

# Highly Sensitive and Fast Response Colorimetric Humidity Sensors Based on Graphene Oxides Film

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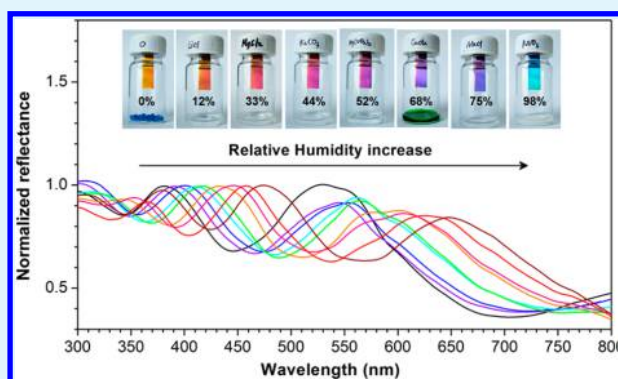
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## S Supporting Information

**ABSTRACT:** Uniform graphene oxide (GO) film for optical humidity sensing was fabricated by dip-coating technique. The resulting GO thin film shows linear optical shifts in the visible range with increase of humidity in the whole relative humidity range (from dry state to 98%). Moreover, GO films exhibit ultrafast sensing to moisture within 250 ms because of the unique atomic thinness and superpermeability of GO sheets. The humidity sensing mechanism was investigated using XRD and computer simulation. The ultrasensitive humidity colorimetric properties of GOs film may enable many potential applications such as disposable humidity sensors for packaging, health, and environmental monitoring.

**KEYWORDS:** humidity sensor, graphene oxide, colorimetric, reflection, carbon



Humidity sensing is of paramount importance in many industrial and domestic applications, including manufacturing processes control, pharmaceutical processing, and intelligent control of living environment.<sup>1</sup> Various types of humidity sensors have been developed over past decades based on different measuring principles such as capacitive,<sup>2</sup> resistive,<sup>3</sup> acoustic,<sup>4</sup> gravimetric,<sup>5</sup> and optical types.<sup>6,7</sup> The frequently used materials for humidity sensing are ceramics (e.g., Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>),<sup>8,9</sup> semiconductors (e.g., GaN, SnO<sub>2</sub>, and In<sub>2</sub>O<sub>3</sub>),<sup>10–12</sup> and polymers (e.g., polyelectrolytes and conducting polymers).<sup>13,14</sup> Recently, carbon materials have attracted considerable interest in gas/vapor sensing and other applications because of their large surface–volume ratio, high surface activity, strong stability, and mechanical stiffness.<sup>15</sup> Zero-dimensional fullerenes (C<sub>60</sub>) and one-dimensional carbon nanotubes (CNT) have been developed for humidity sensing, but their sensitivities are usually nonlinear, and their response and recovery time are relatively slow.<sup>16,17</sup> Two-dimensional graphene showed exceptional promise for biological and chemical sensors because of its large surface area and high chemical stability.<sup>18,19</sup> In particular, the graphene oxide (GO), the most important derivatives of graphene, is very useful for humidity sensing because of its superpermeability that arises from its rich oxygen-containing groups such as hydrophilic hydroxyl, epoxy, and carboxylic groups.<sup>20</sup> Various electrical property-based GOs humidity sensors have been developed, recently.<sup>21–23</sup> However, these electrical type GO-based humidity sensors suffered from low conductivity because of interruption of conjugated electronic state in GOs. Conductivity may be partially

restored by using reduced GOs (rGOs) but it is far behind pristine graphene.<sup>24</sup> Therefore, developing a novel humidity sensor based on GOs by utilizing their unique structure and chemical properties while avoiding their drawback is highly desired.

