

## Photovoltaic Performance Enhancement in Plasmonic Quantum Dot Solar Cells.

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Solar energy, limited by high production costs and low conversion efficiencies, represents only a fraction of global energy generation. Since the 1970s, semiconductor liquid junction solar cells have been proposed as an alternative to expensive solid state photovoltaics; however, the challenge remains to boost liquid junction cell efficiencies to levels comparable to their silicon counterparts. Semiconductor quantum dots (QDs) have unique light harvesting properties, including tunable light absorption, that make them excellent candidates as sensitizers in third generation photovoltaic devices. Despite these favorable characteristics, several issues currently hinder QD solar cell (QDSC) conversion efficiencies: (1) inadequate optical absorption at wavelengths near the band edge transition; (2) high levels of electron-hole recombination within the quantized nanocrystals; and (3) low open circuit potentials.

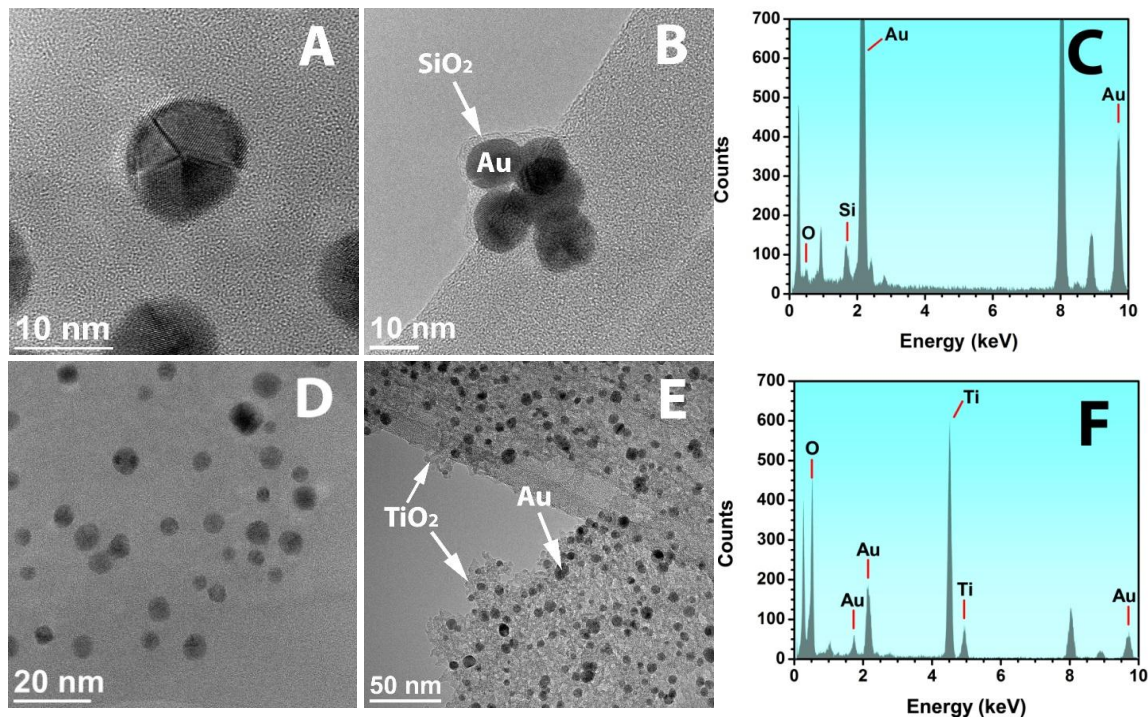
Gold nanoparticles are ideally suited to address current limitations in QDSCs due to their ability to support electron storage and collective electron oscillations known as localized surface plasmons. While gold particles have recently been used to improve the performance of dye sensitized photovoltaics [1], this is the first study to examine these effects in QDSCs. Plasmonic metal particles are thought to influence photovoltaic performance in two ways: (1) enhanced light absorption and charge separation through near-field plasmonic interactions [2] and (2) improved open circuit potential due to charge storage and equilibration between gold and components in the photoanode [3]. To isolate these effects, two different gold-metal oxide (Au-MO<sub>2</sub>) core-shell particles were synthesized. Silica (SiO<sub>2</sub>) served to insulate the gold core, while titania (TiO<sub>2</sub>) facilitated electronic interactions.

