Enhanced CO Sensing Performances of PdO/WO3 Determined by Heterojunction Structure under Illumination

Yue Cao, Chunming Zhou, Yanping Chen, Hongwei Qin, and Jifan Hu*

ABSTRACT: The CO sensing performances and mechanism of PdO/WO3-based sensors were investigated by experiments and density functional theory calculations. The CO sensing performance can be significantly enhanced by decorating WO3 with PdO, which is attributed to the catalyst (chemical sensitization) and P–N junction (electronic effect). On the one hand, PdO is an excellent catalyst used to promote the adsorption of oxygen species. On the other hand, the constructed P–N junction structure between PdO and WO3 can facilitate the migration of carriers and suppress the recombination of electrons and holes, which promote the adsorption of more oxygen species. Furthermore, the calculation results verify that decorating WO3 with PdO can significantly enhance the CO sensing response by providing more adsorption sites available for oxygen species and making more electrons to transfer from CO to PdO/WO3 configuration. Moreover, the band gap energies of the WO3 sensor can be reduced by PdO decoration, and the light absorption range in the visible light region can be expanded. More photogenerated electron–hole pairs can be produced based on the P–N junction structure, which can promote the progress of electrochemical reactions. Thus, the PdO/WO3 material can be a promising candidate to detect CO, and it can effectively utilize the UV–visible light to destruct the CO contaminant.

INTRODUCTION

CO is a colorless, odorless, and toxic gas, which is the product of incomplete combustion of various fuels. Moreover, CO is a common asphyxiating chemical pollutant that seriously endangers the health of individuals. CO prefers to combine with hemoglobin in the body of human to form carboxyhemoglobin (COHb), which makes the hemoglobin lose its ability to carry oxygen. In addition, the tissue of individuals can be threatened and the persons may even die in severe cases. CO has negative effects on whole body tissue cells, especially on the cerebral cortex. Thus, there is an extraordinary significance to research the expensive and highly responsive CO sensors.

In the past decades, tungsten trioxide (WO3)-based sensors have attracted great attention because of their excellent electrical properties. WO3 is also a promising material in the field of CO sensors. For example, Tian et al. investigated CO sensing mechanism on the hexagonal WO3(001) surface by density functional theory (DFT) calculations. Susanti et al. highlighted that WO3 can be a potential material in CO sensors. Moreover, WO3 has excellent optical properties, which can be used in photocatalysis. However, because of the wide band gap of WO3, the absorption of visible light is limited. In order to solve the shortcomings of the wide band gap and improve the CO sensing response of WO3-based sensors using a simple method, many researchers have devoted to decorating the surface of WO3 materials with noble metals or metal oxides. For example, Yao et al. reported that Ag nanoparticles could boost the sensor performance effectively under light illumination because of the localized surface plasmon resonance effect. Yuan et al. reported that the NH3 sensing performance can be enhanced by the formation of a unique WO3–SnO2 core–shell heterojunction structure. Gao et al. proposed that WO3/NiO-based sensors showed excellent xylene sensing performance, which can be attributed to the microspheres and the effect of P–N heterojunctions. Compared with metal oxides, decorating WO3-based sensors with noble metals is not always optimal because the noble metal particles on the support are unstable and tend to aggregate together at a high operating temperature, leading to the decrease in the catalytic activity of noble metal particles.

PdO makes up for the shortcomings of noble metals. Meanwhile, PdO is a typical p-type semiconductor, and decorating WO3 with PdO can construct a P–N junction structure, which can promote the progress of electrochemical reactions.
RESULTS AND DISCUSSION

