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Perovskite Nanoparticle-Sensitized Ga_2O_3 Nanorod Arrays for CO Detection at High Temperature

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Supporting Information

ABSTRACT: Noble metal nanoparticles are extensively used for sensitizing metal oxide chemical sensors through the catalytic spillover mechanism. However, due to earth-scarcity and high cost of noble metals, finding replacements presents a great economic benefit. Besides, high temperature and harsh environment sensor applications demand material stability under conditions approaching thermal and chemical stability limits of noble metals. In this study, we employed thermally stable perovskite-type $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (LSFO) nanoparticle surface decoration on Ga_2O_3 nanorod array gas sensors and discovered an order of magnitude enhanced sensitivity to carbon monoxide at 500 °C. The LSFO nanoparticle catalysts was of comparable performance to that achieved by Pt nanoparticles, with a much lower weight loading than Pt. Detailed electron microscopy and X-ray photoelectron spectroscopy studies suggested the LSFO nanoparticle sensitization effect is attributed to a spillover-like effect associated with the gas-LSFO- Ga_2O_3 triple-interfaces that spread the negatively charged surface oxygen ions from LSFO nanoparticles surfaces over to $\beta\text{-Ga}_2\text{O}_3$ nanorod surfaces with faster surface CO oxidation reactions.

KEYWORDS: semiconductor, nanowire, gas sensor, harsh environment, catalytic effect

■ INTRODUCTION

According to the U.S. Department of Energy, harsh environment sensors are predicted to save 0.25 quadrillion BTU/year of energy across all energy-consuming industries if successfully employed.^{1,2} In automotive and stationary energy industries, monitoring and controlling combustion-related emissions are top priorities for enhancing energy and environmental sustainability. However, commercially available sensor technologies for harsh environments are extremely limited due to the stringent requirements for sensor materials' high sensitivity, selectivity as well as stability in structure and performance under harsh operating conditions. Therefore, there is an urgent need to develop new sensor materials meeting such performance criteria in sensitivity and robustness, which are preferentially combined with low cost.

Traditionally, metal oxides have been used as basic sensor materials, and, in particular, a wide band gap $\beta\text{-Ga}_2\text{O}_3$ (~4.9 eV)³ is promising for high temperature gas sensing, owing to its high thermal and chemical stabilities.^{4–6} Ga_2O_3 thin-film-based gas sensors have been proven as promising oxygen sensors at

high temperature of 600–1000 °C. It also can detect reducing gases such as H_2 , CO, CH_4 , etc., at elevated temperature.⁷ Meanwhile, with decreased size and increased surface-to-volume ratio, metal oxide nanorods have shown good potential for chemical sensors.^{8,9} To further improve the sensor performance, various strategies can be used to directly control and enhance the fundamental material properties affecting sensing characteristics, such as doping,^{10,11} surface functionalization,^{12–14} and heterojunction design.^{15,16} Kim et al. demonstrated that the response of multiple-networked Ga_2O_3 nanowire sensors was enhanced ~17-fold by surface decoration of Pt nanoparticles.¹⁷ Park et al. synthesized Ga_2O_3 -core/ GaN -shell nanowires by directly nitriding the surface of Ga_2O_3 nanowire and the results showed the CO sensing performance can be enhanced at 150 °C by the created heterojunction.¹⁸

Among these approaches described above, the decoration of catalytically active noble metal on sensor material surfaces or interfaces has been one of the most effective and widely used techniques in practice that resulted in substantial improvements in the sensor performance through the catalytic spillover mechanism.¹³ However, due to the earth-scarcity, the concern over high cost of noble metals is an ongoing issue, and therefore, reduction or complete elimination of noble metal usage in the catalysts and related catalytic sensors would promise benefits not only to the relevant industries but also for addressing overarching concerns over global energy and environmental issues.¹⁹ Therefore, finding replacements of noble metals presents a great economic benefit with a significant opportunity for enhancing material and manufacturing sustainability.

