Convenient CNT-Paper Gas Sensors Prepared by a Household Inkjet Printer

Yan Yuan,* Xiaolei Tang, Li Jiang, Yujie Yang, Yanhui Zhou, and Yanmao Dong

**ABSTRACT:** A hydrosoluble light-sensitive polymer named PSAG (poly-styrenesulfonic acid glycidyl methacrylate) was synthesized by acrylic acid (AA), sodium 4-styrenesulfonate (SS), and glycidyl methacrylate (GMA). PSAG is used to modify multiwall carbon nanotubes (MWCNTs) with a length-to-diameter ratio between 0.004 and 0.016. An inkjet conductive ink was formed by well-dispersed MWCNTs in aqueous and organic solvents, which could adjust the surface tension and viscosity of the ink. Gas sensors were then fabricated using this conductive ink on a household inkjet printer. The sensors demonstrated good reproducibility and acceptable recovery time (<200 s) to ammonia, methanol, and acetone. The resistance of the inkjet-printed sensor electrodes remained stable in the process of bending the sensors to different angles because of ultraviolet curing.

**INTRODUCTION**

The United Nations Sustainable Development Goals (SDGs) were put forward in 2012 and came into effect in 2016. Consequently, environmentally friendly chemistry became a research hotspot in the chemical industry. The rapid development of the Internet of Things has spurred demand for devices facilitating human-object interactions. Therefore, increasing attention is being paid to developing eco-friendly sensors and actuators.

In the past, researchers focused on the sensitivity, accuracy, and response speed of sensors. Nowadays, the primary demands are for convenience and environmental friendliness in line with the SDGs. Thus, inkjet-printed paper-based sensors that meet SDG requirements have become a preferred solution for both scientific and industrial applications. Furthermore, they have other advantages including flexibility, portability, low cost, and biodegradability.

Advances in nanomaterial technology have produced many conductive inks for inkjet-printed paper-based sensors, such as poly(3,4-ethylenedioxythiophene) (PEDOT), graphene, Ag, polyaniline, and carbon nanotubes (CNTs). Of these, CNTs have large specific surface areas and high sensitivity to changes in the surrounding vapor, making them appropriate for all types of sensors, including sensors for gas, electrochemical, ultraviolet, humidity, and damage detection. Kim et al. prepared a CNT-coated paper sensor for damage detection. Its sensitivity to location and damage was 73 ppm, and its detection limit was approximately 29 ppm; this detection limit was 30 times higher than that reported previously.

Generally, strong van der Waals forces between CNT walls caused poor dispersion of CNTs in most organic and aqueous solvents. To improve their dispersibility, noncovalent and covalent modification methods have been developed for CNTs.

In a previous study, we reacted sodium 4-styrenesulfonate monomers with acrylic acid and obtained poly(styrenesulfonic acid) (PSA), a water-soluble random copolymer. PSA was then reacted with glycidyl methacrylate (GMA) to obtain a hydrosoluble light-sensitive polymer, which was named PSAG (poly-styrenesulfonic acid glycidyl methacrylate). PSAG was finally used to modify single-wall CNTs such that a stable and homogeneous aqueous dispersion of CNTs after ultraviolet (UV) irradiation cross-linking was obtained.

In the current study, we used PSAG to modify multiwall carbon nanotubes (MWCNTs) with length-to-diameter ratios of 0.004 and 0.016. Consequently, the MWCNTs dispersed well in the aqueous and organic solvents to form an inkjet conductive ink, and its surface tension and viscosity could be adjusted as required. Finally, paper-based gas sensors for...
ammonia and methyl alcohol detection were fabricated using this conductive ink of an inkjet printer.

RESULTS AND DISCUSSION

Dispersibility of PSAG to MWCNTs. UV–vis spectrophotometer is used to determine the dispersibility PSAG to MWCNTs as shown in Figure 1. The concentration of MWCNTs dispersing into the solution is determined using the specific extinction coefficient of MWCNTs at 500 nm according to the Lambert–Beer law. Figure 1 shows the UV–vis absorbance spectra of MWCNTs aqueous dispersions with different PSAG amounts. From Figure 1, the absorbance intensity increases with the increasing amount of PSAG. The absorbance at 500 nm of dispersions 3, 4, 5, and 6 in the right side of Figure 1 appears to increase and then remains stable, indicating that these MWCNTs dispersions are homogeneous. Dispersion 3–6 have similarly higher absorbance, but dispersion 3 needs comparatively less PSAG. Therefore, dispersion 3, with the least PSAG amount among them, is chosen as the original ink.

The detailed amount of MWCNT aqueous dispersion is shown in Table 1.

