sp²-Hybridized Carbon-Containing Block Copolymer Templated Synthesis of Mesoporous Semiconducting Metal Oxides with Excellent Gas Sensing Property

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CONSPECTUS: In recent years, rational design of ordered mesoporous metal oxides, especially metal oxide semiconductors with adjustable pore architecture and framework compositions, has aroused extensive research interest owing to their unique electronic structures, long-range ordered porous framework, uniform mesopore size, and high specific surface area. Research on mesoporous materials has been booming in the past 30 years, and many synthesis methods have been developed, such as templating methods based on amphiphilic copolymers as soft templates or mesoporous carbon/silica as hard templates, respectively. Soft-templating synthesis has been considered as one of the most efficient and flexible methods in designing ordered mesoporous materials through the controllable interfacial induced coassembly process. However, most commercial amphiphilic copolymers, such as poly(ethylene oxide)-*b*-poly(propylene oxide) based Pluronic-type ones, suffer the drawback of poor thermal stability, because they are too easy to be decomposed even in inert atmosphere. Therefore, they are difficult to support the structures of mesoporous metal oxides under high calcination temperatures (>400 °C). To solve this challenge, we designed new amphiphilic block copolymers with high content of sp²-hybridized carbon in the hydrophobic segments that were relatively stable and could be in situ converted into residual carbon to support the mesoporous structure, via living free radical polymerization. We developed a variety of novel synthesis methods based on sp²-hybridized carbon-containing block copolymer, such as ligand-assisted assembly and resol-assisted assembly strategies, achieving a controllable and versatile synthesis of mesoporous semiconducting metal oxides with excellent gas sensing performance. In this Account, we first outline the features of sp²-hybridized carbon-containing block copolymers synthesized via living free radical polymerization, particularly their pyrolysis behavior in converting into residual carbon. Combining the solvent evaporation induced coassembly and the carbon-supported crystallization strategies, we realized the rational design of various ordered mesoporous semiconducting metal oxides (e.g., WO₃, SnO₂, Co₃O₄, In₂O₃, TiO₂, ZnO) and the regulation of their architectural features. To overcome the fast hydrolysis rate of metal precursors and weak interaction between block copolymers and metal precursors, we developed efficient ligand-assisted (e.g., acetylacetone and acetic acid) coassembly and resol-assisted coassembly methods to retard hydrolysis behavior and enhance the interaction via hydrogen bonds, covalent bonds, electrostatic interactions, etc. We also highlight the applications of these ordered mesoporous semiconducting metal oxides of both n-type and p-type in gas sensing fields, and they show tremendous sensing performance due to their abundant active sites on electron depletion layer and rapid gas diffusion via accessible pore channels. Finally, on the basis of the classic surface-electron depletion layer model, we elucidated in depth the surface catalytic reactions between the target gas molecules and the activated species (e.g., the adsorbed oxygen species) in the surface of mesoporous metal oxides during sensing process. These newly developed soft-templating synthesis methods that rely on sp²-hybridized carbon-containing block copolymers will open a new avenue for the design and application of ordered mesoporous semiconducting metal oxides in various fields.

1. INTRODUCTION

Owing to their miraculous electrical, magnetic, and thermal properties, metal oxide semiconductors have been extensively studied for catalysis, sensors, energy storage, etc.^{1–3} With the progress of technology about Internet of things, various intelligent devices, particularly gas sensors based on high-performance sensing materials, have gained unprecedented attention.⁴ Ordered mesoporous semiconducting metal oxides (OMSMOs) have recently emerged as ideal sensing materials

due to their highly porous structure with suitable pore size (2–50 nm), outstanding mass transport efficiency, and high specific surface area.^{5–7} The attempt to synthesize OMSMOs via soft-templating approach can be traced to Yang's work on various metal oxides with semicrystalline frameworks, including TiO₂, ZrO₂, Al₂O₃, and Nb₂O₅ via coassembly between commercial

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amphiphilic block copolymers and metal salts.⁸ Despite the difference in chemical component of the framework, the common feature of soft-templating synthesis is that the coassembly is based on various interactions between the precursor and hydrophilic segments in the template molecules.^{9,10}

Currently, lots of ordered mesoporous materials with amorphous frameworks, including silica and carbon, have been reported based on commercial soft templates (e.g., quaternary ammonium salts and poly(ethylene ether) series).^{11–13} By contrast, it has remained a great challenge to controllably synthesize high-quality OMSMOs through either soft- or hard-templating approaches.^{14,15} It is mainly because most previous attempts to OMSMOs exclusively relied on the commercially widely available Pluronic-type templates. These templates possess low molecular weight and decomposition temperature, and they can be decomposed too fast even at low temperature region (<350 °C).^{16,17} Thus, it is unable to support the reorganization and crystallization of the pore walls during template removal at high temperatures (usually >400 °C), leading to metal oxides with low porosity, disordered porous structure, and low surface areas. These drawbacks seriously hamper their applications in many fields, in which a fast mass transport of guest molecules and efficient host–guest interaction between molecules and solid frameworks are required.

