Ag Nanoparticles Sensitized In\textsubscript{2}O\textsubscript{3} Nanograin for the Ultrasensitive HCHO Detection at Room Temperature

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Abstract

Formaldehyde (HCHO) is the main source of indoor air pollutant. HCHO sensors are therefore of paramount importance for timely detection in daily life. However, existing sensors do not meet the stringent performance targets, while deactivation due to sensing detection at room temperature, for example, at extremely low concentration of formaldehyde (especially lower than 0.08 ppm), is a widely unsolved problem. Herein, we present the Ag nanoparticles (Ag NPs) sensitized dispersed In\textsubscript{2}O\textsubscript{3} nanograin via a low-fabrication-cost hydrothermal strategy, where the Ag NPs reduces the apparent activation energy for HCHO transporting into and out of the In\textsubscript{2}O\textsubscript{3} nanoparticles, while low concentrations detection at low working temperature is realized. The pristine In\textsubscript{2}O\textsubscript{3} exhibits a sluggish response (R\textsubscript{a}/R\textsubscript{g} = 4.14 to 10 ppm) with incomplete recovery to HCHO gas. After Ag functionalization, the 5\%Ag-In\textsubscript{2}O\textsubscript{3} sensor shows a dramatically enhanced response (135) with a short response time (102 s) and recovery time (157 s) to 1 ppm HCHO gas at 30 °C, which benefits from the Ag NPs that electronically and chemically sensitize the crystal In\textsubscript{2}O\textsubscript{3} nanograin, greatly enhancing the selectivity and sensitivity.

Keywords: In\textsubscript{2}O\textsubscript{3}, Ag loading, HCHO detection, Gas sensors

Introduction

All kinds of hazardous volatile organic compounds (VOCs) gases in indoor and outdoor, such as HCHO, ethanol, acetone, benzene, methanol, and toluene, are routinely and daily emitted from agriculture and industrial processes, or released as vehicle exhaust emissions [1]. VOCs, such as HCHO, are harmful to human health and the environment when their concentrations are above a critical threshold, sometimes as low as parts-per-million (ppm) levels [2, 3]. For safety reasons, anything out of limits in HCHO storage systems, appliances, and vehicles, as well as the entire internal environment infrastructure, must be detected immediately [4–6]. The ever-increasing attention concerning indoor and outdoor air quality and workplace safety has brought out the steady development of the gas sensors market over the past few years, and therefore, gas sensors are expected to attain wider application [7–9]. Therefore, formaldehyde sensors will play a critical role on account of formaldehyde’s extensive carcinogenicity range in air [10, 11].

Metal oxide semiconductor based on chemiresistors, mainly including In\textsubscript{2}O\textsubscript{3} [12–14], WO\textsubscript{3} [15–17], SnO\textsubscript{2} [18, 19], ZnO [20, 21] and LaFeO\textsubscript{3} [22–24], is an outstanding technique for detecting VOCs, due to its unique advantages in terms of low cost, good sensitivity, fast response/recovery time, and a large number of gases detected [25]. However, traditional gas sensors based on metal oxide semiconductors usually have a high working temperature of 150–400 °C, which may decrease the sensor stability and life. In addition, high operating temperature leads to high power consumption, which is an important parameter for the new generation of battery-loaded wireless sensors [26, 27]. However, this can be reversed when the sensing materials are elaborately designed. A typical method used for lowering working temperature is the surface modification of the
semiconductor metal oxide with noble metals such as Ag [28, 29], Pt [30], and Pd [31, 32] or different metal oxides [26]. By either chemical sensitization or electronic sensitization, one can modify the semiconductor surface with various metal promoters to achieve an effective room-temperature sensor material. Outstanding sensing performance is attributed not only to the sensitizer effect of noble metals but also to the synergistic effect of large surface area, appropriate particle size, and abundant mesoporous surface of nanostructure [15, 20, 23, 33].

