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Paper-based disposable molecular sensor constructed from oxide nanowires, cellulose nanofibers, and pencil-drawn electrodes

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Keywords

Cellulose nanofiber, Oxide nanowire, Nanocomposite, NO₂ sensor, Paper electronics

Abstract

Progress toward the concept of “a trillion sensor universe” requires sensor devices to become more abundant, ubiquitous, and be potentially disposable. Here, we report a paper-based disposable molecular sensor device constructed from a nanowire sensor based on common zinc oxide (ZnO), a wood-derived biodegradable cellulose nanofiber paper substrate, and a low-cost graphite electrode. The ZnO nanowire/cellulose nanofiber composite structure is embedded in the surface of the cellulose nanofiber paper substrate via a two-step papermaking process. This structure provides a mechanically robust and efficiently bridged network for the nanowire sensor, while ensuring efficient access to target molecules and allowing reliable electrical contact with electrodes. The as-fabricated paper sensor device with pencil-drawn graphite electrodes exhibits efficient resistance change-based molecular sensing of NO₂ as a model gas. The performance of our device is comparable to that of noble metal electrodes. Furthermore, we demonstrate cut-and-paste usability and easy disposal of the sensor device with its uniform in-plane sensing properties. Our strategy offers a disposable molecular sensing platform for use in future sensor network technologies.

Introduction

The recent rapid growth of the Internet of Things (IoT) has generated considerable interest in sensor technologies.^{1,2} Global usage of sensor devices is estimated to reach more than one trillion units per year by 2022.³ In particular, molecular sensing has become a core technology of the IoT, because it offers a powerful tool for generating data to be used in a wide range of fields such as healthcare, environmental monitoring, and industrial safety.^{2,4} The collection of molecular information by sensors will open a new platform for generating chemical “big data” within a trillion-sensor society. To collect accurate molecular information over long periods, reliable molecular sensing approaches are required.

To effectively detect volatile molecules, various types of molecular sensors such as polymer-based chemiresistor sensors,⁵ two-dimensional nanosheet sensors,⁶ and inorganic nanomaterial-based sensors⁷ have been demonstrated. Among these, semiconducting metal oxides show promise from the viewpoint of long-term molecular sensing owing to their thermal/chemical stability in air.⁸ The sensing mechanism of conventional metal oxide sensors is mainly based on changes in the electric potential at grain-boundaries upon exposure to target molecules. However, such mechanisms frequently suffer from deteriorated sensing performances owing to contamination of grain-boundaries during long-term use.^{9,10} Disposable sensor devices might effectively overcome the problem of deteriorating device performance in long-term use. A sensor component suitable for single- or short-term use, could be easily replaced with a fresh component before it deteriorates. Such sensor devices are required to not only be disposable but should also be lightweight, inexpensive, and mechanically robust to handling. These features cannot be achieved in conventional powder-formed metal oxide sensors equipped with precious metal electrodes.¹¹

In this study, we propose a disposable sensor device constructed from a cellulose nanofiber

paper substrate, a zinc oxide (ZnO) nanowire sensor, and a graphite electrode. Cellulose nanofiber paper is expected to be beneficial for disposable sensors, because it is lightweight, thermally/mechanically robust and made from abundant and renewable biomass resources.^{12,13} In previous studies, various cellulose nanofiber paper-based electronic devices, such as transparent conductive films,^{14,15} transistors,^{16,17} antennas,^{18,19} memory,^{20,21} generators,²² and electronic paper²³ have been developed. Such paper-based devices show high performance, paper-like flexibility, and biodegradability.^{24,25} For sensing materials, single crystalline nanowires of highly abundant metal oxides (e.g., ZnO and CuO) have shown great promise as molecular sensors, owing to their large surface/volume ratios and well-defined crystal planes, wide controllability of chemical reactivity by altering the metal ions,^{26–28} and high mechanical robustness.²⁹ Graphite is also suitable as a disposable electrode for molecular sensors because of its low-cost and high stability in air.

From this perspective, the integration of an oxide nanowire sensor, a cellulose nanofiber paper substrate, and a graphite electrode represents a reasonable approach to disposable molecular sensor devices. However, conventional strategies, such as the encapsulation of nanowires or drop casting of nanowires into/onto cellulose nanofiber paper, are unsuitable for molecular sensors, because analytes are not accessible to the oxide nanowires or the nanowires easily peel off from the substrate. One essential requirement is strongly adhered networks of oxide nanowire sensors on the surfaces of the cellulose nanofiber paper substrate. To meet these requirements, here, we tailored robust nanowire/cellulose nanofiber composite networks, which are implanted on the surfaces of cellulose nanofiber paper substrates, by a two-step papermaking process. The as-implanted ZnO nanowires provide strongly adhesive and efficiently bridged network structures on the substrate surface, and enable reliable electrical contact with graphite electrodes (Figure 1). The as-fabricated paper device showed effective molecular sensing performance for nitrogen

oxide (NO_2) as a model gas component. The performance of our device was comparable to that of Pt electrode-based systems. The paper-like cut-and-paste usability of the sensor device with an in-plane uniformity of the sensing property was also demonstrated, suggesting potential for application as disposable and ubiquitous molecular sensor elements.

Results and Discussion

In this study, the sensing material was hydrothermally synthesized single crystalline ZnO nanowires with widths and lengths of approximately 100 nm and 6 μm , respectively (see Supporting Information Figure S1).³⁰ We first investigated the robust integration of the ZnO nanowires with the substrate materials. When the ZnO nanowires were drop-coated on to a conventional substrate, i.e., polyethylene terephthalate (PET) film, they were easily peeled off by a finger touch, even after a hot-pressing treatment at 110 $^{\circ}\text{C}$ for 1 h under high pressure (8.5 MPa) (Figure 2a and d). The adhesion of the ZnO nanowires was improved with the use of the cellulose nanofiber paper substrate (Figure 2b) and the ZnO nanowires adhered to the cellulose nanofiber paper substrate much better than to the PET film substrate. However, a small amount of ZnO nanowires was removed by a finger touch. Thus, simply coating the ZnO nanowires onto the substrate did not result in strong adhesion. To overcome this problem, we deposited the ZnO nanowire/cellulose nanofiber composite networks onto the cellulose nanofiber paper substrate by a two-step papermaking process, as follows (see Supporting Information Figure S2). First, an aqueous dispersion of wood cellulose nanofibers with widths 15–50 nm was filtered through a commercial membrane filter to form a wet cellulose nanofiber gel. Second, an aqueous dispersion of ZnO nanowires with cellulose nanofibers was poured onto the wet nanofiber gel, followed by dewatering under pressure filtration. During the second process, the wet nanofiber gel served as a filter, retaining almost all the ZnO nanowires on the surface. Finally, the resulting wet material

was thoroughly dried by hot pressing at 110 °C for 1 h (8.5 MPa) and then peeled from the membrane filter to form a sheet of paper. The as-prepared ZnO nanowire/cellulose nanofiber composite networks on the cellulose nanofiber paper, denoted as ZnO nanowire@cellulose nanofiber paper, were sufficiently adhesive to withstand finger touch (Figure 2c and e). We attribute this stability to the entanglement of ZnO nanowires and cellulose nanofibers on the surfaces of the cellulose nanofiber paper substrate (Figure 3a and b). Atomic absorption analysis confirmed that the ZnO content in the ZnO nanowire@cellulose nanofiber paper was ca. 5.5 wt%. Thus, our approach is expected as an effective way to construct mechanically robust ZnO nanowire networks on cellulose nanofiber paper substrates.

