



Cite this: *J. Mater. Chem. C*, 2015, **3**, 11397

Highly sensitive, temperature-dependent gas sensor based on hierarchical ZnO nanorod arrays†

Xiaomei Wang,^a Fazhe Sun,^b Yongqing Duan,^a Zhouping Yin,^a Wei Luo,^c YongAn Huang^{*a} and Jiankui Chen^{*a}

The low-cost growth of patterned zinc oxide (ZnO) nanorod arrays (NAs) has attracted much attention with the rapid development of electronics and nanotechnology. A mechanoelectrospinning-assisted continuous hydrothermal synthesis method (MES-CHSM) is proposed to direct-write the precursor patterns for the growth of the ZnO-NAs, in a digital, low-cost, and mask-free manner. The morphology and distribution of the hierarchical ZnO nanorods, having a tremendous impact on the gas response, are determined by the process parameters of the MES-CHSM. It is highly desirable that the diameter, interval, orientation and distribution of the ZnO nanorods can be tuned proactively by changing the growth time, the solution concentration, the nature of the precursor layer, and the pattern by MES. The ZnO-NAs exert excellent Ohmic contact with interdigital electrodes when exposed to dry air, NO₂ gas and then dry air again. The gas response of the ZnO sample is surface-reaction-determining. The gas sensing results show highly sensitive and repeatable response–recovery cycles following NO₂ gas exposure and air purging, respectively. The dynamic response of the gas sensor shows a temperature-dependent response to NO₂, even at low concentrations (1–50 ppm). The best gas response is located between 200 °C and 225 °C. Gas sensors, prepared by different process parameters, show two laws regarding the corresponding responses and the NO₂ concentrations: approximately linear and saturation regions. The optimal process parameters are presented to postpone the occurrence of the saturation region, to enlarge the measuring range.

Received 19th July 2015,
Accepted 29th September 2015

DOI: 10.1039/c5tc02187a

www.rsc.org/MaterialsC

Introduction

Nitrogen dioxide (NO₂) is one of the main pollutant gases generated during automotive engine combustion, and by power plants and factories, and is involved in many disasters like acid rain and photochemical smog.¹ According to health and safety guidelines, humans should not be exposed to more than 2.5 ppm NO₂. Therefore, highly sensitive gas sensors are significant for NO₂ monitoring. A large variety of NO₂ gas sensors have been obtained, *e.g.* piezoelectric sensors,² electrochemical sensors,³ solid electrolyte sensors,⁴ *etc.* However, these sensors have some disadvantages such as moisture permeable absorption, easily poisoned electrodes, poor selectivity, *etc.* Semiconductor oxide resistance-type NO₂ gas sensors can overcome the above shortcomings with a simple circuit.

Therein, ZnO nanomaterials, as functional n-type semiconductors with a wide direct band gap (3.37 eV), have already been utilized in gas sensors^{5,6} for detecting toxic or hazardous gases because of their typical properties, such as high electrochemical stability, non-toxicity, high response, long term stability and recyclability.^{7,8} Solvothermal methods,^{9,10} molecular beam epitaxy,¹¹ and vapor phase methods¹² have been employed to grow ZnO nanorods. But molecular beam epitaxy and vapor phase methods (including thermal evaporation and condensation,¹³ physical/chemical vapor deposition,¹⁴ *etc.*) require high temperature, vacuum or costly equipment. Recent studies have demonstrated that the morphology of ZnO nanorods has a significant influence on their gas sensing performance.^{15,16} So the selective growth of ZnO nanostructures is very important for highly sensitive gas sensors like electronic noses and integrated devices.^{17,18} Various micro-patterning methods, such as monolayer self-assembly,¹⁹ microcontact printing,²⁰ nanoimprinting or soft lithography,^{21,22} the pulsed laser deposition method,²³ the photolithographic method²⁴ and ink-jet printing,^{25,26} have been adopted but are limited by high-temperature treatment, needing a high-vacuum system, complicated lithography, low-resolution patterns, or needing a mask or mold.

The continuous hydrothermal synthesis method^{27,28} has been considered as an excellent procedure to prepare ZnO nanostructures due to its low-cost, low-temperature and controllable²⁹ properties

^a State Key Laboratory of Digital Manufacturing Equipment and Technology, Flexible Electronics Research Center, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: yahuang@hust.edu.cn, chenjk@hust.edu.cn

^b Analysis Testing Center, Shandong University of Technology, Zibo 255100, China

^c School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China

† Electronic supplementary information (ESI) available: Materials and details of mechanoelectrospinning equipment; synthesis of ZnO nanorod arrays; diameter distributions of ZnO-NAs by different process parameters; gas response of ZnO samples at room temperature. See DOI: 10.1039/c5tc02187a

compared to other growth methods. The electrohydrodynamic direct-writing^{30,31} technique can deposit high-resolution patterns directly onto a substrate in an individually controllable, high-resolution, and low-temperature manner. We present a mechano-electrospinning-assisted continuous hydrothermal synthesis method (MES-CHSM) to fabricate an NO₂ sensor based on ZnO nanorod arrays (ZnO-NAs), where the MES is an improved electrohydrodynamic direct-writing process with high controllability over the morphology of the fibers.^{32,33} This method can achieve highly aligned ZnO nanorods on sub-10-micrometer printed patterns, to form hierarchical structures for the highly sensitive sensors. Further, the morphology and distribution of the ZnO-NAs are tunable with different process parameters, such as the growth time, the ZnAc precursor concentration, the Zn(NO₃)₂ concentration in the growth solution and the printed micropattern of the MES. Their relationships with the gas sensing performance are investigated in detail to discover the optimal parameters of process and working.

Experimental section

Preparation

Zinc acetate (ZnAc, Zn(CH₃COO)₂·2H₂O, AR), zinc nitrate (Zn(NO₃)₂, AR) hydrate and hexamethylenetetramine (HMTA, (CH₂)₆N₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. The polyethylene oxide (PEO) used in this study was purchased from Aldrich. The relative molecular mass (*M_r*) of PEO was 600 000. An aqueous solution containing PEO (6 wt%) and ZnAc was fabricated by magnetic stirring for 10 hours (h). Aqueous solutions of Zn(NO₃)₂ (0.2 M) and HMTA (0.2 M) were prepared by magnetic stirring for >0.5 h, then were mixed with equal volume and stirred evenly to fabricate a mixed solution of Zn(NO₃)₂ and HMTA.

