**In situ** gold nanoparticle-decorated three-dimensional tin dioxide nanostructures for sensitive and selective gas-sensing detection of volatile organic compounds

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Sensitive and selective gas sensors for the detection of volatile organic compounds are highly desired. A composite consisting of a specific structure modified with a noble metal catalyst is considered as a promising sensing material candidate. Herein, we present a three-dimensional tin dioxide (SnO2) nanostructure in situ-decorated with gold nanoparticles (AuNPs) on the surface; this nanostructure exhibited high gas-sensing performance including high response and selectivity towards volatile organic compounds. To achieve high-loading of AuNPs, 3-aminopropyltrimethoxysilane (APTMS) functionalization was conducted on the surface of SnO2/carbonaceous precursors prior to the AuNPs growth. The vapors of volatile organic compounds, such as acetone, methanol, and hexane, were employed as analytes for gas-sensing measurements. The results show that the SnO2 nanostructures decorated with dense AuNPs exhibit remarkably better gas-sensing performance as compared to SnO2 with few AuNPs and pure SnO2. In addition, gas sensors based on three-dimensional AuNP-decorated-SnO2 showed high recognition ability towards different analytes in combination with a principal component analysis method, indicating their promising practical application for gas environment monitoring.

1. Introduction

Nanostructured sensing materials have been extensively investigated for environment monitoring applications due to their unique chemical and physical properties.1–6 In recent years, nanomaterial-based gas sensor is one of the important electronic detection devices applied in industrial production and our daily life and has received significant attention.7–11 Significant efforts have been contributed to the synthesis of gas-sensing nanostructures, demonstration of sensing mechanism,12 and fabrication of sensors based on nanomaterials such as single nanowire, nanotube, etc.13–16 For example, Gouma et al. have reported a ferroelectric WO3 nanoparticle-based sensor, which exhibits response to low concentrations of acetone (0.2–1 ppm).17 Karmaoui et al. have shown that In2O3–Pt nanoparticle-based sensors possess a detection limit as low as 10 ppb or less towards acetone.18

As an n-type semiconductor with a wide band gap of 3.6 eV, tin dioxide (SnO2) has been of significant interest for use in chemical gas sensors, transparent conductive electrodes, anodes for lithium-ion batteries, dye-sensitized solar cells, and so on.19–22 Previous reports have confirmed that the performance of SnO2-based gas sensors is greatly influenced by the structure and morphology of the SnO2 materials. For example, Wang et al. synthesized SnO2 nanocrystals with a porous hierarchical structure, and these nanocrystals exhibited high selectivity towards chlorine.23 Fang et al. reported biomorphic SnO2 with an architecture-hierarchy of butterfly wings, which exhibited high sensitivity towards ethanol even at low working temperature (170 °C).24 However, the pure SnO2 nanomaterials still suffer from the limitations of having less defects and active sites that are very important for gas-sensing response. As a result, fabricating nanocomposites that can introduce large amount of active sites for
sensing reactions would be a promising strategy to enhance the performance of the nanostructured SnO2-based gas sensors.

Gold nanoparticles (AuNPs) have been used as Raman sensors, catalysts, and photoelectrochemical materials because of their special electronic and catalytic properties. The AuNPs act as electron traps that prevent the rapid recombination of electrons and holes, leading to the improvement of electronic performance. Singh et al. have reported that a gas sensor based on AuNP-decorated In2O3 nanowires can exhibit a high response towards CO at low concentrations. The presence of AuNPs reduces the Schottky barrier in sensing reactions. To date, fabrication of a specific nanostructure cooperated with AuNPs to achieve a high gas-sensing response and selectivity still remains a great challenge.

