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Humidity-responsive Gold Aerogel for Real Time Monitoring of Human Breath

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ABSTRACT: Humidity sensor has received considerable attention in recent years because of its significance and wide applications in agriculture, industries, goods stores and medical fields. However, the conventional humidity sensors usually possessed the complexed sensing mechanism, low sensitivity, and required a time-consuming, labor-intensive process. The exploring an ideal sensing material to amplify the sensitivity of humidity sensor is still a big challenge. Herein, we developed a simple, low-cost and scalable fabrication strategy to construct a highly sensitive humidity sensor based on polymer/gold nanoparticles (AuNPs) hybrid materials. The hybrid polymer/AuNPs aerogel was prepared by a simple freeze-drying method.

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By taking the advantage of conductivity of AuNPs and high surface area of highly porous structure, the hybrid poly-N-isopropylacrylamide (PNIPAm)/AuNPs aerogel showed high sensitivity to water molecules. Interestingly, the hybrid PNIPAm/AuNPs aerogel based humidity sensor can be used to detect human breath in different states such as normal breath, fast breath and deep breath, or by different individuals such as person in illness, smoking and normal, which is promising in practical flexible wearable devices for human health monitoring. In addition, the humidity sensor can be used in whistle tune recognition.

KEYWORDS: Humidity sensor, gold aerogel, AuNPs, PNIPAm, breath monitoring

1. Introduction

Humidity sensors are widely used in chemical warehouse, air conditioning, paper industries and some food storage areas.[1] Fast response rate, high sensitivity, good stability, and high selectivity are the essential requirements for humidity sensing devices.[2] However, the conventional humidity sensors usually employed ceramics, semiconductors and organic polymers, resulting into some serious drawbacks such as complexed sensing mechanism, time-consuming, labor-intensive process, low-sensitivities, high cost, and non-operational behavior at high temperature.[1, 3-4] Many research efforts have therefore been devoted to develop novel advanced materials for highly sensitive humidity sensing. Until now, different nanomaterials such as ZnO, Ag and Ag/SnO_2, CuO, WS_2, and TiO_2 have been used in humidity sensing.[5-8] For instant, Phan D. T et al [9] fabricated black phosphorous and graphene-based nanohybrid material to monitor humidity with high sensitivity and fast response. Similarly, Li et al [10] designed a humidity sensor based on LiCl-TiO_2 via electrospinning technique. The designed humidity sensors could monitor the relative humidity range from 11% to 95%. The recent progress has

revealed that humidity sensing materials with porous structure show lots of advantageous to improve the humidity sensing performances.[11-13] Liu and coworkers[14] has described polymer/ TiO_2 hybrid porous materials for humidity sensing in a large range from 10% to 90%.

Aerogels have unique ultra-high porous structure, endowing them with various distinctive properties such as low density, larger inner surface area, low dielectric and thermal properties, profuse and large open interconnected pores.[15-17] Following Kistler's pioneering preparation of aerogel,[18] the fascination with aerogel structures, functions and applications has prompted an avalanche of research activity.[19-21] Recently, Nyström and coworkers [22] synthesized a new class of ultra-low density amyloid templated Au-aerogel for catalytic application. Qian et al[23] prepared Ag nanowires based ultralight aerogel with high conductivity. However, to the best of our knowledge, there is no reports about gold aerogels as humidity sensing materials for practical flexible wearable devices for human health monitoring.

Herein, we developed a simple, facile and efficient approach to prepare hybrid PNIPAm/AuNPs aerogel and explored the humidity sensing applications. The designed hybrid PNIPAm/AuNPs aerogel has hydrophilic groups, which can easily interact with water molecules and lead to the formation of hydrogen bond.[24] Hence, due to the high specific surface area, relatively high conductivity and high porosity, the designed hybrid PNIPAm/AuNPs aerogel can instantly capture water molecules at relatively high humidity via dynamic hydrogen bonds and easily detach water molecules at low relative humidity. The designed humidity sensors were employed to detect human breath and whistle tune recognition. In addition, our system exhibits fast response and linear sensitivity to relative humidity as compared to other available systems.[25-26]

2. Experimental Section

2.1. Materials. All chemicals were provided from Sigma-Aldrich and Aladdi. N-isopropylacrylamide (NIPAM), Potassium Persulfate (KPS), Ammonium Persulfate (APS) and N, N'-methylenebisacrylamide (MBA) and Acrylamide (AAm).

