

## **Low-Temperature Solution-processed Zn-doped SnO<sub>2</sub> Photoanodes: Enhancements in Charge Collection Efficiency and Mobility†**

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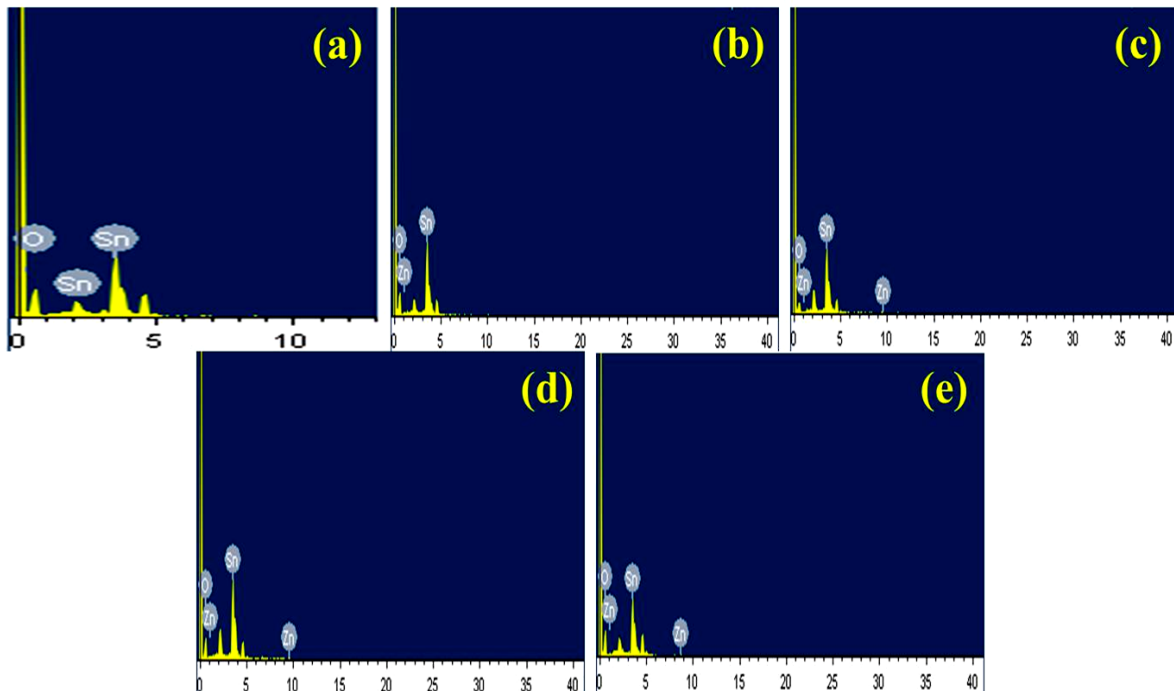
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## Experimental procedure

Zn-doped SnO<sub>2</sub> upright-standing photoanodes were prepared by using a simple, low temperature and cost-effective chemical bath deposition method. In a typical procedure, 0.3M SnCl<sub>4</sub> was initially dissolved in organic ethanol solvent and then 0.6M thioacetamide was added to same solution at room temperature. This transparent solution was then transferred into air-sealed teflon tubes with fluorine-tin-oxide (FTO) substrates vertically inserted into it. Initially FTO substrates were cleaned with acetone and ethanol for 30 min in ultrasonic cleaned and further dried in argon flow. This as-prepared solution was further maintained at 70 °C for 3 h in chemical bath apparatus. For synthesizing Zn-doped SnO<sub>2</sub> photoanodes the wt.% of ZnCl<sub>2</sub> was varied from 1 to 4 and added directly into a solution containing SnCl<sub>4</sub> and thioacetamide before keeping placing it into the water bath. These samples are nomenclatured as A-pristine and B, C, D and E, respectively, according to the dopant concentration. The deposited films were removed off and annealed at 500 °C for 1 h and used for further characterization.

## EDX analysis



**Figure S1.** EDX spectrum obtained for the photoanode (A-E).

Energy-dispersive X-ray spectroscopy (EDX) analysis was carried out to confirm the presence of  $\text{Zn}^{2+}$  in/over the  $\text{SnO}_2$  matrix. A systematic increase of Zn wt% from 0 to 3.89 wt% for B to E photoanodes corroborates that Zn wt% in  $\text{SnO}_2$  increases with increase in the wt% of  $\text{ZnCl}_2$ .

