Supporting Information for:

Highly sensitive and selective chemiresistive sensor based on multidimensional polypyrrole nanotubes

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Methods

Materials. Pyrrole (98%), FeCl₃, and poly(vinyl alcohol) (PVA; Mw 9000~10,000) were purchased from Aldrich. Poly(dimethylsiloxane) (PDMS) substrate was provided from DOW CORNING Co. (product: SYLGARD 184 SILICONE ELASTOMER KIT).

Fabrication of multidimensional polypyrrole nanotubes (MPPy NTs). 6 wt% PVA solution was prepared at 80 °C and PVA nanofibers with an average diameter of 70 nm were electrospun from the PVA solution (Nano NC 120 kV / 1.5 mA). The distance between syringe needle to a cellulose substrate (collector) was *ca.* 10 cm. The resulting PVA nanofibers were immersed into 5 wt% ferric chloride / ethanol solution, as an initiator (40 mL). After drying under vacuum for 5 h, the nanofiber were placed in the pressure-controllable reactor. Subsquently, the liquid monomer (pyrrole) was injected at a controlled temperature and pressure, which reulted in the multidimensional formation of polypyrrole-coated PVA nanofibers with nanonodules (NDs, 60 °C and 760 torr for 10 min) and nanowires (NWs, 40 °C and 760 torr for 10 min) surfaces. The nanofiber with smooth layer (SM, 60 °C and 1 torr for 10 min) surface was also prepared as control experimental data. Finally, the MPPy NT structures with NDs and NWs surfaces were obtained by dissolving the PVA core with distilled water (the diameter was *ca.* 100 nm).

Fabrication of the chemiresistive sensor based on MPPy NTs. First, to construct the platform for the chemiresistive sensor, the patterned PDMS substrate was fabricated by photolithography process. The MPPy NTs was transfer into the surface of the patterned PDMS substrate by dry-transfer method and the microelectrodes was deposited on the MPPy NTs/PDMS substrate by thermal evaportation.

Instrumentation. All electrical measurements were conducted with a Keithley 2612A sourcemeter and probe-station (MS TECH, MODEL 4000). The MPNS device was mounted in a test chamber on the probe-station and the probes were contacted on the microelectrodes. The test chamber were connected with gas inlet/oulet lines connected with MFC and an electrical feed-through. The resistance change

was monitored in real-time at an applied current of 10^{-6} A. The instruments were connected *via* a GPIB interface to a computer and controlled through Labview software. The sensitivity was calculated by measuring the normalized electrical resistance change $\Delta R/R_0 = (R - R_0)/R_0$, where R_0 and R are the measured real-time resistance and initial resistive value, respectively. In addition, the response time was defined as the time required for the conductance to reach 90% of the equilibrium value after a test gas was injected, and recovery time was the time necessary for a sensor to attain a conductance 10% above its original value in air.

SEM image of SM-PPy NT



Figure S1. SEM image of SM-PPy NT. The inset indicate HR-TEM image.



Schematic diagram of the fabrication of PDMS substrate



The designed poly(dimethylsiloxane) (PDMS) substrate of the device was patterned using typical photolithography processes, where its bottom was punched with holes to effectively retain the flow of the analytes (Figure S2).

Schematic diagram of the fabrication of home-made circuit device



Figure S3. Fabrication process of the MPNS by dry-transfer.

Real-time responses of MPNSs exposure to relative humidity (RH)



Figure S4. Real-time responses of MPNSs exposure to RH. The significant resistance chances from MPNSs were recorded over 35 % RH.

The base line in resistance value was RH dependent at room temperature (RT), as shown in Figure S4. The responses to RH increased with the order (NW-MPNS > ND-MPNS > SM-PNS) over ~ 35 % RH (the red area in Figure S4) and the significant response (signal-to-noise: 3.0) was observed from NW-MPNS. These results indicate that the precise measurements of the MPNSs can be produced by controlling the RH (under 35 % RH; the plum area in Figure S4) at RT.



Expanded real-time responses of MPNSs exposure to ammonia gas

Figure S5. Real-time response profiles of MPNSs expanded between 590 s and 630 s. The highlighted area in yellow indicates the saturated portion.