In$_2$O$_3$ is an important n-type semiconductor with about 3.6 eV wide band gap and has been widely studied owing to its high catalytic activity and electronic properties [34, 35]. Unfortunately, the pure In$_2$O$_3$ as sensing material possessing simply poor selectivity and a high response can hardly be obtained at low temperatures, which restricts its further application. To further enhance its sensing properties, In$_2$O$_3$ has been modified by noble metals [36], metal ions [37], and carbon materials [38]. Composites of multi-phase semiconducting metal oxide nanostructures have also been frequently reported [39]. To date, few researches have been carried out on the gas-sensing properties of In$_2$O$_3$ sensor to HCHO. Wang et al. [29] reported that the Ag-loaded In$_2$O$_3$ hierarchical nanostructure sensors showed fast response (0.9 s), recovery (14 s), and high response (11.3) towards 20 ppm HCHO at 240 °C. Dong et al. [40] reported that the as-synthesized 3 wt%Ag-functionalized In$_2$O$_3$/ZnO samples exhibited high response of about 842.9 towards 2000 ppm HCHO at operating temperature of 300 °C. Currently, formaldehyde gas sensors have been reported to require higher operating temperatures. Zhang et al. [28] have reported the results of formaldehyde gas-sensing tests, which revealed that a sensor based on 6%Ag/In$_2$O$_3$ exhibits ultra-high sensitivity (123.97) toward 100 ppm of formaldehyde at a lower operating temperature (160 °C). Wang et al. [33] reported that the graphene oxide in situ modified two-dimensional SnO$_2$ nanosheets with in-plane mesopores was utilized as the sensing material and that the sensor response was larger than 2000 toward 100 ppm HCHO at 60 °C. The problem of formaldehyde gas sensors with high sensitivity and high selectivity to low concentration HCHO at room temperature have remains unsolved.

In this work, we report a high-response formaldehyde gas sensor that operates at room temperature, which is prepared with In$_2$O$_3$ nanograin sensitized by Ag nanoparticles. The comparative study of HCHO gas detection between pure and Ag-loaded In$_2$O$_3$ nanoparticles was investigated, and the influence of Ag loading on sensing performance was revealed. The results show that 5%Ag-In$_2$O$_3$ sensor exhibits an excellent response of 1670 to 5 ppm HCHO at 30 °C and a ultra-low detection concentration of 0.05 ppm (to which the response value is 3.85). Simultaneously, the 5%Ag-In$_2$O$_3$ sensor also presents superior selectivity and stability, all of which reaches the level of metal oxide sensors.

**Methods**

**Sample Preparation**
The pure In$_2$O$_3$ was synthesized through dissolving 6 mmol In(NO$_3$)$_3$·4.5H$_2$O (99.99%, Aladdin), and 24 mmol urea (99%, Aladdin) in 45 mL of deionized water; the mixture was kept in a 50-mL polyethylene reaction pot at 140 °C for 16 h and then cooled to room temperature. The prepared sediment was washed with ethyl alcohol for three times, dried for 20 h at 70 °C, and calcined for 2 h at 600 °C in pure nitrogen flow with a heat rate of 5 °C min$^{-1}$. The pure In$_2$O$_3$ was dissolved in deionized water (1 wt%, 3 wt%, 5 wt%, and 7 wt%) were prepared and named 1%Ag-In$_2$O$_3$, 3%Ag-In$_2$O$_3$, 5%Ag-In$_2$O$_3$, and 7%Ag-In$_2$O$_3$, respectively.

**Characterization**
The X-ray powder diffraction (XRD) of the prepared products was conducted on a D/max-2300 diffractometer (Rigaku Corporation; 35 kV) in a scanning range of 10–90° at a rate of 2°min$^{-1}$ with Cu Kα1 radiation ($I = 1.540$ Å). X-ray photoelectron spectroscopy (XPS) was carried out on a K-Alpha+ spectrometer with Al Kα excitation (Thermo Fisher Scientific Co. Ltd; 1486.6 eV) to observe the chemical binding states of each element. The morphology of the samples was recorded by scanning electron microscopy (SEM, Thermo Fisher Scientific Co. Ltd.). The elemental composition was performed by SEM equipped with an energy dispersive X-ray spectroscopy (EDS) detector. Transition electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) of the size and crystallinity of the grain were performed by a JEM-2100 microscope (JEOL Co. Ltd.) operating at 200 kV. The N$_2$ adsorption–desorption analysis of the obtained samples was collected on Bethe equipment (Bestech Instrument Technology Co. Ltd.) at liquid nitrogen temperature.

