Supplementary Material (ESI) for Chemical Communications

Supporting Information

Formaldehyde Gas Sensing Chip based on Single-Walled Carbon Nanotubes and Thin Water Layer

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EXPERIMENTAL SECTION

Reagents. All the solutions were prepared using DI water that was purified with NANOpure (Barnstead, USA), and all the chemicals were used as received without further purification. Diallydimethylammonium chloride (DADMAC), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (photoinitiator), N,N'-methylenebisacrylamide (cross-linker), 3-(trimethoxysilyl)propylmethacrylate (TMSMA), glacial acetic acid, magnesium chloride, octadecyltrichlorosilane (OTS), anhydrous hexane and o-dichlorobenzene (ODCB) were purchased from Sigma. The negative

photoresist (PR) SU-8 2150 and its developer were supplied from Microchem. Co. USA. The positive PR AZ5214 was purchased from AZ Electronic Materials. Co. USA.

Preparation of gas sensors. The SWCNT-based field effect transistors (FETs) were prepared by following the method reported previously.[1] First, the align key was patterned on the Si/SiO_2 substrate via conventional photography and lift-off process. Then the region of junction was windowed by photolithography followed by the dipping the junction pattern into OTS solutions (OTS : anhydrous hexane = 1:500) for 10 min at room temperature and the humidity of 80%. And then the substrate was rinsed with clean anhydrous hexane, acetone and ethanol followed by heating in a convection oven at the temperature of 60 °C for 10 min to enhance the polymerization of OTS's on SiO_2 layer. SWCNT was assembled by dipping the substrate into 0.05 mg mL^{-1} CNT suspension in ODCB for ~10 s and then rinsing thoroughly with clean ODCB. Source and drain electrodes were patterned by photolithography and thermally deposited Au/Pd (20 nm/10 nm) followed by lift-off process. Then, the electrodes were passivated with PR (AZ5214) to impede any electrochemical reaction with DI water at the surface of the electrodes.

A PR (SU-8 2150) mold as a template for PDMS channels was fabricated by conventional photholithography on a silicon substrate. A silicon wafer was cleaned by submerging it in a piranha solution (H_2SO_4 : H_2O_2 = 3:1, J.T Baker, US) for 40 min and rinsed it with DI water. The wafer surface as cleansed was then blown with air and dried at 150 °C for 10 min on a hot plate. Then, the wafer was cooled down to room temperature, and SU-8 2150 was spin-coated (YS-100MD, Won Corp., Korea) onto the wafer at 2000 rpm for 30 s. Soft baking was performed at 65 °C for 8 min and then at 95 °C for 70 min. The coated wafer was cooled down to room temperature before the patterned mask was neatly placed on the SU-8, over which 365 nm UV light of 21 mW cm^{-2} was illuminated for 20 s. (MDE-4000, Midas,

Korea). After soft baking at 65 °C for 5 min and again at 95 °C for 25 min, the wafer was immersed in SU-8 developer for 5 min and hard-baked at 150 °C for 30 min.

PDMS which was 300 μm thick and 1.5 mm wide casted from the SU-8/Si master and its surface was treated with oxygen plasma (PDC 32G, Harrick Scientific Corp., USA) for 10 min and with piranha solution for 5 min to introduce hydrophilicity. After washing with DI water and drying with air, the hydrophilic PDMS was coated with 0.5% TMSMA in DI water containing 0.5% acetic acid for 30 min. TMSMA acted as a linker between polyelectrolytic gels and the PDMS surface. The PDMS channels were cleaned with methanol and dried with air. 5 M AMPSA solution containing a photoinitiator (2%) and cross-linker (2%) was dropped into the indented PDMS channel, in which the depth was 300 μm and 3 mm in diameter. UV light (365 nm) with an intensity of 21 mW cm^{-2} was shined to photopolymerize the pAMPSA plug for 12 s. Washing out the residual monomers, 4.2 M DADMAC solution containing a photoinitiator (2%) and cross-linker (2%) was delivered to fill out the channel and pDADMAC plug was created next to the previously formed pAMPSA by UV light in the same manner.

To expose SWCNTs to the air, an adhesive layer was perforated to make a hole with several hundreds μm in diameter and carefully attached to the CNT array substrate. Then the PDMS layer with a pattern and polyelectrolyte plugs was put on the top. It follows that 10 mM magnesium chloride aqueous solution was injected into the sample chamber over the SWCNTs and dried it in the air. Finally, the reservoirs, which had 5 mm in diameter, outside the polyelectrolyte plugs were filled with DI water, which started to infiltrate the sample chamber by osmotic pressure and make SWCNTs wet slowly. At equilibrium between evaporation and inward osmotic flux, a thin aqueous layer was formed over the SWCNT array, which was separated from the air. During the experiments, reservoir was sealed to slow

down evaporation of the water and to prevent from exposure of the water in the reservoir to the gaseous formaldehyde.

Measurement. The experiment was conducted in a sealed chamber with an automatic gas control system. Fig. S1 illustrates the gas detection system (GMC1200, Green Advanced Technology Inc., Korea). Formaldehyde vapor of a certain concentration was sent to a sensing chamber by controlling flow rate of formaldehyde gas and N_2 carrier gas. The tests were performed at room temperature. Some experiments were performed under different humidity conditions to observe the humidity effect on our sensor. The change of resistance on the sensor was measured using an electrochemical analyzer (CH750, CH Instruments Inc., USA).

