ABSTRACT: Surface oxygen chemistry of semiconductor metal oxides is the basis for the sensing reaction between the preadsorbed surface oxygen and the target gases or organic vapors that are to be detected, and thus fundamentally determines their sensing performances. Herein, we, for the first time, identify a novel semiconductor spinel oxide, CdGa$_2$O$_4$, that has suitable surface oxygen chemistry and exhibits excellent selectivity and response toward formaldehyde. Moreover, we find that a cation off-stoichiometric CdGa$_2$O$_4$ spinel oxide decorated with a small amount of CdO nanocrystals can further improve the formaldehyde response, without losing the selectivity. This is based on the advantages of an increased amount of adsorbed oxygen in the Ga-rich environment, as well as heterojunctions between CdO nanoparticles and Ga-rich spinel oxide. Sensing performance (e.g., selectivity and response) of the material is much better than that of most reported nanostructured metal oxides used for formaldehyde detection. Our findings propose a general approach for achieving highly selective and sensitive detection of target gases by optimizing the surface oxygen property of semiconductor oxides.

INTRODUCTION
Efficient and selective gas/vapor sensors based on semiconductor metal oxides are in high demand for detection of toxic, volatile, and flammable gases/vapors.$^{1-3}$ Typically, the sensing function of semiconductor oxide (taking the n-type semiconductor as an example) lies in the surface chemistry (Figure 1a−c), which involves adsorbed oxygen molecules being removed from the semiconductor surface by the targeted gas/vapor (e.g., formaldehyde).$^{4,5}$ In particular, the specific reaction between the adsorbed oxygen with targeted gas/vapor is of paramount importance but is still a challenge for the purpose of selective detection.$^{6,7}$ For instance, n-type semiconductors, such as SnO$_2$, ZnO, and In$_2$O$_3$, are some of the most prominent sensing materials studied previously, but they generally suffer from cross-response to other interfering gases/vapors.$^{8-15}$ The major cause of poor selectivity can be attributed to the fact that the surface-adsorbed oxygen on them has too strong ability to oxidize a wide range of reducing gases/vapors including both the targeted gas/vapor and interfering gases/vapors. As shown in Figure 1a,b, when oxygen molecules are adsorbed on the semiconductor surface, they will capture free electrons from the conduction band, until electronic equilibrium between the semiconductor and adsorbed oxygen is reached. In this situation, the redox potential of the adsorbed oxygen is pinned near the Fermi level of the semiconductor.$^{16}$ That is, oxidation potential of absorbed oxygen, which indicates the oxidation ability to different reducing gases/vapors, is mainly determined by the material’s Fermi level. For evaluating the Fermi level of the semiconductor oxide, the work function ($\phi$) is a useful parameter, especially considering that the work function is easily determined by a scanning Kelvin probe method.$^{17}$ Hence, for optimizing the surface oxygen chemistry and subsequently improving selectivity, semiconductor oxides with a relatively low work function value are required.

Spinel-type oxides (MFe$_2$O$_4$, Mg$_2$O$_4$, etc.) have attracted substantial interest for sensing applications because their high compositional flexibility allows for tunable physical and chemical properties, including the work function tuning.$^{18-22}$ Taking Mg$_2$O$_4$ (M = Ni, Cu, Co, Mg, Zn, Cd) as the study object in this work, we first screen suitable sensing materials based on the following criteria: (1) n-type rather than p-type semiconductor oxides, as the shortcomings of p-type oxides are well-illustrated in a previous report; and (2) suitable band gap

Support Information

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CuGa$_2$O$_4$ exhibits a comparatively narrow band gap (because of high carrier concentration) and is not a suitable material for the selective oxidation of formaldehyde, as its resistance change is insensitive to the oxidation of adsorbed oxygen and should have the potential to achieve better selectivity.

Among these spinel gallates, n-type semiconductor CdGa$_2$O$_4$, with its Fermi level pinned at 0.412 mmol of Ga(NO$_3$)$_3$·6H$_2$O, displays too large band gaps (∼5.0 and 4.7 eV). In addition, CuGa$_2$O$_4$ exhibits a comparatively narrow band gap (∼1.8 eV). Among these spinel gallates, CdGa$_2$O$_4$ has a potential to achieve better selectivity.

