



Research article

High-response room-temperature NO₂ gas sensor fabricated with thermally reduced graphene oxide-coated commercial cotton fabric

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ABSTRACT

Electronic textile-based gas sensors with a high response for NO₂ gas were fabricated using reduced graphene oxide (rGO)-coated commercial cotton fabric (rGOC). Graphene oxide (GO) was coated on cotton fabric by simply dipping the cotton into a GO solution. To investigate the relationship between the degree of reduction and the sensing response, the GO-coated fabrics were thermally reduced at various temperatures (190, 200, 300, and 400 °C). The change in the amount of oxygen functional groups on the rGOCs was observed by x-ray photoelectron spectroscopy, Raman spectroscopy, and x-ray diffraction patterns. The maximum sensing response of 45.90 % at 10 ppm of NO₂ gas at room temperature was exhibited by the rGOC treated at 190 °C, which was the lowest heat-treatment temperature. The high response comes from the greater amount of oxygen functional groups compared to other rGOC samples, and the tubular structure of the cotton.

1. Introduction

Interest in the real-time monitoring of harmful molecules has increased due to continuing efforts to monitor and address environmental pollution, and electronic textile (e-textile)-based gas sensors have attracted much attention for this application [1–7]. E-textiles not only have the inherent characteristics of textiles, being light weight, portable, flexible, with adaptable shapes but can also be electrically conducting. As a result, e-textiles are considered suitable for flexible, resistive gas sensors.

Among such applications, e-textile-based wearable NO₂ gas sensors using carbon nanotubes (CNTs) and graphene have been reported [8]. However, graphene and CNTs are presently not suitable for practical application, because of mass production difficulties, and relative cost-inefficiency [9]. In contrast, graphene oxide (GO) can be mass produced by Hummers' method. And because GO contains numerous oxygen functional groups (OFGs) including hydroxyl, epoxy groups, and carboxyl groups [10], it can also be easily attached to commercial textiles. GO also has a notable advantage for detecting NO₂ gas: the hydroxyl groups in GO are rotated to NO₂,

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which leads to a shorter distance between the carbon plane and NO₂ molecules. In addition, they have a large binding energy with NO₂ molecules via hydrogen bonds, compared to other functional groups [11].

To make the GO-coated textiles electrically conducting, a reduction process is used to remove the OFGs, which act as a potential barrier. Two methods, chemical reduction and thermal reduction, have usually been adopted for this process [9]. The chemical reduction approach has the merit of being faster than thermal reduction. However, it uses harmful chemicals such as HI and acetic acid, and these chemicals also generate heteroatomic impurities on GO. In contrast, the thermal reduction process is simple, and it's easy to control the remaining oxygen groups just by changing the annealing temperature and heating rates [12,13]. In previous studies, we synthesized NO₂ gas sensors with rGO-coated commercial silk using thermal reduction at different temperatures (400, 500, and 600 °C) and heating rates (1, 3, and 5 °C/min) [12,14]. We determined that there is a specific temperature and heating rate to use during thermal reduction to get an excellent response to NO₂ gas.

One of the commercial textiles, cotton, has an advantage in the gas sensor application because of its unique structure. A hollow canal called a lumen exists at the core of a cotton fiber [15]. This tubular structure can facilitate NO₂ detection because it provides a potentially large number of active sites compared to other textiles. However, cotton is unstable at high temperatures. Cotton starts to thermally degrade at about 200 °C [16,17]. Hence chemicals were used to reduce the GO in rGO-based cotton (rGOC) gas sensors [2–5]. The responses of those chemically reduced rGOC sensors to NO₂ gas were below 26 % in dry conditions [3], even though the maximum response was 38.07 % in 24 % humidity [4].

Here, we report an e-textile with a high response to NO₂ gas prepared with thermally reduced GO-coated cotton fabric. We found that the suitable reduction temperature for maximum response was 190 °C. The gas-sensing performance was investigated from 500 ppb to 10 ppm of NO₂ gas. The highest response was 45.90 % for 10 ppm of NO₂ when the rGOC was treated at 190 °C with a heating rate of 1 °C/min, rGOC190. (The samples were labeled according to their thermal reduction temperature, i.e., rGOC190 indicates rGOC prepared at 190 °C). This value was higher than the sensing responses of the rGO-silk thermally reduced at 400 °C with a heating rate of 1 °C/min (20.50 % for 10 ppm) [12] and a mesoporous ZnO/rGO hybrid sensor (38.07 % for 10 ppm) [4].

2. Materials and methods

2.1. Preparation of rGO-Cotton

GO was synthesized by the Hummers' method using graphite powder (99.9995 %, metals basis, Alfa Aesar). To make a 0.25 mg/ml GO solution, 75 mg of GO was dissolved in deionized water and sonicated for 3 h. Then, commercial cotton fabric was dipped in the GO solution for 30 min and dried in an oven for 1 h. This procedure was repeated three times to coat GO uniformly onto the cotton. The GO-coated cotton (GOC) was thermally treated at 190 °C with a 1 °C/min heating rate under N₂ conditions.

2.2. Characterization

The morphology of the sample was observed by normal scanning electron microscope (SEM) (XL30 ESEM, Philips, Netherlands).

