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Light-Assisted Room-Temperature NO_2 Sensors Based on Black Sheet-Like NiO †

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Abstract: In this study, we use two-dimensional black flake nickel oxide as the sensitive material which was synthesized by a facile hydrothermal route. The as-synthesized sheet-like NiO possessed a large specific surface area, as verified by BET characterization. The as-prepared NiO nanosheets had strong absorption in the range of 250–800 nm including UV and visible light. Upon exposure to ppb-level NO_2, the presented sensors showed significant responses under light illumination at room temperature. In addition, the light wavelength also had a remarkable effect on the sensing performance in terms of sensitivity, response and recovery kinetics. Furthermore, the sensor showed a low humidity dependence.

Keywords: NiO; NO_2; room temperature; light illumination

1. Introduction

Over the past decades, numerous efforts have been made to investigate the n-type semiconductors used for gas sensing materials. However, less attention has been paid on the p-type semiconductors. In the previous studies, Hübner found that the response of a p-type semiconductor towards a given gas was almost equal to the square root of the counterpart of the n-type ones to the same gas under same conditions [1]. In addition, the p-type semiconductors were less sensitive to humidity when compared with that of n-type ones. Therefore, it is interesting to investigate the p-type semiconductors, especially in room temperature gas sensor applications. Room temperature gas sensors are attractive due to their low power consumption, which simplified the sensor design, improved the sensor stability, facilitating the electronic integration, etc. Our previous studies showed that the sensing properties of pure semiconductors are not good enough in the dark at room temperature, however, its performance was greatly enhanced with UV or visible light stimulation [2,3]. In this study, we use a simple hydrothermal method to prepare black NiO sensitive materials and their sensing properties are studied.

2. Experimental Method

2.1. Synthesis of Materials

2.1.1. Hydrothermal Synthesis from Nickel Nitrate ($Ni(NO_3)_2$) Precursors (Sample 1)

In a typical procedure, 0.7 g $Ni(NO_3)_2.6H_2O$ and 0.5 g Polyethylene glycol 6000 (PEG 6000) are dissolved in 45 mL distilled water under vigorous stirring at room temperature. Subsequently, 2.5 mL triethylamine $N(C_2H_5)_3$ is added to the above system dropwise and stirred for 50 min. The obtained mixture is then transformed into a Teflon-lined stainless steel autoclave, and maintained at 140 °C for 12 h. After cooling to room temperature naturally, the product is filtered, washed with distilled water and ethanol for several times, and dried under vacuum at 80 °C for 12 h. Finally, the synthesized powders were calcined at 400 °C for 1 h.

2.1.2. By Precipitation from Nickel Malonate ($Ni(CH_3CH_2COO)_2$) Precursors (Sample 2)

10 mmol lithium hydroxide added into 5 mmol malonic acid to form an aqueous solution, and then adjusted pH to 7. After 5 min, aqueous nickel chloride solution was added to the previous solution by dropwise, and then the obtained green solution was stirred for 3 h at 90 °C under reflux. The prepared precipitate was respectively washed by deionized water, isopropanol and acetone to remove the impurities. The product was dried in an oven at 70–80 °C, and then calcined in an oven at 500 °C.

2.2. Gas Sensing Test

The sensors prepared by the obtained sensitive materials are measured under different light illumination at room temperature including UV and visible light. Before the test, 1000 mL/min synthetic air is injected into the chamber to stabilize the base resistance. And then a certain flow rate of NO_2 gas is injected into the atmosphere to obtain a desired target gas concentration.

3. Results and Discussion

Figure 1 shows that the as-synthesized samples are well-crystallized NiO phase structure. The peaks located at 37.16°, 43.27°, 62.50°, 75.08° and 79.17° are well assigned to the (111), (200), (220), (311) and (222) planes of face-centered cubic structure NiO (JCPDS 78-0428). As well known, the morphology and microstructure play vital roles in the gas sensing performance. In order to gain more insights into phase structure of the samples, XPS technique is utilized and O1s signals are exhibited in Figure 2. It is obvious that there are peaks which are suited at 529.5 and 531.3 eV, respectively. The 529.5 eV peak is attributed to the lattice oxygen in the stoichiometric NiO. Moreover, the 531.3 eV one is related with the presence of oxygen vacancies. Apparently, the oxygen vacancy concentration for Sample 1 is much higher than that of Sample 2.

