Electronic Supplementary Information

Outstanding Room-Temperature Hydrogen Gas Detection by Plasma-Assisted and Graphene-Functionalized Core–Shell Assembly of SnO₂ Nanoburflower

Anupam Nandi¹#, Pratanu Nag²#, Dipankar Panda¹, Sukanta Dhar¹, Syed Minhaz Hossain³, Hiranmay Saha¹ and Sanhita Majumdar¹*

¹Centre of Excellence for Green Energy and Sensor Systems (CEGESS), Indian Institute of Engineering Science and Technology (IIEST), P.O. Botanic Garden, Shibpur, 711103, Howrah, West Bengal, INDIA.

²Department of Physics, Jadavpur University, Kolkata-700032, West Bengal, INDIA.

³Department of Physics, Indian Institute of Engineering Science and Technology (IIEST), Shibpur, Howrah-711103, West Bengal, INDIA.

*Corresponding author e-mail: email2sm@gmail.com

# These two authors contributed equally.

S1. SENSOR FABRICATION

For sensor unit fabrication, simple Doctors’ glass slides of 1 sq. inch dimension with thickness of 2 mm were used. These glass substrates were sequentially cleaned by liquid soap, followed by DI water and acetone to avoid contaminations from impurities (like, oil, dirt etc.). The glass substrates were sonicated for 15-20 min. in acetone medium in a bath sonicator (Wensar WUC Series-12L) where the temperature of the bath was maintained at 80°C. After acetone cleaning, the substrates were dried by hot nitrogen gun and kept in vacuum desiccators for further use. These glass substrates have been used in deposition unit (e-beam chamber), where conformal SnO₂ thin film were deposited on the surface of the glass substrates followed by two important steps viz., (i) H₂ plasma treatment in PECVD unit (SnO₂ nanoparticle formation) and (ii) Ar plasma treatment in RIE unit (surface etching of SnO₂ NPs to grow desired bidding of SnO₂.
on SnO$_2$ NP, to augment surface area). A thin layer of graphene (rGO) has been developed on the bided SnO$_2$ surface by the help of capillary action (already discussed). The step by step photographs of the samples developed and fabricated on glass substrates by the help of various processes in a series of treatments have been shown in Figure S1a. Glass substrates with the desired formation of SnO$_2$ moiety have been placed on a flat alumina plate and their gas sensing performances have been measured by pressure-contact technique [Figure S1b]. To achieve the desired temperature of the sample, a nichrome (80% Ni-20% Cr; by mass) heating coil was placed under the sensing stage (Al$_2$O$_3$ plate) and connected to DC power supply. The substrate was heated to the desired temperature by the help of conduction heating method and temperature modulation has been calibrated using thermostat and thermocouple placed very near to the sample. The whole unit of sensor set-up measurement is shown in Figure S1b.

**Figure S1:** (a) Real photograph of sensor samples synthesized by various treatments and (b) the front view of the sensor measurement setup used to measure the sensor responses for this work.

### S2. SENSOR MEASUREMENTS

All the samples were pre-heated at a constant temperature of 200°C for one week to achieve the desired stability before measurement of electrical resistance. After achieving thermal stability, the sample was exposed to the desired sensing gas(es) within a thick glass chamber where, one inlet and one outlet keys are attached to inject the target gas and collect the exhaust, respectively. The gas flow rate was controlled by digital mass flow controller (MFC; GE50A) attached with the module. Drop in resistance was observed after exposure to the analyte gas(es) (reducing type) and this change in resistance was recorded using Agilent Multimeter (U1253A).
at room temperature as well as at elevated temperatures, in presence of ambient humidity of ~60% to 65%. The details of the measurements, the elements of sensor fabrication and processing are reported elsewhere. The response towards H₂ as well as other reducing gases were estimated and expressed in percentage as follows:

\[
(\%)S = \left[\frac{(R_a - R_g)}{R_a}\right] \times 100
\]

\[\text{Where, } R_a \text{ and } R_g \text{ are the sensor resistances in air and in presence of reacting gas(es), respectively, at the same operating temperature. The response time } (T_{Res}) \text{ and recovery time } (T_{Rec.}) \text{ were measured respectively, as the time taken for a sensor to read 90% of full-scale reading after being exposed to a given target gas and the time taken by the sensor to come back to its original base resistance when the target gas was removed.}^{3}