To solve the above problems, we designed various sp²-hybridized carbon-containing block copolymers with lower oxygen content and high thermal stability using controllable living polymerization methods.¹⁸ On the basis of the rich phase behaviors of these block copolymers and their interaction with inorganic precursors, we realized the rationally controllable design and synthesis of various OMSMOs (e.g., TiO₂, WO₃, Nb₂O₅, SnO₂, In₂O₃, ZnO, Co₃O₄). These materials possess ordered mesostructure, high surface area (120–200 m²·g^{−1}), tunable pore size (8.0–30 nm), highly crystalline framework, and promising sensing values. After more than 10 years' research on the soft-templating synthesis of mesoporous materials, we are now at a point where we can present a coherent account of various reliable methods for effective synthesis of OMSMOs with excellent gas sensing performance.

2. SP²-HYBRIDIZED CARBON-CONTAINING BLOCK COPOLYMERS

With the development of templating synthesis concept, various functional mesoporous metal oxides have been extensively explored for applications in different fields. Mesoporous structures are mainly synthetically generated from the soft-templating approaches based on interface coassembly of amphiphilic molecules and framework precursors. Although the synthetic route is kaleidoscopic and can produce different mesoporous structures with different properties, the assembly process follows liquid crystalline pathway based on the microphase separation of block copolymers.

Using commercial Pluronic-type poly(ethylene oxide)-*b*-poly(propylene oxide) copolymers (e.g., P123 and F127) as structure directing agent can only generate relatively small mesopores size (<10 nm) and semicrystalline framework, due to the short chain length of poly(propylene oxide) PPO block and poor thermal stability of the template molecules. Thanks to advances in the field of polymer synthetic chemistry, various new amphiphilic block copolymers, especially those non-Pluronic type ones, have been designed and applied for the controllable synthesis of OMSMOs with crystalline or amorphous ordered

mesoporous framework.^{19,20} New amphiphilic block copolymers, such as poly(isoprene)-*b*-poly(ethylene oxide) (PI-*b*-PEO), poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS-*b*-PVP-*b*-PEO), poly(ethylene oxide)-*b*-poly(styrene) (PEO-*b*-PS), and poly(styrene)-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) usually consist of hydrophilic blocks (i.e., PEO, poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP)) that can interact with inorganic precursors and hydrophobic blocks (i.e., PS, PI, polybutadiene (PB), and polyacrylonitrile (PAN)).^{19–24} These copolymers possess high carbon content, lower oxygen content, and rich sp²-hybridized-carbon atoms in the hydrophobic block, which enables them to be carbonized under inert conditions in the assembled mesostructures to support the crystalline frameworks under high temperatures. Thus, the target OMSMOs with well-reserved mesostructures and highly crystalline walls can be obtained after removal of residual carbon by further calcination in air at a temperature lower than that for carbonization. In 2008, Lee et al.²⁰ reported a method combining soft structure-directing assemblies and hard-templating chemistries, termed “CASH” method, and they synthesized many highly crystalline mesoporous metal oxides by using poly(ethylene oxide)-*b*-polyisoprene with rich sp²-hybridized-carbon as the soft template.^{25,26} Inspired by this method, our group designed amphiphilic block copolymers PEO-*b*-PS with different molecular weights and hydrophilic/hydrophobic ratios, via the well-developed atom transfer free radical polymerization (ATRP) method, which is easy to learn even for those who have no experience in polymer synthesis.^{27,28} In the ATRP synthesis process, using PEO-Br with various molecular weights (i.e., 2000–10 000 g·mol^{−1}) as a macro-initiator, adjusting the polymerization time of styrene monomer, we obtained high molecular weight soft templates (10 000–50 000 g·mol^{−1}) with different chain lengths of hydrophilic PEO and hydrophobic PS blocks. Similarly, other amphiphilic block copolymers with PEO hydrophilic block can be readily synthesized through above polymerization reaction, and simply changing the reaction conditions, one can effectively adjust target molecular composition and chain length of templates, which is extremely beneficial for the controllable design and synthesis of OMSMOs.