Previously, we synthesized a three-dimensional (3D) coral-like SnO2 nanostructure that exhibited a fast diffusion and adsorption-desorption performance when used in dye-sensitized solar cell and sensor. In the present investigation, the 3D SnO2 nanostructures were used as host materials for the in situ growth of AuNPs on the surface, as shown in Fig. 1. First, amino groups were modified on the surface of the coral-like SnO2/carbonaceous precursors using 3-aminopropyltrimethoxysilane (APTMS) as a source. Then, the AuNPs in situ grew on the surface of precursors under a refluxing condition. The amino groups could effectively coordinate with the growing nuclei of the gold seeds, thereby improving the density of gold seeds on the SnO2/carbonaceous nanocomposites. Finally, the as-prepared samples were annealed in air to remove the carbonaceous components, resulting in the formation of 3D AuNP/SnO2 nanostructures for fabricating gas sensors. In gas-sensing measurements, volatile organic compounds (VOCs), including acetone, methanol, and hexane, were employed as target analytes. The gas-sensing properties of the AuNP/SnO2 with high or low density of AuNPs as well as those of pure SnO2 were comprehensively compared in. The gas-sensing responses, response and recovery times, and recognizable ability to analytes were investigated using a principal component analysis (PCA) method.

2. Experimental

2.1 Synthesis of the 3D SnO2/carbonaceous precursors

All chemicals were of analytical grade and used without further purification as purchased from Shanghai Chemical Reagents Company. The coral-like SnO2/carbonaceous precursors were synthesized through a hydrothermal route, as reported earlier. Typically, 0.1 g of the SnO2/carbonaceous precursors functionalized by APTMS with ammonia groups was transferred to a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was sealed and heated in an oven at 170 °C for 6 h. After the completion of the reaction, brown precipitates were obtained via centrifugation and alternately washed several times with ethanol and deionized water. Finally, the samples were dried in a vacuum oven at 60 °C for 6 h.

2.2 Functionalization of the SnO2/carbonaceous precursors with APTMS

To achieve a dense growth of the AuNPs, the SnO2/carbonaceous precursors were functionalized with ammonia groups using APTMS prior to the growth process. The as-synthesized precursors (0.2 g) were placed in a solution containing ethanol (20 mL) and APTMS (5 mL) and stirred at room temperature for 12 h. Then, the samples were obtained, washed with ethanol to remove excess APTMS, and dried in a vacuum oven at 60 °C for further use.

2.3 Preparation of the AuNP/SnO2 nanocomposites

The AuNPs were prepared through the reduction of gold chloride (HAuCl4) by sodium citrate (Na3C6H5O7). Typically, 0.1 g of the SnO2/carbonaceous precursors functionalized by APTMS and 2 mL of sodium citrate were added to a boiling aqueous solution (100 mL) that contained 1 mL of HAuCl4. After sometime, the solution turned into brilliant red. Then, it was boiled for half an hour. After the completion of the reaction, the brown precipitates were obtained via centrifugation, alternately washed several times with ethanol and deionized water, and dried in a vacuum oven at 60 °C for 6 h. Finally, the samples were annealed in air at 550 °C for 1 h in a furnace at a ramp rate of 10 °C min⁻¹.

2.4 Characterization

The samples were characterized via a Philips X’Pert Pro X-ray diffractometer (XRD) with Cu Kα radiation (1.5418 Å), an FEI Sirion 200 field emission scanning electron microscope (FESEM), and a JEOL JEM-2010 transmission electron microscope (TEM) equipped with an Oxford INCA energy dispersive X-ray (EDX) spectrometer, operating at an accelerating voltage of 200 kV. The diffraction peaks of the crystalline phases were compared with the patterns in the Joint Committee on Powder
Diffraction Standards (JCPDS). The elemental mappings and the line scans were performed in the high-angle annular dark-field (HAADF) mode using the same TEM. The composition analysis was carried out via an ESCALab MK II X-ray photoelectron spectrometer (XPS) using monochromatized Al Kα X-ray beams as the excitation source. Binding energies were calibrated relative to the C 1s peak at 284.6 eV. Fourier transform infrared (FT-IR) absorption spectrum was obtained via a Shimadzu IR-440 spectrometer. The Brunauer–Emmett–Teller (BET) surface area of the samples was measured using a Coulter Omnisorp 100CX instrument via N₂ adsorption–desorption isotherms.