Characterizations of PdO/WO3 Powders. The X-ray diffraction (XRD) patterns of PdO/WO3 powders are shown in Figure 1. The samples can be well indexed by the WO3 phase with monoclinic structure (according to the JCPDS no. 72-0677). Unfortunately, palladium element cannot be found by XRD as the content of PdO is extremely small. FE-SEM was implemented to investigate the microstructures of 1.0 mol % PdO/WO3 powders, as shown in Figure 2a,b. Figure 2a shows the FE-SEM images at low resolution, which reveal that the size of PdO/WO3 powders ranges from 70 to 600 nm, which is around 200 nm for most particles. Before characterizing the size distribution, the nanopowders need be dissolved in water to form a suspension. During this process, the concentration of the suspension could affect the size of the crystallites; meanwhile, a few particles could be agglomerated because of their small size, which also made the particle size measured by the Zetasizer Nano a little larger. However, the rule of particle size distribution is consistent with that in FE-SEM. To further analyze the microstructure of 1.0 mol % PdO/WO3, high-resolution transmission electron microscopy (HR-TEM) was performed to investigate the distribution, the morphology, and the size of PdO present in the WO3 material, as shown in Figure 2d,e. Several small dots were found on the surface of the WO3 material (see in Figure 2d), and HR-TEM was implemented to analyze the composition of these dots (see in Figure 2e). It is found that these particles are located on the surface of the WO3 material and indicated in the blue circle. These particles are in the form of nanospheres with a diameter of about 5.16 nm, which are conjectured as PdO. Meanwhile, EDX mapping was performed (see in Figure 2g–j) to confirm the existence of the Pd element, and the content of different elements is given in Figure S3. Furthermore, the interplanar spacing of the WO3 particle was analyzed by HR-TEM, as shown in Figure 2f. In the light of the figure, the interplanar spacing of the measured area is 0.3867 nm, which is consistent with that of the (002) film of WO3 obtained from the XRD standard spectrum. There are multiple lattices coexisting in the blue circle region, which are speculated to be WO3 and PdO, and the corresponding area at low resolution is shown in the inset of Figure 2f.

X-ray photoelectron spectroscopy (XPS) of PdO/WO3 powders was accomplished, as shown in Figure 3. Figure 3a shows the wide survey scan of 1.0 and 3.0 mol % PdO/WO3 powders, and the XPS spectra of the elements W, O, and Pd are all displayed. Owing to the low content of Pd element for 1.0 mol % PdO/WO3 powders, the signal-to-noise ratio is relatively low, and the XPS spectrum signal of the Pd element is weak. Thus, the XPS spectra of Pd 3d for 3.0 mol % PdO/WO3 powders were also analyzed. As Figure 3b shows, the XPS spectra of Pd 3d can be deconvoluted into two peaks, which are at around 337.1 eV (337.0 eV) and 342.4 eV (342.3 eV) for 1.0 mol % PdO/WO3 powders (3.0 mol % PdO/WO3 powders), ascribed to the 3d5/2 and 3d3/2 states of PdO. Moreover, as shown in Figure 3c, the peaks of O 1s for 1.0 mol % PdO/WO3 powders centered at 530.5 and 531.7 eV are consistent with the values of lattice oxygen for WO3 and adsorbed oxygen, respectively. Figure 3d shows the XPS spectra of W 4f for 1.0 mol % PdO/WO3 powders, whose peaks are located at around 35.8 and 37.9 eV, which could be assigned to the 4f7/2 and 4f5/2 states of W6+, respectively. Meanwhile, the XPS spectra of pure WO3 powders are shown in Figure S4.

CO Sensing Performances of PdO/WO3-Based Sensors under Natural Illumination. CO sensing performances of PdO/WO3-based sensors are shown in Figure 4. Figure 4a shows the resistances in air as a function of operating temperature for PdO/WO3-based sensors. As the operating temperature rises, the resistances of PdO/WO3-based sensors decrease, which can be attributed to the nature of semiconductors. Meanwhile, the resistances of pure WO3-based sensors are lower than those of PdO/WO3-based sensors at each fixed operating temperature, owing to the formation of P–N heterojunctions. With an increasing PdO content, the resistances of sensors increase. Decorating the WO3 surface with PdO can promote the adsorption of oxygen species and the formation of P–N junctions, which explains why the resistances of sensors are proportional to the PdO content.
The operating temperature dependence of responses for PdO/WO₃-based sensors to 500 ppm CO are shown in Figure 4b. As the operating temperature rises, the CO sensing responses of PdO/WO₃-based sensors gradually increase to a maximum and then decrease. The types of species adsorbed on sensors over different temperature ranges is a crucial reason that can be used to explain this phenomenon. Meanwhile, some other factors are also proposed to explicate the relationship between the operating temperatures and gas sensing responses, such as the rates of adsorption and desorption (of oxygen species, the detected gas, and the products) and the structure and nature of WO₃ material with PdO decoration. Moreover, the CO sensing responses of PdO/WO₃-based sensors are much better than those of pure WO₃ sensors. The best responses of 0.4, 1.0, and 3.0 mol % PdO/WO₃-based sensors to 500 ppm CO are 7.353, 10.392, and 6.933 at the operating temperature of 280, 280, and 240 °C, respectively, whereas the response for pure WO₃-based sensors to 500 ppm CO is around 1, which indicates that decorating WO₃ with PdO can significantly enhance the CO sensing response, and 1.0 mol % PdO/WO₃ powders can be a promising sensor for the detection of CO.