Interdigitated electrodes of Ag were screen printed on an alumina substrate (1 cm × 0.8 cm). The distance between adjacent electrodes was 800 μm. The hierarchical ZnO-NAs were prepared on an alumina substrate and interdigitated electrodes for use as a gas sensor by the following steps: (1) PEO was adopted into the prepared aqueous solution to adjust the solution viscosity, then parallel arrays containing ZnAc along one direction were direct-written on the substrate by MES,¹⁶ and the micropattern of the large-area, well-defined ZnAc-PEO fiber array, which was the first level pattern, was fabricated. The applied voltage, moving speed and flow rate of the MES were 2.25 kV, 200 mm s⁻¹ and 500–750 nl min⁻¹, respectively. (2) The obtained sample was annealed at 200 °C in air for 2 h to form ZnAc nanoparticle nuclei and to ensure the adhesion of the seed particles on the substrate to form a seed layer. (3) The ZnO-NAs were formed by suspending the substrate upside-down in a Teflon-bottle filled with the growth solution for 1–12 h at 90 °C. The selective growth of the ZnO nanorods resulted from the ZnAc nanoparticle nuclei on the MES-assisted pattern through the hydrothermal decomposition of the zinc complex. The growth solution was a mixture of Zn(NO₃)₂ and HMTA. The obtained ZnO-NAs were the second

level pattern. So the preparation of the hierarchical ZnO-NAs had been completed.

Characterization and measurements of the gas sensor

The morphologies of the samples were investigated using field emission scanning electron microscopy (FESEM). The current–voltage (*I*–*V*) characteristics were recorded using a Semiconductor Characterization System (Keithley 4200-SCS) and a typical four-point probe station (CASCADE SUMMIT 11000). The gas responses of the ZnO sensor were tested with homemade measurement equipment.

The test schematic of the custom test circuitry for gas measurement is shown in Fig. 1(a). A DC voltage of 4.096 V is applied and the voltage (*V*₀) across the signal resistor (*R*₀) is continuously recorded, as the sensor is subjected to repeated target gas (NO₂) exposure and removal at a set temperature. According to Ohm's law, the following formula for the resistance *R* of the ZnO sample is obtained from the above-mentioned test schematic:

$$(R + R_0) \cdot V_0 / R_0 = 4.096 \Rightarrow R = (4.096 / V_0 - 1) \cdot R_0 \quad (1)$$

So the dynamic response of the ZnO sample can be calculated when *R*₀ is determined and *V*₀ has been measured.

Fig. 1(b) shows a schematic diagram of the gas sensing measurement system. A gas dilution system is utilized for the sensor response measurements. The ZnO sensors are mounted inside the test chamber and connected into the custom test circuitry shown in Fig. 1(a). A DC power supply provides 4.096 V to the series resistance and sensor electrodes. The temperature is controlled by a resistive heater, to improve the measurement performance. NO₂ gas is injected into the test chamber with dry-air (carrier gas). The gas sensing performance is evaluated by measuring the resistance changes of the ZnO sample related to various NO₂ concentrations at different operating temperatures.

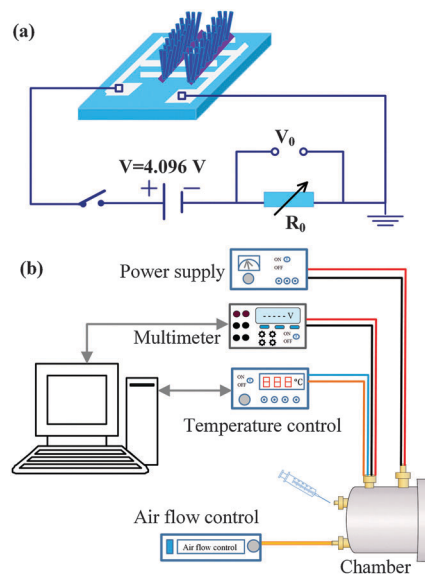


Fig. 1 The test schematic (a) and schematic diagram (b) for NO₂ gas sensing measurement configuration system.

The resistance changes over time during exposure to on-off cycles consisting of specific concentrations of NO₂ ("on") and pure air ("off"). Cycles of different concentrations are tested for NO₂ gas by ramping from a low concentration to a high concentration. Since ZnO is an n-type semiconductor, its resistance R increases with an increase in the oxidizing gas, NO₂, concentration. R of the ZnO sample is measured under dry air to obtain the base line resistance R_a . The resistance of the sample increases to a maximum value R_g when the sample is exposed to different concentrations of NO₂ (1–50 ppm). Sensor response S is defined as $S = (R_g - R_a)/R_a$, where R_a and R_g are the resistances measured in air and an NO₂-air mixture, respectively.

Results and discussion

Morphologies and structures

Due to the anisotropic crystal properties, the growth rates (V) in different directions under hydrothermal conditions are $V_{[0001]} > V_{[0110]} > V_{[1000]}$.³⁴ The as-grown nanorods are c -axis oriented (001) and highly crystalline with less impurities.¹⁶ The crystals of individual nanorods are of good quality in accordance with low index crystallographic face growth. Overall the morphology and distribution of the ZnO-NAs are controlled by process parameters such as the growth time, the ZnAc precursor concentration, the Zn(NO₃)₂ concentration, etc.

The effect of growth time. The growth time in the continuous hydrothermal synthesis can improve the orientation of the ZnO nanorods. Within the first 1 h of growth time, non-directionally oriented ZnO nanorods are obtained, and most nanorods are not vertically aligned to the substrate (Fig. 2(a)). After growing for 4 h, the ZnO nanorods do not have enough space to grow sideways but show consistent orientation, and the axis of the nanorods is

perpendicular to the substrate in the middle area (Fig. 2(b)). After growing for 8 h, it is beginning to appear that the diameters of the nanorods at the edges are larger than those in the middle, which can be observed from the insets of Fig. 2. The growth rate of the marginal nanorods provided with more growing space is greater than that of the middle ones. Well-aligned ZnO-NAs are obtained through growing for 12 h. The consistency becomes greater and the average diameter of the nanorods is larger (Fig. 2(e)) with the increase in growth time.

