Synthesis of Au nanospheres, Au/PVDF nanocomposites and their breath sensing properties

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Abstract

Herein, we report, a simple breath sensor based on Au/PVDF nanocomposites. Au nanostructures have been synthesized by using a simple seed mediated growth method. The synthesized Au nanostructures exhibited uniform spherical morphology with average diameter ~20 nm, confirmed by FESEM analysis. The synthesized nanostructures were further used to form nanocomposites with Polyvinylidene Fluoride (PVDF). The synthesized Au nanospheres as well as Au nanospheres/PVDF nanocomposites were tested for breath analysis. The nanocomposite materials were found to sense breath and uniform breathing patterns were generated. During breathing over sensor, voltage gets generated. The maximum voltage obtained was around 280 mV in breathing cycle.

Introduction:

Gold (Au) is a well-known noble metal with excellent optical, mechanical and electrical properties. Au exhibits various nanostructures like nanospheres[1,2], nanorods[3-5], nanowires[6,7], nanoplates, nanocubes, nanostars etc. These nanostructures have vast area of applications in different fields. Some of them to list are air cleaning, emission management, water purification, power cells, and critical medical applications like anticancer therapy, drug delivery, biomarkers and biosensors applications[8]. Further, Au nanostructures have been used for composite preparation along with various polymers like polypyrene (PPy), polyaniline (Pani), polythiophene (PTh), Polyvinylidene Fluoride (PVDF), Polytetrafluoroethylene (PTFE)[9,10]etc. Theses Au/Polymer nanocomposites have been used for applications such as gas sensing, humidity sensing, dielectric measurements, electrochemical supercapacitors, electrochemical sensors etc. Breath sensing and breath analysis is an emerging technology. There are many traditional breath sensing techniques like Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)[11], Proton Transfer Reaction Mass

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Spectrometry (PTRMS)[12], Gas Chromatography Mass Spectrometry (GC-MS)[13] which are non-invasive as well as highly sensitive. However, all these methods have drawbacks like huge set up, complex machineries and expensive. Nowadays many reports are coming up with various nanostructure based electrical and optical sensors for breath analysis[14-16]. Feiyi Liao et.al[15] have developed a breath sensor to detect apnea syndrome by transfer-printing vanadium dioxide (VO_2) thin films on PDMS substrates. They have obtained the response time and recovery time of 0.5 s. Seon Jin Choi et.al[16] have synthesized WO_3 hemitube nanostructure assisted by O_2 plasma surface modification with functionalization of graphene-based material for the detection of acetone (CH_3COCH_3) and hydrogen sulfide (H_2S) which are biomarkers for the diagnosis of diabetes and halitosis, respectively. They have showcased response times of 11.5 ± 2.5 s and 13.5 ± 3.4 s to 1 ppm acetone as well as 12.5 ± 1.9 s and 10.0 ± 1.6 s to 1 ppm of H_2S, respectively. Danling Wang et al[17] have synthesized novel nanostructured $K_2W_7O_{22}$ and tested on its feasibility for acetone detection in breath with response time of 12 s is achieved. In Our earlier reports we have synthesised Au nanowires and nanorods based nanocomposites[3,6]. They are proved to be excellent humidity sensors and have good sensitivity towards human breath. In the same regard, here, we report breath analyzer based on Au nanospheres and PVDF nanocomposite.

Experimental:

Synthesis of Au nanospheres:

Au nanospheres have been synthesized using earlier reported method[1,2]. The detailed procedure is as follows. Gold chloride trihydrate ($HAuCl_4.3H_2O$, 99%) (Sigma Aldrich) and trisodium citrate dihydrate ($Na_3C_6H_5O_7.2H_2O$, 99 %) (Alfa Aesar) were used as a precursor. For the synthesis of seed solution, 150 mL of 2.2 mM trisodium citrate dihydrate (TSC) was dissolved in DI water and heated at ~100 °C in a 250 mL three necked round bottom flask with a condenser. The solution was stirred continuously. 1 mL of 25 mM $HAuCl_4$ was added to the boiling TSC solution. The color changes to light pink after 15 – 20 min, indicating formation of Au seeds. The solution was allowed to cool down to 90°C, then to this solution, further, 1mL of 60 mM TSC was added followed by addition of 1 mL of 25 mM $HAuCl_4$ after 2 min. The reaction mixture was continued to heat with stirring for 30 mins and again TSC and $HAuCl_4$ were added and kept under same condition for 30 mins. Then the solution was allowed to cool down to room temperature.