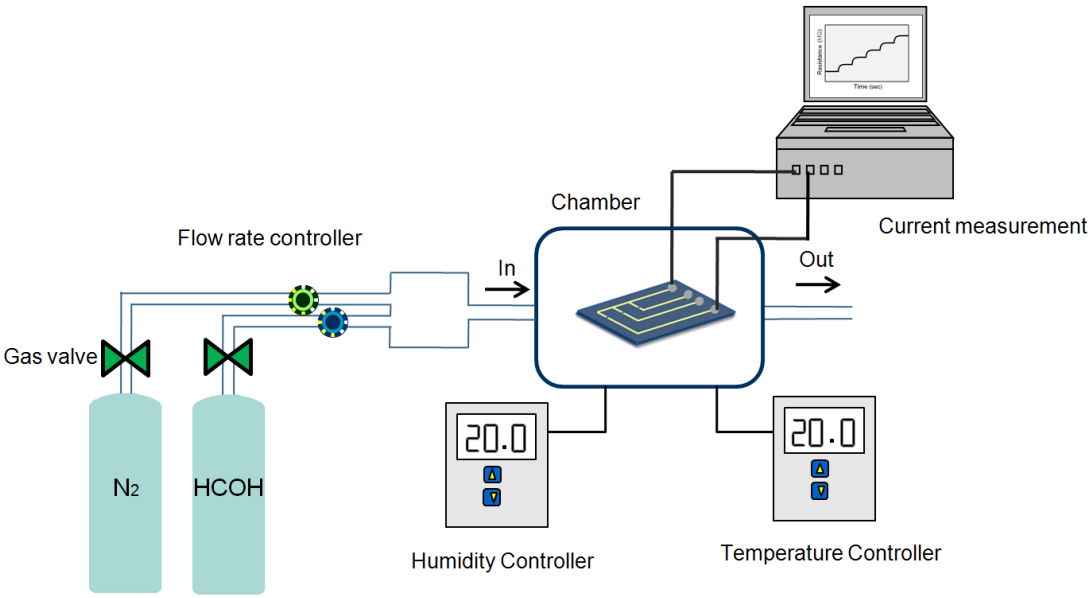

Fig. S1 Schematic diagram depicting the instrument to measure the response of our gas sensor systems upon exposure to formaldehyde.

RESULTS AND DISCUSSION

Properties of SWCNT-FETs. Fig. S2(a) shows a liquid gating effect of SWCNT junctions using a Pt reference electrode in DI water. A gate sweeping between -0.5 V to 0.5 V was applied with V_{ds} = 0.1 V, resulting in typical p-type FET behavior. The transconductance of this device at V_g = 0 V was ~ -0.59 μA V^{-1}.

Fig. S2(b) shows the noise characteristics of the device. The Hooge's model is used for the empirical description of noise phenomena by the following formula.

$$S_I = A\frac{I^2}{f^\alpha} \tag{1}$$

A and α were determined by fitting the noise power spectrum in a log-log scale using equation (1). α was estimated to be 1.079, which indicates a typical 1/*f* noise behavior as previous works.[2-5] A was estimated to be about 7.30 x 10^{-7} and A/R is 6.18 x 10^{-12} which is consistent with previous results ($A/R \sim 10^{-11}$).[6]

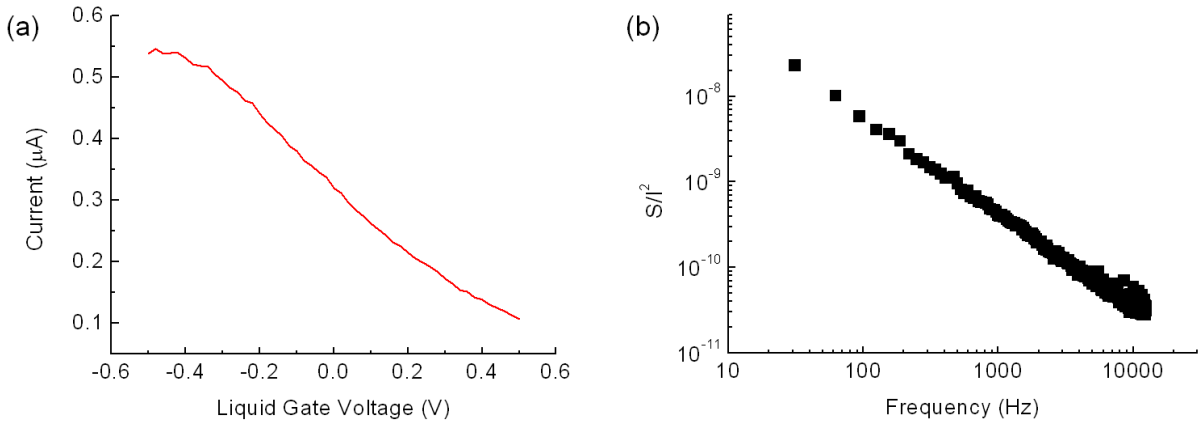

Fig. S2 Liquid gate property and noise property for SWCNT device (a) Liquid gate property of a junction immersed in DI water with Pt liquid gate swept from -0.5 V to 0.5 V, and source-drain bias of 0.1 V. (b) Spectrum density of SWCNT based sensor with source-drain bias of 1 V.

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