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# Enhancement Sensitivity and Selectivity of Ammonium Hydroxide Using Nitrogen-Doped Double-Walled Carbon Nanotubes

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## Abstract

Nitrogen-doped double-walled carbon nanotubes (N-DWCNTs) were synthesized by floating catalytic chemical vapor deposition (FCCVD) at 1300 °C using ethanol and urea as carbon and nitrogen sources. For comparison, the undoped double-walled carbon nanotubes (DWCNTs) were synthesized by FCCVD using ethanol as carbon source. Synthesized DWCNTs and N-DWCNTs were separately dispersed in ethanol and separately dropped onto printed circuit board substrate. The fabricated sensors were detected to ammonium hydroxide ($NH_4OH$), acetone and ethanol vapors at part per million level. The sensor response results show that N-DWCNTs are highly sensitive to $NH_4OH$. In the case of volatile organic compounds detection, DWCNTs and N-DWCNTs exhibit similar response to acetone and ethanol. The fabricated sensor from N-DWCNTs to $NH_4OH$ vapor was 4-fold higher than that of fabricated sensor from undoped DWCNTs. The sensing mechanism of N-DWCNTs can be attributed to the charge transfer between N-DWCNTs and $NH_4OH$ molecule. Nitrogen site has a higher response, resulting in an enhancement the selectivity and sensitivity to $NH_4OH$. The total atomic percentage of N-DWCNTs is approximately 0.90 at%. The results suggest that the heteroatom-doping of nitrogen is a promising approach for improving the sensitivity and selectivity for $NH_4OH$ detection.

**Keywords:** Nitrogen-doped double-walled carbon nanotubes, Chemical vapor deposition, Ammonium hydroxide, Urea

## Introduction

Carbon nanotubes (CNTs) [1-3] have attracted intensive interest due to their distinctive characteristics in structural, optical, thermal, electronic and mechanical properties [3-7]. CNTs have been extensively applied in many fields of nanotechnology. For instance, CNTs have been shown outstanding sensing materials for gas sensor application due to their large specific area [8] and high electrical conductivity [9,10]. Recently, substitution nitrogen atom into CNT structure can improve the electronic properties and enhance the sensitivity of advanced gas sensors devices. To synthesized nitrogen-doped CNTs (N-CNTs), the chemical vapor deposition (CVD) is a simple technique for mass production with controlled diameter, purity and crystallinity. For instance, nitrogen-doped multi-walled carbon nanotubes (N-MWCNTs) were produced using aerosol CVD using benzylamine as carbon and nitrogen sources [11]. The content of nitrogen introduced into the MWCNT structure was approximately 2.2 at%. N-MWCNTs were detected to parts per million (ppm)-level nitrogen dioxide ($NO_2$), carbon monoxide (CO) and ethylene gases at room temperature to 150 °C. N-MWCNTs show the best sensitivity to $NO_2$ and CO gases but insensitive to ethylene gas. Battie *et al.* [12] synthesized the nitrogen-doped single-walled CNTs (N-SWCNTs) by floating catalyst CVD (FCCVD) using CO and ammonia ($NH_3$) as the carbon and nitrogen sources, respectively. The nitrogen concentration in N-SWCNTs is estimated 1.2 at%. Synthesized N-SWCNTs were detected to ppm-level $NO_2$ and $NH_3$ gases. The sensing performance of N-SWCNTs is compared to pristine SWCNTs. The results show that the response of N-SWCNTs to $NH_3$ gas was enhanced 2.3 times than that of pristine SWCNTs. The interaction between $NH_3$ and N-pyridinic defects leads to an important charge transfer from gas molecules to N-SWCNTs. The sensitivity of N-SWCNTs and pristine DWCNTs to $NO_2$ gas is similar, with no obvious difference. Recently, nitrogen-doped double-walled CNTs (N-DWCNTs) were successfully synthesized by high-vacuum CVD (HVCVD) using benzylamine as carbon and nitrogen sources [13]. The nitrogen content of N-DWCNTs was 1.6 at%. The results show that the N-DWCNTs exhibited a 2.7-fold improvement in the response to $NO_2$ gas compared to undoped DWCNTs. The sensing mechanism is attributed to the charge transfer from sensing materials to the adsorbed $NO_2$ molecule. Importantly, the pyridinic nitrogen was proved that it plays greater role than the other types of nitrogen of N-DWCNTs in improving the sensor performance. Although the HVCVD has been considered as a promising method for the synthesis of high nitrogen doping of DWCNTs, this technique requires expensive vacuum apparatuses that high cost.

