

Supporting Information

Surface Treated Nanofibers as High Current Yielding Breath Humidity Sensors for Wearable Electronics

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Preparation of rGO

Materials. Poly[vinylidene fluoride] (PVDF) [commercial grade], aniline, ethanol, ammonium persulfate (APS) from RANKEM, India. Dimethylformamide (DMF) and hydrochloric acid (HCl) were purchased from Sigma Aldrich, hydrogen peroxide (H_2O_2), sulfuric Acid (H_2SO_4), sodium nitrate (NaNO_3), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), phosphorus pentoxide (P_2O_5) and potassium permanganate (KMnO_4) were obtained from Alfa Aesar. Millipore produced de-ionized water ($\sim 18.2 \text{ M}\Omega$) was used throughout the experiments and all the chemicals were used without any further purification.

Preparation of graphite oxide. A modified version Hummer's method¹ was used to synthesize graphite oxide using graphite powder. Briefly, graphite powder (2 g) was added to $\text{K}_2\text{S}_2\text{O}_8$ (4 g) and P_2O_5 (4 g) in concentrated H_2SO_4 (25 mL), and the mixture was heated to 100°C . The resulting dark blue oxidized mixture was isolated and slowly cooled to room temperature over a period of 6 h. The mixture was diluted, filtered and dried overnight at 60°C . About 2 g of this powder was added to H_2SO_4 (92 mL) chilled in an ice bath, to which KMnO_4 (12 g) was gradually added. After 15 min, NaNO_3 (2 g) was added to the mixture. The solution was further stirred for 2 h at 35°C and distilled water (200 mL) was added. Finally, H_2O_2 diluted to 30% in distilled water was added. The product was washed with HCl (1:10) and then with water. The resulting brown dispersion was extensively dialyzed and exfoliated via ultra-sonication for 2 h (300 W). Unexfoliated graphite oxide was removed by centrifugation (12000 rpm, 20 min) using a KUBOTA (Tokyo, Japan) centrifuge.

Preparation of reduced graphene oxide (RGO). About 1 g of the freeze-dried graphite oxide was taken and dispersed in 1 L of deionized water and ultrasonicated for 1 h. Then GO suspension was mixed with NH_3 and aq. KOH to adjust the pH to 10. Under the effect of ultrasound and electrostatic repulsion, the layers of GO were separated. About 1 mL of hydrazine hydrate solution was added to the suspension and it was maintained at 95°C in an oil bath with reflux condenser

overnight.²⁻⁴ The color change from brown to black confirms the formation of rGO. The solution was filtered and washed with deionized water. The washed rGO was dried under vacuum to obtain the desired rGO powder.

Fabrication and testing

Testing breath humidity. The SILAR treated fiber mat was cut into pieces of dimensions, 2.5 cm x 1.5 cm to serve as the sensing element and to maximize the sensor response. Each piece was taped to a glass slide for support. Using commercial grade conducting silver paste, wire contact points were made at opposite ends of the sensing fiber element with a separation of 1 cm. The wire terminals were connected to a CH Instruments Electrochemical Workstation and testing was carried out under the chronoamperometry scan mode. All experiments were carried out at ambient conditions, recorded to be 45 ± 2 %RH and 25 °C, respectively, by standard humidity and temperature sensors. For breath analysis, a standard respiratory mask fitted with holes at its periphery and a central connecting tube was used to carry the exhaled oral/nasal breath directly to the sensing element.

Device fabrication. To use the sensing element as an independent functioning unit for health monitoring purposes, a basic voltage divider circuit was prepared. The entire circuit was designed using a commercially available open-source electronic prototyping platform which can acquire real-time data and relaying it via universal serial bus wire cable or Bluetooth to a PC/mobile device. The data were collected periodically and plotted after basic noise filtration processes. The sensing element has been prepared in such a way that, the over dimension of the sensor are 2.5 x 1.5 cm. The distance between the electrodes is 1 cm. The electrode contact is considered as a point contact, but has a width of around 2-3 mm.

Proximity drop tests. To confirm increased sensitivity and specificity toward atmospheric moisture, pure ethanol and acetone droplets (5 μ L) were separately brought within proximity of the sensing material and current measurements were taken. All experiments were carried out at ambient conditions, recorded to be 45 ± 2 %RH and 25 °C, respectively, by standard humidity and temperature sensors. The analytes were loaded in a 2 mL capacity syringe and the droplets from

the needle tip were initially suspended at a fixed distance of 5 cm. Soon after, the syringe was lowered so that the droplets were at 1, 2 and 5 mm above the surface of the sensing element. This was carried out in approaching-withdrawal and a receding-withdrawal fashion and the current response was noted accordingly.

