Boosting the Photovoltage of Dye-Sensitized Solar Cells with Thiolated Gold Nanoclusters

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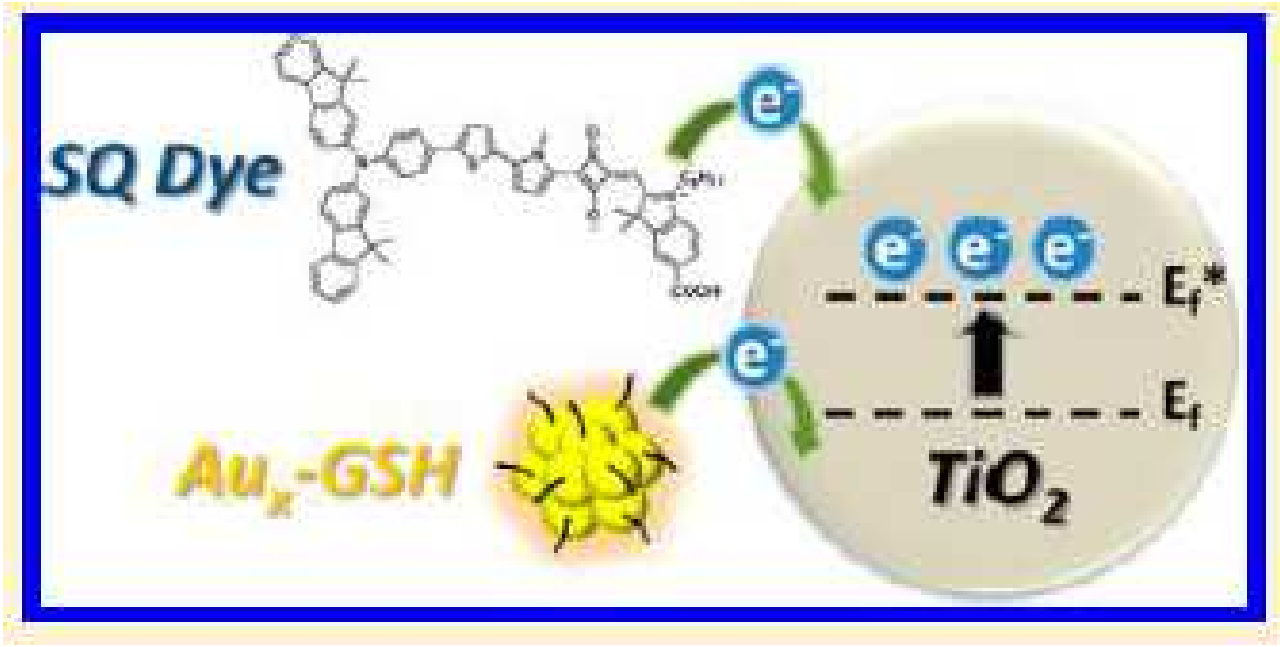

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Introduction

• Sensitization of semiconductor nanostructures with dyes is attractive for capturing a broader range of visible–near-IR photons and improving the performance of solar energy conversion devices.

• Synthetic approaches such as structural modification, surface treatment of mesoscopic oxide films, and use of co-sensitizers have been attempted to improve the performance of dye-sensitized solar cells (DSSCs).

• For example, structural manipulation of ligands of Ru(II) bipyridyl complexes is found to be quite effective for tailoring the absorptivity and excited-state properties of the sensitizing molecule.

• Semiconductor quantum dots (QDs) (CdS, CdSe, PbS, and Sb_2S_3) are another class of sensitizers that are widely used in liquid junction and solid-state solar cells.

• Thiolated gold nanoclusters are a new class of photosensitizers, which are quite effective in the operation of DSSCs and photocatalytic generation of H_2 in a photoelectrolysis cell.

• Glutathione-capped gold nanoclusters were able to inject electrons into mesoscopic TiO_2 films with a relatively high photon to charge carrier generation efficiency (IPCE) and deliver power conversion efficiency of 2%.

• Another approach to broaden the photoresponse of a solar cells is to employ two or more sensitizers with different spectral responses.

• Rational design of coupling organic dyes with semiconducting QDs in a cosensitized solar cell has led to some synergistic effects.

