Supporting information

Sensing Nature's Alarm: SnO_2/MXene Gas Sensor Unveils Methyl Jasmonate Signatures of Plants Insect Stress

Prem Kumar,[a] Sarita Kataria,[a] Kesavan Subaharan,[b] Mahima Chandel,[a] Bandana Kumari Sahu, Parul Sharma[a] and Vijayakumar Shanmugam*[a]

[a]Institute of Nano Science and Technology, Mohali 140306, India

[b]ICAR - National Bureau of Agricultural Insect Resources, Bangalore 560064, India

1. Experimental section

1.1 Materials

Tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$, Himedia, 98%), titanium aluminium carbide (Ti_3AlC_2, Sigma-Aldrich, ≥90%) tert-butanol ($C_4H_{10}O$, SRL, 99.7%), dichloromethane (CH_2C_{l2}, Merck, ≥ 99.8%), β-myrcene ($C_{10}H_{16}$, TCI, >75%) , β-ionone ($C_{13}H_{20}O$, Sigma-Aldrich, 96%), methyl jasmonate ($C_{13}H_{20}O_3$, Sigma-Aldrich, >95%), β-caryophyllene($C_{15}H_{24}$, Sigma-Aldrich, >80%), Methanol (CH_3OH, Sigma-Aldrich), hydrofluoric acid (HF, Sigma-Aldrich, >48%) and carbotrap adsorbent (20-40 mesh, Sigma-Aldrich) were used without additional purification.

1.2 Synthesis of SnO_2 Nanoparticles

For the synthesis of SnO_2 nanoparticles the reported solvothermal process was used with minor modification. The reaction was conducted in teflon-lined autoclave incubated at 180°C for 12 hours. The resultant was collected through precipitation and rinsed three times with distilled water at the speed of 15000 rcf for 15 min. The final samples obtained were calcined at 400°C for 4 hours and characterized using several techniques. [1]

1.3 Synthesis of MXene.

MXene was synthesized through the widely known etching method, with minor modification.[2] Briefly the MAX phase Ti_3AlC_2 powder was allowed to etch at room temperature for five hours in 30% HF, while being stirred with the magnetic bar. The resultant was then repeatedly washed by centrifugation until the pH of the solution reached ≈6.

1.4 Synthesis of SnO_2/MXene Nanocomposite

SnO_2/MXene nanocomposite was synthesized using the SnO_2 synthesis procedure as described above in the presence of MXene. After the addition of tin precursor into DCM and tert-butanol, 1 mol% of MXene powder was added and incubated in hot air oven followed by the washing and calcination step.

1.5 Characterization.

The absorbance spectra of nanomaterials were measured using an Agilent Technologies Cary series UV–visible spectrophotometer. Confocal Raman system (WITEC) coupled with 532 nm

wavelength laser source was used to measure Raman spectra. Powder X-ray diffraction (PXRD) analysis has been carried out in the 2θ angle range of 10° to 80° using Bruker D8 Advance X-ray diffractometer equipped with a Cu-Kα radiation source (λ = 1.54 Å) working at 25 mA and40 kV voltage. The high-resolution transmission electron micrograph (HR-TEM) and TEM images of the nanomaterial were captured using JEOL JEM-2100, (200 kV microscopy). The morphology of the nanomaterial and electrode, after the coating were captured using 2 kV field emission scanning electron micrograph (JSM-7610FFESEM). The X-ray photoemission spectroscopy (XPS) was performed using Thermo Scientific K-Alpha surface analyser coupled with monochromatic Al-Kα source (hν = 1486.6 eV), with micro-focused (400 μm, 12000 V, 72 W) hemispherical analyser and a 128-channel plate detector. The volatile were determined using Shimadzu GC-MS-2014 coupled with a single-quadrupole mass spectrometer Quantum (Shimadzu) and GCMS-QP 2010 plus mass detector (GC-MS) with 100% dimethyl polysiloxane. The Rxi-1ms (30m 0.25mm i. d. 0.25) analytical column was used. Infrared spectra of the MeJA and oxidized MeJA was recorded using FTIR spectroscopy (VERTEX70, Bruker, Switzerland) operated in ATR mode with 4 cm^{-1} resolution and 64 scans. The N_2 adsorption desorption analysis was conducted with Brunauer Emmett-Teller (BET) surface area analyzer (AutosorbiQ2, quantachrome instrument). Park system XE7 atomic force microscopy (AFM) system was used in non-contact mode for thickness measurement.