Synthesis of Au nanosphere/ PVDF nanocomposite

Various concentrations of PVDF (0.5, 1, 2, 5 wt%) were prepared in DMF and 1 mL as-prepared Au nanosphere solution was added to this PVDF/DMF solution. This nanocomposite mixture was stirred for 1 h at 60°C. The resultant as synthesized Au nanosphere solution and nanocomposite solution was used as it is for UV-Visible Spectroscopic and FTIR analysis. The nanocomposite solution was coated on glass slide to form a film for XRD and on interdigitated electrode for breath sensing analysis.

Characterizations:

(a) Physiochemical Characterization of the as prepared composites.

Fourier-transform infrared spectroscopy (FTIR) analysis was done using a Bruker TENSOR37 spectrometer, X-Ray Diffraction analysis is done on a Rigaku Miniflex diffractometer using CuKα radiation (λ = 1.5405 Å; nickel filter). Optical absorption spectra were recorded on a Hitachi UV-Visible Spectrophotometer (model U-3210). Morphological studies were conducted using FE-SEM (Hitachi Model 5890). For the characterization, the samples were prepared by drop casting the material on alumina stub.

(b) Breath – Sensing Characterization.

The breath sensing experiments were conducted for Au nanospheres and Au/PVDF nanocomposite as shown in schematic Fig. 1. For this purpose, the material was dropcasted on an alumina substrate having silver interdigited electrodes printed on it. Once the material is coated on the substrate, it is allowed to dry in an oven @ 120 °C for 1 h. Using this material coated IDE, the breathing tests were carried out. The change in voltage with respect to breathing was recorded on Digital multimeter (Keithley DMM 7510).

Results and discussion:

Polyvinylidene fluoride (PVDF) (-CH_2-CF_2)n is a semi crystalline polymer. There are 3 polymorphs of PVDF viz α, β and γ. Among these, β phased PVDF[18-20] is desirable due to its ferroelectric nature. The formation of β phase was first confirmed from the FTIR analysis. The FTIR spectra of the as prepared Au nanospheres, PVDF and Au / PVDF nanocomposite are shown in Fig 2. From the FTIR spectra of nanocomposite, absorption bands at 410, 478, 510, 876, 1071, 1275, 1402, 1433 related to β phase are observed. Addition of Au nanospheres to PVDF have helped in the β phase formation of the material[3,21].

The XRD patterns of pure PVDF powder, PVDF film drop casted on glass slide and Au/PVDF nanocomposite is presented in Fig 3. Fig 3 (a) exhibits the XRD pattern of PVDF powder. PVDF powder is mainly made up of α- phase. It could be confirmed from the two intensive peaks at 18.34° and 19.90° and a minor peak at 26.66° corresponding to (020), (110) and (021) reflections of monoclinic α – phase crystals. When the film of PVDF was prepared (Fig. 3(b)), the pattern clearly exhibit the semi crystalline nature of the sample in the view of the broad peak within the range of 15 to 22 ° 2θ. Crystalline planes at 2θ = 18.43°, 20.02°, 26.98°, 32.47°, 36.07°, 38.62° are indexed as (020), (110), (021), (121), (200), (131), respectively and it is consistent with β – phase (JCPDS Card No: 42 – 1650). The ferroelectric β phase is characterized by an all – trans (TTTT) conformation. The peak at 18.43° is very minor confirming the formation of β phase. The heat treatment was given to PVDF to obtain the β phase. For Au / PVDF nanocomposite the peaks around 18 ° are broad and minorly present indicating formation of both β and γ phase[21].