Experimental Section

Materials Characterizations. The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2500 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) images were obtained with a JEOL JSM 6700F electron microscope. Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) were performed with a Philips-Fei Tecnai G2STWIN microscope equipped with a field emission gun operating at 200 kV. Thermogravimetric (TG) analysis was performed using a NETZSCH STA 449C thermal analyzer by heating the samples from 35 to 800 °C at a heating rate of 10 °C/min in air. Temperature-programmed desorption (O$_2$-TPD) was performed using a Micromeretics AutoChem 2920 II system. Specific surface area was estimated using the Brunauer–Emmett–Tobin method.

Ga-rich environment and heterojunctions between CdO nanoparticles and Ga-rich spinel nanofibers. The superior sensing properties of Cd–Ga spinel oxide toward formaldehyde have never been reported.

Chemicals and Reagents. Gallium(III) nitrate hydrate (Ga(NO$_3$)$_3$·xH$_2$O), indium(III) nitrate hydrate (In(NO$_3$)$_3$·xH$_2$O), and cobalt(II) nitrate hexahydrate (Co(NO$_3$)$_3$·6H$_2$O) were purchased from Sinopharm Chemical Reagent Co., Ltd. Zinc nitrate hexahydrate (Zn(NO$_3$)$_3$·6H$_2$O) and magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$·6H$_2$O) were purchased from Xilong Chemical Reagent Co., Ltd. Cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O) was purchased from Shanghai Tingxin Chemical Reagent Factory. Nickel(II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) was purchased from Tianjin Huadong Chemical Reagent Factory. Tin(II) chloride dihydrate (SnCl$_2$·2H$_2$O) was purchased from Tianshui Chemical Reagent Co., Ltd. Copper(II) nitrate trihydrate (Cu(NO$_3$)$_3$·3H$_2$O) was purchased from Tianjin Guangfu Fine Chemical Research Institute. N,N-Dimethylformamide (DMF) was purchased from Tianjin Tiantai Fine Chemicals Co., Ltd. Polyvinylpyrrolidone (PVP, Mn ≈ 1 300 000 g/mol) was purchased from Aladdin Chemical Co., Ltd. Ethanol was purchased from Beijing Chemical Factory. Highly purified water (>18 MΩ cm resistivity) was provided by a PALL PURELAB Plus system.

Synthesis of CdO/Ga-Rich CGO. Cd(NO$_3$)$_2$·4H$_2$O (0.206 mmol) and Ga(NO$_3$)$_3$·xH$_2$O (0.412 mmol, x was determined by thermogravimetric (TG) analysis) were dissolved in DMF (2.2 g), ethanol (6.6 g), and PVP (0.8 g), under continuous stirring for >12 h to obtain a homogeneous electrosprun solution. The electrosprun solution was loaded into an injection syringe (5 mL) with a needle, and a piece of aluminum foil (15 cm × 20 cm) was used as a collector. Their distance was set around 20 cm. Then, electrosprun initiation was applied by feeding a voltage of 22 kV between the needle tip and the collector. After electrosprun, the resulting products (Cd- and Ga-embedded PVP nanofibers) were collected and dried at 70 °C for 12 h. Finally, the dried CdO- and Ga-embedded PVP nanofibers were calcined at 600 °C for 3 h in air, giving the CdO/Ga-rich CGO material.

For comparison, stoichiometric CGO and Ga-rich CGO were prepared. For the stoichiometric CGO, the above-obtained CDO- and Ga-embedded PVP nanofibers were calcined at 700 °C for 3 h in air. For the pristine Ga-rich CGO, the as-synthesized CdO/Ga-rich CGO (30 mg) was immersed in 0.1 M HCl solution (10 mL) for 5 min to remove CdO nanoparticles, and then washed several times with water and dried at 70 °C.

Synthesis of Mg$_2$O$_3$ (M = Ni, Cu, Co, Mg, and Zn). Their synthetic procedures were similar to that of CdO/Ga-rich CGO, except that we used Ni(NO$_3$)$_2$·6H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O, or Zn(NO$_3$)$_2$·6H$_2$O to replace Cd(NO$_3$)$_2$·4H$_2$O in the electrosprun solution.

