In–situ integration and surface modification of functional nanomaterials by localized hydrothermal reaction for integrated and high performance chemical sensors

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A R T I C L E   I N F O
Article history:
Received 20 June 2015
Received in revised form 11 November 2015
Accepted 20 November 2015
Available online 30 November 2015

Keywords:
- Nanowire
- Localized synthesis
- Metal nanoparticle
- Surface functionalization
- Gas sensor
- Chemical sensor

A B S T R A C T
We have developed a novel method for simple, rapid and selective synthesis of one dimensional nanomaterials as well as their selective surface functionalization, all in low-temperature and liquid-phase conditions, for highly integrated chemical sensor applications. In specific, localized heating by micro-heater allows selective synthesis and in–situ integration of ZnO nanowires on sensing electrodes. High surface area and chemical reactivity of nanowires enable high sensitivity and fast response to hydrogen (H2) molecules. Furthermore, subsequent localized heating process in metal precursor solution allows facile surface functionalization of ZnO nanowires with catalytic metal nanoparticles (Pt or Pd), which dramatically enhanced the gas sensing performances. This approach has demonstrated a practical method of developing integrated chemical sensors with heterogeneous nanostructures, potentially for multiplexed chemical detection purposes.

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1. Introduction

One dimensional (1D) inorganic semiconductor nanomaterials have received tremendous attention for their potential use as building blocks in the next generation nanodevices [1,2]. Among those nanomaterials, 1D metal oxide nanomaterials (nanowires, nanorods, nanotubes and nanoribbons) have been attracting great research interests due to their facile synthesis, unique material properties and advantages. Therefore, a large number of studies have been conducted to apply them in electronics, catalysis, sensors, displays, energy conversion devices, etc [3,4]. Especially, as environmental monitoring in public and industrial areas has become more important, there is an increasing need for chemical sensors with high sensitivity, selectivity, stability and ultra-compact size. Accordingly, diverse gas sensors based on 1D metal oxide nanomaterials (e.g. ZnO, SnO2 and TiO2) have been developed to detect gaseous molecules such as ethanol (C2H5OH) [5], carbon monoxide (CO) [6], hydrogen (H2) [7], hydrogen sulfide (H2S) [8] and nitrogen dioxide (NO2) [9]. However, vapor phase synthesis processes including chemical vapor deposition (CVD) or pulsed laser deposition (PLD), which are popular methods for the fabrication of metal oxide nanowires in gas sensor applications, often require stringent and expensive process conditions (e.g. high temperature, vacuum and/or toxic gases). On the other hand, solution phase synthesis such as hydrothermal reaction includes less toxic chemical reaction at low temperature conditions in comparison to the vapor phase synthesis method. Another challenge of 1D nanomaterial-based sensor fabrication lies in the integration of nanomaterials on device electrodes: For the fabrication of integrated sensing devices, 1D nanomaterials have to be assembled or integrated on device electrodes after the synthesis process. In particular, they should be harvested from the synthesis substrate and assembled onto the device substrate by various methods such as drop casting [10], contact printing [11], dielectrophoresis [12], optical tweezing [13] or nanomanipulation [14]. Furthermore, to make electrical and mechanical contacts between...
nanowires and electrodes more robust, additional processes for the contact formation such as focused ion beam (FIB) or conventional lithography techniques with metal lift-off process should be carried out [15–17] since the bonding between as-assembled nanomaterials and electrodes is based on weak van der Waals force [18]. Alternative approach to the device integration of nanowires is the in-situ synthesis on device electrodes by using patterned seeds/catalysts [19,20] or lateral synthesis of nanowires on particular crystal planes [21]. However, the first approach requires multiple steps for seed/catalyst patterning and tedious alignment process with device electrodes. Also, the second approach requires nonconventional and expensive substrates with particular crystalline orientations to enable the directional growth of nanowires.