3. CONTROLLABLE ASSEMBLY SYNTHESIS OF OMSMOS

3.1. Different Forms of Assembly

Recently, with the progress in understanding the coassembly process of amphiphilic block copolymers and different precursors in complex solutions, our group realized the controllable synthesis of a series of OMSMOs based on sp²-hybridized carbon-containing block copolymers. Emerging approaches have brought about high-quality OMSMOs, such as solvent evaporation induced coassembly (EICA), which have opened a door in large-scale production of OMSMOs. EICA usually occurs in a typical nonaqueous phase synthesis process, which depends on the kinetically induced evaporation of good solvent (e.g., tetrahydrofuran (THF), chloroform, dioxane) to reach critical concentration of comicellization of copolymers cooperatively assembling with inorganic precursor species, leading to OMSMOs after structure fixing and removal of template molecules.^{29,30} The continuous evaporation of good solvent causes the self-assembly of amphiphilic block copolymers with associated inorganic species into ordered mesostructures (i.e., liquid crystalline phases) in the nonaqueous

Figure 1. (A) The template-carbonization synthesis process of crystalline mesoporous WO_3 . (B) XRD pattern of the ordered crystalline mesoporous WO_3 . (C) FESEM images: (a) surface, (b) cross-section; TEM images taken along the (c) [110], (d) [100], (e) [211], and (f) HRTEM image of the crystalline ordered mesoporous WO_3 . (D) SAXS patterns of the ordered mesoporous WO_3 , (a) as-made and (b) after calcination at 500 °C in air. Adapted with permission from ref 31. Copyright 2014 John Wiley and Sons.

system by virtue of the interface interaction between organic templates and inorganic precursor of metal oxides. With the reduction of the solubility of copolymers with associated inorganic species in the solution induced by various factors (e.g., the decreased content of good solvent, the increased content of nonsoluble inorganic species as a result of hydrolysis and condensation, etc), organic–inorganic micelles occur in two-phase interfaces. Subsequently, when the volatile solvent evaporates completely, preformed mesoscopic liquid-crystal phase is closely packed, forming nanocomposites with specific ordered mesostructures. As a result of the structural supporting of the residual carbon generated by pyrolysis of the sp^2 -hybridized carbon-containing block copolymers, OMSMOs can be obtained without structure collapse.

3.2. Direct Interfacial Coassembly

On the basis of typical EICA method, OMSMOs can be synthesized directly via a direct template-carbonization strategy. For instance, adopting lab-made PEO_{117} - b - PS_{198} with high molecular weight (ca. $25850 \text{ g}\cdot\text{mol}^{-1}$) as a soft template, ordered mesoporous WO_3 was fabricated for the first time through direct EICA strategy based on the strong interaction between the PEO segments of PEO_{117} - b - PS_{198} and W^{6+} species, as shown in Figure 1A.³¹ With the evaporation of THF, closely packed spherical micelles with hydrophobic PS core and hydrophilic PEO-tungsten species form stable ordered mesostructures via strong hydrogen bonds. The carbonization of PS segments can in situ generate stable residual carbon in mesopores, which supports the ordered inorganic framework converting into crystalline WO_3 in high-temperature treatment, ensuring a large mesopore size ($\sim 10.9 \text{ nm}$) and high surface area ($\sim 121 \text{ m}^2\cdot\text{g}^{-1}$). The results of X-ray diffraction (XRD; Figure 1B) showed typical

crystalline monoclinic phase of WO_3 , which exhibited strong diffraction peaks and high crystallization. According to the scanning/transmission electron microscopy (SEM/TEM) images (Figure 1C) and small-angle X-ray scattering (SAXS) spectra (Figure 1D), the obtained mesoporous WO_3 has face-centered cubic (fcc) (space group: $Fm\bar{3}m$) mesostructure. Similarly, PEO-*b*-PS copolymers can directly interact and coassemble with indium chloride to form ordered mesostructures. To avoid the mesostructure collapse during the simultaneous process of framework crystallization and template removal, CaO_2 powder was used to promote the combustion of organic template during calcination via the burst release abundant oxygen, and ordered mesoporous In_2O_3 with large uniform pore size ($\sim 14.5 \text{ nm}$) and highly crystalline nanosheet-assembled framework was obtained via short-time calcination (30 min) at relatively lower temperature (400 °C).³²

