Supporting Information

Wireless hand-held device based on polylactic acid protected, highly stable, CTAB functionalized phosphorene for CO_2 gas sensing

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Red phosphorous to black phosphorous:

Herein, we have converted red phosphorous to black phosphorous (BP) by ball milling. Initially, we took ball to powder ratio as 10:1 in 50 mL tungsten carbide jar under inert atmosphere. The milling time is 12 h with 60 min run time and 15 min rest time. After the milling, the powder is collected inside the glove box and stored it further use.

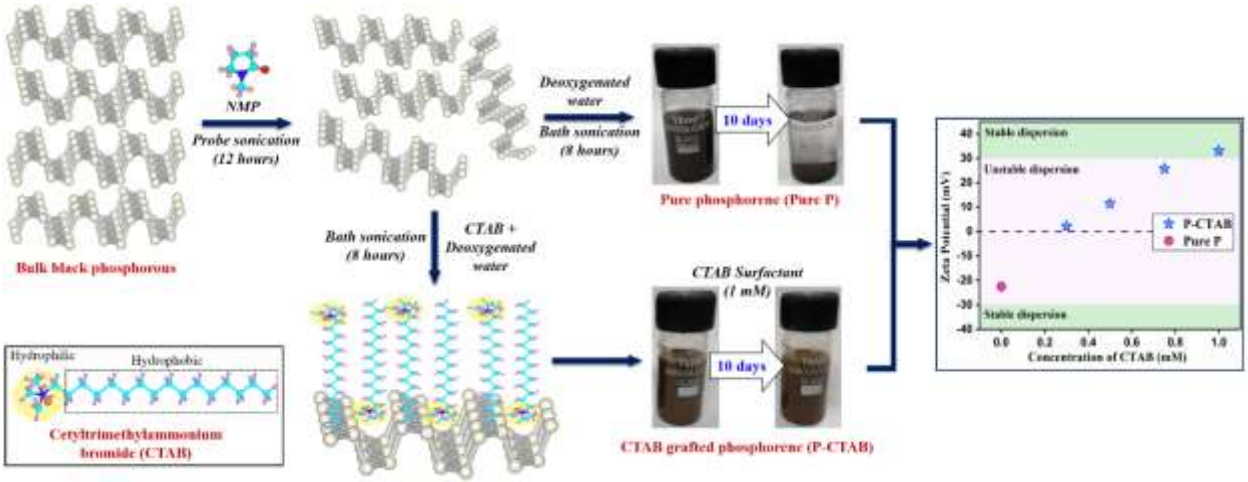

Figure S1. Schematic of the material synthesis and sensor fabrication of pure phosphorene and CTAB grafted phosphorene.

Detailed about hand held device:

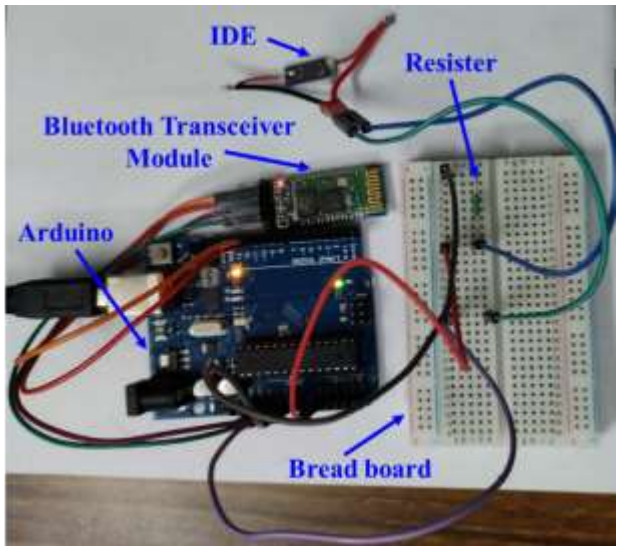

Figure S2. Arduino circuit diagram for resistance calculation and wireless connection via Bluetooth.

Arduino code for resistance calculation:

Arduino board are programmed with the help of Arduino IDE software. The open source Arduino software (IDE) makes it easy to write code and upload it to the board it runs on Windows, Mac OS X, and Linux. The environment is written in Java and based on processing and other open source software.

