High-performance photoluminescence-based oxygen sensing with Pr-modified ZnO nanofibers

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Abstract

Praseodymium (Pr)-modified zinc oxide (ZnO) nanofibers have been fabricated using an electrospinning-calcination method. These Pr-modified ZnO nanofibers present porous morphologies containing numerous ZnO nanocrystallites with average sizes that are much smaller than those found in pure ZnO nanofibers formed by the same procedures. Most Pr is identified at the surface of / interface between the nanocrystallites. In addition to the morphological modifications, addition of Pr is also shown to enhance the crystalline quality of the ZnO. Consequently, the Pr-modified ZnO nanofibers have a higher UV emission efficiency and exhibit a much-enhanced UV emission-based O2 sensing performance than the pure ZnO nanofibers. By way of illustration, the Pr-modified nanofibers show O2 sensing responses of $R = 39\%$ at room temperature and $R = 71\%$ at 115 °C (cf. $R = 19\%$ and 52% with the pure ZnO nanofibers at these same operating temperatures). These results suggest that electrospun Pr-modified ZnO nanofibers hold real promise for high-performance optical gas sensing applications.

Keywords: Zinc oxide; Praseodymium; Nanofibers; Electrospinning; Photoluminescence; Gas sensing

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1. Introduction

Optical gas sensors offer several distinctive advantages, which accounts for the intensity of current research in this area. In contrast to electrical sensors, optical sensors require no electrical contacts, can operate remotely and can be used in the presence of strong electromagnetic radiation or, for example, in aqueous solution [1–8]. Zinc oxide (ZnO) is widely regarded as one of the most promising optical gas sensing materials, on account of its acknowledged electrical sensing properties [9–13], high oxygen-adsorption capacity [14], excellent near-band edge UV emission properties [15,16] and the diversity of methods by which it can be produced at low cost and with different, but controllable, morphologies [17–22]. Various strategies, including controlling the morphology, crystal defects, doping, and surface modification have been reported to improve the UV-emission-based sensing performance of ZnO nanomaterials to target gases like O₂, H₂, CO, H₂S, NO₂, etc. [17–21,23–25]. However, there are at least two challenges that still need to be addressed in order to boost the practical application of ZnO-based optical gas sensors: (1) the UV emission efficiency and the sensing response both need to be improved further; and (2) a low cost and high yield growth technique needs to be adopted, since most ZnO nanomaterials with UV emission efficiencies sufficient for optical gas sensing applications reported to date were produced by high cost, low yield growth techniques like pulsed laser deposition [18–20] and chemical vapor deposition/vapor phase deposition [21,23–26]. Thus there remains a pressing need for a low cost, high yield production method for ZnO nanomaterials that display high UV emission intensities and high UV emission-based gas sensing responses.

The electrical gas sensing performance of ZnO and other oxides/hydroxides like SnO₂, Fe₂O₃ and ZnSn(OH)₆ can be notably enhanced by praseodymium (Pr) doping and modification [27–33]. Mechanistically, Pr species are assumed to facilitate oxygen chemisorption on the oxide surface and thereby enhance the gas sensing properties [28–33]. Addition of Pr has also been shown to influence the structure, morphology and, particularly, the light emission properties of ZnO [34–36]. These findings encouraged the present investigation of Pr-modified ZnO nanomaterials for potential optical gas sensor applications.

Electrospinning, followed by a calcination process, is one facile approach to producing oxide nanofibers with low cost and high yields [37–39]. The electrical gas sensing properties of electrospun oxide nanofibers have been widely explored [40–42], but their photoluminescence
(PL)-based gas sensing properties have not been reported hitherto. In this work, pure and Pr-modified ZnO nanofibers were fabricated using the same electrospinning-calcination production method, and their properties and performance compared. The pure ZnO nanofibers are found to consist of many compact nanocrystallites. The Pr-modified ZnO nanofibers, in contrast, present porous morphologies and are built up from many much smaller nanocrystallites. The latter nanofibers exhibit enhanced UV emission efficiencies, and more importantly, show a much-improved UV emission-based oxygen sensing performance (Fig. 1). Possible mechanisms for the enhanced sensing performance are discussed accordingly.

Fig. 1. Schematic illustration of the fabrication and oxygen gas sensing mechanism of the Pr-modified ZnO nanofibers.