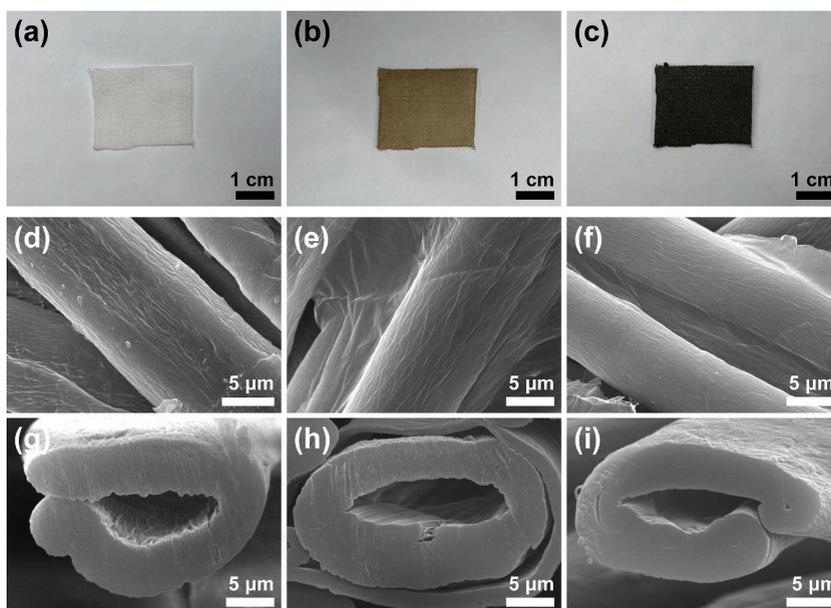


Fig. 1. Optical images of (a) cotton fabric, (b) GOC, and (c) rGOC190. SEM images of (d) cotton fabric, (e) GOC, and (f) rGOC190. SEM images of the cross-section of (g) cotton fabric, (h) GOC, and (i) rGOC190.

Chemical components were investigated using X-ray photoelectron spectroscopy (XPS) (PHI 5000 Versa Probe II, Chigasaki, Japan) with an Al-K α X-ray source. The structural characteristic was obtained by X-ray diffraction (XRD) (SmartLab, Rigaku, Japan) with Cu-K α radiation ($\lambda = 1.5412 \text{ \AA}$) with a range from 5° to 90° . Raman spectra (XperRF, Nanobase, Korea) were carried out using a 532 nm laser. Fourier-transform infrared (FT-IR) spectra were obtained by FT-IR (Vertex 80V, Hyperion2000, Bruker, USA).

2.3. Bending cycle test and gas sensing measurements

Bending-cycle tests were carried out using a homemade bending machine with KEITHLEY 6517A electrometer/high resistance meter. The resistance of the rGOC190 was measured during 5000 bending cycles with 10.0 V of bias voltage (Keithley Instruments, USA). Gas sensing measurements were obtained using a KEITHLEY 6517A electrometer/high resistance meter and a KEITHLEY 7001 switch system (Keithley Instruments, Ohio, USA). The rGOC190 sensor was contacted using the two-probe method, using gold wire with silver paste. The resistance of the sample was measured under 10.0 V of bias voltage at 20°C in dry condition. At first, we flowed air gas (N_2 79 %, O_2 21 %) 500 cc/min for 100 min. And then, the NO_2 environment was maintained for 30 min followed by a recovery process for 1 h. These procedures were repeated with NO_2 conditions from 500 ppb to 10 ppm. The response was defined as $S (\%) = (R_a - R_g)/R_a \times 100$, where R_a and R_g are the resistance in air and NO_2 conditions, respectively. The sample size was about $2.0 \text{ cm} \times 0.5 \text{ cm}$.

3. Results and discussion

GO was easily coated on the cotton by dipping without any adhesive materials, with bonding provided by electrostatic interaction, van der Waals' force, and hydrogen bonding with cotton [18,19]. The color of the cotton changed from white to brown due to the GO on its surface (Fig. 1a and b). After the thermal treatment even at 400°C , the cotton fabric did not decompose and the color changed to black (Fig. 1c and f), which was due to the coated GO. We focused on rGOC190 because it showed the best sensing performance, as will be discussed later. When GO was attached to the surface of the cotton fabric, wrinkles appeared not only on the cotton fiber but between the fibers (Fig. 1d and e). These remained after thermal reduction at 190°C (Fig. 1f). The XRD patterns and FT-IR spectroscopy also supported these results (Figs. S1 and S2, and Table S1, Supplementary material). In the SEM images, voids, known as lumen, were observed to exist at the center of the cotton fiber (Fig. 1g–i). It was possible to coat GO inside this tubular structure because the size of the GO used in this study was approximately 200 nm (Fig. S3, Supplementary material), which is much smaller than the tube size. This hollow structure in the cotton fiber provides more active sites for NO_2 molecules.

Fig. 2a shows the XPS C1s spectrum of pristine cotton. Cotton is composed of cellulose comprised of D-anhydroglucose units linked by β -1,4 glycosidic linkages. The hydroxyl groups (-OH) in cellulose can bond with adjacent hydroxymethyl groups (-CH $_2$ OH) through hydrogen bonds. The related peaks, which are C–C, C–OH, C–O–C, and C=O, appeared at 284.5, 286.06, 287.36, and 288.79 eV, respectively [20]. C=C bonds at 284.5 eV which were observed in the GOC, come from the sp^2 -carbon hexagonal structure of the GO (Fig. 2b).