In this work, we report the facile synthesis of N-DWCNTs by FCCVD method at atmospheric pressure using ethanol and urea as carbon and nitrogen sources. Synthesized DWCNTs and N-DWCNTs were used as gas sensor for ammonium hydroxide ($NH_4OH$) and volatile organic compounds (VOCs) detection at ppm level to investigate the sensitivity and selectivity. The fabricated sensor from N-DWCNTs enabled an approximately 4-fold improvement in $NH_4OH$ detection compared to undoped DWCNTs. Moreover, N-DWCNTs were highly selective to $NH_4OH$ vapor.

## Materials and methods

### Synthesis and characterization of DWCNTs and N-DWCNTs

DWCNTs were synthesized by FCCVD using mixed homogenous ethanol-ferrocene-thiophene solution. The CVD system was raised up to 1300 °C under Ar gas with a flow rate of 500 sccm. The mixed solution was injected into reaction zone by micropumping at a pumping speed of 0.04 $\mathrm{mLmin^{-1}}$, which was introduced by $H_2$ gas at a flowrate of 1000 sccm as carrier gas. The synthesis time was carried out for 20 min. Synthesized CNTs were cooled down under Ar gas. As-synthesized CNTs was further purified by acid and air-annealing treatments repeatedly for 2 times as described elsewhere [13]. For comparison, the N-DWCNTs was synthesized at the same condition by using ethanol-urea (95:5) mixture solution as carbon source and nitrogen sources. The nanostructure was characterized by transmission electron microscopy (TEM, JEOL JE-2010) operated at 200 kV. Raman spectroscopy (Horiba Jobin Yvon) was employed to characterized the crystallinity using a wavelength of 532 nm (2.33 eV). The X-ray photoelectron spectroscopy (XPS, PHI Quantera II, Ulvac-phi inc.) was used to analyze the chemical composition and state.

### Fabrication of sensor devices and gas sensor measurement

DWCNTs and N-DWCNTs were separately sonicated with ethanol solution at the concentration of 0.01 mg/mL for 120 min. A 1000 µL of DWCNTs and N-DWCNTs in ethanol were separately dropped on to the printed circuit board consisting of an interdigitated Cu/Au electrode with a gap of 250 µm. During drop casting the substrate was heated at 90 °C to remove the solvent in the sample material. All sensors were placed into the stainless steel chamber and then $N_2$ gas was introduced into the chamber at a flow rate of 500 sccm for 10 min as a baseline. Acetone, ethanol and $NH_4OH$ vapors were separately injected into the detection chamber by control the volume of solution and monitoring its electrical resistance for 10 min. The concentration of all vapors was 500 ppm. To recover, the fabricated sensors were recovered by $N_2$ gas at a flow rate of 500 sccm for 10 min. The sensor response (*SR*) was defined by the equation;

$$SR = \frac{R_{Vapor}-R_{N_2}}{R_{N_2}} \times 100 \tag{1}$$

where $R_{Vapor}$ and $R_{N2}$ are the electrical resistance of sensor after and before vapor exposure, respectively.

