In Situ Localized Growth of Ordered Metal Oxide Hollow Sphere Array on Microheater Platform for Sensitive, Ultra-Fast Gas Sensing

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Supporting Information

ABSTRACT: A simple and versatile strategy is presented for the localized on-chip synthesis of an ordered metal oxide hollow sphere array directly on a low power microheater platform to form a closely integrated miniaturized gas sensor. Selective microheater surface modification through fluorinated monolayer self-assembly and its subsequent microheaterinduced thermal decomposition enables the position-controlled deposition of an ordered two-dimensional colloidal sphere array, which serves as a sacrificial template for metal oxide growth via homogeneous chemical precipitation; this strategy



ensures control in both the morphology and placement of the sensing material on only the active heated area of the microheater platform, providing a major advantage over other methods of presynthesized nanomaterial integration via suspension coating or printing. A fabricated tin oxide hollow sphere-based sensor shows high sensitivity (6.5 ppb detection limit) and selectivity toward formaldehyde, and extremely fast response (1.8 s) and recovery (5.4 s) times. This flexible and scalable method can be used to fabricate high performance miniaturized gas sensors with a variety of hollow nanostructured metal oxides for a range of applications, including combining multiple metal oxides for superior sensitivity and tunable selectivity.

KEYWORDS: tin oxide, SnO₂, metal oxide, hollow sphere, microheater, on-chip, formaldehyde, gas sensor

INTRODUCTION

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As solid-state gas sensors gain importance in environmental and health monitoring applications, metal oxides remain the most widely used sensing materials due to their chemical stability, ease of synthesis, and sensitivity to numerous gases.¹⁻ However, to achieve the sensitivity and response/recovery rates necessary for practical sensor operation, metal oxides often need to be heated to high temperatures (>250 °C) and are usually paired with heating elements,⁴ whose high power consumption (>500 mW) hinders practical sensor operation in portable, battery-powered devices. Miniaturization of the heater through microfabrication techniques can effectively reduce the power consumption,⁵⁻⁷ but it also decreases the active area available for sensing and the corresponding sensitivity.8 Nanostructured, high surface area metal oxides can be used to compensate for the reduced sensing area. In particular, hollow nanostructures such as nanospheres,9 nanoc $ages_{1}^{20-22}$ and nanotubes $ages_{2}^{23-25}$ can be highly effective sensing materials due to their potential for maximal surface area and permeability, which can facilitate gas diffusion to the active surface sites and drastically increase both the sensitivity and the response/recovery rates.²⁶ Due to their unique properties and applications, various chemical routes have been developed in recent years to synthesize hollow metal oxide nanostructures, using both sacrificial templates (e.g., chemical precipitation/ heterocoagulation^{9,11,14,15,27,28} or layer-by-layer coating^{16,29,30}) and template-free methods (e.g., hydrothermal self-assembly $^{10,12,13,17-19}$ or spray pyrolysis 19,31).

However, the integration of these hollow nanomaterials onto a microheater platform is a significant challenge.^{8,16} Current

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strategies involving drop-casting^{9,10,16,19,24,25,32} or coating^{11,13–15,17,18,20–22} a suspension of the nanomaterials onto the heater platform fail to control their deposition, leading to variable morphology, uncontrolled coverage, loss of surface area from aggregation, and poor electrical contact with the sensing electrodes; these issues are further compounded by the small heated area (<0.01 mm²) available for sensing on a microheater platform. Even the more sophisticated strategy of inkjet printing requires highly specialized nanomaterial suspensions to avoid the risk of clogged printer heads and other equipment damage,^{8,33-35} hindering its utility. Because these challenges in nanomaterial integration arise due to the widespread strategy of off-chip nanomaterial synthesis followed by deposition onto the heater platform, an approach enabling in situ generation of a tailored hollow nanostructure directly on a microheater platform could allow significantly improved control over its morphology and coverage, especially if the microheater surface properties could be suitably managed to facilitate its directed formation.