The effect of ZnAc precursor concentration. The ZnAc precursor concentration in the growth solution has a tremendous impact on the morphology of the ZnO-NAs. The radial growth of flower-type structures is shown in Fig. 3(a) and (b) which correspond to a 0.01 M and 0.025 M ZnAc precursor concentration, respectively. The ZnO nanorods originate from the ZnO seed layer and grow uniformly in all directions. Additionally, the central part of the flower-shape structure, corresponding to the ZnO seed layer, provides a root for the growth of the ZnO nanorods. There are lots of breakpoints in the ZnO-NAs resulting from the 0.01 M ZnAc precursor layer, because the concentration of seed particle nuclei is very low. When the concentration of the ZnAc precursor increases to 0.025 M, the ZnO nanorods can be congregated well. Well-aligned ZnO-NAs are obtained with

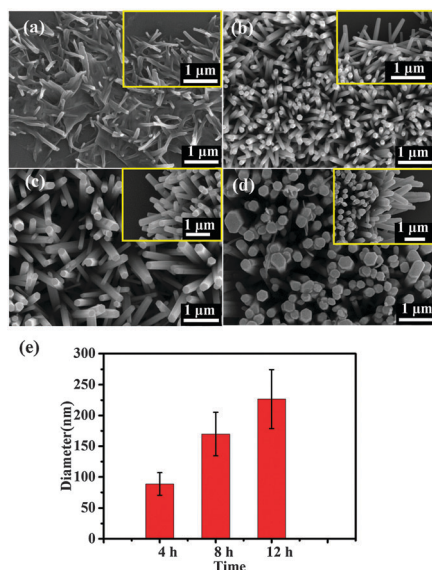


Fig. 2 FESEM images of ZnO nanorods growing for (a) 1 h; (b) 4 h; (c) 8 h; (d) 12 h. The insets are the corresponding FESEM images of the ZnO-NAs edges. (e) Shows the average top diameter distribution of ZnO nanorods obtained with different growth times.

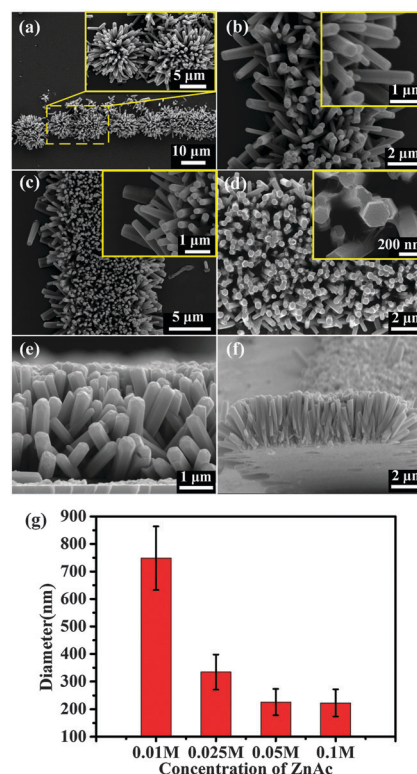


Fig. 3 FESEM images of ZnO nanorods growing from (a) 0.01 M ZnAc, (b) 0.025 M ZnAc, (c) 0.05 M ZnAc, and (d) 0.1 M ZnAc seeds. The insets of (a)–(c) are the corresponding FESEM images of the ZnO-NA edges, and the inset of (d) is the corresponding high magnification FESEM image. The (e) side view and (f) sectional view FESEM images of ZnO-NAs are shown. (g) Shows the average top diameters of ZnO nanorods with different ZnAc concentrations.

0.05 M and 0.1 M ZnAc as the seed (Fig. 3(c) and (d)). The diameter of the array edge is larger than that of the intermediate region for the 0.5 M ZnAc seed layer, which is shown in the inset of Fig. 3(c). For certain ZnAc concentrations, the lateral growing space of the edge array is more sufficient than that of the intermediate region (Fig. 3(e) and (f)). It is easy to form a ZnO nanorod network intersection between parallel arrays, which has advantages for gas sensor devices.³⁵ The ZnO nanorods begin to show a mutual adhesion phenomenon for the 0.1 M ZnAc precursor because of the limited growing space of the individual nanorods owing to the large precursor concentration. The number of nanorods increases as the precursor concentration increases, however the average diameter of the nanorods reduces (Fig. 3(g)).

The effect of $\text{Zn}(\text{NO}_3)_2$ concentration in growth solution. The $\text{Zn}(\text{NO}_3)_2$ concentration in the growth solution has a significant effect on the diameter distributions of the ZnO nanorods. Fig. 4 shows the FESEM images of the ZnO nanorods growing with different concentrations of $\text{Zn}(\text{NO}_3)_2$ in the growth solution. The average top diameter of the ZnO nanorods increases (Fig. 4(g)), when the $\text{Zn}(\text{NO}_3)_2$ concentration increases from 0.01 M to 0.2 M. Radially grown, flower-type structures with uniform and individual nanorods are prepared with 0.01 M $\text{Zn}(\text{NO}_3)_2$ (Fig. 4(a)). The diameter of the array edge is larger than that of the intermediate region for the ZnO-NAs grown

with 0.5 M $\text{Zn}(\text{NO}_3)_2$ growth solution, which is shown in the inset of Fig. 4(b). The ZnO nanorods grown with 0.1 M $\text{Zn}(\text{NO}_3)_2$ solution begin to crowd together, which affects their continued growth and forms stubby nanorods, thereby impacting on the gas response. There are representative joints as seen in Fig. 4(d)–(f), which exhibit that neighboring nanorods grown in a direction deviating from the rigid vertical growth azimuth would fuse together – neighboring nanorods grow and finally combine into one nanorod with a larger diameter. The coalescence of adjacent nanorods renders objective evidence to the issue reported by Li *et al.*,³⁶ which reveals that the growth mechanism should be attributed to the coalescence of ZnO crystals and the secondary growth.