On the other hand, the surface functionalization of metal oxide nanowires with metal nanoparticles (NPs) such as Pt, Pd, Au and Ag leads to great enhancement of the gas sensor performance with high sensitivity, selectivity and fast response speed by the catalytic effect [22–24]. The surface functionalization methods include a physical vapor deposition [25,26] or chemical reaction process [27]. In the physical vapor deposition method, thin films of catalytic materials are deposited on the surface of sensing materials by using thermal evaporation, electron beam evaporation or sputtering process, and then thin films are converted into NPs by additional heating process. These methods require stringent vacuum condition and high power consumption. Moreover, for the surface functionalization of nanomaterial array with different types of metal NPs, additional masking processes with accurate alignment on selected sensing materials are required [28]. Even through the chemical reaction processes are usually conducted in normal pressure and low temperature conditions, additional screening processes are also required to prevent damage and contamination of different material array other than those to be functionalized [29].

In this work, we provide an alternative solution to the critical technical challenges explained above (i.e. device integration and surface functionalization of 1D nanomaterials on microelectronic devices) by utilizing localized heating of integrated microheater array, all in low temperature and liquid phase. This method enables the facile fabrication of low-power and high-performance gas sensing device based on 1D metal oxide nanomaterials and their surface functionalization with catalytic metal nanoparticles [30] In specific, the synthesis of ZnO nanowires and their decoration with catalytic NPs (Pt and Pd) were demonstrated in this work. ZnO with a wide band gap (3.37 eV) and a large excitation binding energy (~60 meV) is a useful material in numerous applications such as optics, optoelectronics, sensors and actuators [31]. ZnO nanowires as sensing elements were locally synthesized and directly integrated into a device by using localized thermal energy generated from the integrated microheater array (Fig. 1A). Subsequently, the surface of locally synthesized ZnO nanowires was decorated through wet-chemical synthesis of catalytic NPs (Pt or Pd) again by local heating method (Fig. 1B).

We have found that metal NP coating on the ZnO nanowires dramatically enhances the sensitivity of sensor and lowers the operation temperature by catalytic effect in the reaction with gas as compared to the pristine ZnO nanowires. Our novel approach presents the following advantages: (1) direct integration of functional nanomaterials on the sensing device is possible with no further integration or assembly processes; (2) selective surface functionalization of nanowires with metal NPs can be achieved with no complicated alignment or vacuum deposition processes; and (3) consumption of energy and resources is minimized due to low power and liquid phase reaction at extremely localized spots. Although this method was applied to a particular combination of materials (ZnO nanowire as a sensing material, Pt or Pd as the metal catalysts and H2 as the target gas), this approach can potentially be extended to a variety of sensing materials and target gases.

2. Material and methods

2.1. Device fabrication

The device is composed of three layers (layer 1: metal microheater; layer 2: electrical insulation layer; layer 3: interdigitated sensing electrode) on thermally oxidized silicon (Si) substrate (Fig. S1A). As the first step, Au/Cr (thickness = 200 nm/10 nm)
microheater array was patterned on Si substrate with 2 μm thick SiO2 layer by using photolithography, electron beam evaporation and lift-off processes. Then, SiO2 thin film (400 nm) was deposited by plasma enhanced chemical vapor deposition (PECVD) for the passivation between lower microheater array and top sensing electrodes. Interdigitated sensing electrodes were fabricated on a SiO2 passivation layer by photolithography, e-beam evaporation and lift-off process. Finally, the passivation layer was removed on the contact pad area by using buffered oxide etchant (BOE) solution.

2.2. Synthesis of ZnO nanowires via localized heating

The synthesis of ZnO nanowires was conducted by using local heating with integrated microheater array as shown in Fig. 1A. First, the substrate was coated with ZnO NPs seed solution and then heated at 150 °C for 20 min to form a thin ZnO seed layer as described in the literature [32]. Second, a PDMS block with a punched hole was attached onto the substrate and filled with 0.01 mL of ZnO nanowire precursor solution that was prepared from zinc nitrate hexahydrate (Zn(NO3)2·6H2O, 25 mM), hexamethylenetetramine (HMTA, C6H12N4, 25 mM), and polyethyleneimine (PEI, C4H9N2, 6 mM) in DI water. Third, a local hydrothermal synthesis of ZnO nanowires was carried out by Joule heating of microheater array with a voltage of 0.85 V and power consumption of 360 mW. The localized thermal energy elevated the temperature of ZnO nanowire precursor solution above 90–95 °C along the microheater and realized the selective synthesis of ZnO nanowires for a period of 20–25 min (Fig. S1B and C).