2.2. Instrument. The morphologies in the experiments were characterized by scanning electron microscopy (SEM) (JEOL JMS-6700F instrument) and transmission electron microscopy (TEM) (TECNAI T20 with an accelerating voltage 200kV). CHI 660D electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China) was used to perform the electrochemical analysis. X-ray diffraction (XRD) data were obtained from Bruker AXS, D8 Advance. X-ray Photoelectron Spectroscope (XPS) data were obtained from AXIS ULTRA DLD. Relative humidity was tuned by Espec SH-24.

2.3. Synthesis of Gold nanoparticles (AuNPs). Firstly, all the glassware were cleaned with aqua regia (HNO_3/HCl = 1:3) and then completely rinsed with water. AuNPs (18 nm) were synthesized according to the previous method.[27] In a typical synthesis, 100 ml of HAuCl4•3H2O (2.5 mM) was added into a three neck bottom flask (250 ml), and stirred at 300 r/min at 120 ^{o}C. Then, 10 ml of 1% sodium citrate (SC) was quickly added. After 20 min, the solution color changed to ruby red, indicating the formation of AuNPs. UV-visible Spectra of AuNPs (Figure S1 and S2) showed the plamonic peak at 522 nm, which is good agreement with previous work.[28-32]

2.4. The preparation of hybrid PNIPAm/AuNPs hydrogels. First, 50 mg of crystalized purified NIPAM monomer, 60 mg of AAM monomer, 4 mg MBA as cross-linking agent and 100 µl (40 mg/ml) KPS initiator were added in a plastic tube. Then a predetermined amount of

$HAuCl_4$ solution and 1.2 mL PVA solution (1%) were added. Furthermore, oxygen has been removed by using nitrogen and the sealed solution was kept in the refrigerator at 4 ºC.

The solution was added into a homemade hollow device by quartz glass plate and Teflon plate, and was kept in the oven at 60 ºC for 6 hours. The prepared hydrogel was taken out and washed with deionized water. The hybrid PNIPAm/AuNPs hydrogels also can be prepared at room temperature by addition of TEMED.

2.5. Preparation of PNIPAm/AuNPs hydrogels using 18 nm AuNPs. 50 mg of NIPAM after crystallization, 60 mg AAm, 4 mg MBA monomer as crosslinking agent and 100μL (40 mg/mL) KPS initiator and 3.5 mL of the synthesized 18 nm AuNPs solution were mixed and dissolved well. Then 10μL of TEMED accelerator was added in the solution to get hydrogel.

2.6. Preparation of PNIPAm/AuNPs Aerogel. The prepared NIPAM/AAm/Au hydrogel was frozen in a refrigerator at -80 ºC for 4 h and then freeze-dried in a freeze dryer for 12 h to obtain NIPAM / AAm / Au aerogel. The formation of Au-aerogel can be carried out by two methods. 1) Direct addition of $HAuCl_4 \cdot 3H_2O$ with AAm, NIPAM, (N, N'-methylenebisacrylamide) MBA and Potassium persulfate KPS mixed solution. 2) The synthesized AuNPs (18nm) were added in AAm, NIPAm, MBA and KPS mixed solution. The different samples with different amount of chemicals were listed in Table 1.