The effect of distance between parallel fibers of ZnAc–PEO in MES technology. The ZnO-NAs are grown with 0.05 M ZnAc seed in 0.05 M $\text{Zn}(\text{NO}_3)_2$ solution for 12 h. The distance between parallel fibers of the ZnAc–PEO is recorded as d . When d is equal to 5 μm , 10 μm , 20 μm , 30 μm , 40 μm and 50 μm in the mechanoelectrospinning (MES) technology, for simplicity, the corresponding samples of the ZnO-NAs are labeled as $D_{5\mu\text{m}}$, $D_{10\mu\text{m}}$, $D_{20\mu\text{m}}$, $D_{30\mu\text{m}}$, $D_{40\mu\text{m}}$ and $D_{50\mu\text{m}}$ respectively. The ZnO-NAs exist independently as parallel fibers for $D_{30\mu\text{m}}$, $D_{40\mu\text{m}}$ and $D_{50\mu\text{m}}$ samples, which can be seen in Fig. 5(a)–(c). There are networks between the ZnO-NA parallel fibers for the sample $D_{20\mu\text{m}}$ (Fig. 5(d)). Enough spaces are still achieved for gas transport and adsorption. The ZnO-NAs are interconnected together to form a densified ZnO nanorod film owing to too close or partial overlap between the ZnAc–PEO seed fibers, when d is equal to 5 μm , and 10 μm (Fig. 5(e) and (f)). The size of the electrode on the sample was decided. The smaller the value of d is, the greater the number of ZnAc–PEO fibers between the electrodes is, and there are more grown ZnO nanorods. The order of the amount of nanomaterial (M) is $M_{50\mu\text{m}} < M_{40\mu\text{m}} < M_{30\mu\text{m}} < M_{20\mu\text{m}} < M_{10\mu\text{m}} < M_{5\mu\text{m}}$.

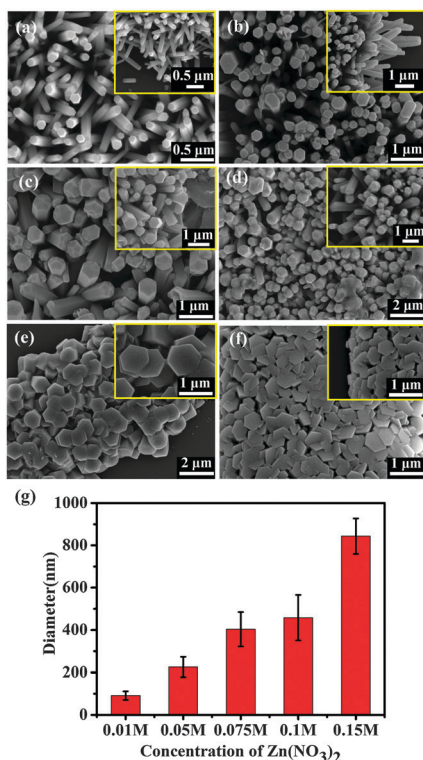


Fig. 4 FESEM images of ZnO nanorods growing in growth solution with (a) 0.01 M $\text{Zn}(\text{NO}_3)_2$; (b) 0.05 M $\text{Zn}(\text{NO}_3)_2$; (c) 0.075 M $\text{Zn}(\text{NO}_3)_2$; (d) 0.1 M $\text{Zn}(\text{NO}_3)_2$; (e) 0.15 M $\text{Zn}(\text{NO}_3)_2$; (f) 0.2 M $\text{Zn}(\text{NO}_3)_2$. The insets of (a–d) and (f) are the corresponding FESEM images of ZnO-NAs edges and the inset of (e) is the corresponding enlarged view. (g) Shows the top diameter distribution of ZnO nanorods with different $\text{Zn}(\text{NO}_3)_2$ concentrations in growth solution.

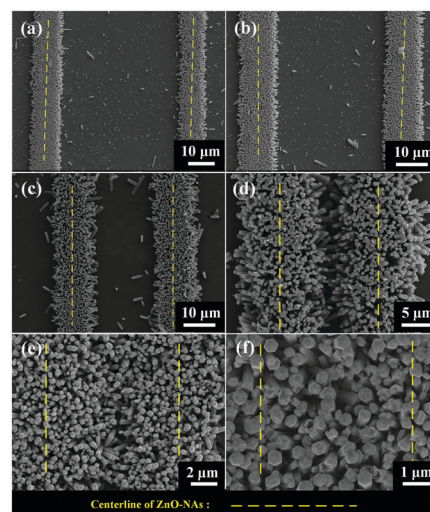
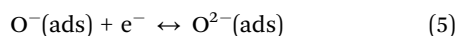
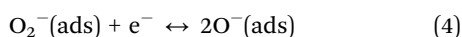
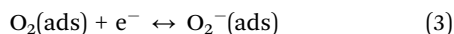
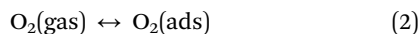


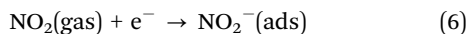
Fig. 5 FESEM images of ZnO-NAs growing from ZnAc–PEO fibers with distances of (a) 50 μm , (b) 40 μm , (c) 30 μm , (d) 20 μm , (e) 10 μm and (f) 5 μm in MES technology. The ZnO-NAs are grown with 0.05 M ZnAc seed in 0.05 M $\text{Zn}(\text{NO}_3)_2$ solution for 12 h.

Characterization of the ZnO gas sensor

The sensing mechanism of the ZnO-NAs for NO₂ can be explained as follows. When a patterned ZnO-NA gas sensor is exposed to air, the chemisorbed oxygen on the surface plays an important role in the electrical transport properties of the ZnO nanorods. Electrons from the ZnO conduction band ionize adsorbed oxygen making it a reactive oxygen species such as O₂⁻, O₂²⁻ and O⁻, and an electron blocking layer (a depletion layer) is formed on the ZnO nanorod surface. The reactive oxygen species depend strongly on temperature. At low temperatures, O₂⁻ is commonly chemisorbed. At high temperatures, O⁻ and O₂²⁻ are commonly chemisorbed while O₂⁻ disappears rapidly.³⁷ The electron blocking layer increases the resistance of the ZnO-NAs.³⁸ The possible reactions can be shown as follows:³⁹



The NO₂ gas molecules are adsorbed on the surface of the ZnO nanorods when the ZnO nanorods are exposed to NO₂ gas. The NO₂ acts as an electron acceptor and attracts the electrons from the ZnO conduction band.



When the NO₂ concentration increases, more electrons will participate in reaction (6), resulting in an increase in the depletion layer width, and leading to the increase in the sensor resistance.⁴⁰

The current-voltage (*I*-*V*) characteristics (Fig. 6(a)) of the ZnO sample's exposure to dry air, NO₂ gas and dry air again indicate that the electrical current is approximately linearly proportional to the intensity of the applied bias voltage (from -10 V to 10 V), which denotes that the ZnO sample has Ohmic behavior. This is beneficial for the gas sensing properties because the response of the gas sensor can be maximized when the metal-semiconductor junction displays Ohmic behavior or has a negligible junction resistance.