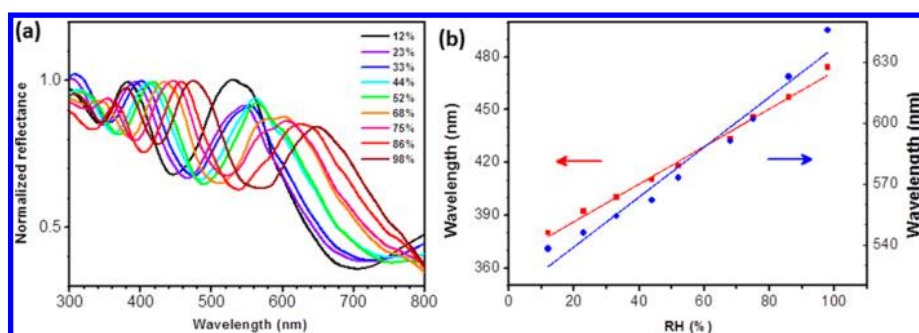
Herein, we show that GO thin films can act as the active layer to detect humidity change in the whole relative humidity (RH) range at an ultrafast speed. The change can be detected by naked eyes without the need of any equipment or power source. Importantly, the reflecting spectra (reflection peaks) of GO film and RHs follows a linear relationship, which makes the quantitative RH measurement possible. The GO-based optical humidity sensor reported here show many interesting features for practical applications such as low cost, fast response, high reproducibility, and suitability for large scale manufacturing.

Graphene oxides are mass producible from natural graphite by chemical oxidation and exfoliation. In this work, GOs used for optical humidity sensors were prepared by modified Hummer's method.<sup>25,26</sup> The formation of GO was confirmed by the Fourier transform infrared spectroscopy (FTIR) spectra, which showed the characteristic vibration peaks from carboxylic group and hydroxyl group. As shown in the FTIR spectra of GOs (Figure S1 in the Supporting Information), stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide

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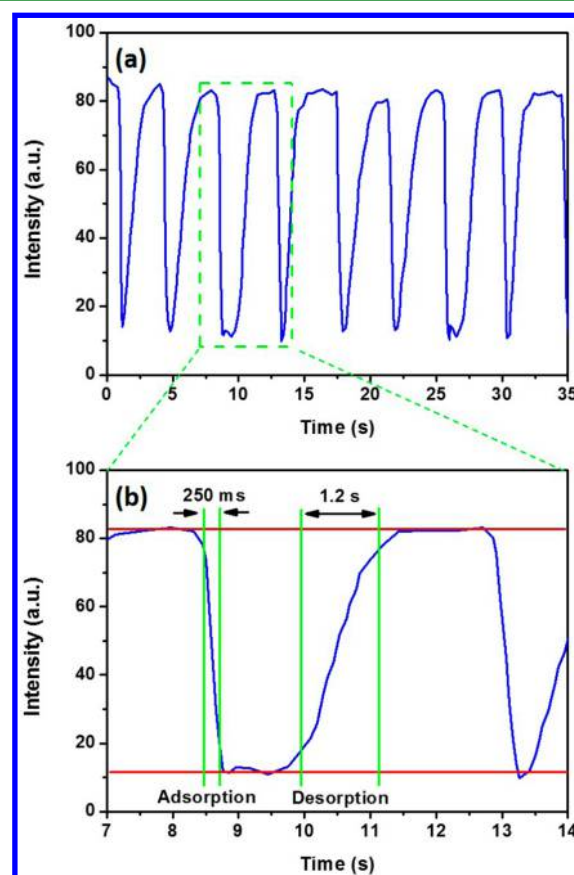
**Figure 1.** (a) UV/vis reflecting spectral shifts of a GOs film under different humidity conditions at 25 °C and (b) the linear wavelength change of the reflection spectra peaks under different RHs.

showed a broad peak between 3000–3700  $\text{cm}^{-1}$ , suggesting that the sample exhibit strong hydrophilicity. The presence of the absorption peaks at 1630 and 1390  $\text{cm}^{-1}$  were attributed to the stretching vibration of C=O and C–O of carboxylic acid groups present at the edges of GOs. The successful exfoliation was confirmed by transmission electron microscope (TEM) analysis, which showed the formation of GO nanosheets, consisting of 1–3 layers with sizes ranging from a few hundred nanometers to a couple of microns (Figure S2).

To fabricate GOs film with good uniformity and controllable thickness, we employed a dip-coating technique for solution processing as it allows continuous large-scale thin film production for practical applications. The formed GOs film was characterized by using electron microscopes analysis. Scanning electron microscope (SEM) image of the formed GOs film showed a smooth surface (Figure S3) and the cross-section image showed a uniform GOs layer with thickness of about  $380 \pm 15$  nm (Figure S4) which stayed constant on the same wafer (6 in.). The thickness of the GOs film was affected by the concentration of GO stock solution and the pulling rate. However, under the same condition, the thickness of the obtained uniform GOs film is reproducible, suggesting that the dip coating is simple and reproducible technique for fabricating GOs film for practical applications.