**S3. HOT PROBE TEST**

Easy and potential standard hot probe technique has been practiced by many researchers to discriminate between p-type and n-type semiconductors using a heated probe and a multi meter. This kind of experiment is carried out by connecting hot probe to the positive terminal of the meter and negative terminal is kept unheated. While applying hot probe in the positive terminal voltage read positive for n-type material and negative for p-type material. Majority free charges at the hot probe attain thermal excitation, which drives the mainstream charges sweep away from the point, making the point opposite to the nature of material. Opposite charges retained at the place near hot probe while the zone in touch with the other probe consists of majority charges creates a potential difference between two probed points. A glass with two gold electrodes at centre was dip coated in af-RGO solution (separation between the two electrode is ~ 500 µm) to get the continuity. The two probes have a distance of ~10 mm in between, are connected with a DC power supply multi meter (Agilent; U3606A) to measure the corresponding voltage and current. When a soldering iron with its maximum heating (450°C) has been touched to the positive terminal of the hot probe, a steep rise in voltage has been noticed. When it has been kept for another 40 sec., a sharp fall of the voltage graph is observed (Fig S2). Positive rise in voltage can be noticed after touching the positive terminal by hot probe due to potential difference created between the two touching points. Near hot probe positive charges accumulated and at the other point negative charges have been accumulated, which measures a positive voltage in between. After withdrawal of the hot probe, thermally created minority charges again recombined and localized potential difference

S3
(developed due to hot probe) diminished. Sharp gradient of voltage rise and fall can be correlated as generation and recombination of minority charges, which is almost same.\textsuperscript{5–6}

![Figure S2: Thermoelectric (hot probe) test showing the type of synthesized amine functionalized rGO.](image)

### S4. X-RAY DIFFRACTION STUDIES

In order to confirm the phase purity, orientations of crystal lattice structures and probable lattice plains of the synthesized materials, room temperature X-ray diffraction studies have been performed in RIGAKU Ultima IV and the corresponding peak positions ranging between 20° and 70° has been presented in Figure S3a and the corresponding degree of strain incorporated during the formation of nanoparticles have been estimated and presented in Figure S3b. The particles under strain can be estimated by plotting \((\beta \cos \theta)/\lambda\) as Y-axis against \(\sin \theta /\lambda\) as X-axis and the slope \((dY/dX)\) of the lines of Figure S3b was considered as the degree of strain. Here, ‘\(\theta\)’ is the Bragg’s diffraction angle, ‘\(\beta\)’ is the full width at the half of the maximum diffraction peak intensity (FWHM) derived from X-ray diffraction peaks and ‘\(\lambda\)’ being the wavelength of Cu K\(_\alpha\) radiation used in X-ray diffraction (XRD) analyses (\(i.e., 1.5406\) Å). The twelve diffractograms of the samples S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11 and rGO
coated S12 are matched well with the JCPDS card no. 77-0447, confirming the formation of tetragonal rutile lattice structure of SnO₂ (mineral form: cassiterite, an anisotropic polar crystal) with space group P4₂/mnm. Four oxygen anions (O²⁻) attached with two metallic cations (Sn⁺⁴) to form unit lattice, wherein the tin atoms are six coordinated and the oxygen atoms are three coordinated oriented in octahedron fashion (a=b≠c; α=β=γ=90°). Therefore, it is regarded as an oxygen-deficient n-type semiconductor. Crystallite sizes (D) of all the synthesized samples were calculated using the equation (2):\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]where, ‘\( \lambda \)’, ‘\( \beta \)’ and ‘\( \theta \)’ are in their usual custom, already explained earlier.