1.6 Sensor Evaluation.

For the sensor measurements, an interdigitated gold electrode with 200 μm inter-lane gap has been used, which is also having continuous Pt heater electrode running at the back. The working temperature of the electrode has been adjusted using a tunable DC supply through a triple channel 2231A-30-3 Keithley. The operating temperature has been measured using a temperature sensor (Selec TC203).

The response or the sensitivity (S) was calculated as:

$$S = \left(\frac{R_{air}}{R_{analyte}}\right) - 1$$

The volatile analyte was prepared by admixing the respective precursor solution in a customized vapor meter maintained with the synthetic air flow using a digitally controlled mass flow

controllers (Cole Parmer flowmeter kit and Aalborg GFCS-010058). Throughout the experiment, wherever it is not specified, a standard gas flow of 2.2 $Lmin^{-1}$ has been maintained. A water bubbler was placed in between synthetic air and analyte mixing chamber to achieve the desired relative humidity, which has been measured using humidity sensor (HM1500LF), (while bubbling the RH varies ±5%). The sensor's selectivity was tested in the presence of additional plant volatiles that are specific to other types of stress. Standard volatile dynamics formula was used to calculate, the concentration of target VOCs:

$$C = \frac{22.4 \times \rho \times V1}{V2 \times M}$$

Here V1 (µL) and V2 (L) is the volume of the gas and the volume of a glass container filled by the VOC, respectively. The ρ (gL^{-1}) is the gas density, C is the concentration of gas in ppm and M (g mol^{-1}) is the molecular weight of the gas. In order to verify the concentration and to quantify the oxidation product of the analyte, a glass tube column with a dimension of 24 cm length and 1 cm diameter was filled with solid adsorbent carbotrap X (20/40 mesh size) and placed at the outlet to adsorb VOCs. To verify the VOCs concentration, the samples were collected for 10 min before exposing it to the sensor and then washed using methanol, such that 1 mL of methanol was collected for the analysis. For the analysis of oxidation product of VOCs, the resultant samples after exposure to sensor were collected and analyzed with GC-MS and FTIR.

1.7 Collection of VOCs and real time sensing.

Tuta absoluta adults were collected in tomato field in Malur, Karnataka in Southern India, and were reared in the laboratory. Tomato plants were exposed to *T. absoluta* adults in cages (30×30×50cm) in Green house. After 24h of exposure to *T. absoluta* adults the tomato plants were transferred to another cage with similar dimension until they reached pupal stage. The pupae were collected and and kept separately until adult emergence and the same were used for rearing. The *T. absoluta* eggs with the leaves were collected and sent INST Mohali to be used in experiments. On hatching five II instar larvae were transferred to the tomato plants (20 – 25 days old) using a fine brush on the upper portion of the plants. Three such replicates were maintained. In case of control plants same conditions were maintained but the larva were not inoculated the plant. Care was taken to cover the potting mixture with a silver foil. Both the setup (Control and treated) were

placed in 2 L glass containers. Two sets of such setup were maintained one for the collecting the volatiles for gas sensor and other for trapping the volatiles for GC MS estimation.[3]

On initiation of feeding damage by larvae after 8h zero air was blown into the setup. Teflon tubes were used to route the flow at a rate of 200 mL min^{-1}. At periodic intervals, the volatiles concentration were allowed to build and delivered on the sensor chamber in the gas detecting setup. Simultaneously, volatiles from another plants that has been exposed to similar insects were collected for 20 min using Carbotrap X sorbent glass tube attached to the outlet. Following this the collected volatile were eluted with 1 mL of methanol and analyzed with GC-MS.