In this paper, we report the controllable fabrication of a closely integrated miniaturized gas sensor through the localized on-chip growth of an ordered two-dimensional metal oxide hollow sphere array directly on a low power microheater/ sensor platform, using a selectively predeposited colloidal sphere array as a sacrificial template. Colloidal sphere arrays^{36,37} are a useful choice as templates for porous and/or hollow metal oxide structures due to their mechanical stability and ability to self-assemble on various substrates, and have been used in applications such as photonic crystals,³⁸ supercapacitors,³⁹ and gas sensors.^{40–43} However, generation of such an ordered metal oxide structure on a miniaturized heater platform has rarely been explored, with only one group reporting the fabrication of an open macropore array through capillary infiltration of a liquid precursor into the interstitials of a colloidal sphere array during transfer to a microheater chip.^{41,42} In this work, the microheater surface energy is first locally modified in situ to enable selective predeposition of the colloidal sphere array on only the active heated area; then, homogeneous chemical precipitation is used to fully coat each colloidal sphere with a thin metal hydroxide shell, resulting in a uniform array of metal oxide hollow spheres localized on the heated area after microheater-induced calcination. The flexibility of growth via chemical precipitation allows control over the crystallinity, grain size, nanoporosity and shell thickness,²⁶ as well as the growth of multiple concentric shells of different metal oxides to form intricate multishelled heterostructures^{13,17–19,44} with controllable morphology and strong intershell contact for enhanced sensing performance. Furthermore, the use of the microheater for prior in situ surface modification as well as subsequent onchip nanomaterial calcination serves as a novel route to restrict the placement of the generated metal oxide nanostructure to precisely the active heated area of the microheater platform, providing an important advantage over the other reported methods of sensing material integration.

To demonstrate the utility of this strategy, a tin oxide (SnO_2) hollow sphere-based sensor is fabricated and used to detect several gases, exhibiting high sensitivity and selectivity toward formaldehyde and extremely fast response and recovery. Indium oxide (In_2O_3) , nickel oxide (NiO), and double-shell SnO_2 (inner shell)/ In_2O_3 (outer shell) hollow sphere arrays are also fabricated to show versatility. The results demonstrate that this simple, flexible, and reproducible method can enable the fabrication of a superior class of miniaturized gas sensors with high sensitivity, ultrafast response and recovery, and tunable selectivity toward specific gases depending on their constituent metal oxide(s).

RESULTS AND DISCUSSION

Sensor Fabrication and Material Characterization. The fully fabricated sensor (shown schematically in Figure 1a)



Figure 1. (a) Cross-sectional schematic of the fabricated sensor, showing the porous metal oxide hollow sphere array and its integration with the microheater platform. (b) Real-color top-view optical image of a blank 3.5×3.5 mm microheater chip, which contains four heaters. Inset: zoomed in view of one heater site, showing the active heated area (scale bar: 20 μ m).

consists of an area-selected close-packed metal oxide hollow sphere array contacting Pt/Ti electrodes on a low power microheater platform (shown optically in Figure 1b), which consists of a polycrystalline 3C silicon carbide (polySiC) heater embedded in a suspended Si_3N_4 membrane on a Si substrate. Full microheater fabrication and characterization details are provided in our prior report.⁴⁵ The thermal isolation of the polySiC heater from the substrate reduces its heat loss, keeping power consumption low (13 mW to reach 500 °C, as shown in Figure S1 of Supporting Information).

Figure 2 schematically outlines the sensor fabrication process, which combines several independent surface chemistry phenomena to ensure control and reproducibility in the onchip synthesis of the tailored metal oxide hollow sphere array and its integration with the microheater platform.

First, to enable selective formation of the hollow sphere array on only the active heated area of the microheater platform, the entire chip is chemically modified by a thin (~1.4 nm) selfassembled monolayer (SAM) coating of perfluorodecyltrichlorosilane (FDTS) to reduce its surface energy. Pretreatment in UV/ozone is used to introduce a dense layer of terminal hydroxyl groups on the chip surface, which covalently bond to the FDTS molecules' hydrolyzed head groups and facilitate SAM formation.⁴⁶ The highly fluorinated SAM coating drastically reduces the microheater chip surface wettability, observed from the large increase in the water contact angle from $\sim 65^{\circ}$ (on the unmodified chip) to $\sim 111^{\circ}$ (on the modified chip) (Figure S2 of Supporting Information). Subsequent ramping of the microheater to >450 °C in air decomposes⁴⁶ the SAM coating on the heated area, restoring its high surface wettability while preserving the low surface wettability of the rest of the chip; this local surface modification causes the template colloidal sphere array to adhere to only the microheater site and dewet from the reset of the chip (shown in Figure 3), thus localizing the formation of the metal oxide hollow sphere array to only the active heated area of the microheater platform.