The dynamic responses of resistance at different operating temperatures to 500 ppm CO for pure WO₃-based sensor and 1.0 mol % PdO/WO₃-based sensor are shown in Figure 4c. As the operating temperature increases, the resistances of sensors in air gradually decrease. When CO gas (reducing gas) is introduced, the resistances of both pure WO₃-based sensor and 1.0 mol % PdO/WO₃-based sensor are greatly reduced until equilibrium is reached. Further, when CO gas is released, the resistances of sensors rise rapidly. Meanwhile, the response time of sensors at high operating temperatures (more than 200 °C) is much shorter than that at lower operating temperatures, at which the equilibrium of resistances for sensors were not realized within 360 s. Moreover, when the operating temperature is below 260 °C, the resistance of 1.0 mol % PdO/WO₃-based sensor cannot be recovered to the initial value in a short time; yet, when the operating temperature is higher than 260 °C, the resistance of 1.0 mol % PdO/WO₃-based sensor will be fully recovered. However, during the whole experiment, the resistance of the pure WO₃-based sensor could not be returned to the initial value within a short
Thus, the decoration of PdO can accelerate the recovery of the WO$_3$-based sensor and has advantages in the reusability of the sensor.

The dynamic response curves to the different concentrations of CO gas for the pure WO$_3$-based sensor and PdO/WO$_3$-based sensors at 280 °C are shown in Figure S5. As the concentrations of CO gas increase, the gas sensing responses of sensors increase, and the responses are linearly related to the concentration of CO (shown in Figure 4d). According to the figures, the response of pure WO$_3$-based sensors is linearly related with the concentrations of CO, and it is much lower than the CO sensing response of PdO/WO$_3$-based sensors. Meanwhile, the decoration of PdO has an effect on the relationship between the responses of sensors and concentrations of CO. When the concentrations of CO are lower than 400 ppm, the relationships between the gas sensing responses of 0.4, 1.0, and 3.0 mol % PdO/WO$_3$-based sensors and the concentration of CO satisfy the linear function $Y = 0.015X + 0.415$, $Y = 0.022X + 0.01$, and $Y = 0.011X + 0.806$, respectively. Also, when the concentrations of CO reach 400 ppm, the functions $Y = 0.005X + 4.631$, $Y = 0.009X + 5.428$, and $Y = 0.003X + 4.205$ are satisfied for 0.4, 1.0, and 3.0 mol % PdO/WO$_3$-based sensors. It is found that the 1.0 mol % PdO/WO$_3$-based sensor has the best response rate to CO gas, and when the concentrations of detected CO exceed 400 ppm, the response rate of the sensors to CO gas is significantly reduced, which may be due to the limitations of the surface area of the sensors and the available adsorption sites for oxygen species. It is promising for the application of PdO/WO$_3$-based sensors to detect the low concentrations of CO gas. Figure 4e shows the dynamic response curves for PdO/WO$_3$-based sensors to 500 ppm CO under natural light and in dark. The CO sensing responses under natural light are 1.294, 10.392, and 5.341, whereas that in dark are 1.237, 9.246, and 3.442 for 0.0, 1.0, and 3.0 mol % PdO/WO$_3$-based sensors, respectively. The response can be greatly improved under natural light for PdO/WO$_3$-based sensors, whereas the CO sensing responses can be hardly affected by natural light for the pure WO$_3$-based sensor, which indicates that the decoration of PdO can promote the utilization of light for the sensor to improve the CO sensing response. Furthermore, the repeated sensing performances of the 1.0 mol % PdO/WO$_3$-based sensor to 500 ppm CO at 280 °C were implemented (see Figure 4f). The resistance of the sensor in air and the repeated responses to 500 ppm CO in long term is shown in Figure S6, which indicates that the 1.0 mol % PdO/WO$_3$-based sensor has excellent stability and can be reused.