2. Experimental

2.1. Synthesis of pure and Pr-modified ZnO nanofibers

Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd; praseodymium nitrate hexahydrate (Pr(NO$_3$)$_3$·6H$_2$O) and poly(vinylpyrrolidone) (PVP, $M_w$ = 1,300,000) were purchased from Aldrich. All chemicals were analytical grade and used as received without further purification. Pr-modified ZnO nanofibers were synthesized via an electrospinning method followed by a calcination process. In a typical procedure, solutions of zinc nitrate (594.8 mg Zn(NO$_3$)$_2$·6H$_2$O) and praseodymium nitrate (8.7 mg Pr(NO$_3$)$_3$·6H$_2$O) dissolved in DMF (4 mL) and of PVP (1.000 g) in ethanol (8 mL) were separately stirred for 6 h. The two solutions were mixed under stirring for 2 h and then loaded into
a glass syringe (needle diameter of 0.5 mm) connected to a high-voltage (15 kV) direct current power supply and composite nanofibers were electrospun onto the grounded collector electrode (an aluminum frame located at a distance of 20 cm), and then transferred to a standard thin mica microscope slide. Finally, a calcination process (at 500 °C in air for 5 h) was employed to selectively remove the organic constituents and achieve crystalline Pr-modified ZnO nanofibers (henceforth denoted as ‘PZNF’). For reference, pure ZnO nanofibers (denoted as ‘ZNF’) were also synthesized using the same process but without the use of praseodymium nitrate hexahydrate.

2.2. Characterization
The products were characterized using scanning electron microscopy (SEM, FEI Quanta 200F, equipped with an energy dispersive X-ray spectrometer (EDS)), high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai-G2-F30), X-ray diffraction (XRD, Rigaku D/MAX-2600/PC with Cu Kα radiation), X-ray photoelectron spectroscopy (XPS, ESCALAB, 250Xi), and spectrofluorometry (Horiba, Fluoromax-4, 325 nm excitation).

2.3. Optical gas sensing measurements
Temperature-dependent PL and UV emission-based gas sensing measurements were carried out using the spectrofluorometer together with a vacuum mini-chamber containing a heating system to allow variation of the sample temperature. The gas composition within the chamber was controlled using two mass flow controllers and one gas mixing chamber. The spectrofluorometer was used in ‘kinetics’ mode to derive real-time PL-based gas sensing data by monitoring the emission intensity at any user selected wavelength with a time resolution of 1 s. The O₂ sensing response of the samples at any temperature of interest is defined as 

$$ R = \frac{(I_0 - I_{100})}{I_0}, $$

where $I_0$ and $I_{100}$ are the maximum values of the UV emission intensity measured in atmospheres of pure N₂ and pure O₂, respectively.

3. Results and Discussion
The morphologies of the as-prepared samples were first characterized by SEM and TEM. Figs. 2a and e present SEM images of the ZNF and PZNF samples, respectively. The ZNF sample is seen to consist of many uniform nanofibers with an average diameter, $d \sim 180$ nm. The Pr-modified ZnO nanofibers, in contrast, show a rough surface and larger average diameters, $d \sim 330$ nm. TEM
measurements further reveal that the pure ZnO nanofibers are comprised of many densely packed nanocrystallites with an average size of ~50 nm (Figs. 2b and c) whereas the PZNF samples present more porous structures containing many more, smaller crystallites with an average size of ~22 nm (Figs. 2f and g).

![SEM image, TEM images, and HRTEM image of ZNF and PZNF samples](image)

**Fig. 2.** SEM image, TEM images, and HRTEM image of (a–d) the ZNF sample and (e–h) the PZNF sample.

The two samples were further characterized by HRTEM and XRD to reveal their crystal structures. As shown in Figs. 2d and h, the HRTEM images of both samples reveal parallel crystal planes with a measured spacing of ~0.24 nm characteristic of the (101) plane of ZnO. The XRD patterns of both samples (Fig. 3a) show diffraction peaks that can be indexed to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (202) and (104) planes of the ZnO wurtzite...
crystal structure (JCPDS 89-0510), and no diffraction peaks related to any impurity phases. These HRTEM and XRD data confirm the crystalline quality of the ZnO in both nanofiber samples.

![XRD Patterns and XPS Spectra](image)

**Fig. 3.** (a) XRD patterns and (b) XPS survey spectra of the ZNF and PZNF samples. (c) High-resolution XPS spectrum of the Pr 3d region for the PZNF sample. High-resolution XPS spectra of (d) the Zn 2p region and the O 1s region for the ZNF and PZNF samples.

XPS was used to explore the chemical compositions of the nanofiber samples. Survey spectra of the ZNF and PZNF samples are shown in Fig. 3b. In addition to the Zn and O peaks, the PZNF sample shows two peaks that confirm the presence of Pr. XPS is a surface sensitive technique, so the finding that the measured Pr/Zn atomic ratio (0.11:1.00) is much larger than that in the precursor mixture (0.01:1.00) implies that a large fraction of the Pr is at the surface of (or at the interface between) the ZnO nanocrystallites. The O/Zn atomic ratios derived from the XPS data
for the PZN and ZNF samples are, respectively, 1.57:1.00 and 1:03:1.00 – indicating that the PZN sample supports relatively more oxygen containing species on its surface.