Fig. 6(b) shows the dynamic response of the ZnO-NAs to NO₂ at various concentrations from 1 to 50 ppm at 180 °C. The resistance increases to a maximum resistance within minutes of the injection of the oxidizing NO₂ gas into the testing chamber, suggesting a rapid response to NO₂ and a steady state. The resistance recovers completely to the original baseline level with the removal of NO₂. The response of the ZnO sensor increases as the NO₂ concentration increases. The response of the ZnO-NAs to NO₂ gas is stable and reproducible for repeat tests.

The response time is defined as the time taken by the sensor to attain 90% of the maximum increase in resistance on exposure to the target gas and the recovery time is defined as the time to get back 90% of the maximum resistance when

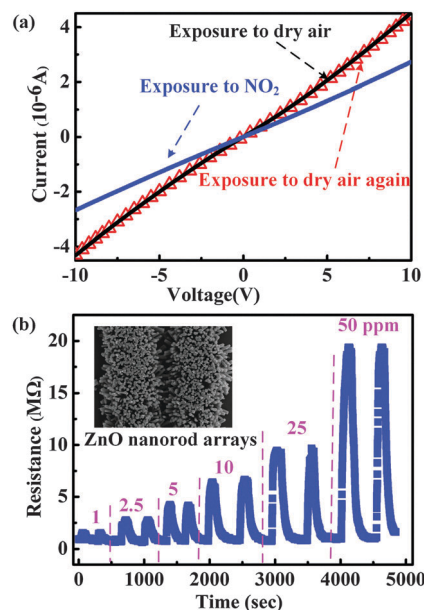


Fig. 6 (a) Room-temperature *I*-*V* characteristics measured when ZnO-NAs gas sensor is exposed to dry air, NO₂ gas and then dry air again. (b) Dynamic response of ZnO sample for two measurement cycles to different concentrations of NO₂ at 180 °C. The ZnO-NAs are grown with 0.05 M ZnAc seed in 0.05 M Zn(NO₃)₂ solution for 12 h.

exposed to clean air. Fig. 7(a) shows the dynamic response of the ZnO samples at different working temperatures from 150 °C to 250 °C and different concentrations of NO₂ from 1 ppm to 50 ppm. The working temperature has a significant effect on the gas response. Usually, the NO₂ gas sensing tests are carried out at a high operation temperature (working temperature).⁴¹ Hamaguchi *et al.*⁴² reported that the gas sensing responses and recovery times became much longer as the operation temperature decreased. NO₂ gas sensing at low working temperatures by a ZnO nanorod based sensor can be achieved by doping and using a spiral electrode.⁴³ The hierarchical ZnO-NAs exhibit a repeatable, fast response and recovery towards NO₂ at 150 °C (Fig. 7(a)) in this study. The response times (less than 120 s) and recovery times (less than 150 s) for every test concentration of NO₂ at all working temperatures (150–250 °C) are in the order of minutes.⁶

The gas response increases with the working temperature up to a range from 200 °C to 225 °C and then decreases sharply (Fig. 7(b)). The optimal working temperature is 200–225 °C.

The gas response (sensor conductance) is believed to be affected by many factors, including adsorbed oxygen species, rates of adsorption and desorption, and the charge-carrier concentration, which are all functions of temperature. All of the factors together determine the quantity of active electrons in the surface reaction. Therefore, the gas response becomes temperature-dependent, and an optimal temperature (200–225 °C) is induced here, which corresponds to the optimal conditions where the largest number of active electrons are involved in the surface reactions of the ZnO nanorods. The gas sensing performance is with respect to the tangent slopes of the response curves. The tangent slopes in Fig. 7(c) at different gas concentrations for the optimal temperatures

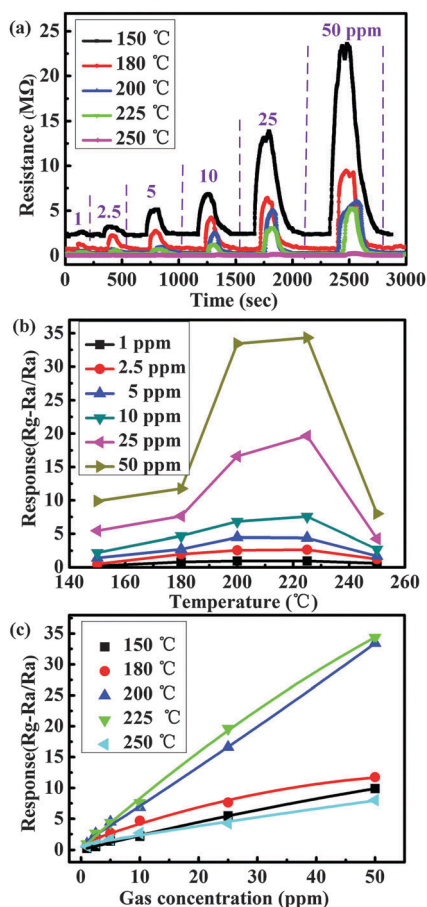


Fig. 7 (a) Shows the dynamic response of ZnO samples exposed to different concentrations of NO₂ at high working temperatures. Response (b and c) of the ZnO sensor to different concentrations of NO₂ at different working temperatures. The ZnO-NAs are grown with 0.05 M ZnAc in 0.05 M Zn(NO₃)₂ growth solution for 12 h.

are larger than those for other temperatures. So the gas sensor has the best sensing performance at 200–225 °C.

It is obvious that the gas response values increase with the increase in gas concentration (Fig. 7(c)). An approximately linear increase relationship between the corresponding responses and the NO₂ concentrations at optimal working temperatures is observed. However, the gas response values reach saturation gradually as the NO₂ gas concentration increases at other working temperatures. The sensor surface reaction will become saturated at higher NO₂ concentrations (> 50 ppm). The available surface area of the ZnO nanorods is enough to let the NO₂ molecules interact with the ZnO at low NO₂ concentrations. So the gas response is mainly dependent on the NO₂ concentration before the sensor reaches the saturation stage. However, if the NO₂ concentration increases, there are insufficient adsorption sites and the NO₂ molecules have to compete for adsorption sites.