On the other hand, the significantly decreased melting points of noble metal nanoparticles (for example, the melting point of Pt nanoparticles could be reduced to ~ 600 °C) due to a size effect coupled with inherent chemical instabilities also hinder their usage at elevated temperatures as sensitizers for harsh environment chemical sensors.^{20–22} Tietz et al. reported perovskite material $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ shows good thermal stability at high temperature. After sintering at 900–1300 °C for 6 h, the crystalline phases essentially remain the same.²³ In addition, rare-earth-based perovskite oxides have shown their potentials for catalytic and functional applications as in our recent demonstrations of the improved performance of various metal oxide nanowire arrays via the application of thin film perovskites.^{24–29}

Herein, we report a new discovery in which trace amounts of alternative perovskite oxide nanoparticles dramatically sensitize metal oxide nanorod gas sensors at high temperature. In the present work, we conducted a comparative study on the sensing properties of pristine, Pt-nanoparticle-, and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (LSFO)-nanoparticle-sensitized Ga_2O_3 nanorod arrays and clearly show that the perovskite-nanoparticle decoration can enhance the gas sensitivity by an order of magnitude at high temperature with excellent dynamic gas sensing response characteristics, which overall rivals the performance of Pt sensitizing effects.

■ EXPERIMENTAL METHODS

First we grow $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays by combining a hydrothermal method and high temperature calcination. A Si (100) wafer with 1 μm SiO_2 insulator layer is used as a substrate. To remove surface grease and organic deposits, the Si/ SiO_2 substrates were immersed in acetone solution and sonicated for 5 min. A 50 nm thick tin dioxide (SnO_2) film was sputter-coated as a seed layer followed by postdeposition ambient-annealing at 900 °C for 2 h in order to make it crystalline. A $\text{Ga}(\text{NO}_3)_3$ solution was prepared by dissolving 0.6 g $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 40 mL of deionized (DI) water, with the pH of solution controlled at ~ 2 . The SnO_2 -coated substrates were then incubated in $\text{Ga}(\text{NO}_3)_3$ solution at 150 °C for 12 h for the hydrothermal growth of the intermediate products, vertically aligned gallium hydroxide (GaOOH) nanorod arrays. After the growth, GaOOH nanorod arrays were washed by DI water, dried overnight in air at 80 °C, and finally subjected to annealing at 1000 °C for 4 h to be converted into pure $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays. To prepare Pt nanoparticles, a glycol solution of NaOH (50 mL, 0.5M) was added into a glycol solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1.0 g, 1.93 mmol in 50 mL) via stirring to obtain a transparent yellow platinum hydroxide or oxide colloidal solution. The solution was then heated at 160 °C for 3 h, with a N_2 flow passing through the reaction system to take away water and organic byproducts, finally yielding a transparent dark-brown homogeneous colloidal solution of the Pt metal nanocluster without any precipitates. Pt nanoparticles

were dip-coated with a control of ~ 3.0 wt % loading on the $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays, followed by a post heat-treatment at 450 °C for 2 h in order to remove the surface residual glycol ligands. The decoration of LSFO nanoparticles on Ga_2O_3 nanorod arrays was achieved by depositing LSFO (nominal thickness of 5–10 nm, monitored by a quartz microbalance) on $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays by radio frequency (RF) magnetron sputtering followed by postannealing to improve the crystallinity of LSFO nanoparticles.

The structural characteristics of intermediate GaOOH and final $\beta\text{-Ga}_2\text{O}_3$ nanorods with either Pt- or LSFO-nanoparticle surface decoration were studied by X-ray diffractometry (XRD, Bruker D8 Advance), scanning electron microscopy (SEM, JEOL JSM-6335F), and transmission electron microscopy (TEM, FEI Tecnai T12, acceleration voltage 120 keV). The selected area electron diffraction (SAED) in TEM was used to further confirm the crystal structures of the grown intermediate and final nanorods while scanning TEM (STEM, FEI Tecnai G2 F30, acceleration voltage: 300 keV) was used to examine the detailed morphology and composition distributions of $\beta\text{-Ga}_2\text{O}_3$ based nanorods. The Pt and perovskite loadings on Ga_2O_3 nanowire array sensors were measured using an inductively coupled plasma (ICP) optical emission spectrometer (PerkinElmer Optima 7300DV).