## Results and discussion

**Figures 1(a)** and **1(b)** shows TEM images of DWCNT and N-DWCNT bundles. TEM images reveal the DWCNTs in a bundle structure. The well-aligned DWCNTs and N-DWCNTs stick together due to Van der Waals interaction. TEM image of the individual DWCNTs and N-DWCNTs with 2 graphene layers stacked in parallel on each side. The average diameter of DWCNTs and N-DWCNTs were 1.78±0.31 and 1.68±0.27 nm, respectively. The results show that average diameter of N-DWCNTs is narrower than that of DWCNTs, which implies that the nitrogen doping plays role in decrease of diameter of N-DWCNTs. In addition, the interlayer spacing of isolated DWCNTs and N-DWCNTs is approximately 0.34-0.41 nm, which is consistent with interlayer distance in graphite [14-16]. Raman spectroscopy was employed to characterize the structure and crystallinity of DWCNTs and N-DWCNTs.

**Figure 2(a)** shows the 4 significant Raman peaks: Radial breathing mode (RBM) at ~150-270 cm$^{-1}$, disordered carbon-derived at ~1340 cm$^{-1}$, graphitic structure-derived G-band at ~1590 cm$^{-1}$ and second-order of D-band-derived at ~2670 cm$^{-1}$. The intensity ratio between the *D*- and *G*-bands ($I_D/I_G$) ratio of DWCNTs and N-DWCNTs were 0.021 and 0.030, respectively. The $I_D/I_G$ value of N-DWCNTs were higher than that of DWCNTs, indicating the lower crystallinity of N-DWCNTs due to nitrogen doping induced structural damage. The *2D*-band of the N-DWCNTs shift to lower frequency because of success of nitrogen doping in DWCNT structure [13], corresponding to the $I_D/I_G$ intensity of N-DWCNTs as shown in **Figure 2(b)**. The diameter of DWCNTs and N-DWCNTs can be determined by the equation;

$$\omega_{RBM} = \frac{234}{d_t} + 10 \tag{2}$$

where $\omega_{RBM}$ and $d_t$ are RBM frequency (cm$^{-1}$) and tube diameter (nm), respectively [17,18].

The calculated diameters of DWCNTs and N-DWCNTs from RBM spectra at 153, 184 and 265 cm$^{-1}$ were 1.64, 1.35 and 0.91 nm. The calculated interlayer spacing of DWCNTs and N-DWCNTs from RBM spectra ranges from 0.36-0.43 nm, which is in the same range as that observed the TEM results.