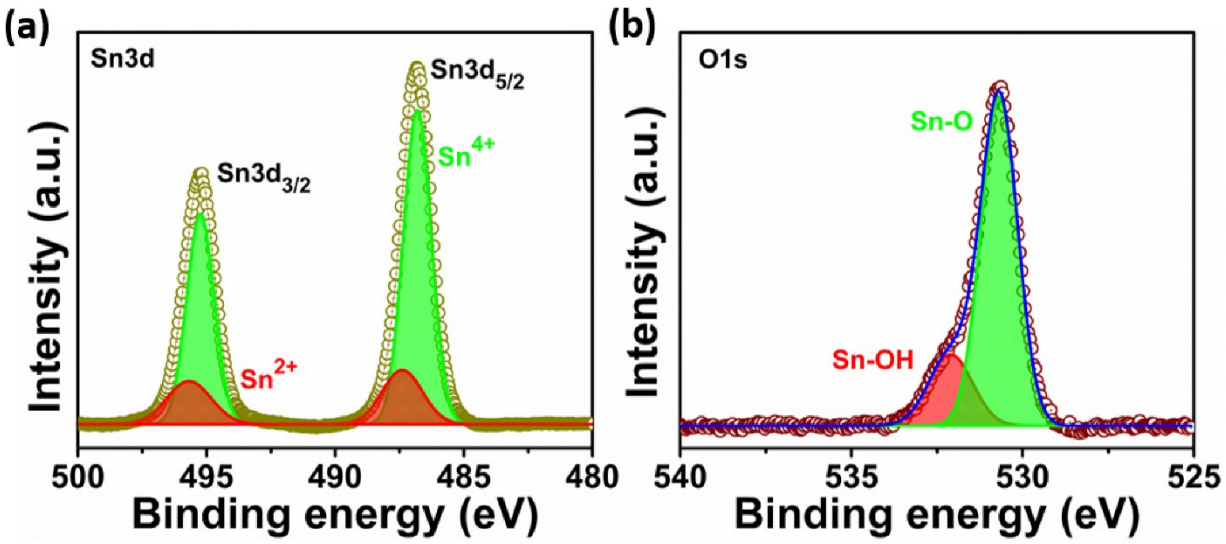

Figure S1. XPS spectra of SnO_2 (a) Sn3d and (b) O1s.