	AAm mg	NIPAM mg	MBA mg	KPS (40mg/ml) uL	TEMED uL	T ºC	PVA (1%) mL	$HAuCl_4$ %
A	30	25	2	50	-	60	0.6	-
B	30	25	2	50	-	60	0.6	0.097
C	30	25	2	50	-	60	0.6	0.97
D	30	25	2	50	-	60	0.6	9.70
E	30	25	2	50	-	60	0.6	24.3
F	60	50	4	100	-	60	1.2	0.97
G	60	50	4	100	-	60	1.2	0.97
H	60	50	4	100	10	25	1.2	0.97
I	30	80	4	100	10	25	1.2	0.97

Table 1. Chemical content and temperature variation for the preparation of hybrid PNIPAm/AuNPs aerogels

3. Results and Discussion

Initially, PNIPAm/AuNPs hydrogel as an intermediate is obtained by the polymerization of NIPAM (N-isopropylacrylamide) and in-situ reduction of $HAuCl_4 \cdot 3H_2O$. The prepared PNIPAm/AuNPs hydrogel was further treated by freeze-drying to acquire light weight and porous PNIPAm/AuNPs aerogel. Super critical drying method is the widely used approach to get nanomaterials with high porosity and high surface area.[33] In present study, freeze-drying method was used to get the desired aerogel from the intermediate hydrogel. This one-step strategy is promising because it is very simple, facile and efficient to large-scale get Au-aerogel with

tunable Au concentrations. **Figure 1** shows the synthetic roadmap towards the functional Au-aerogel and its application.

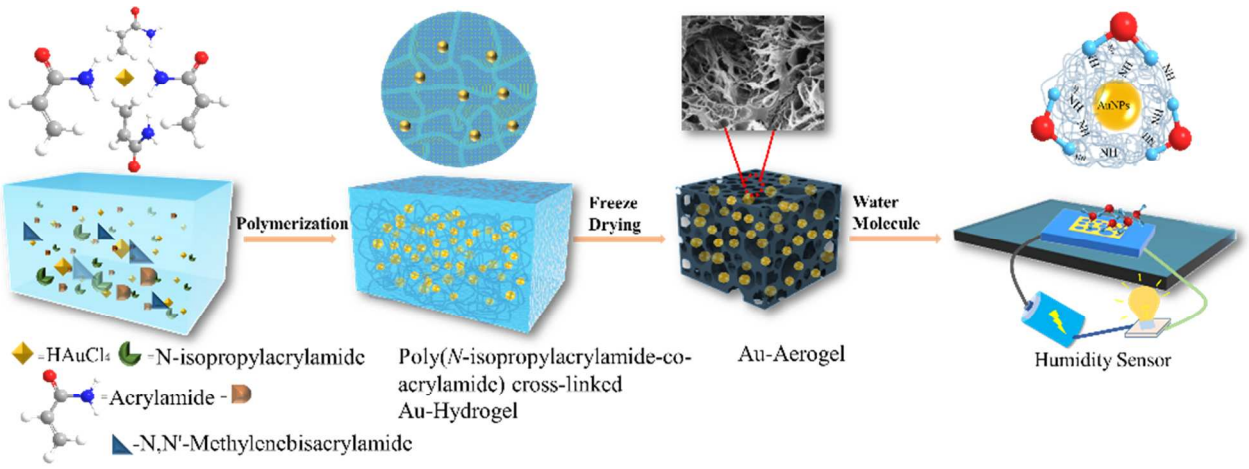

Figure 1. Schematic illustration of the fabrication of hybrid PNIPAm/AuNPs aerogel and its application in humidity sensor.

The optimized experiential parameters are necessary to tune the desired structure of Au aerogel. Table 1 illustrates the different chemical concentrations of $HAuCl_4$ and other chemicals used for the preparation of Au-aerogel (Table 1). Figure S3 and Figure S4 demonstrate the effect of $HAuCl_4$ concentration and temperature on the preparation of Au-aerogel. The increase of Au concentration would lead to color changes of hybrid PNIPAm/AuNPs aerogel from white to pink, then to purplish red, and finally to orange. Actually, the hybrid PNIPAm/AuNPs aerogel can be prepared with/without tetramethylethylenediamine (TEMED). Without TEMED, N-isopropylacrylamide (NIPAM) required a high temperature about 60 ºC in the presence of Potassium Persulfate (KPS) for polymerization. While polymerization reaction was achieved at room temperature by the addition of TEMED, because TEMED can act as an activator for the activity of KPS.