The code for resistance calculation-

```
const float Voltpin =A0;
        void setup()
{
   Serial.begin(9600);
}
  void loop()
{
   float V1 =analogRead(Voltpin);
     float V2 =(V1/1024)*5;
   float I =(5-V2)/1000; // 1000 ohm is resistance of known resistor
   float R =(V2/I);
   float I2 = I*1000000;

   Serial.print(V2);
   Serial.print("Volts,");
   Serial.print(I2);
   Serial.print("MicroAmps");
   Serial.print(R);
   Serial.println("ohms");

   delay(2000);
}
```

Casing fabrication:

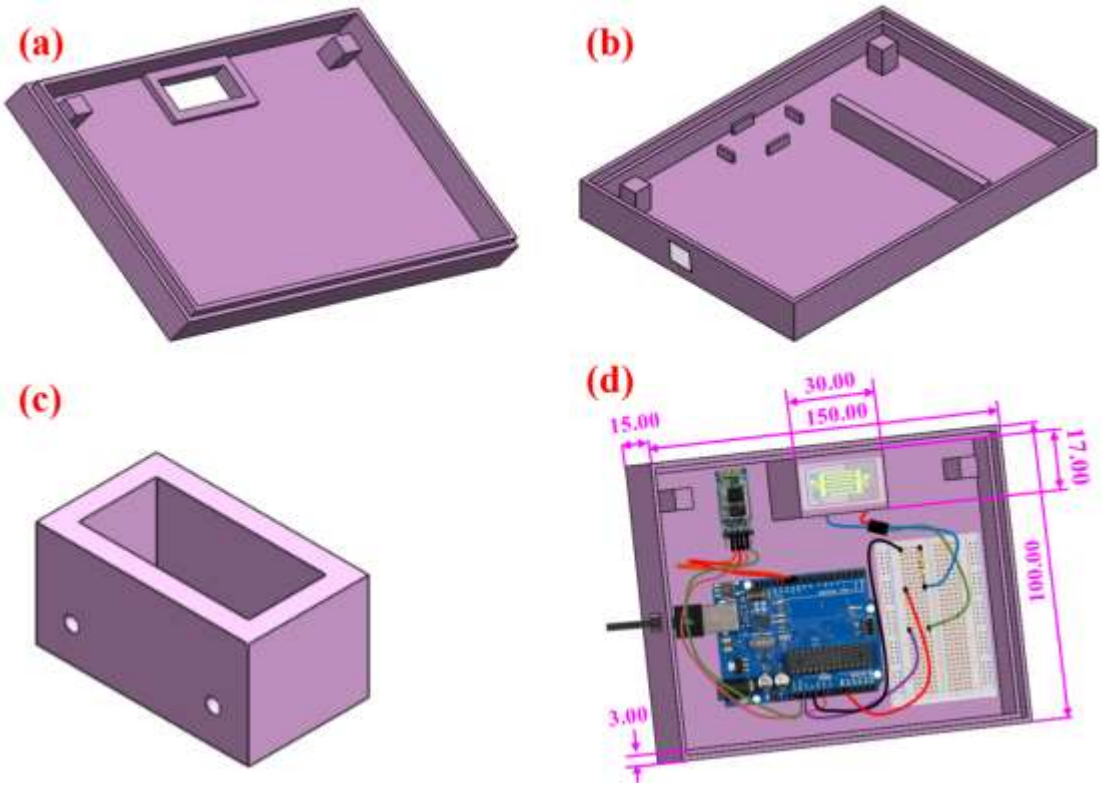

Figure S3. 3D printed model of casing (a) top part, (b) bottom part, (c) sensor part (d) box with dimension.

For device fabrication we have used ABS (Acrylonitrile Butadiene Styrene) polymer because it is suitable for 3D printing.

Fabrication of sensor and Experimental setup:

All the gas sensors are fabricated by using the interdigitated electrode (IDE). An IDE (10 x 4.5 mm^2) having a thickness of 0.5 mm is cut from 4 inch Si/SiO wafer (University wafer; Boston MA) and is designed with 0.3 mm gap for gas sensing test. For patterning IDE electrodes, 4 inch Si/SiO wafer is used for photolithography and metallization. At first, the wafer is cleaned using piranha solution, which removes all inorganic and organic contamination from the surface. Next, a positive photoresist (Microposit S1800) is coated at 3000 rpm for 1 min, followed by prebake for 2 min at 120 °C on a hot plate. After prebaking, the wafer is processed for mask alignment and exposure (EVG 620 mask aligner), 35 mJ/cm^2 energy is considered. Later, the wafer is developed (MG positive photoresist developer) to achieve IDE patterned. A thin Titanium (15 nm) and Gold (70 nm) are deposited through an electron beam evaporator (Enerjet evaporator) onto a substrate. The photoresist layer is then stripped out using acetone in an ultrasonic bath and the final IDE has been prepared. Before drop-casting the sample onto the IDE, initially, IDE has been cleaned by acetone followed by isopropyl alcohol and then distilled water for 2 min each in a bath sonicator. A tin-coated copper wire (dia: 0.1 mm) is joined by soldering process at both ends of the IDE for electrical connection. For sensor preparation, 1 µL of pure phosphorene nanoflakes and CTAB grafted phosphorene nanoflakes solutions are dropped onto the honeycomb area of the designed IDE from the top followed by vacuum dry at 55 °C temperature for 1 h.