**Table 1:** EDX analysis confirming the Zn doping for 3wt % (atomic and weight) into  $\text{SnO}_2$  photoanodes.

<b>Element</b>	<b>Weight%</b>	<b>Atomic%</b>
<b>O K</b>	<b>30.40</b>	<b>76.28</b>
<b>Zn K</b>	<b>0.91</b>	<b>0.43</b>
<b>Sn L</b>	<b>68.69</b>	<b>23.29</b>
<b>Totals</b>	<b>100.00</b>	

## XPS analysis

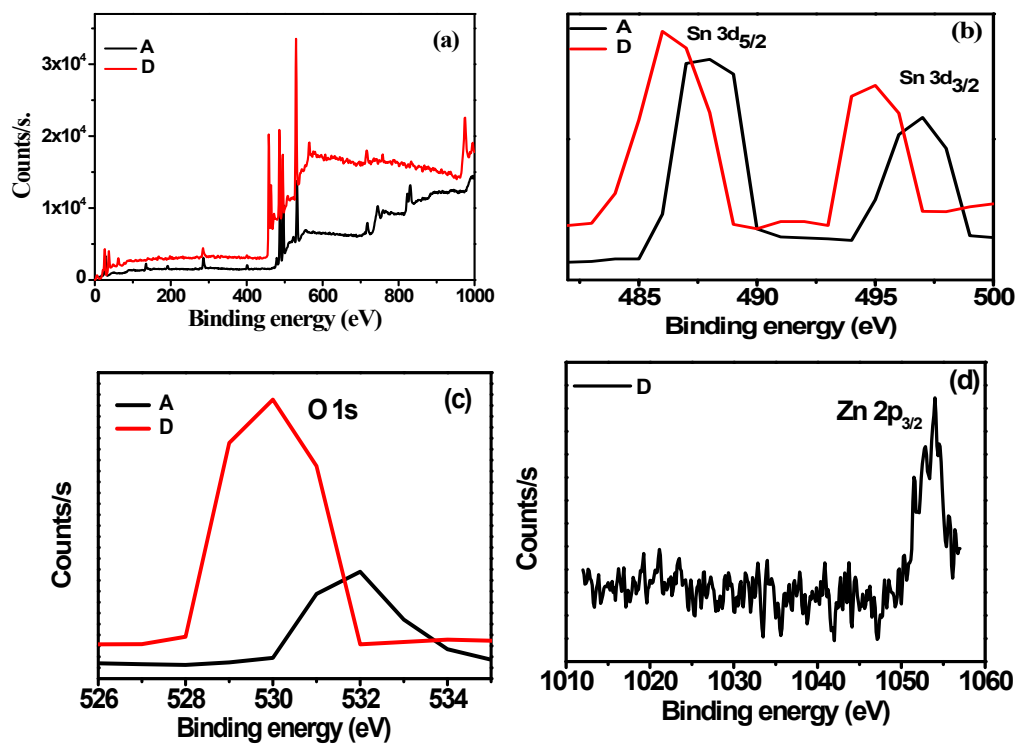
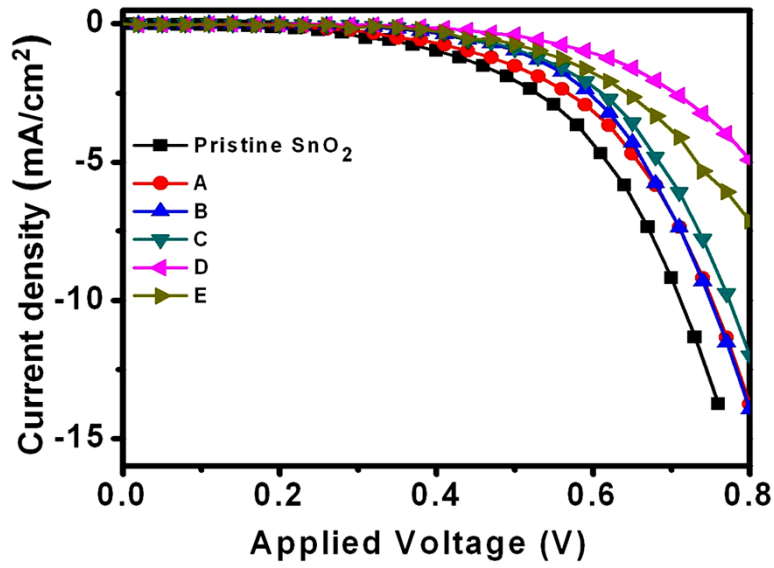