Formation of a ZnO nanowire network on the substrate surface is also important to ensure efficient molecular sensing response (i.e., a detectable change in the electrical resistance upon adsorption/desorption of analytes). The network can offer additional modulation to the sensor resistance owing to the potential barrier at the nanowire/nanowire junctions as well as the surfaces of individual nanowires.³¹ Field-emission scanning electron microscope (FE-SEM) and energy dispersive X-ray spectrometry (EDX) images of the surface and a cross section of the ZnO nanowire@cellulose nanofiber paper are shown in Figure 3c-f. The EDX Zn element mapping images show that the ZnO nanowires were well-dispersed and implanted over the whole surface of the cellulose nanofiber paper substrate (see also Supporting Information Figures S3 and S4). The cellulose nanofiber paper without ZnO nanowires showed a surface resistance as high as $10^{14} \Omega \text{ square}^{-1}$ owing to the high electrical insulation properties of the cellulose nanofibers.²⁵ The ZnO nanowire@cellulose nanofiber paper exhibited a relatively low surface resistance of approximately $1.0 \times 10^8 \Omega \text{ square}^{-1}$ under atmospheric conditions. These results indicated successful formation of efficiently bridged networks of ZnO nanowires in the cellulose nanofiber paper substrate. When an aqueous mixture of ZnO nanowires and cellulose nanofibers

was introduced into the paper by a one-step papermaking process, most of the ZnO nanowires were buried inside the cellulose nanofiber matrix, leading to difficulty in forming a nanowire-bridging structure on the cellulose nanofiber paper (see Supporting Information Figure S5). Thus, the ZnO nanowire@cellulose nanofiber paper with a dual-layered structure (Figure 3), which was prepared by a two-step papermaking approach (Figure S2), provided a robust nanowire-bridging structure over its entire surface.

The ZnO nanowire@cellulose nanofiber paper was used as a molecular sensing platform for NO₂ as a model gas component. When the n-type ZnO semiconductor is exposed to an oxidizing gas such as NO₂, gas molecules adsorb to the ZnO surface and extract electrons from the conduction band of ZnO, leading to the formation of an electron-depletion region on the surface.³² Furthermore, in the case of a ZnO nanowire sensor, a potential barrier develops at nanowire/nanowire junctions of the bridging nanowire network, which blocks electron flow more efficiently than surface depletion of a single nanowire and thus enhances sensitivity (i.e., induces an effective increase in the resistance).³¹ To evaluate the sensing performance of the ZnO nanowire@cellulose nanofiber paper, Pt electrodes were first sputtered on the surfaces of the paper to fabricate the paper sensor device (Figure 4a). The paper sensor showed ohmic behavior in current-voltage characteristics, indicating the formation of good electrical contacts between the ZnO nanowire sensor networks and Pt electrodes (see Supporting Information Figure S6). The sensing performance of the paper sensor for 98 ppm NO₂ at 150 °C is shown in Figure 4b. The electrical resistance of the ZnO nanowire@cellulose nanofiber paper clearly increased upon exposure to 98 ppm NO₂ gas. Then, following exposure to air, the resistance decreased owing to desorption of NO₂ from the ZnO nanowires. These results suggested that the ZnO nanowire-bridging structure on the cellulose nanofiber paper substrate (Figures 3d and S3) enabled NO₂ sensing. The paper sensor provided sufficient sensitivity to detect NO₂ down to concentrations as

low as 3.9 ppm (Figure 4c and d). The NO₂ sensing characteristics of the ZnO nanowire@cellulose nanofiber paper were almost similar up to 30% of relative humidity (RH 30%), while further increase of relative humidity decreased its sensitivity (Figure S7). This is plausibly because the adsorption of NO₂ molecules was suppressed by the presence of water molecules on the surfaces of ZnO nanowires. However, the ZnO nanowire@cellulose nanofiber paper still could detect 28 ppm NO₂ at RH 70%.

As described above, the adsorption/desorption behaviors of NO₂ onto/from ZnO nanowires govern their sensing performances. As shown in Figure 4e, the NO₂ sensing behavior of the paper sensor depended on the surrounding temperatures, indicating that temperature affected the adsorption/desorption of NO₂ onto/from the ZnO nanowire-bridging structure. The relative resistance values of the paper sensor after the first exposure to 98 ppm NO₂ for 10 s (NO₂ introduction) and the following exposure to air for 10 s (NO₂ subtraction) at different temperatures are shown in Figure 4f. Upon introducing NO₂, the relative resistance values increased with increasing temperature, suggesting that NO₂ adsorption onto the ZnO nanowires was promoted as the surrounding temperature increased. At temperatures below 50 °C, the relative resistance values were greater than 1.0 for both the introduction of NO₂ and its attempted removal under an air flow, indicating that NO₂ hardly desorbed from ZnO nanowires at low temperatures. These results suggest that low-temperature use of the paper sensor can improve sensitivity (resistance change) for single-use and long-term sensing. When the paper sensor was used at relatively high temperatures exceeding 100 °C, the relative resistance values were less than 1.0 upon loss of NO₂, owing to the promotion of NO₂ desorption from the ZnO nanowires. Because both adsorption and desorption of NO₂ onto and from the ZnO nanowire-bridging structure occurred over 100 °C, such high-temperature use of the paper sensor would be

advantageous for short-term and repeat sensing. Thus, the paper sensor is expected to be suitable for single-use at room temperatures and repeated use at high temperatures over 100 °C.

Although the ZnO nanowire@cellulose nanofiber paper acted as a molecular sensing platform, the use of precious metal electrodes (i.e., Pt) prevents easy disposal of the sensor device. One of the most important properties of electrodes for gas sensors is stability to air. However, inexpensive metals, such as aluminum, copper, and titanium, easily form an insulation layer on their surfaces owing to oxidation in air, which limits their applicability as electrodes. Graphite is a promising candidate for disposable electrodes, because it is earth-abundant, low-cost, and air-stable. Therefore, we investigated graphite as an electrode for the ZnO nanowire@cellulose nanofiber paper. Pencil lead generally contains high-purity graphite. As shown in Figure 5a and b, graphite electrodes, drawn from a commercial pencil lead, were successfully deposited onto the surfaces of the ZnO nanowire@cellulose nanofiber paper by a drawing process. The success of the pencil drawing can be attributed to both the nanoscale rough surfaces (Figure 3b) and high mechanical robustness (Figure 2c and e) of the ZnO nanowire@cellulose nanofiber paper. The electrical resistance of the pencil-drawn graphite electrodes was of the order of $10^4 \Omega$, which is much lower than that of the sensing layer, i.e., ZnO nanowire@cellulose nanofiber paper ($1.0 \times 10^8 \Omega \text{ square}^{-1}$). In addition, the as-prepared paper sensor exhibited ohmic behavior in its current-voltage characteristics, suggesting the formation of a reliable electrical contact between the ZnO nanowire sensor networks and graphite electrodes (see Supporting Information Figure S8). The paper sensor with pencil-drawn graphite electrodes showed good NO₂ sensing performance, comparable to that of the Pt electrodes (Figure 5c). It has been reported that flexible pencil lead composed of graphite/polymer composites can act as a sensing material for volatile organic compounds owing to absorption/desorption-induced swelling/recovery of polymer binders.³³ The pencil-drawn graphite used in this study showed no clear sensitivity toward NO₂ gas, indicating

that the graphite behaved as an electrode rather than a sensing layer (Figure S9). Thus, we constructed a paper sensor device based on graphite electrodes rather than precious metal electrodes, while maintaining the molecular sensing performance of the device.