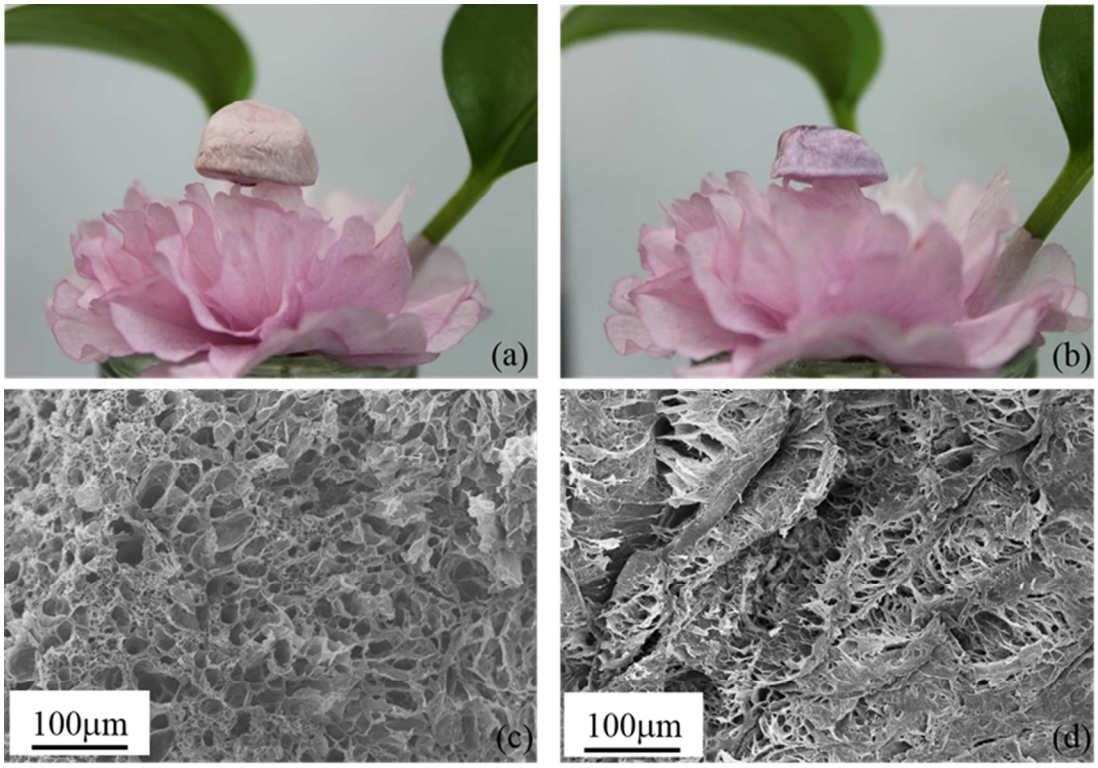

Figure 2. The photographic images and scanning electron microscopy (SEM) images of hybrid PNIPAm/AuNPs aerogel with different Au concentrations (a, c: 0.97%; b, d: 0.097%).

Figure 2a and b show photographic images of the hybrid PNIPAm/AuNPs aerogel with different Au concentrations, which clearly show their distinctive low-density feature by standing on the tip of the flower. The density of hybrid aerogel can be tuned in a range from 0.001 to 0.5g/cm^{-3}. The lowest density is about 0.177g/cm^{-3}, approximately one hundred forty-five times heavier than air density (0.00122g/cm^{-3}). Figure 2c and 2d shows SEM images of hybrid aerogel. The hybrid PNIPAm/AuNPs aerogel with Au concentration of 0.97% shows a honeycomb-like structure. While the hybrid aerogel with low Au concentration of 0.097% shows broken multilayer structure. It is clear to see porous structure in hybrid PNIPAm/AuNPs aerogel, and as Au concentrations increased, the number and size of porous increased. The previous work about PNIPAm-catechol2@Au hydrogel also shows the similar structure.[27] Additionally, different

well-designed shapes of Au-aerogel can be obtained by present approach, which is an easy method to acquire versatility in shapes of Au-aerogel **(Figure S5)**.