Fig. 4 (a) depicts the UV-Vis spectrum of Au/PVDF nanocomposite. Here both the signature peaks of PVDF (observed at 240 nm and 278 nm) as well as Au nanosphere (observed at 522 nm) could be observed in the UV-Vis spectrum of nanocomposite. The PVDF peaks in nanocomposite are observed to be slightly blue shifted than pristine PVDF film which confirms the formation of Au/PVDF nanocomposite[3]. In pristine PVDF film (Fig. 4 (b)) two signature peaks at 242 nm and 292 nm are observed. Whereas, optical absorption spectrum of Au nanosphere (Fig. 4 (c)) exhibited surface plasmon resonance (SPR) peak[22-24] at around 522 nm confirming the formation of Au nanospheres.

The FESEM images of Au nanospheres, pristine PVDF and PVDF/Au nanosphere composite are as shown in Fig. 5(a), (b) and (c) respectively. From the Fig 5 (a) uniform sized Au nanoparticles with more or less spherical shape are observed. The size of the Au nanoparticles is ~20 nm in diameter. Fig.5 (b) depicts the FESEM image of PVDF matrix which shows the smooth porus structure of the polymer. In case of Au/PVDF nanocomposite (Fig. 5(c)) this smooth polymer structure was found to be disintegrated probably due to incorporation of Au nanospheres inside polymer matrix[21]. Moreover, due to nano size (~ 20 nm), it is difficult to spot the Au nanospheres in FESEM.

Further, these Au nanospheres and Au/PVDF nanocomposites were tested for breath sensing analysis. As reported earlier, Au nanostructures are excellent humidity sensing materials[6,25] and can also be sensitive towards human breath[3] since human breath contains 90% humidity. For the breath sensing tests, the breath samples of a 34 years old female have been used. When tested for breath exposure, our materials exhibited change in resistance and also change in voltage. The resultant waveforms pertaining to change in voltage were recorded for normal breathing with nose and forced breathing with mouth. Fig. 6 (a) shows the change in voltage of Au nanospheres for normal breath-in and breath-out. The pattern is uniform and the peaks are Sharpe showing good sensitivity of Au nanospheres towards breath. Fig. 6 (b) shows the change in voltage of the Au nanosphere after the forced inhale and exhale of breath on the material. It is observed that ~200 mV voltage is generated in the material. Also, the response to breath is uniform, showing good sensitivity of the material towards breath. The sensor response was studied over a period of 6 months, and found to be stable. Fig. 7 (a) and (b) shows the normal breathing pattern and forced exhale pattern of Au/PVDF nanocomposite. Here, from the generated patterns, it could be observed that there is storage of charge with each breath in case of normal breathing pattern. Here PVDF plays an important role in charge storage which is not the case with normal breathing pattern of Au nanosphere. From the Fig. 7 (b) the Au/PVDF nanocomposite has generated a voltage of 250 mV which is higher than that of Au nanospheres. Thus Au/PVDF nanocomposite is excellent material for breath analysis and its property of charge generation and storage can be useful to fabricate self-powered device.

Mechanism of breath sensing:

The breath sensing mechanism can be explained on the basis of Grotthus chain mechanism[26]. Grotthus chain mechanism is based on the absorption of moisture on the material surface and in turn, change in the electrical properties. It is well known that, breath contains 90% of humidity. Here, the Au surface chemisorbed water molecule, on exposure to breath, forming hydroxyl species. With increase in humidity, the process of physisorption initiated through hydrogen bonding on previously chemisorbed hydroxyl species. The process of physisorption continues as humidity increases further. Hopping of protons between the hydroxyl groups forms series of dipoles which can conduct charge easily. Therefore, there is sharp change of conductance/resistance and consequent high sensitivity in this region. If the humidity increases further, number of layers of hydroxyl group being adsorbed increases, resulting in weak electrostatic force between the chemisorbed layer and the physiosorbed layer. hence, less hydronium ions are released, and small change is detected in the resistance resulting in decreased sensitivity in higher humidity conditions.