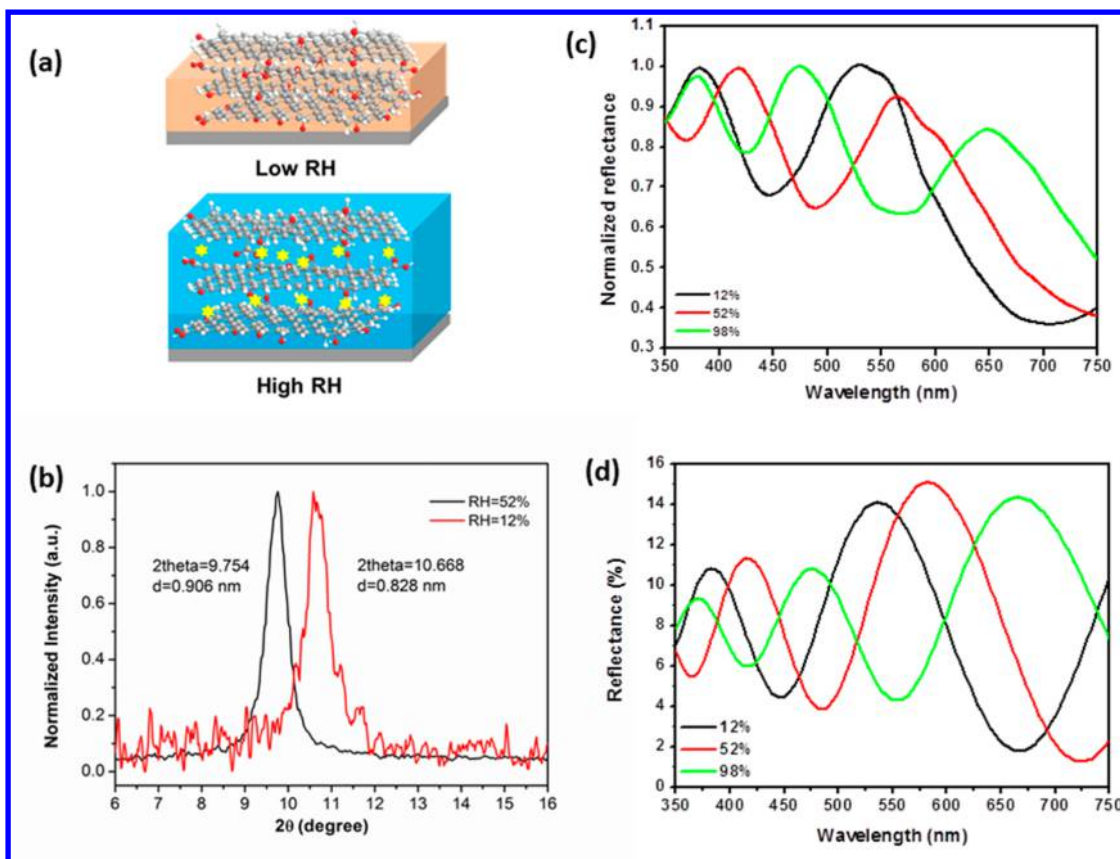
We studied the GOs film response to RH by extensive measurement of the reflectance spectra in a quartz chamber at room temperature, where RH was controlled by vapor pressure from a series of saturated salt solution, ranging from dry to a high humid state (RH = 98%). Figure 1a shows reflectance spectra of GOs film upon exposure to different humidity environments. In the relatively dry state (RH = 12%), the sensor shows two main reflection peaks at 386 and 526 nm. With the increase of RH, these two reflection peaks gradually red-shifted. When RH reaches 98% (in the vapor of saturated  $\text{PbNO}_3$  solution), these two reflection peaks shifted to 474 and 645 nm, respectively. On the basis of the measured spectra, both reflection peaks showed nearly linear relationships with the change of RH (Figure 1b). In the relative humidity range from 12 to 98%, the first reflection peak shifted from 386 to 474 nm with a slope of 1.07, and the second reflection peak shifted from 526 to 645 nm with a slope of 1.23 as shown in Figure 1b. It is interesting to note that the spectra changes cover the whole visible range from deep blue to red, making it very promising to develop the dual-colorimetric humidity sensors that can detect the humidity change by naked eyes.

