## **Supporting Information**

## SnO<sub>2</sub> quantum dots decorated on RGO: A superior sensitive, selective and reproducible performance for H<sub>2</sub> and LPG sensor

R. K. Mishra,<sup>a</sup>\* S. B. Upadhyay,<sup>b</sup> Ajay Kushwaha,<sup>c</sup> Tae-Hyung Kim,<sup>d</sup> G. Murali,<sup>a</sup> Ranjana Verma,<sup>e</sup> Manish Srivastava,<sup>f</sup> Jay Singh,<sup>g</sup> P. P. Sahay,<sup>b</sup> Seung Hee Lee<sup>a</sup>\*

<sup>a</sup>Applied Materials Institute for BIN Convergence, Department of BIN Fusion Technology and Department of Polymer-Nano Science and Technology, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea

<sup>b</sup>Department of Physics, Motilal Nehru National Institute of Technology, Allahabad 211004, India. <sup>c</sup>Department of Physics, IIT Bombay, Powai, Mumbai-400076, India.

<sup>d</sup>Graduate School of Flexible & Printable Electronics Engineering, Chonbuk National University, Jeonju, Jeonbuk 561-756, Korea.

eSolar Energy Material Laboratory, Department of Energy, Tezpur University, Tezpur, Assam, 784 028, India.

<sup>f</sup>Department of Physics & Astrophysics, University of Delhi, Delhi -110007, India.

<sup>g</sup>Department of Applied Chemistry, Delhi Technological University, Shahbad Daulatpur, Main Bawana Road, Delhi-110042, India.

\*Correspondence to Prof. Seung Hee Lee, lsh1@chonbuk.ac.kr, Tel: +82-63-270-2343; Dr. Rajneesh Kumar Mishra (R.K. Mishra), rajneeshmishra08@gmail.com

## X-ray diffraction spectrum (XRD):

Phase identification was carried out by powder X-ray diffraction (XRD) using Bruker AXS C-8 advanced diffractometer with Cu K<sub>a</sub> radiation ( $\lambda = 1.5406$  Å). The XRD spectra of the RGO/SnO<sub>2</sub> QDs, RGO and SnO<sub>2</sub> QDs are presented in Fig. S1(a-c). All the diffraction peaks in the spectra corresponding to the tetragonal rutile structure of polycrystalline SnO<sub>2</sub> QDs are well matched with JCPDS card no. 72-1147. In addition, a broad peak denoted by '\*' at an angle 2 $\theta$  = 24.2775° (d-spacing = 0.37 nm) is observed which correspond to RGO.<sup>1</sup> These results confirm that the synthesized product is RGO/SnO<sub>2</sub> QDs nanocomposite. The XRD spectrum of RGO shows a broad peak centered ~ 24.2782° Fig. S1(b).



Fig. S1: XRD spectra of the as synthesized (a) RGO/SnO<sub>2</sub> QDs, (b) RGO and (c) SnO<sub>2</sub> QDs.



Fig. S2: XPS spectra (a) survey spectrum of RGO/SnO<sub>2</sub> QDs, (b) C 1s deconvoluted spectra of RGO and (c) survey spectrum of SnO<sub>2</sub> QDs and inset shows Sn 3d deconvoluted spectra.

The elemental analyses of the RGO/SnO<sub>2</sub> QDs, RGO and SnO<sub>2</sub> QDs have been studied by X-ray photoelectron spectroscopy (XPS). The XPS measurements were made with a K-Alpha Thermo Scientific equipped with a monochromatic Al-Ka X-ray and 100-4000 eV ion gun. Fig. S2(a) show presence of C, O and Sn only; no other elements were detected in the RGO/SnO<sub>2</sub> QDs sample. The band corresponding to 282.5 eV and 530.8 eV are attributed to the C1s and O1s, respectively.<sup>2</sup> Further, several other Sn band exists corresponding to 757.0 eV (Sn 3p<sub>1/2</sub>), 714.9

eV  $(3p_{3/2})$  and 25.2 eV (4d).<sup>3</sup> The Sn 3d spectrum indicates two symmetrical peaks at 484.3 eV and 495.1 eV, which are due to the Sn  $3d_{5/2}$  and Sn  $3d_{3/2}$ , respectively and confirms the formation of SnO<sub>2</sub>.<sup>4</sup> In Fig. 2(b), the presence of C1s corresponding to 284.0 eV, attributed to C-C band in the graphene based materials.<sup>5</sup> Fig. 2(c) shows the XPS spectrum of bare SnO<sub>2</sub> QDs where several bands matched with XPS spectrum of RGO/SnO<sub>2</sub> QDs, while shifting of the bands. The shift in 3d (487.6 eV, Sn  $3d_{5/2}$ ) and (495.4 eV, Sn  $3d_{3/2}$ ) correspond to bare SnO<sub>2</sub> and RGO/SnO<sub>2</sub> QDs composite, respectively, is attributed to the interaction between the graphene and the SnO<sub>2</sub> QDs.<sup>6</sup>





Fig. S3: TEM and HR-TEM images of the as synthesized (a) RGO and (b) SnO<sub>2</sub> QDs.