Furthermore, the ZnO nanowire@cellulose nanofiber paper was easily shaped, as for normal paper. The paper could be easily cut with scissors into a desired shape. Then graphite electrodes were formed on the paper by simply drawing with a pencil, before application as a NO₂ sensor (Figure 5d). As shown in Figure 5e, these paper sensors showed similar NO₂ sensing performance, regardless of the area of the cut-out. We attribute this result to the high spatial uniformity of the ZnO nanowire networks on the cellulose nanofiber paper. As shown in Figure 6, the paper sensor could also be disposed of simply and rapidly, through burning within several seconds. Such cut-and-paste usability and easy disposal are features required for a ubiquitous molecular sensor network; our paper sensor is light and could be easily cut into a range of shapes and sizes, and mounted as required for sensing, and disposed after use. Integration of the heating system into the paper sensor without sacrificing its flexibility and disposability is a further challenge. Drawing graphite layer all over the back surfaces of the ZnO nanowire@cellulose nanofiber paper might be a promising strategy; the as-drawn graphite layer would allow joule heating of the sensing layer.

Conclusion

To conclude, we fabricated a paper-based disposable molecular sensor device. A cellulose nanofiber paper substrate, ZnO nanowire sensor, and graphite electrodes were robustly integrated by two-step papermaking and pencil-drawing processes. The as-fabricated paper sensor device offered efficient molecular sensing performance for NO₂, cut-and-paste usability, and easy

disposability. This strategy can be extended to a variety of oxide nanowires and thus spur development of disposable molecular sensors to support a future trillion-sensor society.

Experimental Section

Materials. Cellulose nanofibers with widths 15–50 nm were prepared from never-dried softwood dissolving sulfite pulp, which was provided by Nippon Paper Group. Inc., Tokyo, Japan, as follows. An aqueous suspension of the pulp (0.5 wt%, 2 L) was treated by a high-pressure water-jet system (Star Burst, HJP-25005E, Sugino Machine Co., Ltd, Uozu, Japan). The pulp suspension was ejected from a 0.15-mm diameter nozzle at 245 MPa with 50-cycle repetitions. ZnO nanowires were hydrothermally synthesized based on a previously reported method,³⁰ as follows. An aqueous solution (100 mL) of precursor was prepared at room temperatures from zinc nitrate hexahydrate (25 mM), hexamethylenetetramine (25 mM), polyethylenimine (2.5 mM), and ammonia (500 mM). Then, ZnO (thickness: ca. 75 nm)/Cr (thickness: ca. 7 nm)/Si wafer substrate (size: 2.25 cm × 2.25 cm), which was prepared by successive sputtering on the Si wafer, was immersed upside down into the precursor solution in a sealed beaker and maintained at 95 °C for 12 h, followed by washing with distilled water and drying. The ZnO nanowires obtained were peeled from the substrate by ultrasonication in an aqueous dispersion of cellulose nanofibers for 3 min. Zinc nitrate hexahydrate (>99.0% purity), hexamethylenetetramine (>99.0% purity), and ammonia solution (28 wt%) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Polyethylenimine solution (50 wt%, average molecular weight: ~2000) was obtained from Aldrich, Ltd., Tokyo, Japan. Si wafer (4" P(100) 1-10) and a pencil (9800, Hardness: 2B) were purchased from SUMCO corp., Tokyo, Japan, and Mitsubishi Pencil Co., Ltd, Ohi, Japan, respectively. The polyethylene terephthalate (PET) films (G2, thickness: 50 μm, Teijin DuPont Films Japan, Ltd., Tokyo, Japan) were treated at 150 V and 10 mA for 30 s with a plasma etching

device (AP-T02-L, Sekisui Chemical Co., Ltd., Osaka, Japan) to improve their wettability before use.

Preparation of the ZnO nanowire/cellulose nanofiber composite networks on cellulose nanofiber paper. To prepare the ZnO nanowire/cellulose nanofiber composite networks on cellulose nanofiber paper, i.e., the ZnO nanowire@cellulose nanofiber paper, with a diameter of 35 mm, an aqueous dispersion of cellulose nanofibers (0.3 wt%, 20 mL) was first dewatered on a membrane filter (H020A090C, hydrophilic polytetrafluoroethylene (PTFE) membrane, 0.1 μm pore diameter, Advantec Toyo Kaisha, Ltd., Tokyo, Japan) under pressure filtration (KST-47, Advantec Toyo Kaisha, Ltd., Tokyo, Japan). Then, the aqueous mixture of cellulose nanofibers and ZnO nanowires at a specific concentration (30 mL) was added and filtered in the same manner. The obtained wet sheet was covered with a hydrophobic glass plate, treated by hot pressing at 110 $^{\circ}\text{C}$ for 1 h (8.5 MPa) and then peeled from the membrane. As a control, the ZnO nanowire networks on PET film were also prepared by drop coating, as follows. An aqueous dispersion of ZnO nanowires (2 mL) at a specific concentration was cast onto a PET film (diameter: 35 mm), followed by drying at 50 $^{\circ}\text{C}$ for 2 h and then hot pressing at 110 $^{\circ}\text{C}$ for 1 h (8.5 MPa).

Preparation and evaluation of the paper sensor. The paper sensor was constructed by depositing the electrode materials on the ZnO nanowire@cellulose nanofiber paper. A Pt electrode with a thickness of ca. 200 nm was deposited by a metal mask-assisted sputtering technique with sputtering power of 50 W in Ar 0.3 Pa atmosphere at room temperatures. The graphite electrode was deposited by line-drawing with a commercial pencil. The amount of deposited graphite was controlled by the number of pencil strokes. Typically, we drew the

graphite electrode at least 30 times to ensure electrical conduction of electrode. The gap size of the electrodes was carefully controlled to be ca. 200 μm . The electrical conduction measurements and NO_2 sensing measurements of the paper sensor and the graphite electrode were conducted on a temperature programmable probe station. All measurements were performed by a two-probe method. For the measurements, the temperature was modulated in the range of 25–200 $^{\circ}\text{C}$ by a state heater and the NO_2 concentration varied in the range of 3.9–98 ppm with a mass-flow control system using dry air as a carrier gas. For NO_2 sensing, the dry air (N_2 80%, O_2 20%) was first flown for 100 s and then NO_2 mixed with Ar was flown for 100 s. This process was cycled 5 times and one another cycle with varying the flow time to be 300 s was tested for a reliability of sensing characteristics. During the gas flow, the flow rate was controlled to be 250 mL min^{-1} . The resistance values during the NO_2 sensing were readout by applying 1 V between the contact electrodes. The NO_2 sensing characteristics at different relative humidity (dry, 10%, 30%, 50%, 70%) were measured at the flow rate of 1.4 L min^{-1} (0.4 L min^{-1} for NO_2 and 1.0 L min^{-1} for humidity control).

Analyses. Surface and cross-section observations were performed using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7610F) and an optical microscope (Olympus, BXFM-N22MBS-D). Compositional image analyses were conducted by energy dispersive X-ray spectrometry (EDX) fitted to the FE-SEM. To avoid charging issues that disturb the FE-SEM and EDX analysis, Pt thin films with a thickness of 10 nm were deposited onto the paper sensor prior to these measurements. The ZnO nanowire content was determined by atomic absorption spectrophotometry using a ZA3300 instrument (Hitachi High-Tech Science Corp., Tokyo, Japan). Sheet resistance values were measured using a resistivity meter with a ring-type probe (Hiresta-UX, MCP-HT800, Mitsubishi Chemical Analytech Co., Ltd., Chigasaki, Japan).

Associated content

Supporting Information

An FE-SEM image of the ZnO nanowires hydrothermally synthesized on the ZnO/Cr/Si wafer substrate; Schematic of the preparation of the ZnO nanowire@cellulose nanofiber paper by a two-step papermaking process; Top-view FE-SEM and EDX elemental mapping images of the ZnO nanowire@cellulose nanofiber paper; Cross-section-view FE-SEM and EDX elemental mapping images of the ZnO nanowire@cellulose nanofiber paper; Optical and top-view FE-SEM images of the paper composite prepared from an aqueous mixture of ZnO nanowires and cellulose nanofibers by a one-step papermaking process; Temperature dependent current versus voltage characteristics of the ZnO nanowire@cellulose nanofiber paper with Pt electrodes; Current versus voltage characteristics of the ZnO nanowire@cellulose nanofiber paper with pencil-drawn graphite; Change in the resistance of the ZnO nanowire@cellulose nanofiber paper and the graphite electrode upon exposure to 98 ppm NO₂ gas at 150 °C.

