Electronic Supplementary Information

Efficient energy harvesting in SnO₂ based dyesensitized solar cell utilizing nano-amassed mesoporous zinc oxide hollow microspheres as synergy boosters

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I. FESEM image of SnO₂ nanoparticles based photoanode.



Figure S1. Low resolution (a) and high resolution (b) FESEM images of SnO₂ nanoparticle based photonode

II. Cross-sectional FESEM image of champion photoanode (SZ₂₀)



Figure S2. (a) Lower magnification and (b) Higher magnifiation cross-sectional FESEM image of photoanode SZ₂₀.



III. Top View FESEM image of champion photoanode (SZ20)

Figure S3. (a) Lower magnification and (b,c,d) Higher magnifiation top-view FESEM image of photoanode SZ₂₀.

IV. High-magnification TEM images of meso-ZnO hollow spheres



Figure S4. (a,b) Higher magnifiation TEM images of *meso*-ZnO Hollow spheres.

V. BET surface area analysis of SnO2 nanoparticle.



Figure S5: Nitrogen adsorption-desorption isotherms for SnO₂ nanoparticle.

VI. Current density-Voltage (Jsc-V) curve for bare ZnO HS based DSSC.



Figure S6: Short circuit current density- Voltage curve for bare ZnO HS DSSC

VII: Photovoltaic parameters of ZnO HS based DSSC

Table S1: Short-Circuit Photocurrent Density (J_{sc}) , ^{*a*} Open-Circuit Voltage (V_{oc}) , ^{*a*} Fill Factor (FF), ^{*a*} Power Conversion Efficiency (PCE, η) for the ZnO HS based fabricated DSSCs employing I⁻/I₃⁻ Redox couple.

| Device | J_{sc} (mA/cm ²) | $V_{oc}(mV)$ | FF (%) | PCE (%) |
|-------------|--------------------------------|--------------|-------------|---------|
| Meso-ZnO HS | 6.95 (±0.3) | 616 (±8) | 63.1 (±1.3) | 2.71 |

^aData reported are the results of the best performed devices out of a minimum of five devices. The standard deviations for evaluated for five devices are included.

VIII: Chemisorption analysis

Table S2: Amount of dye chemisorbed for various photoanodes.

| Photoanodes | Dye Adsorbed (mol.cm ⁻²) |
|-------------|--------------------------------------|

| SnO ₂ | 4.21×10^{-8} |
|--|-----------------------|
| SnO ₂ NP_ZnO HS (9:1), SZ ₁₀ . | 4.78×10^{-8} |
| SnO ₂ NP_ZnO HS (8:2), SZ ₂₀ . | 4.91×10^{-8} |
| SnO ₂ NP_ZnO HS (7:3), SZ _{30.} | 4.46×10^{-8} |

Quantity of dye chemisorbed onto the photoanodes was estimated by employing a dye adsorption–desorption process using a 0.1 mM NaOH in equal proportion of ethanol/water (1:1, v/v). Briefly, each of the dye sensitized photoanodes were immersed in a 0.1mM NaOH solution in 1:1 ethanol: water mixture. The dipped photoanodes were then removed from the solution after complete desorption and the UV-vis absorption was recorded. The concentration of the dye desorbed per sq. cm area was then evaluated using Beer's law.¹

IX. Energy dispersive X-ray spectroscopy (EDS) Analysis.



Figure S7: Energy dispersive X-ray spectroscopy (EDS) mapping of the best performing composite photoanode i.e. SnO₂ NP_ZnO HS (8:2), SZ₂₀.

X: A comparative study of various SnO2_ZnO based Photovoltaics

| Table S3: A comparative study of various SnO2_ZnO based Photovoltaics. | |
|--|--|
| | |