2.3. Surface modification of ZnO nanowires with metal NPs via localized heating

The surface of ZnO nanowires was selectively decorated with noble metal (Pt or Pd) NPs by using the same protocol as that for the nanowire synthesis (Fig. 1B), but within the precursor solutions for metal NPs. Pt and Pd precursor solutions were prepared by adding sodium citrate solution (30 mM) into the aqueous solutions of potassium tetrachloroplatinate (K2PtCl4, 1 mM) or potassium chloropalladitate (K2PdCl4, 1 mM), all in DI water. Sodium citrate was used as a reducing agent and a stabilizer. Also, aqueous sodium hydroxide solution (0.1 mM) was added to the Pt and Pd precursor solutions in order to prevent the surface etching of ZnO nanowires. For the surface modification of ZnO nanowires, the aqueous Pt or Pd precursor solution was dispensed into the PDMS block attached on the device with locally grown ZnO nanowires. The device was heated by microheater array supplying the electrical power of ~300 mW for 15–25 min. In order to avoid the contamination of nanowires by reaction byproducts, remaining reactants or other impurities in the precursor solution, the device was thoroughly cleaned after the surface modification process.

2.4. Material characterization

Scanning electron microscopy (SEM) images of the samples were obtained with a field emission scanning electron microscope (FESEM, Phillips Model XL30 FEG). Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) characterization were performed with an FEI Technai G2 F30 Super twin transmission electron microscope operating at 300 kV. X-ray diffraction (XRD) spectrum was measured with a Bruker AXS D8 DISCOVER diffractometer using Cu Kα (λ = 0.5412 nm) radiation.

2.5. Hydrogen sensing measurement

The chemical sensing experiments were conducted to investigate the hydrogen sensing performances of gas sensors based on pristine and metal NP coated ZnO nanowires. The sensors were annealed at 300 °C for 2 h in an atmospheric condition to eliminate organic residues remaining in the synthesized nanostructures and to improve their sensing performance. They were mounted on a chip carrier inside a sealed quartz tube furnace with an electrical circuit and gas inlet/outlet. The chip carrier was connected to a source meter unit (KEITHLY, 2400) in order to measure the resistance change of gas sensors. A voltage of 1 V was supplied to the sensing electrodes and the operating temperature of a gas sensor was controlled by changing the temperature of quartz tube furnace. The experiments were operated in a LabView™ measurement system. Various concentrations of H2 (gas flow: 1 L/min) were generated by controlling the mixture of pure H2 and synthetic air gas (N2:O2 = 79%-21%) at different volume ratios.