This paper

• Used a glutathione-capped gold nanoclusters (Au_x-GSH NCs) as a cosensitizer in DSSCs employing a squaraine (SQ) dye.

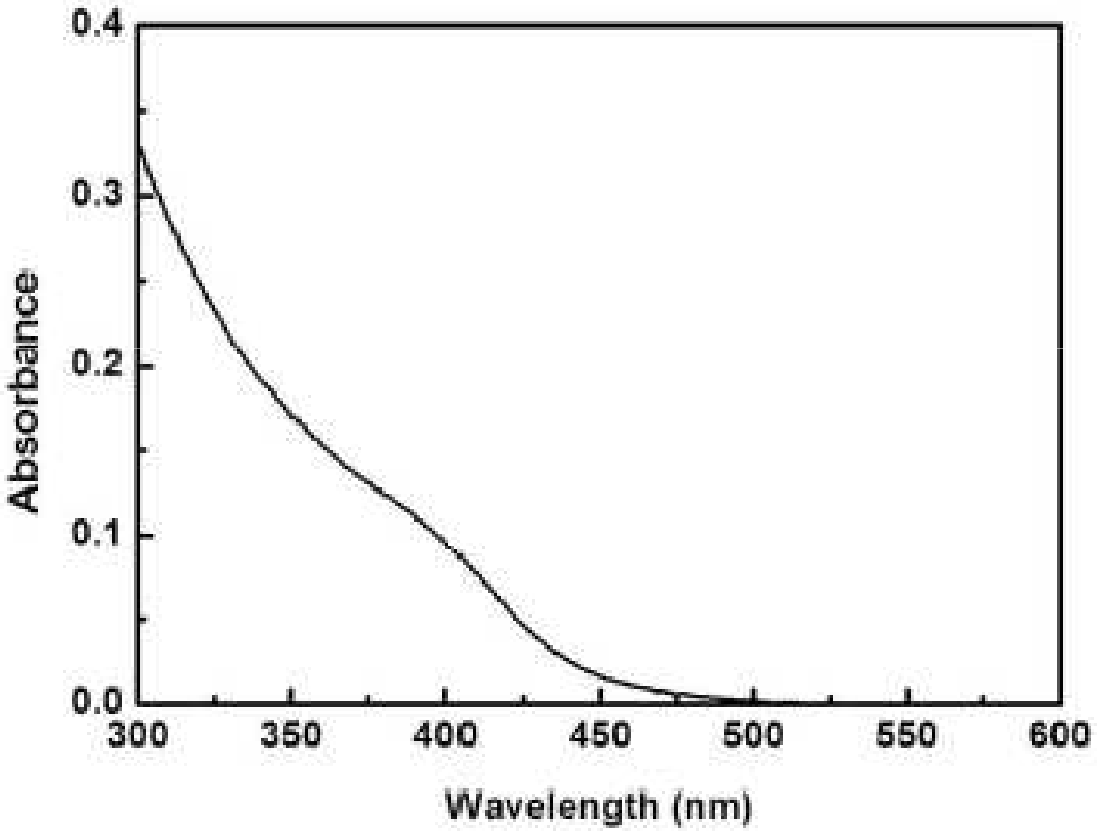
• Au_x-GSH NCs and the SQ dye selectively absorb in the spectral region below 500 nm and between 550 and 800 nm, respectively, and thus enable the broadening of the overall photoresponse of the DSSCs