Instrumentation

SEM (Scanning electron microscopy) of fibers. To determine the size and morphology of the bare PVDF/rGO fibers and SILAR treated fibers, they were characterized using a FEI QUANTA 200 SEM.

IR/ATR and real-time Raman spectral analysis. In order to confirm the various organic functional groups present in the nanofibers, IR spectral data were collected using Perkin Elmer Spectrum System One FTIR in attenuated total reflectance (ATR) mode. Raman analysis was performed using WiTec GmbH confocal Raman microscope (alpha-300S). A 532 nm (Nd-YAG) laser was used for Raman excitation with a power of 0.2 - 0.5 mW, which was maintained throughout the experiment. Oral breath was exhaled onto the sensor to the point of humidity saturation and it was later placed under the objective lens for the collection of time lapse Raman spectra. Spectra were collected for a time period of 25 s, marked from the time of oral exhalation, at an interval of 2 s.

Cyclic Voltammogram of PANi and LCR measurement. To understand the redox states of PANi, CV of PANi was performed by using 0.5 M H₂SO₄ aqueous solution as electrolyte. Indium doped tin oxide coated (ITO) glass was used as electrode and PANi was coated via SILAR. After 12 cycles, a greenish coat was observed on the ITO glass and after drying the ITO was used as electrode. Ag/AgCl electrode was used as reference and Platinum wire was used as anode. The electrode was cycled between -0.4 – 0.8 V with a sweep rate of 50 mVs⁻¹ using a CH Instruments Electrochemical Analyzer.

Sensor calibration. To study the sensitivity of the sensor towards various humidity levels, a standard calibration was performed by controlling the humidity of the chamber in which the sensor

was placed. Initially, the current during continuous purging of N₂ was noted as ($I_{\text{Dry air}}$) and we observed the output to be 0.012 mA. Aqueous solutions of K₂CO₃ and K₂SO₄ and finally mist generated via nebulizing water was used to obtain humidity levels of 43±5 %, 85±5 % and ~100 %RH, respectively⁵. The sensor was placed in each of the humidity condition for calibration. The corresponding calibration curve is presented in Figure S5.

TEM of rGO and the composite fiber. In order to visualize the synthesized rGO, the rGO flakes were dispersed in DMF and it was drop-casted on transmission electron microscope (TEM) grid. Later this grid was placed inside a JEOL 3010 TEM operating at 300 kV. Similarly, PVDF/rGO nanofibers were directly electrospun on the TEM grid to visualize the surface morphology and location of rGO in PVDF matrix.

Contact angle studies. Surface contact angle measurements were performed using a sessile water droplet with a volume of 3 μL using a Holmarc contact angle meter. A fresh sample of PVDF/rGO was electrospun onto glass slides for a period of 20 min. SILAR was performed for one slide and the other was taken as is. These glass slides were placed under the syringe needle and the droplet was brought to make contact with the surface and the contact angle was measured. These tests were performed to confirm the hydrophobicity of PVDF nanofibers and its hydrophilicity in presence of a PANi coating.