The high-temperature gas sensing properties of $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays were tested by monitoring the potentiostatic current response of the $\beta\text{-Ga}_2\text{O}_3$ nanorod array device to carbon monoxide (CO) exposure in a high-temperature tube furnace equipped with an alumina tube, electrical feedthroughs (Ni/Cr lead wires), and a gas injection system. The resistor-type $\beta\text{-Ga}_2\text{O}_3$ -based nanorod arrays were installed on an Al_2O_3 ceramic holder, shown in Figure S1. Two Pt wires (10 μm in diameter) were used to connect the nanorod gas sensor placed in the center position of the tube to Ni/Cr lead wires, which were externally connected to an electrochemical workstation (CHI 601C). The nanorod sensor was subjected to a fixed 1 V direct current (DC) bias while being heated from room temperature to 500 °C in air with a ramp rate of 20 °C/min. Gas sensing tests were then performed at 500 °C under varying concentration of CO (N_2 balance; from 20, 50, 80, to 100 ppm; total chamber pressure 1 atm). The responses of the nanorod sensor to CO were evaluated by measuring the magnitude of current change upon the exposure to various concentrations of CO under a dynamic gas flow condition with a constant flow rate of 1.5 L/min (with high purity N_2 as carrier gas), which was regulated by a computer-controlled gas mixing system (S-4000, Environics Inc., USA). The desired CO concentrations can be achieved by a 2% CO cylinder connected to one port of the system and diluted by a pure N_2 cylinder connected in another port of the gas mixing system. In detail, the nanorod sensor device was first exposed to CO/N_2 mixture for 16 min, followed by high purity N_2 purge for 24 min (i.e., one gas exposure cycle) to recover the sensor, and then multiple exposure cycles were repeated. We define the device gas sensitivity as $(R_0/R_{\text{CO}}) - 1$, where R_{CO} is the resistance under CO/N_2 mixture and R_0 is the resistance under high purity N_2 . The response time is defined as “the time duration required for gas sensitivity to reach 90% upon exposure of a sensor to CO”, and recovery is defined as “the time duration required for the gas sensitivity to decrease to 10% of the sensitivity upon the termination of CO injection”.

To investigate the chemical characteristics of nanoparticle-decorated $\beta\text{-Ga}_2\text{O}_3$ nanorods, we conducted X-ray photoelectron spectroscopy (XPS) analysis (PHI 5600ci with monochromatic Al K α characteristic X-ray) with the pass energy of the analyzer at 58.7 eV. Measured binding energies were referenced to the Ga 2p $_{3/2}$ peak, which was assigned a binding energy of 1117.9 eV for Pt/ Ga_2O_3 and 1117.5 eV for LSFO/ Ga_2O_3 , based on its position relative to the C 1s peak at 284.6 eV, which originates from adventitious carbon on the samples. Charge neutralization was employed to minimize the effects of sample charging. Treatments with O_2 , N_2 , and CO (10% in N_2) gases were performed at atmospheric pressure for 20 min at 500 °C in a reaction chamber directly attached to the XPS instrument, which permitted sample transfer between the reaction and analysis chambers without exposure to air.

RESULTS AND DISCUSSIONS

X-ray diffraction (XRD) analysis successfully resolved the crystal phases of intermediate GaOOH and final β -Ga₂O₃ nanorods before and after Pt or LSFO nanoparticle surface decoration (Figure 1). As shown in Figure 1a, most of the peaks

Figure 1. X-ray diffraction (XRD) patterns of (a) GaOOH nanorod arrays, (b) β -Ga₂O₃ nanorod arrays, (c) β -Ga₂O₃/Pt particles nanorod arrays, (d) β -Ga₂O₃/LSFO nanorod arrays.

in the GaOOH XRD spectrum are assigned to orthorhombic GaOOH phase (JCPDS #06–0180), with a preferred growth orientation perpendicular to (111) plane, instead of (110) plane typically observed in GaOOH powder.^{30,31} Strongly *c*-axis-oriented GaOOH nanorods were deposited by the hydrothermal method. Heterogeneous nucleation of GaOOH was efficiently induced on crystalline SnO₂ seed layers and further annealing converted the GaOOH nanorods to Ga₂O₃ nanorods without structural disintegration.³² Minor peaks present in the spectrum are originating from the underlying SnO₂ seed layer. After postgrowth annealing at 1000 °C for 4 h, the GaOOH phase is completely converted to monoclinic β -Ga₂O₃ (JCPDS # 41–1103) as shown in Figure 1b. These β -Ga₂O₃ nanorod arrays have a preferred growth orientation perpendicular to (111) plane of the monoclinic structure. The XRD spectrum of Pt-coated β -Ga₂O₃ (Figure 1c) displays no clear peaks corresponding to Pt due to its much smaller amount than Ga₂O₃. Similarly, the LSFO-nanoparticle-decorated β -Ga₂O₃ nanorod array does not display peaks corresponding to the LSFO perovskite, other than apparent Ga₂O₃ peaks (Figure 1d).

