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Hybrid Semiconductor-Metal Nanorods as Photocatalysts

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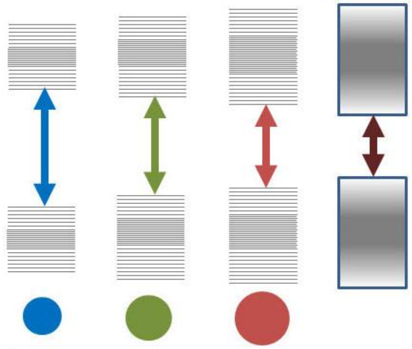
Institute of Chemistry
& the Center for Nanoscience and Nanotechnology
The Hebrew University of Jerusalem
Jerusalem, Israel

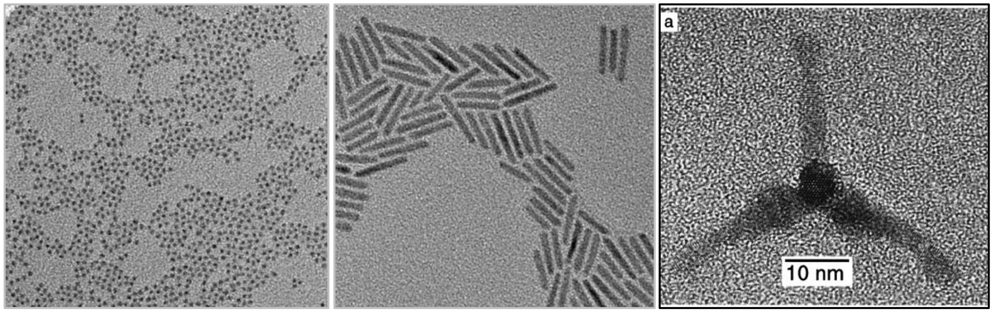
21st Sede Boqer Symposium on Solar Electricity Production
8 March 2018

Manipulating NCs Electronic Structure

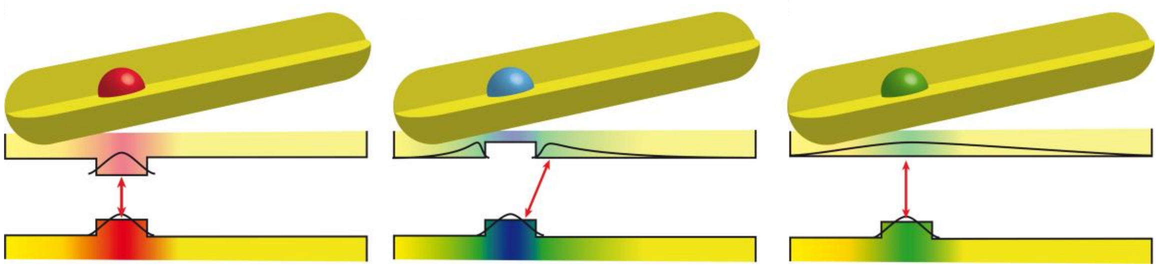
- Size



- Shape



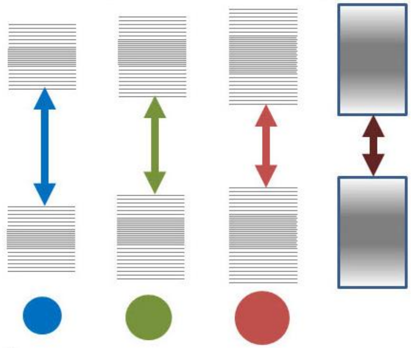
- Composition



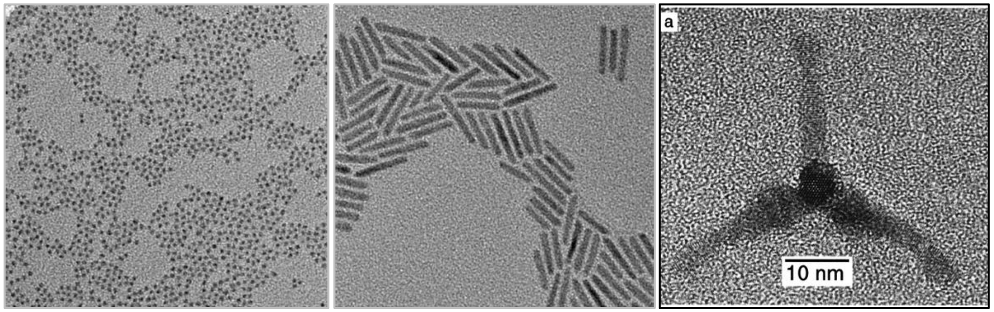
Sitt A., Hadar I. and Banin U.,Nano Today, 8, 494-513, (2013)