A customized test setup is designed to perform the gas sensing studies (see Supporting Information, Figure S4), where a known and fixed volume of the test chamber is made including mass flow controllers (MFCs; 5850E, Brooks Instrument), for controlling the dry synthetic air (79% N_2, 21% O_2) flow including desired target gas inside the test chamber. A hygrometer (Neoteck, India) is also attached with the test chamber for checking the humidity level (Accuracy = ±0.2 %RH) during the entire experiment. Two-wire electrodes with copper endpoints are tailored at the top side of the chamber for electrical connection purposes. The schematic of the experimental setup is shown in Figure S4.

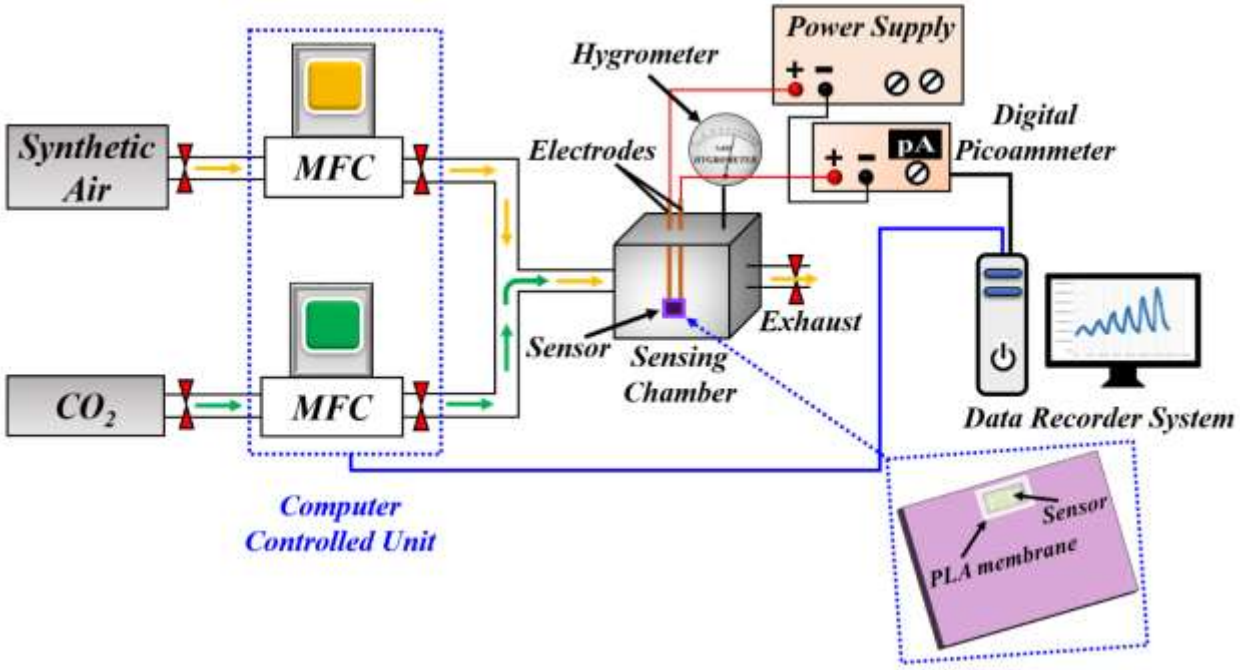

Figure S4. Schematic of the experimental setup.