Control in the morphology of the sensing material and its integration with the microheater platform is further achieved by

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Figure 2. Sensor fabrication scheme. (a) Microheater chip cross section (microstructural details omitted for clarity). (b) Surface modification of the microheater chip via perfluorodecyltrichlorosilane (FDTS) self-assembled monolayer (SAM). (c) Localized SAM removal using the microheater. (d) Directed PS sphere array self-assembly at the water—hexane interface and transfer to the surface-modified microheater chip. (e) Selective deposition of the PS sphere array onto only the hydrophilic area of the microheater platform. (f) Localized growth of the metal hydroxide (MOH) shell on the PS sphere array template by aging in aqueous chemical bath (consisting of the metal salt, urea, and polyvinylpyrrolidone). (g) Rapid calcination of the grown PS–MOH core—shell array. (h) Fully synthesized porous metal oxide hollow sphere array integrated with the microheater platform.



Figure 3. Real-color optical top-view images of (a) the microheater chip membrane, showing the selective deposition of the PS sphere array on the four heater sites, and (b, c) zoomed in views of one heater site.

use of the highly ordered polystyrene (PS) sphere array (Figure S3 of Supporting Information) as an on-chip sacrificial template for metal oxide chemical growth. Prior self-assembly and transfer of the PS sphere array to the hydrophilic area of the microheater chip provide a uniform, reproducible template for metal oxide growth without the risk of template aggregation, which is a common $issue^{14,15,28}$ in off-chip template-based synthesis that undermines the uniformity of the resulting nanostructure. For simplicity and flexibility, the metal oxide shell is grown by chemical bath precipitation without PS sphere functionalization, electrophoretic deposition, or any such active driving force for metal oxide deposition. A generalized aqueous precursor solution is used, comprising the metal salt, urea, and polyvinylpyrrolidone (PVP). Without an active driving force for material deposition onto the PS spheres, slow and controlled precipitation is essential to obtain uniform growth on their surface rather than in solution.^{26-28,47} At slightly elevated temperatures (~50 °C), aqueous urea decomposes reversibly into ammonia, releasing OH⁻ ions and causing precipitation of the metal hydroxide; this homogeneous generation of OHthroughout the whole solution via in situ urea decomposition, rather than its direct addition in the form of ammonia or other alkaline species, enhances the uniformity of the precipitated nanomaterial.^{27,28,47,48} The presence of PVP as a dispersant also reduces precipitation in solution, resulting in growth primarily on the surface of the PS spheres.^{27,49} For easily hydrolyzed metal salts (e.g., SnCl₄ and TiCl₄), HCl is added to further

control the precipitation rate, as it is a product in the hydrolytic precipitation reaction:

$$MCl_{n(aq)} + nH_2O_{(1)} \rightarrow M(OH)_{n(s)} + nHCl_{(aq)}$$

where M is a general metal. The metal oxide shell thickness and diameter can be easily modified by varying the reaction time and template PS sphere size, respectively. Due to the scalability of the ordered PS sphere array deposition and homogeneity of the precursor solution, uniform metal oxide shell growth can be achieved over an extremely large area, allowing fast and reliable wafer-scale sensor fabrication. Furthermore, because this approach does not require template functionalization, growth of multiple concentric shells of different metal oxides can be accomplished by stepwise immersion and aging of the PS sphere-coated microheater chip in the appropriate precursor solutions. As several reports have shown, these heterostructures can have drastically superior sensing performance, including enhanced sensitivity and selectivity, due to the introduction of heterojunctions and other synergistic effects.^{13,17–19,44}

After the chemical growth step(s), thermal removal of the PS template and full oxidation of the metal hydroxide shell are simultaneously achieved by ramping the microheater to 350 °C for 1 h, creating the metal oxide hollow sphere array. *In situ* calcination using the microheater avoids the need for exposure of the entire chip to external high temperature, which can damage the normally unheated microheater contacts by



Figure 4. (a–c) FESEM images of the SnO_2 hollow sphere array. (d) TEM image of individual SnO_2 hollow spheres. (e) HRTEM image of the SnO_2 hollow sphere shell wall. Inset: HRTEM image showing the SnO_2 shell wall thickness. (f) HRTEM image showing individual SnO_2 grains, with a lattice spacing of 0.33 nm, corresponding to the (110) plane. (g) Relevant SAED pattern of the SnO_2 structure.

