Forced Assembly of Water-Dispersible Carbon Nanotubes Trapped in Paper for Cheap Gas Sensors

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Because of the increasing number of cars and power plants, air pollution is becoming worse and is taking a major toll on global health. Detection and elimination of harmful gases, including amide, nitride, and some other volatile organic compounds, are of particular interest and importance.[1,2] Gas chromatography mass spectrometry has been a reliable tool for precisely analyzing harmful gases. However, this instrument, in addition to being expensive, is huge and hard to carry, which limits its monitoring use to the laboratory rather than factories or the open air.[3] The demand for low cost, low power-consuming, portable, reproducible, and at the same time highly sensitive and selective detection of the harmful gases is thus increasing. Emerging nanomaterials with one-dimensional structures, e.g., nanowires, nanotubes, and nanoribbons, are routinely evaluated as promising building units for detection nanotechnology.[4] Among them, carbon nanotubes are one of the most exciting discoveries because of their unique electrical, mechanical, and chemical properties.[5] An essential feature of carbon nanotubes is their electrical conductance, which is extremely sensitive to the local environment. Notably, single-walled carbon nanotubes (SWCNTs) are broadly used to detect electron-donating (e.g., ammonia) and -withdrawing gas molecules (e.g., nitrogen dioxide).[6] Physical adsorption of these molecules is considered able to transfer or withdraw electrons from SWCNTs, which thereby dopes free electrons or holes into the SWCNTs. Theoretical simulations have also validated that a weak charge transfer occurs between adsorbed molecules and SWCNTs.[7,8] As a result, such an electrochemical activation induced by gas molecules dramatically changes the conductivity of SWCNTs.[9,10]

After the early inspiration by Dai and co-workers,[11] many efforts have been devoted to integrating carbon nanotubes into electrical devices to test gas species based on their conductance change.[12] Recent research involves two major strategies to decorate carbon nanotubes on the surface of various matrices, including in situ growth and solution-based deposition. The former improves control over density and orientation of SWCNTs, while the fabrication is equipment-dependent and time-consuming. The latter is growing in popularity because of its ease of use, cost, and operation in most ambient conditions. Because it is low-cost, insulating, flexible, and portable, paper has been recognized as a particular class of supporting matrix for accommodating sensing materials.[13] There are examples of SWCNT decoration on paper surfaces using solution-based deposition.[14] Also, a powerful method by Swager and co-workers mechanically wrote SWCNTs on paper using a compressed SWCNT pellet.[15]

Paper-based gas sensors are intriguing and promising although the research is still in its infancy. From a brief survey, several amendments that may improve the sensing performance can be noted: 1) Sensing materials are always formulated on paper surfaces. This formulation may impair the mechanical stability and continuity of the SWCNT network. 2) Enlargement of the sensing area amplifies gas-adsorption capacity while the resistance is also changed, which may impact the sensitivity. 3) Dispersible SWCNT ink is conventionally prepared by binding chemical agents onto the SWCNT surface. However, such a chemical layer may hamper the gas molecules in close contact with the SWCNTs. With these concerns in mind, we have formulated a concept of forced assembly to drive water-dispersible SWCNTs to become trapped in paper, which forms sensing arrays with a high throughput. The continuous arrays consisting of chemically carboxylated SWCNTs exhibit a rapid and sensitive response to ammonia.

A forced assembly procedure was designed to make SWCNTs trapped in paper. The typical preparation process is outlined in **Figure 1**. First, a commercially available filter paper with an average pore size of 2.5 μm was drop-cast with a thin layer of photoresist. As a result, the paper pores were fully sealed. Second, the thin layer of photoresist was subjected to UV light with a mask. The region exposed to light was cured and solidified, and the region away from light recovered to become porous paper after washing off the uncured photoresist. Third, water-dispersible SWCNTs were sucked into the porous paper at low pressure. As the paper pores covered by crosslinked photoresist were entirely sealed, SWCNTs were only able to be assembled in the open areas, which lead to formation of sensing arrays on the paper. After an adequate lyophilization, gold electrodes were deposited on the paper containing trapped SWCNTs for further gas-sensing tests.