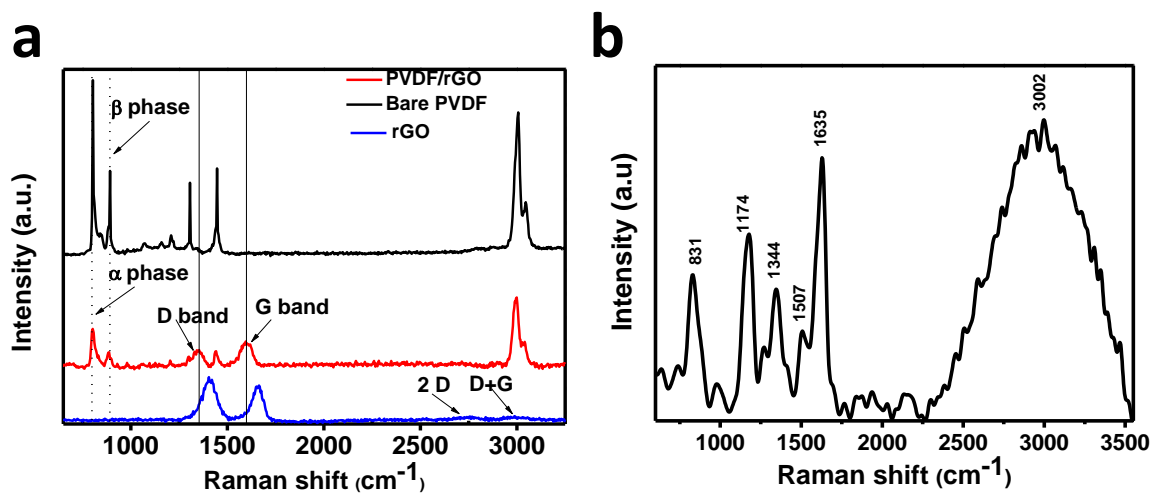


Figure S1. Raman spectra showing α and β phases of PVDF and D & G bands of rGO. (a) Comparison of bare PVDF with rGO and PVDF/rGO. (b) Electrospun composite fiber saturated with humidity.

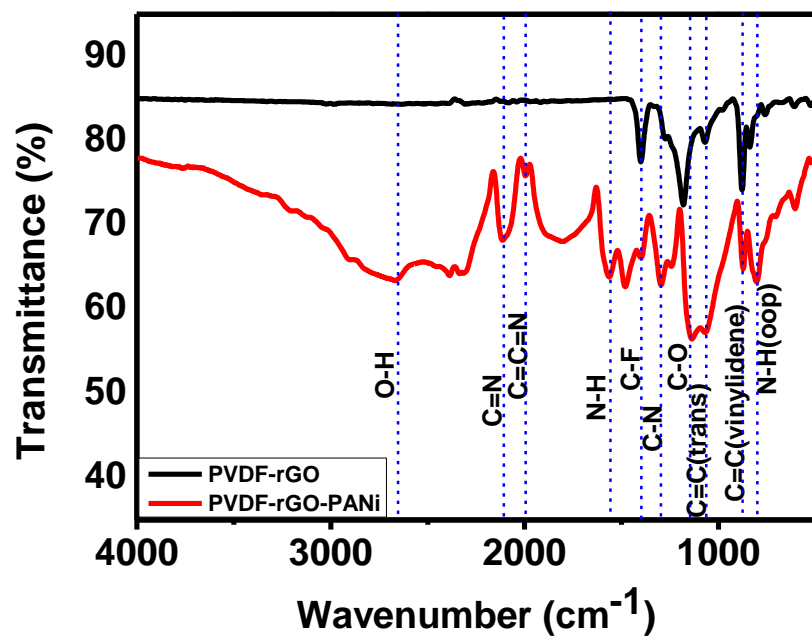


Figure S2. IR spectra of electrospun nanofibers before and after PANi coating via SILAR.