Manipulating NCs Electronic Structure

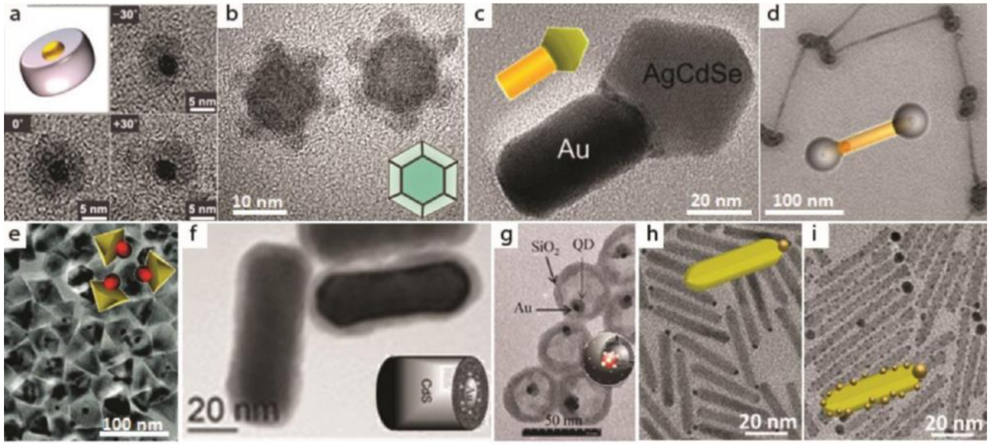
- Size



- Shape



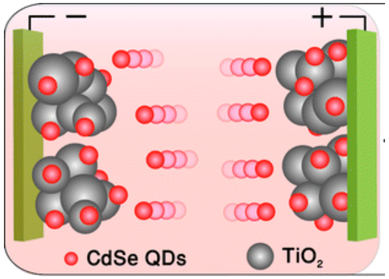
- Composition



Banin U., **Ben-Shahar Y.** and Vinokurov K. , *Chemistry of Materials*, 26(1), 97-110, (2014)
Ben-Shahar Y. and Banin U. ,*Top Curr Chem.* , 374:54, (2016)

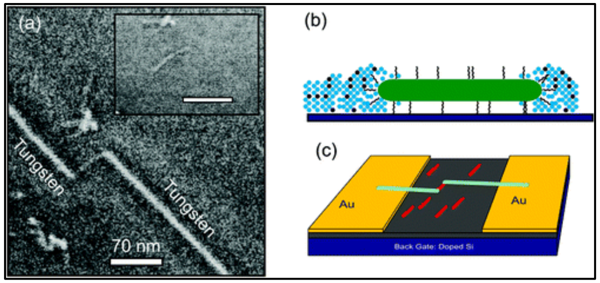
Semiconductor & Hybrid Nanocrystals Research Towards Applications