Figure 2 shows the response and recovery curves of the GOs film measured at room temperature when RH alternately changes between atmosphere (RH ~50%) and high humidity



**Figure 2.** (a) Response and recovery properties of the GOs film based sensors under alternate atmosphere and high humidity at 25 °C. (b) Magnified view of one cycle showing the response and recovery time of the adsorption and desorption processes, respectively.

(RH ~98%). The reflectance wavelength at 550 nm was used for tracking. GOs film showed good repeatability and rapid response/recovery characteristics. The response time of the adsorption process as the RH increases from 50 to 98% for the GO film is around 250 ms, while the recovery time for the desorption process is about 1.2 s. The big difference in the response and recovery times could be attributed to the abundant hydrophilic groups on GOs 2D nanosheets. These polar hydrophilic groups cover the surface of 2D GO nanosheets, forming hydrogen (H) bonding with the absorbed water molecules. The H bonds between GOs and water molecules made desorption of water much more difficult than the absorption process. However, such a response/recovery time is still much faster than many of the reported humidity sensors.<sup>27,28</sup>



**Figure 3.** GOs film humidity sensing mechanism studies. (a) Schematic illustration of GO multilayers at low humidity and high humidity environment. Carbon, oxygen, and hydrogen atoms are represented by gray, red and white spheres, respectively. Water molecules are represented by yellow stars. (b) Normalized XRD pattern of GOs film at RH = 12 and 52%. (c, d) UV/vis spectral comparison of the (c) experimental and (d) simulated results of GOs film with thickness of 386 nm when exposed to different humidity conditions (RH = 12, 52, and 98%) at 25 °C.

The rapid humidity response and the complete recovery was attributed to the superpermeability of GOs to water molecules and nanoscale thickness of the GOs film.<sup>20</sup> The fast and reversible color changes can be repeated many times without detectable decrease of sensitivity and speed (Video S1).

The humidity dependence of color change of the GOs film can be attributed to the moisture-induced swelling of the GO multilayers as illustrated in Figure 3a. Our GO multilayer-based humidity sensor system consists of three layers: an incident medium (air layer), a top layer (GO multilayers), and a bottom layer (Si substrate). When the incident light irradiate on the GO multilayers, optical interference occurs that the incident light is reflected by the upper and lower interfaces of the GOs film. Because of the superpermeability of GOs to water molecules, the increase in RH will lead to more nanopores opening in GOs film and insertion of more water molecules. At higher RH, the H bonds between functional groups and water molecules that interlinked the adjacent GO layers will be replaced by the H bonds between water molecules, which lead to an increase of spacing between adjacent GO layers and thus the swelling of GOs film.<sup>29</sup> As a result, the newly formed optical interference resulted from the swelled GOs film causes a redshift of the reflection peaks, leading to visual range spectra shifts as shown in Figure 1. It is worth mentioning that the measured spectra and the observed colors caused by the optical interference are highly repeatable and reversible with the controlled humidity change, indicating that the GOs film is very stable and the uptake and release processes of water molecules by the GOs film are highly reversible as well.

To confirm the above-mentioned mechanism, we carried out X-ray diffraction patterns of a GOs film before and after swelling. Figure 3b showed a displacement of the (002) diffraction peak of GO multilayer to lower  $2\theta$  value in humidity environment. The water uptake increased the interlayer distance from 8.28 Å (RH = 12%) to 9.06 Å, (RH = 52%), indicating that the GO film on Si wafer were heavily swollen with water. This is in excellent agreement with our assumption.