The perpendicular distance between two successive parallel planes of the crystals, i.e., d-spacing of lattices of the synthesized materials have been estimated by the help of equation 3 and the results are revealed in the Table 2 (of main article) to identify any deviations present in the ‘d’ values, due to the introduction of strain in terms of defects and disorders in between two planes, lattice twinning and/or void incorporation in the lattice.

\[ n\lambda = 2d \sin \theta \]It should be mentioned here that, the ‘d’ spacing of a perfect lattice of the tetragonal SnO₂ crystal is 0.176 (JCPDS. 77-0447). From the above mentioned table it could be seen that the ‘d’ value of S1 is almost identical with the ideal one but, for the samples S2, d-value decreases abruptly probably due to the presence of crystal defect(s) originated from layer growth due to electron beam deposition. On further movement from S3 to S8, wherein samples are treated with H₂ plasma with different time and power, d-values gradually increases and for the sample S7, d-value is exactly identical with the ideal one. It is noteworthy here, that plasma treatment time and power play a key role for nanoparticle formation. Higher plasma time produces larger sized nanoparticles probably due to particles agglomeration by the help of plasma bombardment. In this turn, incomplete and disordered lattice are also formed on the surface, but not in significant ratio. However, with the reduction in particle sizes, surface to bulk ratio is also increased and as the surface of the nanoparticles is comparatively defect rich segment, the pure bulk characteristics of the core segment of the nanoparticles is suppressed by the defect related surface characteristics.

From the Figure S3a it could also be seen that diffraction peaks of sample S1 have very sharp intensity indicating its high degree of crystallinity. However, this crystalline nature decreases abruptly if one may proceed to the sample S2 and S3 since, they possess very thin layer of coating with very tiny particles. The diffractograms of sample S4 are broad, hump-like
structure. But, if we move to sample S5 to S8, peak intensity as well as crystalline properties of the sample gradually increases, indicating sequential overgrowths of the nano-particles (SnO₂) due to time amplifying of H₂ plasma flow. Sample S8 is much crystalline in nature though, its crystallinity is not comparable with Sample S1. However, peak broadness or peak intensity change is not the only reason of size reduction effect. It can also be generated due to i) introduction of interstitial defect and disorder in lattice, ii) presence of unfilled atomic spaces, iii) interstitial void, iv) presence of unbounded cation(s) (Sn⁺⁴) and/or anion(s) (O⁻²), which is/are not necessary to from perfect tetragonal lattice structure, v) incomplete growth of particle under the various plasma time and treatment condition and vi) generation of defect induced strain inside the lattice structure. However, peak intensity decreases and peak broadening increases again from the samples S9 to S11 due to the formation of nano-bids on the surface, because of Ar plasma treatment which ultimately amend the surface to volume ratio. Sample S12 is basically a composite material consists of SnO₂ and C (rGO), which can be acknowledged by its peak identification (JCPDF impression of graphite, Card No.: 75-2078 and x-ray diffractogram of rGO have also been provided for the sake of comparison).

Figure S3: (a) X ray diffractogram of SnO₂ nanoparticles synthesized by different synthesis procedure viz., chemical as well as physical method along with standard JCPDS impression of SnO₂ and graphite (b) Degree of strain incorporated during the formation of nanoparticles under different condition.

It is also noticeable from the Figure S3a and the data table [Table 2, presented in the main article] that the broadening of peak and consequent comparable increment of FWHM of the peaks, confirms the nanoparticle formation and reduction in size up to sample S4. After that decreasing value of FWHM indicates the particle size increment. Calculation of ‘c/a ratio’ is also a convincing method to evaluate the twinning force originated due to the incorporation of defect and other unwanted void space within the molecule(s) having basic crystal structure,
which in turn, are responsible to produce strain in the lattice crystal. With the reduction of particles size, deviations have predominantly been noticed in lattice parameters. ‘c/a ratio’ also supports the increment of the degree of defects at the crystals, as the size of the nanoparticles has been decreased. From the lattice parameter deviations, it is also evident that the unwanted void and atom incorporation has been occupied at intra-plane and inter-plane, as the value of a and c has been deviated from the ideal value of lattice parameter(s).