Calibration and Sensing Measurements of the device:

To investigate the sensing response of CO_2 gas for all the prepared sensor devices, separate digital picoammeter (DPM-111, SES Instruments Pvt. Ltd., Roorkee) has been used for individual sensor to measure the real-time DC electrical resistance by supplying a continuous potential bias of +1 V through a regulated DC power supply (L-3210, Aplab, India) to the sensor devices. Before introducing the prepared sensors inside the test chamber, all the sensors were pre-heated at 55 °C for 30 min to remove any earlier unwanted moisture and gas adsorption from the sensor's surface. After that, all the prepared sensors were inserted in the test chamber to normalize under synthetic air background for 20 min before purging the CO_2 and other target gases (during selectivity test) to get a steady baseline resistance. Throughout the experiment, the CO_2 gas concentrations were varied from 500 to 5000 ppm by controlling the mass flow controller at room temperature (i.e. 27 ˚C), respectively. The measured baseline DC electrical resistance (in synthetic air) of all the sensors was found to be in the range of 3.33 to 5.09 MΩ and 3.12 to 3.95 MΩ for P-CTAB and P-CTAB / PLA, respectively. After exposing to CO_2 and other gases, the initial baseline resistances of the sensors were recovered by purging desired synthetic air inside the test chamber for 20 min. During the test, the simultaneous changes in DC electrical resistance of the prepared sensors were recorded through a data recorder system with instant time. The dynamic sensing response was calculated in terms of sensor response (i.e. percentage relative changes in DC electrical resistance) vs. experimental time, where sensor response $(\frac{\Delta R}{R_a}\%)$ was determined as follows:

$$\left(\frac{\Delta R}{R_a}\%\right) = \frac{R_g - R_a}{R_a} \times 100 \qquad \text{(i)}$$

Where, R_g and R_a denote the sensor resistance in target gas (CO_2 gas) and in synthetic air background (baseline resistance), respectively. In this study, the response and recovery time are found to be as the experiment time reached 90% of the final DC electrical resistance change after exposing the sensors to the test gas and synthetic air background, respectively. The sensitivity of both sensors was measured using the slope of the fitting line between dynamic sensing response $\left(\frac{\Delta R}{R_a}\%\right)$ and gas concentration (ppm).

I-V characteristics of sensors:

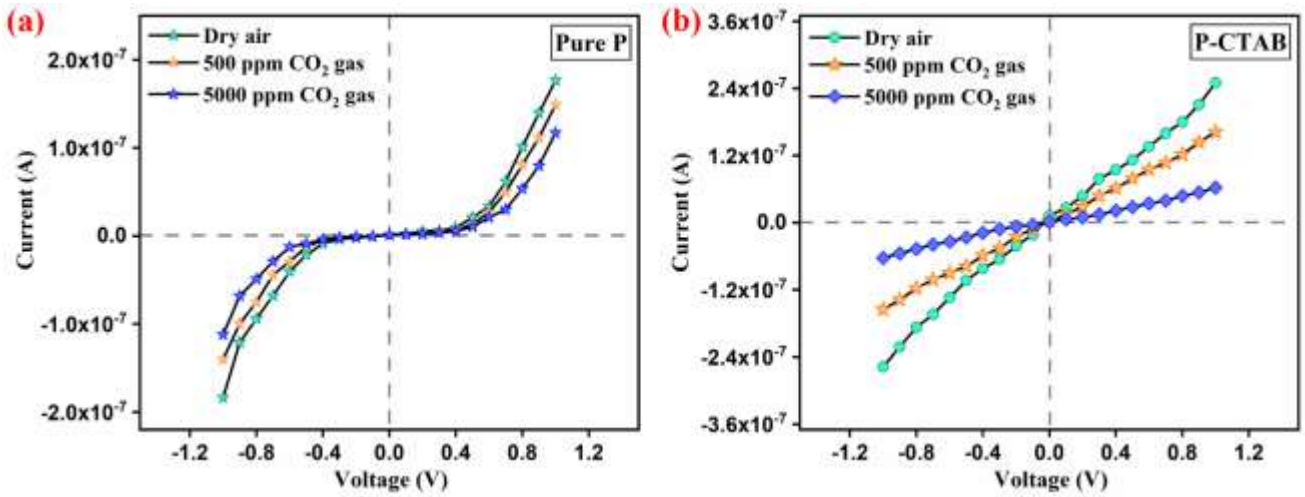

Figure S5. I-V curve of (a) Pure P and (b) P-CTAB at dry air, 500 ppm and 5000 ppm of CO_2 gas.