Solar Cells



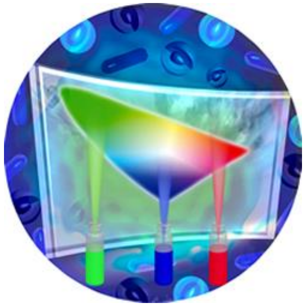
Salant A. et al. *Nano Lett*. 2012

Electronics



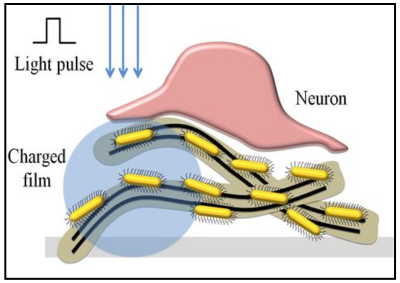
Steinberg, H. et al. *Nano Lett*. 2009

Displays



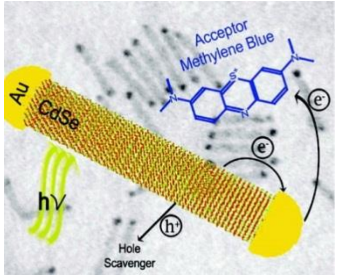
Panfil Y.E. et al. Angew. Chem. 2018

Biological Activations



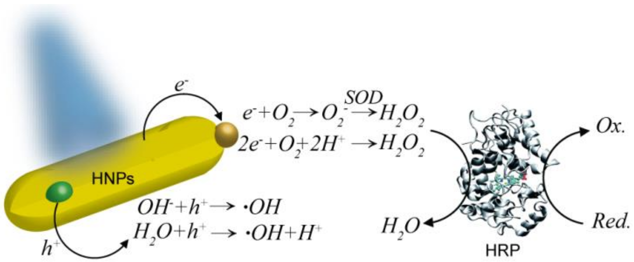
Waiskopf N. et al. *Nano Lett*. 2014

Dye Reduction



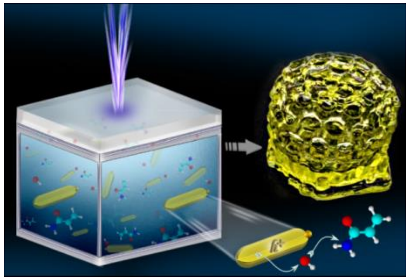
Costi R. et al. *Nano Lett.* 2008

Light-Induced Biological Modulation



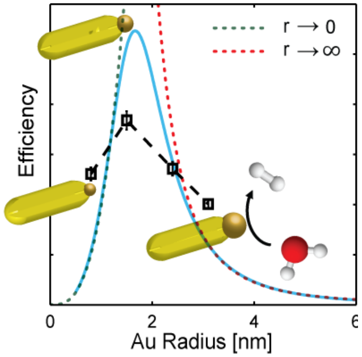
Ben-Shahar Y. et al. *Nano Lett.* 2016

Photo-polymerization



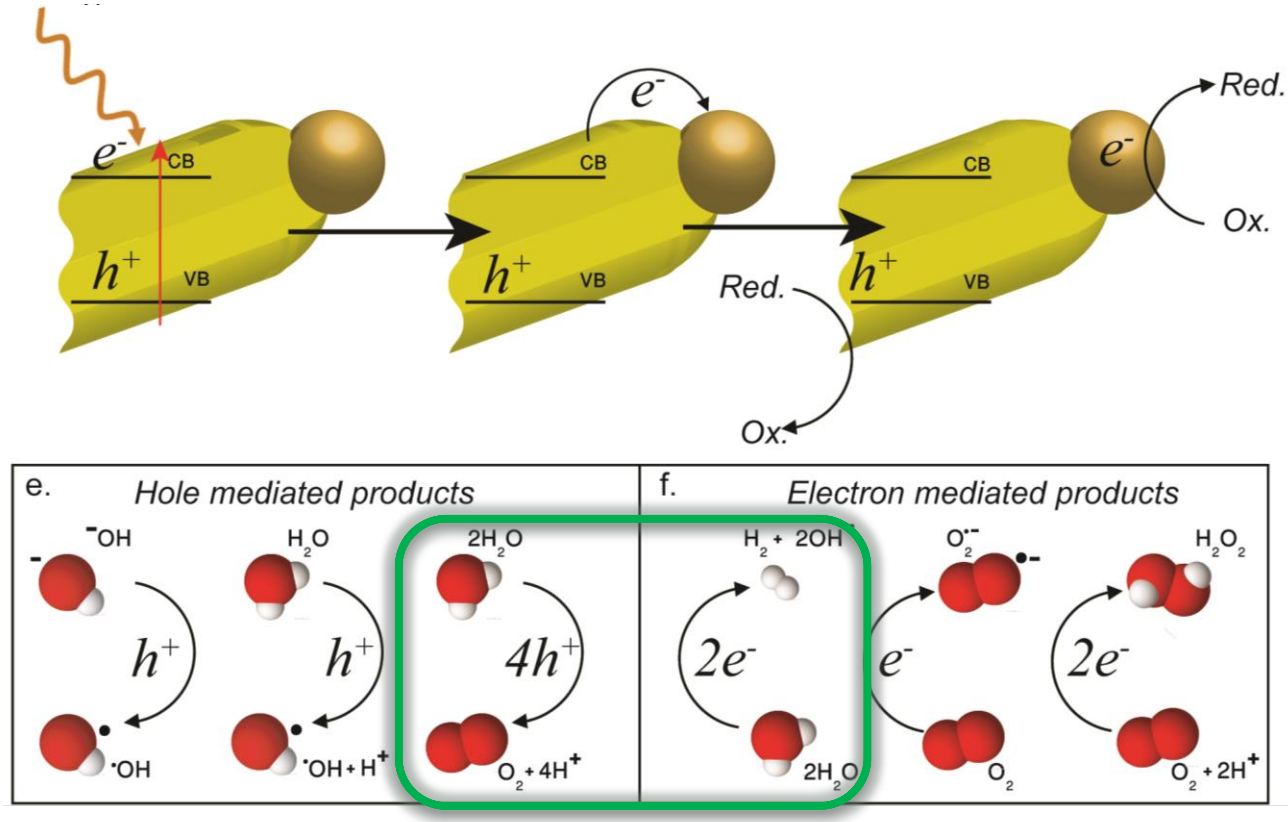
Pawar A.A., H.S., W.N., **Ben-Shahar Y.** et al. Nano Lett. 2017