Besides PEO-*b*-PS, PS-*b*-P4VP copolymers were also designed and used as template to directly assemble with inorganic precursors.^{33–35} In this case, by using the electrostatic interactions between the protonated P4VP segments and the hydrolyzed titanium tetrabutoxide in acidic THF solution, ordered mesoporous titania with in situ N-doped crystalline anatase framework has been synthesized by using P4VP as the nitrogen source.³³ By contrast, because of the limitation of the weak interaction between late transition-metal precursors and block copolymers, other common metal oxides with low crystallization temperature, including ZnO , Co_3O_4 , Fe_2O_3 , etc., are difficult to synthesize through the simple direct coassembly strategy. To solve the key issue of weak interactions, our group developed a series of techniques to strengthen the

Figure 2. TEM images of the large-pore mesoporous titania MPTi-600N viewed from (a) [100], (b, d) [111], and (c) [210] directions. HRTEM images (d, f) of ordered mesoporous titania MPTi-600N, (e) is the corresponding SAED pattern from (c), exhibiting diffraction rings indexed to anatase phase. Adapted with permission from ref 36. Copyright 2011 John Wiley and Sons.

Figure 3. Chelation-assisted synthesis process of crystalline mesoporous ZnO. Adapted with permission from ref 42. Copyright 2016 Royal Society of Chemistry.

interaction between precursors and template molecules, including ligand-assisted and resol-assisted strategies.

3.3. Ligand-Assisted Assembly Strategy

In the synthesis of inorganic nanomaterials like nanocrystals, various ligands with different functional groups (thiol, carboxyl, amino), have been frequently employed to suppress the growth of nanoparticles into large ones or to achieve a controllable synthesis in terms of shape and morphology by using their strong ability to bind metal atoms. For the synthesis of mesoporous materials based on the soft-templating method, a ligand with multiple functional groups as an efficient “bridge” can not only reduce the hydrolysis and condensation rate of precursors of metal oxides but also facilitate the organic/inorganic coassembly process through interaction with PEO segments via hydrogen bonds and simultaneous coordination bonding with metal ions.

Early in 2011, we for the first time studied large-pore mesoporous TiO_2 with attractive crystalline framework via a novel ligand-assisted assembly strategy based on copolymer $\text{PEO}_{125}\text{-}b\text{-PS}_{130}$ as a template. Acetylacetone (AcAc) was used as the crucial coordination agent to retard the hydrolysis and condensation of Ti precursor (titanium isopropoxide (TIPO)) and avoid the phase separation of organic and inorganic species in the acidic THF solution.³⁶ As shown in Figure 2, the obtained titania materials exhibited ordered mesoporous framework, and the pore wall was composed of anatase nanocrystals. Thereafter, much effort has been devoted to design ordered mesoporous TiO_2 using various precursors, such as titanium alkoxide $[\text{Ti}(\text{OR})_4]$, soluble peroxytitanate $[\text{TiO}_2(\text{OH})(\text{H}_2\text{O})]\text{OH}$, titanium tetrachloride (TiCl_4), and tetrabutyl titanate (TBOT). Except for pure mesoporous TiO_2 , element-doped (Cu^{2+} and Mn^{4+}) and organic–inorganic hybrid materials of g-

C₃N₄ and mesoporous TiO₂ have also been synthesized using acetic acid-assisted and *p*-hydroxybenzoic acid assisted EICA strategy, respectively.^{37,38}

Recently, with the assistance of HCl-AcAc dual-ligand, ordered mesoporous crystalline SnO₂ can be obtained via classic EICA method with robust PEO-*b*-PS copolymer directed coassembly.³⁹ The acetylacetone-stabilized inorganic species were found to be ultrafine SnO₂ nanoclusters (ca. 2.5 nm), because the SnCl₄ precursor could be hydrolyzed even in the presence of trace water in THF. These SnO₂ nanoclusters can coassemble with PEO₁₁₄-*b*-PS₂₄₈ to form uniform spherical micelles via strong hydrogen bonds. Although ordered mesoporous WO₃ can be obtained through the direct EICA technique by carefully controlling the conditions (humidity, THF evaporation speed, precursor concentration, etc.), the textural parameters (e.g., pore dimension, wall thickness, porosity) are difficult to regulate, and the introduction of extra functional compositions (e.g., Pt, Au, Pd precursors) can interfere with the coassembly of WCl₆ with PEO-*b*-PS copolymers. Thus, the AcAc-assisted assembly method was extended to synthesize mesoporous WO₃, allowing for a highly reproducible, reliable, and scalable production of high-quality mesoporous WO₃ within a large synthesis window due to the complexation of AcAc with WCl₆ to form WCl_{6-x}(AcAc)_x. With this method, a series of lab-made PEO-*b*-PS copolymers with various molecular weights can be used for the controllable templating synthesis of crystalline ordered mesoporous WO₃ with different pore sizes,⁴⁰ and more importantly, hydrophobic (1,5-cyclooctadiene) dimethylplatinum(II) (i.e., Pt precursor) can be introduced in the synthesis system, leading to Pt nanoparticles sensitized ordered mesoporous WO₃.⁴¹