2.5 Gas sensor fabrication and measurements

The as-prepared nanostructures were dispersed in absolute alcohol and coated onto the surface of a SiO₂ substrate that was covered with comb-like gold electrodes and a RuO₂ layer as a heater on the back side. The sensors were dried in an oven at 80 °C. To enhance the repeatability of gas-sensing performance, gas sensors were aged for 48 h before each measurement. The gas-sensing measurements were conducted using a computer-controlled gas-detecting system in which a Keithley-6487 picoammeter/voltage sourcemeter was used as both the current and voltage source. All measurements were carried out at the same working temperature (200 °C) of gas sensors and humidity in the detecting chamber (ca. 60% RH). Volatile organic compounds including acetone, methanol, and hexane at a series of concentrations ranging from 50 to 300 ppm were employed as gas analytes. For comparing the gas-sensing performances of different samples, the gas responses towards each analyte at 100, 200, and 300 ppm were also measured.

\[
S = \frac{R_{\text{air}}}{R_{\text{gas}}} \left( \frac{I_{\text{gas}}}{I_{\text{air}}} \right) V
\]

The response of the sensor is defined as eqn (1), where \( R_{\text{air}} \) is the resistance of the sensor in pure air and \( R_{\text{gas}} \) is the resistance of the sensor in the gas mixture of pure air and target gas. According to Ohm’s Law, \( S \) can be presented by the ratio of the currents in gas mixture (\( I_{\text{gas}} \)) and pure air (\( I_{\text{air}} \)) under a constant measuring voltage. In addition, the response and recovery times were determined by the times required for the sensor to achieve 90% of the total resistance change in the cases of gas injection and discharge, respectively.

3. Results and discussion

3.1 Structure and composition of the as-prepared nanostructures

The XRD patterns of the pure samples and those decorated with AuNPs are shown in Fig. 2. Note that AuNP-decorated SnO₂ with APTMS functionalization indicates that APTMS functionalization treatment towards the SnO₂/carbonaceous precursors was successfully conducted before the AuNPs growth. In contrast, for the AuNP-decorated SnO₂ without APTMS, no APTMS functionalization treatment was carried out. In the XRD patterns, the peaks corresponding to the rutile structure of SnO₂ (JCPDS No. 41-1445) are presented. For samples decorated with AuNPs with APTMS functionalization (Fig. 1c), the diffraction peaks of gold were clearly detected as compared to the those of the samples without APTMS functionalization, indicating higher loading of gold in the AuNP/SnO₂ nanostructures with APTMS functionalization. The APTMS functionalization was able to provide additional amino groups (–NH₂) to enhance the attraction of gold seeds onto the SnO₂/carbonaceous precursors because of the coordination effect between the isolated pair of electron in the nitrogen atom and the gold nuclei. In addition, the enlarged full width at half maximum (FWHM) of the AuNP-decorated SnO₂ as compared to that of pure SnO₂ indicated a reduced grain size. The XRD patterns of (a) pure SnO₂, (b) AuNP-decorated SnO₂ without APTMS functionalization, and (c) AuNP-decorated SnO₂ with APTMS functionalization.

Fig. 3 shows the FESEM and TEM images of the AuNP/SnO₂/carbonaceous precursors and AuNP/SnO₂ without or with APTMS functionalization. All the samples show a 3D corallike morphology. In Fig. 3a and b, there are a few gold particles on the surface of the AuNP/SnO₂/carbonaceous precursors without APTMS functionalization. In contrast, for the AuNP/SnO₂/carbonaceous precursors with APTMS (Fig. 3c and d), there were dense particles decorated on the surface of corallike nanostructures, exhibiting high loading of AuNPs as compared to that on the samples without APTMS functionalization. In Fig. 3e–h, after the annealing treatment, the density of the AuNPs in the AuNP/SnO₂ composites with APTMS functionalization remarkably exceeded that of the composites without APTMS treatment.