Conclusions:

Au nanospheres and their composite with PVDF have been synthesized successfully. Here quasi spherical shaped Au nanoparticles have obtained with an average diameter of 20 nm. The XRD and UV-Vis spectrum of the Au/PVDF nanocomposite have confirmed the presence of Au nanoparticles in PVDF matrix. The FTIR spectrum of the nanocomposite shows the presence of β phase PVDF in the nanocomposite. All the synthesized composites were tested for breath sensing. The Au/PVDF nanocomposite with 2 wt % PVDF has shown excellent sensitivity towards breath and has generated a voltage of 280 mV, just by breathing on it.

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Figures:

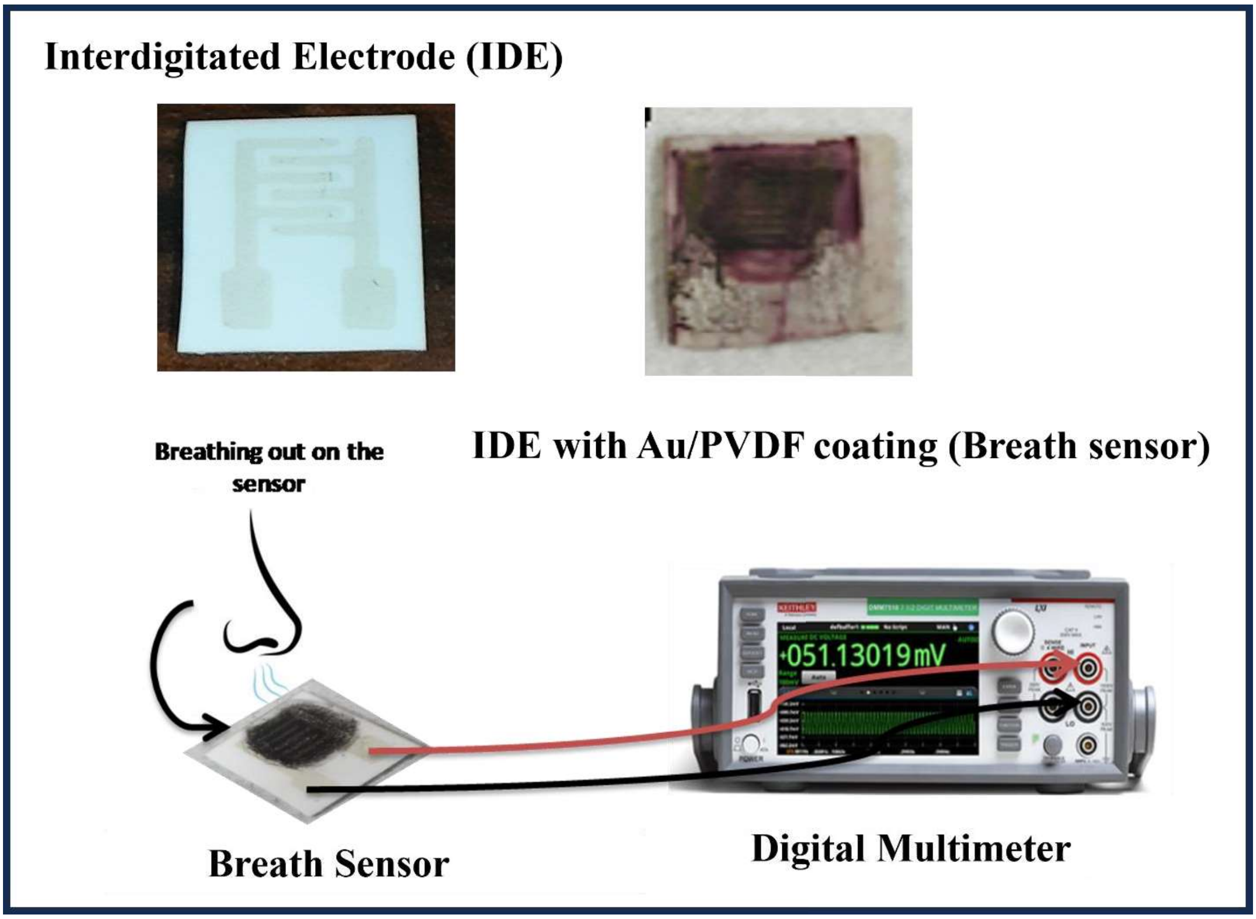

Fig. 1. Breath sensing set up.