**Sensor Fabrication and Sensing Test**
In the as-prepared of gas sensing materials (pure In$_2$O$_3$, 1%, 3%, 5%, and 7% Ag-loaded In$_2$O$_3$), 2 mg gas-sensing
material samples were mixed with 2 mg printing oil in mortar, which was ground for 1 min in agate mortar for forming a uniform mash. The mash sensing materials were screen-printed with a mesh on the outer surface of substrate and dried at 60 °C for 10 min in a drying oven. The gas sensing material forming on the surface of substrate has a thickness of about 10 mm. Figure 1 presents the schematic diagram of the gas sensor. Finally, the devices were sintered at 400 °C for 2 h in an electric furnace to ensure its stability. Afterwards, the sensing properties were evaluated by HCRK-SD101 gas sensing analyzer (Wuhan HCRK Technology Co. Ltd.) at the relative humidity of 16 ± 10%. The prepared sensors were installed in the test chamber (2.7 L) and then injected with different concentrations of tested gas by a micro syringe. The response of the gas sensor can be defined as the ratio of the resistance value Ra to the resistance value Rg, where Ra and Rg refer to the resistance in air and target gas, respectively [41]. Response and recovery times refer to the time required to achieve 90% of the maximum sensing value during adsorption and desorption.

Results and Discussion

Morphology and Structure Characterization

The crystal phase of the pure and Ag-loaded dispersed In$_2$O$_3$ were investigated utilizing XRD. XRD patterns of the pure and Ag-loaded dispersed In$_2$O$_3$ were shown in Fig. 2. It can be seen from Fig. 2a that the diffraction peaks of the In$_2$O$_3$ sample are similar according to the JCPDS card NO. 06-0416, which can be assigned to the cubic structure of In$_2$O$_3$. The diffraction peaks of In$_2$O$_3$ samples are located at 2θ of 30.58, 35.46, 51.03, and 60.67, which are ascribed to the 222, 400, 440, and 622 planes, respectively. For Ag-loaded In$_2$O$_3$ samples, in Fig. 2b, the XRD curves corresponding to 1%Ag-In$_2$O$_3$, 3%Ag-In$_2$O$_3$, 5%Ag-In$_2$O$_3$, and 7%Ag-In$_2$O$_3$ are similar to those pure In$_2$O$_3$, indicating that the crystalline phase of In$_2$O$_3$ is barely influenced during the surface functionalization process. As the loading amount of Ag is increasing, the diffraction peaks of 200 and 111 agreeing with Ag (JCPDS card NO.04-0873) can be gradually detected by small bulges and continuously shift to larger angles. No impurity phase was examined from the XRD patterns, which further confirmed the prominent purity of the samples.

To further demonstrate the component and the chemical states of the as-synthesized samples in the surface region, XPS was presented. The full XPS spectra (Fig. 3a) reveal that the 5%Ag-In$_2$O$_3$ sample mainly contains In, O, Ag, and C elements. The presence of elemental C in the spectrum is due to the binding energy of C 1 s, which is usually used as an internal reference in the spectrum during XPS measurements. All XPS spectra were calibrated with a C1s peak of 284.8 eV, as shown in Fig. 3. The high-resolution In 3d XPS spectrum can be fitted with two strong peaks with binding energies at 452.08 eV (In 3d$_3/2$) and 444.48 eV (In 3d$_5/2$) in Fig. 3b. Compared with the reported In 3d$_5/2$ (443.60 eV) signal of metallic indium, there is no metallic indium peak in our samples, demonstrating that the elemental indium exists only in the form of oxide and the major state is In$^{3+}$. The high-resolution XPS spectra of the Ag peak is sketched, where the peak corresponding to metallic silver can be assigned to 374.0 eV (Ag 3d$_3/2$) and 368.0 eV (Ag 3d$_5/2$) in Fig. 3c, indicating that the Ag species loaded on the surface region are metallic silver.
The morphology of the pure In$_2$O$_3$ and 5\%Ag-In$_2$O$_3$ samples was preliminarily demonstrated in Fig. 4a–e by SEM analysis. All samples showed nanograin morphologies with diameters ranging from 20 to 50 nm and ranged from a few hundred nanometers to over 1 \( \mu \)m in lengths. For the pure In$_2$O$_3$ samples, from Fig. 4a–c, we can see that the surface of each nanograin is smooth. After functionalization processes, we can plainly see that the surface of the In$_2$O$_3$ nanograin is a little rough in Fig. 4d–e, and that the Ag NPs are distributed on the surface of In$_2$O$_3$ nanograin. The presented SEM images show that the loading of Ag has no significant effect on the morphology of In$_2$O$_3$.