Fig. 4 shows the FT-IR spectrum of the SnO₂/carbonaceous precursors after APTMS functionalization. The peaks at 1140 cm⁻¹ can be assigned to the stretching and bending vibrations of C–N; the characteristic band of N–H vibration locates at ca. 1610 cm⁻¹, indicating that the APTMS has been modified onto the surface of the SnO₂/carbonaceous precursors. The quantitative results were further investigated using XPS analysis and elemental mappings. In Fig. 5, the gold signals were detected in AuNP/SnO₂ with and without APTMS. In addition, we found...
that the intensity and area of the gold peak of the AuNP/SnO$_2$ nanostructures with APTMS were remarkably larger than those of AuNP/SnO$_2$ without APTMS, confirming that the amount of gold in AuNP/SnO$_2$ with APTMS was much more than that in the samples without APTMS.

Fig. 6 shows the BET surface area and pore-size distribution of the AuNP-decorated SnO$_2$ with APTMS functionalization. The BET surface area of AuNP/SnO$_2$ with APTMS was ca. 55.3 m$^2$ g$^{-1}$, which was obviously larger than that of pure SnO$_2$ (35.6 m$^2$ g$^{-1}$), indicating that the presence of AuNPs increased the BET surface area. As shown in Fig. 6b, the pore diameter centers at about 13.1 nm. The elemental distribution of the AuNP/SnO$_2$ nanostructures with APTMS was further obtained via the elemental mappings of Sn L$_{\alpha_1}$ and Au L$_{\alpha_1}$, as shown in Fig. 7. The profile of Au L$_{\alpha_1}$ was close to that of Sn L$_{\alpha_1}$, indicating that gold was uniformly and densely distributed throughout the 3D coral-like SnO$_2$ nanostructures.

Fig. 3 TEM images of the AuNP/SnO$_2$/carbonaceous precursors (a) and (b) without and (c) and (d) with APTMS functionalization; FESEM images of the AuNP-decorated SnO$_2$ composites (e) and (f) without and (g) and (h) with APTMS functionalization.

Fig. 4 FT-IR spectrum of the SnO$_2$/carbonaceous precursors after APTMS functionalization.

Fig. 5 (a) XPS survey spectra of the AuNP/SnO$_2$ nanostructures with (red line) and without (black line) APTMS functionalization; (b) XPS spectrum of the Au 4f region of AuNP/SnO$_2$ with APTMS.
Fig. 6  (a) Typical N\textsubscript{2} adsorption–desorption isotherm and (b) the pore-size distribution curve of the AuNP/SnO\textsubscript{2} nanostructures with APTMS functionalization.

Fig. 7  (a) TEM image of AuNP/SnO\textsubscript{2} with APTMS functionalization; elemental mappings of (b) Sn L\textsubscript{a}1 and (c) Au L\textsubscript{a}1.

Fig. 8  Real-time gas-sensing curves of the sensors based on the AuNP/SnO\textsubscript{2} nanostructures with APTMS functionalization towards (a) hexane, (b) acetone, and (c) methanol; (d) the calculated responses; and (e) logarithm relationship between the gas response and concentration.
Table 1  Comparison of the gas-sensing responses among the as-prepared AuNP/SnO$_2$ nanostructures with APTMS functionalization and the nanostructures reported in previous studies