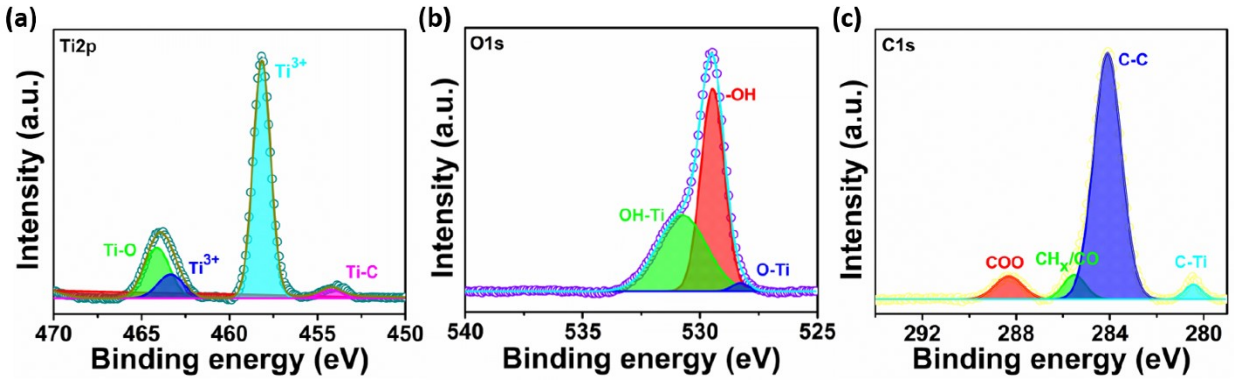

Figure S2. XPS (a) survey spectra of MXene (b) Ti2p (c) O1s and (d) C1s

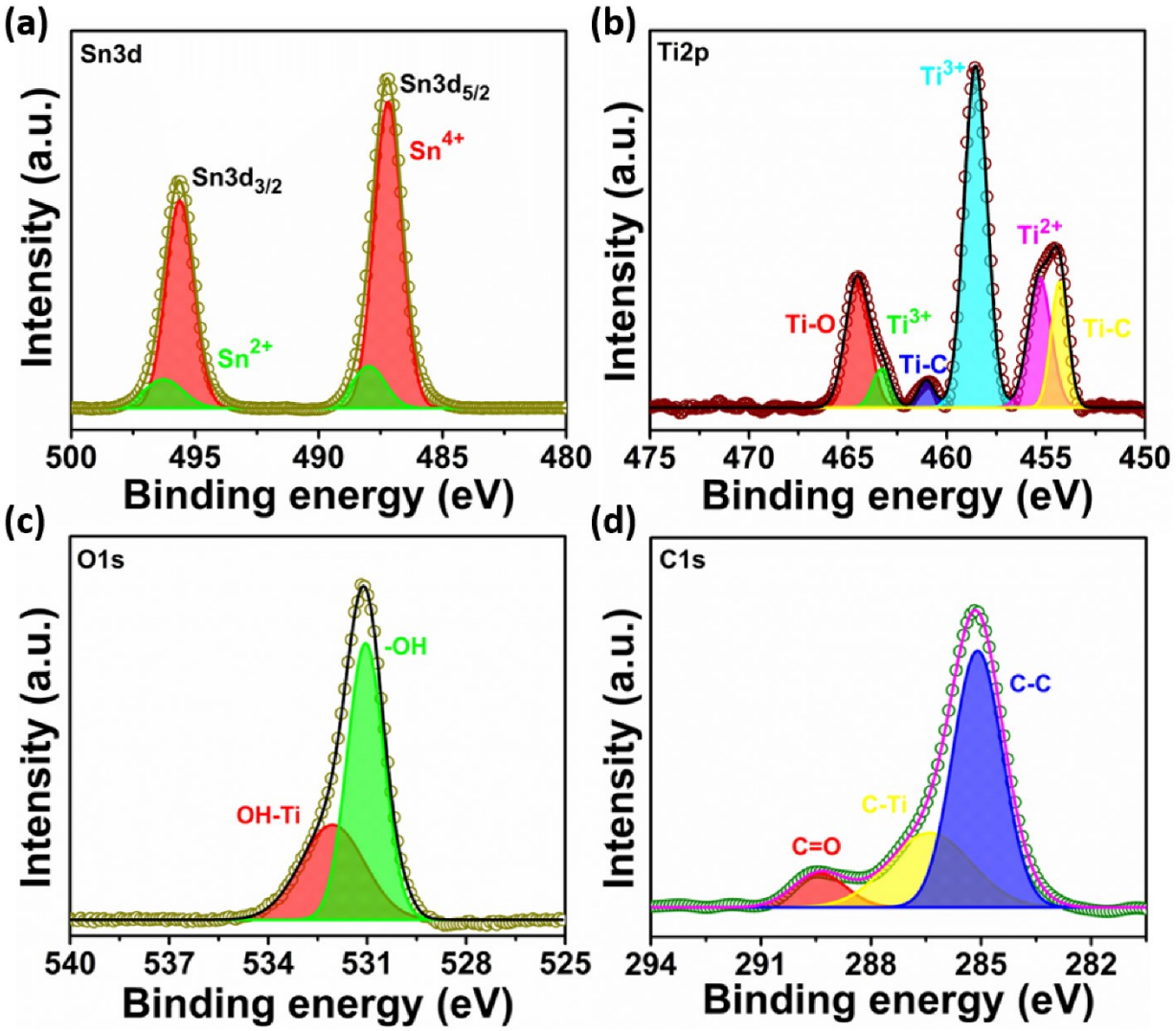

Figure S3. XPS (a) survey scan of SnO_2/MXene Nanocomposite (b) Sn3d (c) Ti2p(d) O1s and (e) C1s

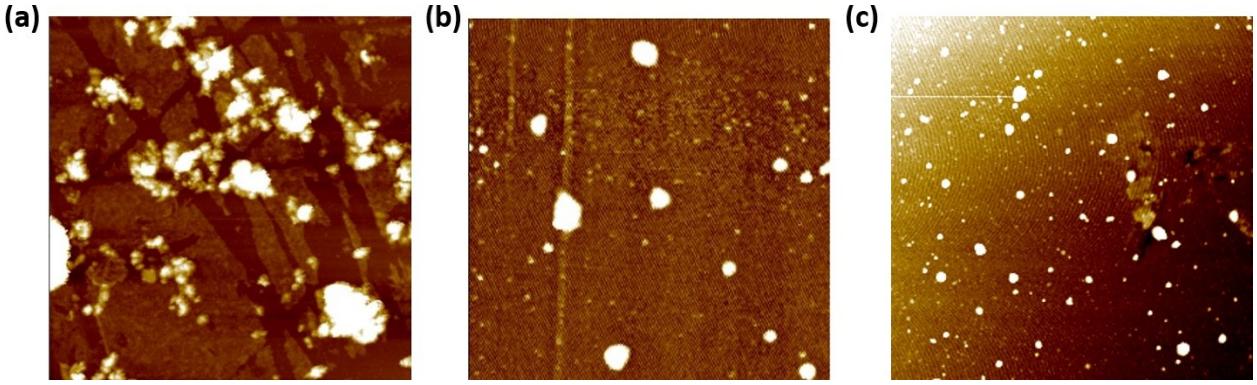

Figure S4. AFM image of (a) MXene, (b) SnO_2, (c) SnO_2/MXene (area scanned 5 μm)