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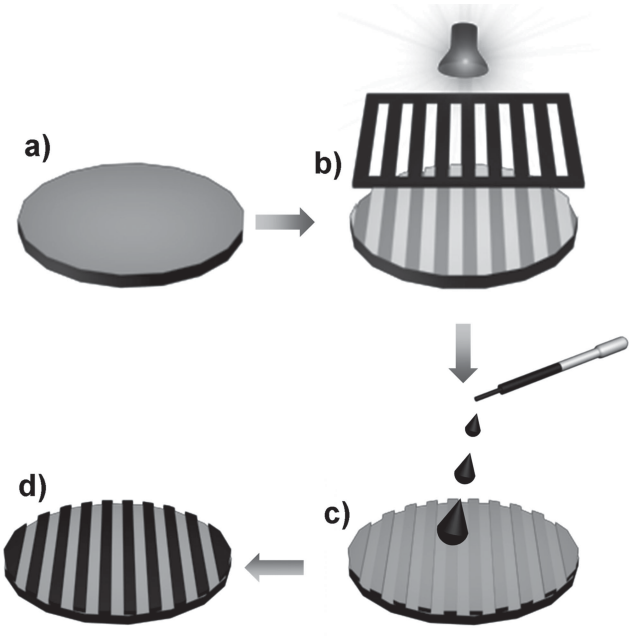

Figure 1. Schematic illustration of preparation of SWCNT-based paper sensors: a) A filter paper coated with photoresist; b) selective crosslinking of photoresist; c) suction filtration of SWCNTs through the paper under low pressure; d) a paper chip with sensing arrays.

To avoid the hindrance of the passage of gas through the paper by the surface coating, SWCNTs were acidified to increase their water solubility instead of covering their surface with amphiphilic agents. SWCNTs were chemically functionalized with carboxylic acid groups according to a previous procedure.[16] As shown in **Figure 2**a, the acidified SWCNTs retained a filamentous structure and did not aggregate excessively. In contrast to unfunctionalized SWCNTs, the acidified SWCNTs could be easily dispersed in water and did not precipitate in over two weeks, as shown by photographic images in Figure 2b. Carboxylic acid functional groups were hypothesized to be generated on the sidewall and ends of the SWCNTs. The appearance of the carboxylic acid group was verified by IR spectroscopy, as shown in Figure 2b. The peak at 1712 cm^{-1} refers to the stretching vibration of the C=O bond. The peaks at 2907 and 3119 cm^{-1} are ascribed to stretching vibrations of the O–H bond within the –COOH, which exists in the form of dimers in the solid state. The carboxylic acid on the wall of the SWCNT is assumed to facilitate ammonia adsorption onto the SWCNTs due to the substantial interaction of this group with Lewis bases, such as ammonia. In addition, the surface functional groups are small and they have no steric effect on the adsorbed ammonia molecules that distort the electrical cloud of the SWCNTs.

Water-dispersible SWCNTs were sucked into porous filter paper to be assembled there. However, paper covered with crosslinked photoresist could not take up any SWCNTs, because these paper pores were sealed with hydrophobic photoresist that did not allow water to penetrate. The surface wettability of the filter paper, both with and without photoresist covering, was assessed by means of contact-angle measurements, as shown in Figure 2c and d. The photoresist-coated