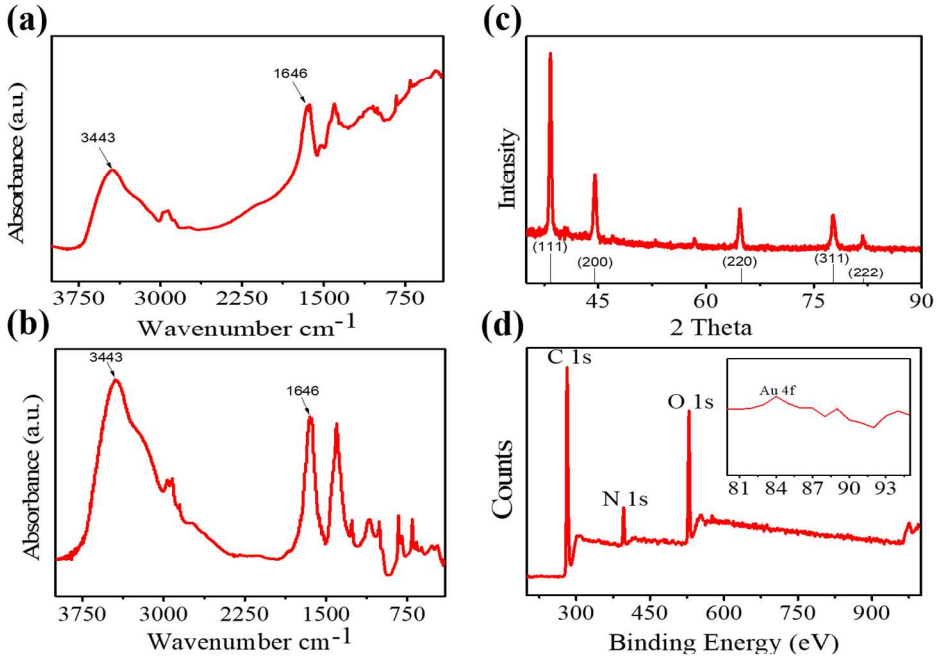

Figure 3. FTIR spectra of (a) PNIPAm and (b) PNIPAm/AuNPs aerogel; (c) XRD spectra and (d) XPS spectra of hybrid PNIPAm/AuNPs aerogel.

In order to characterize the structure of PNIPAm/AuNPs aerogel, different instrumental techniques have performed, and corresponding data were shown in **Figure 3**. The FTIR spectra of PNIPAM and Au-PNIPAM has shown its characteristic peaks in **Figure 3(a, b)**. The carbonyl (C=O) stretching vibration at nearly 1646 cm^{-1} and the amine (N-H) stretching frequency at 3443cm^{-1} can be ascribed into the side chain of PNIPAm.[34-35] XRD was used to predict the monocrystalline structure of AuNPs. The obtained results (**Figure 3(c)**.) showed the diffraction peaks appeared at 2θ=38.3°, 44.4°, 64.7°, 77.6°, and 81.5° correspond to (111), (200), (220), (311) and (222) of characteristics peaks of gold metal, respectively [2,26] XPS spectra

(**Figure 3(d)**.) of Au-aerogel has clearly shown information about the Au (B.E=81-85eV) and other major chemical contents such as carbon, oxygen, and nitrogen from PNIPAm**.**

