourier-transform infrared (FTIR) spectra were collected on a Nicolet Fourier spectrophotometer using KBr pellet method. Powder X-ray diffraction (XRD) patterns were recorded on Bruker D4 X-ray diffractometer (Germany) equipped with Ni-filtered Cu Kα radiation (40 kV, 40 mA). The X-ray photoelectron spectroscopy (XPS) spectra were collected on an RBD 147 upgraded PHI 5000C ESCA system with a dual X-ray source. The Mg Kα (1253.6 eV) anode and a hemispherical energy analyzer were used in the measurements. All of the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The average sizes of micelles were tested using a dynamic light scattering (DLS) instrument (Malven, Zetasizer Nano ZS, UK).

2. **Gas sensing tests**

Before the tests, the Si-WO$_3$ hollow hemispheres powder was mixed with ethanol and grounded in an agate mortar to form a paste. The resulting paste was coated on an alumina tube on which a pair of Au electrodes had been printed previously, followed by drying at 100 °C for about 2 h and subsequently annealing at 250 °C for about 2 h. Finally, a small Ni-Cr alloy coil was inserted into the tube as a heater to adjust and optimize the working temperature of the gas sensor. To improve the long-term stability, the sensors were kept at the working temperature for 3 days. The gas sensing performance of the fabricated Si-WO$_3$
sensors was performed using a dynamic gas distribution test system (JF02F, China). The gas sensing response \( S \) in the measurement was deduced using the following equation, \( S=R_a/R_g \), where \( R_a \) and \( R_g \) are the resistance of materials in air and in the test gas, respectively. In addition, the gas sensing performance working at different temperatures was investigated to find the optimal working temperature, which is determined by the voltage of the heating electrode. The commercial acetone gas was purchased from Shanghai Weichuang Company. The acetone in the dry air with an accurate concentration can be controlled by the gas distribution box.

3. Computational methods

First-principles were used to describe the ions behavior in the anode based on density functional theory (DFT) with the Vienna ab initio simulation package (VASP) code. In addition, Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method were used to describe the ion-electron interactions in our systems. In this study, the plane-wave cutoff energy was set to 450 eV, and van der Waals corrections (optPBE-vdW) were adopted during structural optimization for the layer materials, and the vdWs interactions were described exactly by using DFT-D3 correction method of Grimme’s scheme. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than \( 10^{-6} \) eV. A geometry optimization was considered convergent when the energy change was smaller than 0.05 eV Å\(^{-1}\). The vacuum spacing in a direction perpendicular to the plane of the structure is 15 Å. The Brillouin zone integration is performed using \( 3\times3\times1 \) Monkhorst-Pack k-point sampling for a structure. Finally, the adsorption energies \( (E_{ads}) \) were calculated as \( E_{ads} = E_{ad/sub} - E_{ad} - E_{sub} \), where \( E_{ad/sub} \), \( E_{ad} \), and \( E_{sub} \) are the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively.

4. Principle of wireless gas sensor module

The circuit diagram of the wireless gas sensor module is as follows:
The inverting amplifier can convert the resistance information into voltage information. The operational amplifier OPA376 (Texas Instrument, TI) was adopted in the system, which provides extremely high input impedance and rail to rail input/output range.

MUX (multiplexer) is connected to the feedback resistance of the inverting amplifier as a switch, which can change the measuring range of the resistance. In this system, ADG704 from Analog Devices Company is adopt as MUX to provide extremely low on-resistance (<8 Ω) to ensure measurement accuracy, and extremely low leakage current (<0.3 nA) to ensure large resistance measurement in the order of GΩ.

ADS1115 from TI Company was adopted as the Analog to Digital Converter (ADC). The ADC was integrated with a differential input Programmable Gain Amplifier (PGA), which can be used to realize voltage subtraction calculation. The voltage is collected by ADC and processed by Micro Controller Unit (MCU). The resistance value can be calculated and the concentration can be fitted, which can be sent to the smart phone via Bluetooth.

In addition, the heating power of the heating resistor can be controlled by Pulse Width Modulation (PWM), and the heating current can be collected by measuring the voltage of the resistor in series, and the data can be sent to the MCU for power management or sent to a smart phone.
According to the schematic,

\[ \frac{V_{ref1} - V_{cc}}{R_x} = \frac{V_{out} - V_{ref1}}{R_{ref}} \]

\[ V_{out} = V_{ref1} + \frac{R_{ref}}{R_x} \cdot (V_{ref1} - V_{cc}) \]

in which, \( V_{out} \) is the output voltage, \( V_{ref1} \) is the voltage reference, \( R_x \) is the resistance value of gas sensor, and \( V_{cc} \) is the supply voltage.