The bright-field TEM and HR-TEM images of the as synthesized RGO and  $SnO_2$  QDs are shown in Fig. S3(a, b). Fig. S3(a) shows RGO sheet and the corresponding HR-TEM image depicts 3-4 RGO sheets. Fig. S3(b) indicates the TEM images of the  $SnO_2$  QDs having particle size of ~7 nm. The HR-TEM image is consistent with the tetragonal rutile structure of  $SnO_2$  where the lattice fringes are assigned to (110) and (101) planes and proves the high crystallinity of the  $SnO_2$  QDs.





Fig. S4: FE-SEM images and corresponding elemental mapping of the as synthesized (a) RGO/SnO<sub>2</sub> QDs, (b) RGO and (c) SnO<sub>2</sub> QDs.

The morphology and elemental composition of the as-prepared RGO/SnO<sub>2</sub> QDs, RGO and SnO<sub>2</sub> QDs were investigated by JEOL scanning electron microscope (SEM) along with elemental mapping. Fig. S4(a-c) present FE-SEM images of the RGO/SnO<sub>2</sub> QDs, RGO and SnO<sub>2</sub> QDs. The micrographs of the RGO/SnO<sub>2</sub> QDs, RGO and SnO<sub>2</sub> QDs show the different resolution images and corresponding elemental mapping. It can be seen that the associated elements in the mapping are C, Sn, O for RGO/SnO<sub>2</sub> QDs, C for RGO and Sn, O for SnO<sub>2</sub> QDs.



Fig. S5: UV-Vis. spectra of (a) RGO/SnO<sub>2</sub> QDs, (b) SnO<sub>2</sub> QDs.

Analysis of the optical absorption spectra is one of the most powerful techniques for understanding the band structure and energy gap of the materials. Fig. S5(a, b) shows the absorption spectra of RGO/SnO<sub>2</sub> QDs and SnO<sub>2</sub> QDs. The UV-Vis spectra shows absorption peak at ~268 nm and ~270 nm for RGO/SnO<sub>2</sub> QDs and SnO<sub>2</sub> QDs, respectively, corresponding to a significantly wider band gap compared to the bulk band gap (3.6 eV) of SnO<sub>2</sub>. The observations confirmed the quantum confinement feature of RGO/SnO<sub>2</sub> QDs and SnO<sub>2</sub> RGO/SnO<sub>2</sub> QDs and SnO<sub>2</sub> QDs and SnO<sub>2</sub> QDs and SnO<sub>2</sub>.

The H<sub>2</sub> and LPG gas sensing response of the bare RGO and  $SnO_2$  QDs based sensor have been investigated and shown in Fig. S6(a, b) and Fig. S7(a, b), respectively. Fig. S6(a, b) shows the H<sub>2</sub>

and LPG sensing response profiles of the RGO sensor. It is observed that the response increases for all concentrations up to 200 °C and thereafter decreases. The H<sub>2</sub> response is observed to be saturated in the temperature region 250-275 °C as shown in Fig. S6(a). But in the case of LPG, the gas sensing response increases with all concentration and temperature up to 250 °C after that it was slowed down [Fig. S6(b)]. It may be due to the scattering of electrons by defect levels, which reduces the conductivity of the electrons.



Fig. S6: The gas sensing response characteristics of the (a) H<sub>2</sub> and (b) LPG based on RGO sensor.



Fig. S7: The gas sensing response characteristics of the (a) H<sub>2</sub> and (b) LPG based on SnO<sub>2</sub> QDs sensor.

Fig. S7(a, b) shows the H<sub>2</sub> and LPG gas sensing characteristics of the bare  $SnO_2$  QDs. It is seen that the sensing response first increases up to 200 °C and after that found to be saturated except at 300 ppm, where the response decreases [Fig. S7(a)]. It may be due to the dense environment around the sensor surface which leads to decrease in response. However, in case of LPG sensor [Fig. S7(a)], the test gas response increases for all the concentration and temperature and attains its maximum value at 275 °C. It is due to the more interaction of test gas molecules with the sensing sites present on the surface of sensor.

## **References:**

- 1 L.J. Cote, F. Kim, J. Huang, J. Am. Chem. Soc., 2009, 131, 1043-1049.
- 2 C. Zhu, S. Guo, Y. Fang, S. Dong, ACS Nano, 2010, 4, 2429-2437.
- 3 Q. Zhao, Z. Zhang, T. Dong, Y. Xie, J. Phys. Chem. B, 2006, 110, 15152-15156.
- 4 F.H. Li, J.F. Song, H.F. Yang, S.Y. Gan, Q.X. Zhang, D.X. Han, A. Ivaska, L. Niu, *Nanotechnol.*, 2009, 20, 455602.
- 5 S. Pei, J. Zhao, J. Du, W. Ren, H.M. Cheng, *Carbon*, 2010, 48, 4466-4474.
- 6 H. Seema, K.C. Kemp, V. Chandra, K.S. Kim, Nanotechnol., 2012, 23, 355705.
- 7 H. Liu, S. Xu, M. Li, G. Shao, H. Song, W. Zhang, W. Wei, M. He, L. Gao, H. Song, J. Tang, *Appl. Phys. Lett.*, 2014, **105**, 163104.
- 8 M. Srivastava, A. K. Das, P. Khanra, M. E. Uddin, N. H. Kim, J. H. Lee, J. Mater. Chem. A, 2013, 1, 9792-9801.
- 9 M. Srivastava, M. E. Uddin, J. Singh, N. H. Kim, J. H. Lee, J Alloy Compd. 2014, 590, 266-276.