After Ag nanoparticles are decorated onto the dispersed In$_2$O$_3$ nanograin, the morphology and crystalline phases of 5\%Ag-In$_2$O$_3$ samples are presented through the TEM images in Fig. 5. It can be seen that Ag NPs with a size from 30 nm to about 100 nm are well pinned on the surfaces of the dispersed In$_2$O$_3$ nanoparticle, which will be helpful for enhancing gas-sensing properties. In order to further observe the detailed microstructure of In$_2$O$_3$ and Ag NPs, high-resolution TEM images of the 5\%Ag-In$_2$O$_3$ sample were obtained (Fig. 5b, c).

The dispersed In$_2$O$_3$ are assembled into a single crystal in Fig. 5b and c. The high-resolution TEM images from Fig. 5c show that the lattice plane is 0.293 nm, corresponding to the (222) crystal plane of cubic In$_2$O$_3$, while the crystal spacing of 0.236 nm is in good agreement with the (111) spacing of Ag. In addition, the interface reveals the existence of strong electronic interaction between In$_2$O$_3$ nanostructures and Ag nanoparticles.

The energy dispersive X-ray spectroscopy pattern (Fig. 5d) is eloquent proof of the existence of In, O, and a few Ag without any impurity elements. The atomic percentages of In, O, and Ag are 33.99\%, 62.43\%, and 3.59\%, respectively. The atomic ratio of In and O is about 1:2, indicating that 5\%Ag-In$_2$O$_3$ samples are the major phase component in selected region. To further determine the distribution of Ag, the 5\%Ag-In$_2$O$_3$ samples were performed by the EDS. As observed from Fig. 5e–h, the Ag-loaded In$_2$O$_3$ sample was evenly distributed by elemental mappings of O, In, and Ag, respectively. The results show that there are obvious loads of Ag NPs onto the surface of dispersed In$_2$O$_3$ nanoparticle and dispersed In$_2$O$_3$ nanostructure does not accumulate with the decoration of Ag.
**Fig. 4** SEM images of pure In$_2$O$_3$ (a, b, and c) and 5%Ag-In$_2$O$_3$ (d and e) samples.

**Fig. 5** a TEM image of 5%Ag-In$_2$O$_3$ samples. b, c HRTEM images of 5%Ag-In$_2$O$_3$ samples. d EDS spectra pattern of 5%Ag-In$_2$O$_3$ samples. e–h The EDS mapping picture of O, In, and Ag elements of 5%Ag-In$_2$O$_3$ samples.
In order to obtain the porosity and the specific surface area of the pure In$_2$O$_3$ and 5%Ag-In$_2$O$_3$ samples, N$_2$ adsorption-desorption experiment method was employed. On the basis of the current IUPAC classification, Fig. 6a and b show the classic type III isotherm to relative pressure (0.1 < P/P$_0$ < 1.0) with a type H3 hysteresis loop, which consist of granular material and have no obvious saturated adsorption platform, indicating that the pore structure is very irregular. The pore volume and surface area of 5%Ag-In$_2$O$_3$ are 0.0650 cm$^3$ g$^{-1}$ and 14.4 m$^2$ g$^{-1}$ characterized with the Brunauer–Emmett–Teller (BET) method, both of which are larger than the pure In$_2$O$_3$ (6.5 m$^2$ g$^{-1}$ and 0.0204 cm$^3$ g$^{-1}$), demonstrating that the specific surface area gradually raises as being loaded certain content of Ag NPs. The pore-size distribution was measured by using the Barrett–Joyner–Halenda (BJH) way. One can see that the pore sizes of the pure In$_2$O$_3$ distributes in the range from 2 to 54 nm. For 5%Ag-In$_2$O$_3$ samples, the pore sizes are all distributed between 2 and 65 nm.