Designing Photoanodes for DSSCs

$HAuCl_4$ (aq)) **70°C**

+ → **Yellow Au- GSH NCs**

L-glutathione **24 hr**

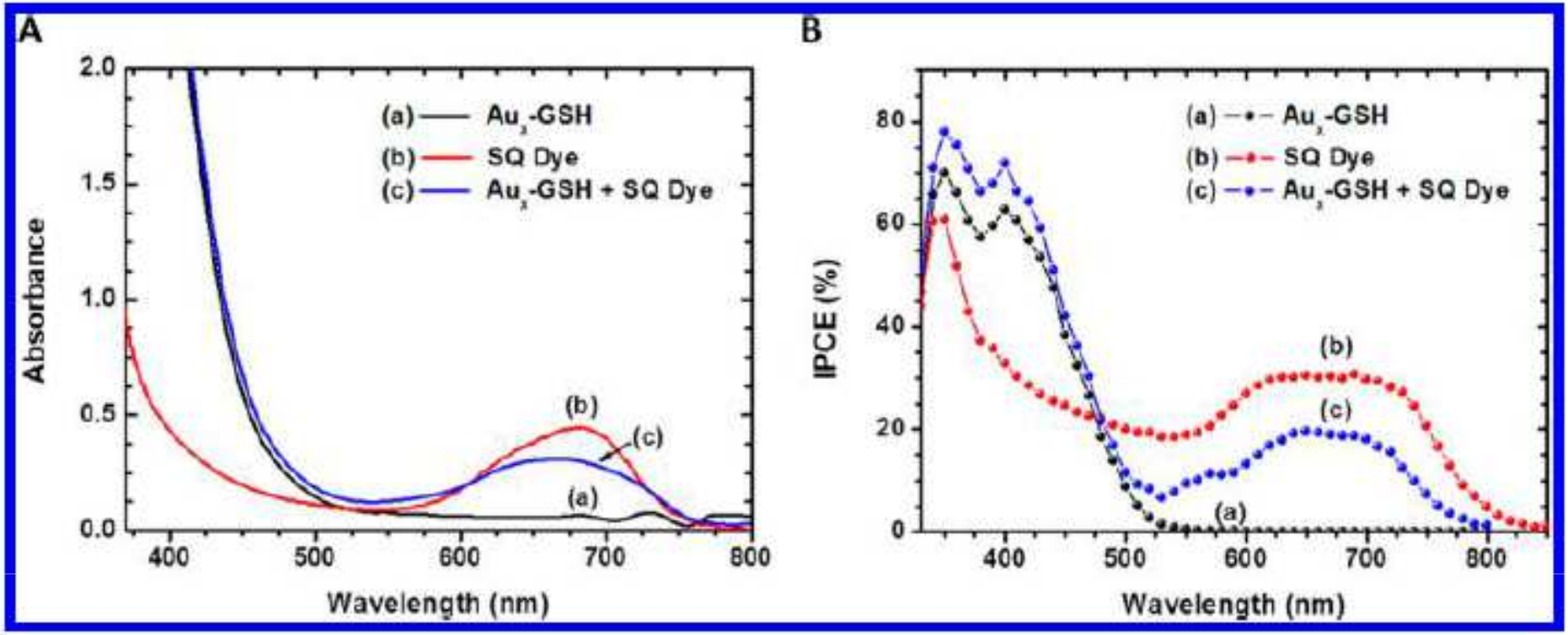


•The absorption spectrum shows a characteristic onset of absorption at 520 nm with a shoulder at ~400 nm

• The mesoscopic TiO_2 film was deposited on a transparent conductive electrode (fluorine-doped SnO_2 on glass, FTO glass) using a doctor blade technique.

• This electrode was first sensitized with Au_x-GSH NCs by immersing the TiO_2 film electrode in a concentrated Au_x-GSH NCs solution for 48 h. Electrode turned yellow.

• The TiO_2 electrode and Aux-GSH NCs sensitized TiO_2 electrode were further modified with squaraine (SQ) dye by immersing the electrode in the dye solution in ethanol overnight



(A) Absorption and (B) IPCE (incident photon to charge carrier generation efficiency) spectra recorded using (a) Au_x-GSH, (b) SQ dye, and (c) Au_x-GSH + SQ dye-sensitized TiO_2 photoanode. Note that nonzero absorbance above 520 nm in trace a is due to light scattering by the TiO_2 layer

- The SQ dye that exhibits absorption in the range of 550 and 800 nm, with a maximum around 680 nm