To further confirm the GO film sensing mechanism, we carried out optical simulation. We considered the GO film with the bottom in contact of Si substrate and the top in contact with air. The thickness of the GO film was varied under different RHs. We adopted the Fresnel matrix formalization to calculate the reflectance of the multilayered film. At normal incidence, the characteristic matrix for the GO layer is given by

$$M_{\text{GO}} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = \begin{bmatrix} \cos\left(\frac{2\pi n_{\text{GO}} d_{\text{GO}}}{\lambda_0}\right) & -\frac{i}{g_{\text{GO}}}\sin\left(\frac{2\pi n_{\text{GO}} d_{\text{GO}}}{\lambda_0}\right) \\ -ig_{\text{GO}}\sin\left(\frac{2\pi n_{\text{GO}} d_{\text{GO}}}{\lambda_0}\right) & \cos\left(\frac{2\pi n_{\text{GO}} d_{\text{GO}}}{\lambda_0}\right) \end{bmatrix}$$

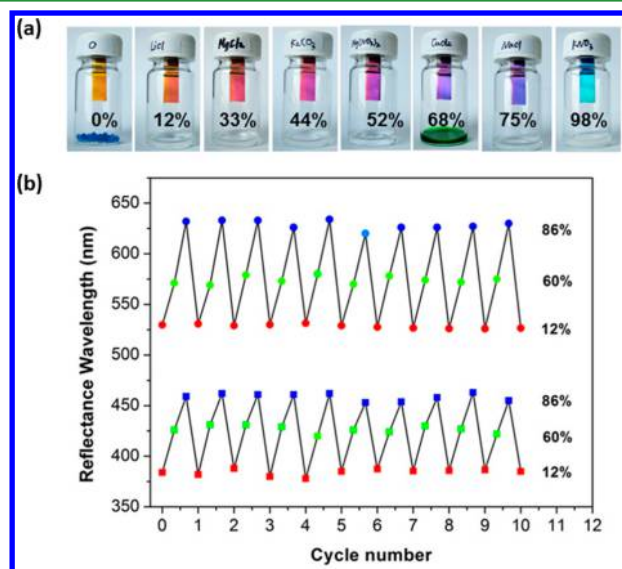
where  $g_{\text{GO}} = (\epsilon_0/\mu_0)^{1/2}n_{\text{GO}}$  for s-polarization and  $g_{\text{GO}} = (\epsilon_0/\mu_0)^{1/2}(1/n_{\text{GO}})$  and for p-polarization.

The reflection coefficient,  $r_{s,p}$  can then be calculated by the equation below, which takes into account the substrate and air

$$r_{s,p} = \frac{g_{\text{air}}(m_{11} + g_{\text{substrate}}m_{12}) - (m_{21} + g_{\text{substrate}}m_{22})}{g_{\text{air}}(m_{11} + g_{\text{substrate}}m_{12}) + (m_{21} + g_{\text{substrate}}m_{22})}$$

The reflectance is given by  $R_{s,p} = |r_{s,p}|^2$ . For unpolarized light, the reflectance is  $R_0 = (1/2)(R_s + R_p)$ . As can be seen from Figure 3d, the simulated results are nearly consistent with the measured spectra (Figure 3c), indicating that the color change of the GOs film under different RHs was attributed to water induced thickness change of the GOs film.

To demonstrate their practical applications as humidity sensors, we cut a silicon wafer with thin layer of GOs film into chips and then put into vials containing various saturated salt solution at the vial bottom as shown in Figure 4a (Sat. LiCl: 12%,



**Figure 4.** (a) Color change of GOs film when exposure to various RH. (b) Reversible conversion from the dual-colorimetric of GO multilayers by alternately exposing to selected RHs.

Sat.  $\text{MgCl}_2$ : 33%, Sat.  $\text{K}_2\text{CO}_3$ : 44%, Sat.  $\text{Mg}(\text{NO}_3)_2$ : 52%, Sat.  $\text{CuCl}_2$ : 68%, Sat. NaCl: 75 and Sat.  $\text{PbNO}_3$ : 98%). The saturated salt solution was used to provide certain vapor pressure. An immediate color change can be seen when the chip was put into the vial. In addition, remarkable vivid color change can be observed when the RH was changed in the whole range, from dry state to high humid (98%) states. Figure 4b shows the response and reflectance peak positions of our GOs based humidity sensor with multicycle change humidity from RH 12%, 60%, to 86%. GO film sensor showed excellent durability and reversibility over nearly the entire humidity range. Thus, we can conclude that our GO sensor shows good performance when working under a relatively broad humidity range. It is also interesting to note that the thickness of GO film affects both the film color and humidity response (Figure S5), which will be reported elsewhere.