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Author contributions

H. K., K. N., M. N., and T. Y. designed this work. H. K. and K. N. prepared the manuscript. H. K., K. N., H. Y., G. Z., C. W., A. I., H. Y., Y. H. carried out the experiments. H. K., K. N., T. T., K. U., M. K., Y. H., M. N. and T. Y. analyzed the results and discussed the manuscript during the preparation. All authors discussed the results and implications and commented on the manuscript at all stages.

Note

The authors declare no competing financial interests.

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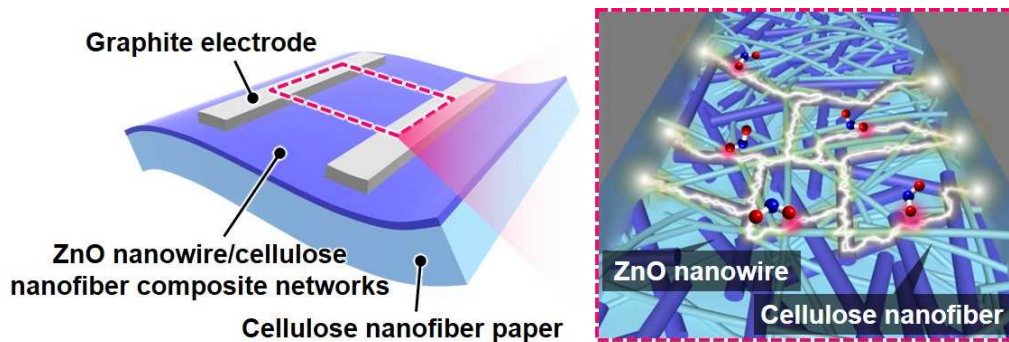


Figure 1. Schematic of the disposable molecular sensor device consisting of a cellulose nanofiber paper substrate, a ZnO nanowire sensor, and a graphite electrode.

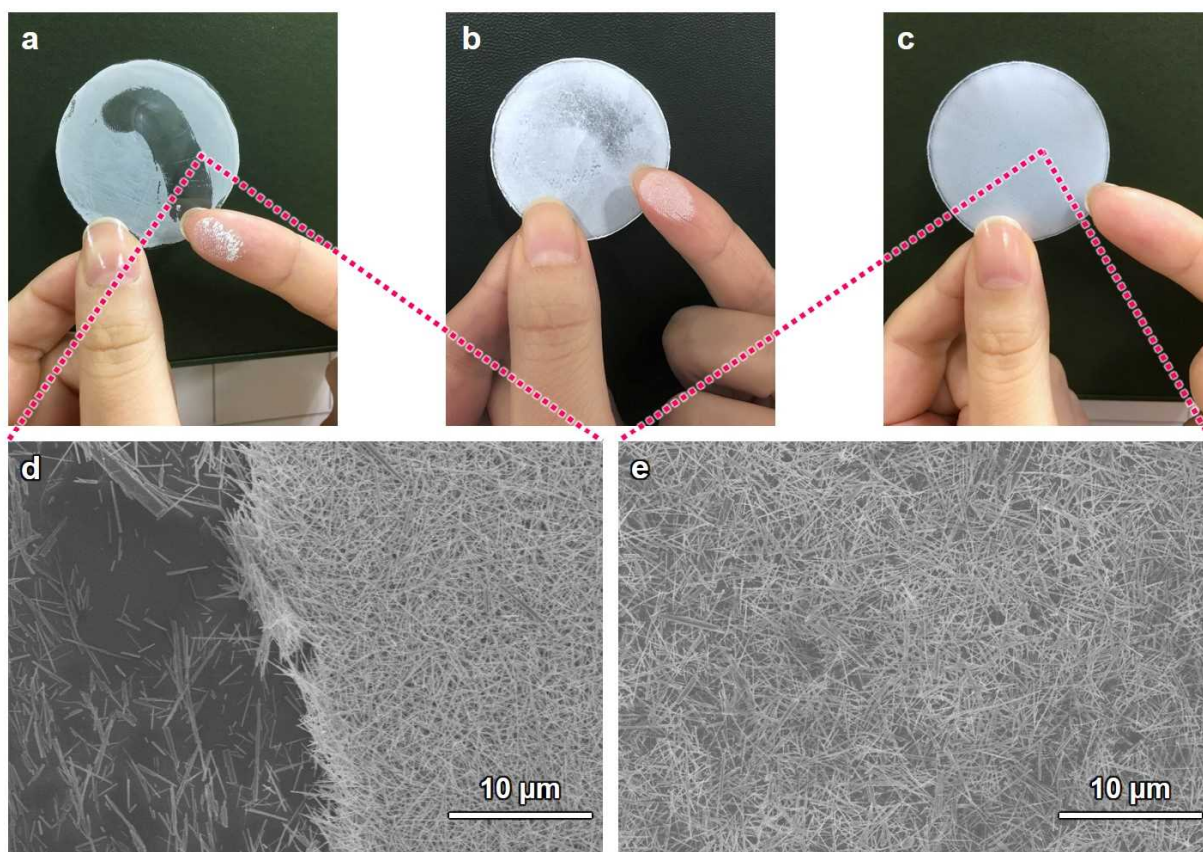


Figure 2. Adhesion performance of the ZnO nanowire/cellulose nanofiber composite networks on a cellulose nanofiber paper substrate. (a, b, c) Optical and (d, e) FE-SEM images of (a, d) ZnO nanowires on a PET film substrate, (b) ZnO nanowires on a cellulose nanofiber paper substrate, and (c, e) ZnO nanowire/cellulose nanofiber composite networks on a cellulose nanofiber paper substrate after running a finger over their surfaces. In each case, hot pressing was conducted at 110 °C for 1 h (8.5 MPa) before adhesion performance testing.