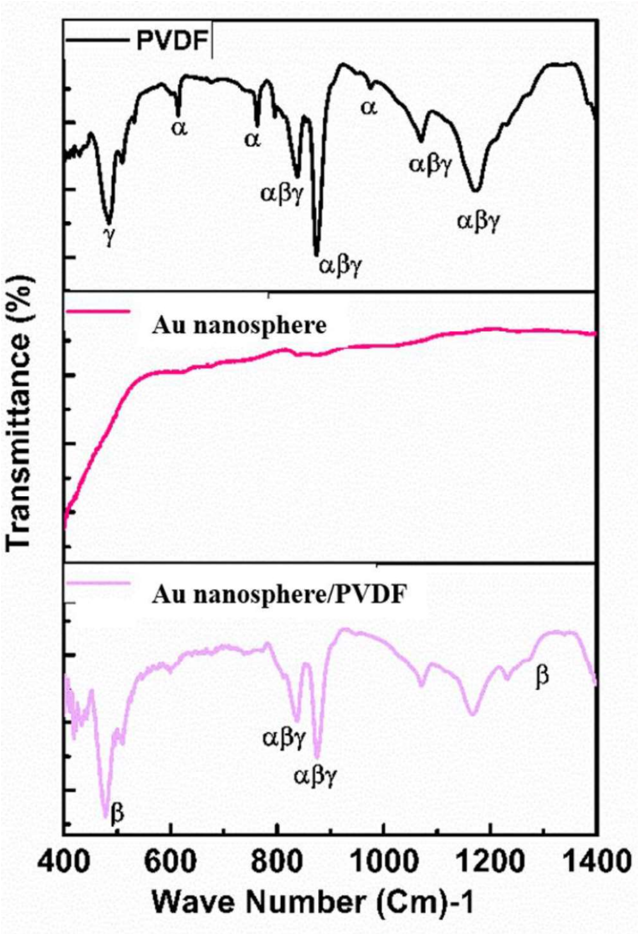

Fig. 2. FTIR spectrum of PVDF, Au nanosphere & PVDF/Au nanosphere nanocomposite.