Gas-Sensing Performance

The gas response upon exposure to 1 ppm HCHO was investigated by increasing the operating temperature of the sensor device to observe the relation between the operating temperature and gas response, and to determine the optimized operating temperature. The pure In$_2$O$_3$, 1%Ag-In$_2$O$_3$, 3%Ag-In$_2$O$_3$, 5%Ag-In$_2$O$_3$, and 7%Ag-In$_2$O$_3$ were continuously tested under the 5 ppm gaseous formaldehyde conditions at operating temperatures of 30–300 °C, respectively. The sensing responses of each gas sensor were measured at a fixed temperature, and the recorded values of the gas sensors are shown at room temperature in Fig. 7.

It can be seen that the 5%Ag-In$_2$O$_3$ sensor has maximum response to formaldehyde gas at 30 °C, and the response is 1670. It tends to increase at lower operating temperatures (5%Ag-In$_2$O$_3$: 1670, 844, 366, 191, 113, 87, 56, 46.3, 39, and 44.2 at 30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 °C; 7%Ag-In$_2$O$_3$: 400, 143, 49, 33.1, 29.3, 37.8, 20.3, 23.3, 8.66, and 12.8 at the same operating temperatures). The gas responses of the Ag-In$_2$O$_3$ sensors show higher values than pure In$_2$O$_3$ in all operating temperature ranges, which can fix the optimal operating temperature and the optimum HCHO response of the sensors. Among them, it can be clearly seen that 5%Ag-In$_2$O$_3$ sensor has the highest responses (1670) to 5 ppm HCHO at room temperature demonstrating the superior sensing properties of the sensor, which is higher than other sensors. The reason the higher gas response appears
At room operating temperatures can be attributed to Ag NPs catalytic (spill-over effect) and electronic (generation of schottky barrier) sensitization. After loading the Ag NPs, the operating temperature is reduced and the formaldehyde sensitive response enhanced significantly. Nevertheless, with the loading of Ag NPs further enhancing, the response value decreases. This can be ascribed to the reduction in number of surface active sites of In$_2$O$_3$, which indicates that the excessive coverage of Ag NPs and the permeability of gas are affected, and then the catalytic action of Ag NPs is weaken, causing a decrease in adsorbed oxygen ions [28]. Compared with other previously reported gas sensors based on In$_2$O$_3$ sunflower, In$_2$O$_3$/ZnO nanocomposites, or In$_2$O$_3$ nanorods, our gas sensor shows notable gas response at room temperature [28, 29, 40].

To further confirm the selectivity of the synthesized gas sensors toward HCHO, the selectivity sensing performance of pure In$_2$O$_3$, 1%Ag-In$_2$O$_3$, 3%Ag-In$_2$O$_3$, 5%Ag-In$_2$O$_3$, and 7%Ag-In$_2$O$_3$ sensors was tested at room temperature toward 10 ppm of several volatile organic compounds, including benzene, toluene, xylene, methane, formaldehyde, acetone, ethanol, and ammonia, 5%Ag-In$_2$O$_3$ and 7%Ag-In$_2$O$_3$ toward this gases with a concentration of 1 ppm at room temperature. As shown in Fig. 8, the Ag-In$_2$O$_3$ sensors demonstrate superior selectivity to formaldehyde, whereas they have poor responses to other typical interference gases at the same temperature, especially the 5%Ag-In$_2$O$_3$ sensor. This indicates that the prepared sensor has quite excellent selectivity towards formaldehyde.

Furthermore, the stability of the 5%Ag-In$_2$O$_3$ sensor is shown in Fig. 9. The 5%Ag-In$_2$O$_3$ sensor was investigated toward 1 ppm HCHO for 6 cycles at room temperature (Fig. 9a), which demonstrates the excellent reproducibility to HCHO at room temperature. As demonstrated in Fig. 9c, the 36-day response test results show that the 5%Ag-In$_2$O$_3$ sensor not only possesses high gas-sensing performance but also excellent long-term stability. Meanwhile, the gas-sensing properties of 5%Ag-In$_2$O$_3$ sensor under different humidity conditions were investigated (Fig. 9b). Obviously, the sensor has not been significant affected on the sensing performance under a relative humidity range of 10−30%. Nevertheless, when the relative humidity range increases from 30 to 80%, the gas-sensing properties begin to reduce gradually.