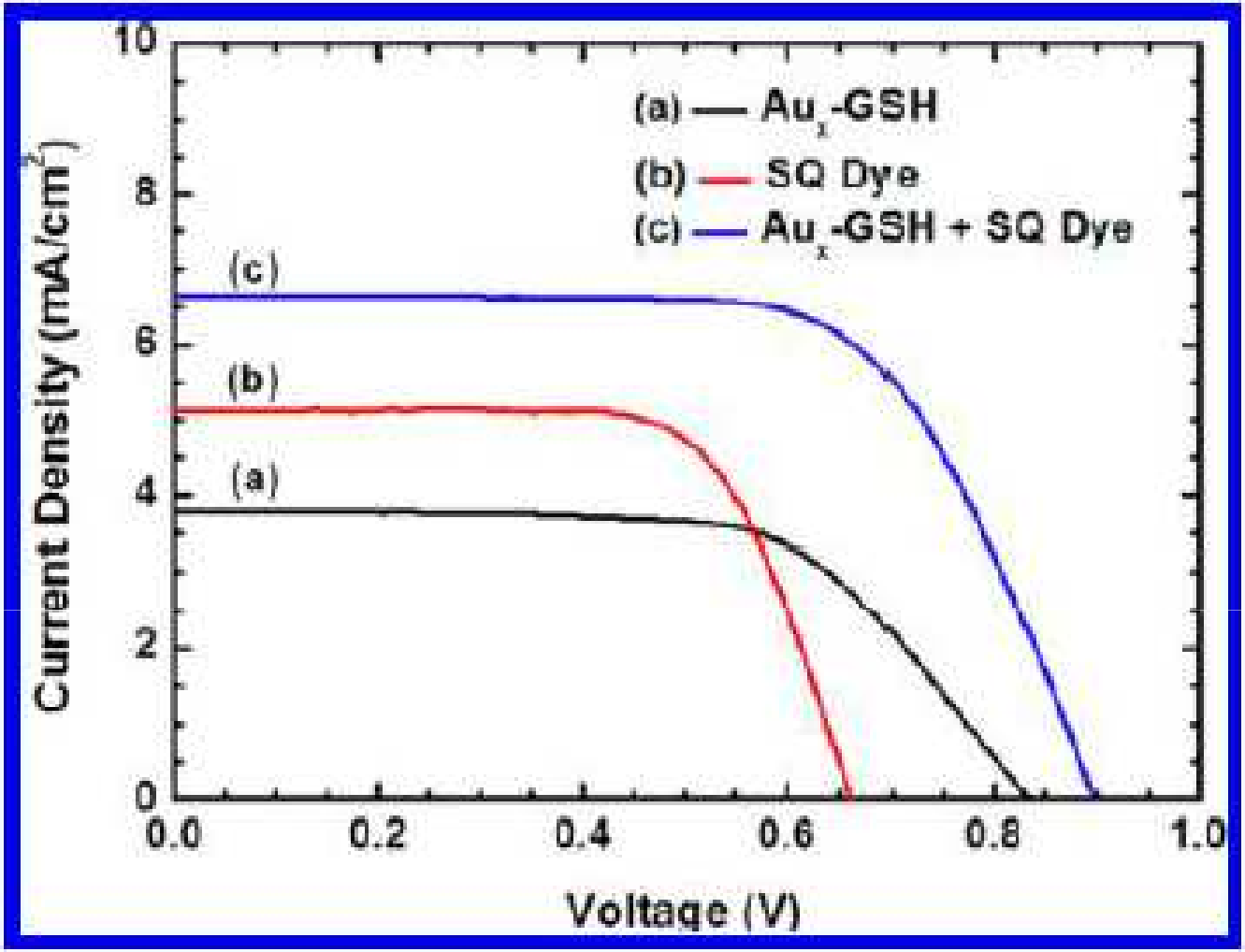
DSSCs Performance

• Solar cell was constructed using a TiO_2 electrode modified with sensitizers (photoanode) and Pt-deposited FTO counter electrode in a sandwich configuration with a 50 µm hot-melt ionomer film (Surlyn SX 1170−25, Solaronix) as a spacer.

• A redox electrolyte of [Co(III)(bpy)3](PF6)3/[Co(II)(bpy)3]/(PF6)2 was introduced between the two electrodes.

• The IPCE of the photoelectrochemical cell employing Aux-GSH NCs sensitized TiO2 electrode shows photocurrent response below 520 nm, in agreement with the absorption feature.

• The TiO2 photoanode consisting of both SQ dye and Aux-GSH NCs as sensitizers shows the characteristic photoresponse in the red (550−800 nm) and blue (<500 nm) regions of the visible spectrum, thus confirming the participation from both SQ dye and Aux-GSH NCs.