Synthesis of CdO, ZnO, SnO$_2$, Ga$_2$O$_3$, and In$_2$O$_3$. Their synthetic procedures were similar to that of CdO/Ga-rich CGO, except that we used single metal salt (0.618 mmol Cd(NO$_3$)$_2$·4H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, SnCl$_2$·2H$_2$O, Ga(NO$_3$)$_3$·xH$_2$O, or In(NO$_3$)$_3$·xH$_2$O) to replace two metal nitrates (0.206 mmol of Cd(NO$_3$)$_2$·4H$_2$O and 0.412 mmol of Ga(NO$_3$)$_3$·3H$_2$O) in the electrosprun solution.
Teller (BET) method on a Micromeritics ASAP 2020 M system. UV−vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda 20 UV−vis spectrometer. X-ray photoelectron spectroscopy (XPS) analyses were performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatic X-ray source (Al Kα hν = 1486.6 eV). Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer with a 20 mW air-cooled argon ion laser (532 nm) as the exciting source. The work function was determined using a scanning Kelvin probe system (KP Technology Ltd.) in air environment.

Sensor Fabrication and Measurement. The obtained sample was ground with ethanol to make a viscous slurry. Then, the slurry was uniformly coated onto the outside surface of a special ceramic tube (4 mm in length and 1 mm in diameter) equipped with Au electrodes and Pt wires on both ends of the tube, forming a sensing layer. A Ni−Cr alloy coil was inserted into the ceramic tube as a heater to control operating temperature. For improvement in stability, the as-fabricated sensor was preheated at 200 °C for 24 h in air before the gas-sensing measurement. A schematic diagram of the sensor is shown in Figure S3 (Supporting Information). The sensing measurement was performed on a commercial CGS-8 gas-sensing measurement system (Beijing Elite Tech Co., Ltd.) equipped with a testing chamber (2.5 L) to control gas species and concentrations. A typical measurement procedure was as follows. After a certain amount of tested gas was injected into the testing chamber by a microinjector and sufficiently diffused for above 10 min, the sensor was positioned from fresh air into the testing chamber. Until its resistance reached a steady state in the testing chamber, the sensor was taken out to fresh air, and its resistance gradually recovered to its original value. Throughout the whole process, resistance of the sensor was recorded by the measurement system. The upper resistance detection limit of the sensor connected with the system was 500 MΩ. The sensor response is defined as $S = R_a/R_g$ (n-type semiconductor) or $S = R_g/R_a$ (p-type semiconductor), where $R_a$ and $R_g$ are sensor resistance in air and in test gas, respectively. The response and recovery times of the sensor are the times required to reach 90% of the final steady resistance in the case of response and recovery processes.

RESULTS AND DISCUSSION

Choice of Materials. The n-type semiconductor of Cd−Ga spinel oxide was considered to be a good candidate for sensing applications originating from its intriguing electronic and crystal structural features, which result in the well-tuned surface oxygen chemistry. First, the high Fermi level position of Cd−Ga spinel oxide indicates the low oxidation potential of adsorbed oxygen, facilitating selective detection of a strong reducing gas (e.g., formaldehyde) against others with relatively weak reducibility (e.g., ethanol, methanol, acetone). Second, two cations Cd2+ and Ga3+ in CdGa2O4 spinel tend to deviate from the stoichiometry of a precise 1:2 ratio and become Ga3+-rich due to a large ionic size difference, inducing n-type doping which produces free electrons and promotes oxygen adsorption. Electrospinning techniques were employed for synthesizing porous Cd−Ga spinel oxide nanofibers. This technique has the advantages of easy operation, high yield, low cost, excellent reproducibility, and high controllability, and represents one of the most effective strategies to generate complex one-dimensional nanomaterials (e.g., porous, hollow, core/shell, or heterostructure nanofibers) which has been extensively proven to be feasible to promote gas sensing. Among the obtained Cd−Ga spinel oxide nanofibers, CdO/Ga-rich CGO exhibits the remarkably enhanced formaldehyde response without losing the selectivity, and therefore most of the characterizations, results, and discussions in this work focus on the special material.
Material Synthesis and Characterizations. The synthesis process of CdO/Ga-rich CGO heterostructure is shown in Figure 2a, which involves electrospinning preparation of Cd(II) and Ga(III) ions (1:2 ratio) embedded PVP nanofibers (Figure S4, Supporting Information), followed by calcination in air at 600 °C. During the calcination process, PVP decomposed completely, and metal ion species are oxidized to mixed metal oxide nanofibers, composed of both Ga-rich CdGa2O4 spinel phase and a small amount of CdO phase, rather than an ideal stoichiometric CdGa2O4 spinel. Note that the stoichiometric CdGa2O4 adopts a normal spinel structure (Figure 2b), with O2− anions forming face-centered cubic packing in which Cd2+ ions reside on tetrahedral (Td) sites, and Ga3+ ions reside on octahedral (Oh) sites, respectively. Once in Ga-rich conditions, some Ga3+ ions substitute Cd2+ cations in Td sites, and the system creates oxygen vacancies spontaneously to maintain charge neutrality.30,31