Adsorption Process of CO on Sensors Based on DFT Calculations. In order to simulate the adsorption process of CO on sensors in experiments, DFT calculations were carried out.

First, the band gap energies of pure WO$_3$ and PdO/WO$_3$ structures were calculated, as shown in Figure 5. Pure WO$_3$ and the PdO/WO$_3$ structure have band gap energies of 2.053 and 1.081 eV, respectively, which proves that the decoration of PdO can decrease the band gap energy of WO$_3$, and it is consistent with the conclusion in the experiment. However, because of the limitation of Dmol3, the DFT + U treatment cannot be implemented, which makes the calculated band gap energy smaller than that in experiment. Then, the gas sensors in experiment were simulated by adsorbing the oxygen species (O$^-$, O$_2^-$) and hydroperoxyl radical (OOH) on the...
surface of WO$_3$ and PdO/WO$_3$ configurations as substrates (shown in Figure S7). A variety of initial models for CO adsorption on different substrates were calculated to find the optimized structures, as shown in Figure 6. Simultaneously, the corresponding calculated results [the adsorption bond length $D$ (Å), the electron transfer amount from the CO molecule $Q_{\text{CO}}$ (e), and the adsorption energy $E_{\text{ads}}$ (eV)] are shown in Table S1. The calculated results prove that CO can not only be adsorbed to the W site and Pd site of the substrate (see in Figure S8) but also prefer to react with the species pre-adsorbed on the substrate to form CO$_2$. In mode (a−c), the CO$_2$ molecules exist in free form, whereas in mode (d−f), the generated CO$_2$ molecules can be adsorbed on the PdO surface by physical adsorption, corresponding to the adsorption bond lengths of 2.301, 2.244, and 2.306 Å, respectively. During these processes, the adsorption energies are 3.81, 3.36, 4.98, 2.94, 3.32, and 4.06 in modes (a−f), respectively, which indicates that all of the above processes can be carried out spontaneously with the release of heat. Moreover, during the adsorption reaction, CO molecules can release electrons to substrates. Further, the electron transfer from CO to the substrates in modes (a−f) are 0.353 e, 0.284 e, 0.366 e, 0.394 e, 0.443 e, and 0.421 e, respectively, which explains theoretically the reason why the resistance of the gas sensor decreases after CO is introduced. Meanwhile, compared with the pure WO$_3$(001) surface, more electrons can be transferred from CO to WO$_3$(001) with the PdO-decorated surface, which proves that the decoration of PdO can greatly enhance the CO sensing response of WO$_3$-based sensors in experiment.

On the other hand, when more oxygen molecules were introduced, the PdO/WO$_3$ configurations can provide more adsorption sites for oxygen species, compared with the pure WO$_3$(001) surface (see in Figure 8), so that more CO molecules would be prone to react with the preadsorbed oxygen species, which can theoretically explain that the CO gas sensing response for the WO$_3$ sensor can be significantly improved by decorating WO$_3$ with PdO (chemical sensitization).

**CO Sensing Performances of PdO/WO$_3$-Based Sensors under UV−Visible Illumination.** As Figure 9a shows, the UV−visible absorption spectrum of sensors was measured. It is found that the absorption edge of the pure WO$_3$-based sensor is at around 500 nm, whereas the absorption edge of PdO/WO$_3$-based sensors gradually red-shifts. In addition, as the content of PdO increases, the absorbance of light for PdO/WO$_3$-based sensors can be significantly increased at each fixed wavelength, and a wider wavelength range of light can be absorbed for PdO/WO$_3$-based sensors in the visible region, compared with the pure WO$_3$-based sensor. Based on Figure 9a, the $(ahu)^2=-(hu)$ curves for pure WO$_3$ and 1.0 and 3.0 mol % PdO/WO$_3$ are plotted, as is shown in Figure 9b. Meanwhile, the band gap energies of pure WO$_3$ and 1.0 and 3.0 mol % PdO/WO$_3$ are estimated to be 2.83, 2.80, and 2.70 eV, respectively, and the band gap energy of the pure WO$_3$ material is substantially identical to that mentioned in ref 27. All these results can be obtained by the following formula:

$$\text{CO adsorption models on WO}_3(001) \text{ surfaces and PdO/WO}_3(001) \text{ surfaces with pre-adsorbed species.}$$

$$\text{DOS of free CO, free CO}_2, \text{ and CO}_2 \text{ generated in modes (a−f).}$$

$$a(ahu)^2=A(h-E_g)$$

(1)
where \( a \) is the absorbance; \( h \nu \) is the photon energy; \( A \) is a constant; and \( E_g \) is the band gap energy of the material. It is clearly seen that the band gap energies of PdO/WO\(_3\) materials gradually decrease with the PdO content increasing. In a word, the decoration of PdO has significant effects on the absorption range of light and band gap energies for WO\(_3\) sensors.

The photon energy is inversely proportional to the wavelength of light, and the photon energies are 3.45, 3.07, and 2.80 eV for light at 365, 410, and 450 nm, respectively, according to the following formula30

\[
E = \frac{hc}{\lambda}
\]

where \( c \) is the speed of light, about \( 3.0 \times 10^8 \) m/s; \( h \) is the Planck constant, approximately \( 4.2 \times 10^{-15} \) eV·m; and \( \lambda \) is the wavelength of light. The photon energy of light at 365 and 410 nm are much larger than the band gap energies of both the pure WO\(_3\)-based sensor and PdO/WO\(_3\)-based sensors, whereas the photon energy of light at 450 nm is lower than the band gap energies of the pure WO\(_3\)-based sensor and a little larger than that of PdO/WO\(_3\)-based sensors. Only when the energy of light is larger than the band gap energy of the sensor, light can be absorbed, forming photogenerated electron–holes, and then undergoing a redox reaction, which is a crucial reason why the CO sensing responses of sensors can be significantly enhanced under 365 and 410 nm illumination. Meanwhile, the 450 nm illumination can also be adsorbed, and the CO sensing responses of sensors can be enhanced under 450 nm illumination, after decorating WO\(_3\) with PdO. Thus, it is concluded that the decoration of PdO can widen the absorption range of visible light.

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Figure 8. Oxygen species adsorption configurations on pure WO\(_3\)(001) surfaces and PdO/WO\(_3\)(001) surfaces.

Figure 9. (a) UV–visible absorption spectrum of PdO/WO\(_3\) powders; (b) \((ah\nu)^2-(h\nu)\) curves for 0.0, 1.0, and 3.0 mol % PdO/WO\(_3\) powders; (c) dynamic response curves of 0.0, 1.0, and 3.0 mol % PdO/WO\(_3\)-based sensors to 500 ppm CO exposed to ultraviolet light (96 \( \mu \)W cm\(^{-2}\)); the dynamic response curves of (d) 0.0, (e) 1.0, and (f) 3.0 mol % PdO/WO\(_3\)-based sensors to 500 ppm CO under dark, 410, and 450 nm illumination (732 \( \mu \)W cm\(^{-2}\)), respectively.
CO Sensing Mechanism of PdO/WO₃-Based Sensors under Illumination. According to all the experimental results above, the CO sensing mechanism of PdO/WO₃-based sensors under illumination can be concluded (see in Figure 10). The decoration of PdO does not only participate in the gas sensing reactions as the catalyst to promote the adsorption of oxygen species (chemical sensitization) but also modify the electronic structure of the WO₃ material through the formation of P–N junctions (electronic effect).²² WO₃ is a typical n-type semiconductor material with electrons as carriers, whereas PdO is a p-type semiconductor with holes as carriers. The electrons would transfer from the valence band of WO₃ to PdO and the holes would transfer from the conduction band of PdO to WO₃ until their Fermi levels equalize,¹⁷ which results in the formation of an electron depletion layer around WO₃ and a hole accumulation layer around PdO.³⁰ In this process, the energy bands would bend, and a p–n heterojunction would be formed at the interface between WO₃ and PdO. The p–n heterojunction can promote the migration of carriers and suppress the recombination of electrons and holes compared with the pure WO₃-based sensor, which contributes to the adsorption of more oxygen species. Thus, the CO sensing performance can be enhanced by decorating the WO₃-based sensor with PdO. Furthermore, for WO₃-based sensors with a trace amount of PdO decorated, the nature of n-type semiconductors does not change, which can be manifested by the reduction of the resistance when CO (reducing gas) is detected.