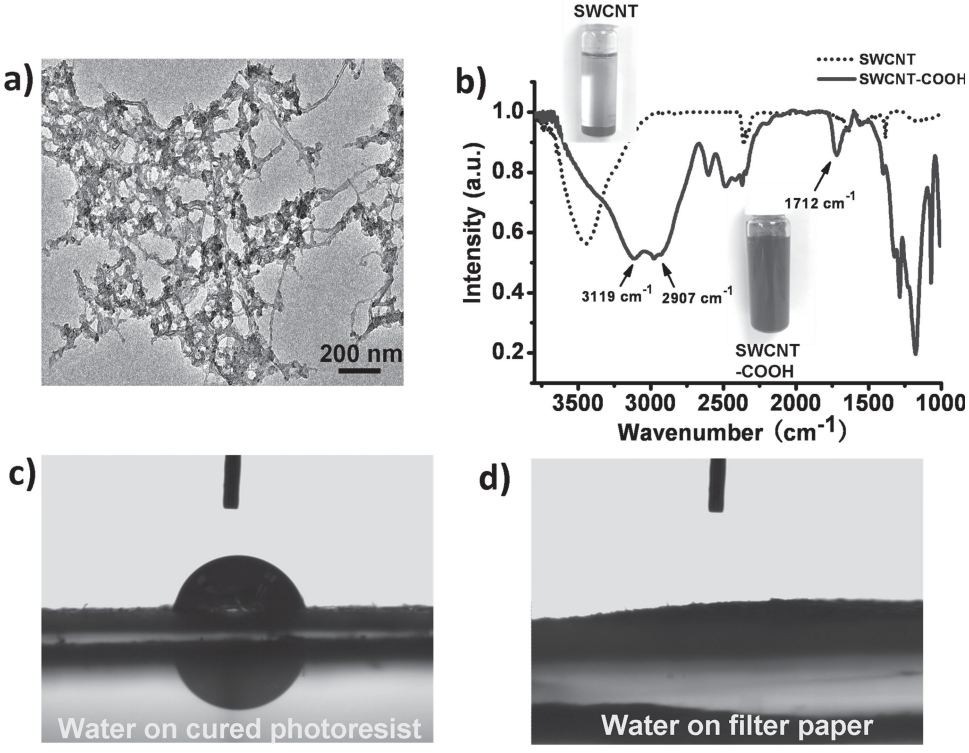

Figure 2. a) Transmission electron microscopy (TEM) image of well-dispered carboxylated SWCNTs; b) IR absorbance of surface-acidified SWCNTs in comparison to purified SWCNTs without surface modification. Insets are photographic images of treated and untreated SWCNTs in aqueous solution; c) contact-angle measurements on the filter paper covered with the cured photoresist; and on d) a filter paper. The volume of the water droplet was 2 μL.

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paper was relatively hydrophobic, with a contact angle of 79°, while the pristine paper rapidly took up the water droplet. As a result, a lithographically treated paper can selectively take up SWCNTs in the open pores if the paper is drop-cast with a solution of SWCNTs. The stability and continuity of SWCNTs in the paper were extremely improved by applying suction. In our work, three set-ups were tested with open areas of widths: 400, 600, and 1200 μm. The gap length covered by the photoresist was set as 500 μm. As shown in **Figure 3**, SWCNTs were successfully assembled in the open areas, forming uniform arrays on a large scale. Microscopic inspection showed that the assembled SWCNTs possessed a distinct continuity. It should be noted that the porous paper was fully filled with SWCNTs. Top and side views of a paper chip demonstrated that SWCNTs were well distributed through the paper, affording robust sensing arrays with the same thickness as the paper.

The sensing ability of the paper chips for ammonia was tested. Typical sensing devices were made by manually cutting SWCNT-containing paper and subsequently depositing it with gold electrodes to form the desired chips, with precise control over array length and number. The signal output of the sensors was recorded on an electrochemical workstation with an applied direct voltage, by following the normalized change of conductivity as demonstrated in Equation (1):

$$-\Delta G/G_0\% = [(I_0 - I)/I_0] \times 100\% \quad (1)$$

where G_0 and I_0 are the initial conductivity and current before exposure to the analytes, and I is the current after exposure to the analytes. Detection sensitivity routinely relies on how fast the gas comes into contact with the SWCNTs and how much the SWCNT responds to the adsorbed gas molecules.