3. Results and discussion

3.1. Synthesis of ZnO nanowires

The device to realize directly integrated ZnO nanowire sensor using localized thermal energy of microheater array was fabricated by conventional photolithography, thin film deposition and lift-off process. Fig. 2A and B present the photograph and top view SEM images of the fabricated device. It consists of interdigitated sensing electrodes (upper layer) and microheater array (lower layer) that are separated by an insulating layer as shown in Fig. S1A. The experimental setup is also simple, it consists of the microheater device, DC power supply for electrical energy supply and microscope for monitoring the synthesis process (Fig. S1B). It should be noted that two separate microheaters (heater A and B) were used to control the local heating in two individual zones. Numerical simulation of the steady-state temperature distribution generated by microheater array during the hydrothermal synthesis process of ZnO nanowires was conducted by using COMSOL Multiphysics® software (Fig. 2C–E; details about numerical simulation is explained in the Supplementary Information). The simulation results indicate that the temperature of ZnO precursor solution can be locally elevated to the desired values (90–95 °C) for ZnO nanowire synthesis in the region of sensing electrodes while being maintained at low values (~27 °C) at the surrounding regions. The temperature on the top surface of the sensing electrode is slightly lower than that on the microheater. Also, the heat generated from microheater is mostly transferred to upper direction (ratio of heat transfer to upper and lower directions = 8.23:1) due to thick underlying SiO2 layer with low thermal conductivity (i.e., thickness ≈ 2 μm and k ≈ 1.48 W/(mK) at 100 °C) [33]. Therefore, the thermal energy can be effectively transferred to the precursor solution during the synthesis process without considerable waste of energy to the substrate. Fig. S2 shows time-lapse microscope images of ZnO nanowires synthesized for various time periods (0, 5, 10, 15, 20 and 25 min) during hydrothermal synthesis process. In these images, ZnO nanowire bundles appear to be dark and hazy spots along the serpentine microheater. They grew from microheater and became bigger along the increased synthesis time period. Fig. 3A and B display the SEM images of fully (using both heaters A and B) and partially (using heater B only) grown ZnO nanowires on the sensing electrodes by localized thermal energy generated from microheater array. These results indicate that ZnO nanowires were selectively grown and directly integrated on the local hot spot created by microheater array in a single step without the need of complicated alignment or integration process. The ZnO nanowires synthesized on interdigitated electrodes exhibit hexagonal structures with diameter of 50–300 nm and length of 2–4 μm as shown in the high resolution SEM images (Fig. 3C and D). In addition, they form a network structure with
Fig. 2. Fabricated gas sensing device and numerical simulation of localized heating in the device. (A) Photograph of the fabricated sensor device. (B) Top view SEM image of microheater array (lower layer) and interdigitated electrodes (upper layer). (C) Three dimensional temperature distribution of the device by microheater array operation. Two dimensional temperature profiles on the surface for the upper side of (D) microheater array and (E) interdigitated sensing electrodes.

numerous junctions between individual nanowires. Fig. 3E and F shows TEM and HRTEM images of ZnO nanowires peeled off from the substrate. The HRTEM image of single nanowire reveals a lattice spacing of 0.52 nm corresponding to the d spacing of (0 0 1) crystal plane, which indicates the preferential growth of ZnO nanowires along the [0 0 1] direction [34]. From the experimental results, it was confirmed that high-crystalline ZnO nanowires with nanojunction-network could be synthesized directly between

Fig. 3. Morphology and structural characterization of ZnO nanowires synthesized by localized hydrothermal reaction method. SEM images of (A) fully (by both heaters A and B) and (B) partially (by heater B only) grown ZnO nanowires synthesized by local thermal method on interdigitated electrodes. (C and D) High resolution SEM images of ZnO nanowires prepared on sensing electrodes by local heating of heat A. (E and F) TEM and HRTEM images of ZnO nanowires and a single nanowire measured after segregating them from substrate.
interdigitated electrodes by localized thermal energy of microheater array.

It has been studied that the temperature plays an important role for the control of ZnO solubility in ammoniacal aqueous solutions [35]. The ZnO solubility in ammoniacal solutions is much greater at lower temperature than at higher temperature. In our process, we apply localized heating to a ZnO precursor solution by using microheater embedded on the device substrate. Localize heat provides a steep temperature gradient in the precursor solution due to a very small area of heating. This induces a vigorous interaction between hot (i.e. in the vicinity of microheater) and cool (i.e. surrounding precursor) zones. As a consequence, this method creates a significantly larger convective flow than the bulk-phase heating of ZnO precursor solution that is done in the conventional hydrothermal synthesis. In other words, local heating acts as a fluidic pump to continuously supply fresh precursor during the synthesis period. Therefore, synthesis rate (0.2 µm/min) of ZnO nanowire is much higher by localized heating than by bulk phase synthesis (0.008–0.06 µm/min) [19,36,37]