(A) J−V characteristics of solar cell recorded under AM 1.5G illumination (100 mW/cm2) using (a) Au_x-GSH, (b) SQ dye, and (c) Au_x-GSH + SQ dye-sensitized TiO_2 as photoanode.

Table 1. Comparison of Solar Cell Performance with Au_x-GSH and SQ Dye as Photosensitizers[a]

photosensitizer	J_{sc} (mA/cm^2)	V_{oc} (V)	ff	η (%)
Au_x-GSH	3.82	0.83	0.63	2.0
SQ dye	5.12	0.66	0.70	2.4
Au_x-GSH + SQ dye	6.70	0.90	0.66	4.0

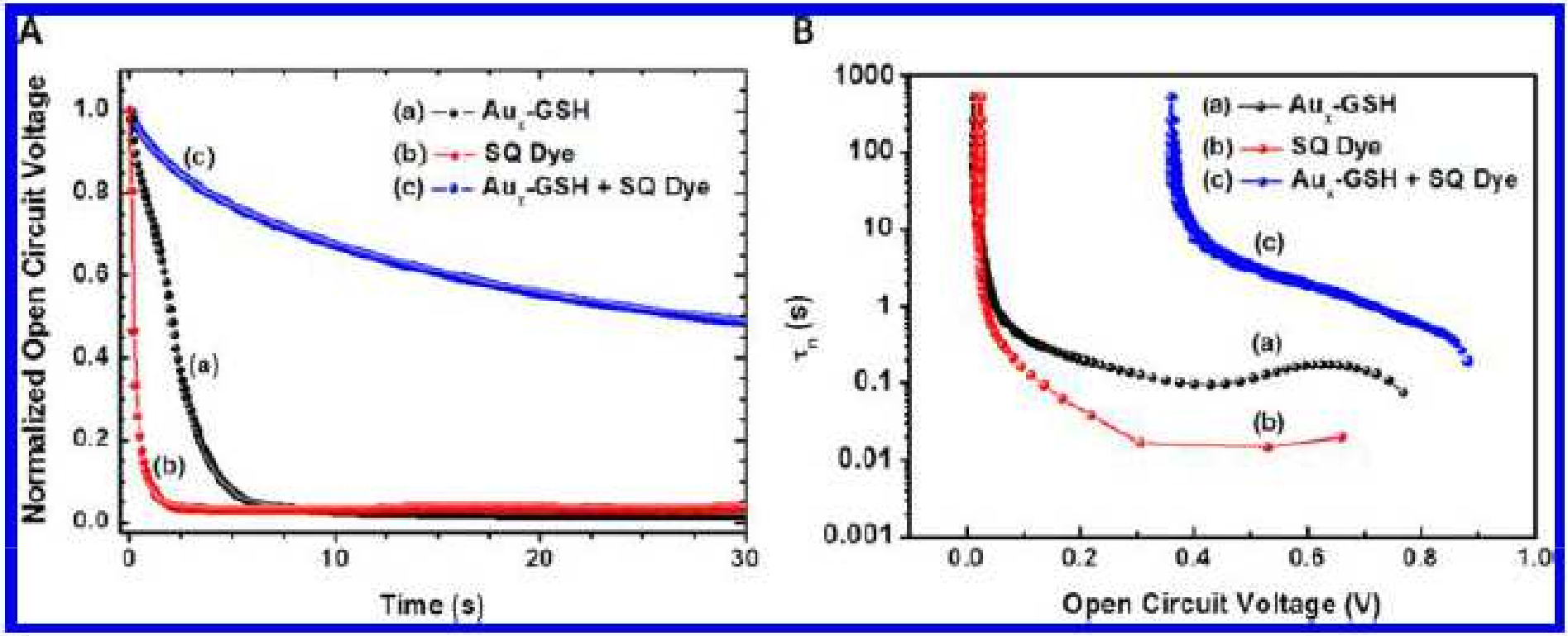
[a]Performance of solar cells measured with 0.18 cm^2 working area under AM 1.5G illumination (100 mW/cm^2). Electrolyte: 0.22 M $Co(bpy)_3(PF_6)_2$, 0.033 M $Co(bpy)_3(PF_6)_3$, 0.3 M *tert*-butylpyridine, and 0.1 M $LiClO_4$ in acetonitrile. ff and η correspond to fill factor and power conversion efficiency, respectively.