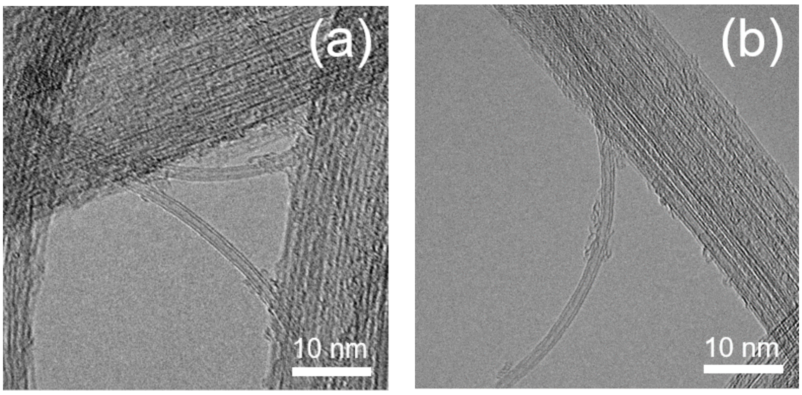

**Figure 1** TEM images of (a) DWCNTs and (b) N-DWCNTs.

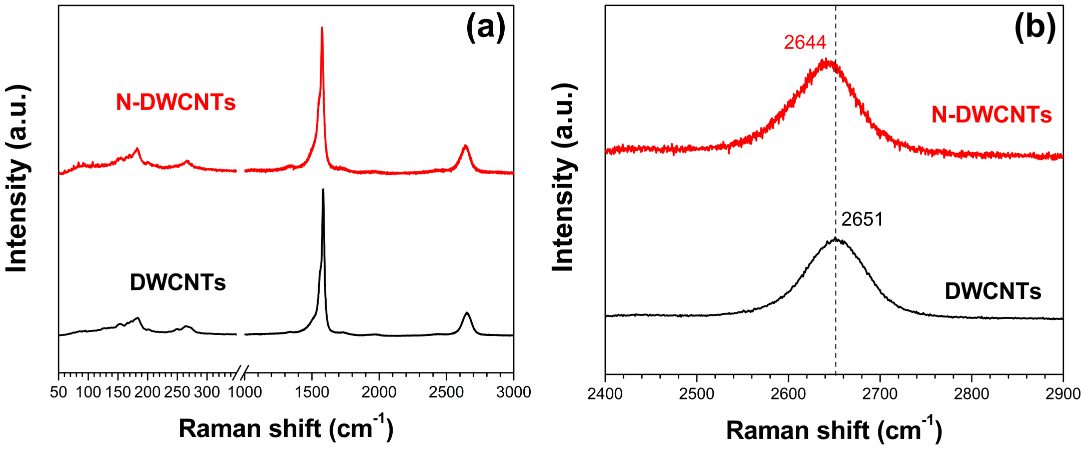

**Figure 2** (a) Raman spectra and (b) *2D*-band of DWCNTs and N-DWCNTs.

XPS was used to analyze the chemical composition and chemical state of DWCNTs and N-DWCNTs. The XPS survey spectra of DWCNTs and N-DWCNTs consist of strong C1s and O1s peaks at ~284 and ~532 eV, respectively, as shown in **Figure 3(a)**. For the C 1s peak, there are 3 different carbon group in the XPS spectrum: sp$^2$ C=C at 284.8 eV, C-O bands at 286.2 eV and shake-up satellite line at 290.5 eV [19-20]. **Figure 3(b)** shows the C1s spectrum of N-DWCNTs. For the O 1s peak, there are 2 different oxygen groups in the XPS spectrum: C=O at 532.6 eV and C-O at 533.9 eV [21] (data not shown). In the case of N-DWCNTs, there are 2 types of nitrogen; pyridinic at 399.7 eV and graphitic at 401.4 eV [22] as shown in **Figure 3(c)**. The total atomic percentage of N-DWCNTs is approximately 0.90 at%. The XPS results show the success of nitrogen doping in DWCNTs, which correspond to the Raman spectra, resulting a decrease the degree of crystallinity the CNT structure that in an increase of $I_D/I_G$ intensity. The C1s, O1s and N1s composition of DWCNTs and N-DWCNTs is shown in **Table 1**.