3.2. Surface modification of ZnO nanowires

To improve the performance (e.g. sensitivity, transient response and power consumption) of the fabricated ZnO nanoheater sensor, the surface of ZnO nanowires was modified with metal (Pt or Pd) NPs by applying local heating in aqueous metal (Pt or Pd) precursor solution with sodium citrate. The mechanism of metal NP decoration on the surface of nanowires by local heating process is suggested as shown in the schematic illustration of Fig. 4A. Thermal energy generated by the microheater migrates from the microheater to ZnO nanowires by thermal conduction due to higher thermal conductivity of the nanowires (6.5 W/(mK) at 100 °C) [38] than that of metal precursor liquid (0.7676 W/(mK) at 90 °C) [39]. In this process, sodium citrate contained in the metal precursor solution is utilized as a reducing agent of metal salts ions as well as a stabilizer, and the reduction reaction of metal salt ions by sodium citrate can be highly activated by increasing the temperature [40,41]. Also, the convective flow of metal precursor solution can continuously provide fresh metal ions to the locally heated region. Fig. 4B shows the temperature distribution and velocity field in the metal precursor solution during the local heating process. The density and viscosity of solution are changed by the locally increased temperature, causing a substantial influence on the flow field. When the solution is heated at the center of the device, the local density degreases, thereby inducing an upward flow in the vicinity of the heated nanowires and continuous filling with new metal precursor solution from the lateral direction. This phenomenon can be clearly observed in the velocity field and streamline plot obtained by computational fluid dynamics (CFD) analysis (Fig. 4B and C). As a consequence of this convective flow field and local heating of nanowires, fresh metal ions are continuously supplied to the heated nanowires and metal NPs are deposited along the surface of nanowires. Fig. 5 shows the TEM, HRTEM images and EDS spectra of ZnO nanowires decorated with Pt NPs (Fig. 5A–C) and Pd NPs (Fig. 5D–F). From the TEM images (Fig. 5A and D), it can be observed that the Pt and Pd NPs with diameters of 2–5 nm were formed uniformly along the surface of ZnO nanowire by the reduction of metal salt ions (PtCl₄)²⁻ and (PdCl₄)²⁻ with sodium citrate [40,41]. HRTEM images (Fig. 4B and E) identified the lattice planes of metal NPs with single crystalline structures. A d-spacing of 0.230 nm and 0.224 nm between adjacent lattice planes of Pt and Pd NPs present on nanowire surface correspond to the {111} planes of face-centered cubic (fcc) phase of Pt and Pd, respectively [42,43]. In the EDS spectra (Fig. 5C and F), Pt and Pd element could be observed. These results reveal that metal (Pt and Pd) NPs could be coated selectively on the surface of ZnO nanowires in the presence of localized thermal energy. Moreover, not only single type metal NPs but also multiple heterogeneous metal NPs can be decorated on an array of nanowires in the same microelectronic device by selective and sequential heating of microheaters in different precursor environments. We have demonstrated this selective and multiplexed surface functionalization by using Pt and Pd NPs on two neighboring ZnO nanowire bundles (Detailed experimental process is explained in the

Fig. 4. (A) Schematic illustration for decoration mechanism of metal NPs on the surface of ZnO nanowires. (B) Temperature distribution and velocity arrows in a metal precursor solution and (C) velocity field visualized with streamlines during local heating process.
Supplementary Information). Fig. S4C and D shows the SEM images and EDS spectra of the identical sample based on the ZnO nanowires array coated with Pd NPs on heater B (Fig. S4C) and Pt NPs on heater A (Fig. S4D). The Pt peak can be found only on microheater A while the Pd peak can be observed only on microheater B, which verifies the selective and multiplexed surface functionalization of nanowires. This heterogeneous material array can be potentially used for enhancing the sensitivity and selectivity for multiple gas detection [44].