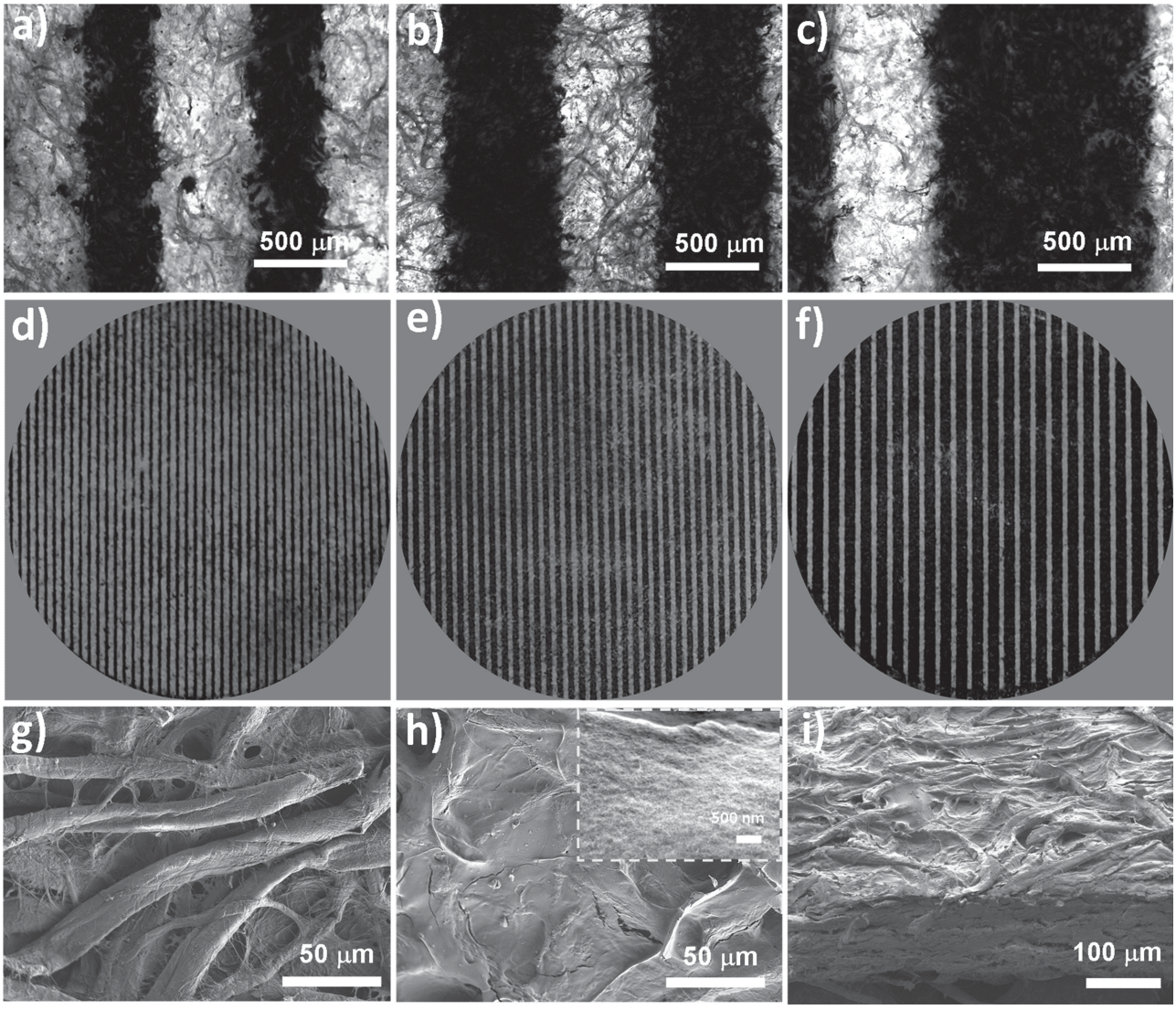

Figure 3. Characterization of the paper chip consisting of SWCNT arrays. Optical micrographs of the paper chips containing trapped SWCNTs in open areas with a width of a) 400; b) 600; c) 1200 μm. Photographic images of a full view of the paper chip with SWCNT arrays of d) 400; e) 600; f) 1200 μm. Scanning electron microscopy (SEM) image of g) a pristine filter paper; h) the paper fully filled with SWCNTs; i) side view of the paper chip containing trapped SWCNTs.