| Primary photoanode | Secondary /Composite | Sensitizer | PCE , η (%) | Reference |
|--------------------------------|----------------------------|------------|--------------------|-----------|
| material used | Material used | Used | | |
| | | | | |
| | | | | |
| SnO ₂ nanoparticle | ZnO nanorod overlayer | N719 | ~2.62 % | 2 |
| SnO ₂ nanoparticles | ZnO nanotetrapods | N719 | ~ 4.91 % | 3 |
| | | | | |
| SnO ₂ nanoparticles | ZnO microparticles | N719 | ~4.96 % | 4 |
| SnO ₂ | Li Doped ZnO nanoparticles | N719 | ~2.06% | 5 |
| | (LZN) | | | |
| SnO ₂ Nanoparticles | ZnO Nanotetrapods | N719 | ~6.31 % | 6 |
| SnO ₂ Nanoparticle | ZnO Nanoparticle | D149 | ~3.6 % | 7 |
| SnO ₂ Nanoparticle | ZnO Nanoparticle | N3 | ~ 1.5 % | 7 |
| | | N10 | | |
| SnO ₂ Nanoparticle | ZnO Hollow Sphere | N719 | ~4.37 % | Present |
| | | | | Work |



XI: Stability tests of SnO₂ and SZ₂₀ based DSSCs

Figure S8: Stability tests for SnO₂ and SZ₂₀ based DSSCs.

Figure S8 depicts the stability tests for the fabricated $SnO_2 NP$ based and the best performed composite device i.e. $SnO_2 NP_ZnO$ HS (8:2), SZ_{20} and here and included in the supporting information of the revised version. In order to check the stability of the devices, dependence of photovoltaic parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), Fill factor (FF) and the power conversion efficiency (η) on time durations (over 48 h) are shown in Fig. R1. The photovoltaic characteristics are collected at an interval of 2h for 12h and then up to 48h in ambient condition and it has been found that $SnO_2 NP$ based and SZ_{20} based devices show a ~39.1% and ~38.4% reduction of efficacy respectively after 48h duration.

XII: Table S4: EIS fitting parameters for devices

| DSSC | R _s ^a | R _{ct1} ^a |
|--|------------------------------------|-------------------------------|
| photoanode | (Ohm) | (Ohm) |
| SnO ₂ NP | 22.51 | 3.97 |
| SnO ₂ NP _ ZnO HS (9:1), SZ ₁₀ | 21.83 | 4.17 |
| $SnO_2 NP _ ZnO HS (8:2), SZ_{20}$ | 20.11 | 3.91 |
| SnO ₂ NP _ ZnO HS (7:3), SZ ₃₀ | 21.65 | 4.06 |

References:

- Fan, K.; Liu, M.; Peng, T. Y.; Ma, L.; Dai, K., Effects of paste components on the properties of screen-printed porous TiO₂ film for dye-sensitized solar cells. *Renew. Energy* 2010, *35* (2), 555-561.
- Huu, N. K.; Son, D. Y.; Jang, I. H.; Lee, C. R.; Park, N. G., Hierarchical SnO₂ Nanoparticle-ZnO Nanorod Photoanode for Improving Transport and Life Time of Photoinjected Electrons in Dye-Sensitized Solar Cell. *Acs Appl Mater Inter* 2013, 5 (3), 1038-1043.
- Chen, W.; Qiu, Y. C.; Yang, S. H., A new ZnO nanotetrapods/SnO₂ nanoparticles composite photoanode for high efficiency flexible dye-sensitized solar cells. *Phys Chem Chem Phys* 2010, *12* (32), 9494-9501.
- Milan, R.; Selopal, G. S.; Epifani, M.; Natile, M. M.; Sberveglieri, G.; Vomiero, A.; Concina, I., ZnO@SnO₂ engineered composite photoanodes for dye sensitized solar cells. *Sci Rep* 2015, *5*, 1-12.
- Hung, I. M.; Bhattacharjee, R., Effect of Photoanode Design on the Photoelectrochemical Performance of Dye-Sensitized Solar Cells Based on SnO₂ Nanocomposite. *Energies* 2016, 9 (8), 1-11.
- Chen, W.; Qiu, Y. C.; Zhong, Y. C.; Wong, K. S.; Yang, S. H., High-Efficiency Dye-Sensitized Solar Cells Based on the Composite Photoanocles of SnO₂ Nanoparticles/ZnO Nanotetrapods. *J Phys Chem A* 2010, *114* (9), 3127-3138.

 Arai, T.; Kondo, S.; Nakano, S.; Kuramoto, T., Performance improvement of a tin(II) dioxide-modified electrode for the dye-sensitized solar cell by the addition of zinc(II) oxide and niobium(V) oxide. *Inorg Chim Acta* 2013, 395, 19-23.