oxidation and/or thermal shock. The microheater's fast thermal response time allows an extremely fast heating rate ($\sim 10^5 \, ^{\circ}\text{C} \, \text{s}^{-1}$), which not only preserves the shape of the hollow spheres by preventing deformation ¹⁶ of the template PS spheres from significant time at their glass transition temperature ($\sim 100 \, ^{\circ}\text{C}$) but also substantially increases the porosity of the shell walls through the rapid expulsion of gaseous combustion products, ^{8,16} allowing for fast target gas diffusion to all parts of the inner and outer surfaces during sensor operation.

Figure 4 shows various magnification field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the synthesized SnO₂ hollow sphere array, which is chosen as the main metal oxide sensing material. To demonstrate versatility, In2O3, NiO, and doubleshell SnO_2 (inner shell)/ In_2O_3 (outer shell) hollow sphere arrays are also synthesized and characterized by FESEM in Figure S4 of Supporting Information. As observed from low magnification FESEM (Figure 4a,b), the SnO₂ structure consists of an array of 1-µm diameter hollow spheres that mirrors the template PS sphere array (Figure S3), indicating that there is no movement of the spheres or change in their ordering during the metal oxide chemical growth process. The consistency in the structure and morphology of the hollow spheres is evident, showing the full and uniform material growth; furthermore, the spheres have maintained their shape with none showing signs of collapse, indicating the robustness of the structure. High magnification FESEM (Figure 4b,c) additionally suggests some surface roughness, which can be attributed to the polycrystallinity of the nanostructure. Overall, the hollow sphere array appears well-interconnected by a continuous SnO₂ film, enhancing both its conductivity and mechanical stability.

Low magnification TEM (Figure 4d) further shows the hollow nature of the SnO_2 spheres, as well as significant shell porosity on multiple length scales. A magnified view of the typical SnO_2 hollow sphere shell wall is shown in Figure 4e, where it is seen to be made up of interconnected nanoparticles ~4 nm in diameter separated by abundant and uniformly distributed nanopores. Both the nanoparticles and nanopores

are small and highly monodisperse, the result of uniform and simultaneous nanoparticle nucleation in the chemical bath solution through *in situ* urea decomposition.^{27,28,47,48} The shell wall, a cross section of which is shown in the inset of Figure 4e, is 20 nm thick. Thin shell walls and small constituent nanoparticles enhance both the sensitivity and response/recovery rates during sensor operation due to their increased gas permeability and number of grain contacts in the conductive path.^{1,8,16} From Figure 4f, a lattice spacing of 0.33 nm is observed in the individual nanoparticles, consistent with the (110) plane⁸ of the SnO₂ rutile phase. Complete formation of tetragonal rutile SnO₂ is additionally verified by the corresponding selected area electron diffraction (SAED) ring patterns (Figure 4g), which are readily indexed to its (110), (101), (211), and (310) crystal planes⁸ and show the polycrystallinity of the structure.

X-ray photoelectron spectroscopy (XPS) is conducted to confirm further the composition of the SnO_2 hollow sphere array. From the survey XPS spectrum (Figure S5 of Supporting Information), the presence of Sn and O can be clearly identified from their characteristic binding energies. High resolution spectra of the Sn 3d and O 1s regions are shown in Figure 5a,b, respectively. The Sn 3d region shows two peaks at binding energies of 487.2 and 495.7 eV, which can be indexed to the Sn $3d_{3/2}$ and Sn $3d_{5/2}$ spin states, respectively, and indicate a Sn oxidation state of 4+. The O 1s peak can be separated into two



Figure 5. High-resolution XPS spectra of the (a) Sn 3d and (b) O 1s regions.

peaks, one at 531.2 eV, which can be indexed to O–Sn bonding, and another at 533.4 eV, which is likely from O–Si bonding from a layer of SiO₂ on the substrate; the presence of this SiO₂ layer is further confirmed by analyzing the Si 2p region (Figure S5), which exhibits a peak at 103.5 eV, attributed to a Si oxidation state of 4+. Thus, the measured Sn⁴⁺ and O²⁻ oxidation states and the absence of an O–H bonding or Cl peak verify full conversion of the SnCl₄ precursor into SnO₂, with no residual presence of SnCl₄ or Sn(OH)₄. From the peak areas, the calculated O to Sn ratio is 1.85, further confirming the chemical composition of the SnO₂ structure; the slight oxygen deficiency compared to the stoichiometric ratio of 2 can be attributed to surface defects such as O vacancies and/or Sn interstitials that can readily form given their low activation energies.^{50,51}