Mechanism

$$TiO_2 + S^* \rightarrow TiO_2(e) + S^+ \quad (1)$$

$$S^+ + Red \rightarrow S + Ox \quad (2)$$

$$TiO_2(e) + Ox \rightarrow TiO_2 + Red \quad (3)$$



(A) Open-circuit voltage decay−time profile and (B) electron lifetime as a function of V_{oc} using (a) Au_x-GSH, (b) SQ dye, and (c) Au_x-GSH + SQ dye-sensitized TiO_2 as photoanode

• The suppression of the back electron transfer is seen only when Au_x-GSH NCs are loaded onto TiO_2 film along with a visible sensitizer.

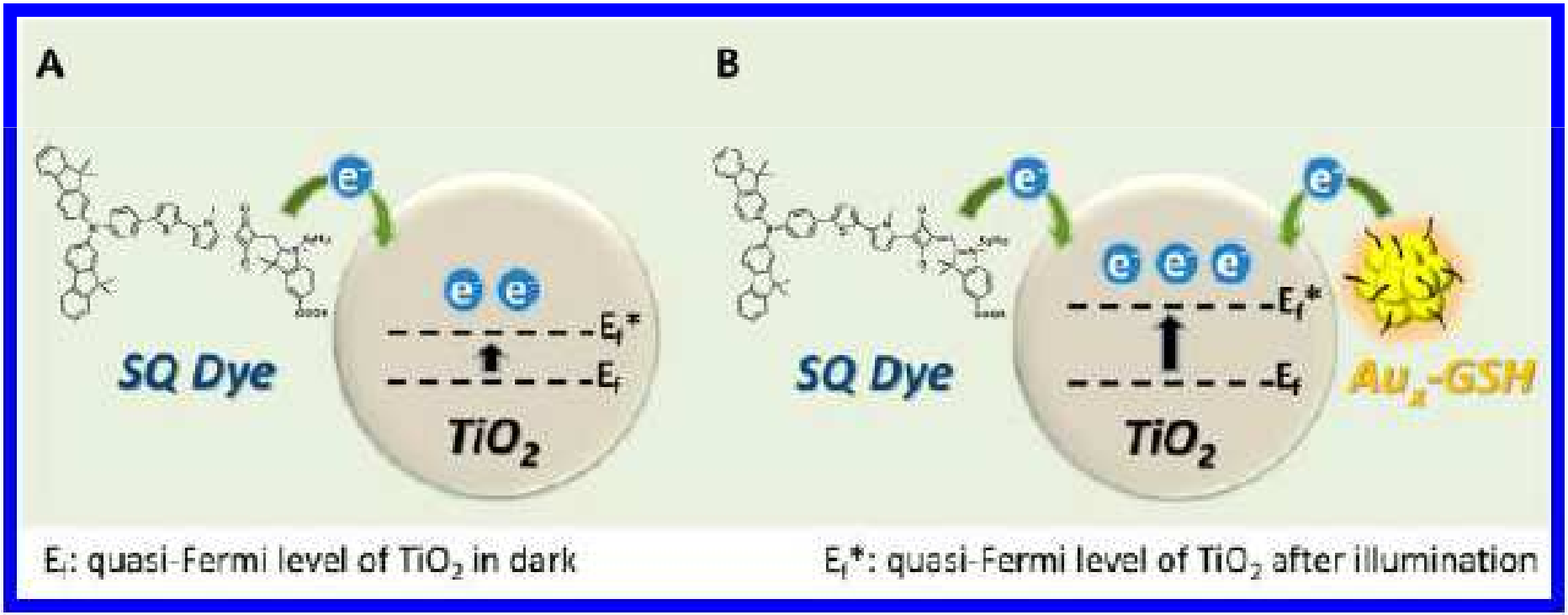
•Probably the partial coverage of the TiO_2 surfaces by the AuGSH minimizes the probability of back electron transfer.

• The higher photovoltage that arises from the shift in the Fermi level is the result of electron accumulation at the photoanode during the illumination

Role of Metal Nanoclusters in Boosting the V_{oc} of DSSCs

• Au_x-GSH NCs play a dual role in improving the overall performance of DSSCs: (i) as a photosensitizer and (ii) as a voltage booster.