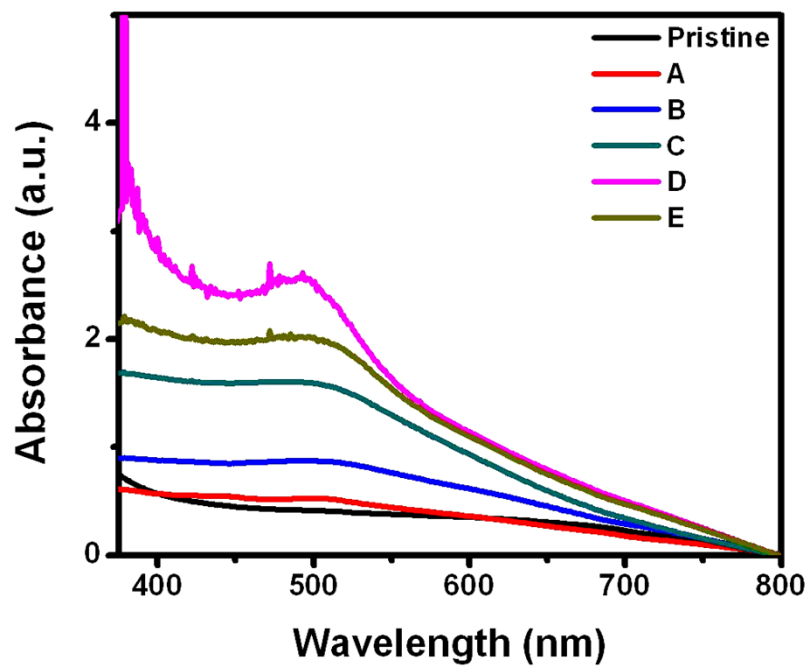
Fig. S2, XPS analysis of pristine and 3 wt.% Zn-doped SnO<sub>2</sub> photoanode.

**Table 2:** Photovoltaic parameters of all the photoanodes.

<b>Sample</b>	<b><math>J_{sc}</math> (mA/cm<sup>2</sup>)</b>	<b><math>V_{oc}</math> (V)</b>	<b>FF</b>	<b>PCE (%)</b>
<b>Pristine SnO<sub>2</sub></b>	<b>6.73</b>	<b>0.55</b>	<b>0.51</b>	<b>1.87</b>
<b>A</b>	<b>11.02</b>	<b>0.66</b>	<b>0.35</b>	<b>2.54</b>
<b>B</b>	<b>11.84</b>	<b>0.67</b>	<b>0.43</b>	<b>3.41</b>
<b>C</b>	<b>12.28</b>	<b>0.65</b>	<b>0.47</b>	<b>3.76</b>
<b>D</b>	<b>15.13</b>	<b>0.67</b>	<b>0.48</b>	<b>4.87</b>
<b>E</b>	<b>13.15</b>	<b>0.66</b>	<b>0.48</b>	<b>4.16</b>