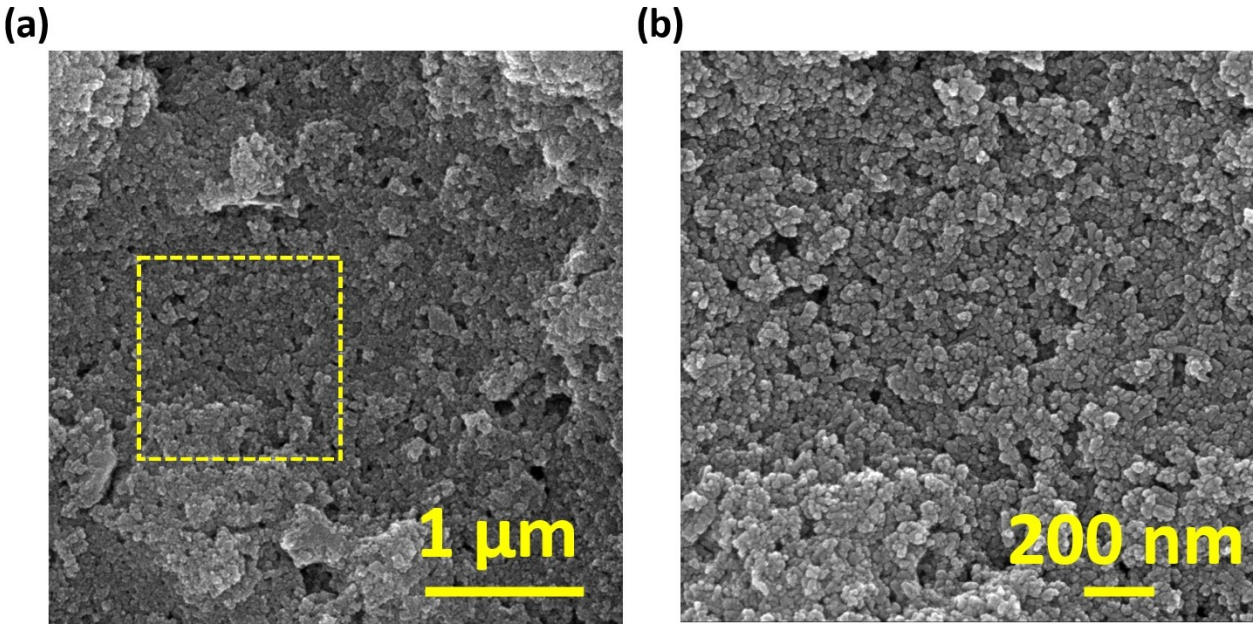

Figure S5. SEM of SnO_2/MXene coated electrode.