The high-resolution Pr 3d XPS spectrum (Fig. 3c) reveals Pr 3d_{3/2} and Pr 3d_{5/2} peaks at, respectively, 953.7 eV and 933.6 eV with an energy separation of 20.1 eV, implying that the Pr in the PZN sample is present as Pr^{3+} or Pr^{4+} [43]. The high-resolution Zn 2p spectra of the two samples (Fig. 3d) are quite similar, but the profiles of the high-resolution O 1s spectra of the PZN and ZNF samples (Fig. 3e) are clearly different. Both O 1s spectra can be deconvolved into two sub-peaks. The peak centered at 530.3 eV is a signature of the O^{2-} ion in the ZnO wurtzite structure, while the 531.8 eV peak is attributable to adsorbed oxygen species on the surface and/or oxygen ions in oxygen-deficient regions [44–46]. The different sub-peak ratios in the O 1s spectra reinforce the findings from the XPS data that the PZN sample supports relatively more surface adsorbed oxygen species than the ZNF sample.

PL spectra of the ZNF and PZN samples measured in air at temperatures ranging from room temperature (RT) to $T = 210$ °C are presented in Figs. 4a and b, respectively. The RT PL spectrum of the ZNF sample consists of a sharp near-band-edge UV emission centered at 382 nm and a broad, defect-related, visible-band emission. The latter can be further partitioned into an oxygen-deficiency-related green emission centered at 520 nm [47] and an oxygen-rich-related orange emission centered at 600 nm [48]. With increasing temperature, both the UV and visible-band emissions from the ZNF sample shift to longer wavelengths and decline in intensity – observations that match previous findings [18] and are not considered further. The PL spectra of the PZN sample show similar profiles and temperature-dependences to those of the ZNF sample, but also two clear differences: (1) The ratio of the peak intensities of the visible band and UV emissions ($I_{\text{visible}}/I_{\text{UV}}$) from the PZN sample at any given temperature is much smaller than that from the ZNF sample, implying that the ZnO in the PZN sample has a higher crystalline quality and thus a higher UV emission efficiency; (2) The visible band emission of the PZN sample is dominated by an oxygen-deficiency-related component, the relative importance of which falls as $T$ is increased, e.g. $I_{\text{visible}}/I_{\text{UV}}$ declines from 0.98 at RT to 0.20 at $T = 115$ °C. The ZNF sample, in contrast, shows a relatively strong oxygen-rich-related emission which decreases more slowly than the oxygen-deficiency-related emission with increasing temperature and dominates the visible band emission at $T \geq 80$ °C. The $I_{\text{visible}}/I_{\text{UV}}$ ratio for the ZNF sample declines from 2.19 at RT to
0.65 at $T = 115 \, ^\circ\text{C}$.

![Diagram showing temperature-dependent PL spectra for ZNF and PZNF samples.]

**Fig. 4.** (a–b) Temperature-dependent PL spectra, (c–d) PL spectra measured in nitrogen, air and oxygen atmospheres at RT, and (e–f) PL spectra measured in nitrogen, air and oxygen atmospheres at $T = 115 \, ^\circ\text{C}$ of the ZNF and PZNF samples.

A sample temperature of 115 °C is too low to cause any substantial reduction of defects in the inner (bulk) part of the crystallites but could have a substantial influence on surface defects related to the physical and chemical adsorption of gaseous species. Thus, it is rational to conclude that the ZnO in the ZNF sample has relatively poorer crystalline quality with some oxygen-rich-related defects located inside the crystallites, while the ZnO in the PZNF sample has higher crystalline quality and contains a higher density of oxygen-deficiency-related defects at the crystallite
surfaces and interfaces – which are beneficial to the adsorption of oxygen species and thus improve the sensing performance of such gas sensors [49]. The $T$-dependent PL properties of the $PZNF$ sample can be understood if the surfaces and interfaces of the ZnO nanocrystallites are Pr-rich, and the smaller average crystallite size facilitates higher crystalline quality via the calcination process.

The oxygen gas sensing properties of the $ZNF$ and $PZNF$ samples were evaluated by measuring their PL in nitrogen, air and oxygen atmospheres, respectively. The RT PL measurements show that the peak intensity of the UV emission, $I_{UV}$, from the $ZNF$ and the $PZNF$ samples both decrease as the $O_2$ concentration is increased (Figs. 4c and d). Compared to $R = 19\%$ for the $ZNF$ sample, the $PZNF$ sample presents a much higher RT sensing response, $R = 39\%$. This exceeds the value ($R = 30.7\%$) reported for $O_2$ sensing at $T = 150 \degree C$ with ZnO nanorods grown by pulsed laser deposition [18]. Even more promisingly, sensing responses of $R = 52\%$ and $71\%$ were obtained with the $ZNF$ and $PZNF$ samples when measuring the PL at $T = 115 \degree C$. The latter value surpasses most reported optical oxygen sensing responses using ZnO nanomaterials [18,26].