The powder XRD pattern of CdO/Ga-rich CGO (Figure 2c), combined with the XRD pattern comparison of CdO/Ga-rich CGO with pristine CdO and Ga2O3 (Figure S5, Supporting Information), reveals that the CdO/Ga-rich CGO nanofibers contain CdGa2O4 (JCPDS 20-0863) and CdO (JCPDS 05-0640) phase, without any detectable Ga2O3 phase. The peak positions at 2θ = 29.4°, 34.6°, 36.2°, 42.9°, 52.1°, 55.5°, 60.9°, and 69.1° are assigned to (220), (311), (222), (400), (422), (511), (440), and (620) of CdGa2O4 phase, respectively, and the peak positions at 2θ = 33.0°, 38.3°, 55.3°, 65.9°, and 69.3° are assigned to (111), (200), (220), (311), and (222) of CdO phase, respectively. EDS analyses in Figure 2d show that the atomic ratio of Cd/Ga is near 1:2 in the two-phase mixture. These results indicate the Ga-richness in the CdGa2O4 phase. In addition, diffraction peaks of CdO in the XRD pattern are much sharper than those of Ga-rich CdGa2O4, implying that CdO has a larger crystallite size. From XRD analysis using the Scherrer equation, mean crystallite sizes of CdO and Ga-rich CGO are estimated to be about 31.5 and 13.9 nm, respectively. SEM images in Figure 2e show that the morphology of CdO/Ga-rich CGO is uniform nanofibers with a diameter of 50–150 nm, and these nanofibers are highly interconnected and randomly oriented. TEM images (Figure 2f,g, Figure S6 in the Supporting Information) show that CdO/Ga-rich CGO is porous nanofibers assembled from CdO nanofibers and Ga-rich CdGa2O4 nanoparticles with respective sizes of 50–100 and 5–20 nm, in line with the XRD analysis using the Scherrer equation. Ga-rich CdGa2O4 and CdO nanoparticles in Figure 2g are further investigated by high-resolution TEM (HRTEM). As shown in Figure 2h, the observed lattice spacings on Ga-rich CdGa2O4 are 0.248 and 0.259 nm, which correspond to crystal planes of CdGa2O4 (222) and (311), respectively. In addition, the existence of the CdO phase was confirmed by observing the (100) crystal plane with lattice spacing of 0.470 nm.

To compare with the CdO/Ga-rich CGO, we also synthesized pristine CdO particles and pristine Ga-rich CdGa2O4 nanofibers (e.g., Ga-rich CGO) as control samples. Pristine CdO was synthesized by a similar electrospinning method as shown in Figure 2a, but without containing Ga3+ ions in the electrospinning solution (see the Experimental Section). Pristine Ga-rich CGO was obtained by directly removing CdO from CdO/Ga-rich CGO composites using dilute HCl solution (see the Experimental Section). Sample characterizations (Figures S7 and S8, Supporting Information) suggest that pristine CdO is regular crystals with sizes above 100 nm, and pristine Ga-rich CGO with single CdGa2O4 phase maintains a uniform porous nanofiber morphology. The composite structure of CdO/Ga-rich CGO is further confirmed by comparison of UV–vis diffuse reflection spectra, sample colors, and Raman spectra of CdO/Ga-rich CGO with pristine Ga-rich CGO and pristine CdO (Figures S9 and S10, Supporting Information). Furthermore, two EDS spectra of pristine Ga-rich CGO (Figure S8b, Supporting Information) and CdO/Ga-rich CGO (Figure 2d) reveal that CdO content is about 6.63 wt % in CdO/Ga-rich CGO.