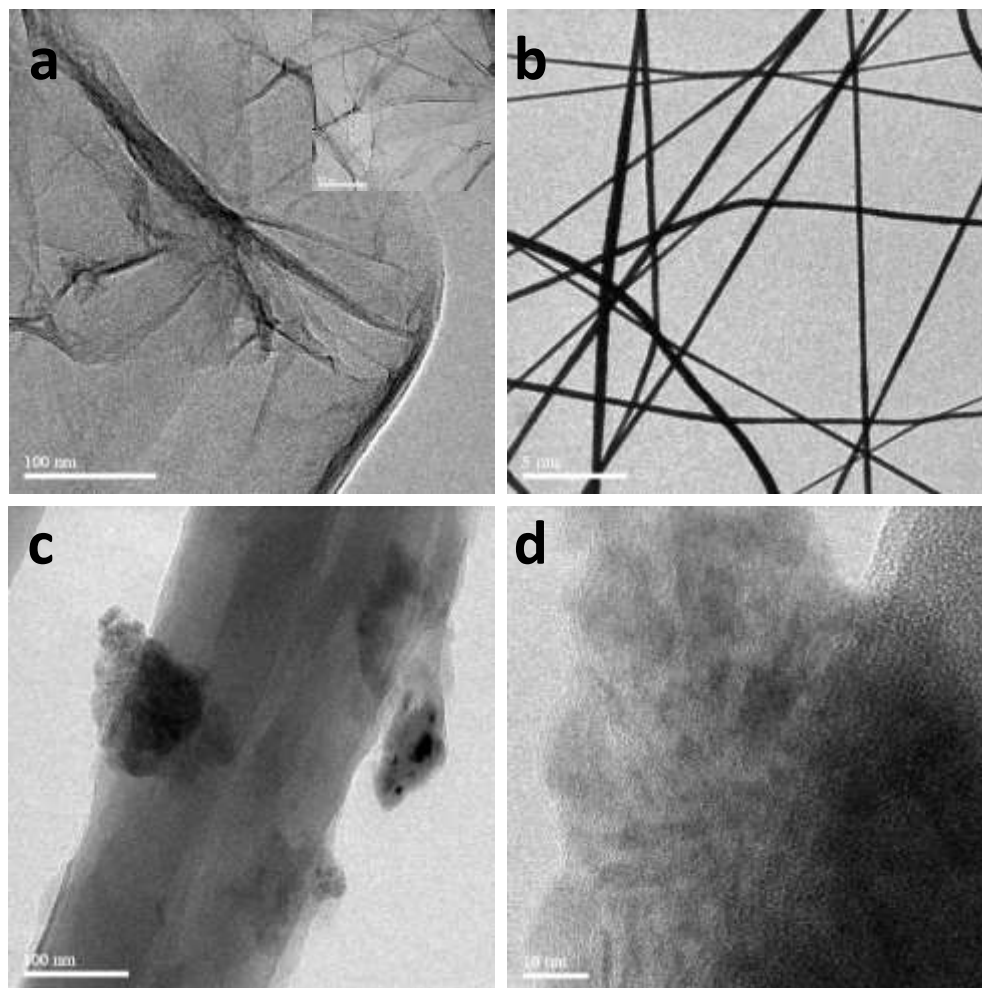


Figure S3. TEM images of (a) rGO and an expanded view of parent graphene shown in the inset. (b, c and d) PVDF/rGO nanofibers in different magnifications and expanded view of the fibers in (d) shows the embedded graphene.

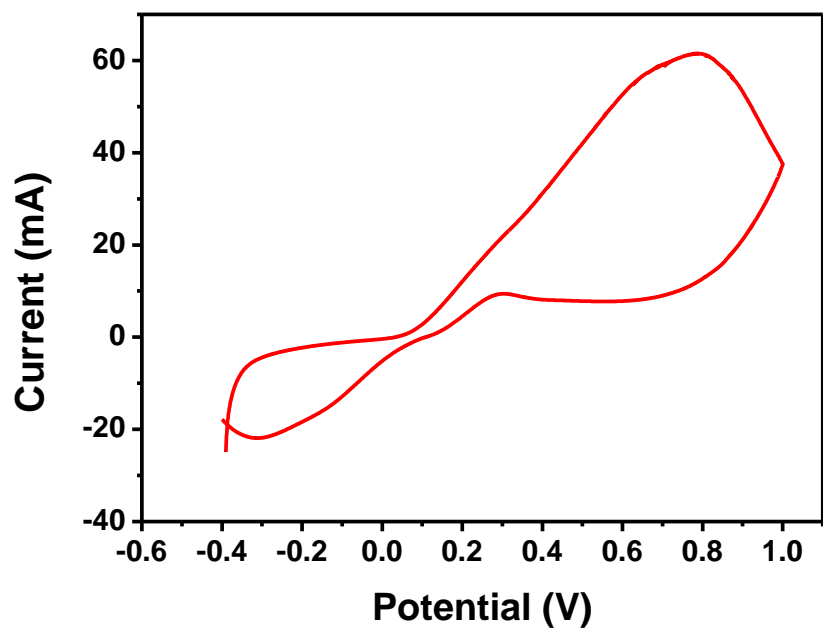


Figure S4. Cyclic voltammogram of PANi coated on ITO via SILAR, with a scan rate of 50 mVs^{-1} using $0.5 \text{ M H}_2\text{SO}_4$ as electrolyte.

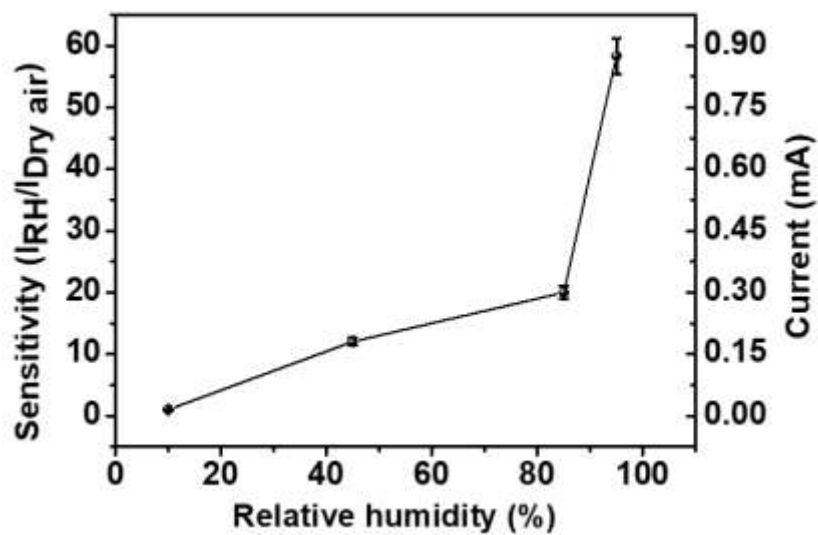


Figure S5. Calibration curve of humidity with respect to sensitivity and current.