<table>
<thead>
<tr>
<th>Sensing nanomaterials</th>
<th>Operating temperature (°C)</th>
<th>Gas concentration: sensing response ((I_{gas}/I_{air}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D hierarchical carbon-doped ZrO$_2$</td>
<td>25</td>
<td>500 ppm acetone: 63.5</td>
<td>38</td>
</tr>
<tr>
<td>Co$_3$O$_4$ nanocubes</td>
<td>240</td>
<td>500 ppm acetone: 4.88</td>
<td>39</td>
</tr>
<tr>
<td>Porous In$_2$O$_3$–CeO$_2$ binary oxide nanotubes</td>
<td>300</td>
<td>300 ppm acetone: ~30</td>
<td>40</td>
</tr>
<tr>
<td>Nb-Doped ZnO nanowall</td>
<td>200</td>
<td>100 ppm acetone: ~20</td>
<td>41</td>
</tr>
<tr>
<td>2-Fe$_2$O$_3$ nanorods</td>
<td>280</td>
<td>100 ppm acetone: 32.5</td>
<td>42</td>
</tr>
<tr>
<td>ZnO/graphene (ZnO–G) hybrid composites</td>
<td>280</td>
<td>100 ppm acetone: 13.3</td>
<td>43</td>
</tr>
<tr>
<td>WO$_3$ nanotubes</td>
<td>340</td>
<td>300 ppm hexane: ~3.5</td>
<td>44</td>
</tr>
<tr>
<td>Nanocrystalline perovskite oxides LnFeO$_3$ (Ln = La, Nd, and Sm)</td>
<td>200</td>
<td>300 ppm hexane: ~2</td>
<td>45</td>
</tr>
<tr>
<td>Ti(n) chelate with 2,2-bipyridine-N$_2$N-dioxide</td>
<td>30</td>
<td>1000 ppm methanol: 8</td>
<td>46</td>
</tr>
<tr>
<td>Zn doped MoO$_3$ nanobelts</td>
<td>273</td>
<td>1000 ppm methanol: 55</td>
<td>47</td>
</tr>
<tr>
<td>PbS quantum dots/TiO$_2$ nanotubes arrays</td>
<td>Room temperature</td>
<td>100 ppm methanol: ~3</td>
<td>48</td>
</tr>
<tr>
<td>Honeycomb-like SnO$_2$ grown on silicon nanoporous pillar array</td>
<td>320</td>
<td>300 ppm methanol: 33</td>
<td>49</td>
</tr>
<tr>
<td>Co$_3$O$_4$ nanorod arrays</td>
<td>160</td>
<td>500 ppm methanol: 38.8; 500 ppm acetone: 13.3</td>
<td>50</td>
</tr>
<tr>
<td>3D AuNPs/SnO$_2$ nanostructures with APTMS functionalization</td>
<td>200</td>
<td>300 ppm hexane: 69.2</td>
<td>Our study</td>
</tr>
</tbody>
</table>

3.2 Gas-sensing performance

Fig. 8 shows the gas-sensing performance of the sensor based on AuNP-decorated SnO$_2$ with APTMS functionalization towards hexane, acetone, and methanol. In Fig. 8a–c, it can be observed that when the gas analytes are injected into the test chamber, the current of the sensors rapidly increases, indicating that the AuNP/SnO$_2$ nanostructures are sensitive to target gases. It was supported by the calculated responses, as shown in Fig. 8d. For example, the gas responses to 50, 100, 150, 200, 250, and 300 ppm hexane were ca. 6.1, 18.7, 33.1, 42.1, 57.7, and 69.2, respectively. The gas-sensing responses towards hexane, acetone, and methanol were far high as compared to those of previously reported nanostructures, as shown in Table 1; this indicates potential application of the semiconductor-based sensors in trace VOCs monitoring, which have attracted extensive attention. In addition, both the response and recovery times were short. The response and recovery times towards 300 ppm hexane were about 4.5 and 32.5 s, respectively. The sensitive performance perhaps can be ascribed to the nano-sized SnO$_2$ with high reaction activity, the 3D structure, which is beneficial for gas diffusion and target adsorption, and the electron transfer effect of the gold nanoparticles. It was considered that both the reactivity of sensing materials and gas diffusion performance would be significant impact factors for the response/recovery time. To shorten the response/recovery time, improvement of the reactivity of the sensing materials via reducing the size of materials, doping, and decorating with noble metal particles was promising. In addition, a porous and 3D structure was beneficial for the adsorption of a target gas molecule and sensing desorption of reaction products, which was helpful for increasing the response/recovery speeds. The decoration of AuNPs on the SnO$_2$ nanostructures would induce electronic sensitization, resulting in larger amount of the electrons being transferred from the conduction band of SnO$_2$ to gold than to the SnO$_2$, as illustrated in Fig. 9. Thus, it forms a greater band bending at the Au/SnO$_2$ interface with a broad depletion layer. The existence of this additional depletion layer at the Au/SnO$_2$ interface enables greater change in the resistance of the sensor when it is exposed to the target gases. Fig. 8e shows a good linear relationship between the logarithm of gas concentration and the logarithm of response, indicating that the sensors possess a wide detection range of the gas analytes. The linear relationship of \(\lg C\) versus \(\lg S\) towards hexane, acetone, and methanol can be presented as \(y = 1.34x - 1.46, y = 1.89x - 2.30,\) and \(y = 1.19x - 0.90,\) respectively.