The voltage collected by ADC is

\[ V_{ADC} = A_{PGA} \cdot (V_{ref2} - V_{out}) = A_{PGA} \cdot \frac{R_{ref}}{R_x} \cdot (V_{cc} - V_{ref2}) \]

where \( A_{PGA} \) is the voltage gain of PGA inside ADS1115.

When the resistance to be measured is too small, the voltage measured by the ADC is relatively large. The measurement range of the circuit can be adjusted by reducing the PGA gain \( A_{PGA} \), or switching the reference resistance through MUX (reducing the value of \( R_{ref} \)).

When the resistance to be measured is too large, the voltage measured by the ADC is low. The measurement range of the circuit can be adjusted by increasing the PGA gain \( A_{PGA} \), or switching the reference resistance through MUX (increase the value of \( R_{ref} \)).
Figure S1. Schematic illustration of the micelle structures formed by the coassembly of block copolymer and polyoxometalates in n-hexane/THF dual solvent solution. The self-assembled structures are determined by the packing parameter ($p$).

Figure S2. Dynamic light scattering (DLS) characterization of the PEO-b-PS/H₄SiW/THF colloidal solution, showing an interesting bimodal narrow size distribution. The first distribution peak centered at 34.5 nm corresponds to PEO-b-PS/H₄SiW spherical micelles, and the peak at 2.5 nm is attributed to free SiW₁₂O₄₀⁴⁻ anions. The insets are optical photograph and the Tyndal effect of the PEO-b-PS/H₄SiW/THF colloidal solution.
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Figure S4. X-ray photoelectron spectroscopy (XPS) of PEO-\textit{b}-PS/H_4SiW_{12}O_{40} cylindrical micelles (without \textit{n}-hexane) supported on silicon wafer before and after Ar\textsuperscript{+} sputtering: (a) Si 2p, (b) W 4f, (c) O 1s and (d) C 1s. (e) Element contents measured by XPS and (f) the corresponding structural models of the PEO-\textit{b}-PS/H_4SiW_{12}O_{40} cylindrical micelles before and after Ar\textsuperscript{+} sputtering.

Firstly, the nanocomposites film composed of PEO-\textit{b}-PS/H_4SiW_{12}O_{40} cylindrical micelles was tested without treatment, the elements content calculated by XPS results was Si = 1.38 at\%, W = 3.46 at\%, O = 24.51 at\% and C = 70.65 at\% respectively. After Ar\textsuperscript{+} sputtering for 180 s, the Si and O content was decreased to 0.82 at\% and 14.53 at\% respectively, which was caused by etching of PEO/SiW_{12}O_{40}\textsuperscript{4-} species on the surface of the film, conforming the PEO-\textit{b}-PS/H_4SiW_{12}O_{40} cylindrical micelles structure with PS chain as core and PEO/SiW_{12}O_{40}\textsuperscript{4-} domain as shell. The unpredictable rise of W content could be explained by that it is difficult to be etched, the sputtering speed is much slower compared with the surrounding Si, C, O elements, which agrees well with the appearance of W species with low chemical state (W\textsuperscript{4+}).
**Figure S5.** X-ray photoelectron spectroscopy (XPS) showing the C 1s core level peak regions of PEO-$b$-PS/H$_4$SiW$_{12}$O$_{40}$ hybrid film supported on silicon wafer before Ar$^+$ sputtering: (a) cylindrical micelles, (b) spherical vesicles.

**Figure S6.** TEM images at low magnification and from different directions at high magnification of the Si-WO$_3$ hollow hemispheres, showing a nanobowl-like morphology.
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**Figure S8.** (a) Schematic illustration of the structural evolution of PEO-\textit{b}-PS/H$_4$SiW$_{12}$O$_{40}$ spherical vesicles into Si-WO$_3$ nanobowls via a thermal-induced structural transformation process, SEM image of the Si-WO$_3$ nanobowls obtained after calcination at 500 °C for different time: (b) 0.5 h, (c) 1.0 h, (d) 2.0 h.
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