Sensor Performance. The sensing performance toward formaldehyde and other common polluting gases is investigated for the SnO₂ hollow sphere-based sensor. Formaldehyde (CH₂O) is a toxic and carcinogenic reducing gas that may cause poisoning at concentrations as low as 1 ppm,⁵² making its accurate detection important. The typical conductometric gas sensing mechanism for SnO₂, an *n*-type metal oxide, is based on the reaction between chemisorbed oxygen species on the metal oxide surface and the reducing gas, which releases electrons back into the metal oxide bulk and decreases the thickness of the depletion layer initially caused by the oxygen chemisorption, thus decreasing the metal oxide resistance.^{1,44,51} It is known that the sensor operating temperature affects both the response and response/recovery times due to its simultaneous effects on gas adsorption/desorption, diffusion, and reaction rates.¹ Figure 6a shows the effect of temperature on the SnO₂ sensor's response (calculated as $R_{\rm air}/R_{\rm gas}$, where $R_{\rm air}$ and $R_{\rm gas}$ are the resistance of the sensing material when exposed to air and the target gas, respectively) toward 0.5 ppm of CH₂O. As can be observed, the response rises to a maximum at 250 °C and then declines with increasing temperature. At low temperatures the response is limited by the surface reaction rate, which increases with temperature, whereas beyond a certain temperature the response decreases due to both a decrease in the initial concentration of chemisorbed oxygen as well as mass transfer limitations (compared to the fast reaction kinetics) that decrease the penetration of the CH₂O to all the metal oxide surface sites.^{1,17} Figure 6b shows the effect of temperature on the response and recovery times (calculated as the time taken for the resistance to reach 90% of its total change, t_{90}) for the sensor toward 0.5 ppm of CH₂O. Both the response and recovery times decrease with increasing temperature, due to the increase in gas reaction, adsorption/desorption, and diffusion rates.²⁶ To balance both the sensitivity and response/recovery time, 300 °C is chosen as the operating temperature, at which the microheater consumes only ~7.5 mW, significantly lower than commercial sensors.

A representative plot of the dynamic resistance of the SnO_2 sensor over time for increasing exposures to CH_2O at 300 °C is shown in Figure 6c. When the sensor is exposed to CH_2O , the resistance rapidly drops to a steady state level, and when the gas is removed, rises back to its baseline. Both the baseline and response resistances are stable with low noise, due to the strong material contact and close integration of the sensing material with the microheater platform. Figure 6d shows the sensor response as a function of CH_2O concentration. At lower concentrations (up to 1 ppm) the response is linear as most of the SnO_2 surface sites are unoccupied, whereas at higher



Figure 6. (a) Temperature dependence of the SnO₂ sensor response to 0.5 ppm of CH₂O. (b) Temperature dependence of sensor response and recovery time to 0.5 ppm of CH₂O. (c) Real-time sensor resistance when exposed to increasing concentrations of CH₂O at 300 °C. (d) Sensor response versus CH₂O concentration at 300 °C. Inset: zoomed in plot of the sensor response to <0.3 ppm of CH₂O. (Error bars indicate the standard deviation of the response of multiple devices; if not visible, error bars are within their respective markers.) (e) Real-time sensor response when exposed to 0.5 ppm of CH₂O at 300 °C, showing the ultrafast response and recovery (t_{90} values provided).