The real-time dynamic gas responses of the 5%Ag-In$_2$O$_3$ sensors toward HCHO at various concentrations at room temperature are presented in Fig. 10. The responses to 1, 0.8, 0.6, 0.4, 0.2, 0.1, 0.08, and 0.05 ppm formaldehyde were calculated to be $R_a/R_g = 135, 108, 75, 65, 34, 23, 11, \text{ and } 3.85$, respectively. The sensitivity amplitude increases monotonically with gas concentration and is far from saturation until the gas concentration reaches 0.05 ppm, which is beneficial to the quantitative measurement of formaldehyde. Notably, the response is still as high as 3.85 when sensor is exposed to concentrations of formaldehyde as low as 0.05 ppm, indicating the ultra-low detection concentration of the sensor.

**Mechanism of the Gas Sensor**

The In$_2$O$_3$ semiconductor is a chemical resistancesensing material, and its electrical property changes mainly with the reaction of HCHO on the surface of In$_2$O$_3$. A HCHO sensing schematic diagram is shown in Fig. 11. When the sensor is exposed to air, an abundance of oxygen molecules in air will be absorbed onto the surface of In$_2$O$_3$, and the oxygen captures electron from the material’s conductive band and converts them into more active chemical adsorbed oxygen, thereby creating a space charge area (depletion layer) that greatly increases initial resistance. The electron depletion layer has a great influence on the initial resistance of the sensor in the air. The major forms of chemisorbed oxygen species are $O^2-$ and $O^-$, which can be described as Eqs. (1)-(3):

![Fig. 8](image_url) The gas response of pure In$_2$O$_3$, 1%Ag-In$_2$O$_3$, and 3%Ag-In$_2$O$_3$ (benzene, toluene, xylene, methane, formaldehyde, acetone, ethanol, and ammonia) with a concentration of 10 ppm at 30°C, 5%Ag-In$_2$O$_3$, and 7%Ag-In$_2$O$_3$ toward this gases with a concentration of 1 ppm at 30°C.
When the sensor is placed in an environment inflated with HCHO, the chemical adsorption oxygen reacts with HCHO, discharging electrons back to the conductive band, reducing the space charge area thickness, and thus decreasing the sensor resistance. The occurred reaction can be explained as followed in Eqs. (4) and (5):

\[ O_2(g) \rightarrow O_2(ads) \]  
\[ O_2(ads) + e^- \rightarrow O_2^-(ads) \]  
\[ O_2^- (ads) + e^- \rightarrow 2O^-(ads) \]

\[ HCHO + O_2^- (ads) \rightarrow CO_2 + H_2O + e^- \]  
\[ HCHO + 2O^-(ads) \rightarrow CO_2 + H_2O + 2e^- \]

Obviously, the sensor performances based on 5%Ag-In$_2$O$_3$ are much higher than those of pure In$_2$O$_3$. This excellent response is ascribed to the electronic sensitization and chemical effect of Ag NPs. The Ag NPs have high availability for the catalytic activation of the dissociation of molecular oxygen, and the activated oxygen species created are then spilled onto the metal oxides surface and interact with the adsorption-desorption reactions of oxygen [42]. The chemisorbed oxygen plays
a critical role in the gas sensing of sensors by regulating the reaction with tested gases [43]. Pure In$_2$O$_3$ and 5%Ag-In$_2$O$_3$ based on sensors were investigated by XPS to confirm the ratio of the chemisorbed oxygen in the samples. The O$_1$ spectra of the pure In$_2$O$_3$ and 5%Ag-In$_2$O$_3$ (Fig. 12a, b and Table 1) show that the adsorbed oxygen content (2.46% of O$^{-}$ and 19.54% of O$_2^{-}$) of 5%Ag-In$_2$O$_3$ is higher than that of pure In$_2$O$_3$ (1.83% of O$^{-}$ and 16.05% of O$_2^{-}$), which is mainly due to the Ag Nps spill-over effect on metal oxide semiconductors [44]. Owing to the high conductivity and catalytic properties of Ag NPs [28, 42, 45, 46], Ag NPs on the surface of the metal oxides enhance the chemical activity of the chemisorbed oxygen species and spill the oxygen species.