Comparison of sensing response:

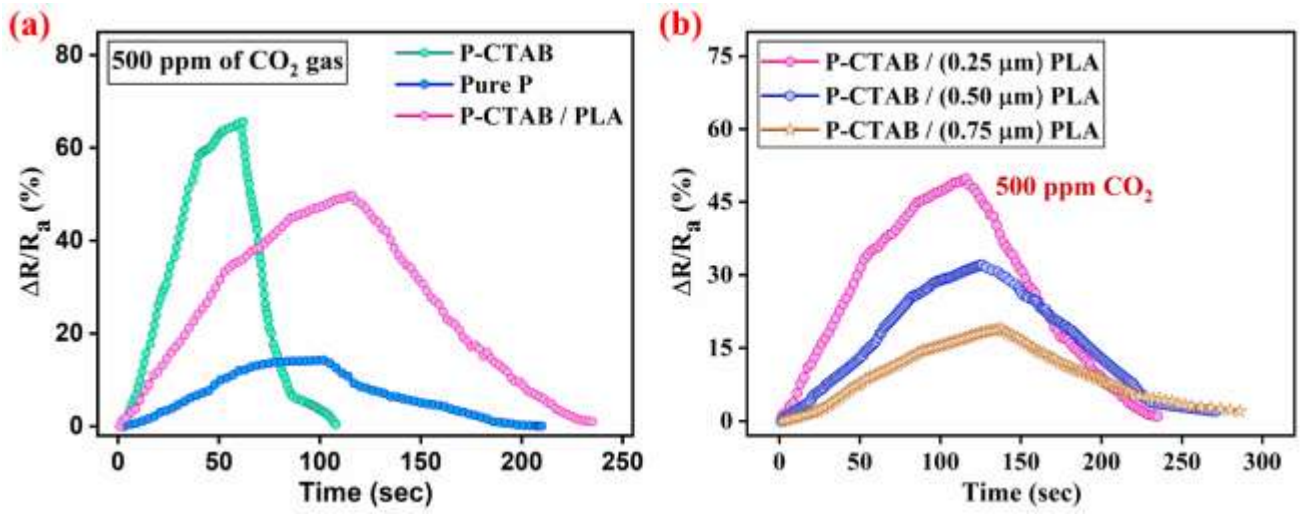

Figure S6. Dynamic sensing response of (a) Pure phosphorene, P-CTAB and P-CTAB/ (0.25 µm thick) PLA (b) P-CTAB/ (0.25 µm thick) PLA, P-CTAB/ (0.50 µm thick) PLA and P-CTAB/ (0.75 µm thick) PLA based sensor under CO_2 gas at 500 ppm.

Effect of humidity without gas:

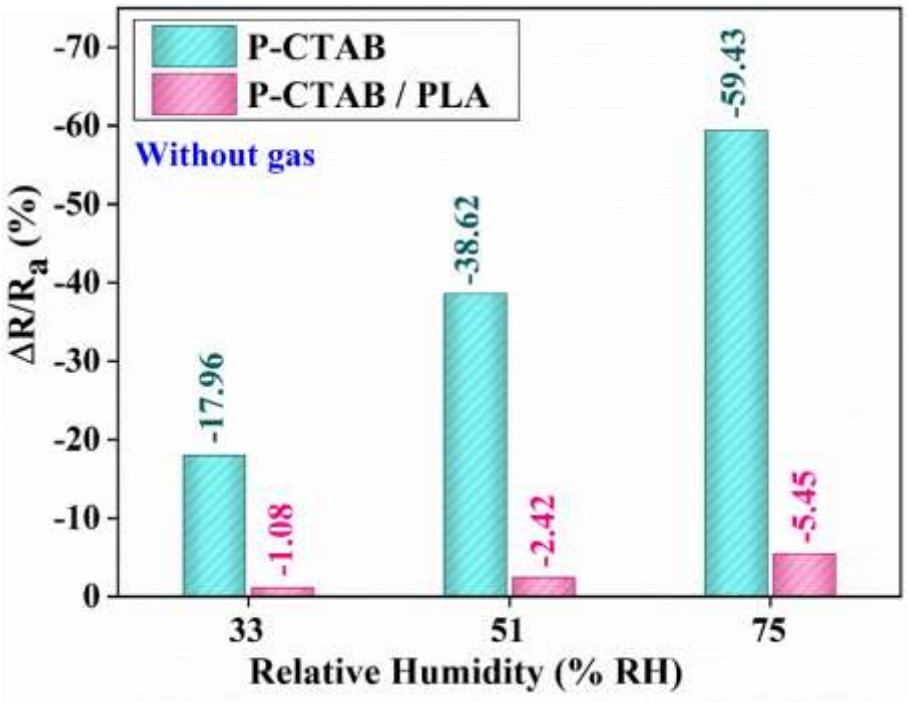

Figure S7. Sensing response of P-CTAB and P-CTAB/PLA without gas.