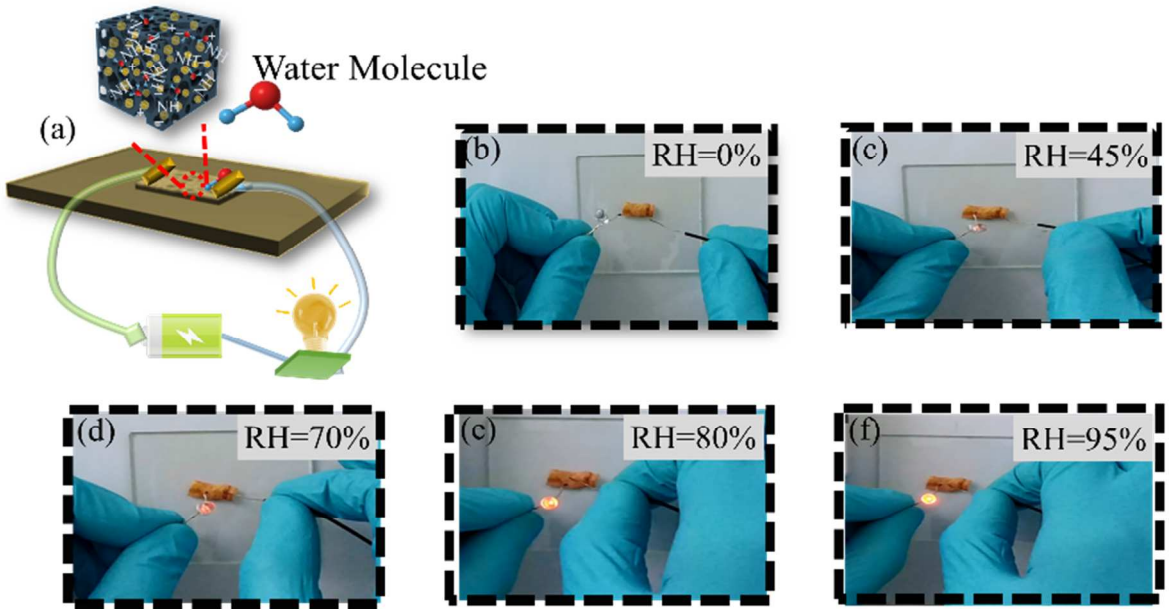

Figure 4. Schematic (a) for hybrid PNIPAm/AuNPs aerogel in a circuit to detect humidity sensing from water molecule; b-f shows the conductivity changes with respect to relative humidity (RH).

Figure 4 shows that the conductivity of hybrid PNIPAm/AuNPs aerogel is very sensitive to humidity. As the contents of gold nanoparticles increase in hybrid aerogel, it is expected to get the high conductive properties. The conductivity can be precisely controlled by simply tuning Au concentrations in hybrid aerogel. Aerogel can be used as switch in the circuit (**Figure 4a**) to turn on/off the light by connection of circuit with aerogel exposing to water molecules. **Figure 4b-f** shows the relationship between the conductivity of hybrid aerogel and Au concentrations. It is clear to see that the conductivity can be tuned from nanoampere to microampere, which is promising in an electronic circuit without utilization of semiconductors. The humidity sensing

mechanism can be explained based on the conductivity signals. AuNPs in the hybrid PNIPAm/AuNPs aerogel are not connected each other by themselves, leading to the low conductivity. While, water molecules would interact with hybrid aerogel, and results in the clear conductivity change. Water molecules may cause the additional pathways of proton transport, beyond the distance between two AuNPs. Water molecules tend to interact with C=O and amine groups of PNIPAm through hydrogen bond and act as a bridge between two AuNPs. Yamauch et al[36] explained theoretically and experimentally the formation of hydrogen bond between N-H group of PNIPAm with the oxygen of water molecules. In FTIR spectra (Figure S6), it is clearly to see two peaks. One is at 1625cm-1, which can assigned to C=O bound to water molecules. The second peak at 1650cm-1 can be assigned to amide group (C=O----HN) from hydrogen bond.