• These metal clusters are highly photoactive with excited-state lifetimes as high as 780 ns, they are quite effective in injecting electrons into TiO2 and deliver a photoconversion efficiency of 2% in a DSSC.



Schematic Illustration of the Increase in Quasi-Fermi Level of TiO_2 after Illumination Using (A) SQ Dye and (B) SQ Dye and Aux-GSH as Photosensitizer(s)[a]

Conclusion

• This study highlight the unique role of metal NCs as photosensitizers in light energy conversion Devices.

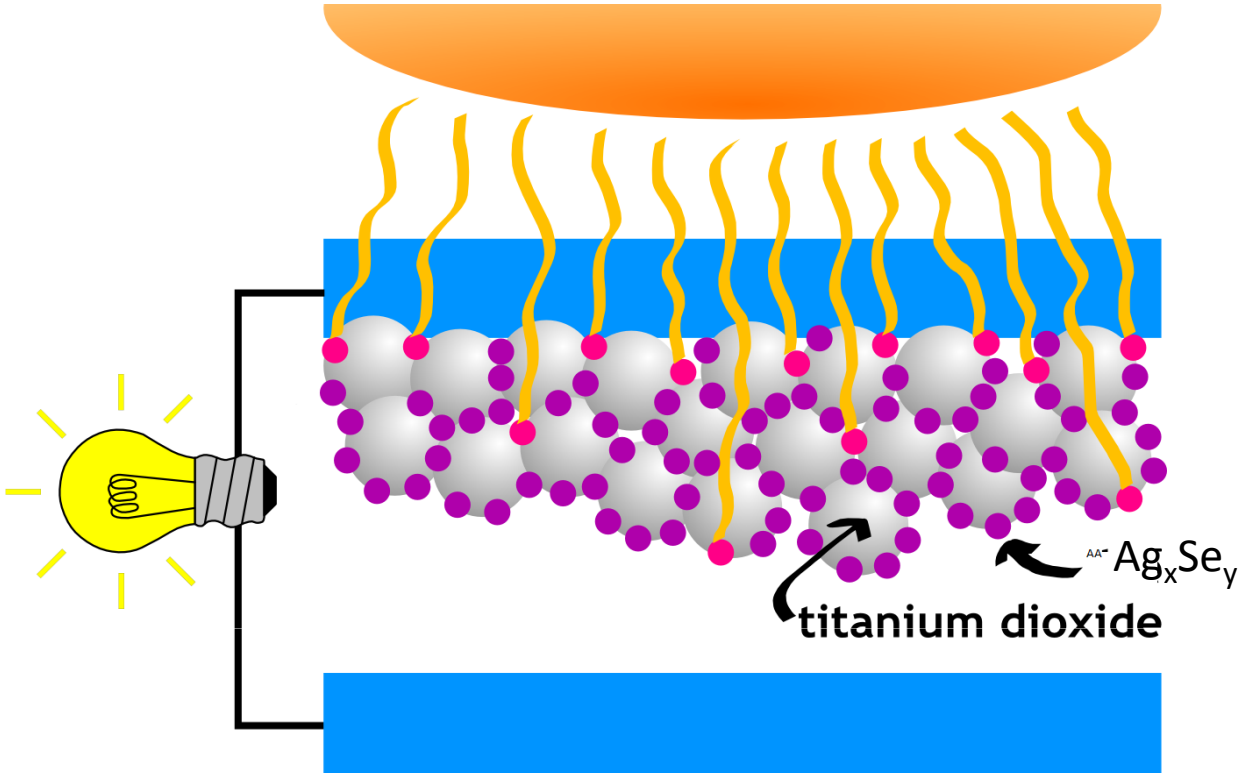
• The presence of Au_x-GSH NCs as a cosensitizer increases the power conversion efficiency of squaraine dye-sensitized solar cell from 2.4 to 4% under AM 1.5G illumination.

• The unique charge-storage properties of metal NCs plays a major role in attaining higher photovoltage in DSSCs

• The high open-circuit voltage (0.90 V) observed in this system results from the quantized charging of the Au_x-GSH NCs.

• Optimizing the loading of Au_x-GSH NCs and SQ dye in the photoanode could further lead to tunable photovoltage and photocurrent output of a DSSC.

Thank You



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