The former is a physical diffusion process which is affected by the size of sensing area and surface chemistry of SWCNTs. A larger sensing area can allow more gas molecules to contact the SWCNTs. However, the sensing test shown in **Figure 4**b indicated that thinner arrays afforded a stronger response to ammonia gas at a concentration of 20 ppm than did the thicker arrays. A similar rule also applies to the sensing arrays with the same feature width but different line numbers. As shown in Figure 4d, the increase of array number depressed the sensitivity of the sensor. In the presence of 20 ppm ammonia, the normalized conductivity change of two lines of arrays is four times larger than that of a sensor with eight lines. As defined in Equation 1, conductivity change is ascribed to current change. To explain the effect of sensor array size, a comparison was made between eight lines and two lines of 400 μm arrays. The current changes ($\Delta I = I_0 - I$) of the two sensors caused by ammonia at a concentration of 20 ppm are very close, even though their initial currents (I_0) are different (Figure 4c). As such, the normalized conductivity change of a two line array is bigger since the I_0 value of two lines is much smaller than that of eight lines. Assuming that the gas density (ρ) adsorbed on the SWCNT arrays is the same, the total gas amount on an array is proportional to the feature size $l \times w$, where l is the array length and w is the sum of array widths. As the ammonia adsorption simply contributes to distorting the electrical delocalization of SWCNTs, current change should be related to array width and thickness (d), $\Delta I \propto (\rho\ l\ w)/(w\ d) = \rho\ l/d$. In this case, eight-line and two-line 400 μm arrays should have similar current changes, as they both have a length of 5.0 mm and a thickness of 0.2 mm.