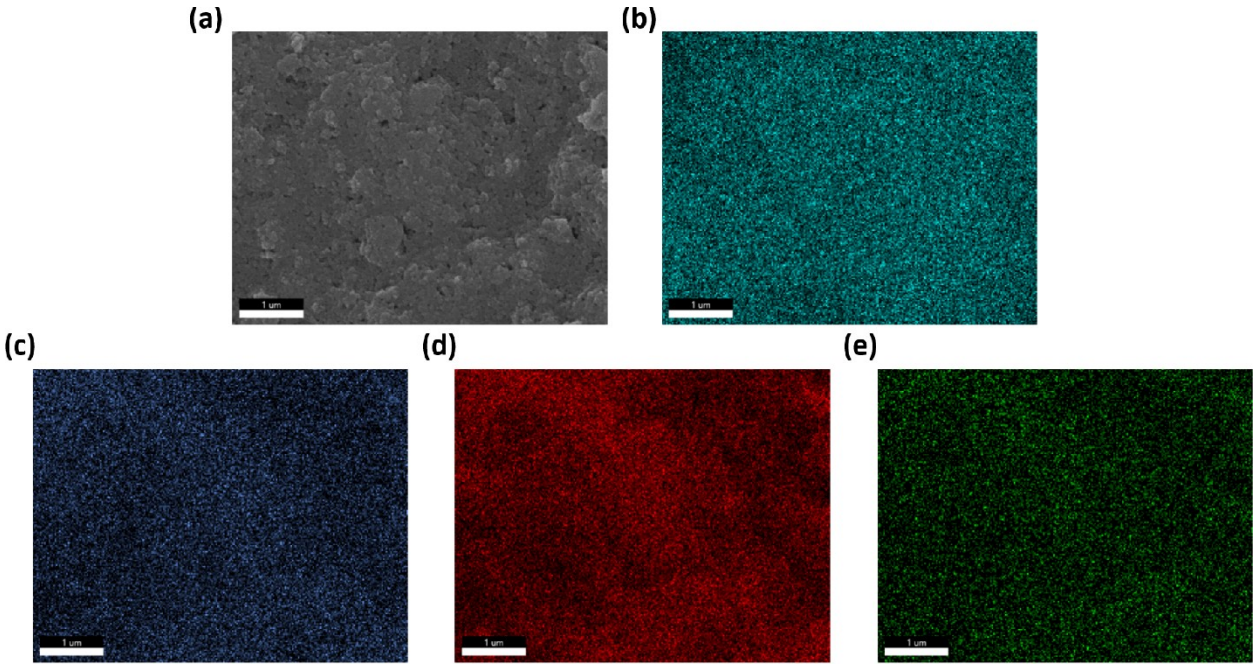

Figure S6. Elemental mapping SnO_2/MXene coated electrode (a) SEM image of electrode (b) EDS elemental analysis of Sn (c) EDS elemental analysis of Ti (d) EDS elemental analysis of O (e) EDS elemental analysis of C.

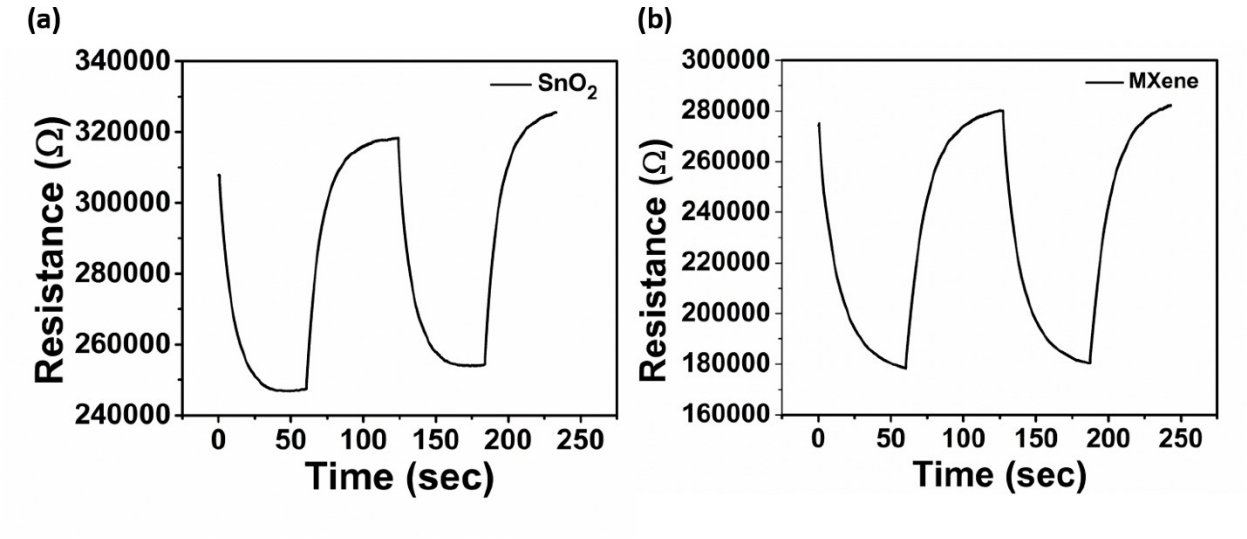

Figure S7. Raw data (a) of the SnO_2 (b) MXene, sensor for the detection of Methyl jasmonate.