After coating with GO, the amount of C elements increased a little bit (Fig. S4 and Table S2, Supplementary material). During the thermal reduction, the OFGs in GO were removed and the peak for sp^2 -carbon hexagonal structure was relatively enhanced (Fig. 2c). As a result, the ratio of C=C bonds in rGOC190 dramatically increased from 28.18 % to 67.25 %, and the full width at half maximum (FWHM) was sharpened, while the ratio of C–C bonds and oxygen-related components decreased.

Raman peaks for cellulose characteristics of cotton were clearly exhibited in the pristine cotton (Fig. S5, Supplementary material). After the GO coating, D and G bands appeared at 1324.5 and 1563.1 cm^{-1} , which originated from defects, disordered carbon structure, and the bond stretching of the sp^2 carbon structure, respectively (Fig. 3a) [21]. Subpeaks related to defects, D^* , D'' , and D' bands, were observed. The D^* band is induced by disordered graphitic lattices, provided by the sp^2 - sp^3 bonds at the edge. The D'' band is related to amorphous phases and the D' band is due to sp^3 hybridization [22,23]. When the GOC was thermally treated, the D and G bands were blue-shifted because of reduction (from 1324.47 cm^{-1} to 1308.9 cm^{-1} for the D band and from 1563.1 cm^{-1} to 1553.9 cm^{-1} for the G band, respectively, Fig. 3b). The I_D/I_G ratio decreased from 1.74 to 1.44 after the thermal reduction. The D^* and D'' bands also changed. Both the I_{D^*}/I_G (from 0.58 to 0.41) and $I_{D''}/I_G$ ratios (from 0.33 to 0.12) decreased after thermal reduction (Fig. 3c).

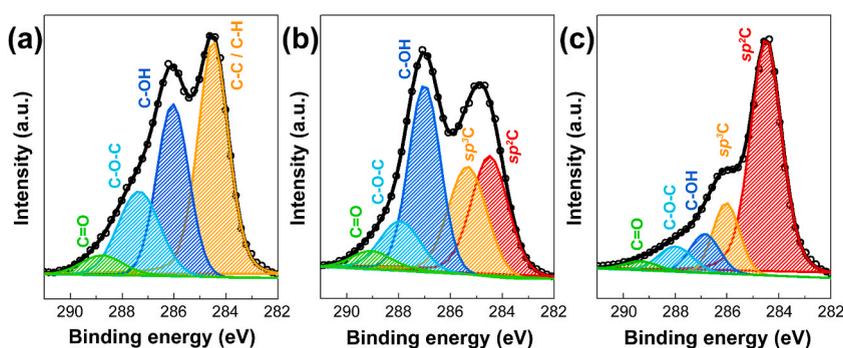


Fig. 2. XPS C1s spectra of (a) cotton, (b) GOC, and (c) rGOC190.

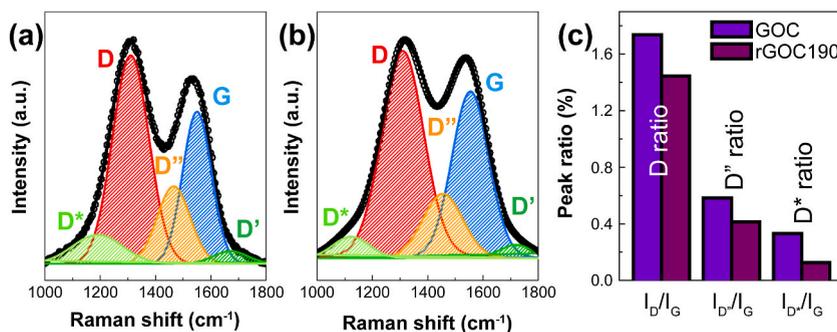


Fig. 3. Raman spectra of (a) GOC and (b) rGOC190. (c) The ratios of I_D/I_G , $I_{D''}/I_G$, and I_{D^*}/I_G of GOC and rGOC190.

Mechanical durability and electrical stability during bending are essential factors for a flexible gas sensor. To confirm these properties in rGOC190, we performed a 5000-cycle bending test as shown in Fig. 4a. The resistance (R_0) of rGOC190 was 19 M Ω . The response S was less than 1 % even after 5000-cycles of bending and stretching. This indicates that the structure and electrical properties of rGOC190 remained even after applying physical stimuli such as bending and stretching. The flexibility of rGOC was also investigated using twisting and grabbing rGOC190. The rGOC190 had structural stability even under twisting (Fig. 4b) and repeated grabbing (Movie S1). This shows that the flexibility of rGOC190 is comparable to pure cotton (Movie S1). Based on these results, it is expected that rGOC190 is suitable for use in flexible NO₂ gas sensors.