The effect of process parameters on the ZnO-NAs sensing performance

The gas response of the ZnO sensor is dependent on the surface-reaction rate which is determined by the adsorption

sites on the ZnO nanorod surface and the quantity of NO₂ gas molecules. The adsorption sites are related to the surface area of the nanomaterial (the amount of nanomaterial) and the quantity of NO₂ molecules is determined by the gas concentration. The gas sensing performance is affected by the morphology of the ZnO-NAs prepared under different conditions including the growth time, the solution concentration and the concentration of the precursor. If there is insufficient nanomaterial or NO₂ concentration, the gas response of the ZnO sensor easily reaches saturation.

Gas sensing performance with growth time. The NO₂ sensing properties of the ZnO-NAs/ZnO sensors grown with 0.05 M ZnAc seed in 0.05 M Zn(NO₃)₂ growth solution for different growth times (1 h, 4 h, 8 h, 12 h) are measured. There is no visible response to NO₂ when ZnO nanorods are grown for 1 h, because the baseline resistance R_a is more than 10^9 ohms, and the resistance change of dozens of MΩ is too small to be sensed. The signal resistance is $R_0 = 156$ MΩ, 78 MΩ and 1 MΩ, when the growth time is 4 h, 8 h and 12 h respectively. It is observed that the gas response S of the ZnO samples increases in an order of $S_{4h} < S_{8h} < S_{12h}$ (Fig. 8(a)). For 4 h, the increases slow down gradually, and the response becomes saturated with an increase in the gas concentration. When the growth time is 8 h and 12 h, an approximately linear increase relationship between the corresponding responses and NO₂ concentrations is observed. The tangent slopes T of the response curves to the same test gas concentration are in the order: $T_{4h} < T_{8h} < T_{12h}$. So the gas sensor using ZnO-NAs growing for 12 h has the best sensing performance. When the growth time is too short (1 h), there are barely any ZnO nanorods on the substrate, and thus the sensor has no signal. With the increase in the growth time, the lengths and diameters of the ZnO nanorods are both increased, and there are more adsorption sites on the surfaces of the ZnO nanorods, which can enhance the gas sensing performance.

Gas sensing performance with concentration of ZnAc precursor. There is a critical concentration of the ZnAc seed for fabricating the ZnO-NAs/ZnO sensors. The ZnO-NAs are grown with different concentrations of the ZnAc seed in 0.05 M Zn(NO₃)₂ growth solution for 12 h. When the concentration of the ZnAc precursor is lower than 0.01 M, the ZnO sensor becomes a failed product owing to breakpoints in the nanorod arrays. When the ZnAc concentration is in the range of 0.025–0.1 M, there are significant gas responses, and the responses increase as the NO₂ concentration increases (Fig. 8(b)). There is an approximately linear relationship between the response and the NO₂ concentration (1–50 ppm) for samples using a 0.05 M and 0.1 M ZnAc precursor. However, the increase in the gas response for the 0.025 M ZnAc precursor sample slows down gradually when the NO₂ concentration increases, and the response reaches saturation. When the NO₂ concentration is less than or equal to 2.5 ppm, the gas response of the 0.025 M ZnAc samples is not obvious. Even if the NO₂ concentration is larger than 2.5 ppm, the response is also small. So the lowest detection limit is 2.5 ppm. As the concentration of the ZnAc precursor increases, the gas response increases at first and then decreases. The tangent slopes T of the response curves under the same gas concentration are in the order: $T_{0.025M} < T_{0.1M} < T_{0.05M}$. So the ZnO sample grown from

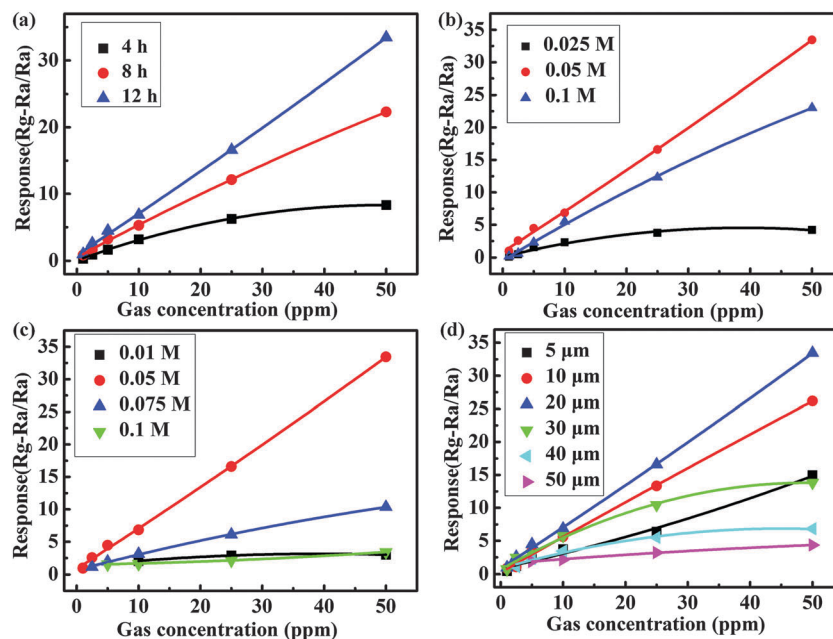


Fig. 8 Response of ZnO samples with (a) different growth time (1 h, 4 h, 12 h), growing from (b) different concentrations of ZnAc seeds (0.025 M, 0.05 M, 0.1 M), growing with (c) different concentrations of $Zn(NO_3)_2$ in growth solution (0.01 M, 0.05 M, 0.075 M, 0.1 M) and with (d) different distances between fibers of ZnAc-PEO to different concentrations of NO_2 measured at 200 °C are listed.

the 0.05 M ZnAc precursor has the best gas sensing performance. Therefore, a low concentration of the ZnAc seeds leads to a small amount of the ZnO nanorods which tend to reach saturation for the adsorption of NO_2 molecules. However, a too high concentration of the ZnAc seeds results in an excess amount of the ZnO nanorods (the adhesion phenomenon) affecting the NO_2 gas transmission and adsorption, and thus the response of the sensor becomes lower. The optimal concentration of the ZnAc seeds leads to an appropriate amount of the ZnO nanorods, which could absorb a large amount of NO_2 molecules. The critical concentration for the ZnAc precursor is 0.05 M for the best sensing performance.

Gas sensing performance with $Zn(NO_3)_2$ concentration.

