Plasma treated MXene/Ag-based humidity sensor with ultrahigh sensitivity for gesture tracking

Hui’an Liu¹, Ning Li¹, Yue Jiang¹, Qiang Wang¹, Zhengchun Peng*¹

¹ College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518061, China
* Corresponding author’s e-mail: zcpeng@szu.edu.cn

Abstract. A novel humidity sensor based on MXene (Ti₃C₂) combined with Ag nanoparticles was prepared in this paper. Owing to high surface-to-volume ratio and outstanding hydrophilicity of sensing film, the humidity sensor shows ultrahigh sensitivity. Moreover, this kind of sensor exhibits fast response speed which can detect human breath. Meanwhile, with a 7×7 sensor array, hand gesture can be tracked without direct contact of these sensors by hand which provides an unique approach for human–machine interaction without using machine vision.

1. Introduction

Highly sensitive humidity sensors are widely used in daily life. High sensitivity humidity sensors with fast RH-response speed are necessary to support human needs. In order to achieve this goal, the development of humidity-sensitive materials, especially two-dimensional (2D) nanomaterials, has attracted considerable attention, such as MoS₂ and graphene [1-2]. Due to the hydrophilic and large specific surface area of their nanosheets, these distinct 2D nanomaterials demonstrate great potential for humidity sensing application.

MXenes, which is a new series of 2D materials obtained by removal of the intermediate element from MAX phases, have attracted tremendous attention to fuel cells, lithium ion batteries, and supercapacitors since the discovery of Ti₃C₂-MXenes [3-5]. Owing to the distribution of abundant hydroxyl (OH) and fluorine (F) surface groups in the chemically active surfaces after HF etching, MXene obtained excellent hydrophilicity which made it a promising humidity sensing material[6].

It is an effective way to combine inorganic semiconductors or polymers with Ag nanoparticles (AgNPs) for fabricating the new function of materials [7]. Due to its excellent catalytic properties, it has been proved that AgNPs were the effective additive that can improve the humidity performance through create much more adsorption sites for water molecules [8-9].

In this work, we demonstrate the matrix panel based on MXene/Ag-based humidity sensor with ultrahigh humidity sensitivity for non-contact gesture tracking, which can realize non-contacting close proximity sensing with high sensitivity and fast response speed.
2. Fabrication and Characterization

Figure 1. (a) Schematic diagram of 2D Ti$_3$C$_2$ MXene nanosheets fabrication process. (b-d) SEM image of Ti$_3$AlC$_2$, Bulk Ti$_3$C$_2$ and Ti$_3$C$_2$ nanosheets. (e) FTIR image of Ti$_3$C$_2$ nanosheets. (f, g) TEM and EDS images of Ti$_3$C$_2$/Ag hybrid. (h-k) the water contact angle images of Ti$_3$AlC$_2$, Ti$_3$C$_2$ and Ti$_3$C$_2$/Ag hybrid with plasma treatment.

Figure 1 shows the schematic diagram and characterization of Ti$_3$C$_2$ nanosheets (MXene). Ti$_3$C$_2$ nanosheets were prepared by selective hydrofluoric-acid-etching (HF-etching) of the aluminum (Al) layers in Ti$_3$AlC$_2$, followed by liquid-phase exfoliation (LPE) in N-methylpyrrolidone (NMP), as shown in figure1(a). Each of these products were shown in the field emission scanning electron microscopy (FE-SEM) images (figure 1(b-d)). As shown in figure 1(c), the Al layer was selectively removed in HF-etching process, which rise the distance between Ti$_3$C$_2$ layers and the bulk part exhibits loosely packed accordion-like structures. After intense ultrasonic treatment, the Ti3C2 nanosheets was peeled away, as shown in figure 1(d)[10].

The FTIR spectroscopy of Ti$_3$C$_2$ is showed in figure 1(e). It is clear a big absorption spectrum is at 3437 cm$^{-1}$, other peaks at 1630 cm$^{-1}$ and 1390 cm$^{-1}$, which are the characteristic vibration peaks of hydroxyl group and carboxylic group. The broad peak at ~3437 cm$^{-1}$ attributed to the stretching and bending vibration of OH groups on the Ti$_3$C$_2$, the peaks at 1630 and 1390cm$^{-1}$ were due to stretching vibration of C=O and C-O of Ti$_3$C$_2$Tx. The results indicate that Ti$_3$C$_2$ nanosheet are terminated by -O, -OH groups, and give the sample good hydrophilicity.