**S5. FTIR**

Fourier transform-infrared (FT-IR) spectra have been recorded for SnO₂ samples (S1, S4, S6, S7, S8, S10) along with rGO and rGO coated sample S12 in between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹ and is presented in Figure S4a. Figure S4b shows the enlarged view (450-725 nm) of Figure S4a to clearly identify the changes in surface oxygen vacancy, lattice strain, introduction/withdrawal of lattice voids and stoichiometric alteration in the lattices. It is already known that the discrepancies in the positions of IR spectra arise due to many factors, such as the non-stoichiometry of the oxide *i.e.*, the presence of intrinsic defects and positional defects in the lattice, variation in relative intensity and the width variations (band stretch and band shrinkage) of the IR absorption bands, which are strongly affected by the size, orientation, state and induced lattice disorder, aggregation of the particles etc. Since SnO₂ being an n-type semiconductor with inherent oxygen vacancy defects, the IR bands of Sn-O bonds is highly subjected to undergo shift due to the variation in the concentration of surface oxygen defects. Hence, greater the oxygen vacancy defects, the Sn-O bond absorption will be at higher wave numbers *i.e.*, blue shift will occur due to phonon stiffening, which incorporate an anomaly in the intrinsic natural vibration of Sn²⁺ (where O²⁻ considered as the centre) and O²⁻ (where Sn²⁺ considered as the centre). This indicates that the decrease of crystallite size below 6 nm gives rise to a more non-stoichiometric nature of SnO₂₋δ containing more surface oxygen vacancy defects (acts as lattice voids) in the H₂ plasma treated surface modified samples. Moreover, the FTIR bands of the nanoparticles (S6 to S10) grown by the plasma treatment also exhibited splitting nature with three well defined, strong and highly resolved sharp peaks at around 660-675 cm⁻¹, 608-618 cm⁻¹ and 515-520 cm⁻¹, along with a shoulder at around 465-475 cm⁻¹, all of which can be attributed to the two IR active modes namely (E_u) and (A₂_u) of tin (IV) oxide, respectively. Infact, the peaks at 608-618 cm⁻¹ assign to the anti-symmetric Sn-O-Sn stretching mode of the surface-bridging oxide formed by condensation of adjacent surface hydroxyl groups (which produce water) and 465-475 cm⁻¹ shoulders assign to symmetric Sn-
O-Sn stretching mode.\textsuperscript{11} After calcination at 600°C, the band corresponding to water at $\sim 3437$ cm$^{-1}$ is expected to almost disappear. However, we could still observe a very small weak peak here, which is probably due to the fact that the spectra were not recorded in situ and some re-adsorption of water from the ambient atmosphere has taken place.\textsuperscript{12} The broad band between 3200–3600 cm$^{-1}$ and the band centred at 1620 cm$^{-1}$ found on materials are assigned to O–H stretching and deformation vibrations of weak-bound water.\textsuperscript{13} Therefore, only the broad bands between 400–800 cm$^{-1}$ are attributed to the framework vibrations of tin oxide crystal matrix.