Table 1. Detailed Amount of MWCNTs Aqueous Dispersion

| dispersion | MWCNTs (mg) | PSAG (mg) | H2O (mL) | PSAG content (mg/mL) |
|------------|-------------|-----------|----------|----------------------|
| 1          | 10          | 10        | 10       | 0.1                  |
| 2          | 10          | 20        | 10       | 0.2                  |
| 3          | 10          | 40        | 10       | 0.4                  |
| 4          | 10          | 60        | 10       | 0.6                  |
| 5          | 10          | 80        | 10       | 0.8                  |
| 6          | 10          | 100       | 10       | 1.0                  |

Raman Characterization of MWCNTs Inkjet-Printed Sensor Electrodes. Figure 2 is the Raman spectra of pure MWCNTs and MWCNTs paper-based sensor electrodes. It can be seen from the figure that there are two peaks in the electrodes at 1312 and 1594 cm⁻¹, which respectively correspond to the disordered structure characteristic peak (D) and the tangential C–C vibration graphite structure characteristic peak (G). The ratio of the D-band to G-band of the MWCNTs is a direct indication of the degree of modification of the MWCNTs. The inkjet-printed electrodes showed almost the same Raman spectra as pristine MWCNTs. This observation confirmed the noncovalent functionalization of PSAG onto the MWCNTs. However, the slight decreases in the \( I_D/I_G \) values of the inkjet-printed electrodes were probably because of the extra \( \pi \) atom from the \( \pi \)-conjugation of the benzene ring on PSAG.

Characterization of the Stability of Inkjet-Printed Sensor Electrodes. Figure 3 displays the resistance-angle curves of the inkjet-printed sensor electrodes before and after UV curing. The resistance of both sensors fluctuated slightly with the increase of the folding angle and remained between 20 and 50 MΩ without significant changes. This indicated that the resistance of the inkjet-printed sensor electrodes was stable.

Sensitivity of Inkjet-Printed Sensor Electrodes. The organic gases selected for testing were ammonia, methanol, acetone, toluene, dichloromethane (DCM), and tetrahydrofuran (THF). The response results under different gases are presented in Figure 4. For all gases, the resistance value decreased sharply after the inkjet-printed sensor was placed in organic gases, and it eventually stabilized. When the sensor was moved into the air, the resistance value of the sensor increased gradually with the release of the gas, finally returning to the initial resistance value. Therefore, all tests revealed a n-type response behavior.

The response curves for ammonia, methanol, and acetone demonstrated good reproducibility, acceptable recovery time (<200 s), and a smooth baseline. However, poor reproduci-
bility and significant baseline drift were observed for toluene, DCM, and THF, indicating that the inkjet-printed sensor had a stable response to polar solvents. Figure 5 presents a cylindrical diagram for the maximum response values of inkjet-printed sensors to six organic gases.

Figure 5. $\Delta R_{\text{max}}/R$ of the inkjet-printed sensors under six organic gases atmosphere.

The sensors have the largest $\Delta R_{\text{max}}/R$ in an atmosphere of ammonia and methanol. Therefore, with respect to reproducibility, recovery time, and $\Delta R_{\text{max}}/R$, the inkjet-printed sensors demonstrated the best responses to ammonia and methanol.

Comparison of Gas Sensitivity Behavior between Dip-Coated (DC) Sensor and Inkjet-Printed (IJP) Sensor Electrodes. To compare gas sensitivity behaviors among dip-coated sensors and inkjet-printed sensor electrodes, ammonia, and methanol were used. Figure 6A,B presents the response curves for a dip-coated sensor in ammonia and methanol. Therefore, the response of dip-coated sensors to ammonia and methanol was also found to be n-type response behavior, and their response to ammonia was better than that to methanol. Figure 6C presents the maximum response values of each cycle: The baseline responses of the inkjet-printed sensor to ammonia and methanol were relatively flat, with no obvious drift. By contrast, the baseline responses of the dip-coated sensor to ammonia and methanol were uneven, with an obvious baseline drift. In particular, the inkjet-printed sensor had better responsiveness to ammonia and methanol than did the dip-coated sensor, indicating that the inkjet-printing process produces sensors with better properties than those of the dip-coating process.

Enhanced Performance of Inkjet-Printed Sensors after UV curing. Figure 7 presents the response curves of inkjet-printed sensors in ammonia (Figure 7A) and methanol (Figure 7B) before and after UV irradiation. The reproducibility and recovery time for both gases did not show considerable changes after UV curing, indicating that UV irradiation had no negative effect on the gas-sensing performance of the inkjet-printed sensors.

■ CONCLUSIONS

In summary, we prepared paper-based inkjet-printed sensors using PSAG–MWCNT inks on a household inkjet printer. The sensors had good reproducibility and acceptable recovery...
time (<200 s) for ammonia, methanol, and acetone. These sensors had better responsiveness to ammonia and methanol than did dip-coated sensors. Moreover, their resistance was stable in the process of bending sensors to different angles because of the UV curing process.