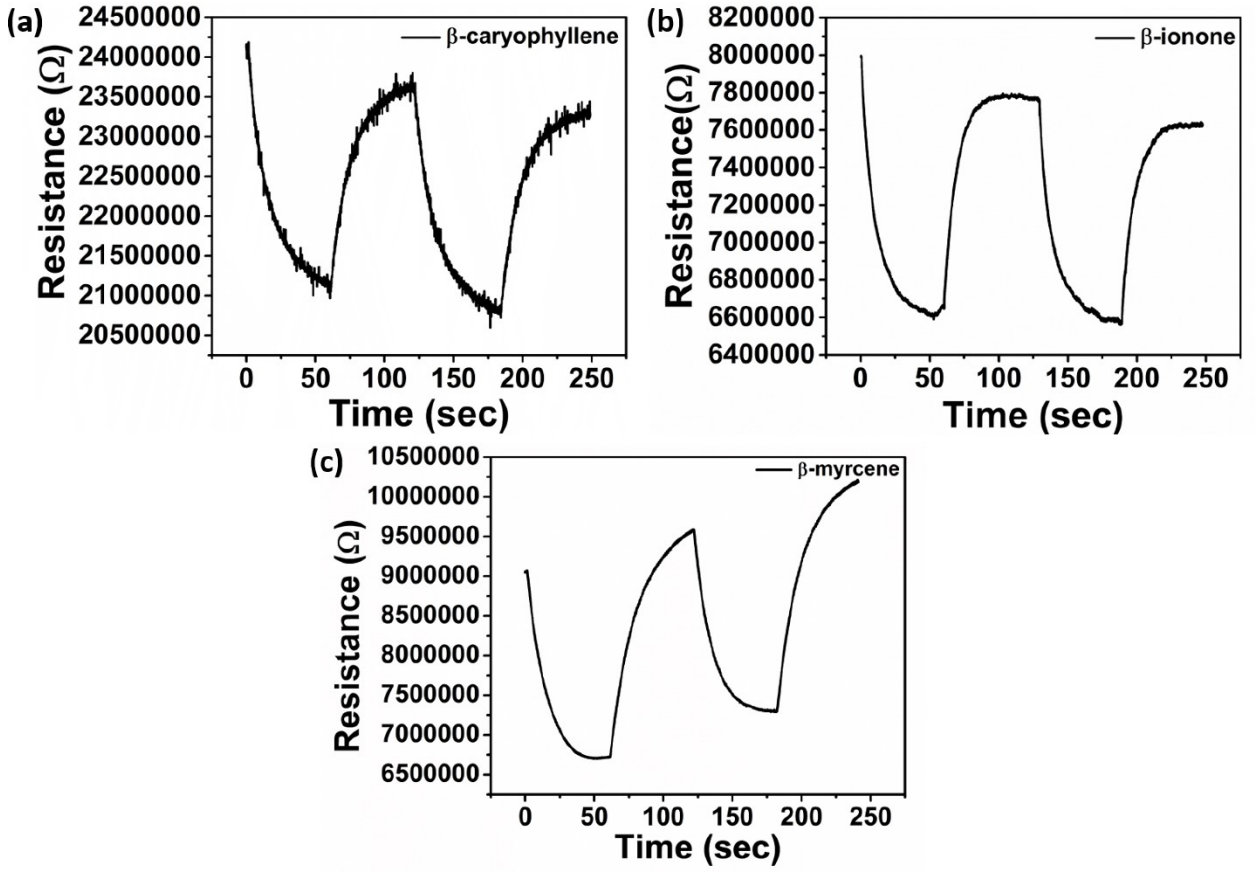

Figure S8. Raw data of the SnO_2/MXene sensor for the detection of (a) β-caryophyllene (b) β-ionone and (c) β-myrcene.

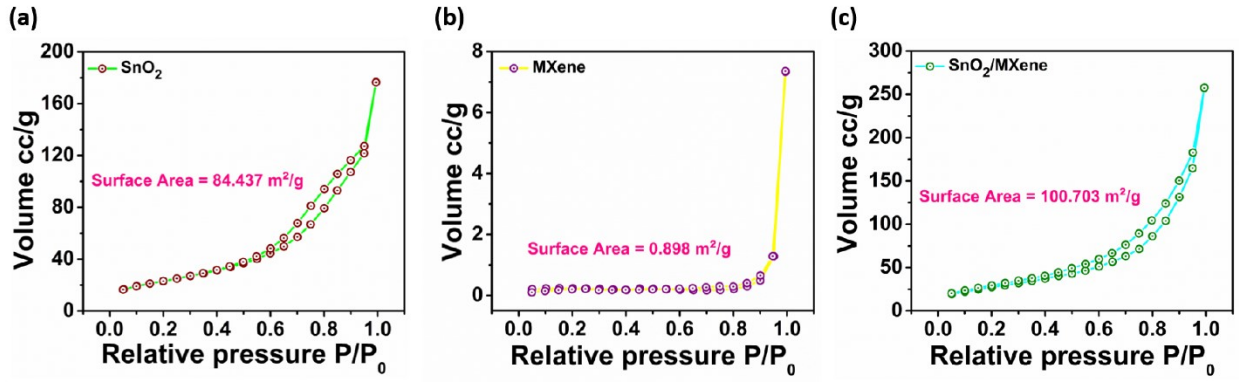

Figure S9. BET isotherm of (a) MXene (b) SnO_2 and (c) SnO_2/MXene.