concentrations the response gradually plateaus as the surface sites begin to saturate. However, even at 10 ppm the response has not plateaued completely, suggesting that the sensor can detect higher CH₂O concentrations as well. Additionally, there is a clear response to 0.05 ppm of CH₂O, the lowest concentration accurately deliverable by our gas delivery system, with a signal-to-noise ratio of 23. Using the conventional signalto-noise threshold of 3, we calculate the detection limit of the SnO_2 sensor to be 6.5 ppb; considering that >1 ppm of CH_2O is required for poisoning,⁵² the sensor shows excellent sensitivity for practical use. The high sensitivity is enabled by the high surface area and small grain size (\sim 4 nm diameter) of the SnO₂ nanostructure, which maximizes the effect of the changing electron depletion layer thickness on its overall resistance.¹ It has been shown that in nanostructures with grains of diameter less than twice the Debye length (~3 nm for SnO₂ at 300 °C),⁴¹ the electron depletion layer extends throughout the entire grain and therefore results in maximal sensitivity.^{1,26,44} Furthermore, due to the high gas permeability afforded by its porous hollow structure and thin shell (~20 nm), the sensor exhibits extremely fast response and recovery at 300 °C (shown for 0.5 ppm of CH₂O in Figure 6e), with average t_{90} response and recovery times of 1.8 and 5.4 s, respectively, over all concentrations; this is significantly faster

than most other porous and hollow nanostructure-based sensors, which often take >5 s for response and >20 s for recovery.^{12,15,17–19} Vital to preventing prolonged undetected exposure to CH₂O and other toxic gases, the fast response and recovery further demonstrates the merits of this hollow nanostructure-based sensor fabrication method.

In addition to sensitivity and response/recovery rate, selectivity is a crucial metric of sensor performance, and one that has been a source of difficulty^{44,51} in metal oxide sensor development. The selectivity of the SnO₂ sensor is probed by testing its response to high concentrations of other typical toxic and combustible reducing gases, specifically carbon monoxide (CO), propane (C_3H_8), and methane (CH₄). As shown in Figure 7, the SnO₂ sensor's response at 300 °C to 1 ppm of



Figure 7. Selectivity of the SnO₂ sensor at 300 °C.

CH₂O is considerably greater than its response to 30 ppm of CO, 500 ppm of C₃H₈, and 500 ppm of CH₄, all much higher concentrations. Clearly, the sensor shows excellent selectivity to CH₂O over the other typically encountered gases. Although the exact mechanism behind this selectivity is not certain, it is well-known that a sensing material's surface structure and electronic characteristics have a strong effect on its interaction with various gases.^{1,51} The observed selectivity may be due to preferential adsorption and reaction of the CH₂O molecules at the defect sites on the SnO₂ surface, or a catalytic effect that accelerates the CH₂O surface reaction over those of the other gases.

CONCLUSION

In summary, we have developed a simple, controllable, and versatile route for the localized on-chip growth of an ordered metal oxide hollow sphere array directly on a low power microheater platform to form a closely integrated miniaturized gas sensor. Localized surface modification of the microheater chip ensures selective deposition of a colloidal sphere array template on only the active heated area, and the use of this highly ordered array as a template for metal oxide chemical growth allows controllability in nanomaterial morphology and porosity, lending reproducibility to the sensor fabrication. Using SnO₂ as the sensing material, the resulting sensor exhibits high sensitivity (6.5 ppb detection limit) and selectivity to formaldehyde and ultrafast response (1.8 s) and recovery (5.4 s) due to its small grain size (\sim 4 nm) and high surface area. This strategy of in situ hollow nanostructure growth greatly simplifies and strengthens the integration of the sensing material with the microheater platform, avoiding issues of nanomaterial aggregation and poor electrical contact that conventional methods of presynthesized material integration

face and maximizing sensing performance. Furthermore, due to its flexibility and scalability, this method can be extended to various other metal oxides as well as combinations thereof, thus enabling the fabrication of hollow nanostructure- and heteronanostructure-based gas sensors with optimized sensitivity, response/recovery rate, and selectivity for increasingly diverse applications.

EXPERIMENTAL SECTION

Microheater Fabrication and Localized Surface Modification. The microheater platform consisted of a polycrystalline 3C silicon carbide heater embedded in a suspended Si_3N_4 membrane on a Si substrate, and was fabricated using micromachining technology as detailed in our prior report.⁴⁵ A monolayer of perfluorodecyltrichlorosilane was self-assembled on the microheater chip to reduce its surface energy, based on our previously developed procedure.⁴ Briefly, the microheater chip was cleaned with deionized water, acetone, and isopropanol for 5 min each and UV/ozone for 20 min, followed by immersion in 0.1 vol % FDTS (Alfa Aesar) in isooctane in a low humidity chamber (<10% RH) for 60 min. The chip was then cleaned with isooctane and isopropyl alcohol for 5 min each and heated at 130 °C in air for 30 min to stabilize the FDTS coating. The contact angle of deionized water on the microheater chip was measured using a Ramé-Hart model 290 tensiometer. The microheater was then powered to 600 °C for 5 min to decompose thermally the FDTS self-assembled monolayer at the heater site and ensure the selective growth of the sensing nanostructure.