In summary, we reported that uniform GO thin film could be a new type of highly sensitive and fast colorimetric humidity sensor. The optical studies showed a linear relationship between the reflecting wavelengths and relative humidity. Importantly, the color change of GOs film is in the visible range, making the sensing process quite easy to be discriminated over the whole humidity range from dry to 98% by naked-eye without any sophisticated instrument. The mechanism studies showed that the humidity induced color change was attributed to the swelling of GOs film at higher relative humidity and the ultrafast sensing

was attributed to the superpermeability of GOs. The easy preparation, low cost, high sensitivity, and fast response of the GO-based humidity sensors provide a promising opportunity for the design of new humidity sensing systems for industry and domestic applications.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06883.

Materials, detailed experimental procedures, TEM of graphene oxide sheets, and SEM analysis of the GO film (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Chen, Z.; Lu, C. Humidity Sensors: A Review of Materials and Mechanisms. *Sens. Lett.* **2005**, *3*, 274–295.
- (2) Liu, J.; Sun, F.; Zhang, F.; Wang, Z.; Zhang, R.; Wang, C.; Qiu, S. *In situ* Growth of Continuous Thin Metal–organic Framework Film for Capacitive Humidity Sensing. *J. Mater. Chem.* **2011**, *21*, 3775–3778.
- (3) Kim, M.-J.; Gong, M.-S. Water-resistive Humidity Sensor Prepared by Printing Process Using Polyelectrolyte Ink Derived from New Monomer. *Analyst* **2012**, *137*, 1487–1494.
- (4) Li, Y.; Deng, C.; Yang, M. A Novel Surface Acoustic Wave-impedance Humidity Sensor Based on the Composite of Polyaniline and Poly(vinyl alcohol) with a Capability of Detecting Low Humidity. *Sens. Actuators, B* **2012**, *165*, 7–12.
- (5) Yu, H.; Xu, P.; Lee, D. W.; Li, X. Porous-layered Stack of Functionalized AuNP–rGO (Gold Nanoparticles–reduced Graphene Oxide) Nanosheets as a Sensing Material for the Micro-Gravimetric Detection of Chemical Vapor. *J. Mater. Chem. A* **2013**, *1*, 4444–4450.
- (6) Tian, E.; Wang, J.; Zheng, Y.; Song, Y.; Jiang, L.; Zhu, D. Colorful Humidity Sensitive Photonic Crystal Hydrogel. *J. Mater. Chem.* **2008**, *18*, 1116–1122.
- (7) Liu, Y. J.; Shi, J. J.; Zhang, F.; Liang, H. N.; Xu, J.; Lakhtakia, A.; Fonash, S. J.; Huang, T. J. High-speed Optical Humidity Sensors Based on Chiral Sculptured Thin Films. *Sens. Actuators, B* **2011**, *156*, 593–598.
- (8) Cheng, B.; Tian, B.; Xie, C.; Xiao, Y.; Lei, S. Highly Sensitive Humidity Sensor Based on Amorphous  $\text{Al}_2\text{O}_3$  Nanotubes. *J. Mater. Chem.* **2011**, *21*, 1907–1912.
- (9) Li, Z. Y.; Zhang, H. N.; Zheng, W.; Wang, W.; Huang, H. M.; Wang, C.; MacDiarmid, A. G.; Wei, Y. Highly Sensitive and Stable Humidity Nanosensors Based on LiCl Doped  $\text{TiO}_2$  Electrospun Nanofibers. *J. Am. Chem. Soc.* **2008**, *130*, 5036–5037.
- (10) Sahoo, P.; Oliveira, D. S.; Cotta, M. A.; Dash, S. D. S.; Tyagi, A. K.; Raj, B. Enhanced Surface Potential Variation on Nanoprotuberations of GaN Microbelt As a Probe for Humidity Sensing. *J. Phys. Chem. C* **2011**, *115*, 5863–5867.
- (11) Kuang, Q.; Lao, C.; Wang, Z. L.; Xie, Z.; Zheng, L. High-Sensitivity Humidity Sensor Based on a Single  $\text{SnO}_2$  Nanowire. *J. Am. Chem. Soc.* **2007**, *129*, 6070–6071.

(12) Liang, Q. C.; Xu, H. L.; Zhao, J. X.; Gao, S. Micro Humidity Sensors Based on ZnO–In<sub>2</sub>O<sub>3</sub> Thin Films with High Performances. *Sens. Actuators, B* **2012**, *165*, 76–81.