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NO₂ molecules withdraw an electron from the rGO, which has p-type semiconducting behavior, generating holes in the rGO [1–7]. As a result, the electrical resistance of the rGO decreases. We prepared rGOCs reduced at different temperatures (190, 200, 300, and 400 °C). The change in the resistance of rGOC190 during exposure to various concentrations of NO₂ gas under dry conditions at 20 °C is shown in Fig. 5a (The sensing response of rGOC190 at 60 °C is displayed in Fig. S7, Supplementary material). When rGOC190 was exposed to NO₂ gas, the resistance decreased, and then the resistance recovered to the initial condition under dry air. As the NO₂ concentration increased, the resistance decreased. Fig. 5b shows the response of rGOCs to different concentrations of NO₂ gas under the same conditions. We found that the response increased as the thermal reduction temperature decreased. For example, the response was 9.5 % for rGOC400 but it increased up to 45.9 % for rGOC190. The gas sensing responses were 24.77 % at 0.5 ppm and 45.90 % at 10 ppm of NO₂ gas. In other words, it exhibited a superior NO₂ gas sensing response not only at the ppm level but also at low concentrations (ppb level). This value was 25.5 % and 19.9 % higher than our previous research with rGO-coated silk fabric [12], and than rGOC sensors reduced by chemicals [3], respectively. Moreover, the observed response of rGOC190 is the highest reported response among commercial textile-based gas sensors without any functionalization to the best of our knowledge. This performance was achieved by a low concentration GO solution and low thermal reduction temperature as well as the unique structure of cotton. The tubular structure of cotton fibers can effectively detect NO₂ gas molecules because it provides a large number of active sites compared to other textiles as mentioned before. In previous research, we used a 1.0 mg/ml GO solution and thermal reduction at 400 °C with a heating rate of 1 °C/min, which was a denser GO solution and higher reduction temperature than were used in this study. At a high GO concentration, GO is thickly stacked on the cotton fabric, and NO₂ molecules cannot penetrate rapidly to the inner space of the GO [24]. In addition, the amount of OFGs decreased more at higher temperatures, resulting in a decrease in active sites. This results in relatively lower sensitivity.

Fig. 5c compares the NO₂ sensing performance before and after bending rGOC190 (Fig. S8, Supplementary material). After bending, the NO₂ sensing property was found to be similar to before bending, until 2.5 ppm of NO₂ gas. From 5.0 ppm, a larger

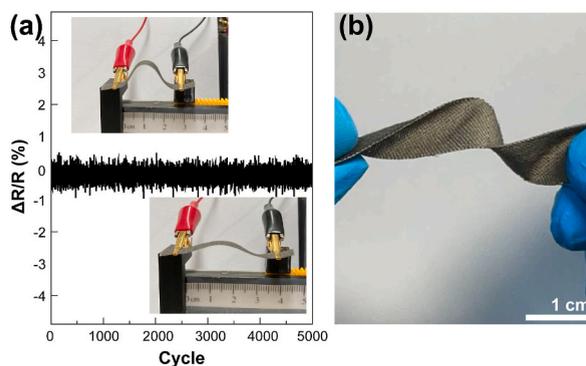


Fig. 4. (a) Resistance variation of rGOC190 during 5000 bending cycles. The upper and lower images in the inset show the stretched and bent rGOC190. (b) The optical image of twisted rGOC190.

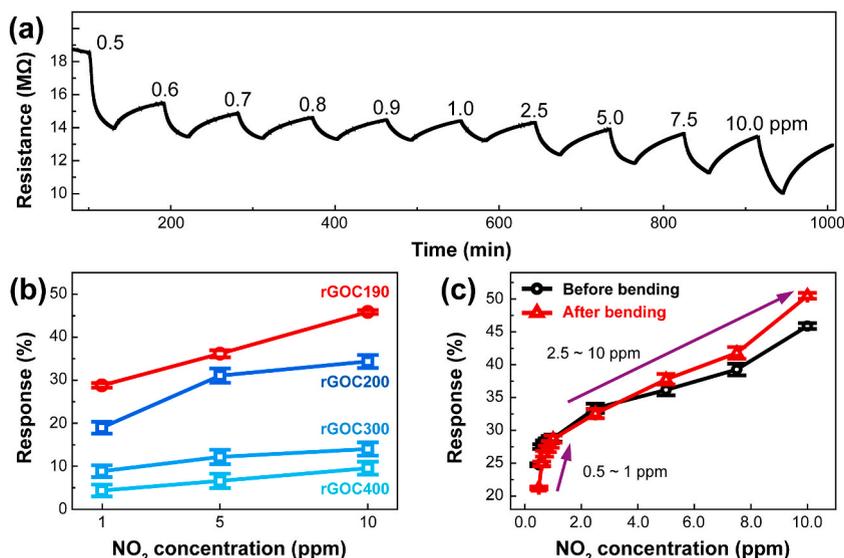


Fig. 5. (a) The resistance variation of rGOC190 exposed to 500 ppb–10 ppm of NO₂ gas. (b) Responses of rGOCs reduced at different temperatures. (c) Comparison of sensing response before and after bending (black circle: before bending, red triangle: after bending). The blank test is shown in Fig. S6. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

response was observed, compared to the response of the unbent sensors. The maximum response of bent rGOC190 was only 50.47 % at 10 ppm of NO₂. The enhanced response is considered to originate from the tubular structure of the cotton. Generally, the gas molecules travel in a laminar flow on the flat surface, but this laminar flow is broken at bent regions inside the tube due to the collision of gas molecules. Therefore, a relatively large number of the molecules interact with the surface of a bent region in the hollow structure of cotton. In this study, we found that this effect occurred with 5.0 ppm of NO₂ gas. Table 1 shows the sensing response, sensing conditions, sensing temperature, and synthesis method of rGO-coated textile sensors. The best sensing response is shown in rGOC190 except the functionalized sensors with organic materials [2] and MoS₂ [6]. This indicates that the low-temperature thermal reduction in this work seems to be important for the high response. In addition, the structural change of rGOC190 was investigated before and after the gas sensing process with XPS and FT-IR (Figs. S9 and S10, Supplementary material) to show the reusability. Although there was no structural change after the sensing process, the response time, recovery time, and repeatability need to be improved (Fig. S11, Supplementary material) and addressed in further studies.