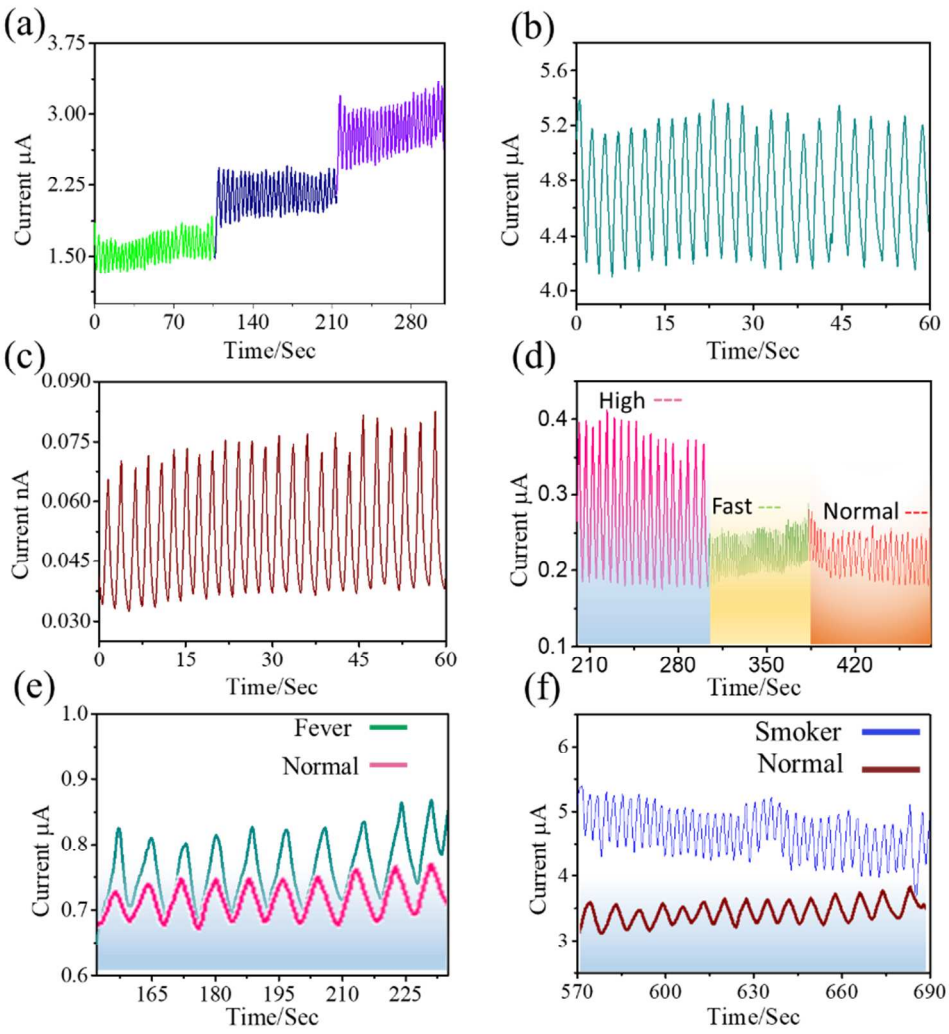

Figure 5. Real-time breath analysis by using Au-aerogel sensor at different states of subject. (a) The detection of normal breath with sneezing; (b) Au-aerogel sensor with high Au concentration for the detection of normal breath; (c) Au-aerogel sensor with low Au concentration for the detection of normal breath; (d) The detection of breath at different breath rate (high breath, fast breath and normal breath); (e) The detection of breath from normal and sick person; (f) The detection of breath from smoker and normal person.

The humidity sensing of hybrid Au aerogel to water molecules allow us to monitor human breath. The hybrid Au aerogel was employed in a designed smart mask for the detection of humidity sensing. The mask is very simple and have great advantages such as non-invasive