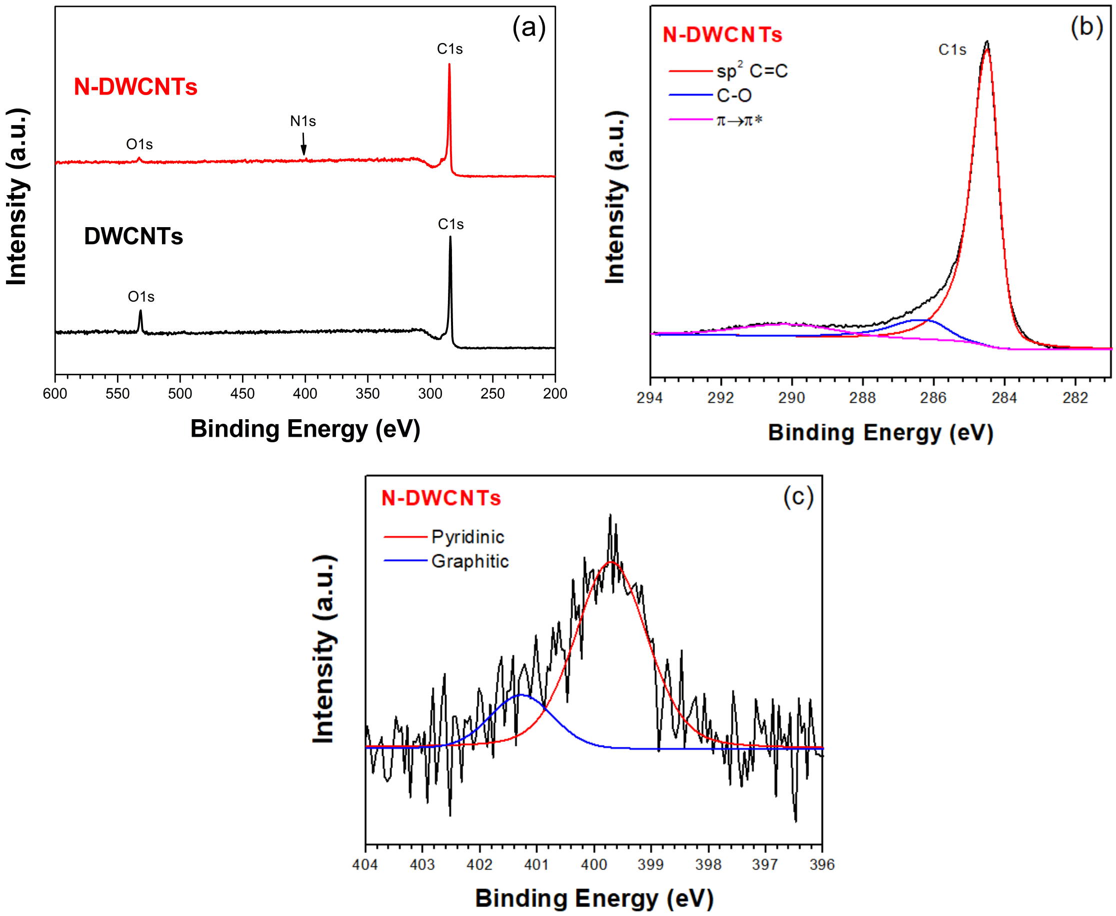

**Figure 3** (a) XPS survey spectra of DWCNTs and N-DWCNTs. (b) C1s and (c) N1s spectra of N-DWCNTs.

**Table 1** The C1s, O1s and N1s composition of DWCNTs and N-DWCNTs.

| Sample | Content (at%) | | | N/C ratio (at%) |
|---|---|---|---|---|
| | C | O | N | |
| DWCNTs | 91.69 | 8.31 | - | - |
| N-DWCNTs | 97.12 | 2.00 | 0.88 | 0.90 |

Next, fabricated sensors based on DWCNTs and N-DWCNTs for ethanol, acetone and $NH_4OH$ vapors detection were investigated at room temperature. The initial resistance of DWCNTs and N-DWCNTs are 6.02 and 3.59 kΩ, respectively. The initial resistance of N-DWCNTs slightly decrease from that of DWCNTs due to the incorporation of nitrogen in the structure of DWCNTs, which corresponds to the $I_D/I_G$ intensity and XPS results. **Figures 4(a)-(c)** show sensor responses as a function of time of DWCNTs and N-DWCNTs exposure to ethanol, acetone and $NH_4OH$ vapors at 500 ppm. The electrical resistance of DWCNTs increased upon ethanol, acetone and $NH_4OH$ exposure and decreased after replacing vapor with $N_2$ gas. In the case of VOC detection, the sensing mechanism can be explained by the dielectric constant that involves the solvent polarity of VOCs. The solvent polarity of ethanol is higher than that of acetone [23]. The molecule with higher polarity can hold moving holes and interrupt the movement of holes along CNTs, resulting in a large increase in resistance [24-26]. For $NH_4OH$ detection, sensing mechanism is attribute to the charge transfer between $NH_4OH$ molecule and N-DWCNTs. The electron transfers from $NH_4OH$ molecules to N-DWCNTs. The hole density of N-DWCNTs decrease, resulting in an increase of the electrical resistance [12, 27,28]. The sensor response of fabricated sensor from N-DWCNTs to $NH_4OH$ vapor greatly improved by 4.1-fold compare to that of undoped DWCNTs, whereas the fabricated sensor from N-DWCNTs is sensitive to acetone and ethanol vapors similar with undoped DWCNTs. These results imply that the improvement of sensitivity and selectivity of N-DWCNTs to $NH_4OH$ could be attributed by nitrogen-doping in N-DWCNTs [12,13,29]. The acetone, ethanol and $NH_4OH$ are physically adsorb onto the undoped DWCNTs via van der Waals forces, which is a weak interaction. The molecules were easily removed by using $N_2$ gas purging. In the case of N-DWCNTs, $NH_4OH$ molecule strongly interact with the nitrogen-site N-DWCNTs through chemisorption, which is stronger interaction than that of physisorption, resulting in difficulty in removing $NH_4OH$ molecule from N-DWCNTs. However, the reversibility of the sensor can be improved by applying heat or UV exposure [30,31].