Meanwhile, the decoration of PdO can significantly lower the band gap energy of the pure WO₃ material and expand the absorption range of light, on the basis of the UV–visible absorption spectrum of PdO/WO₃-based sensors (shown in Figure 9b) and DFT calculations (shown in Figure 5). When PdO/WO₃-based sensors were irradiated with UV–visible light, the light would be absorbed, whose energy is larger than the band gap energy of the sensor, and then makes the electrons from the valence band of the photocatalyst to be excited to the conduction band, leaving the photogenerated holes. Thus, the separation of photogenerated electrons and holes is realized.³⁴ When the oxygen molecules in air contact PdO/WO₃-based sensors, they would react with the photogenerated electrons to form oxygen species (O₂⁻, O⁻, O₂⁻⁻) and then adsorb on the surface of sensors. The different oxygen species can be produced and adsorbed on the sensor with the operating temperature changing. The process can be described by the following formula:

\[
O_2(gas) + e^- \rightarrow O_2^-(ads) \quad (T < 100 \degree C) \quad (3)
\]

\[
O_2^-(ads) + e^- \rightarrow 2O^-(ads) \quad (100 \degree C < T < 300 \degree C) \quad (4)
\]

\[
O^-(ads) + e^- \rightarrow O^2-(ads) \quad (T > 300 \degree C) \quad (5)
\]

In addition, H⁺ in air could react with partial preadsorbed O₂⁻ on the surface of PdO/WO₃ powders to form a hydroperoxyl radical (OOH), and the remaining photogenerated holes would combine with the electrons in OH⁻, resulting in the formation of free radicals (OH).²⁷–³⁹

\[
2CO(gas) + O_2^-(ads) \rightarrow 2CO_2(gas) + e^- \quad (T < 100 \degree C) \quad (6)
\]

\[
CO(gas) + O^-(ads) \rightarrow CO_2(gas) + e^- \quad (100 \degree C < T < 300 \degree C) \quad (7)
\]

\[
CO(gas) + O^2-(ads) \rightarrow CO_2(gas) + 2e^- \quad (T > 300 \degree C) \quad (8)
\]

When the sensors were exposed to air, O₂ molecules in air can capture electrons from the PdO/WO₃-based sensors, forming a wider electron depletion layer and a hole accumulation layer. When the sensors were exposed to CO atmosphere, CO reacted with the oxygen species preadsorbed on the sensor and released electrons back to the PdO/WO₃-based sensors, resulting in the narrowing of the electron depletion layer and the hole accumulation layer.³⁰ This is the main reason why the PdO/WO₃-based sensors show response to CO, and this explanation is defined as the “electronic effect”.

**CONCLUSIONS**

In summary, the CO sensing performances of PdO/WO₃-based sensors prepared by an easy and affordable method were investigated under illumination. The results indicate that decorating WO₃ with PdO can significantly enhance the responses to CO, which is due to the “chemical sensitization” and “electronic effect”. The DFT calculations prove that decorating the WO₃ surface with PdO can provide more adsorption sites for oxygen species, which can promote the reaction between CO molecules and species. Meanwhile, decorating WO₃ with PdO can promote the formation of p–n heterojunctions, the migration of carriers, and suppress the recombination of electrons and holes, which contributes to the adsorption of more oxygen species. With the content of PdO increasing, the band gap energies of PdO/WO₃-based sensors would gradually decrease and the absorption range of light would be expanded. More light can be absorbed by decorating the WO₃ sensor with PdO, which can lead to the emergence of more photogenerated electron–hole pairs and then promote the progress of electrochemical reactions. Thus, the PdO/WO₃
material can be considered as a promising sensor device to detect CO by effectively utilizing the energy of light.