Photocatalysis



Ben-Shahar Y. et al. *Nat. Commun.* 2016

Photocatalysis by HNPs

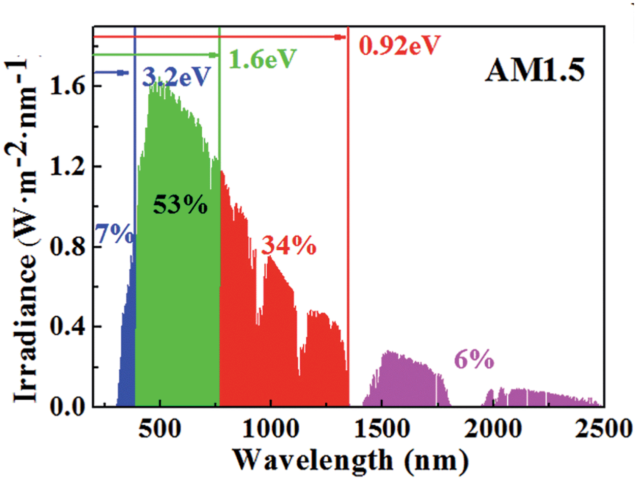


Ben-Shahar Y., Waiskopf N., Banin, U. (2018), *Advanced Materials* , in press

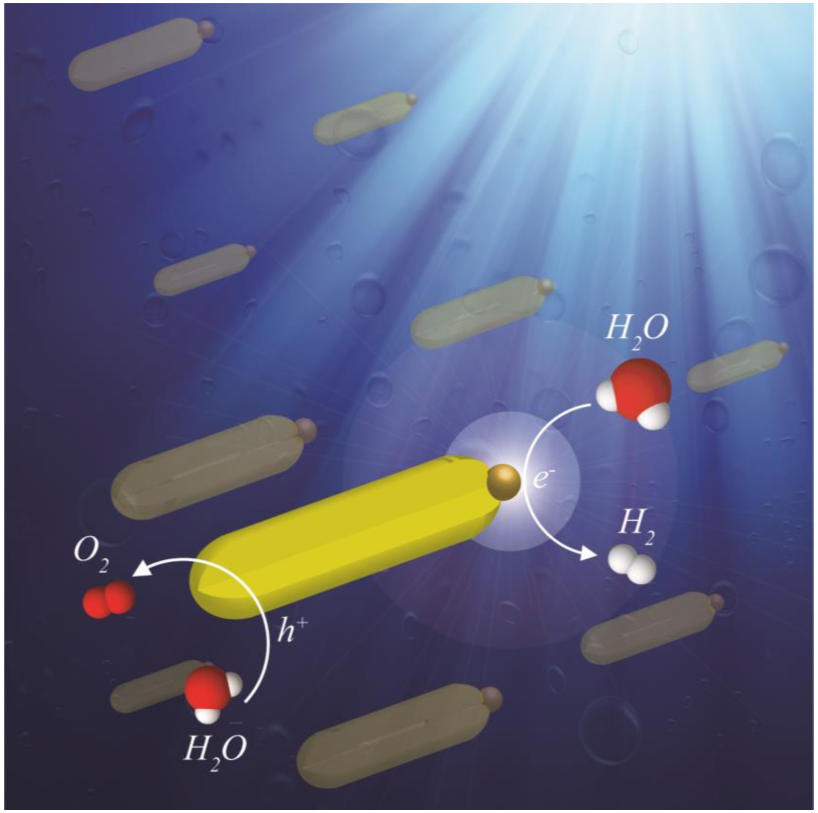
Photocatalytic Water Splitting – Renewable Energy Source towards Hydrogen Production

Solar energy harvesting in the form of chemical energy stored in a hydrogen fuel:

- Synthetic and non-toxic.
- Produced from renewable energy sources.