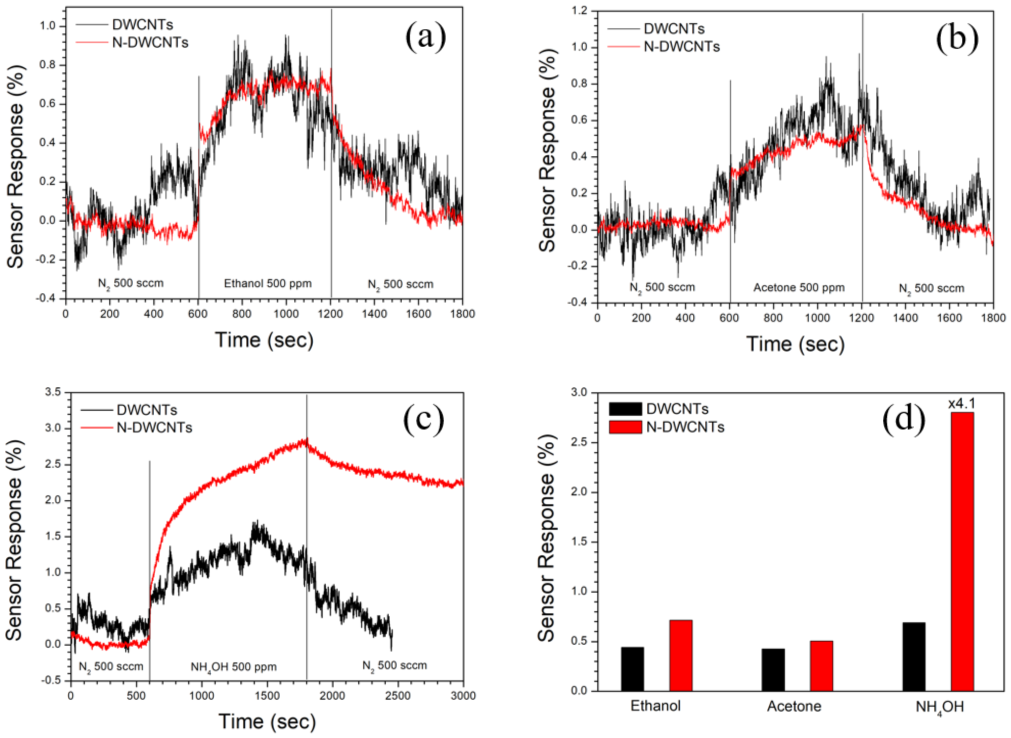

**Figure 4** Sensor response as a function of time of DWCNTs and N-DWCNTs (a) ethanol (b) acetone and (c) ammonium hydroxide. (d) Sensor response of DWCNTs and N-DWCNTs exposed to all vapors.

## Conclusions

We successfully fabricated the high sensitivity and selectivity of $NH_4OH$ sensor using N-DWCNTs as sensing material. The fabricated sensor from N-DWCNTs exhibited a 4.1-fold improvement in the sensor response to $NH_4OH$. The improvement of sensitivity and selectivity can be explained by nitrogen site in N-DWCNTs. These results suggest that nitrogen doping in DWCNTs is a promising approach for the improvement of the sensitivity and selectivity for $NH_4OH$ detection.

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