We also measured the response of rGOC190 with NO, CO, and SO₂ gas using the same conditions as NO₂ and the responses were plotted with that of NO₂ to compare the sensing performance (Fig. 6a). The resistances of rGOCs decreased when rGOCs were exposed to all gases. For CO and SO₂, the response was only half of the response to NO₂ gas. Interestingly, many studies have reported that rGO without additional materials has no response to SO₂ molecules but the response of rGOC190 is 22.06 % at 10 ppm of SO₂ gas. This could be due to the numerous OFGs remaining after the low-temperature thermal reduction. It has been reported that the adsorption energy of SO₂ increased when the degree of oxidation of the carbon basal plane increased. In particular, hydroxyl groups can enhance the charge transfer from the carbon basal plane to SO₂ [25]. For NO, the response reached up to 48.4 % for 10 ppm of NO gas. This value is larger than the response for NO₂ gas and than the previous report [26]. However, the sensing response at the low concentration of NO gas is much lower than the response for NO₂ gas.

In addition, the relative humidity (RH)-dependent resistance of rGOC190 was provided (Fig. 6b). At low RH (below 60 %), the hopping distance was increased by the swelling effect caused by the physisorbed water molecules. Hence, the resistance of rGOC190 increased. In contrast, the absorbed water molecules were ionized, generating hydronium ions (H₃O⁺) which act as charge carriers. This ionic conductivity lowered resistance at high RH [27–30]. We also investigated the NO₂ gas sensing response of rGOC190 under various humid conditions, 20, 40, 60, and 70 % RHs (Fig. 6c). At 20 and 40 % RHs, the responses were about 20 % for 10 ppm of NO₂ gas. It was ascribed by a resistance increase below 60 % RH as shown in Fig. 6b. The response reached 30.18 % for 10 ppm of NO₂ gas under 60 % RH. Although the variation of the response was smaller than that under dry conditions, the response increased as NO₂ gas concentration increased until 60 % RH. However, the response was almost constant from 1.0 to 10 ppm at 70 % RH. The results show that the competition between the response to water molecules and NO₂ molecules determines the gas-sensing property rGOC190 and rGOC190 is inappropriate for NO₂ sensors under humid conditions.

4. Conclusions

NO₂ gas sensing responses of 45.90 % and 50.47 % were respectively obtained with unbent and bent rGOC190. This gas-sensing performance is superior to the performance previously reported using textile-based NO₂ sensors. Based on systematic heat treatment and structural investigations with XPS, Raman spectroscopy, and XRD, the high response of rGOC190 could be attributed to the large

Table 1The response of the rGO-based e-textiles NO₂ sensors.

	Sensing Material	GO coating method (adhesive material)	Synthesis Method (chemical agent and reduction temperature)	Concentration (ppm)	Response (%)	NO ₂ Expose Time	RH (%)	Temp. (°C)	Ref.
Cotton yarn	rGO	Dipping	Chemical Reduction (Hydrazine)	3	25	300 s	25	R.T.	[2]
	HFBA-GO		Functionalized with organic materials		45				
	MPP-GO				55				
	KBIP-GO				65				
Cotton yarn	rGO	BSA	Chemical reduction (HI, acetic acid, NaHCO ₃)	0.45	6	30 min	45	R.T.	[6]
				2.5	~20				
	rGO/MoS ₂		Chemical reduction (HI, acetic acid, NaHCO ₃)	0.45	28		45		
			Dipping MoS ₂ solution	2.5	40				
				4.5	25		Dry		
					48		45		
					40		80		
Cotton yarn	rGO	BSA	Chemical reduction (HI, acetic acid, NaHCO ₃)	1.25	~12	30 min	–	R.T.	[5]
Polyester yarn									
Cotton thread	rGO/ZnO NSs	APTES	Synthesize ZnO NWs (ZnO powder, NaOH) Chemical reduction (Hydrazine, Ammonia)	15	44	~140 s	Dry	~23	[3]
Cotton/spandex fabric	rGO/Pd–ZnO NRs/ AgNWs	Dipping	Synthesize AgNWs (AgNO ₃ , CuCl ₂ , PVP) Synthesize ZnO NRs (Zn(NO ₃) ₂ •6H ₂ O, HMTA) PdNP decorated-ZnO NRs (PVP, Na ₂ PdCl ₄) Chemical reduction (Hydrazine)	100	12	~600 s	Dry	R.T.	[31]
Cotton yarn	rGO	Dopamine	Chemical reduction (HI, acetic acid, NaHCO ₃)	100	46	15 min	24	23	[4]
Polyester sheet	rGO	Dopamine	Chemical reduction (HI, acetic acid, NaHCO ₃)	100	36.01 ± 0.63	4 min	20	19	[32]
Spandex/ polyester yarn	rGO	BSA	Chemical reduction (HI, acetic acid, NaHCO ₃)	10	~60 ~30	30 min	Wet Dry	R.T.	[33]
Nylon6 mesh fabric	rGO	BSA	Chemical reduction (HI, acetic acid, NaHCO ₃)	8	26.5	30 min	80	R.T.	[1]
Nylon fiber	rGO/ZnO QDs	Dipping	Thermal reduction (800 °C, 10 °C/min) Synthesize ZnO QDs (Zn(CH ₃ COO) ₂ •2H ₂ O, KOH, anhydrous methanol)	100	49.6	~4 min	–	R.T.	[34]
Silk fabric (satin)	rGO	Dipping	Thermal reduction (400 °C, multi-step)	10	10	30 min	Dry	27	[14]
Silk fabric (satin)	rGO	Dipping	Thermal reduction (400 °C, 1 °C/min)	10	20.4	30 min	Dry	25	[12]
Cotton fabric	rGO	Dipping	Thermal reduction (190 °C, 1 °C/min)	10	45.9	30 min	Dry	20	This work