## EXPERIMENTAL SECTION

### Preparation and Gas Sensing Test of PdO/WO3-Based Sensors

Pure WO3 nanopowders were obtained by calcining tungstic acid (H2WO4) at 500 °C. Then, the powders obtained above were mixed with an appropriate amount of palladium chloride (PdCl2) and milled for 2 h, followed by annealing the mixture of WO3 and 0.0, 0.4, 1.0, and 3.0 mol % PdCl2 in an oven at 500 °C for 3 h to obtain samples. All the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Finally, these obtained powders were mixed with deionized water to make the slurry and pasted onto the outer surface of a ceramic tube with a pair of Au electrodes, four Pt wires, and a Ni–Cr heating wire. The schematic diagram of the gas sensor is shown in the inset of Figure S1a. The optical images of the microstructures of the ceramic tube and the slurry on the ceramic tube are shown in Figure S1a, b. The thickness of the gas sensing film coated on the ceramic tube is about 180 μm. Then, the PdO/WO3-based sensors were heated in air at 240 °C for 2 days to make them more stable and reusable. The gas sensing response of the sensor was defined as the ratio of the resistance in air (R空气) to that in the testing gas (R气体), that is, response = R气体/R空气.

### Characterizations of PdO/WO3 Powders

The structures of PdO/WO3 powders were characterized by XRD using a Bruker D8 ADVANCE spectrometer with Cu Kα radiation. The optical images of microstructures were recorded by an optical microscope DP70 (OLYMPUS, Japan). The microstructures were obtained by a field emission scanning electron microscope (S-4800, Japan) and a high-resolution transmission electron microscope (JEM-2100F, Japan). The size distribution by intensity (Zetasizer Nano) was carried out to estimate the particle size of nanopowders. Meanwhile, XPS (Thermo Escalab 250Xi, America) was used to analyze the composition and electronic states of samples. Moreover, the absorption spectrum of the experimental samples was measured using an UV–vis–NIR spectrophotometer (Cary 5000). The gas sensing performances were implemented by the test system (WS-30A, China).

### Theoretical Calculations

The CO sensing mechanism of the PdO/WO3 configuration was studied by DFT calculations, and all the calculations were performed with the program package DMol3.13,14 The exchange–correlation function was constructed by the Perdew–Burke–Ernzerhof functional of generalized gradient approximation.15,16 Further, the double-numerical-quality basis set with polarization functions (DNP) was utilized to describe the valence orbital of the atoms.17 A 2 × 2 × 2 Monkhorst–Pack k-point mesh was used for the bulk, and 2 × 1 × 1 was adopted for the films during the geometry optimization calculation process. The convergence criteria of displacement, force, and energy were set to 5.0 × 10−3 Å, 4.0 × 10−3 Ha/Å, and 2.0 × 10−7 Ha, respectively. Meanwhile, the DOS was obtained by using a 3 × 1 × 1 Monkhorst–Pack grid, and the Mulliken population analysis was used to obtain the charge transfer.

The geometrical configuration of WO3 is a monoclinic structure, with the lattice constants a = 7.429 Å, b = 7.545 Å, and c = 7.711 Å. The WO3(001) surface was cleaved from the optimized bulk WO3 model, and then a 20 Å vacuum was added to the layers, which was used to simulate the periodic slab model with boundaries. Meanwhile, all the calculations were performed with the geometrical structures fully relaxed.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/DOI/10.1021/acsomega.0c04137.

Schematic diagram and the optical images of the gas sensor; FE-SEM and TEM images of the sensors; content of different elements for 1 mol % PdO/WO3-based sensor; XPS spectra of pure WO3 powders; dynamic response curves to different concentrations of CO gas; resistance of the sensor in air and the repeated responses to 500 ppm CO in long term; optimized models of WO3(001) surfaces with oxygen species; CO adsorption configurations; and corresponding calculated parameters (PDF)

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### Notes

The authors declare no competing financial interest.

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