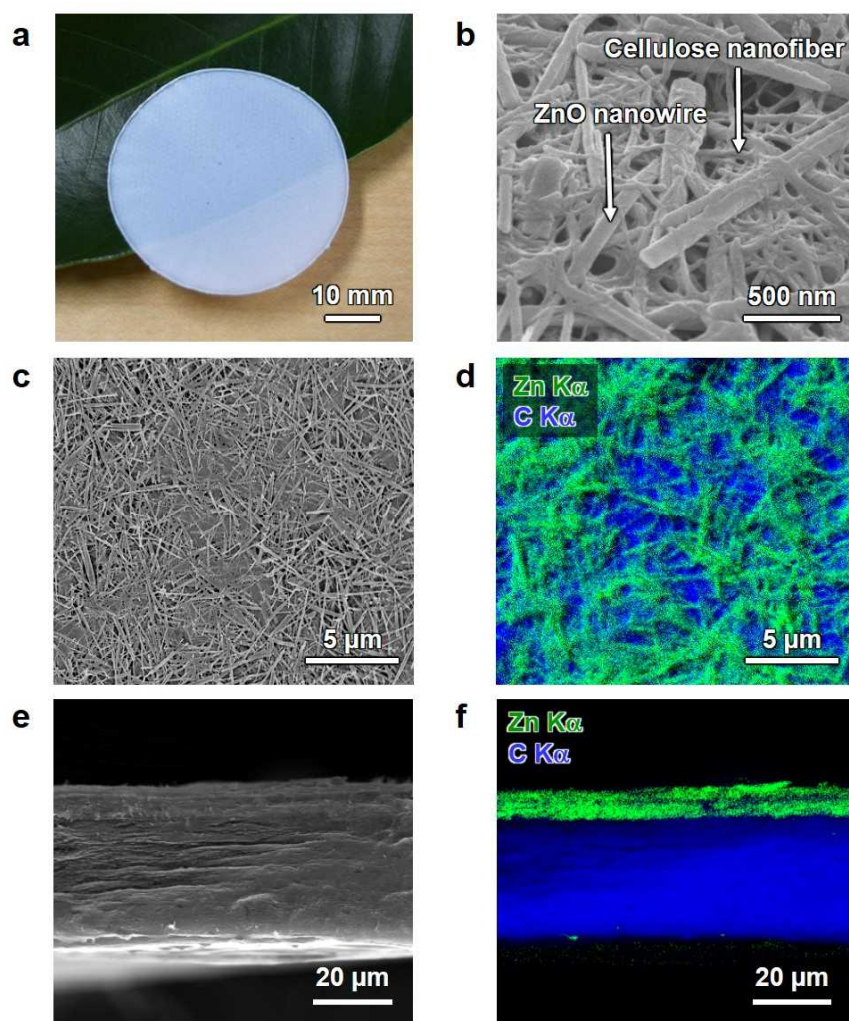


Figure 3. Characterization of the ZnO nanowire/cellulose nanofiber composite networks on a cellulose nanofiber paper substrate, denoted the ZnO nanowire@cellulose nanofiber paper. (a) optical, (b) top-view FE-SEM, (c, d) top-view, and (e, f) cross-section FE-SEM and EDX mapping images of the ZnO nanowire@cellulose nanofiber paper. Paper size: 35-mm diameter.

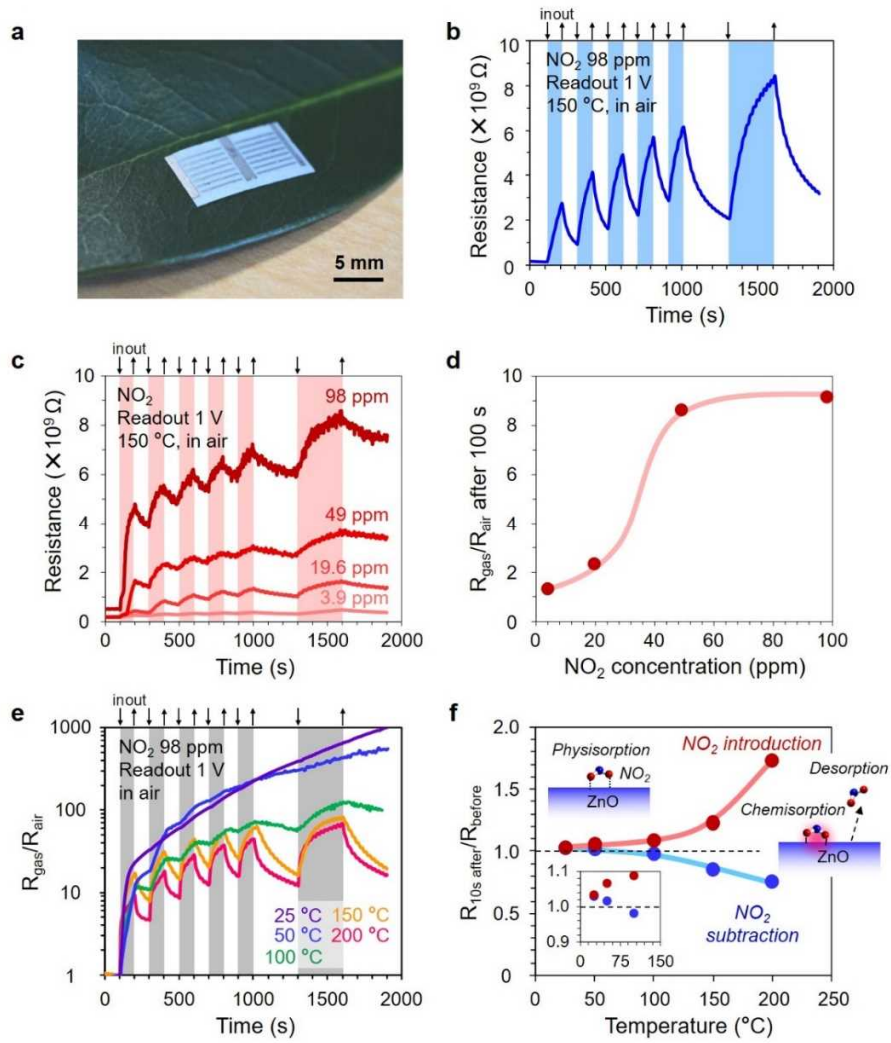


Figure 4. NO₂ sensing performances of the paper sensor consisting of ZnO nanowire@cellulose nanofiber paper and Pt electrodes under dry condition. (a) A photograph of sensor, (b) resistance versus time on exposure to 98 ppm NO₂ gas at 150 °C, (c) resistance versus time upon exposure to NO₂ gas with concentrations ranging from 3.9 to 98 ppm at 150 °C, (d) relative resistance change upon exposure to NO₂ gas with concentrations ranging from 3.9 to 98 ppm at 150 °C for 100 s, (e) relative resistance change versus time upon exposure to 98 ppm NO₂ gas at temperatures ranging from 25 to 200 °C, (f) relative resistance change upon exposure to 98 ppm NO₂ gas for 10 s (red) and the following exposure to air for 10 s (blue) at temperatures ranging from 25 to 200 °C.

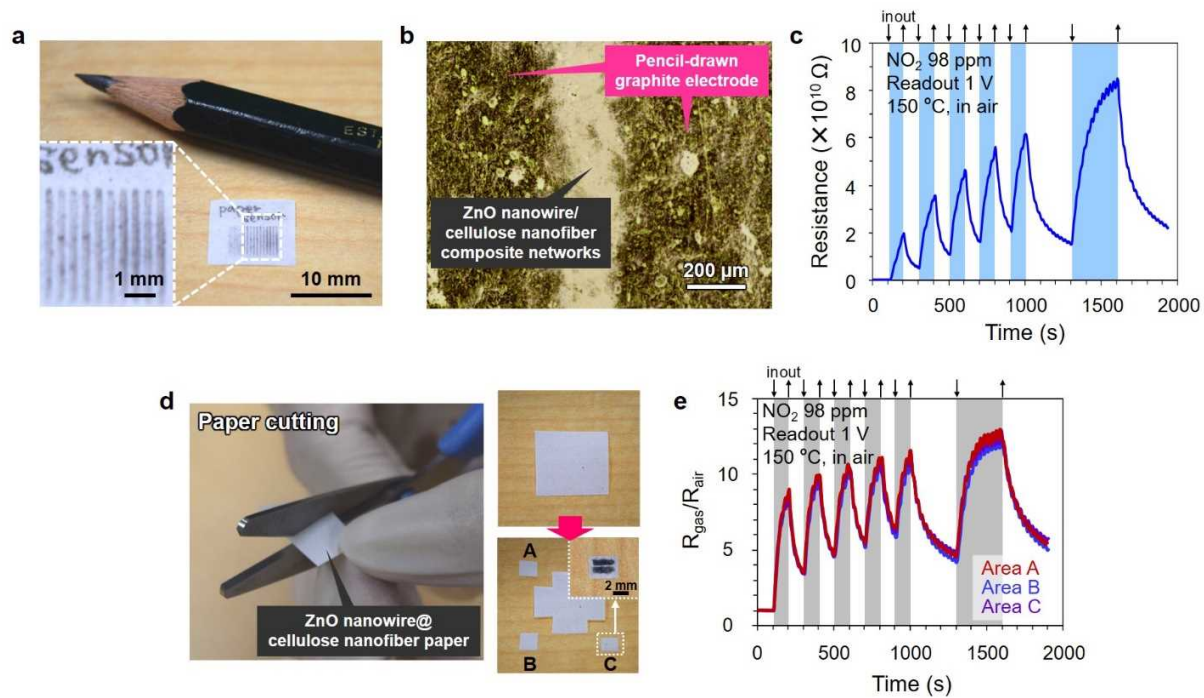
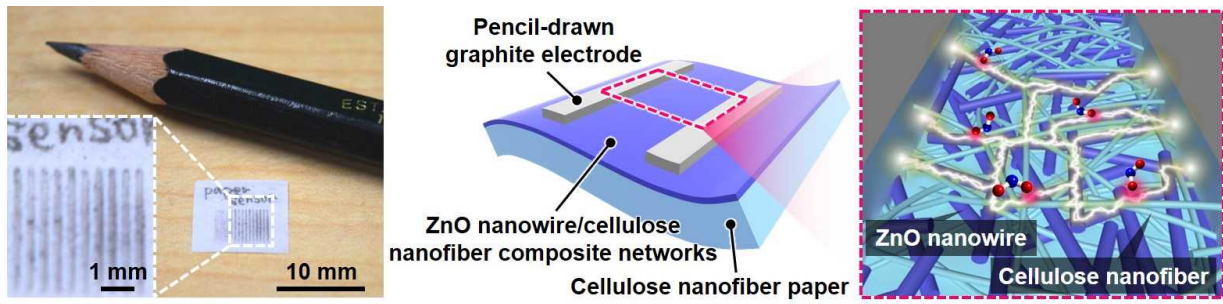