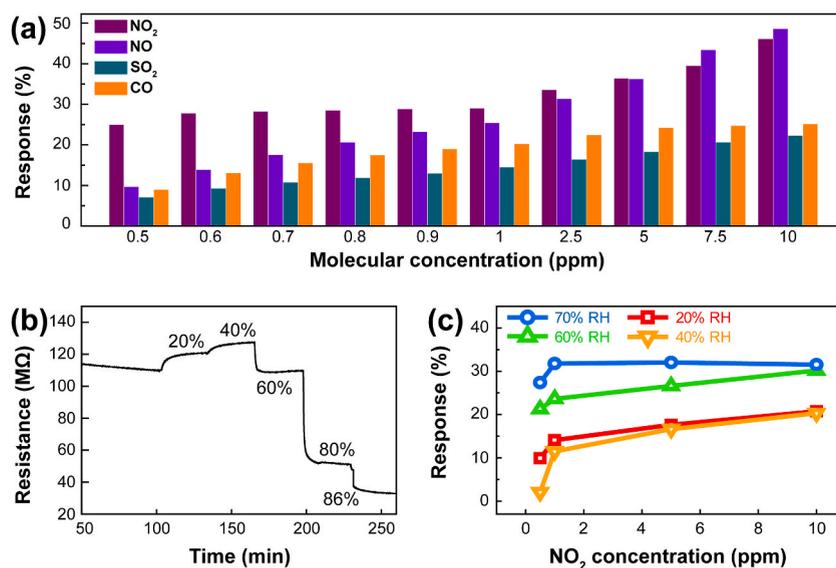


Fig. 6. (a) The gas sensing responses for NO₂, NO, CO, and SO₂. (b) The relative humidity-dependent resistance. (c) NO₂ sensing response under various RH.

amount of oxygen functional groups, as well as the tubular structure of the cotton fibers. Based on the results of this study, we expect that cotton-based e-textiles prepared with low-concentration GO solution and fabricated at low reduction temperature can be a promising wearable NO₂ gas sensor.

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This research received no external financial or non-financial support.

Relationships

There are no additional relationships to disclose.

Patents and intellectual property

There are no patents to disclose.

Other activities

There are no additional activities to disclose.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Won Taek Jung: Writing - original draft, Methodology, Investigation, Formal analysis, Data curation. **Hyun-Seok Jang:** Writing - original draft, Methodology, Investigation, Formal analysis, Data curation. **Sang Moon Lee:** Methodology, Formal analysis, Data curation. **Won G. Hong:** Methodology, Investigation, Formal analysis, Data curation. **Young Jin Bae:** Methodology, Data curation. **Hyo Seon Lee:** Methodology, Data curation. **Byung Hoon Kim:** Writing - review & editing, Writing - original draft, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors have declared no conflict of interest

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e24425>.