For the production of Au-SiO<sub>2</sub> particles, aqueous gold nanoparticles were first synthesized by the sodium citrate reduction method. The gold particles were then functionalized with 3-aminopropyl trimethoxysilane followed by addition of sodium silicate and slow polymerization of the SiO<sub>2</sub> shell. A novel approach was taken for the synthesis of Au-TiO<sub>2</sub> core-shell particles. First, aqueous gold particles stabilized by the TiO<sub>2</sub> precursor titanium bis(ammonium lactato)dihydroxide (TALH) and reduced by sodium borohydride were prepared. The solution was then heated slowly to 70 °C where TALH hydrolyzes to form TiO<sub>2</sub>. This resulted in 5–10 nm Au particles suspended in a matrix of amorphous TiO<sub>2</sub>. Particles were characterized by transmission electron microscopy and energy dispersive X-ray spectroscopy (EDS). Core-shell particles were then incorporated at low concentrations (<1 wt%) into working electrodes of QDSCs sensitized with CdSe for photovoltaic characterization. Improvement in conversion efficiency was achieved for QDSCs incorporating both Au-TiO<sub>2</sub> ( $\eta_{\text{Au-TiO}_2}$  = 5.0%) and Au-SiO<sub>2</sub> ( $\eta_{\text{Au-SiO}_2}$  = 5.7%) particles compared to the highest efficiency reference cell containing no

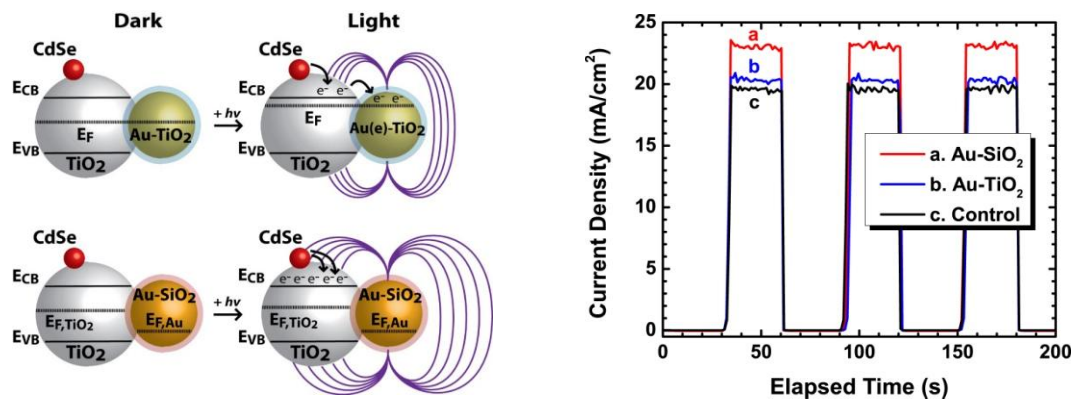
plasmonic particles ( $\eta_{\text{ref}} = 4.9\%$ ). The plasmonic effect of Au-SiO<sub>2</sub> particles resulted in a nearly 15% increase in efficiency over reference cells, constituting a record efficiency for CdSe QDSCs.

#### References:

- [1] Choi, H. *et al*, ACS Nano **6** (2012), p. 4418  
 [2] Brown, M. D. *et al*, Nano Letters **11** (2011), p. 438  
 [3] Thimsen, E. *et al*, Nano Letters **11** (2011), p. 35



**Figure 1.** Bright field TEM images of (A) gold particles stabilized by sodium citrate, (B) Au-SiO<sub>2</sub> core-shell particles, (D) gold particles stabilized by TALH, and (E) Au-TiO<sub>2</sub> particles. EDS spectra of (C) Au-SiO<sub>2</sub> and (F) Au-TiO<sub>2</sub>.



**Figure 2.** Schematic demonstrating electronic and plasmonic interactions between Au-MO<sub>2</sub> core-shell particles and components in QDSC photoanodes (left). Photocurrent response as a function of time for the best performing reference and plasmonic CdSe QDSCs (right).