Polystyrene Sphere Array Deposition. A suspension of unfunctionalized PS spheres (Polysciences, 1 μ m diameter, 2.5 wt % in water) was further diluted with deionized water and ethanol to form a 1:49:50 wt % PS:water:ethanol suspension. 50 μ L of the PS sphere suspension was added to a beaker filled with layers of water and hexane, and 10 μ L of 3 wt % sodium dodecyl sulfate (aq) was added to promote self-assembly of the PS spheres into a close-packed two-dimensional array at the water-hexane interface. The PS sphere array was then carefully picked up by the surface-modified microheater chip, which was dried overnight in air.

Metal Oxide Growth. For SnO2 shell growth, the PS spherecovered microheater chip was immersed in a 10 mL aqueous solution containing 0.001 M SnCl₄ (Allied Chemicals), 0.05 M urea (Qiagen), 0.25 M HCl, and 10 g/L polyvinylpyrrolidone (Sigma-Aldrich, MW 360 000 g/mol) in a capped vial and aged for 22 h at 50 $^\circ$ C. For In₂O₃ shell growth, the PS sphere-covered microheater chip was immersed in a 10 mL aqueous solution containing 0.001 M InCl₃ (Strem Chemicals), 0.05 M urea, and 10 g/L PVP in a capped vial and aged for 4 h at 50 °C. For NiO shell growth, the PS sphere-covered microheater chip was immersed in a 10 mL aqueous solution containing 0.001 M Ni(NO₃)₂ (Alfa Aesar), 0.05 M urea, and 10 g/L PVP in a capped vial and aged for 4 h at 85 °C. For all sensors, after the growth steps the microheater chip was rinsed several times with deionized water and dried in air. Finally, the microheater was powered to 350 °C for 1 h to remove thermally the PS templates and fully oxidize the grown shell into hollow spheres, using an instantaneous heating rate (~10⁵ °C s⁻¹).

Material Characterization. Morphology characterization was performed using a Zeiss Gemini Ultra-55 FESEM and a Hitachi S-5000 FESEM. Further characterization was performed using a JEOL 2010 HRTEM, for which the grown material was removed from the substrate by sonication in isopropyl alcohol. Elemental composition was characterized by XPS using an Omicron Dar400 system with an achromatic Al K α X-ray source, for which the material was grown on a Si substrate with interdigitated Au (100 nm) electrodes or a Au (100 nm)-coated Si substrate, in order to prevent extraneous signals from the various elements of the microheater chip.

Gas Sensor Testing. The microheater chip containing the previously grown SnO_2 hollow sphere array was wire-bonded to a 14-pin ceramic dual inline package and placed within a 1 cm³ gas flow chamber. A LabView-controlled gas delivery system was used to flow individually formaldehyde (Praxair, 21.4 ppm in N₂), carbon monoxide

(Praxair, 5000 ppm in N_2), propane (Praxair, 50 000 ppm in N_2), and methane (Praxair, 50 000 ppm in N_2) at room temperature at a constant flow rate of 300 sccm using Bronkhorst mass flow controllers to vary their concentration. The stream balance and purge consisted of house air that was dehumidified using a pressure swing adsorption dryer and decontaminated using an activated carbon scrubber. Sensor measurements were conducted with a Keithley 2602 source-meter, which applied a bias voltage through both the sensor and heater channels and measured their currents to monitor the sensor response and heater temperature, respectively. An open-source Java-based software called Zephyr was used to control and collect data from both the gas delivery system and the source-meter.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b12677.

Characterization of microheater power consumption; characterization of microheater chip surface modification; FESEM images of large-area polystyrene sphere array deposition; FESEM images of In_2O_3 , NiO, and SnO_2/In_2O_3 (double-shell) hollow sphere array; survey XPS spectrum of the SnO_2 hollow sphere array; survey and high-resolution XPS spectra of the SnO_2/In_2O_3 (double-shell) hollow sphere array (PDF)

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Notes

The authors declare no competing financial interest.

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