Ag nanoparticles dispersion (purchased in Xianfeng Nano. Tech, 0.1mg/ml) was added into Ti$_3$C$_2$ dispersion with the same volume ratio, then followed with ultrasonic treatment (90W, 2 hour). The morphologies of the hybrid of Ti$_3$C$_2$ MXene nanosheets and Ag nanoparticles were also examined by using TEM and EDS. As shown in figure 1(f,g), the Ag nanoparticles with about 20nm in diameter were spread out evenly on Ti$_3$C$_2$ nanosheets and the atomic ratio of Ag in hybrid is 2.5%.
Interdigitated electrodes (IDEs) were prepared with magnetron sputtering and lithography method. Ti/Au layers with the thickness of 100 nm/400 nm formed the electrode structure with a 50µm-wide gap. The IDEs were ultrasonic pre-treated with acetone, ethanol and water for 5 min and dried in N2. And then, the IDEs was treated in plasma cleaning machine (500mW) for 5 minutes. A drop of dispersion (Ti3C2/Ag, 4:1) was added onto the IDEs through a microsyringe, followed by drying in N2. As shown in figure 1 (h-k), the water contact angle of Ti3C2/Ag hybrid treated with plasma is 23.1°, which is smaller than that on Ti3C2 nanosheet based film (57.8°) and Ti3AlC2 (86°), indicating the hydrophilicity of hybrid with plasma treatment has been greatly improved.

Humidity Performance

![Figure 2](image)

Figure 2. (a) Capacitance dependence on relative humidity of Ti3AlC2, bulk Ti3C2, Ti3C2 nanosheet, Ti3C2/Ag hybrid with and without plasma treatment. (b) Hysteresis characteristic of Ti3C2/Ag hybrid with plasma treatment. (c) Response and recovery time. (d) Long-term stability. (e) RH-response at different breathing rates.

To evaluate the humidity-sensing performance, the fabricated sensors were placed in the chamber of temperature and humidity generator (Hongzhan, LP-80U, China). The capacitance response and AC complex impedance spectroscopy of all the sensors were characterized by using an LCR meter with a 250-ms acquisition time (Wayne Kerr, 6500, UK). All experiments were tested at 25°C.

As shown in figure 2(a), the capacitance of sensor based on Ti3C2/Ag hybrid with plasma treatment increased by approximately three orders of magnitude toward RH, which varies from 11% to 97% RH, with large variations from 1150pF to 87442pF (the parameter of the ac driving voltage is 100mV and 100Hz). A sensitivity of 1003pF/%RH is obtained, which is more than 2.5 times higher than that of sensor based on pure Ti3C2 nanosheet films, surpassing the previous MXene based humidity sensors.
Moreover, as shown in Table 1, Ti3C2/Ag exhibited more sensitive performance than GO and MoS2 [16]. The hysteresis (between humidification and desiccation and measured over an RH range of 10%–90% RH) was less than 5% RH (figure 2(b)), which indicated that the hysteresis was very small. The long-term stability of the sensor was shown in Figure 2(d).

As shown in Figure 2(c), the measured response and recovery times were about 180 ms and 230 ms respectively, ahead of all previous sensors in Table 1. The measurement could be ascribed to the large surface area and wide interlayer spacing in the Ti3C2/Ag films, which can accelerate the absorption and desorption of water molecules. Given to the fast response speed, the humidity variations could be monitored by placing the sensors in a respiratory mask at a distance of 5 cm from the nose for monitoring human breathing. Figure 2(e) shows the capacitance change of the sensor toward a person’s breath. The sensor can accurately reflect the whole breathing variation range, regardless of the breathing speed (normal to fast). Such a device is appealing for healthcare, anti-choking, and breathing monitoring.

Table 1. Performance contrast with reported RH sensors

| Sensor type     | Meas. range | Sensitivity | Response time | Ref.   |
|-----------------|-------------|-------------|---------------|--------|
| GO              | 15–95%      | 46.3 pF/%RH | 10.5s         | [11]   |
| rGO/poly        | 11-97%      | 0.465Ω/%RH  | 108s          | [12]   |
| MoS2            | 17-90%      | 80.9 pF/%RH | 140s          | [13]   |
| MoS2            | 10-60%      | 91.8kΩ/%RH  | 12s           | [14]   |
| MXene           | 0-95%       | 0.52Hz/%RH  | --            | [15]   |
| MXene/Poly      | 10-90%      | 1.5 Ω/%RH | 200ms         | [6]    |
| Ti3C2/Ag        | 11-97%      | 1003pF/%RH  | 180ms         | This paper |

3. Gesture Tracking

Figure 3. (a) Capacitance and resistance response during the approach of water droplet, (b) The schematic of sensor arrays, (c) Hand gestures detection.
Due to the ultrahigh RH sensitivity and fast response speed of Ti₃C₂/Ag-based sensors, the matrix panel was utilized to trace the moisture around fingertips in noncontact mode. To demonstrate the noncontact RH sensing of the sensor accurately, one water-droplet on the measuring plane of microcalliper approached the RH sensor on another plane and the capacitance and resistance response was measured (figure 3(a)). Figure 3(b) shows the prepared 7×7 devices array on the PCB substrate. Individual sensor can be regarded as one pixel, and its bias voltage of the resistance shows an exponentially relationship to the finger-device distances. Therefore, the sensors array can detect the RH change in real time. According to figure 3(c), different hand gestures can be identified through the distribution of RHs and LEDs accurately. The noncontact sensing capability shows excellent application in using Ti₃C₂/Ag-based sensor array for long range interaction or localization applications.