Long-term stability:

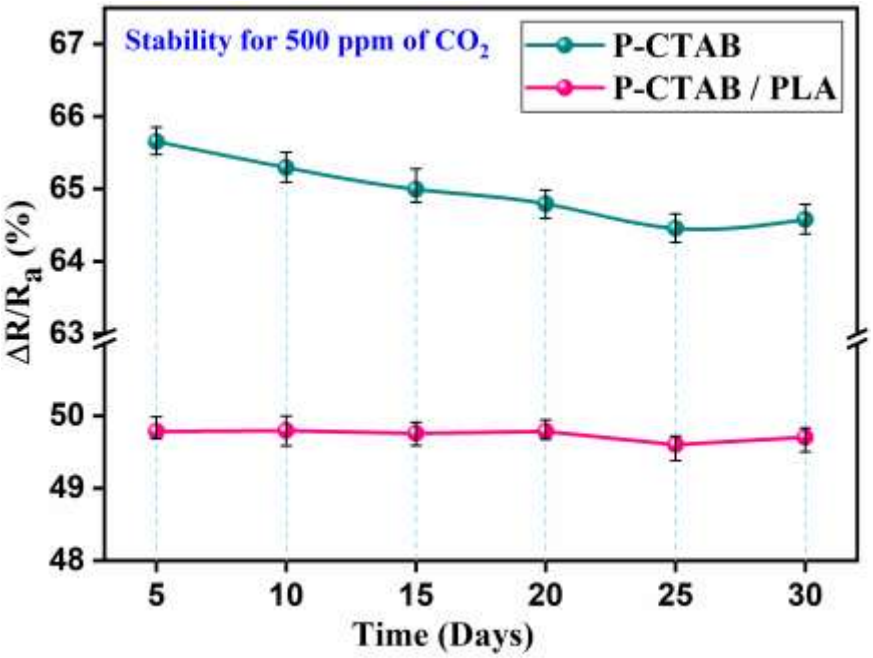

Figure S8. Long-term stability of P-CTAB and P-CTAB/PLA sensors toward CO_2 gas.

Repeatability of sensors:

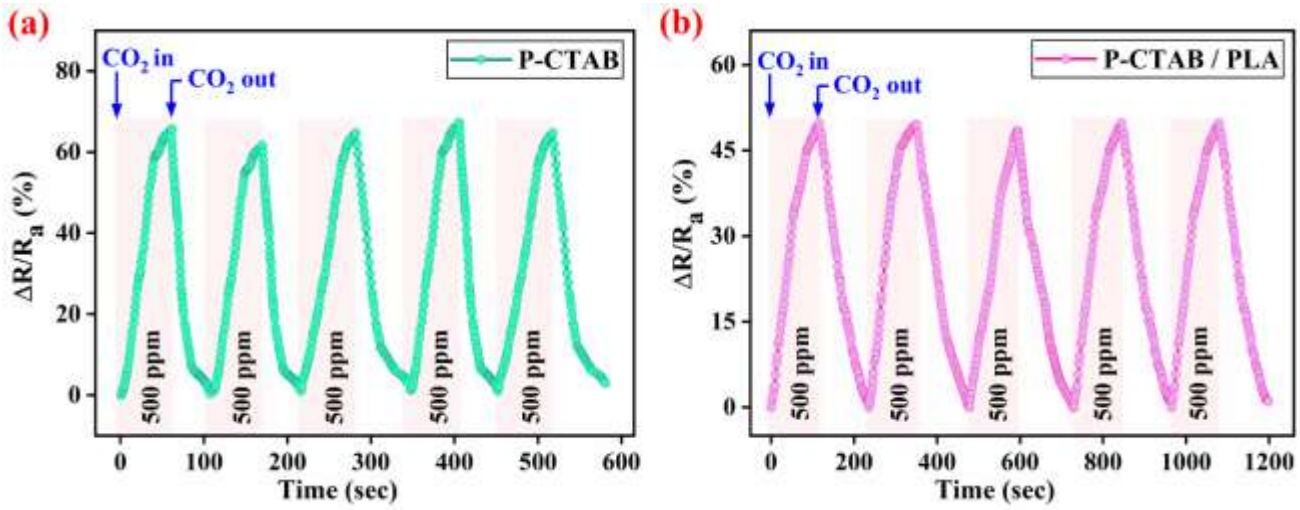

Figure S9. Repeatability studies of the sensors (a) P-CTAB and (b) P-CTAB/PLA at 500 ppm of CO_2 gas.