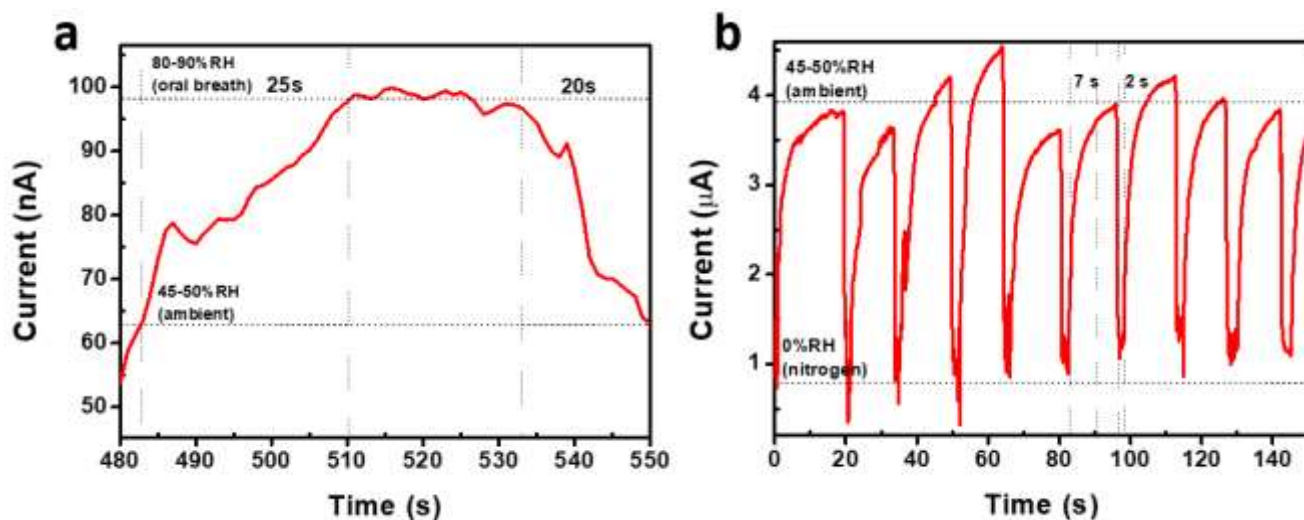


Figure S6. Chronoamperometric response of PANi-coated (a) PVDF and (b) PVDF/4 mg rGO.