By contrast, ZnO has a lower crystallization temperature (200–400 °C), and due to the weak interaction between its salts and amphiphilic block copolymers, it maintains a great challenge to obtain ordered mesoporous structures. Citric acid as powerful chelating agent was recently found to be able to enhance the interaction between PEO-*b*-PS and Zn(NO₃)₂·6H₂O via hydrogen bonds, that is, Zn²⁺–O–C–O···H⁺···EO (Figure 3).⁴² Interestingly, in addition to the large mesopores (29.0 nm) generated by the block copolymers, numerous small mesopores (3.2 nm) were formed in the pore walls due to the decomposition of ZnCO₃ intermediate and the random packing of the resultant ZnO nanoparticles during thermal treatment. The ligand-assisted coassembly strategy can enhance the inorganic–organic interaction, avoid incompatibility among components in assembly system, and thus hold a great promise for controllable synthesis of functional semiconducting metal oxides with ordered mesoporosity and multicomponents.

3.4. Resol-Assisted Coassembly Strategy

In fact, except for ligand-assisted strategy based on various chelating agents, our group developed a general resol-assisted coassembly by utilization of the multiple phenolic hydroxyl groups of resol with complex transition-metal oxide precursors. Resol is a soluble macromolecule synthesized by condensation polymerization of phenol and formaldehyde in alkaline solutions. Resol can simultaneously interact with hydrophilic blocks of PEO-*b*-PS (P4VP-*b*-PS) and transition-metal salts, enabling an effective multicomponent coassembly into ordered mesostructures. During pyrolysis in inert atmospheres, the residual carbon derived from both resol and template molecules can support the crystallization of metal oxides, forming mesoporous carbon–metal oxide nanocomposites,⁴³ and upon

calcination in air, mesoporous carbon–metal oxide nanocomposites can be converted into mesoporous metal oxides which provide that metal oxides have a high content in the nanocomposites.⁴⁴ For example, by using resol as a robust bridge that connects PEO segments through hydrogen bonds and meanwhile complex Co²⁺ ions via coordination interactions, ordered mesoporous carbon–cobalt oxide hybrid materials with large pore size (13.4–16.0 nm) and high surface area (394–483 m²·g^{−1}) were synthesized (Figure 4).⁴³ Similarly, crystalline mesoporous Nb₂O₅ spheres were synthesized after sequential pyrolysis and calcination using NbCl₅ precursor (Figure 5).⁴⁴ The obtained mesoporous Nb₂O₅ spheres have large pore size (~11.4 nm), high surface area (131 m²·g^{−1}), and highly crystalline framework. As shown in Figure 5, PEO-*b*-PS copolymers could form rodlike micelles as the fast evaporation of THF, and hydrophilic resol as the sacrificial carbon source

Figure 4. Formation process of ordered mesoporous CoO_x/C nanocomposites with large mesopores and graphitic walls. Adapted with permission from ref 43. Copyright 2016 American Chemical Society.

could interact preferentially with PEO and served as a glue to bridge the metal species and block copolymers. Furthermore, by changing the relative amount of resol, dual mesoporous metal oxides with tunable pore size and window size can be readily synthesized.⁴⁵ Thus, this resol-assisted coassembly strategy can efficiently enhance the interaction between copolymers and metal precursors whose hydrolysis and condensation are difficult to control.

Thus, the available ligand or auxiliary components can adjust flexibly the interaction between block copolymers and target metal precursors. Moreover, these ligands can also chelate or complex with metal species to form stable ordered mesoporous framework by controlling the kinetic hydrolysis behavior. More novel OMSMOs with crystalline framework, diverse compositions, and pore structures can be created for applications in multidisciplinary fields.

Figure 5. Formation process of the ordered mesoporous Nb_2O_5 spheres by the resol-assisted EICA approach. Adapted with permission from ref 44. Copyright 2013 John Wiley and Sons.