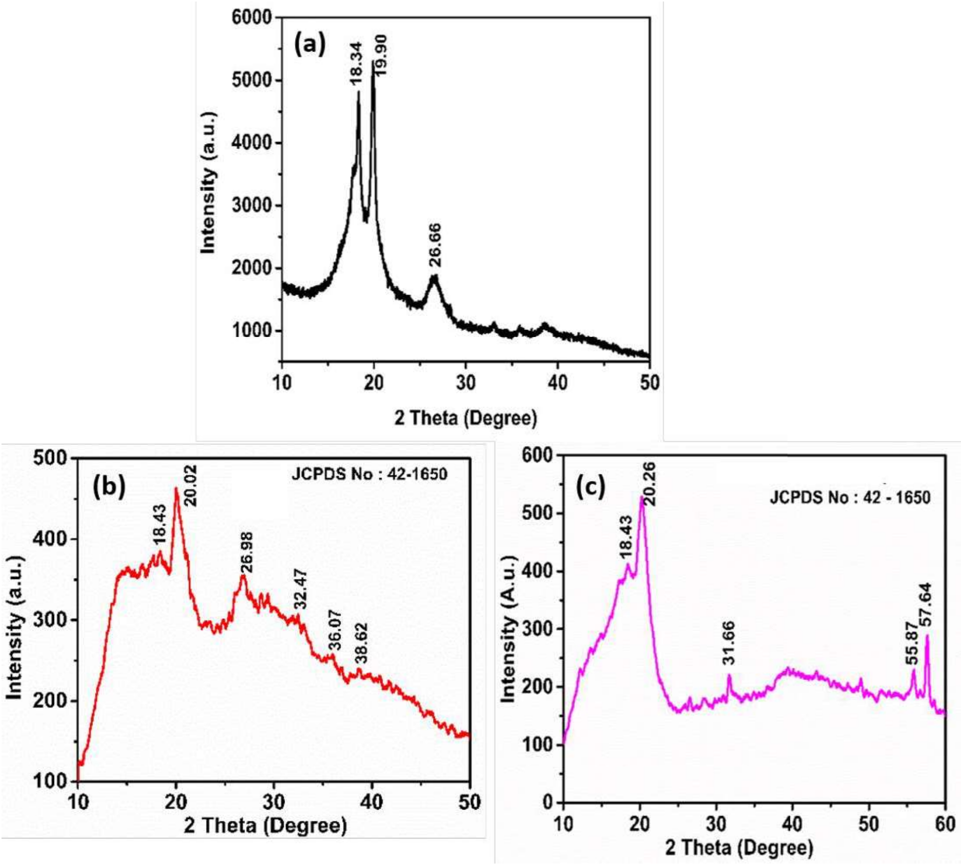

Fig. 3 (a) XRD spectrum of PVDF/DMF solution casted on glass slide. (b) XRD spectrum of PVDF powder. (c) XRD spectrum of PVDF/Au nanosphere nanocomposite

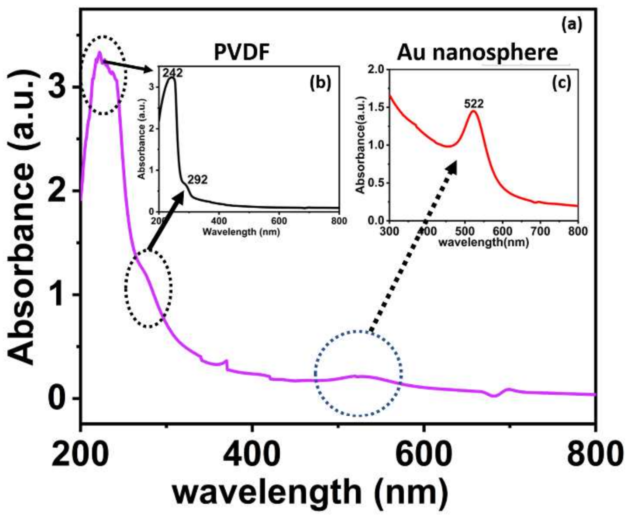

Fig.4. (a) UV Visible spectrum of Au/PVDF nanocomposite, inset: (b) PVDF film. (c) Au nanosphere

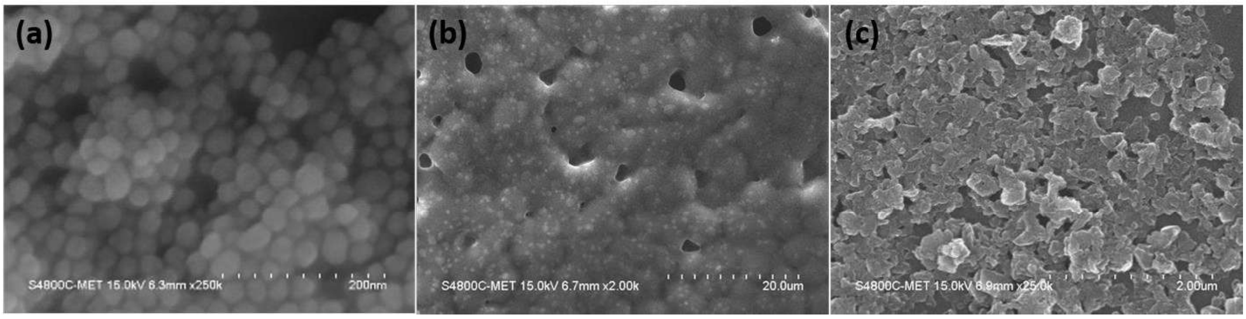

Fig. 5. FESEM images of (a) Au nanospheres (b) PVDF (c) Au nanosphere/PVDF composite