**Figure S3.** *J-V* curves of all DSSCs measured in dark.



**Figure S4.** UV-*vis* spectra of pristine SnO<sub>2</sub> and Zn-doped SnO<sub>2</sub> nanoplates after dye loading.

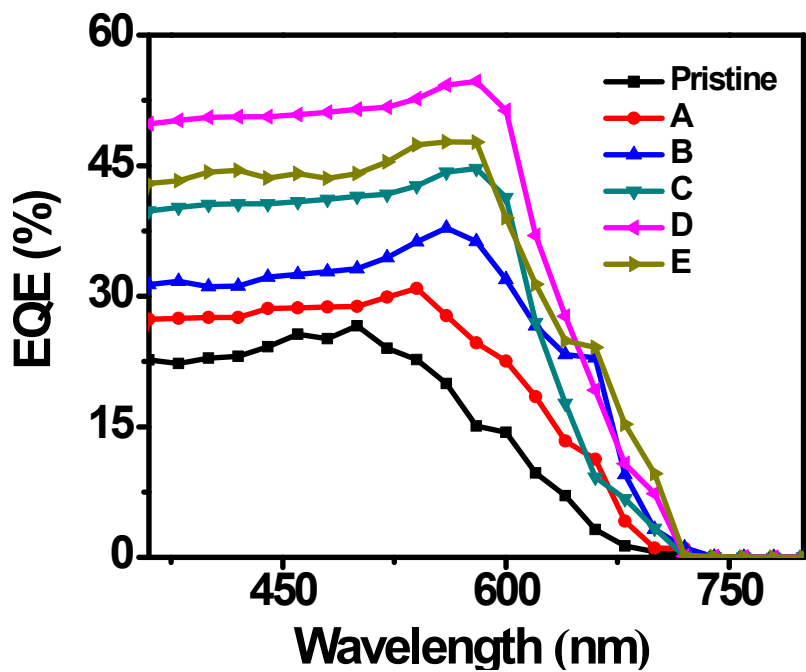
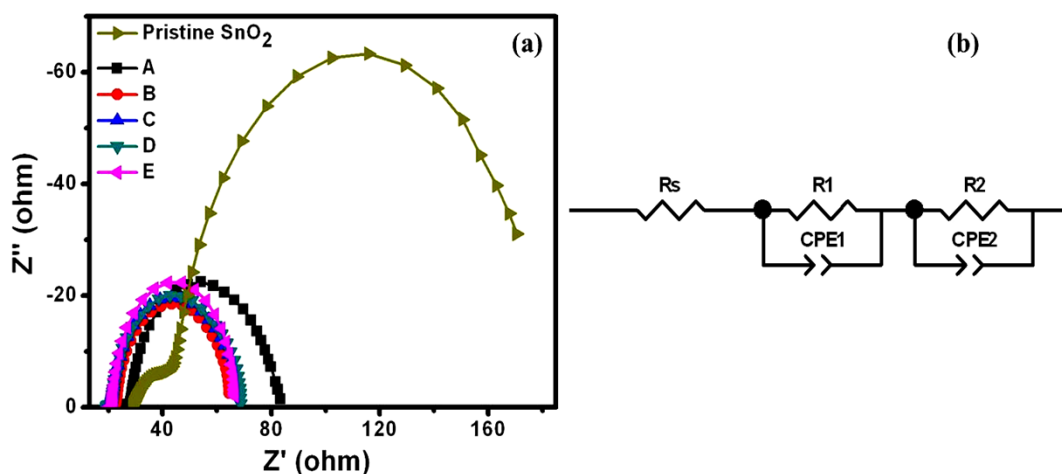


Figure S5. IPCE measurement of various photoanodes.

## EIS analysis



**Figure S5.** (a) Nyquist plot with pristine  $\text{SnO}_2$  and Zn-doped  $\text{SnO}_2$  nanoplates, and (b) An equivalent circuit used for fitting the Nyquist plots.

The EIS measurements were performed to analyze the electron transport behavior in the DSSCs, which distinguishes the charge transport resistance and chemical capacitance of the device. The impedance spectrum for all photoanode shows two semicircles which can be attributed to high frequency represents interaction between counter electrode/electrolyte interfaces whereas low frequency region represents charge transfer resistance at the fluorine-tin-oxide/ $\text{SnO}_2$  or Zn- $\text{SnO}_2$ -dye/electrolyte interface.<sup>1,2</sup>

The second semicircle represents the charge transport resistance from which the mean electron life time ( $\tau_n$ ) can be calculated by using the relation,

$$\tau_n = (2\pi f_{max})^{-1} \quad (1)$$



where,  $f_{max}$  is the frequency at the highest value of recombination region arc.<sup>3</sup> The mean electron transit time ( $\tau_d$ ) is obtained from the relation between the electron transportation resistance ( $R_t$ ) and interfacial charge transport resistance ( $R_{ct}$ )<sup>4</sup> using the relation,

$$(\tau_{d,EIS} / \tau_{n,EIS}) = (R_t / R_{ct}) \quad (2)$$

Here,  $\tau_d$  and  $\tau_n$  are also critical parameters to determine the charge collection efficiency ( $\eta_{cc}$ ) of the photoanode. The photogenerated electrons transport towards the front contact (FTO), to have the maximum probability of recombination with the redox couple (iodide/tri-iodide), hence the charge collection rate at FTO interface is given by,

$$(1/ \tau_{cc}) = (1/ \tau_{d,EIS}) - (1/ \tau_{n,EIS}) \quad (3)$$

where,  $\tau_{cc}$  is the time constant for charge collection. Accordingly  $\eta_{cc}$  is given by the relation

$$\begin{aligned} \eta_{cc} &= (1/ \tau_{cc}) / (1/ \tau_{cc}) + (1/ \tau_{n,EIS}) \\ &= 1 - (\tau_{d,EIS} / \tau_{n,EIS}) \end{aligned} \quad (4)$$