From SEM, we find that the grown vertical nanorod arrays have diameters of ~100–300 nm and lengths up to ~2 μ m. Figure 2a shows a representative top-view SEM micrograph of as-synthesized GaOOH nanorods grown on the Si(100) substrate. The tips of the nanorods reveal diamond-shaped cross sections with diagonal lengths of 150–350 nm, originating from its orthorhombic crystal symmetry (Figure S2). The 45°-tilted view of as-grown GaOOH nanorod arrays (Figure 2b) shows a well aligned vertical structure, while the energy dispersive X-ray spectra (EDXS) confirm the presence of Ga and O from the nanorods and Si from the underlying Si substrate (Figure 2c). From the cross-sectional view of growth substrate (Figure 2d), the length of vertical GaOOH nanorod arrays was determined to be ~1.8 μ m. After thermal annealing

Figure 2. (a) Top-view and (b) 45° tilt-view SEM images of GaOOH nanowires grown at 150 °C. (c) Corresponding GaOOH energy-dispersive X-ray (EDX) spectrum. (d) Cross-sectional view SEM image of GaOOH nanorod array. (e) Top-view SEM image of the β -Ga₂O₃ nanorods from GaOOH nanorods annealed at 1000 °C for 4 h, and coated with (f) LSFO and (g) Pt particles. All scale bars are 1 μ m.

at 1000 °C for 4 h, the converted pure Ga₂O₃ phase retained the diamond-shaped tips, which were not affected by the following Pt or LSFO nanoparticle decoration (Figure 2f, g). In addition, the average diagonal length of each sample is similar, which is shown in Figure S2. The composition analyses from ICP (Figure S3) showed that the Pt nanoparticle loading was ~3.39 wt % on β -Ga₂O₃ nanorod arrays, while 5 nm LSFO nanoparticle decoration led to ~0.61 wt % loading on β -Ga₂O₃ nanorod arrays, suggesting 10 nm LSFO nanoparticle decoration would result in ~1.22 wt % loading, only ~30% of Pt loading amount.

The low-magnification bright-field TEM combined with SAED analysis provide further structural details of grown nanorods and nanoparticle surface decoration. The as-synthesized GaOOH nanorod, with smooth side walls, has single-crystalline orthorhombic crystal structure (lattice constants $a = 4.58$ Å, $b = 9.8$ Å, $c = 2.97$ Å) and growth orientation perpendicular to the (111) plane (Figure 3a). The Ga₂O₃ nanorod converted from GaOOH on the other hand has seemingly roughened surfaces as the bright-field TEM micrograph features local variation in contrast, which is generally resulting from the density variation (Figure 3b). A more detailed examination by STEM reveals that the contrast variation was in fact caused by the porous structure of β -Ga₂O₃ nanorod (Figure S4). The porous β -Ga₂O₃ nanorod is however textured with monoclinic structure ($a = 12.22$ Å; $b = 3.038$ Å; $c = 5.807$ Å; $\alpha = 90^\circ$, $\beta = 103.82^\circ$, $\gamma = 90^\circ$) with a growth orientation normal to (001) plane as confirmed by SAED analysis (Figure 3b inset). The perovskite LSFO-nanoparticle decoration by sputter deposition yields sparsely distributed LSFO nanoparticles of <10 nm size on the surface of β -Ga₂O₃ nanorod (Figure 3c); no diffraction peaks of LSFO was revealed in the SAED pattern due to its small quantity. The more detailed distribution of LSFO nanoparticles is provided in

Figure 3. (a) TEM image of a GaOOH nanorod grown at 150 °C, and the inset is the corresponding electron diffraction pattern indicating the GaOOH nanorod growth plane is parallel to (111). (b) TEM image of a β -Ga₂O₃ nanorod annealed at 1000 °C for 4 h, and the inset is the corresponding electron diffraction pattern indicating the growth plane is parallel to (001). (c) TEM image of postannealing β -Ga₂O₃ coated with LSFO 5 nm, and inset is the electron diffraction pattern corresponding to the nanowire in c, which shows the preferred growth plane of β -Ga₂O₃ nanorod is (001). (d) TEM image of postannealing β -Ga₂O₃ coated with Pt particles.