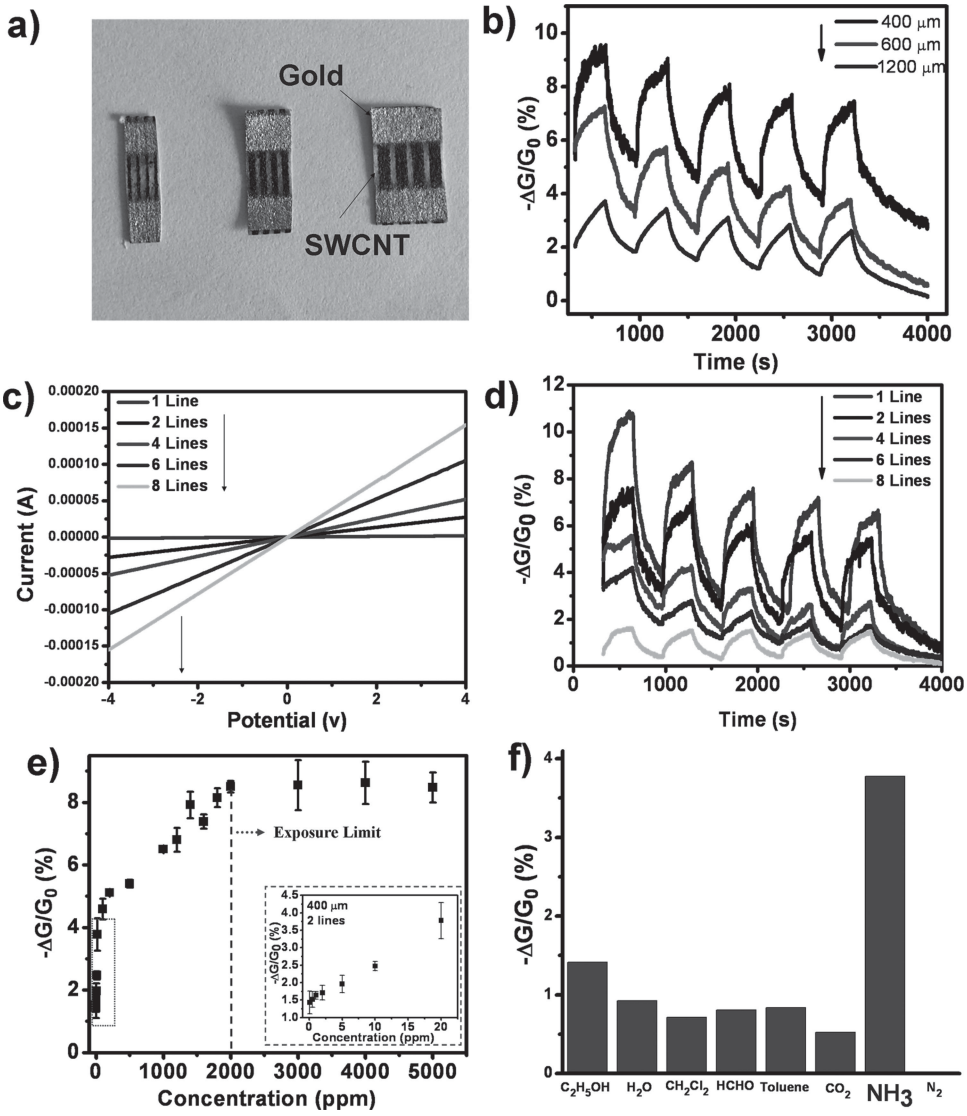

Figure 4. a) Photographic image of paper sensors with four SWCNT arrays. b) NH_3 response of paper chips with two SWCNT arrays with line widths of 400, 600, and 1200 μm. The NH_3 concentration was 20 ppm. c) *I–V* curves of paper chips with 400 μm arrays with one, two, four, six, and eight lines. d) NH_3 response of paper chips with 400 μm arrays with one, two, four, six, and eight lines. The NH_3 concentration was 20 ppm. e) Sensing test of paper chips with two lines of 400 μm arrays in the presence of NH_3 with concentration ranging from 0.1–5000 ppm. The inset shows seven early points in the graph. f) Selective response of paper chips to various volatile organic gases. The gas concentration was 20 ppm.

Because of the fragility of a paper chip with a single line of SWCNT array, sensing limit and selectivity were evaluated by using the optimized paper chip with two lines of 400 μm SWCNT arrays. The paper chip exhibited high sensitivity to ammonia gas. Conductivity change was still visible even when ammonia concentration was as low as 0.1 ppm, which indicates that the detection limit (DL) is even lower than 0.1 ppm. The theoretical detection limit was estimated by analyzing a sensing curve at 0.1 ppm ammonia. DL varies with the standard deviation (SD) of blank values and the average peak height (APH), DL = 3SD×0.1/APH. Thus, the detection limit of the paper chip with two 400 μm lines is 7 ppb. Excessive exposure did not cause the sensing chip to output stronger signals when the ammonia concentration was over 2000 ppm, as shown in Figure 4e. However, this exposure limit is 65 times above the point at which ammonia can be smelt by the human nose. The paper chip also had a specific response to ammonia in comparison with other volatile organic compounds, as shown in Figure 4f. The distinct sensing selectivity could be attributed to the acidified surface of SWCNTs that may strengthen the interaction of SWCNTs with ammonia.

In addition to the ease of fabrication, price is another critical criterion for the universal application of a new device. The cost of a paper-based gas sensing chip was estimated. SWCNTs on a piece of 100 cm^2 patterned paper were weighed as 0.345 mg, so a 4 cm^2 paper chip containing two sensing arrays traps 13.0 μg SWCNTs. The gold electrode sputtered on the paper has thickness of 180 nm, length of 2 cm, and width of 0.5 cm. The weight of gold is 346.7 μg as gold density is 19.3×10^3 kg m^{-3}. Considering the market prices of SWCNTs and gold are 16.08 \$ g^{-1} and 53.6 \$ g^{-1}, the costs of SWCNTs and gold on a paper chip are 0.5 cents and 9.0 cents, respectively. Including all other costs, like equipment usage and energy and labour consumption, the total price of a paper chip is still less than one dollar.

Reproducibility and the ease of scaling are basic criteria for the fabrication of new functional devices with high performance. Herein, we described a versatile and readily scalable approach for fabricating a cheap and sensitive gas sensor embedded in paper. A sensing material of acidified SWCNTs was forcibly assembled in the photoresist paper. Both stability and continuity of sensing arrays were improved over a layer of sensing materials straightforwardly deposited on an unmodified paper surface. The carboxylated surface strengthened the detection sensitivity of the SWCNTs. The study of our sensing arrays revealed that thinner arrays with fewer line numbers were more effective. Additionally, the paper chip displayed a low detection limit and high detection selectivity to ammonia gas. We believe that this approach offers a generally applicable approach for integrating active nanomaterials into paper matrices, opening opportunities in flexible sensors and optoelectronics strategies. High-level methods for generating multifunctional paper sensors are extremely urgently sought. Alternative methods to photolithography such as wax printing could be adopted for lower-cost mass production of patterned papers. Detection of some other gases broadly found in polluted air is also of vital importance. This demand may be solved by stepwise implantation of multiple detectors in a paper chip. However, the challenge of synchronous gas detection and elimination still remains. It is possible for paper chips to act as an antenna to recognize the target gas, deliver the information, and then catch, even eliminate, the toxic gas. We hope this work will open the door to new, exciting applications of paper chips.