sensor and no-contact with skin for diagnosing different diseases such as asthma, cancer, diabetes etc.[31,37] Theoretically, human breath monitoring by hybrid Au aerogel based sensor is possible due to the increase of humidity during exhaling breath process. Therefore, the designed Au aerogel-based sensor can measure the different breath response. The breath air usually is humid, and contains lots of water molecules. When breath air comes out from the mouth, there is an increase in conductivity and contrary it would show decrease in conductivity during inhaling process. Figure 5a shows the detection of normal breath with sneezing. The hybrid Au aerogel still shows response. High concentration of Au in Au-aerogel causes the conductivity change during breath response to about microampere **Figure 5b**, while low concentration (0.25mM) of $HAuCl_4$ also shows a good response to breath while conductivity value decreases to nanoampere **Figure 5c.** Similarly, **Figure 5d** shows detection of breath at different breath rate (high breath, fast breath and normal breath. It is clear to see a clear difference between the normal and fast breath rate. In addition, the irregular breath were tested. Normal and ill person breath are monitored and obtained a clear difference in **Figure 5e**, as the breath rate of a normal person is lower than the person with disease. A smoker breath is different from a normal person breath (**Figure 5f)**. Smoking cause damage to lungs and respiratory system, after few years of regular smoking, a person shows uncontrollable breath rate. The breath from non-smoker normally changes regularly at a long time. While in case of smokers, the breath normally changes irregularly, which lead to a clear difference in humidity sensing signals.

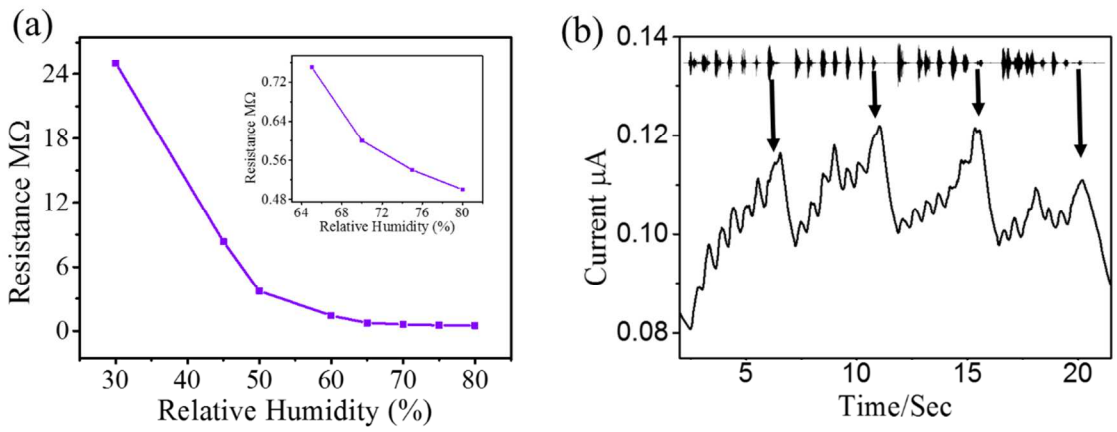

Figure 6. The relationship (a) between the resistance and relative humidity range (30%-80%) and (b) Au-aerogel sensor used in whistle tune recognition.

The response of Au-aerogel to relative humidity is much stronger in humidity value from 25 to 60% (**Figure 6a).** It is very interesting to find that response of Au aerogel can be used to get the response of whistle. F**igure 6b** shows that when a person blows whistle near aerogel, hybrid Au aerogel can detect the humidity, and show a proper change of conductivity value during whistle. Interestingly, the Au aerogel system showed similar signal peaks by the audio signals of a tune, which is promising in practical applications such as voice recognition, song notes recognition and noise identification.

4. Conclusions

In summary, we successfully synthesized low-density and highly porous hybrid PNIPAm/AuNPs aerogel. By taking the advantage of conductivity of AuNPs and high surface area of highly porous structure, the hybrid Au aerogel showed high sensitivity to water molecules. The designed humidity sensor can be used to detect human breath and whistle tune recognition, which is promising in practical flexible wearable devices for human health monitoring or some other advanced applications in near future.

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Supporting Information Available: UV-Vis spectra of synthesized AuNPs, TEM image of AuNPs, different shapes of synthesized Au-aerogel and breath response. This material is available free of charge via the Internet at http://pubs.acs.org

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