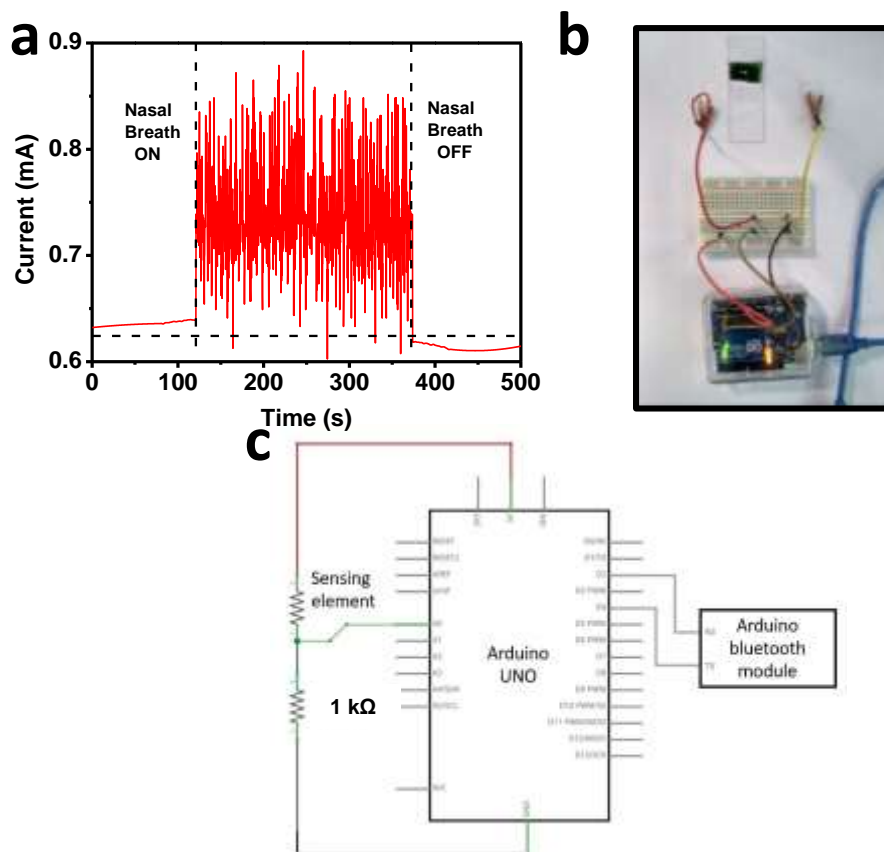


Figure S7. (a) Breath analysis data collected from the sensing element combined with the prototyping platform. (b) Sensor device set-up with circuit, (c) Circuit diagram of the sensor assembly using Arduino UNO and Bluetooth module for data transfer to mobile.

The Arduino interface code used is shown below:

```
int analogPin= 0;
int raw= 0;
int Vin= 5;
float Vout= 0;
float R1= 1000; //specifies the resistance rating of series load in Ohm
float R2= 0;
float buffer= 0;
void setup()
{
  Serial.begin(9600);
}
void loop()
{
  raw= analogRead(analogPin);
  if(raw)
  {
    buffer= raw * Vin;
    Vout= (buffer)/1024.0;
    buffer= (Vin/Vout) -1;
    R2= R1 * buffer;
    Serial.print("Vout: ");
    Serial.println(Vout);
    Serial.print("R2: ");
    Serial.println(R2);
    delay(1000); //specifies time interval between measurements in ms
  }
}
```

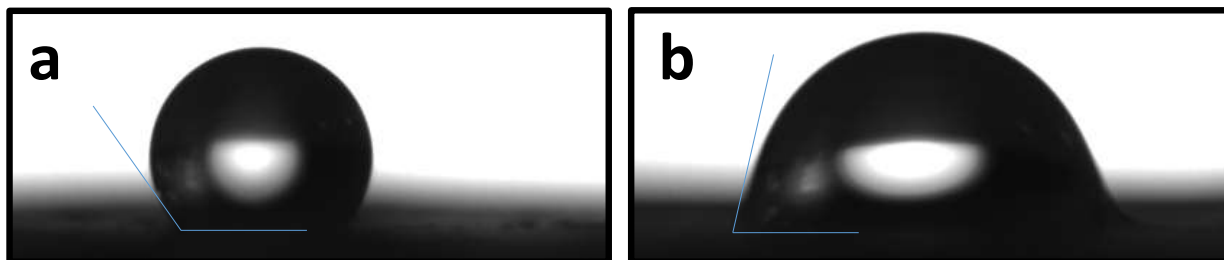


Figure S8. Contact angle measurements performed for PVDF/rGO nanofibers (a) before SILAR and (b) after SILAR treatment.

Table S1. Comparison of the sensing performance between our sensor and previously reported ones.

Sensing element	Sensing Range (% RH)	Response time (s)	Sensitivity	Reference
Supramolecular nanofibers	10-80	0.01	2200	6
Graphene oxide	35-80	0.03	10	7
Polyaniline/poly (vinyl butyral) nanofibers	20-90	1-2	1	8
Amphiphilic Dyad fibers	0-75	0.026	5	9
MoS₂ modified ZnO quantum dots composite	11-95	20	1000	5
Graphene oxide/ polyelectrolyte nanofilm	11-97	1	1000	10
Supramolecular modified graphene oxide	11-95	1	600	11
PVDF/rGO/ PANi based nanofibers	10-95	1	60	Present work
Black phosphorus/ Al₂O₃	20-80	200	6	12
rGO/GO/rGO	6.3-100	1.9	8	13
CNT/PVA filament	60-100	40	220	14
CNT/polyimide composite	10-95	-	1.5	15
CNT/cellulose paper	10-90	6	0.67	16
MWCNT	25-95	3	1.4	17
Silica nanoparticle	10-80	2.4	0.001	18
Paper based	0-90	3	2	19
Wrinkled graphene	11-95	0.0125	1.1	20

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