Temperature has been suggested to have a key influence on the gas sensing performance of many oxides. Fig. 5a shows the $T$-dependence of $R$ for both the $ZNF$ and $PZNF$ samples over the temperature range from RT to $T = 208 \degree C$. For both samples, $R$ increases steeply up to $T \approx 115 \degree C$ but thereafter increases only slowly. This behavior is likely to be attributable to adsorbed water-related species. Since $I_{UV}$ decreases with increasing $T$ (Figs. 4a and b) and small $I_{UV}$ values are not conducive to good signal detection or $R$ determination, $115 \degree C$ was selected as the optimal working temperature.

The dynamic $I_{UV}$ response of the $PZNF$ sample to oxygen at $T = 115 \degree C$ was investigated by changing the partial pressure of $O_2$ in an $N_2/O_2$ mixture maintained at a total pressure $p = 1$ bar. As Fig. 5b shows, $I_{UV}$ decreased with increasing oxygen concentration and yielded a clearly measurable response even at low (e.g. 3\%) oxygen concentrations. The measured response and recovery times of the $PZNF$ sample are of the order of 2 and 8 min, respectively, which are both some 5 min shorter than the corresponding response and recovery times of the $ZNF$ sample. The dynamic $I_{UV}$ of the $PZNF$ sample in 0\% $O_2$ (i.e. 100\% $N_2$) and in 100\% $O_2$ at $T = 115 \degree C$ and $p = 1$ bar is shown in Fig. 5c. These data confirm the good recoverability and reproducibility of the oxygen sensing and illustrate the promise of the $PZNF$ sample as an optical oxygen sensor.
Fig. 5. (a) Temperature-dependent $R$ of the ZNF and PZNF samples. (b) Dynamic UV emission intensity of the PZNF sample to different concentrations of O$_2$ (in N$_2$) at $T = 115$ °C and $p = 1$ bar. (c) Dynamic UV emission intensity of the PZNF sample in 0% O$_2$ (100% N$_2$) and in 100% O$_2$.

It is well known that adsorption/desorption of oxygen species on a ZnO surface can trap or release electrons, causing an expansion or contraction of the electron depletion layer at the surface (Fig. 1) [18,19]. Since the depletion layer makes little or no contribution to the UV emission [19], $I_{UV}$ is mainly dependent on the volume of the “non-depleted” region beneath the depletion layer. Thus the response of an $I_{UV}$-based oxygen sensor is very dependent on the surface conditions (e.g. the surface area to volume ($S/V$) ratio and the number and nature of the active sites for oxygen adsorption) of the ZnO material. Based on the above sensing mechanisms, likely reasons for the superior oxygen sensing performance of the PZNF sample (cf. the ZNF sample) include: (1) The PZNF sample has a much larger $S/V$ ratio (as shown in Fig. 2); and (2), as noted previously, Pr introduces additional active sites on the sample surface that facilitate oxygen adsorption [28–31]. Further, the PL data indicates that the PZNF sample has higher crystalline quality (i.e. less defect-related visible emission from the inner part of the sample, Fig. 4) and thus a higher UV emission efficiency. This is important: high intrinsic emission efficiencies and emission intensities are critical for high-performance $I_{UV}$-based gas sensing, since the sensing relies on the accurate measurement of reductions in emission intensity.
4. Conclusions

Pure and Pr-modified ZnO nanofibers have been synthesized using a common electrospinning-calcination technique. Compared with the pure ZnO nanofibers – which are found to contain many compact nanocrystallites – the Pr-modified ZnO nanofibers have larger diameter and present more porous structures incorporating many smaller nanocrystallites of higher crystalline quality. Pr preferentially locates at the surface of the nanocrystallites and facilitates further adsorption of oxygen species. As a result, the Pr-modified ZnO nanofibers exhibit a higher UV emission efficiency and a much-enhanced UV emission-based $O_2$ sensing performance relative to that of the pure ZnO nanofibers. $O_2$ sensing responses $R = 39\%$ and $71\%$ have been demonstrated at room temperature and at $T = 115$ °C, respectively – values that exceed most optical oxygen sensing performances of ZnO nanomaterials reported hitherto. The present study illustrates the considerable promise of electrospun Pr-modified ZnO nanofibers for optical gas sensing applications.

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