The electron diffusion lengths for the pristine and Zn-doped SnO<sub>2</sub> photoanodes are calculated by using,

$$L_n = \sqrt{D_n \times \tau_n} = L \sqrt{R_{ct}/R_t} \quad (5)$$

where, L is thickness of the photoanode and  $D_n$  is diffusion coefficient. The electronic mobility ( $\mu$ ) is given by the Einstein's relation,

$$\mu = (D_n e / K_B T) \quad (6)$$

where,  $e$  is the elementary charge of the electron,  $K_B$  is Boltzmann constant and  $T$  is absolute temperature in Kelvin. Hence after replacing the constants and considering the absolute temperature as 298 K (room temperature), the above equation 6 can be directly reduced to,

$$\mu = D_n \times 38.9 \quad (7)$$

Where,  $D_n$  can be measured by using the relation,

$$D_n = L_n^2 / \tau_n \quad (8)$$

**Table 3:** Comparison of Zn doped SnO<sub>2</sub> photoanodes from literature.

<b>Sr. no.</b>	<b>Pristine SnO<sub>2</sub> <math>\eta</math> (%)</b>	<b>Optimized Zn doped SnO<sub>2</sub> <math>\eta</math> (%)</b>	<b>Method used for synthesis</b>	<b>Reference</b>
<b>1</b>	<b>0.81</b>	<b>3.73</b>	<b>Double replication</b>	<b>5</b>
<b>2</b>	<b>-</b>	<b>2.21</b>	<b>Autoclave</b>	<b>6</b>
<b>3</b>	<b>-</b>	<b>3.8</b>	<b>Hydrothermal</b>	<b>7</b>
<b>4</b>	<b>1.66</b>	<b>3.96</b>	<b>Sol-gel</b>	<b>8</b>
<b>5</b>	<b>1.87</b>	<b>4.87</b>	<b>Chemical bath deposition</b>	<b>Present case</b>

**Table 4:** Electrochemical parameters calculated by using EIS for pristine and Zn-doped SnO<sub>2</sub> photoanodes.

<b>Samples</b>	<b>Rt</b>	<b>Rct</b>	<b><math>\tau_n * 10^{-2}</math> (S)</b>	<b><math>T_d * 10^{-3}</math> (S)</b>	<b><math>\eta_{cc}</math> (%)</b>	<b><math>L_n * 10^{-6}</math></b>	<b><math>D_n * 10^{-4}</math></b>	<b><math>\mu * 10^{-3}</math> <math>\text{cm}^2\text{V}^{-1}\text{s}^{-1}</math></b>
<b>A</b>	<b>1.7</b>	<b>55.45</b>	<b>5.09</b>	<b>10.97</b>	<b>78.45</b>	<b>29.69</b>	<b>5.83</b>	<b>22.68</b>
<b>B</b>	<b>1.92</b>	<b>56.76</b>	<b>4.69</b>	<b>8.73</b>	<b>81.39</b>	<b>28.29</b>	<b>6.03</b>	<b>23.46</b>
<b>C</b>	<b>1.50</b>	<b>47.61</b>	<b>4.01</b>	<b>5.99</b>	<b>85.04</b>	<b>29.28</b>	<b>7.30</b>	<b>28.40</b>
<b>D</b>	<b>1.22</b>	<b>41.79</b>	<b>3.22</b>	<b>3.44</b>	<b>89.32</b>	<b>30.42</b>	<b>9.45</b>	<b>36.76</b>
<b>E</b>	<b>1.73</b>	<b>44.83</b>	<b>3.68</b>	<b>5.61</b>	<b>84.76</b>	<b>26.47</b>	<b>7.19</b>	<b>27.97</b>

## References

1. S. Sun, G. Meng, G. Zhang and L. Zhang, *Cryst. Growth Des.*, 2007, **7**, 1988.
2. N. Du, H. Zhang, J. Yu, P. Wu, C. Zhai, Y. Xu, J. Wang and D. Yang, *Chem. Mater.*, 2009, **21**, 5264.
3. M. Adachi, M. Sakamoto, J. Jiu, Y. Ogata and S. Isoda, *J. Phys. Chem. B*, 2006, **110**, 13872.
4. Q. Wang, Z. Zhang, S. M. Zakeeruddin and M. Grätzel, *J. Phys. Chem. C*, 2008, **112**, 7084.
5. E. Ramasamy and J. Lee, *Eng. Env. Sci.*, 2011, **4**, 2529.
6. X. Dou, N. Mathews, Q. Wang, S. S. Pramana, Y. M. Lam and S. Mhaisalkar, *Nanoscale*, 2011, **3**, 4640.
7. B. Tan and Y. Wu, *JACS*, 2007, **129**, 4162.
8. J-H, Lee, N-G, Park and Y-J, Shin, *Sol. Eng. Mat. Sol. Cell*, 2011, **95**, 179.