Figure S4. Pt nanoparticle decoration on the β -Ga₂O₃ nanorod surface has a more uniform spatial distribution of Pt

nanoparticles, which have a mean diameter of ~ 4 nm (**Figure 3d**).

We find that the LSFO nanoparticle decoration has an excellent gas sensing catalytic performance on β -Ga₂O₃ nanorods, comparable to that of Pt nanoparticle decoration. We tested the high-temperature (500 °C) CO gas sensing properties of β -Ga₂O₃ nanorod arrays with three different surface conditions: pristine, Pt-nanoparticle-decorated, and LSFO-nanoparticle-decorated (5 or 10 nm nominal film thicknesses). **Figure 4a** shows the dynamic sensing characteristics of the above materials to four different CO gas concentrations (20, 50, 80, and 100 ppm in N₂ balance), where CO sensitivity in general increases for higher CO concentrations, regardless of the type of sample. While the pristine Ga₂O₃ nanorod array shows a base sensitivity ~ 8 at 100 ppm of CO exposure, the sensitivity of 10 nm-LSFO-nanoparticle-decorated sample exceeds ~ 70 at the same CO concentration. This is approaching the sensitivity performance of Pt-nanoparticle-decorated Ga₂O₃ nanorod (sensitivity ~ 95 at 100 ppm of CO). In fact, at lower CO concentrations, sensing performances of 10 nm LSFO and Pt nanoparticles are nearly identical (**Figure 4b**). Meanwhile, 5 nm LSFO nanoparticle decoration has a decreased sensitivity by $< \sim 30\%$ compared with 10 nm LSFO nanoparticle decoration, which most likely results from smaller nanoparticle surface coverage, as supported in **Figure S4**, which revealed the sparse distribution of LSFO nanoparticles on Ga₂O₃ nanorods.

In addition to the excellent CO sensitivity, the LSFO-nanoparticle-decorated Ga₂O₃ nanorod array has a faster

Figure 4. Carbon monoxide gas sensing test results: (a) Current–time characteristics of β -Ga₂O₃; β -Ga₂O₃/LSFO 5 nm; β -Ga₂O₃/LSFO 10 nm; β -Ga₂O₃/Pt composite nanorod tested at 500 °C with N₂ as background atmosphere; (b) sensitivity versus CO concentrations characteristics of β -Ga₂O₃; β -Ga₂O₃/LSFO; β -Ga₂O₃/Pt composite nanorod tested at 500 °C; (c) response time versus CO concentrations characteristics of β -Ga₂O₃; β -Ga₂O₃/LSFO; β -Ga₂O₃/Pt composite nanorod tested at 500 °C; (d) recovery time versus CO concentrations characteristics of β -Ga₂O₃; β -Ga₂O₃/LSFO; β -Ga₂O₃/Pt composite nanorod tested at 500 °C.

Figure 5. X-ray photoemission spectra of (a) La 3d, (b) Fe 2p, and (c) O 1s for LSFO/ β -Ga₂O₃.

response time to a given CO exposure than Pt-nanoparticle decoration. For all the examined CO concentrations, the LSFO-nanoparticle decoration has shorter response time than Pt-nanoparticle decoration, while having comparable or slightly longer response times compared with pristine Ga₂O₃ nanorods (Figure 4c). In particular, at the highest CO concentration (100 ppm), LSFO nanoparticle decoration has a response time of ~200 s, ~400 s shorter than that for Pt-nanoparticle decoration. Meanwhile, the recovery time of Ga₂O₃ nanorod sensors having LSFO nanoparticle decoration was either comparable or slower (especially for 10 nm-LSFO) than that of Pt nanoparticle decoration (Figure 4d), but faster than that of the pristine Ga₂O₃ sensor.