One basic question based on these results is why does the CdO phase prefer to separate from the “ideal CdGa2O4 spinel”. To answer the question, we performed extended experiments by replacing Cd2+ ions with Ni2+, Cu2+, Co2+, Mg2+, or Zn2+ ions in the original electrospinning solution. We found that these synthses ultimately produce a pure phase of ideal stoichiometric MgGa2O4 (M = Ni, Cu, Co, Mg, Zn; Figure S11, Supporting Information), rather than composite phases of MO/Ga-rich spinels. Considering that cation sizes significantly influence structural stability of spinels, we examined them in the six spinel oxides (Table S2, Supporting Information). Cation sizes decrease in the order Cd2+ > Zn2+ > Co2+ > Cu2+ ≥ Mg2+ > Ni2+ > Ga3+, whether in Td sites or in Oh sites. This implies that nonstoichiometry deviation of CdGa2O4 is correlated with the too large ionic size differences between Cd2+ ions and Ga3+ ions, making it difficult to introduce Cd2+ ions in oxygen interstitial sites, and thus, the CdO phase tends to separate to reduce internal stress of the spinel.32 To be more specific, DFT calculations (Table S3, Supporting Information) were conducted to compare the formation energies of stoichiometric CdGa2O4 and ZnGa2O4 phases; the two spinel oxides are both normal spinel structures, in which Cd2+/Zn2+ ions occupy Td sites, and Ga3+ ions occupy Td sites. The calculated enthalpies of CdGa2O4 and ZnGa2O4 are −0.47 and −0.68 eV, respectively, confirming that formation of the stoichiometric CdGa2O4 spinel is more unfavorable. Thus, for preparation of the stoichiometric CdGa2O4, a higher temperature is required to overcome cation diffusion barriers. As shown in Figure S12 (Supporting Information), we obtained stoichiometric CdGa2O4 porous nanofibers (e.g., stoichiometric CGO) as a control sample, by calcination of Cd and Ga-embedded (1:2 ratio) PVP nanofibers at 700 °C (see the Experimental Section).

Gas-Sensing Property. High selectivity and response toward formaldehyde, well-known as a highly toxic and carcinogenic indoor pollutant, are highly desired, and thus, formaldehyde sensors have been vigorously developed in recent years.33–38 Herein, for the first time, the formaldehyde-sensing properties of Cd–Ga spinel oxide including CdO/Ga-rich CGO, Ga-rich CGO, and stoichiometric CGO were investigated. Detailed fabrication and measurement procedures for sensors based on these metal oxides are described in the Experimental Section. Fresh air of 20% relative humidity (RH) at room temperature (20 ± 5 °C) was employed as both background gas and diluting gas. Given that operating temperature strongly affects sensing performances, we first aim at identifying the optimal operating temperature of the sensors, based on major parameters including response value and response/recovery time. Sensors based on CdO/Ga-rich CGO, Ga-rich CGO, and stoichiometric CGO exhibit notable responses in 10 ppm formaldehyde atmosphere (Figure 3a), and their responses decrease promptly with increasing operating temperatures from 100 to 140 °C. The decreased responses may be attributed to the fact that adsorbed
formaldehyde molecules are easily desorbed before their reaction at higher temperature. In addition, response times of the three sensors are very short (<10 s), while their recovery times monotonically decrease in the operating temperature range (Figure S13, Supporting Information). Although the largest responses of the three sensors are reached at 100 °C, their recovery speeds in the operating temperature are very slow (>120 s). Taken together with the factors above, 110 °C was determined as the optimal operating temperature to evaluate sensing properties in subsequent detections. When exposed to 10 ppm formaldehyde at 110 °C, CdO/Ga-rich CGO ($R/R_g = 60.1$) exhibits superior response as compared to Ga-rich CGO ($R/R_g = 38.5$) and stoichiometric CGO ($R/R_g = 18.4$). Dynamic response and recovery curves in Figure 3b point to the fact that the three sensors all have good response/recovery features, with their responses increasing with increasing formaldehyde concentrations from 0.5 to 10 ppm. Once again, their responses drop in the order of CdO/Ga-rich CGO > Ga-rich CGO > stoichiometric CGO at the same formaldehyde concentration. These results imply that Cd–Ga spinel oxides are ideal sensing materials for formaldehyde detection, and the enhanced response of CdO/Ga-rich CGO is achieved by CdO phase deviation from the “ideal CdGa$_2$O$_4$ spinel”.