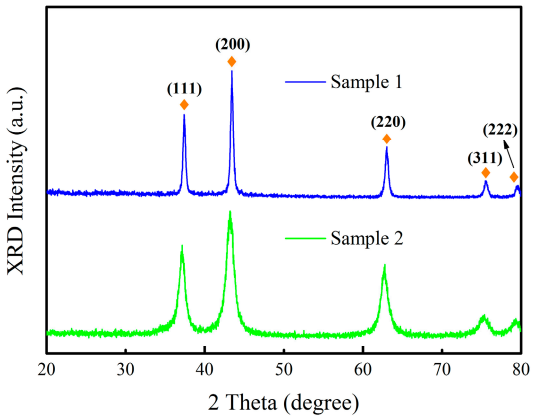

Figure 1. XRD pattern of the samples.

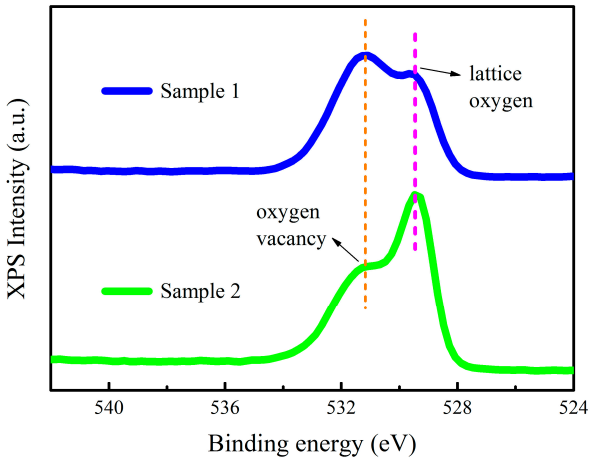

Figure 2. XPS spectra of the samples.

Figure 3 depicts the FE-SEM images of Samples 1 and 2. Sample 1 exhibits a sheet-like morphology, while Sample 2 shows a layer-like morphology on account of the agglomeration of the nanoparticles. From Table 1, it can be found that Sample 1 has a high specific surface area, which is much higher than the counterpart of Sample 2 (the data is not shown).

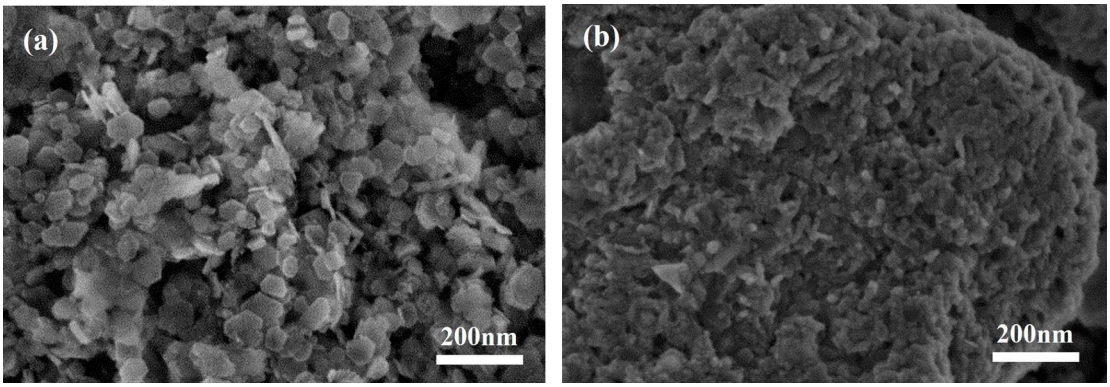

Figure 3. FE-SEM images of (**a**) Sample 1 and (**b**) Sample 2.

Table 1. BET dates for the as-synthesized Sample 1.