4. GAS-SENSING APPLICATIONS OF OMSMOS

4.1. Gas-Sensing Performance

Chemiresistive gas sensor is one of the most important techniques for the real-time monitor and detection of toxic gas and flammable or explosive gas, which is crucial to public healthcare and environmental safety. Semiconducting metal oxides have been considered as ideal candidates, as the sensing layers for fabrication of high-performance gas sensor based on their dramatic resistance change upon contact target gases. The resistance of these materials may increase or decrease owing to their inherent physicochemical property and variable conductivity in atmosphere of reducing or oxidizing analytes (e.g., H_2S , CO , NO_x , alcohol, aldehyde, and low-molecular weight alkane and aromatic compounds). According to the variation of current carrier and sensing mechanism, semiconducting metal oxides can be divided into two typical categories, namely, n-type (e.g., WO_3 , In_2O_3 , SnO_2 , etc.) and p-type (e.g., NiO , CuO , Co_3O_4 , etc.). To evaluate the sensing efficiency, five main indicators have been adopted and used in practical applications including detection temperature, response sensitivity (gas response (S) = R_a/R_g , where R_a and R_g refer to the resistance in air and target gas, respectively), response/recovery time, selectivity, and stability. The performance of semiconducting metal oxides usually depends on the nature of sensing materials, including porosity, surface area, crystallinity, interface effect, grain size, etc. Thus, exploring and designing functional metal oxides with high activity and unique microstructure is essential for the enhancement of sensing performance.

Typical gas-sensor nanodevice is shown in Figure 6a–c; the mesoporous ZnO powder was dispersed in deionized water to form a homogeneous paste, which was coated on alumina ceramic tube twined with Au electrodes, and a Ni–Cr alloy wire was then inserted into the tube as a heater. On the basis of the as-synthesized ordered mesoporous ZnO materials, the nano-

devices showed superior sensing performance to ethanol with a fast response and recovery time (6/7 s) due to the unique hierarchical mesopores and crystalline framework of ZnO materials. Especially, compared with ZnO sensors with other nanostructures, including nanosheet, nanowires, nanodisks, nanostars, nanorods, microspheres, flakes, etc., the ordered mesoporous ZnO sensors showed superior sensing properties to ethanol.⁴² Similarly, ordered mesoporous In_2O_3 exhibited high response values (10.5) to oxidative NO_2 , one of the main culprits of air pollution, at low temperature of 150 °C even in concentration as low as 250 ppb (Figure 6d–f) because of their unique nanosheets-assembled pore wall and abundantly exposed active sites. The ordered mesoporous structure shows excellent performance to NO_2 compared with nonporous structure, such as nanowires, spheres, and nanoparticles, revealing the tremendous advantages of mesoporous structure in gas sensing.³² Very recently, mesoporous In_2O_3 modified with highly dispersed Pd nanodots were synthesized, which exhibited high response to H_2 even in the low concentration range of 0.5–100 ppm.⁴⁶ Crystalline mesoporous WO_3 materials exhibit attractive sensing performance to H_2S at low concentration (0.25 ppm) with fast response of 2 s and recovery of 38 s (Figure 6g,h).³¹ Moreover, they show selective response to H_2S , with a large response value of at least 6 times higher than those of interfering gases (Figure 6i). Compared with n-type metal oxides, p-type ones show relatively low response and selectivity because of their weak electrical conductivity. To address this problem, ordered mesoporous CoO_x/C composites with large pores and good electric conductivity of graphitic carbon matrix were recently designed, which showed superior response to H_2 at a concentration of 0.25%.⁴³

Besides the composition and crystalline framework, other key factors (e.g., porosity, active sites, surface defects) can also affect the gas sensing performance of OMSMOs. Through changing the molecule weight and the PS chain length of PEO-*b*-PS

Figure 6. (a) Photo of the assembled device. (b) The electric circuit of gas sensing measurements. (c) Sketch of the structure of the side-heated mesoporous ZnO-based gas sensor. Adopted with permission from ref 42. Copyright 2016 Royal Society of Chemistry. (d–f) The response of mesoporous In_2O_3 -based sensor to NO_2 . Adopted with permission from ref 32. Copyright 2016 American Chemical Society. (g–i) The response of the crystalline mesoporous WO_3 sensor to H_2S . Adapted with permission from ref 31. Copyright 2014 John Wiley and Sons.

copolymers, the pore size and specific surface area of the obtained ordered mesoporous WO_3 can be readily adjusted.⁴⁰ Four groups of gas sensors with different surface areas were fabricated by using mesoporous WO_3 from templates of different molecular weights (Table 1). The sensors demonstrated high sensitivity and selectivity to low-concentration 3-hydroxy-2-butanone, a typical biomarker of exhaled gas from *Listeria monocytogenes*, and their response increases with increasing surface area. Because of their high surface area, uniform pore size, and rich exposed sites, these ordered mesoporous WO_3 showed ~5–10 times higher sensitivity than that of commercial WO_3 nanoparticles, making it possible to monitor the microbial contamination of food indirectly by measuring biomarker of exhaled gas from *Listeria monocytogenes* (Figure 7).