Figure 5. NO₂ sensing performances under dry condition and paper-like usability of the paper sensor consisting of the ZnO nanowire@cellulose nanofiber paper and the pencil-drawn graphite electrodes. (a) Optical and (b) optical microscope images, (c) resistance versus time upon exposure to 98 ppm NO₂ gas at 150 °C, (d) fabrication of the paper sensor by scissor-cutting and pencil-drawing, (e) influence of cutting position of the ZnO nanowire@cellulose nanofiber paper on the NO₂ sensing performance of the paper sensors.



Figure 6. Disposability test by burning of the paper sensor consisting of the ZnO nanowire@cellulose nanofiber paper and the pencil-drawn graphite electrodes.

Table of Contents Graphic



Supporting Information

Paper-based disposable molecular sensor constructed from oxide nanowires, cellulose nanofibers, and pencil-drawn electrodes

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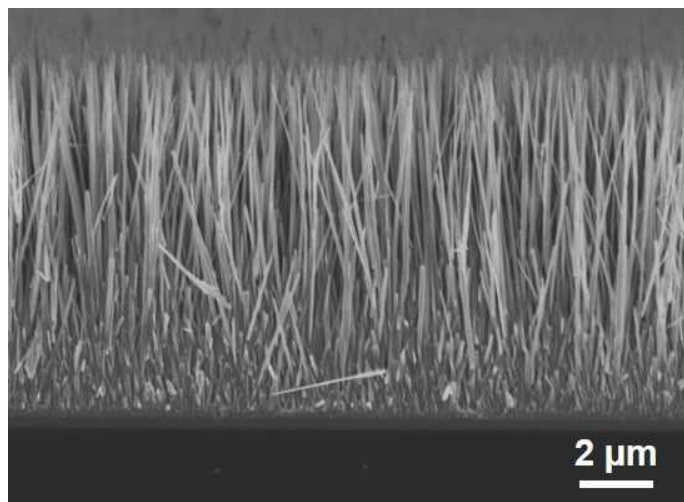


Figure S1. FE-SEM image of the ZnO nanowires hydrothermally synthesized on the ZnO/Cr/Si wafer substrate.

The ZnO nanowires were peeled from the wafer by ultrasonication in an aqueous dispersion of cellulose nanofibers for 3 min, and then used to prepare the ZnO nanowire/cellulose nanofiber composite networks on a cellulose nanofiber paper substrate. After peeling from the wafer by ultrasonication, the widths and length of the ZnO nanowires were approximately 100 nm and 6 μm, respectively.

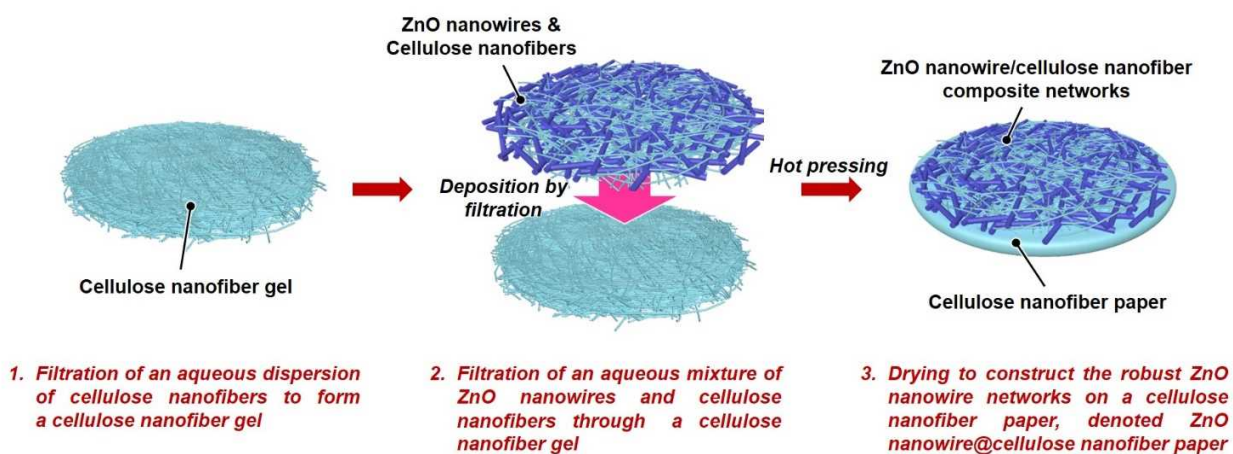


Figure S2. Schematic diagram of the preparation of the ZnO nanowire/cellulose nanofiber composite networks on cellulose nanofiber paper (denoted ZnO nanowire@cellulose nanofiber paper) by a two-step papermaking process.