(13) Huang, J.; Tao, C.-A.; An, Q.; Lin, C.; Li, X.; Xu, D.; Wu, Y.; Li, X.; Shen, D.; Li, G. Visual Indication of Environmental Humidity by Using Poly(ionic liquid) Photonic Crystals. *Chem. Commun.* **2010**, *46*, 4103–4105.

(14) Pandey, R. K.; Hossain, M. D.; Moriyama, S.; Higuchi, M. Real-time Humidity-sensing Properties of Ionically Conductive Ni(II)-based Metallo-supramolecular Polymers. *J. Mater. Chem. A* **2014**, *2*, 7754–7758.

(15) Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Carbon Nanomaterials for Electronics, Optoelectronics, Photovoltaics, and Sensing. *Chem. Soc. Rev.* **2013**, *42*, 2824–2860.

(16) Saab, A. P.; Laub, M.; Srdanov, V. I.; Stucky, G. D. Oxidized Thin Films of C<sub>60</sub>: A New Humidity-Sensing Material. *Adv. Mater.* **1998**, *10*, 462–465.

(17) Zilberman, Y.; Ionescu, R.; Feng, X.; Müllen, K.; Haick, H. Nanoarray of Polycyclic Aromatic Hydrocarbons and Carbon Nanotubes for Accurate and Predictive Detection in Real-World Environmental Humidity. *ACS Nano* **2011**, *5*, 6743–6753.

(18) Mannoor, M. S.; Tao, H.; Clayton, J. D.; Sengupta, A.; Kaplan, D.; Naik, R. R.; Verma, N.; Omenetto, F. G.; McAlpine, M. C. Graphene-based Wireless Bacteria Detection on Tooth Enamel. *Nat. Commun.* **2012**, *3*, 763–781.

(19) Park, S. J.; Kwon, O. S.; Lee, S. H.; Song, H. S.; Park, T. H.; Jang, J. Solution-Gated Graphene Field Effect Transistors Integrated in Microfluidic Systems and Used for Flow Velocity Detection. *Nano Lett.* **2012**, *12*, 5082–5090.

(20) Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K. Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes. *Science* **2012**, *335*, 442–444.

(21) Wang, Z.; Xiao, Y.; Cui, X.; Cheng, P.; Wang, B.; Gao, Y.; Li, X.; Yang, T.; Zhang, T.; Lu, G. Humidity-Sensing Properties of Urchinlike CuO Nanostructures Modified by Reduced Graphene Oxide. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3888–3895.

(22) Bi, H. C.; Yin, K. B.; Xie, X.; Ji, J.; Wan, S.; Sun, L. T.; Terrones, M.; Dresselhaus, M. S. Ultrahigh Humidity Sensitivity of Graphene Oxide. *Sci. Rep.* **2013**, *3*, 2714.

(23) Borini, S.; White, R.; Wei, D.; Astley, M.; Haque, S.; Spigone, E.; Harris, N.; Kivioja, J.; Ryhänen, T. Ultrafast Graphene Oxide Humidity Sensors. *ACS Nano* **2013**, *7*, 11166–11173.

(24) Yuan, W.; Liu, A.; Huang, L.; Li, C.; Shi, G. High-performance NO<sub>2</sub> Sensors Based on Chemically Modified Graphene. *Adv. Mater.* **2013**, *25*, 766–771.

(25) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339–1339.

(26) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-based Composite Materials. *Nature* **2006**, *442*, 282–286.

(27) Buvailo, A.; Xing, Y.; Hines, J.; Borguet, E. Thin Polymer Film Based Rapid Surface Acoustic Wave Humidity Sensors. *Sens. Actuators, B* **2011**, *156*, 444–449.

(28) Farahani, H.; Wagiran, R.; Hamidon, M. N. Humidity Sensors Principle, Mechanism, and Fabrication Technologies: A Comprehensive Review. *Sensors* **2014**, *14*, 7881–7939.

(29) Medhekar, N. V.; Ramasubramaniam, A.; Ruoff, R. S.; Shenoy, V. B. Hydrogen Bond Networks in Graphene Oxide Composite Paper: Structure and Mechanical Properties. *ACS Nano* **2010**, *4*, 2300–2306.