It is worth noting that, because of the large pore size, the OMSMOs allow for in-pore deposition of foreigner nanoparticles (e.g., Pt, Pd, Au) without blocking pore channels, which provides numerous active metal oxide-metal interfaces to catalyze the reaction of target gases, leading to improved gas sensing performance with lower working temperature and better selectivity or sensitivity.^{41,46}

Table 1. Texture Properties and Sensing Performance of the Obtained WO_3 -PEO_x-b-PS_y and Commercial WO_3 Particles⁴⁰

samples	BET surface area (m ² /g)	total pore volume (cm ³ /g)	pore size (nm)	sensitivity (R_s/R_0)	response/recovery (s)
commercial WO_3	6			6.2	18.0/43.0
WO_3 -PEO ₁₁₇ -b-PS ₂₉₇	76	0.17	15.3	32.7	12.0/30.0
WO_3 -PEO ₁₁₇ -b-PS ₂₃₂	95	0.15	12.1	46.2	10.0/26.0
WO_3 -PEO ₁₁₇ -b-PS ₁₈₆	136	0.13	10.6	56.1	4.0/13.0

4.2. Gas-Sensing Mechanism

In general, the current carrier of n-type semiconductor is electrons, and adsorbed oxygen molecules tend to capture electrons from the surface of metal oxides to produce abundant active oxygen species (e.g., O_2^- and O^-), which can reduce the

Figure 7. (a) The principle for detection of *Listeria monocytogenes* using the sensor-based WO_3 -PEO₁₁₇-b-PS₁₈₆. (b–e) The responses of the sensors base on 3-hydroxy-2-butanone (S_a , S_b , S_c , and S_d based on commercial WO_3 particles, WO_3 -PEO₁₁₇-b-PS₂₉₇, WO_3 -PEO₁₁₇-b-PS₂₃₂, and WO_3 -PEO₁₁₇-b-PS₁₈₆, respectively). Adapted with permission from ref 40. Copyright 2017 American Chemical Society.

electron density and increase the resistance of metal oxides. In addition, the surface charge density is dependent on the surface-limited depth derived from these active oxygen species, and the affected region usually endows low electron density, which defines the depletion layer. On the basis of the depletion layer, once n-type semiconducting metal oxides contact reducing gases (e.g., CO, ethanol, and acetone), electrons return to the sensing layer, inducing the rapid decrease of resistance. In the opposite, exposure to oxidizing components (e.g., Cl_2 , NO_x , SO_2) can

intensify the electron depletion and result in increasing resistance of metal oxides. By contrast, p-type semiconductors possess distinct sensing mechanism, the effective holes (h^+) as current carrier endowed inversed response of resistance when exposed in reducing or oxidizing gases.

Our group performed a series of investigations about the gas sensing mechanism of the sp^2 -carbon containing copolymers templated OMSMOs. For example, the sensing process of n-type mesoporous WO_3 complies with the surface-depletion

Figure 8. (a) 3-Hydroxy-2-butanone sensing mechanism of the sensors based on n-type mesoporous WO_3 material. (E_v = valence band edge; E_c = conduction band edge; E_f = Fermi energy). Adapted with permission from ref 40. Copyright 2017 American Chemical Society. (b) H_2S sensing mechanism of the sensors based on mesoporous n-type SnO_2 material. Adapted with permission from ref 39. Copyright 2018 American Chemical Society. (c) H_2 sensing mechanism of the sensors based on mesoporous p-type CoO_x/C . Adapted with permission from ref 43. Copyright 2016 American Chemical Society. (d) CO sensing mechanism of the sensors based on mesoporous WO_3 exposed in air (i) and CO (iii), and Pt-doped ordered mesoporous WO_3 exposed in air (ii) and CO (iv), respectively (E_v , valence band edge; E_c , conduction band edge; E_f , Fermi energy). Adapted with permission from ref 41. Copyright 2017 John Wiley and Sons.