For comparison, sensors based on pristine CdO and Ga$_2$O$_3$ have also been fabricated and tested for formaldehyde detection. The pristine CdO-based sensor is almost insensitive ($R/R_g < 1.5$) to 10 ppm of formaldehyde, and its response is much lower than that of the three sensors based on Cd–Ga spinel oxides (Figure 3). The pristine Ga$_2$O$_3$-based sensor cannot be used for formaldehyde sensing because its base resistance in air is beyond the upper detection limit (500 MΩ) at operating temperatures below 500 °C. The high base resistance of pristine Ga$_2$O$_3$ originates from its wide band gap (4.4–4.9 eV), as confirmed by our previous work. Furthermore, the formaldehyde-sensing properties of sensors based on as-prepared MgGa$_2$O$_4$ (M = Ni, Cu, Co, Mg, and Zn) were investigated. Among them, sensors based on NiGa$_2$O$_4$ and CoGa$_2$O$_4$ show p-type sensing behaviors, and the CuGa$_2$O$_4$-based sensor shows an n-type sensing behavior; the three sensors all exhibit quite low response ($R/R_g < 2$) to 10 ppm of formaldehyde (Figure S14, Supporting Information). MgGa$_2$O$_4$ and ZnGa$_2$O$_4$ with a wide band gap cannot be used for formaldehyde detection on the test system because of their too high base resistances. Sensing-property comparisons (Figure S15, Supporting Information) of Cd–Ga spinel oxide with CdO, Ga$_2$O$_3$, and MgGa$_2$O$_4$ (M = Ni, Cu, Co, Mg, and Zn) identify the high intrinsic sensing activity of Cd–Ga spinel oxide for formaldehyde detection.

For a further assessment of the sensing properties of the CdO/Ga-rich CGO-based sensor, dynamic resistance transitions to formaldehyde in two concentration ranges containing a ppb level range (100–1000 ppb, Figure 4a) and a ppm range (1–50 ppm, Figure 4b) were carried out. Pleasantly, the sensor works very well over the formaldehyde concentration ranges. For determination of detection ranges and limit of detection, the sensor response versus formaldehyde concentration (0.05–2000 ppm) was investigated in Figure 4c. The response increases rapidly with increasing formaldehyde concentration until 800 ppm, suggesting that the sensor can detect formaldehyde at a wide concentration range. When the formaldehyde concentration is above 800 ppm, the sensor responses show a slow increasing trend, because the surface coverage of formaldehyde molecules on the sensor surface reaches saturation. At very low formaldehyde concentrations, the response–concentration plot of the sensor shows a good linearity (Figure 4c, inset). The linear dynamic range (LDR) is investigated from 0.05 to 1 ppm (linearly, $R^2 = 0.989$). The sensitivity, defined by the slope of the linear curve or $Δ(R/\ R_g)/Δ(\text{concentration})$, is about 4.454. The limit of quantification (LOQ) and limit of detection (LOD) of the sensor toward formaldehyde are calculated to be about 50 and 20 ppb (at a signal-to-noise ratio of 3), respectively. The LOD is below the formaldehyde emission standard (40 ppb) set by the U.S. Environmental Protection Agency. For an investigation into the selectivity of the CdO/Ga-rich CGO-based sensor, sensing properties to formaldehyde and potential interfering gases were investigated at the 10 and 100 ppm level, respectively (Figure 4d). The sensor shows the highest response to formaldehyde and a slight cross-response to ethanol ($S_{\text{formaldehyde}}/S_{\text{ethanol}} > 5$) and methanol ($S_{\text{formaldehyde}}/S_{\text{methanol}} > 20$), and is almost insensitive to gases such as acetone, xylene, toluene, benzene, CO, NH$_3$, and H$_2$, demonstrating the outstanding selectivity.

The reproducibility study of the CdO/Ga-rich CGO-based sensor was performed under 10 cycles of a dynamic response-recovery test (Figure 5a), over which initial resistance of the sensor remained unchanged, and responses to 10 ppm formaldehyde were uniform in each trial. Intraday and interday repeatabilities (Figures S16 and S17, Supporting Information) of the sensor were measured, showing good repeatability. For
identification of the long-term stability, the sensor responses to 10 ppm formaldehyde were recorded for up to 45 days. As shown in Figure 5b, the observed sensor responses remained quite steady with relative standard deviations (RSDs) of less than 10%. Taken together, the above results present that CdO/Ga-rich CGO is not only highly sensitive and selective but also a remarkably stable sensing material for formaldehyde detection. In fact, the formaldehyde-sensing function of the CdO/Ga-rich CGO-based sensor in terms of response, selectivity, and operating temperature is more competitive than those of sensors based on most of the nanostructured metal oxides reported in the recent literature (Figure 5c and 5d).
Table S4 in the Supporting Information). For established validation, the CdO/Ga-rich CGO-based sensor was applied to detect formaldehyde in real samples according to previous methods. The results (Table S5, Supporting Information) revealed that the sensor is suitable and reliable for ambient formaldehyde detection.