There is an optimal concentration of $Zn(NO_3)_2$ in the growth solution for fabricating the ZnO-NAs/ZnO sensors. The ZnO-NAs are grown with different concentrations of $Zn(NO_3)_2$ in the growth solution with a 0.05 M ZnAc seed for 12 h. When the concentration of $Zn(NO_3)_2$ was from 0.01 M to 0.1 M, the gas response increases at first and then decreases, as is shown in Fig. 8(c). The sample using 0.05 M $Zn(NO_3)_2$ exhibits the best response within the measured NO_2 concentrations. There is an approximately linear increase relationship between the corresponding responses and NO_2 concentrations (1–50 ppm) for samples of 0.05 M, 0.075 M and 0.1 M $Zn(NO_3)_2$. The curve slopes T under the same gas concentration are in the order: $T_{0.1M} < T_{0.01M} < T_{0.075M} < T_{0.05M}$. So the gas sensor using 0.05 M $Zn(NO_3)_2$ has the best NO_2 sensing performance. The response of the 0.01 M $Zn(NO_3)_2$ sample also increases with respect to the NO_2 concentration, and the increase slows down gradually until the response values become saturated with a larger gas concentration (25 ppm). When the NO_2 concentration

is less than or equal to 10 ppm, the gas response is not visible for the 0.01 M and 0.1 M $Zn(NO_3)_2$ samples. Even if the NO_2 concentration is larger than 10 ppm, the response is also small. So the lowest detection limit is 10 ppm. Therefore, a low concentration of $Zn(NO_3)_2$ leads to less surface area of the ZnO nanorods, which tend to reach saturation for the adsorption of NO_2 molecules. A too high concentration of $Zn(NO_3)_2$ results in fused together ZnO nanorods with a large diameter, which affects the gas transmission and adsorption, and has a significant influence on the gas response of the sensor. The optimal concentration of $Zn(NO_3)_2$ leads to an appropriate amount of the ZnO nanorods, which could absorb large amount of NO_2 molecules. The optimal concentration for $Zn(NO_3)_2$ is 0.05 M for the best sensing performance.

Gas sensing performance with distance between parallel fibers. The ZnO-NAs are grown with a 0.05 M ZnAc seed in 0.05 M $Zn(NO_3)_2$ solution for 12 h. The signal resistance R_0 of the $D_{5\mu m}$, $D_{10\mu m}$, $D_{20\mu m}$, $D_{30\mu m}$, $D_{40\mu m}$, and $D_{50\mu m}$ samples is 0.1 M Ω , 1 M Ω , 1 M Ω , 78 M Ω , 156 M Ω and 156 M Ω , respectively. Fig. 8(d) shows the gas response of the ZnO sensors versus the NO_2 concentration plots in the range of 1–50 ppm at 200 °C. It is found that the gas responses increase with the increasing gas concentration for all curves ($D_{5\mu m}$ – $D_{50\mu m}$). However, the increasing tendencies are different for the varying distances between the ZnAc-PEO fibers. For the $D_{30\mu m}$, $D_{40\mu m}$, and $D_{50\mu m}$ sensors, the increase slows down gradually until the response values become saturated with a larger gas concentration (50 ppm). While for the $D_{5\mu m}$, $D_{10\mu m}$, and $D_{20\mu m}$ sensors, the increase shows an approximately linear increase relationship as the gas concentration increases. That is because there are such large amounts of the ZnO-NAs that the sensing reaction does not easily reach

saturation. The lowest detection limit is 2.5 ppm NO₂ for the D_{40μm} and D_{50μm} samples. There are fewer ZnO-NAs, and the gas responses are lower. There is a significant response to NO₂ even at a low concentration (1 ppm) for the D_{5μm}, D_{10μm} and D_{20μm} samples. The ZnO-NAs of the D_{5μm} and D_{10μm} samples are much too dense, which impacts on the diffusion of the NO₂ molecules and the gas sensing reaction on the surface of the nanorods, and reduces the gas sensing properties. Therefore, the response of the D_{5μm} and D_{10μm} samples is very low. It can be concluded that neither too large nor too small distances between the ZnAc-PEO fibers are beneficial for the gas response. The D_{20μm} sample has the highest response and the largest tangent slope of response curve under each test concentration because of the optimal intensity of the nanorods. Additionally, the intersection between the parallel arrays can contribute to the response.⁴⁴ The above analyses indicate that 20 μm is the optimal distance for the best sensing performance.

Conclusions

ZnO-NAs, prepared by the MES-CHSM, are used for an NO₂ gas sensor and exhibit good sensing performance, and exert excellent Ohmic contact rather than diode-like behaviour. The gas sensing results show fast responses and recovery after NO₂ gas exposure and air purging, respectively, and they are stable and reproducible for repeat tests. Several critical influencing factors for the gas response are investigated: (1) the seed concentration of ZnAc, where there is an optimal value for the best response; (2) the morphology (diameter, interval and orientation) of the ZnO nanorods, which are determined by different process parameters such as the growth time, ZnAc precursor concentration and Zn(NO₃)₂ concentration in the growth solution; (3) the distribution of the ZnO-NAs depending on the distances between the parallel ZnAc-PEO fibers, which can be individually controlled by MES; (4) the optimal working temperature between 200 and 225 °C, at which the ZnO sensor shows the best response to NO₂; and (5) the saturation behavior for low NO₂ concentrations (1–50 ppm), which is delayed to enlarge the measuring range of the gas sensor. The gas response is surface-reaction-rate-determining according to the gas sensing mechanism. The MES-CHSM is a digital, low-cost, low-temperature, and mask-free manufacturing technique to fabricate highly sensitive, temperature-dependent gas sensors.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51322507, 51475195, 51421062), and New Century Excellent Talents in University (NCET-11-0171).