3.3. Hydrogen gas sensor

In order to investigate the response of pristine ZnO nanowire sensors to H2 gas, they were exposed to different concentrations of H2 and at different operating temperatures (100, 250 and 350 °C) as shown in Fig. 6. The response of the sensor to H2 was defined as response(S) = (Gt2 - Gair)/Gair × 100%, where Gair is the conductance of the sensor in the standard air environment and Gt2 is the conductance during the exposure to H2 gas. The response and recovery times were defined as the time required to reach 90% of the equilibrium value after the sensor exposure to H2 gas and fresh air, respectively. Regardless of the temperature and concentration, H2 gas supply was controlled with the same turn-on time (150 s), due to the given time constraint. Therefore it should be noted that the sensor response could not reach saturation before the turn-off cycle. As shown in Fig. 6A, ZnO nanowire sensor has high sensitivity and reproducibility to H2 gas in a wide range of concentrations (100–5000 ppm) at the temperature of 350 °C. For example, the responses to 5000, 1000 and 100 ppm were 534%, 347% and 109%, respectively (Fig. 6D). However, the sensitivity to H2 gas was drastically reduced with the decrease of operation temperature from 350 °C to 250 °C (Fig. 6B). For example, the response to 1000 ppm H2 was reduced from 347% to 57% by lowering the operation temperature from 350 °C to 250 °C (Fig. 6D). Furthermore, the response and recovery times (16 s and 69 s, respectively) at 350 °C became much longer (76 s and 257 s, respectively) at 250 °C (Fig. 6E). When the temperature was decreased further down to 100 °C, the sensor exhibited very small sensitivity, slow response speed, and poor recovery performance (Fig. 6C). As shown in this figure, no recovery and severe drifting of the sensor response can be observed at 100 °C. This temperature dependence of H2 sensing by ZnO nanowires is similar to the result observed in the previous study [45].

The sensing mechanism of H2 gas by ZnO nanowires can be explained by the coaxial cable model [46]. The nanowire-networks consist of myriads of interconnection of individual nanowires. The electrical current passes through the connecting nodes between interconnected nanowires which are surrounded by an electron depletion layer. The adsorption of gas molecules and their reaction with the nanowire surface alters the surface potential and affects the electron depletion layer. In air, it is well known that oxygen is adsorbed on the surface of ZnO nanowires to form oxygen ions such as O2−, O−, and O−2 by extracting electrons from the conduction band of ZnO [47]. When ZnO nanowire sensor is exposed to H2 gas, negatively charged oxygen ions on the surface react with hydrogen atom and produce H2O molecules. This reaction consumes chemisorbed oxygen ions from the surface and releases free electrons back to the ZnO nanowires. Thus, the potential barrier at the nodes becomes lower, which then leads to the reduction in the electrical resistance of ZnO nanowire networks between the sensing electrodes. To explain more about the parameters for sensor response, Srivastava et al. [48] reported the change in the electrical conductance affected by the concentration of reducing gas and the operating temperature of the sensor, which relate to the barrier height at the interface between adjacent grains, degree of surface coverage and Freundlich adsorption isotherm. 

\[ G = \frac{(ATq)}{K} \cdot \exp \left[ \frac{\epsilon^2 N_d^2 (KC)^2}{2 \varepsilon \varepsilon_0 k T N_D} \right] \]

Above Equation provides the relationship between the conductance (G) of a gas sensor, and concentration (C) of gas and temperature (T). Here, A is the Richardson constant, Ni is the number of surface charge per unit area, \( K = \alpha R T n a^\prime \), \( a^\prime = \exp (-\Delta E/kT) \), \( \varepsilon/\varepsilon_0 \) is the permittivity of the semiconductor, Nd is the number of ionized donor states, \( R \) is gas constant and \( \alpha \) is a constant. When the concentration of reducing gas is increased, the degree of surface coverage is increased and the barrier height is decreased by the supplied electrons from the gas molecules. Therefore the conductance of ZnO nanowire is increased by increasing the concentration of H2 gas. The surface potential barrier height is decreased at high temperature due to the increase of charge.
density. It increase the conductance of ZnO nanowire and decrease response time. The response—concentration and response time—concentration curves at different temperatures shown in Fig. 6D and E, correspond well with the abovementioned theory.