\textsuperscript{14} The intensity of the splitting nature of the IR peaks, however, prominently increases and also all the peaks undergo a blue shift with gradual optimization of plasma irradiation induced surface defects. The FTIR spectra of primitive S1 and S4 samples having crystallite size of 10-12 nm are of unsplitted nature, indicating less non-stoichiometry. The presence of only two weak bands at around 456 cm$^{-1}$, and a shoulder at around 498 cm$^{-1}$ in S1 sample whereas the same for S4 is at 460 cm$^{-1}$ and 505 cm$^{-1}$ and another weak band at around 598 cm$^{-1}$, gradually shifted towards higher wavenumbers with increase in non-stoichiometry in S4, S6, S7, S8 and vice versa. Sample S2 on the other hand, did not show any noteworthy shifting or changes in the peaks than S1. Therefore, in S1, two well defined poor peaks around 505 cm$^{-1}$ and 460 cm$^{-1}$ of S4 merged together and becomes an unresolved weak shoulder at around 456 cm$^{-1}$ and a band at around 598 cm$^{-1}$. The similar logic is applicable for S3 and S5 samples also as those two samples didn’t show any substantial change than S4. Infact, the transmittance peaks in S4 exhibited more shifted peaks (towards higher wavenumber) with higher splitting nature than the S3 and even S5. The principle bands mentioned above at 608-618 cm$^{-1}$ and 660-675 cm$^{-1}$ in the FTIR spectra of prepared SnO$_2$ can be assigned to fundamental vibration frequencies ($\nu_{\text{Sn-O}}$) and ($\nu_{\text{O-Sn-O}}$) of SnO$_2$, respectively. Similarly, the bands at around 515-520 cm$^{-1}$ and shoulder at around 465-475 cm$^{-1}$ can both be assigned to fundamental vibrations ($\nu_{\text{Sn-O}}$ and T; T = terminal).\textsuperscript{15} The blue shifting of the corresponding frequencies of the FTIR spectral bands of S6, S7 and S8 compared to S1 and S4 samples and also the disappearance of the splitting nature of the spectral bands in the latter samples indicate the presence of more surface vacant oxygen defects in the former samples (S6, S7 and S8) having crystallite diameter in the order of 2 times of Debye length ($L_D$) of SnO$_2$ i.e., 6 nm. Due to the presence of more vacant oxygen defect lattice sites ($V_O$) in S7, the Sn-O bond in O-Sn-V$_O$ is comparatively shorter and stronger than the corresponding Sn-O bond in S1 (O-Sn-O) due to reduced mass effect. Therefore, the Sn-O bond in S7 having higher bond strength requires much higher energy (i.e. wavenumber or frequency) for its stretching mode of vibration compared to the much lower energy
requirement for S1, i.e. $\nu_{\text{Sn-O}} (S7) > \nu_{\text{Sn-O}} (S8) > \nu_{\text{Sn-O}} (S6) >> \nu_{\text{Sn-O}} (S4-S1)$. The Ar plasma application hardly produced any stoichiometric defect in the later samples i.e., in S9, S10, S11 and S12 samples. However, for the sake of confirmation and satisfaction, the FTIR spectra of the S10 and S12 samples are also given in both the Figure S4a and b. The FTIR spectra of rGO stretching vibration peaks of C=O of carboxylic groups are observed at 1050 cm$^{-1}$. The peak at 1630 cm$^{-1}$ is related to the vibrations of adsorbed water molecules. However, the absence of broad and wide peak at 3447 cm$^{-1}$ related to the O-H stretching vibrations of the C-OH groups and water (as can be seen in graphene oxide) confirms the presence of rGO.$^5$