References

- [1] H.J. Park, W.-J. Kim, H.-K. Lee, D.-S. Lee, J.-H. Shin, Y. Jun, Y.J. Yun, Highly flexible, mechanically stable, and sensitive NO₂ gas sensors based on reduced graphene oxide nanofibrous mesh fabric for flexible electronics, *Sens. Actuators B-Chem.* 257 (2018) 846–852, <https://doi.org/10.1016/j.snb.2017.11.032>.
- [2] M.-A. Kang, S. Ji, S. Kim, C.-Y. Park, S. Myung, W. Song, S.S. Lee, J. Lim, K.-S. An, Highly sensitive and wearable gas sensors consisting of chemically functionalized graphene oxide assembled on cotton yarn, *RSC Adv.* 8 (2018) 11991–11996, <https://doi.org/10.1039/C8RA01184B>.
- [3] W. Li, R. Chen, W. Qi, L. Cai, Y. Sun, M. Sun, C. Li, X. Yang, L. Xiang, D. Xie, T. Ren, Reduced graphene oxide/mesoporous ZnO NSs hybrid fibers for flexible, stretchable, twisted, and wearable NO₂ e-textile gas sensor, *ACS Sens.* 4 (2019) 2809–2818, <https://doi.org/10.1021/acssensors.9b01509>.
- [4] S.W. Lee, H.G. Jung, I. Kim, D. Lee, W. Kim, S.H. Kim, J.-H. Lee, J. Park, J.H. Lee, G. Lee, D.S. Yoon, Highly conductive and flexible dopamine-graphene hybrid electronic textile yarn for sensitive and selective NO₂ detection, *ACS Appl. Mater. Interfaces* 12 (2020) 46629–46638, <https://doi.org/10.1021/acscami.0c11435>.
- [5] Y.J. Yun, W.G. Hong, N.-J. Choi, B.H. Kim, Y. Jun, H.-K. Lee, Ultrasensitive and highly selective graphene-based single yarn for use in wearable gas sensor, *Sci. Rep.* 5 (2015) 10904, <https://doi.org/10.1038/srep10904>.
- [6] Y.J. Yun, W.G. Hong, D.Y. Kim, H.J. Kim, Y. Jun, H.-K. Lee, E-textile gas sensors composed of molybdenum disulfide and reduced graphene oxide for high response and reliability, *Sens. Actuators B-chem.* 248 (2017) 829–835, <https://doi.org/10.1016/j.snb.2016.12.028>.
- [7] E. Singh, M. Meyyappan, H.S. Nalwa, Flexible graphene-based wearable gas and chemical sensors, *ACS Appl. Mater. Interfaces* 9 (2017) 34544–34586, <https://doi.org/10.1021/acscami.7b07063>.
- [8] Z. Xiao, L.B. Kong, S. Ruan, X. Li, S. Yu, X. Li, Y. Jiang, Z. Yao, S. Ye, C. Wang, T. Zhang, K. Zhou, S. Li, Recent development in nanocarbon materials for gas sensor applications, *Sens. Actuators B-Chem.* 274 (2018) 235–367, <https://doi.org/10.1016/j.snb.2018.07.040>.
- [9] K.K.H. De Silva, H.-H. Huang, R. Joshi, M. Yoshimura, Restoration of the graphitic structure by defect repair during the thermal reduction of graphene oxide, *Carbon* 166 (2020) 74–90, <https://doi.org/10.1016/j.carbon.2020.05.015>.
- [10] W.S. Hummers Jr., R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339, <https://doi.org/10.1021/ja01539a017>.
- [11] Y.R. Choi, Y.-G. Yoon, K.S. Choi, J.H. Kang, Y.-S. Shim, Y.H. Kim, H.J. Chang, J.-H. Lee, C.R. Park, S.Y. Kim, H.W. Jang, Role of oxygen functional groups in graphene oxide for reversible room-temperature NO₂ sensing, *Carbon* 91 (2015) 178–187, <https://doi.org/10.1016/j.carbon.2015.04.082>.
- [12] W.T. Jung, H.-S. Jang, J.W. Jeon, B.H. Kim, Effect of oxygen functional groups in reduced graphene oxide-coated silk electronic textiles for enhancement of NO₂ gas-sensing performance, *ACS Omega* 6 (2021) 27080–27088, <https://doi.org/10.1021/acscomega.1c03658>.
- [13] S.J. Yang, T. Kim, H. Jung, C.R. Park, The effect of heating rate on porosity production during the low temperature reduction of graphite oxide, *Carbon* 53 (2013) 73–80, <https://doi.org/10.1016/j.carbon.2012.10.032>.
- [14] W.T. Jung, J.W. Jeon, H.-S. Jang, D.Y. Kim, H.-K. Lee, B.H. Kim, Commercial silk-based electronic textiles for NO₂ sensing, *Sens. Actuators B-Chem.* 307 (2020) 127596, <https://doi.org/10.1016/j.snb.2019.127596>.
- [15] A. Chithra, P. Wilson, S. Vijayan, R. Rajeev, K. Prabhakaran, Thermally insulating robust carbon composite foams with high EMI shielding from natural cotton, *J. Mater. Sci. Technol.* 94 (2021) 113–122, <https://doi.org/10.1016/j.jmst.2021.02.064>.
- [16] S. Basak, K.K. Samanta, S.K. Chattopadhyay, Fire retardant property of cotton fabric treated with herbal extract, *J. Text. Inst.* 106 (12) (2015) 1338–1347, <https://doi.org/10.1080/00405000.2014.995456>.
- [17] Z. Xia, C. Yao, J. Zhou, W. Ye, W. Xu, Comparative study of cotton, ramie and wool fiber bundles' thermal and dynamic mechanical thermal properties, *Textil. Res. J.* 86 (8) (2016) 856–867, <https://doi.org/10.1177/0040517515596937>.