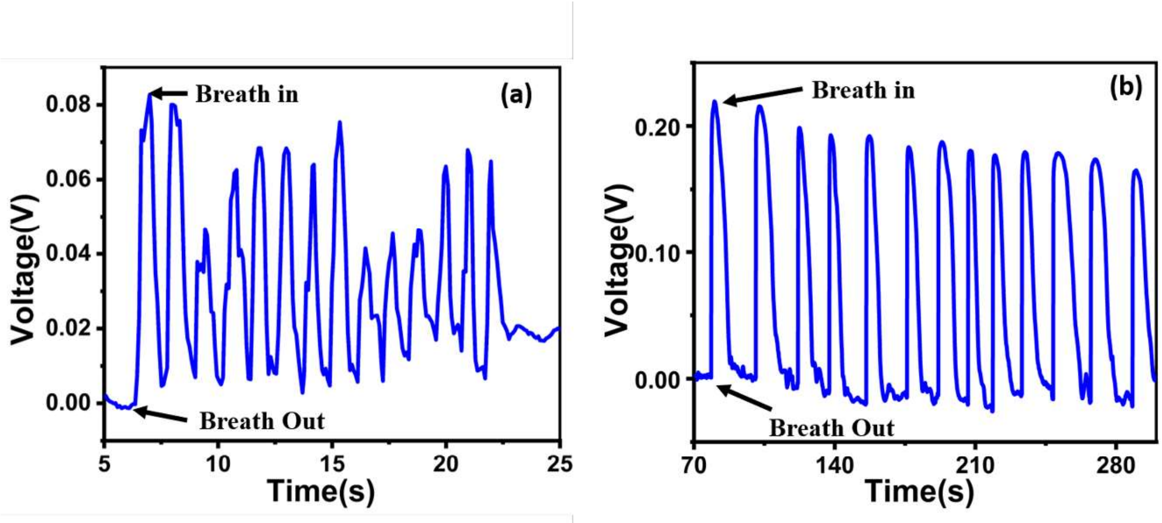

Fig. 6. (a) Normal breathing pattern (with nose) (b) forced exhale pattern (with mouth) for Au nanospheres

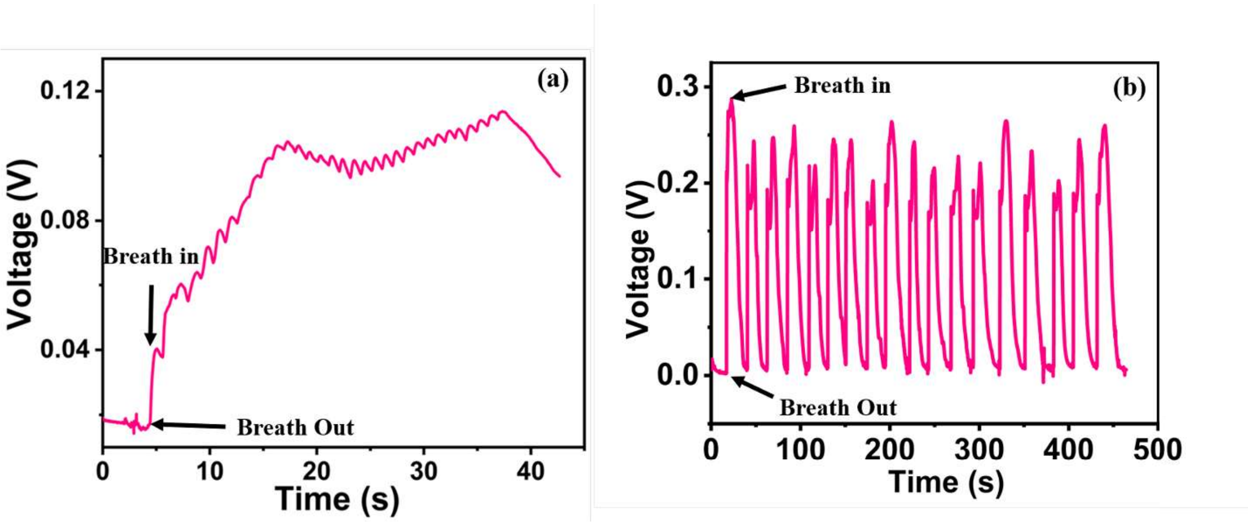

Fig. 7. (a) Normal breathing pattern (with nose) (b) forced exhale pattern (with mouth) for Au/PVDF nanocomposite

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