**EXPERIMENTAL SECTION**

Materials and Characterization Analysis of MWCNT Inks. Polystyrene sulfonic sodium (PSS, $M_w = 75,000$), glycidyl methacrylate (GMA), acrylic acid (AA) with a purity of 99%, and sodium 4-styrenesulfonate (SS) with a purity of 90%, which were supplied by Shanghai Aladdin Chemical Reagent Company, Shanghai (China). MWCNTs were purchased from Chengdu Organic Chemicals Institute, Chinese Academy of Sciences (China). Isopropanol (IPA), acetone, toluene, ammonia, methanol, dichloromethane (DCM), and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co., Shanghai (China). 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiofenone (2959) with a purity of 98% was provided by Changzhou Trony New Electronic Materials Co., Ltd., Changzhou (China).

Surface tension was measured by a contact-angle measurement with the model number of OCA 40 purchased from DataPhysics Co. UV−visible (UV−vis) absorption spectra were performed on a spectra photometer with the model number of TU-1901, which was bought from Beijing Purkinje General Instrument Co., Ltd. Viscosity was tested by an AMETEK Brookfield’s DV-S rotational viscometer. Both surface tension and viscosity are tested in room temperature. Raman spectroscopy analysis was recorded on Renishaw’s inVia Reflex confocal Raman microscope. Inkjet printing was performed using an EPSON R230 inkjet printer (Epson (China) Co., Ltd.), the printing head-type is piezoelectric with a resolution of 5760 × 1440 dpi, and the diameter is ≤300 nm.

Preparation of MWCNTs Aqueous Dispersion. Photosensitive water-soluble copolymer PSAG was synthesized according to our former work. Ten milligrams of MWCNTs...
was dispersed in 10 mL of H$_2$O, followed by the addition of a certain amount of PSAG. The mixture solution was diluted 20 times and under ultrasonic treatment for 1.5 h, obtaining a well-dispersed MWCNTs aqueous dispersion with a concentration of 0.05 g/L. The detailed amount of PSAG is listed in Table 1, and UV-visible (UV-vis) spectrophotometer was used to determine the optimal original ink as dispersion 3.

Preparation of Conductive Inks of Inkjet Printing. Generally speaking, commercial jet ink should have the viscosity of 10 to 40 cps and the surface tension of 33–48 mN/m to ensure good flowability and droplet morphology. Therefore, to achieve inkjet printing, the viscosity and surface tension of the initial ink is adjusted by H$_2$O, IPA, and acetone. The detailed amount can be found in Table 2. The surface tension and viscosity of MWCNT inks (named as J-ink) decreased with the addition of IPA and acetone. J-ink 2 was chosen for the closest approximation of commercial Epson ink, which had a viscosity of 17.6 cps and surface tension of 36 mN/m.

Fabrication of Inkjet-Printed Sensor Electrodes. Five milliliters of J-ink 2 added to 0.5 wt % of photoinitiator 2959 was poured into print cartridges of EPSON R230 inkjet printer (Shanghai industrial Marley Painting Co., Ltd., China) and sensor electrodes were printed on a photographic paper purchased from Eastman Kodak Co. After one layer was printed on a paper substrate, the paper was dried at 40 °C for 5 min. The process was repeated 20 times and paper-based electrodes with 20 layers of MWCNT conductive inks to obtain UV-cured ink films. The fabrication procedure is shown in Scheme 1 (Routing 1).

Fabrication of Comparative Dip-Coating Sensor Electrode and Measurements for Sensor Electrodes. Thirty microliters of J-ink 2 was added in an injector and then dipped onto the interdigital gold electrode (Siping Jihua Advanced Technology Co., Ltd., China). The dipped coating sensor electrode was dried at 40 °C for 1 h and exposed under UV lamps (Scheme 1, Routing 2). The surface resistance of inkjet-printed and dip-coating sensor electrodes was measured by an RTS-9 four-point probe instrument purchased from Guangzhou Four-Point Probe Technology Co., Ltd. The resistance of sensors at different angles is measured by an Agilent digital multimeter with a model number of 34401A. The stability of inkjet-printed sensor electrodes was tested by bending sensors into different angles (0, 30, 60, 90, 120, 150, and 180°).

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**Table 2. Ink Formula of the MWCNTs Conductive Inks with Quality Percentage (%)**

| ink            | dispersion 3 (%) | IPA (%) | acetone (%) | H$_2$O (%) | viscosity (cps) | surface tension (mN/m) |
|----------------|------------------|---------|-------------|------------|----------------|------------------------|
| commercial Epson ink |                  |         |             |            | 18             | 34                     |
| dilute original ink    | 25               |         |             | 75         | 25             | 64                     |
| J-ink 1               | 25               | 16      | 9           | 50         | 18.2           | 45                     |
| J-ink 2               | 25               | 20      | 9           | 46         | 17.6           | 36                     |

**Scheme 1. Schematic of Preparation for PSAG-MWCNTs Sensor Electrons by Inkjet Printing**

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Notes
The authors declare no competing financial interest.

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