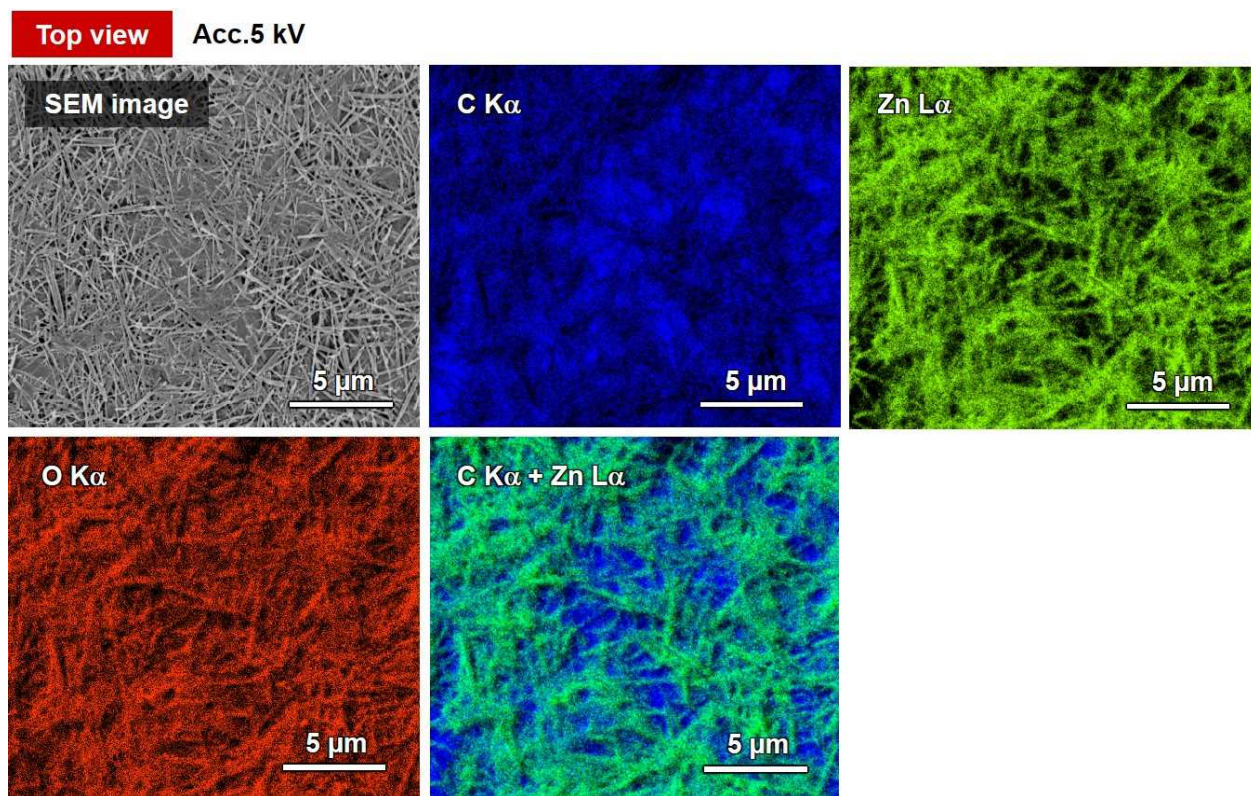


Figure S3. Top-view FE-SEM and EDX elemental mapping images of the ZnO nanowire@cellulose nanofiber paper.

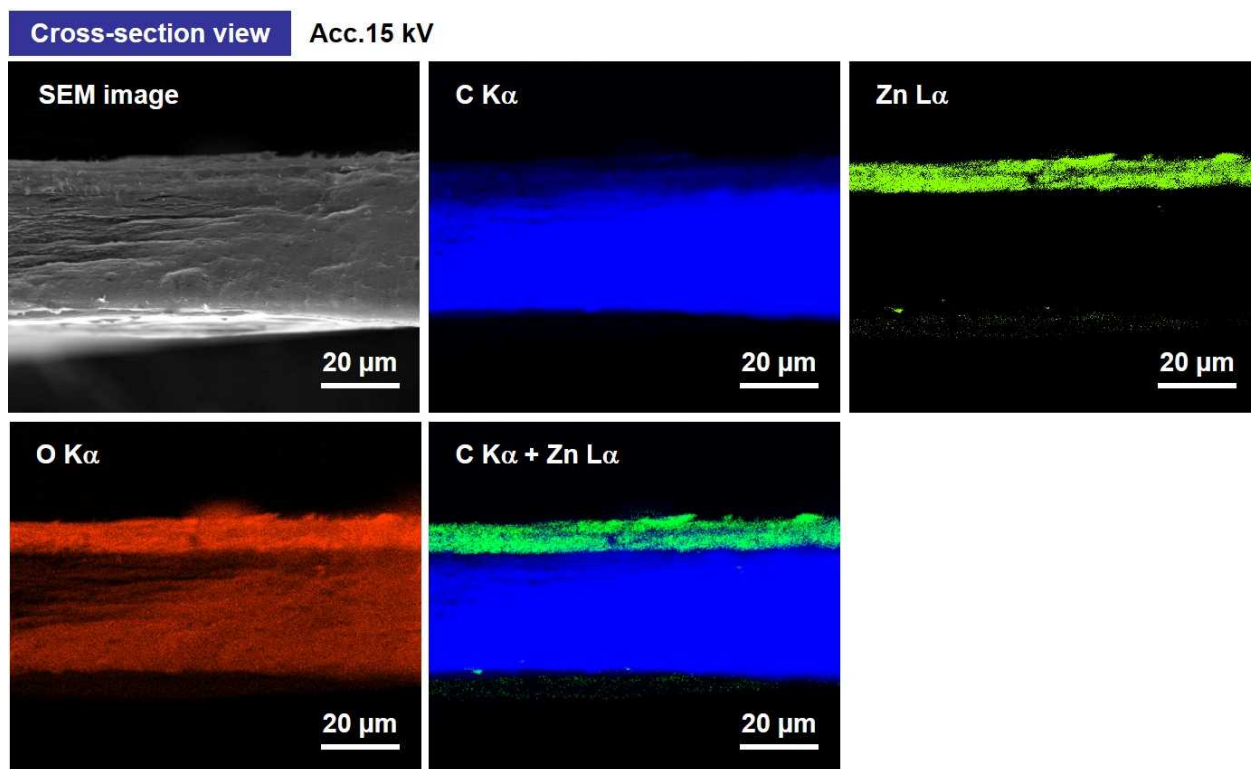


Figure S4. Cross section-view FE-SEM and EDX elemental mapping images of the ZnO nanowire@cellulose nanofiber paper.

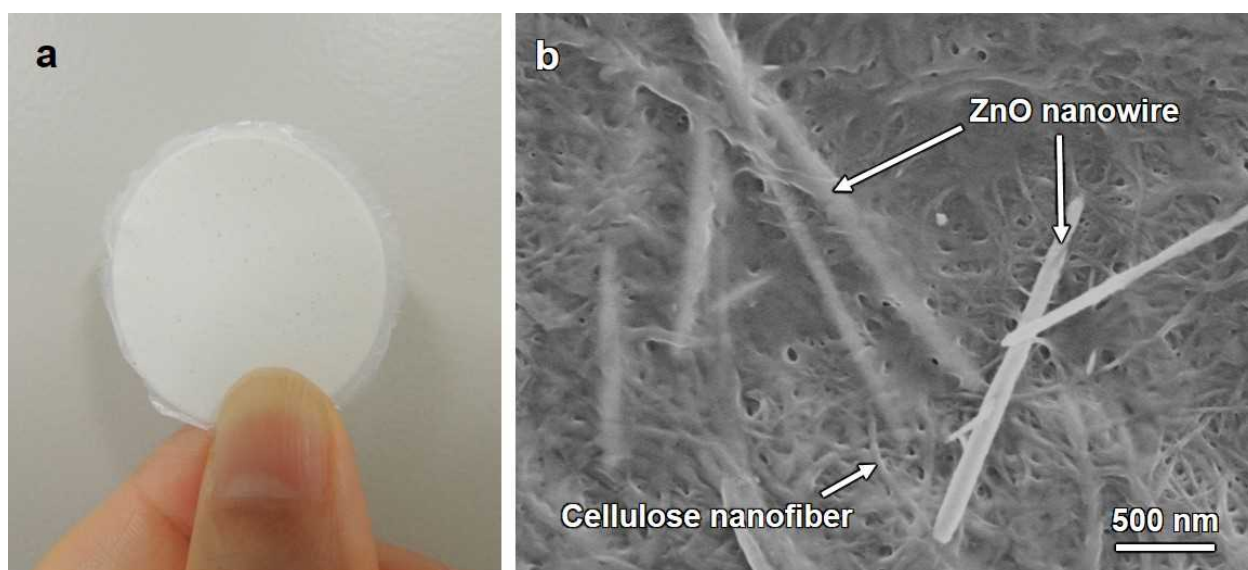


Figure S5. (a) Optical and (b) top-view FE-SEM images of the paper composite prepared from an aqueous mixture of ZnO nanowires and cellulose nanofibers by a one-step papermaking process. For the paper composite prepared from the simple mixture of ZnO nanowires and cellulose nanofibers, most of ZnO nanowires were buried inside the cellulose nanofiber matrix, resulting in a high surface resistance comparable to that of the cellulose nanofiber paper without ZnO nanowires. These results suggested that this simple mixing approach prevents the formation of the nanowire sensing networks on the surfaces of the cellulose nanofiber paper substrate.