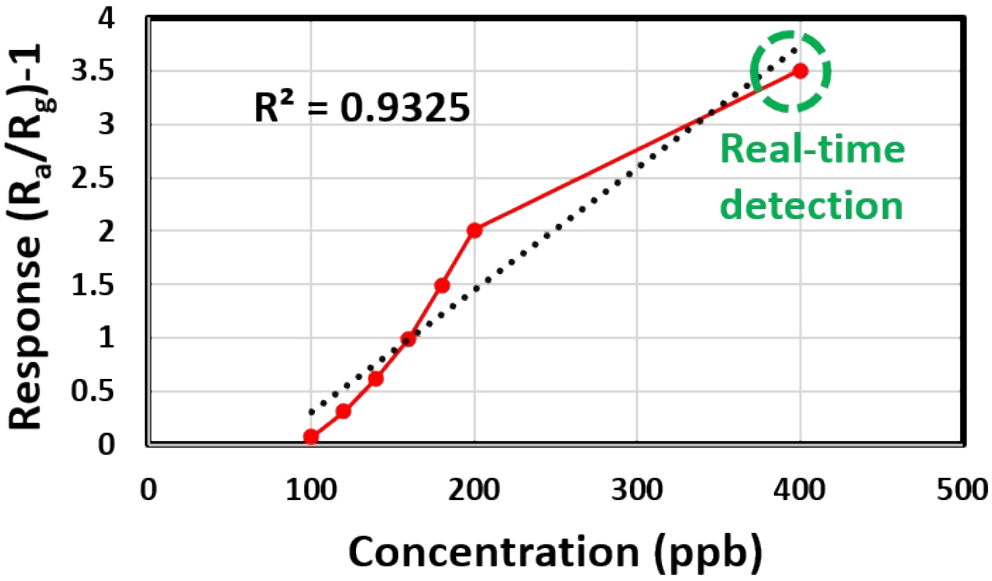

Figure S10. Linear plot of SnO_2/MXene sensor response to proportional change in the concentration and real time detection of methyl jasmonate.

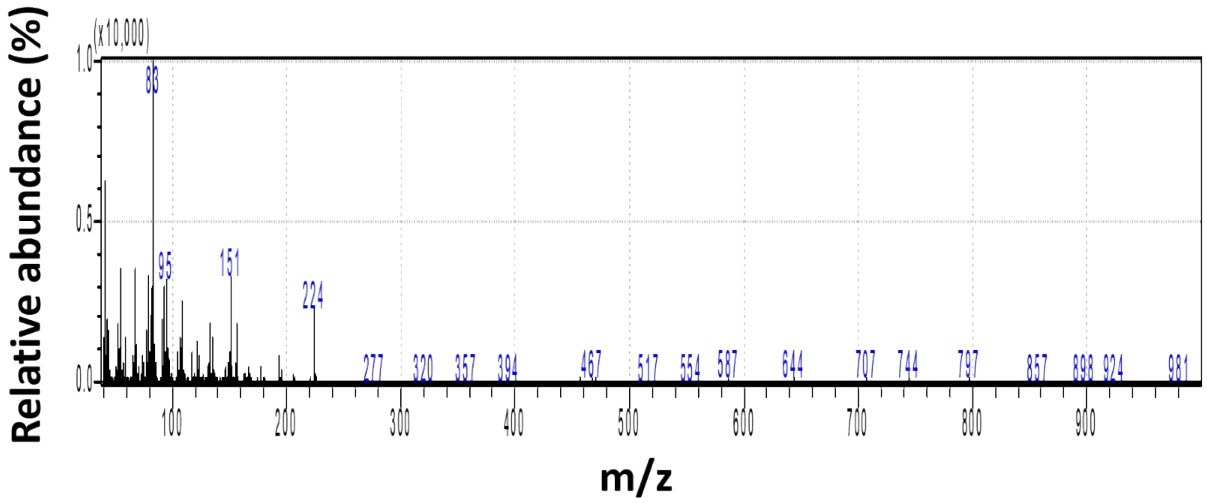

Figure S11. M/Z ratio of methyl jasmonate (GC-MS spectra).

Figure S12. Digital image of infected plant with *Tuta absoluta* (inset infected leaf)

References

1 K. Peters, P. Zeller, G. Stefanic, V. Skoromets, H. Němec, P. Kužel and D. Fattakhova-Rohlfing, *Chem. Mater.*, 2015, **27**, 1090–1099.

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