4. Conclusion

Ti₃C₂/Ag hybrid based humidity sensor with high performance was demonstrated. In addition to the high sensitivity (over 3 orders of magnitude) and millisecond scale response and recovery times. Integrated sensor array was demonstrated for noncontact mapping of hand gesture tracking. It can potentially be used in future apindoid untouched localization systems.

Acknowledgements

This work was supported by the Science and Technology Innovation Commission of Shenzhen (JCYJ20180305124942832), the China Postdoctoral Science Foundation (2018M633130) and the Department of Education of Guangdong Province (2016KZDXM005).

References

[1] Yao, Y., Chen, X., et al. (2014) Investigation of the stability of QCM humidity sensor using graphene oxide as sensing films. Sensors and Actuators B: Chemical, 191: 779-783.
[2] Zhao, J., Li, N., et al. (2017) Highly sensitive MoS2 humidity sensors array for noncontact sensation. Advanced Materials, 29: 1702076.
[3] Liang, X., Garsuch, A., et al. (2015) Sulfur cathodes based on conductive MXene nanosheets for high-performance lithium–sulfur batteries. Angewandte Chemie International Edition, 54: 3907-3911.
[4] Ren, C.E., Hatzell, K.B., et al. (2015) Charge-and size-selective ion sieving through Ti3C2T x MXene membranes. The journal of physical chemistry letters, 6: 4026-4031.
[5] Seh, Z.W., Fredrickson, K.D., et al. (2016) Two-dimensional molybdenum carbide (MXene) as an efficient electrocatalyst for hydrogen evolution. ACS Energy Letters, 1: 589-594.
[6] Muckley, E.S., Naguib, M., et al. (2018) Multi-modal, ultrasensitive, wide-range humidity sensing with Ti 3 C 2 film. Nanoscale, 10: 21689-21695.
[7] Tomer, V.K., Devi, S., et al. (2016) Fast response with high performance humidity sensing of Ag–SnO2/SBA-15 nanohybrid sensors. Microporous and Mesoporous Materials, 219: 240-248.
[8] Li, N., Chen, X.-D., et al. (2017) Ultra-high sensitivity humidity sensor based on MoS 2/Ag composite films. IEEE Electron Device Letters, 38: 806-809.
[9] Li, N., Chen, X., et al. (2017) Ultrahigh humidity sensitivity of graphene oxide combined with Ag nanoparticles. Rsc Advances, 7: 45988-45996.
[10] Xing, C., Chen, S., et al. (2018) Two-dimensional MXene (Ti3C2)-integrated cellulose hydrogels: toward smart three-dimensional network nanoplatforms exhibiting light-induced swelling and bimodal photothermal/chemotherapy anticancer activity. Acs Applied Materials & Interfaces, 10: 27631-27643.
[11] Bi, H., Yin, K., et al. (2013) Ultrahigh humidity sensitivity of graphene oxide. Scientific reports, 3: 2714.
[12] Zhang, D., Tong, J., et al. (2014) Humidity-sensing properties of chemically reduced graphene oxide/polymer nanocomposite film sensor based on layer-by-layer nano self-assembly. Sensors and Actuators B: Chemical, 197: 66-72.

[13] Tan, Y., Yu, K., et al. (2014) The combinations of hollow MoS2 micro@nano-spheres: one-step synthesis, excellent photocatalytic and humidity sensing properties. Journal of Materials Chemistry C, 2: 5422-5430.

[14] Zhang, S.L., Choi, H.H., et al. (2014) Controlled exfoliation of molybdenum disulfide for developing thin film humidity sensor. Current Applied Physics, 14: 264-268.

[15] An, H., Habib, T., Shah, S., et al. (2019). Water Sorption in MXene/Polyelectrolyte Multilayers for Ultrafast Humidity Sensing. ACS Applied Nano Materials. 2:948−955

[16] Longaresi, R.H., Pereira-da-Silva, M.A. (2015) Soft-lithography of ordered block copolymer nanostructures. Micro & Nano Letters, 10: 414-418.