Fig. 11 a–d HCHO sensing mechanism of schematic illustration for 5%Ag-In$_2$O$_3$ and pure In$_2$O$_3$, respectively.

Fig. 12 XPS spectra of 5%Ag-In$_2$O$_3$ (a) and pure In$_2$O$_3$ (b) in the vicinity of O1s. Dynamic resistance transition characteristics of the 5%Ag-In$_2$O$_3$ (c) and pure In$_2$O$_3$ (d) toward 40 ppm of formaldehyde at 30°C.
over the substrate, which accelerates for gas sensing at low temperature.

Moreover, the Schottky junction can be formed at the interface between In$_2$O$_3$ and Ag due to the difference in band gap and work function [47, 48]. When the 5%Ag-In$_2$O$_3$ material is exposed to the atmosphere, compared with pure In$_2$O$_3$, the depletion region in 5%Ag-In$_2$O$_3$ composites is further broadened due to the presence of Schottky junction between Ag and In$_2$O$_3$ interface. The charged species such as O$^-$ and O$_2^-$ adsorbed on the surface of In$_2$O$_3$ also contribute to electron depletion by capturing free electrons from the sensing materials [15] (Fig. 12a, b). The base resistance of 5%Ag-In$_2$O$_3$ was investigated to 206000 kΩ, far higher than the resistance (7.8 kΩ) of pure In$_2$O$_3$ (Fig. 12c, d), further demonstrating that the Ag NPs can remarkably enhance baseline resistance. When the 5%Ag-In$_2$O$_3$ material is exposed to HCHO in the sensing process, the Schottky junction forming at the interface between Ag and In$_2$O$_3$ produces more overflow electrons and donates it to the In$_2$O$_3$ matrix, resulting in efficient modulation of the depletion layer. Besides, with more oxygen substances adsorbed on the surface of Ag/In$_2$O$_3$, the redox reactions occurred between HCHO and chemical adsorbed oxygen are enhanced. The redundant electrons generated by these increased surface reactions result in a greater reduction in resistance of the 5%Ag-In$_2$O$_3$-based sensors in HCHO (Fig. 12c, d). Hence, 5%Ag-In$_2$O$_3$ sensor possesses superior sensing performance to HCHO.

Conclusion

In summary, we realized an ultra-high performance HCHO chemiresistor with Ag nanoparticles sensitized dispersed In$_2$O$_3$ semiconductor. The 5%Ag-In$_2$O$_3$ sensor demonstrates ultra-high response (135), short response time (102 s) and recovery time (157 s) to 1 ppm HCHO gas, and an ultra-low detection concentration (0.05 ppm) at room temperature. Compared with other HCHO sensors, the sensor has good reproducibility and strong responsivity at room temperature, and will have an excellent practical application prospect.

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Not applicable.

Authors’ Contributions

SZ and MC contributed to the conceptualization of the study. SZ contributed to the methodology of the study. SZ and YZ were assigned for the software in the study. QL and JH contributed to the validation of the study. HW contributed to the formal analysis of the study. HW and BL contributed to the investigation of the study. JZ and QL contributed to the resources of the study. SZ contributed to the data curation of the study. SZ contributed to the writing—original draft preparation of the study. SZ and MC contributed to the writing—review and editing of the study. JZ contributed to the visualization of the study. QL contributed to the supervision of the study. QL contributed to the project administration of the study. QL contributed to the funding acquisition of the study. All authors read and approved the final manuscript.

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Availability of Data and Materials

The datasets supporting the conclusions of this article are included within the article, and further information about the data and materials could be made available to the interested party under a motivated request addressed to the corresponding author.

Competing Interests

The authors declare that they have no competing interests.

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Table 1 The ratio of chemical component of 5%Ag-In$_2$O$_3$ and pure In$_2$O$_3$.

| Content      | O$^{−}$ | O$^2$− | O$^−$  |
|--------------|---------|--------|--------|
| 5%Ag-In$_2$O$_3$ | 78.00   | 2.46   | 19.54  |
| pure In$_2$O$_3$ | 82.13   | 1.83   | 16.05  |
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