Notes and references

- 1 M. Breedon, M. J. S. Spencer and I. Yarovskiy, *J. Phys. Chem. C*, 2010, **114**, 16603–16610.
- 2 M. Matsuguchi, Y. Kadowaki and M. Tanaka, *Sens. Actuators, B*, 2005, **108**, 572–575.
- 3 J. W. Fergus, *Sens. Actuators, B*, 2007, **121**, 652–663.
- 4 J. W. Yoon, M. L. Grilli, E. D. Bartolomeo, R. Polini and E. Traversa, *Sens. Actuators, B*, 2001, **76**, 483–488.
- 5 R. Zou, G. He, K. Xu, Q. Liu, Z. Zhang and J. Hu, *J. Mater. Chem. A*, 2013, **1**, 8445–8452.
- 6 R. Kumar, O. Al-Dossary, G. Kumar and A. Umar, *Nano-Micro Lett.*, 2015, **7**, 97–120.
- 7 X. Pan, X. Liu, A. Bermak and Z. Fan, *ACS Nano*, 2013, **7**, 9318–9324.
- 8 A. Gurlo, *Nanoscale*, 2011, **3**, 154–165.
- 9 C. Wu, L. Shen, Y.-C. Zhang and Q. Huang, *Mater. Lett.*, 2011, **65**, 1794–1796.
- 10 K. Mahmood, S. B. Park and H. J. Sung, *J. Mater. Chem. C*, 2013, **1**, 3138–3149.
- 11 S. P. Chang, R. W. Chuang, S. J. Chang, Y. Z. Chiou and C. Y. Lu, *Thin Solid Films*, 2009, **517**, 5054–5056.
- 12 M. Ahmad and J. Zhu, *J. Mater. Chem.*, 2011, **21**, 599–614.
- 13 N. I. Rusli, M. Tanikawa, M. R. Mahmood, K. Yasui and A. M. Hashim, *Materials*, 2012, **5**, 2817–2832.
- 14 J. Liu, W. Wu, S. Bai and Y. Qin, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4197–4200.
- 15 S. Ozturk, N. Kilinc and Z. Z. Ozturk, *J. Alloys Compd.*, 2013, **581**, 196–201.
- 16 X. Wang, F. Sun, Y. Huang, Y. Duan and Z. Yin, *Chem. Commun.*, 2015, **51**, 3117–3120.
- 17 W. Wu, X. Wen and Z. L. Wang, *Science*, 2013, **340**, 952–957.
- 18 Y. Wei, W. Wu, R. Guo, D. Yuan, S. Das and Z. L. Wang, *Nano Lett.*, 2010, **10**, 3414–3419.
- 19 H. Shao, X. F. Qian and B. C. Huanga, *Mater. Sci. Semicond. Process.*, 2007, **10**, 68–76.
- 20 H. W. Kang, J. Leem, S. H. Ko, S. Y. Yoon and H. J. Sung, *J. Mater. Chem. C*, 2013, **1**, 268–274.
- 21 M.-H. Jung and H. Lee, *Nanoscale Res. Lett.*, 2011, **6**, 159.
- 22 F. M. Wisser, B. Schumm, G. Mondin, J. Grothe and S. Kaskel, *J. Mater. Chem. C*, 2015, **3**, 2717–2731.
- 23 M.-H. Chu, S.-Y. Kim, S.-Y. Sung, J.-H. Lee, J.-J. Kim, D. P. Norton, S. J. Pearton and Y. W. Heo, *J. Nanoelectron. Optoelectron.*, 2010, **5**, 186–190.
- 24 B. Postels, M. Kreye, H.-H. Wehmann, A. Bakin, N. Boukos, A. Travlos and A. Waag, *Superlattices Microstruct.*, 2007, **42**, 425–430.
- 25 C. P. Chun and L. J. Grace, *ZnO Nanowire Field-Effect Transistors*, Institute of Electrical and Electronics Engineers, New York, NY, ETATS-UNIS, 2008.
- 26 C.-J. Chang, S.-T. Hung, C.-K. Lin, C.-Y. Chen and E.-H. Kuo, *Thin Solid Films*, 2010, **519**, 1693–1698.
- 27 L. J. Chen and Y. J. Chuang, *Mater. Lett.*, 2012, **68**, 460–462.
- 28 M.-H. Jung and M.-J. Chu, *J. Mater. Chem. C*, 2014, **2**, 6675–6682.
- 29 C. Wang, B. Mao, E. Wang, Z. Kang and C. Tian, *Solid State Commun.*, 2007, **141**, 620–623.
- 30 L. Xu, X. Wang, T. Lei, D. Sun and L. Lin, *Langmuir*, 2011, **27**, 6541–6548.
- 31 D. Sun, C. Chang, S. Li and L. Lin, *Nano Lett.*, 2006, **6**, 839–842.

- 32 Y. Huang, Y. Duan, Y. Ding, N. Bu, Y. Pan, N. Lu and Z. Yin, *Sci. Rep.*, 2014, **4**, 5949.
- 33 N. Bu, Y. Huang, X. Wang and Z. Yin, *Mater. Manuf. Processes*, 2012, **27**, 1318–1323.
- 34 H. Yang, Y. Song, L. Li, J. Ma, D. Chen, S. Mai and H. Zhao, *Cryst. Growth Des.*, 2008, **8**, 1039–1043.
- 35 M.-W. Ahn, K.-S. Park, J.-H. Heo, D.-W. Kim, K. J. Choi and J.-G. Park, *Sens. Actuators, B*, 2009, **138**, 168–173.
- 36 Z. Li, X. Huang, J. Liu, Y. Li and G. Li, *Mater. Lett.*, 2008, **62**, 1503–1506.
- 37 D. Kohl, *Sens. Actuators, B*, 1990, **1**, 158–165.
- 38 L. Shi, A. J. T. Naik, J. B. M. Goodall, C. Tighe, R. Gruar, R. Binions, I. Parkin and J. Darr, *Langmuir*, 2013, **29**, 10603–10609.
- 39 Y. Şahin, S. Öztürk, N. Kılınc, A. Kösemen, M. Erkovan and Z. Z. Öztürk, *Appl. Surf. Sci.*, 2014, **303**, 90–96.
- 40 S. Park, S. An, Y. Mun and C. Lee, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4285–4292.
- 41 A. Z. Sadek, S. Choopun, W. Wlodarski, S. J. Ippolito and K. Kalantar-zadeh, *IEEE Sens. J.*, 2007, **7**, 919–924.
- 42 T. Hamaguchi, N. Yabuki, M. Uno, S. Yamanaka, M. Egashira, Y. Shimizu and T. Hyodo, *Sens. Actuators, B*, 2006, **113**, 852–856.
- 43 C.-J. Chang, J.-K. Chen and T.-L. Yang, *J. Taiwan Inst. Chem. Eng.*, 2014, **45**, 1876–1882.
- 44 M.-W. Ahn, K.-S. Park, J.-H. Heo, J.-G. Park, D.-W. Kim, K. J. Choi, J.-H. Lee and S.-H. Hong, *Appl. Phys. Lett.*, 2008, **93**, 263103.