To identify potential mechanisms of high gas-sensing catalytic activity of LSFO nanoparticles, it is useful to examine the general gas sensing principles in Ga₂O₃ and Pt nanoparticle catalysts. Ga₂O₃, due to its wide band gap (4.9 eV), has a relatively high electrical resistance at room temperature. At a sufficiently elevated temperature (500 °C in this case), reactive oxygen species such as O⁻ and O²⁻ are known to be chemisorbed on the surface of the Ga₂O₃ and, importantly, to experience electron transfer with Ga₂O₃.⁴⁻⁶ Specifically, these chemisorbed oxygen molecules trap mobile electrons from the conduction band of β -Ga₂O₃, creating charge carrier depletion at the surface. However, different oxygen species are dominant in several temperature ranges, usually O₂⁻ ions are adsorbed/desorbed at room temperature to ~200 °C, whereas in 200 °C to ~550 °C range O⁻ ions are dominant and O²⁻ ions exist above 550 °C. Under such a condition, when CO gas molecules are introduced to the Ga₂O₃ surface, CO molecules react with preadsorbed oxygen ions via the following reaction paths^{9,17,33-35}

The result is then the release of mobile electrons back to Ga₂O₃, which induces the increase in carrier density in Ga₂O₃

(i.e., decrease in depletion depth) and, ultimately, the apparent current response of the sensor. The process is reversed when CO exposure is terminated as residual ambient oxygen molecules are rechemisorbed on the surface, resulting in the decrease of current response in Ga₂O₃ back to the original base level (i.e., recovery). It is worth pointing out that the residual gas analysis confirmed that ambient oxygen molecules existed in both ultrahigh purity N₂ and CO/N₂ flows used in the experiment (Figure S5). Although the series of steps generally explain the gas sensing mechanism of the pristine Ga₂O₃ nanorod array, the enhancement of gas sensing performance by the Pt nanoparticle decoration is believed to be originating from, so-called, spillover effects.¹⁷ In the spillover process, CO molecules are first efficiently adsorbed on the Pt nanoparticles surface and react with preadsorbed oxygen species on the nanorods with reduced activation energy, resulting in an efficient electron back-feeding into the charge depletion layer of Ga₂O₃. In addition, the Pt electric sensitization effect is further enhancing the gas sensing: this is caused by the difference between work function of Pt (5.65 eV)³⁶ and Fermi level (approximately electron affinity, considering n-type characteristics) of Ga₂O₃ (4.9 eV),³⁷ which renders the electronic properties of the Ga₂O₃ surface further charge-depleted.

For the observed enhancement of CO sensing performance by LSFO nanoparticle decoration, we find that the spillover effect is one of the likely responsible mechanisms, as supported by XPS analysis of the LSFO-nanoparticle-decorated Ga₂O₃ nanorod array (Figure 5). XPS analyses performed on the LSFO-nanoparticle-decorated β -Ga₂O₃ nanorod array after 500 °C treatment in CO (20 min) show negligible differences in binding energies for Fe 2p, La 3d, and Sr 3d (not shown), compared with the control LSFO-nanoparticle-decorated Ga₂O₃ nanorods treated at 500 °C under pure N₂ (Figure 5a). The lack of evidence for a strong chemical interaction between LSFO nanoparticles and β -Ga₂O₃ nanorods is consistent with the good high-temperature sensing stability as well as the observed fast sensing response of LSFO-nanoparticle-decorated nanorods. Meanwhile, there is a small but

Figure 6. Gas sensing enhancing mechanism. (a) $\beta\text{-Ga}_2\text{O}_3$ and LSFO decorated $\beta\text{-Ga}_2\text{O}_3$ nanorods in N_2 atmosphere. (b) $\beta\text{-Ga}_2\text{O}_3$ and LSFO decorated $\beta\text{-Ga}_2\text{O}_3$ nanorods in CO/N_2 atmosphere. (c) Spillover-like effect model in LSFO nanoparticle decorated $\beta\text{-Ga}_2\text{O}_3$ nanorod surface in CO/N_2 atmosphere; DL, carrier depletion layer.