Experimental Section

Materials: Filter paper (thickness 200 μm, pore size 2.5 μm) was purchased from Whatman Co. SWCNTs (95% purity, length ca. 5 – 15 μm, inner diameter < 2 nm) were purchased from Shenzhen Nanotech Port Co. Deionized water (18.2 MΩ cm^{-1}) was obtained from a Milli-Q water-purification system. A previously reported work was followed to acidify SWCNTs.[16] Briefly, 50 mg SWCNTs were added to 120 mL H_2SO_4:HNO_3 (3:1, 96% and 70%, respectively) solution and ultrasonicated in a water bath at 40 °C overnight. The SWCNTs were subsequently centrifuged at 4000 rpm and redispersed in deionized water. Photoresist SU-8 2010 was purchased from MICROCHEM Co. Propylene glycol methyl ether acetate (PGMEA; 99% purity, with 50 ppm butylated hydroxytoluene) was purchased from Alfa Aesar Co.

Characterization Method: TEM (JEMO electron microscope) was used to visualize the dispersibility of carboxylated SWCNTs. A commercial digital SLR camera was employed to acquire some distinct and macroscopic pictures. SEM images were captured on a Hitachi S-4800 instrument at a voltage of 2.0 kV. Fourier transform infrared (FTIR) spectra were collected on a Bruker IFS66v FTIR spectrometer. Standard IR pellets were prepared by compressing SWCNT dry powder into KBr. Surface wettability was assessed at room temperature on an optical contact-angle measuring device (OCA 20, Dataphysics Instruments GmbH) by a sessile-drop measuring method: 2 μL water droplet was dispensed onto the substrates for contact-angle investigation. A lyophilizer (FD-1–50, Beijing Boyikang Co.) was used to remove ice from frozen wet papers.

Photolithography on Filter Paper: Photoresist (SU-8–2010) was spread uniformly on a piece of filter paper by hand. The thin film of photoresist was gently baked at 65 °C for 1 min and harder baked at 95 °C for 5 min. The baked photoresist was then subjected to UV irradiation for 25 s (365 nm, 9.1 mW cm^{-2}) on a URE-2000/25 mask aligner (IOECAS, Chengdu). A photomask was aligned on the filter paper before light irradiation to generate the desired photoresist arrays. The uncrosslinked photoresist was washed off with a developer of PGMEA solution. Excess PGMEA on the paper was cleaned by using isopropyl alcohol.

Assembly of Sensing Arrays on a Paper Chip: The photolithographic filter paper was fixed into a suction system. A diluted SWCNT solution (4.2×10^{-2} mg mL^{-1}) was added to the system. Dark stripes formed after a few minutes as SWCNTs were trapped in the open papers. The wet papers were fully frozen in a refrigerator at the temperature of −5 °C for an hour. The frozen papers were then quickly transferred into a lyophilizer with a low pressure (less than 10 Pa) to sublimate ice at −50 °C over 4 h. The lyophilization prevented SWCNT arrays from being ruptured, leading to a continuous robust SWCNT array on the paper. Afterwards, a thin layer of gold (ca. 180 nm) was sputtered onto the paper chips by using a JCP-200 magnetron sputtering coating machine. The deposited gold acted as electrodes and the gap between two electrodes was 0.5 cm.

Gas-Sensing Test of Paper Chips: Gas-sensing properties were measured by using a statistic test system which contained a test chamber and a data acquisition system. Dry nitrogen was used both as reference and diluting gas to obtain desired concentrations of analytes. A circuit was set by connecting a paper chip with an electrochemical workstation which acted as a direct current source (1.0 V) and a current reader. The response of the sensor was followed by the normalized change of conductivity, $-\Delta G/G_0$, which was calculated by the normalized change of current,

$$-\Delta G/G_0\% = [(I_0 - I)/I_0] \times 100\%.$$

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