theory as follows. When they contact air (Figure 8a),⁴⁰ oxygen molecules can adsorb on the pore wall surface of mesoporous WO_3 to grasp electrons (conduction band) and produce abundant oxygen species. Consequently, the formed thick space-charge layer increases the potential barriers with a higher resistance, which accounts for the electrical resistance of metal oxides. In our recent research, we proved that the gas sensing behavior is dependent on the crystal size of metal oxides in the pore wall of OMSMOs (Figure 8b).³⁹ In this regard, metal oxide homojunctions were generated between nanograins in the crystalline mesoporous framework, which could accelerate the diffusion of active oxygen species, and these oxygen species usually covered the surface of nanograins. It can capture electrons of these nanograins and generate electron depletion layer, generating potential barriers among the grain boundaries. Thus, the resistance of metal oxides can be adjusted through these potential barriers in target gases. In comparison, during the sensing process of p-type Co_3O_4 , oxygen molecules can trap and react with electrons from conduction band of CoO_x/C (Figure 8c),⁴³ forming the depletion layer consisting of negative oxygen species on the surface of Co_3O_4 nanoparticles. In the atmosphere of reducing H_2 , H_2 molecules can react with these negative oxygen species to form H_2O , and electrons flow back to Co_3O_4 and recombine with hole to increase its resistance. Apart from n-type and p-type semiconductors, various heterojunctions, such as p-n, n-n junctions, can significantly enhance chemical activity and sensing performance based on the strong

synergistic effect. For example, Pt-doped ordered mesoporous WO_3 can be regarded as an excellent gas sensor to CO (Figure 8d).⁴¹ It is not only attributed to the high active and sensitization of Pt nanoparticles highly dispersed in the mesoporous WO_3 matrix but also formed p-n heterojunction at the surface/interface among Pt NPs, PtO_x , and WO_3 , which is beneficial for the efficient allocation of the surface depletion layer and electron depletion.

5. CONCLUSION AND PERSPECTIVES

In this Account, we elucidate recent advances in the synthesis of OMSMOs, especially transition-metal oxides, based on sp^2 -hybridized carbon-containing block copolymers through various coassembly strategies. On the basis of their intrinsic phase-separation behavior and their interaction with inorganic precursors, various OMSMOs have been synthesized by virtue of the supporting effect of residual carbon derived from the soft template during pyrolysis at high temperatures. Recent progress in the synthesis of OMSMOs, such as WO_3 , In_2O_3 , SnO_2 , and ZnO , has been in detail discussed, with emphasis on explaining the unique role of sp^2 -hybridized carbon-containing block copolymers in solving the bottlenecks in the synthesis of mesoporous metal oxides with high crystallization and ordered mesoporous structures.

Despite the current achievements in the synthesis and applications of OMSMOs, there are still considerable challenges and opportunities existing in this field. (1) Since the gas sensing

performance of OMSMOs is directly determined by their pore characteristics including pore structure, pore size, composition, and thickness of pore walls, it is of great importance to widely explore the efficient structural regulation using various sp^2 -hybridized carbon-containing block copolymers. Larger pore is beneficial for the gas diffusion but usually leads to smaller surface area, and thin pore walls can enhance the changes of conductometric chemiresistance in gas sensing process but easily lead to structure collapse. Thus, rational regulation of connectivity of channels, pore size, and thickness of pore walls is meaningful for gas sensing through controlling the ratio and length of hydrophilic/hydrophobic segments. (2) Because doping materials with nonmetal components (e.g., N, C, S, P) or metal ions (e.g., Ni^{2+} , Fe^{3+} , Cr^{3+} , Ce^{4+}) can change energy band and adjust the electronic structure/resistance of OMSMOs, lattice doping or replacement of basal atoms is a promising approach for the design of multifunctional OMSMOs with improved performances in terms of sensitivity and selectivity. (3) Large mesoporous materials can provide abundant adsorption sites for the deposition of noble metals (e.g., Au, Ag, Pt), and these loading active components can reduce the resistance and form heterojunction or Schottky barrier, which is beneficial for the gas sensing process at low working temperatures. (4) Considering that p-n or n-n heterojunction can significantly decrease the steric hindrance and transition distance of electron/hole, designing diverse OMSMOs with novel heterostructures is another important pathway to fabricate gas sensing materials with high sensitivity. (5) Amorphous components like SiO_2 can not only prevent metal oxides from sintering to increase long-term stability but also regulate the adsorption/diffusion behavior of target gas species to adjust the selectivity of gas sensing. Through exploring new synthesis strategies based on the interfacial coassembly of sp^2 -hybridized carbon-containing amphiphilic copolymers, precursors of metal oxides and additives (doping elements, amorphous components, precious metals, etc.), the above-mentioned OMSMOs with improved porous structure, multi-components, and tailored surface property can be created to boost the development of gas sensing. Notably, the development of new OMSMOs is beneficial for their applications in gas sensing and other fields such as catalysis, environmental protection, energy conversion and storage, etc.

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