nonzero broadening of the O 1s peak; a potential indication of change in electron distribution around oxygen on the LSFO surface upon CO treatment (Figure 5c), which points to the possibility of spillover effects operating on LSFO nanoparticles. On the basis of an XPS analysis of Pt-nanoparticle-decorated Ga_2O_3 nanorod arrays exposed to different gas treatments, we believe that the sensing performance enhancement by Pt is related to typical spillover effects,^{11–13} whereas the slow Pt– Ga_2O_3 sensor response we observed may be originating from varying oxidation states of Pt (Figures S6 and S7). In addition to the spillover effect, the LSFO nanoparticle sensitization may be also contributed to by the space-charge effect generally observed in metal oxide sensor systems.³⁵ Similar to the electric sensitization by Pt on Ga_2O_3 , LSFO can generate a charge depletion layer on the Ga_2O_3 nanorod surface upon contact due to the difference in Fermi levels and resulting spontaneous charge transfer (Figure 6a). When a reducing CO gas is introduced, the surface depletion layer becomes thinner, increasing the overall electrical conductance of the nanorod (Figure 6b). We note that there are many potential material properties that can also affect the observed sensitization, such as surface states, oxygen vacancies, and interfaces between LSFO nanoparticles and the Ga_2O_3 nanorod, which can act as adsorption sites for the CO gas molecules.^{38,39} Also, LSFO itself might have an active sensing functionality, but this possibility is thought to be minimal based upon the little or negligible CO sensing response at the 20–100 ppm of CO concentration range we observe for continuous LSFO thin films (Figure S8a).

Figure S8b revealed the good sensitivity of LSFO thin films for the oxidative gas NO_2 with increased current observed upon exposure, a p -type semiconductor characteristic. Therefore, a p – n junction is formed between LSFO and Ga_2O_3 . Due to its surface dominant nature, it is possible the built-in-potential of this p – n junction may regulate the electrons and holes involved in surface conduction upon gas exposures. The gas-LSFO- Ga_2O_3 triple-interface may function as a sink that attracts negatively charged surface oxygen species such as O^- from the LSFO nanoparticle surface causing it to spread over to the

Ga_2O_3 nanorod surface (Figure 6c) as indicated by the surface reactions described earlier. Meanwhile, the insensitive response of LSFO film upon CO exposure indicates the slow or negligible reactions between O^- and CO on LSFO surfaces, which enables the formation of a concentration gradient driving the spread of less-consumed LSFO surface oxygen ions toward the LSFO/ Ga_2O_3 interfaces and Ga_2O_3 nanorod surfaces. On the other hand, the resulting populated oxygen dissociation events and subsequently generated surface oxygen species on LSFO nanoparticle surfaces may contribute to the shorter response time in LSFO- Ga_2O_3 nanorod sensors than Pt decorated ones, beside the possible effect associated with changing surface oxidation states of Pt as revealed in the XPS study. It is worth noting that perovskite-type ABO_3 materials have good lattice oxygen storage capability^{38–42} at high temperature directly attributed to their tunable oxygen deficiency. This lattice oxygen may still add to the O^- distribution and the adsorbed residual O_2 species that can enhance recovery upon termination of CO from the gas stream, although at 500 °C bulk defects may play a secondary role on the surface reaction dynamics compared to the surface defects.

CONCLUSIONS

In summary, large-scale LSFO-nanoparticle-modified Ga_2O_3 vertical nanorod arrays have been successfully fabricated using a two-step synthetic procedure. The structural and CO-sensing characteristics of the pristine, Pt-nanoparticle-, and LSFO-nanoparticle-modified $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays show that 10 nm LSFO nanoparticle decoration greatly enhances the high-temperature (500 °C) CO sensitivity of pristine $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays by an order of magnitude, rivaling the sensitizing performance of Pt noble metal nanoparticle catalysts. Further, the decorated LSFO nanoparticles are only accounted for ~10–30% of that of Pt weight loading on $\beta\text{-Ga}_2\text{O}_3$ nanorod arrays. A “catalytic spillover” effect is identified in LSFO- Ga_2O_3 nanorod sensors as regulated by the LSFO- Ga_2O_3 p – n semiconductor junction. Meanwhile, Pt oxidation state changes and surface oxygen ion populating sites of LSFO may help to enable the faster CO sensing response for LSFO

decorated nanorod sensors than that for Pt decorated sensors. The demonstrated perovskite LSFO-nanoparticle-modified Ga₂O₃ nanorod represents a promising candidate for high-performance sensor material for high-temperature gas detection.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b01709.

Detailed scanning electron microscopy image of GaOOH nanorod arrays, scanning transmission electron microscopy image of LSFO-decorated β -Ga₂O₃ nanorod, X-ray photoelectron spectra of Pt- β -Ga₂O₃ nanorod arrays under different atmosphere treatments at 500 °C, and gas sensing property of LSFO thin film test at 500 °C (PDF)

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Notes

The authors declare no competing financial interest.

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