- [18] L.-L. Xu, M.-X. Guo, S. Liu, S.-W. Bian, Graphene/cotton composite fabrics as flexible electrode materials for electrochemical capacitors, *RSC Adv.* 5 (2015) 25244–25299, <https://doi.org/10.1039/C4RA16063K>.
- [19] B.B. Etana, S. Ramakrishnan, M. Dhakshnamoorthy, S. Saravanan, P.C. Ramamurthy, T.A. Demissie, Functionalization of textile cotton fabric with reduced graphene oxide/MnO₂/polyaniline based electrode for supercapacitor, *Mater. Res. Express* 6 (2019) 125708, <https://doi.org/10.1088/2053-1591/ab669d>.
- [20] Y. Li, Y. Zhang, C. Zou, J. Shao, Study of plasma-induced graft polymerization of stearyl methacrylate on cotton fabric substrates, *Appl. Surf. Sci.* 357 (2015) 2327–2332, <https://doi.org/10.1016/j.apsusc.2015.09.236>.
- [21] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in graphene, *Phys. Rep.* 473 (2009) 51–87, <https://doi.org/10.1016/j.physrep.2009.02.003>.
- [22] D. López-Díaz, M.L. Holgado, J.L. García-Fierro, M.M. Velázquez, Evolution of the Raman spectrum with the chemical composition of graphene oxide, *J. Phys. Chem. C* 121 (2017) 20489–20497, <https://doi.org/10.1021/acs.jpcc.7b06236>.
- [23] S. Claramunt, A. Varea, D. López-Díaz, M.M. Velázquez, A. Cornet, A. Cirera, The importance of interbands on the interpretation of the Raman spectrum of graphene oxide, *J. Phys. Chem. C* 119 (2015) 10123–10129, <https://doi.org/10.1021/acs.jpcc.5b01590>.
- [24] Y. Wang, L. Zhang, N. Hu, Y. Wang, Y. Zhang, Z. Zhou, Y. Liu, S. Shen, C. Peng, Ammonia gas sensors based on chemically reduced graphene oxide sheets self-assembled on Au electrodes, *Nanoscale Res. Lett.* 9 (2014) 251, <https://doi.org/10.1186/1556-276X-9-251>.
- [25] H. Zhang, W. Cen, J. Liu, J. Guo, H. Yin, P. Ning, Adsorption and oxidation of SO₂ by graphene oxide: a van der Waals density functional theory study, *Appl. Surf. Sci.* 324 (2015) 61–67, <https://doi.org/10.1016/j.apsusc.2014.10.087>.
- [26] W. Li, X. Geng, Y. Guo, J. Rong, Y. Gong, L. Wu, X. Zhang, P. Li, J. Xu, G. Cheng, M. Sun, L. Liu, Reduced graphene oxide electrically contacted graphene sensor for highly sensitive nitric oxide detection, *ACS Nano* 5 (2011) 6955–6961, <https://doi.org/10.1021/nn201433r>.
- [27] N. Agmon, The Grothuss mechanism, *Chem. Phys. Lett.* 244 (1995) 456–462, [https://doi.org/10.1016/0009-2614\(95\)00905-J](https://doi.org/10.1016/0009-2614(95)00905-J).
- [28] A.A. Haidry, Z. Wang, Q. Fatima, A. Zavabeti, L. Xie, H. Zhu, Z. Li, Thermally reduced graphene oxide showing n- to p-type electrical response inversion with water adsorption, *Appl. Surf. Sci.* 531 (2020) 147285, <https://doi.org/10.1016/j.apsusc.2020.147285>.
- [29] D. Zhang, J. Tong, B. Xia, Humidity-sensing properties of chemically reduced graphene oxide/polymer nanocomposite film sensor based on layer-by-layer nano self-assembly, *Sens. Actuators B-Chem.* 197 (2014) 66–72, <https://doi.org/10.1016/j.snb.2014.02.078>.
- [30] H. Bi, K. Yin, X. Xie, J. Ji, S. Wan, L. Sun, M. Terrones, M.S. Dresselhaus, Ultrahigh humidity sensitivity of graphene oxide, *Sci. Rep.* 3 (2013) 2714, <https://doi.org/10.1038/srep02714>.
- [31] T.H.P. Doan, Q.T.H. Ta, A. Sreedhar, N.T. Hang, W. Yang, J.-S. Noh, Highly deformable fabric gas sensors integrating multidimensional functional nanostructures, *ACS Sens.* 5 (2020) 2255–2262, <https://doi.org/10.1021/acssensors.0c01083>.

- [32] S.W. Lee, H.G. Jung, J.W. Jang, D. Park, D. Lee, I. Kim, Y. Kim, D.Y. Cheong, K.S. Hwang, G. Lee, D.S. Yoon, Graphene-based electronic textile sheet for highly sensitive detection of NO₂ and NH₃, *Sens. Actuators B-Chem.* 345 (2021) 130361, <https://doi.org/10.1016/j.snb.2021.130361>.
- [33] Y.J. Yun, D.Y. Kim, W.G. Hong, D.H. Ha, Y. Jun, H.-K. Lee, Highly stretchable, mechanically stable, and wearable reduced graphene oxide yarn with high NO₂ sensitivity for wearable gas sensors, *RSC Adv.* 8 (2018) 7615–7621, <https://doi.org/10.1039/C7RA12760J>.
- [34] Q. Lin, F. Zhang, N. Zhao, L. Zhao, Z. Wang, P. Yang, D. Lu, T. Dong, Z. Jiang, A flexible and wearable Nylon fiber sensor modified by reduced graphene oxide and ZnO Quantum Dots for wide-range NO₂ gas detection at room temperature, *Materials* 15 (2022) 3772, <https://doi.org/10.3390/ma15113772>.