**Mechanism Investigation.** The mechanism responsible for reducing gas sensing in real-world conditions (existence of background oxygen) was illustrated in the Introduction. Semiconductor oxides identify reducing gases (e.g., formaldehyde, ethanol) through a change in resistance caused by reactions between surface chemisorbed oxygens and targeted gas molecules. For confirmation of the important role of absorbed oxygen, additional measurements in the absence of background oxygen were carried out. The experiments were performed by three processes (Figure S18a, Supporting Information): (1) positioning the CdO/Ga-rich CGO-based sensor at the operating temperature of 110 °C in a sealed chamber, (2) pumping out air in the chamber and filling with argon as background gas, and (3) injecting formaldehyde or ethanol into the chamber. In the meantime, the sensor resistance was monitored throughout the processes. In the oxygen removal process before equilibrium was reached, the base resistance of the sensor decreased remarkably (Figure S18b,c, Supporting Information). The result suggests that surface-absorbed oxygen, in the form of O2, is important for the detection of reducing gases such as formaldehyde and ethanol. In the meantime, the sensor resistance further decreased drastically. The notable responses could be attributed to the fact that reducing gas molecules (e.g., formaldehyde or ethanol) directly adsorb on the material as electron donors in the absence of background oxygen.

In this case, the sensor selectivity toward formaldehyde against ethanol has disappeared (S_{formaldehyde}/S_{ethanol} = 0.67), and the result is very different to that in the presence of background oxygen (S_{formaldehyde}/S_{ethanol} = 5.1). The comparison confirms that excellent selectivity of CdO/Ga-rich CGO in real-world conditions is achieved according to the different activity of formaldehyde and ethanol to the reaction with surface oxygen. Furthermore, the above results also indicate that the surface oxygen of CdO/Ga-rich CGO can maintain a low oxidation potential to distinguish formaldehyde and ethanol.

As confirmed by the scanning Kelvin probe method, the work function of CdO/Ga-rich CGO is close to that of stoichiometric CGO, and much lower than that of ZnO, In2O3, and SnO2 in air (Table S6 in the Supporting Information). The sensing properties of stoichiometric CGO, ZnO, In2O3, and SnO2 are given in Figure S19 (Supporting Information), and the detailed syntheses and structural characterizations of ZnO, In2O3, and SnO2 are shown in the Experimental Section and Figure S20 (Supporting Information). As expected, stoichiometric CGO also exhibited high selectivity toward formaldehyde. In addition, CdO/Ga-rich CGO and stoichiometric CGO have much better selectivity than ZnO, In2O3, and SnO2 toward formaldehyde. For example, the response ratio of S_{formaldehyde} to S_{ethanol} for CdO/Ga-rich CGO and stoichiometric CGO is about 5, while those for ZnO, In2O3, and SnO2 are less than 2.5 (Figure S21 in the Supporting Information). On the basis of all our results obtained above, the superior formaldehyde selectivity of CdO/Ga-rich CGO originated from its optimal surface oxygen activity. However, although our studies show that the work function greatly affects surface oxygen activity and selectivity of semiconductor oxides, we cannot quantitatively provide an optimum work function range for good selectivity because of the complexity of the gas-sensing mechanism and many other factors influencing the surface reactions. The factors related to sensing selectivity include operating temperature, surface modification, etc. In particular, operating temperature is an important parameter that influences the chemical activity of adsorbed oxygen and gas-adsorption and gas-desorption processes. Temperature-dependent selectivity curves in Figure S22 (Supporting Information) show that the selectivity (S_{formaldehyde}/S_{ethanol}) of the CdO/Ga-rich CGO-based sensor gradually degrades with the increasing temperatures. In addition, selectivity enhancements by suitable modifications are found in previous works, for example, enhanced formaldehyde selectivity of ZnO-SnO2 by Ag coating, and improved toluene selectivity of NiO by α-Fe2O3 decoration.