The H$_2$ gas sensing performance of ZnO nanowire sensors can be dramatically improved by their surface functionalization with noble metal (Pt, Pd) NPs via local heating process. Fig. 7A–D shows the sensing response of the Pt NP and Pd NP-coated ZnO nanowire sensor to H$_2$ gas with concentrations of 100–5000 ppm at 250 and 100 °C. The sensor based on Pt NP-coated ZnO nanowires shows much higher sensitivity to H$_2$ gas than Pd NP-coated ZnO nanowire sensor. For example, the responses of ZnO nanowire sensors decorated with Pt NP and Pd NPs to 5000 ppm H$_2$ gas are 18170% and 2377% at 250 °C, and 1517% and 248% at 100 °C, respectively. However, the sensitivities of Pt NP and Pd NP-coated ZnO nanowire sensors are both higher than that of the pristine ZnO nanowire sensor in the entire range of H$_2$ gas concentrations as shown in Fig. 7E and F. Pt NP-coated ZnO nanowire sensor exhibits 160 times higher sensitivity (response = 18170%) than the pristine ZnO nanowire sensor (response = 113%) to 5000 ppm H$_2$ gas at 250 °C. Furthermore, the sensors based on Pt NP and Pd NP-coated ZnO nanowires could detect H$_2$ gas in various concentrations at 100 °C with high responses, fast response and complete recovery as shown in Fig. 7B and D, while the pristine ZnO nanowire sensor did not show strong response and complete recovery to H$_2$ gas at 100 °C. The results prove that the surface functionalization of ZnO nanowires with metal NPs such as Pt and Pd is very effective not only to enhance the sensitivity and transient response, but also to decrease the sensor operation temperature. The sensing performances (sensitivity and response time) are comparable not only to state-of-the-art nanomaterial-based sensors in the literature [22,49–53] but also to widely used commercial sensors [54,55] (see Table S1). The dramatic performance enhancement can be attributed to the improved chemical reaction by the reduction of activation energy between the surface of ZnO nanowires and H$_2$ gas by metal (Pt and Pd) NPs. In general, the sensitivity of gas sensors based on 1D metal oxide nanomaterials are strongly influenced by the activation energy for the chemical reaction with target gas analytes on their surface. The metal NPs act as catalysts for the dissociation of H$_2$ and O$_2$ by spill-over effect. They provide lower energy path for the adsorption of gas analytes and diffusion onto the surface of supporting metal oxides, thereby enhancing the reaction between gas analytes and metal oxides [57]. In addition, the work function of Pt and Pd are higher than that of ZnO, attracting some free electrons. Therefore the width of depletion layer is increased at the junction of metal NPs and metal oxides. These wide depletion layer enhances the sensitivities to the reducing gases by increasing the margin of resistance decrease [58,59].

The long-term reliability of the Pd NP-coated ZnO nanowire sensor was investigated by comparing its sensing performance before
and after storage for 90 days in a regular deposit-box without any protection from the environment. As shown in Fig. S5, the sensor maintained almost identical performance (sensitivity, response time and recovery time) after 90 days. This verifies that functionalized noble metal NPs do not affect the long-term stability of semiconductor gas sensor [60].

4. Conclusions

In summary, a novel method for the localized synthesis and direct integration of metal oxide nanowires and their selective and in-situ surface functionalization was developed for the facile fabrication of high performance gas sensors with ultra-high sensitivity, fast response and high selectivity. This method based on localized hydrothermal synthesis in low temperature, liquid environment enabled controlled fabrication of ZnO nanowires and their surface functionalization with Pt and Pd NPs also in low-temperature, liquid environment. These catalytic NPs realized a substantial enhancement of the sensitivity and response speed to H2 gas. Although we have demonstrated the applicability of this method to a particular combination of sensing material (i.e. ZnO nanowire), catalytic materials (i.e. Pt and Pd) and target gas (i.e. H2), this can be a generic approach to different combinations. Other metal oxide nanomaterials (e.g. TiO2, CuO, SnO2, etc.) can be synthesized and surface-modified by this method for sensing other toxic gases (e.g. CO, NO2, H2S, etc.), which will be reported in our upcoming research articles. We expect that the advances made in this study shall pave the way for the eco-friendly, economical and facile manufacturing of high performance, ultra-low power, ultra-compact and multiplexed chemical sensor array that can enable ubiquitous sensor network and personalized, ultra-compact environmental sensing platform.

Acknowledgements

This work was supported by (1) Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning, (2013006809), (2) Global Frontier Project through the Center for Integrated Smart Sensors funded by the Ministry of Science, ICT & Future Planning (CISS-2012M3A6A6054201), and (3) National Research Foundation of Korea (NRF) Grant funded by the Korean Government (MSIP) (No. 2015R1A5A1037668).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2015.11.095.
References

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