Material	Surface Area ($m^2 \cdot g^{-1}$)	Pore Size (nm)	Pore Volume ($cm^3 \cdot g^{-1}$)
Sample 1	111.63	15.141	0.4225

In this study, we intended to adopt light as the activation source instead of heating, so the optical property research of the as-synthesized samples is very important. The optical absorption properties of the samples are displayed in Figure 4. The UV-Vis spectra show that the as-prepared samples possess strong absorption in the entire UV and visible light region, and the absorption intensities of Sample 1 is a bit higher than the counterpart of Sample 2.

The samples towards 372 ppb NO_2 gas sensing tests are performed under different light illumination at room temperature results, and the relevant results are displayed in Figure 5. Several results can be drawn from this figure. Sample 2 almost has no response to NO_2. Compared with that, the sensing properties of Sample 1 exhibits a remarkable response to hundreds of ppb of NO_2 under UV or visible light illumination at room temperature. In addition, the base resistance of Sample 1 is lower than that of Sample 2.

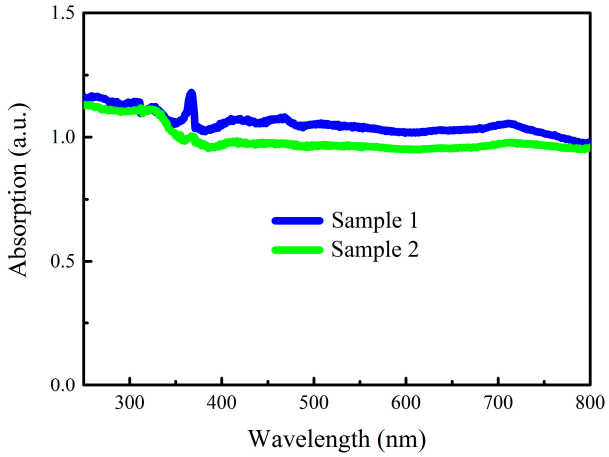

Figure 4. UV-Vis spectra of the as-synthesized samples.