![Figure S4](image)

**Figure S4:** (a) FTIR spectra of the sample S1, S4, S6, S7, S8, S10 and S12 along with reduced graphene oxide (rGO), (b) Enlarged view (450-725 nm) of FTIR spectra of (a).

## S6. RAMAN SPECTRAL STUDIES

Raman spectra for the samples of S1, S4, S6, S7, S8, S10 and S12 are given in Figure S5. The figure shows the Raman bands of SnO$_2$ at $\sim 633$ cm$^{-1}$ (actually 633.81 to 628.17 cm$^{-1}$), $\sim 476$ cm$^{-1}$ (479.58 to 476.57 cm$^{-1}$) and $\sim 775$ cm$^{-1}$ (775.89 to 768.32 cm$^{-1}$) correspond to $A_{1g}$, $E_g$ and $B_{2g}$ vibrational modes, respectively.$^{16-17}$ These Raman features confirm the tetragonal rutile structure of SnO$_2$. Of these three main bands, the one at $\sim 633$ cm$^{-1}$ is the sharpest. Here, $E_g$ is related to the vibration of oxygen in the oxygen plane, while $A_{1g}$ ($\sim 633$ cm$^{-1}$) and $B_{2g}$ ($\sim 775$ cm$^{-1}$) are related to the expansion and contraction of vibrational modes of Sn–O bonds. Raman shifts were observed for SnO$_2$ large particles like S1 at 476.57, 633.81 and 775.89 cm$^{-1}$. These band positions are in good agreement with the reported values at 479 cm$^{-1}$ ($E_g$), 638 cm$^{-1}$ ($A_{1g}$), and 779 cm$^{-1}$ ($B_{2g}$) of SnO$_2$ by Dieguez et al.$^{19}$ Here, the intensities of the $A_{1g}$, $E_g$ and $B_{2g}$ vibrational modes of plasma treated powders are larger than the S1 sample,
indicating improved crystallinity. Similarly, peaks at 631.58 (A1g), 476.44 (Eg) and 775.94 (B2g) cm\(^{-1}\) became sharp and their FWHM decreased with decrease in crystallite size. This suggests that plasma treatment after the calcination leads to relaxation in the interface surface and makes the grain’s lattice more regular. When the samples were exposed to plasma treatment, the crystallite size or grain size begins to increase initially, which might influence the local crystal disorder at the interface. Therefore, the crystal distortion which is related to the local crystal disorder also disappears.\(^{20}\) Relatively low intensified and broader peaks observed in S1 sample at room temperature compared to those calcined at higher temperatures, probably due to the presence of imperfect lattice sites and surface disorders. The E1g and B2g vibrational modes are also absent here. For calcined samples with increase in crystallite or grain size, the Raman bands increase in intensity and SnO\(_2\) samples become free from confined vibration effects.\(^{21}\) The Raman profile also confirms the absence of phase change by plasma treatment. From the Figure S5b, one can infer that with decrease in calcination temperature, some appreciable line shift and broadening of peak in the Raman spectrum have occurred due to the phonon confinement effect. This figure also indicates that the mode A1g shifts toward higher wavenumbers (blue shift) as the particle size increases.\(^{22}\) The phonon confinement effect of the SnO\(_2\) nanocrystal weaken rapidly with increase in particle size.\(^{23}\) Further from our results, the appearance of the B2g mode and observation of other modes as the plasma treatment intensified indicated that the grown nanostructured materials were itself composed of many nanoparticles having diameters more than 3 nm.\(^{24}\) In most of the cases Raman scattering is sensitive to the degree of crystallinity of the sample. Typically a crystalline material yields a spectrum with very sharp, intense Raman bands. The FWHM of the A1g mode of the as-grown nanocrystalline SnO\(_2\) material is found to be more than that of the other plasma treated samples. For both Eg and B2g modes of nanocrystalline SnO\(_2\) material, the width decreases with increase in the plasma treatment. The area of the peak also decreases with increasing optimised plasma treatment. Therefore, it is possible to accurately calculate, which can then be used as a quantitative measure of crystallinity. The rGO sample exhibits D band at around 1584 cm\(^{-1}\), which corresponds to a splitting of the E2g stretching mode and reflects the structural intensity of the sp\(^2\)-hybridized carbon atoms, and G band at around 1356 cm\(^{-1}\).\(^{25-26}\)
Figure S5: (a) Comparison of Raman spectra of sample S1, S4, S6, S7, S8, S10 and S12 nanoparticles along with rGO; (b) Magnified 3D profile of the same Raman spectra in the range of 400 – 800 cm\(^{-1}\) wavenumber.