Furthermore, the high sensing response of CdO/Ga-rich CGO toward formaldehyde is interpreted as follows. In the composite, Cd and Ga exist in the trivalent and divalent states, respectively, as supported by the XPS spectrum of Cd 3d and Ga 2p. The two peaks at 405.9 eV (Cd 3d) and 1142.6 eV (Cd 3d) indicate the oxidation state of Cd^{2+} (Figure 6a),

![Figure 6. High-resolution XPS spectra of CdO/Ga-rich CGO in the region of the (a) Cd 3d level and (b) Ga 2p level. (c) Schematic illustration of the coordination environment of Cd^{2+} ions and Ga^{3+} ions, and resulting donor level doping in Ga-rich CdGa2O4 spinel. (d) O2-TPD profiles of CdO/Ga-rich CGO, Ga-rich CGO, and stoichiometric CdGa2O4. (e) Estimate of the relative amount of O2 adsorbed onto the surface of CdO/Ga-rich CGO, Ga-rich CGO, and stoichiometric CGO, based on comparison of integration areas of O2-TPD spectra and the integration areas normalized by specific surface areas.](Image 326x250 to 563x485)
substitution has proven to be efficient for increasing the amount of adsorbed oxygen and thus improving sensing response. This deduction was verified by the O$_2$-TPD profiles (Figure 6d), in which the amounts of O$_2$ adsorbed on the surface of CdO/Ga-rich CGO, Ga-rich CGO, and stoichiometric CGO were observed. The three sensing materials are both porous nanofibers assembled by nanoparticles, with BET surface areas of 43, 45, and 27 m$^2$/g for CdO/Ga-rich CGO, Ga-rich CGO, and stoichiometric CGO, respectively. After normalization by their surface area, the specific O$_2$ desorption capabilities of CdO/Ga-rich CGO and Ga-rich CGO are at least 2 times higher than that of stoichiometric CGO (Figure 6e), indicating the increasing adsorbed oxygen in the Ga-rich environment. Combining the advantages of aliovalent substitution (Ga$^{i+}$) in the off-stoichiometric spinel and higher surface area, CdO/Ga-rich CGO achieved a larger amount of adsorbed oxygen and thus higher response toward formaldehyde than stoichiometric CGO.

Moreover, heterojunctions between CdO nanoparticles and Ga-rich CdGa$_2$O$_4$ nanofibers were confirmed as another vital factor contributing to the high response of CdO/Ga-rich CGO. Previous reports suggested that forming heterostructures between two different oxides (e.g., ZnO/ZnCo$_2$O$_4$ and NiO/NiMoO$_4$) is effective to enhance gas response. In addition, some studies found that CdO-decorated n-type sensing materials, such as CdO/ZnO and CdO/In$_2$O$_3$, exhibit an enhanced response toward formaldehyde. In our case, the enhanced sensing properties by CdO functionalization might be related to large electron mobilities in CdO particles, beneficial to local electrical conduction at the CdO and Ga-rich CGO heterojunction and thereby to surface reaction kinetics when sensing occurs. However, the synergistic enhanced effects still call for further experimental and theoretical investigation.

**CONCLUSION**

In summary, an efficient and selective sensing material composed of CdO nanoparticle-decorated, Ga-rich off-stoichiometric CdGa$_2$O$_4$ porous nanofibers is reported for formaldehyde detection. This material is obtained by a facile method involving electrospinning preparation of Cd and Ga-embedded PVP nanofibers, followed by a calcination process, in which the CdO phase separates from the ideal CdGa$_2$O$_4$ spinel, and heterostructures between the CdO phase and Ga-rich CdGa$_2$O$_4$ spinel phase form simultaneously. The material shows high response, short response/recovery time, superior selectivity, and remarkable sensing stability toward formaldehyde at 110 °C. The superior selectivity is attributed to the low oxidation potential of surface-adsorbed oxygen. Moreover, sufficient amounts of adsorbed oxygen, and heterojunctions between CdO and Ga-rich CdGa$_2$O$_4$ have been demonstrated to be responsible for the high response. The results presented herein can bring new insights into the design or search of efficient sensing materials to achieve highly selective and sensitive detection.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b05251.

Band gaps and conductivity types; work functions; schematic diagram of sensor; DFT calculations of formation energies; structural parameters; details of XPS spectra, TG curve, EDS spectra, SEM images, TEM images, XRD patterns, Raman spectra, photographs, and UV–vis diffuse reflection spectra; additional measurements and properties of gas sensors (PDF)

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**Notes**

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