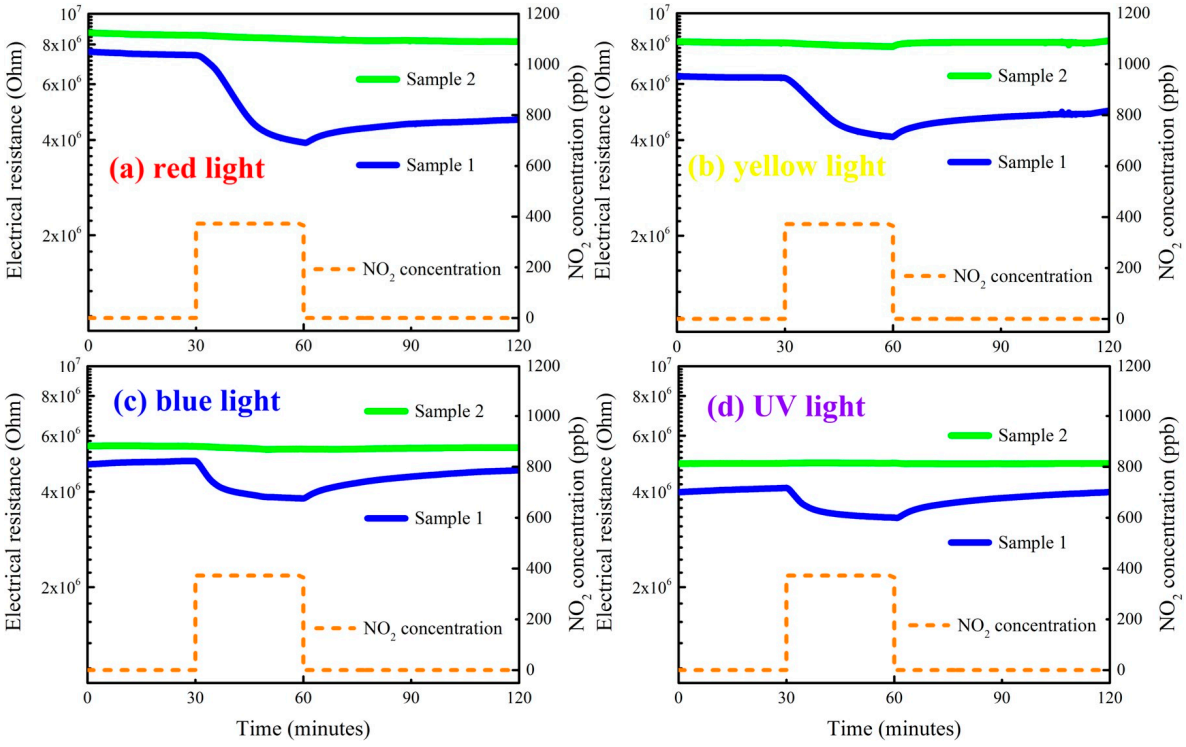

Figure 5. The electrical resistance of Sample 1 and 2 versus 372 ppb NO_2 gas under different light illumination at room temperature.

The difference between these two samples is ascribed to the different oxygen vacancy concentration, morphology, light absorption ability and specific surface area. Oxygen vacancies are considered as the electron donors [4,5], so the electron concentration of Sample 1 is higher than that of Sample 2. Additionally, oxygen vacancies are preferential absorption sites for oxidizing gases, plus with the larger specific surface area, so Sample 1 has a much more enhanced gas sensing properties. Due to the greater light absorption intensities, Sample 1 can absorb more light energies to accelerate the gas sensing speed, which considerably enhances the response and recovery rate.

In addition, it was found that the light wavelength had a great effect on the sensing performance. The gas sensing curve of Sample 1 by different light wavelength irradiation is shown in Figure 6. With the decrease in light wavelength, the base resistance and sensor response decreased, whereas the response and recovery time shortened. Moreover, the response of the as-synthesized NiO towards humidity was weak (in Figure 7).

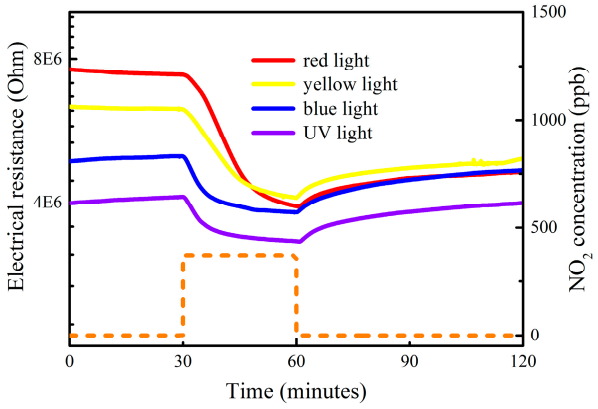

Figure 6. The electrical resistance of Sample 1 versus 372 ppb NO_2 gas illuminated by different light at room temperature.

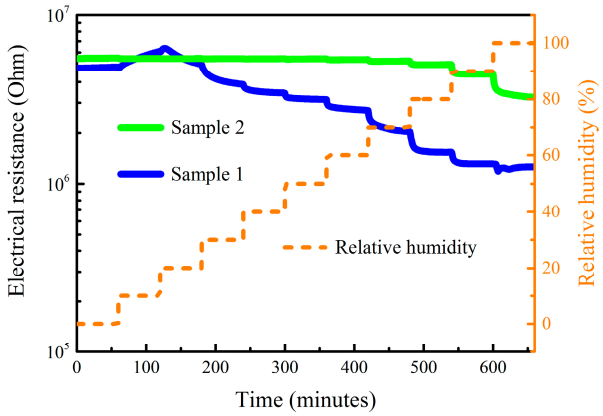

Figure 7. Effect of humidity on the base resistance of the samples illuminated by blue light at room temperature.

4. Conclusions

In this study, we tried to use the black NiO prepared by two different methods as the room-temperature sensitive materials, and their sensing characteristics were enhanced with visible or UV light stimulation. The results found that the NiO samples synthesized by the two routes had different morphologies, phase composition and microstructure, which played a remarkable role in the final performance. The NiO samples with high oxygen vacancy concentration, larger specific area and higher light absorption range would possess a much better gas sensing properties. In addition, the light wavelength had a great effect on the sensing process, the sensing performance would be improved as the decrease in light wavelength. Furthermore, the as-synthesized NiO had a weak independence towards humidity.

Conflicts of Interest: The authors declare no conflict of interest.

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