

Supplementary Information

Enhanced Power Conversion Efficiency of Dye-Sensitized Solar Cells by Band Edge Shift of TiO₂ Photoanode

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1. Fabrication Conditions of DSSCs

The FTO glass samples were sonicated for 20 min in deionized water (DIW), acetone, and ethyl alcohol, and were then thoroughly rinsed with DIW and ethanol. The cleaned FTO glasses were dipped in a hydrolyzed TiCl₄ solution (40 mM) at 70 °C for 30 min, and then washed with DIW and ethanol. A TiO₂ (15–20 nm) paste was coated on the TiCl₄-treated FTO glass via doctor-blade method, and successively a TiO₂ layer composed of particles with a diameter of over 100 nm was deposited. The two layers were then sintered at 500 °C for 60 min to produce both the mesoporous and scattering TiO₂ layers. Finally, the TiO₂ films were again treated with a hydrolyzed TiCl₄ solution (40 mM) and annealed at 500 °C for 60 min. Thus, TiO₂/FTO photoanodes with scattering layers were prepared. The anodes were soaked in an aqueous Na₂S solution (80 mM) for 0–20 min to modify the TiO₂ surfaces. Next, the resultant electrodes were rinsed with DIW and ethanol, and then dried at 65 °C for 10 min to produce the modified photoanodes (Na₂S-TiO₂/FTO). Finally, both the pristine TiO₂/FTO and the Na₂S-TiO₂/FTO photoanodes were sensitized by separately dipping them in a 0.5 mM ethanolic N719 dye solution for 24 h to obtain the working electrodes.

For the preparation of the counter electrode, the FTO glasses were drilled to form two holes, and then cleaned by ultrasonication as described above. A Pt paste was deposited via the doctor-blade method on the cleaned FTO glasses and followed by sintering at 400 °C for 30 min to form Pt catalyst layers. The prepared counter and working electrodes were sealed using a 60-µm-thick hot melt adhesive (Surlyn). The electrolyte was injected into the cells through one of the two small holes drilled into the counter electrodes to produce DSSCs with an active area of 25 mm².

2. Averaged Photovoltaic Performance of DSSCs

Table S1. Averages and standard deviations of cell performance, which were measured using 4 cells, with the time of soaking in the Na₂S solution.

| Soaking time (min) | V_{oc} (mV) | J_{sc} (mA/cm ²) | FF (%) | η (%) |
|--------------------|---------------|--------------------------------|---------------|--------------|
| 0 | 0.675 ± 0.004 | 17.04 ± 0.523 | 67.28 ± 1.006 | 7.73 ± 0.115 |
| 5 | 0.697 ± 0.002 | 16.69 ± 0.530 | 69.66 ± 0.002 | 8.10 ± 0.212 |
| 10 | 0.697 ± 0.007 | 16.21 ± 0.090 | 69.14 ± 0.342 | 7.81 ± 0.141 |
| 15 | 0.699 ± 0.002 | 15.99 ± 0.371 | 68.76 ± 0.279 | 7.68 ± 0.193 |
| 20 | 0.693 ± 0.003 | 15.98 ± 0.185 | 69.12 ± 0.271 | 7.66 ± 0.122 |

3. Current Density-Voltage Profiles of DSSCs

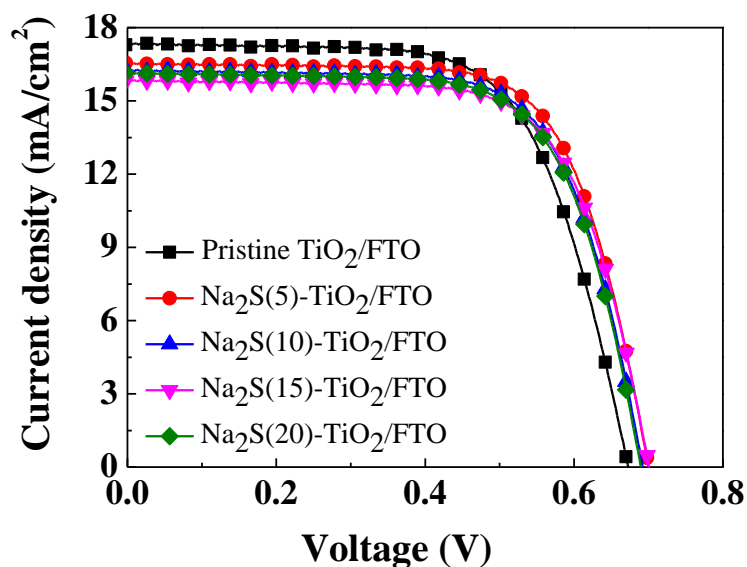


Figure S1. J - V characteristics of selected DSSCs which showed PCEs similar to the averaged values in each soaking time.

Table S2. Photovoltaic parameters of selected cells which showed PCEs similar to the averaged values in each soaking time.

| Applied photoanodes | V_{oc} (mV) | J_{sc} (mA/cm^2) | FF (%) | η (%) | R_{se} (Ωcm^2) | R_{sh} (Ωcm^2) |
|---|---------------|--------------------------------------|----------|------------|----------------------------------|----------------------------------|
| Pristine TiO_2/FTO | 671 | 17.35 | 66.16 | 7.70 | 6.96 | 1418 |
| $\text{Na}_2\text{S}(5)\text{-TiO}_2/\text{FTO}$ | 700 | 16.53 | 69.81 | 8.08 | 6.05 | 2347 |
| $\text{Na}_2\text{S}(10)\text{-TiO}_2/\text{FTO}$ | 692 | 16.21 | 69.41 | 7.79 | 6.32 | 2169 |
| $\text{Na}_2\text{S}(15)\text{-TiO}_2/\text{FTO}$ | 700 | 15.86 | 69.15 | 7.68 | 6.46 | 1835 |
| $\text{Na}_2\text{S}(20)\text{-TiO}_2/\text{FTO}$ | 690 | 16.13 | 68.85 | 7.66 | 6.20 | 2375 |

4. UV-Vis Absorbance and UPS Valence Band Spectra

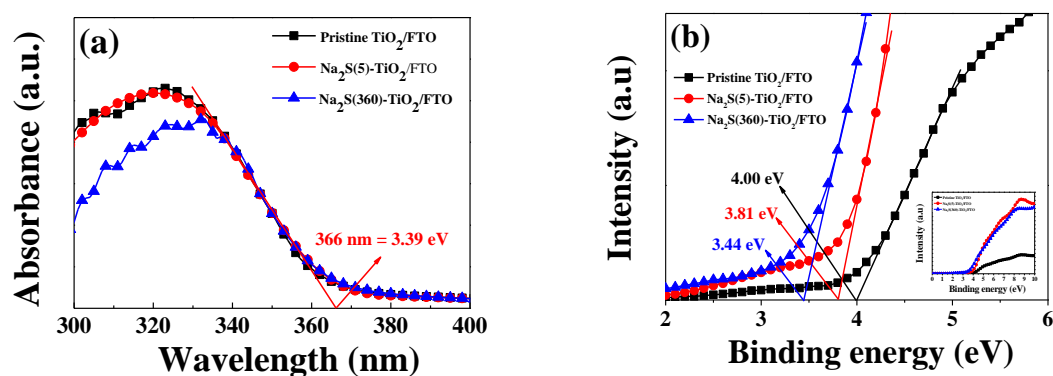


Figure S2. UV–vis absorbance (a) and UPS valence band (b) spectra for pristine TiO₂/FTO, Na₂S(5)-TiO₂/FTO, and Na₂S(360)-TiO₂/FTO.



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