Table S1: Respective peaks positions of different SnO\(_2\) nano-spheres and their shifting

|       | S1   | S4   | S6   | S7   | S8   | S10  | S12  |
|-------|------|------|------|------|------|------|------|
| Eg (cm\(^{-1}\)) | 476.57 | 479.41 | 477.70 | 477.11 | 476.54 | 479.36 | 479.58 |
| A\(_{1g}\) (cm\(^{-1}\)) | 633.81 | 628.17 | 631.03 | 632.70 | 633.75 | 628.67 | 628.89 |
| B\(_{2g}\) (cm\(^{-1}\)) | 775.89 | 768.32 | 773.50 | 774.60 | 775.70 | 768.52 | 768.69 |

**S7. XPS ANALYSES**

As gas sensing activities are basically surface driven phenomena, therefore, to understand the oxidation state of the elements present on the outermost surface, the surface composition of the sample was analysed by x-ray photoelectron spectroscopic (XPS) analysis which is a surface-sensitive analytical technique that is useful to determine the chemical environment of atoms, as shown in Figure S6a to c. Figure S6a shows the survey photoemission data collected on the SnO\(_2\) powder for S1, S4, S6, S7, S8, S10, S12 samples along with rGO. Figure S6b and c show Sn3d and O1s binding energies, respectively. The Sn 3d\(_{5/2}\) for all the samples were observed around 487.6 eV, while that of 3d\(_{3/2}\) were around 496 eV, and both were assigned to Sn\(^{4+}\) in bulk SnO\(_2\).\(^9\) The separations between the two peaks of all the corresponding samples were nearly 8.4 eV, which again is in good agreement with that of pure SnO\(_2\).\(^{27}\) Figure S6c shows the O1s spectra (around 532 eV) which further confirm the presence of oxygen in O\(^{2-}\) form.
exist on the surface of all the prepared SnO$_2$. From the XPS analyses it can be confirmed that in the investigated samples, Sn is basically present in the tetravalent state and O in the divalent state and interestingly, the prepared SnO$_2$ samples did not show the presence of any Sn$^0$ or Sn$^{+1}$ signal. XPS was also employed to analyse the structure of reduced graphene oxide (rGO) to confirm the results obtained by the Raman spectroscopy. The resolution of XPS spectrometer does not allow analysing peaks of C=C and C=O separately, therefore it is treated as signal binding energy derivatives at nearly 285 eV. However, rGO is prepared from reduction of graphene oxide by thermal and chemical treatments.

![X-ray photoelectron spectra of the samples S1, S4, S6, S7, S8, S10 and S12 along with rGO; (b) Magnified 3D profile of the Sn3d peaks in the range of 485–503 cm$^{-1}$ wavenumber; (c) O1s 3D spectra in the 528–538 cm$^{-1}$ wavenumber range for the previously mentioned seven different samples](image)

**Figure S6:** (a) X-ray photoelectron spectra of the samples S1, S4, S6, S7, S8, S10 and S12 along with rGO; (b) Magnified 3D profile of the Sn3d peaks in the range of 485–503 cm$^{-1}$ wavenumber; (c) O1s 3D spectra in the 528–538 cm$^{-1}$ wavenumber range for the previously mentioned seven different samples

Therefore, in the reduced graphene oxide, there was always some defects present in the structure and some trace amount of oxygen functional groups were also present on the rGO surface. Different reducing agents will lead to various carbons to oxygen ratio and different chemical compositions in reduced graphene oxide moiety, which can be confirmed from XPS.
studies. Using simple de-convolution procedure of Sn3d and O1s, with the assumption that the energetic distance between Sn$^{4+}$ and Sn$^{2+}$ components is equal to 0.7 eV, whereas the same between Sn$^{4+}$ and Sn$^{0}$ components is equal to 2.2 eV.\textsuperscript{29-30} According to these assumptions, a shift of Sn3d peak of $\sim$0.5 eV towards lower binding energy, after H$_2$ exposure, can only be interpreted as a true chemical shift due to an increase of Sn$^{4+}$ component with higher non-stoichiometry. Figure S6c shows the characteristic XPS spectra of O1s, which shows the core-level O1s spectra for rGO, along with O1s originated from the other sources.

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