In contrast, Fig. 10a and b show the real-time response curves of the sensors based on the AuNP/SnO$_2$ nanostructures without APTMS functionalization and pure SnO$_2$ towards hexane, acetone, and methanol, respectively. The responses of AuNP/SnO$_2$ without APTMS were higher than those of pure SnO$_2$. Moreover, the responses of both AuNP/SnO$_2$ without APTMS and pure SnO$_2$ were remarkably lower than those of AuNP/SnO$_2$ with APTMS, as shown in Fig. 11. Since the density of the AuNPs in the nanocomposites without APTMS functionalization was low, it indicated that the gas-sensing response
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significantly improved by dense AuNPs. The mechanism for this enhancement can be described as follows: the AuNPs decorated at the boundary of the conjoint SnO$_2$ particles reduced the particle size of SnO$_2$, which was supported by the XRD patterns, as demonstrated above. Smaller particle size improved the surface area for gas adsorption and surface reactions, also leading to an improved sensing response.

Furthermore, the recognizable ability of the proposed gas sensors based on AuNP/SnO$_2$ with APTMS functionalization towards different targets was also studied by PCA method, as shown in Fig. 12. The PCA method is a conventional approach for data classification with specific characters, which transforms originally correlated variables to a new set of principal components (PCs). The PCs are sorted in an order such that the first few PCs (such as PC1 and PC2) remain in most of the variations shown in the original variables. Herein, the variances explained in PC1 and PC2 were 74.5% and 13.7%, respectively. It clearly showed that the characters extracted from the gas-sensing processes towards different analytes and some interference gases, such as benzene and diethyl ether (the concentrations were 50, 100, 150, 200, 250, and 300 ppm) for measurements, were located at a specific region far from each other, suggesting that different analytes could be obviously identified by the sensors combined with a PCA method.

4. Conclusions

In summary, a 3D SnO$_2$ nanostructure decorated with dense AuNPs was presented for the fabrication of gas sensors. The loading of AuNPs in AuNP/SnO$_2$ can be significantly improved...
via APTMS functionalization towards the SnO$_2$/carbonaceous precursors before the AuNPs growth. The fabricated gas sensors exhibited high gas-sensing performance for the detection of volatile organic compounds, which was attributed to the specific structure, enabling a gas diffusion environment, and the gold particles, providing numerous catalytic sites for gas-sensing surface reactions. Compared to the AuNP/SnO$_2$ without APTMS particles, providing numerous catalytic sites for gas-sensing structure, enabling a gas diffusion environment, and the gold volatile organic compounds, which was attributed to the specific functionalization and the pure SnO$_2$ nanostructures, AuNP/SnO$_2$ with APTMS functionalization exhibited both higher response and shorter response/recovery times. In addition, the proposed gas sensors show high recognizable ability towards different targets by combining with a PCA method, thereby indicating a promising application in practice.

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Notes and references