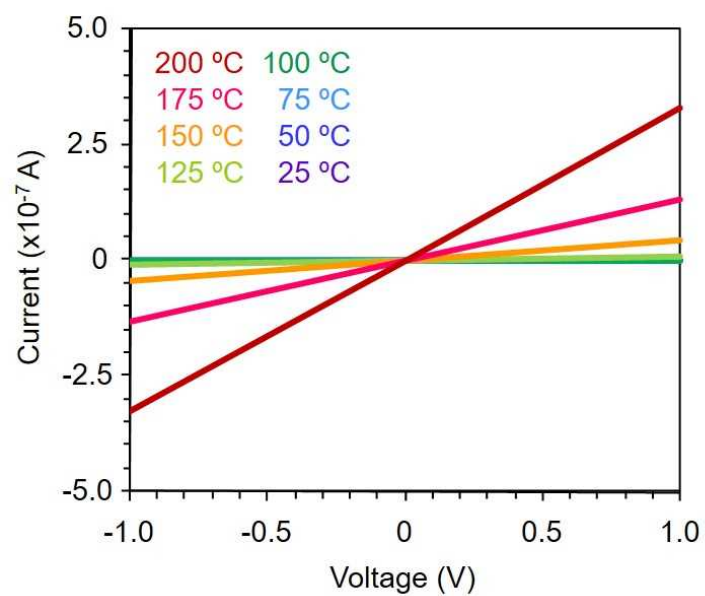


Figure S6. Temperature dependent current versus voltage characteristics of the ZnO nanowire@cellulose nanofiber paper. Electrode: sputtered Pt.

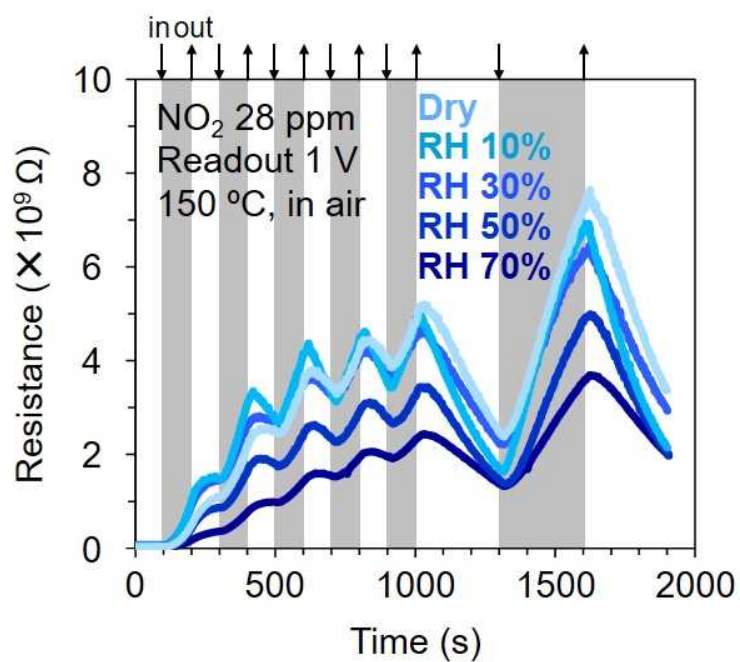


Figure S7. Effect of relative humidity (RH) on the NO₂ sensing performances of the paper sensor consisting of ZnO nanowire@cellulose nanofiber paper and Pt electrodes.

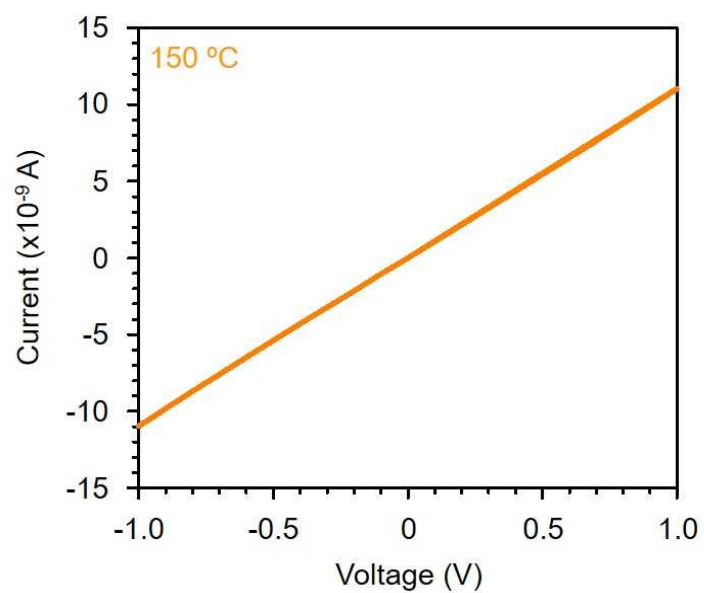


Figure S8. Current versus voltage characteristics of the ZnO nanowire@cellulose nanofiber paper. Electrode: pencil-drawn graphite.

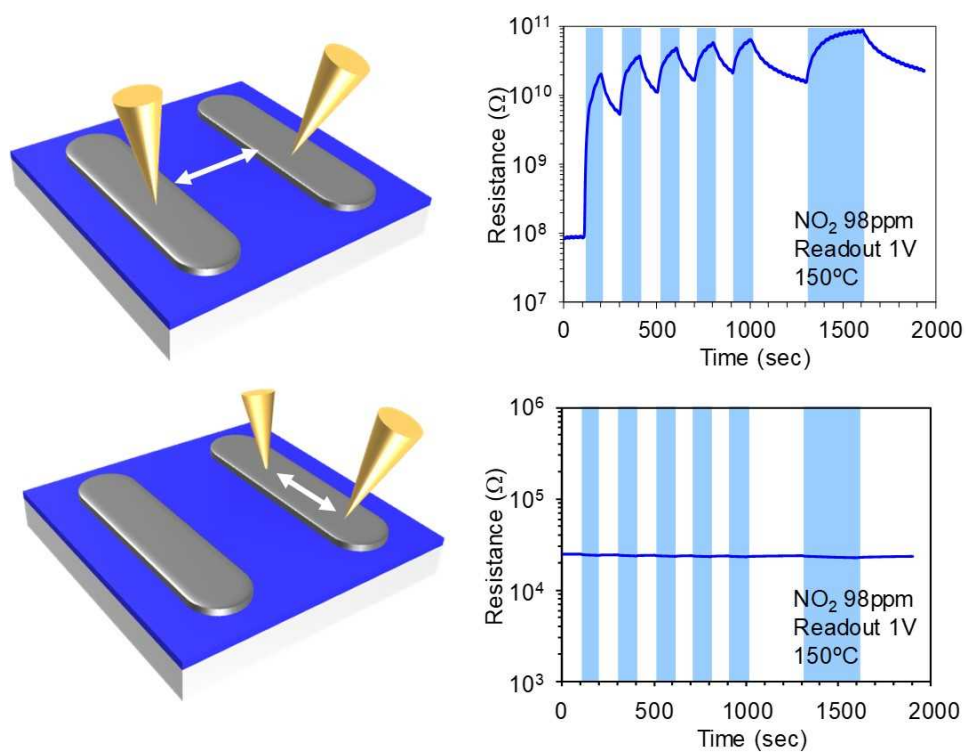


Figure S9. NO_2 sensing performance of the paper sensor consisting of the ZnO nanowire@cellulose nanofiber paper and the pencil-drawn graphite electrodes. Change in the resistance of the ZnO nanowire@cellulose nanofiber paper (top) and the graphite electrode (bottom) upon exposure to 98 ppm NO_2 gas at 150 °C.