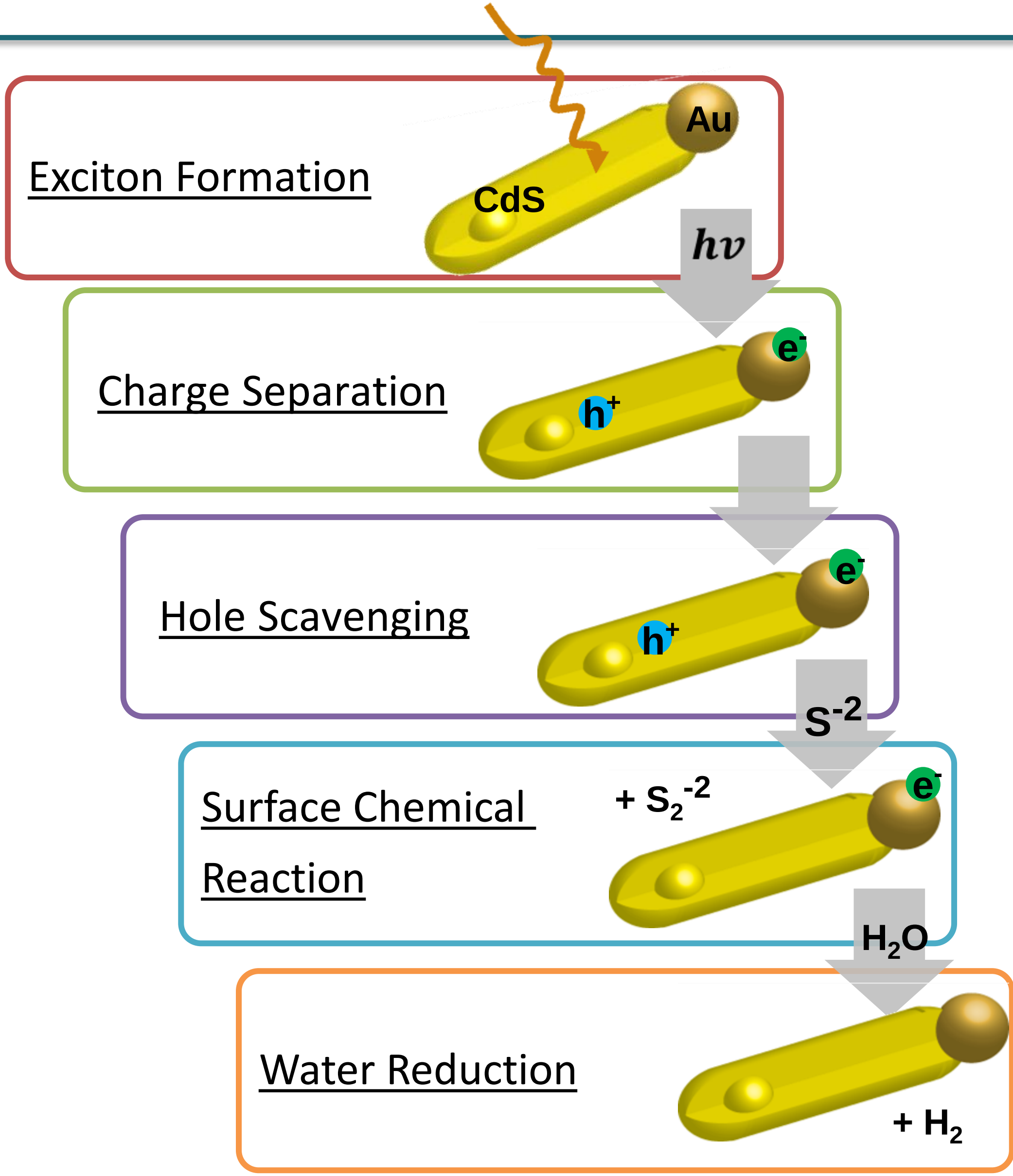


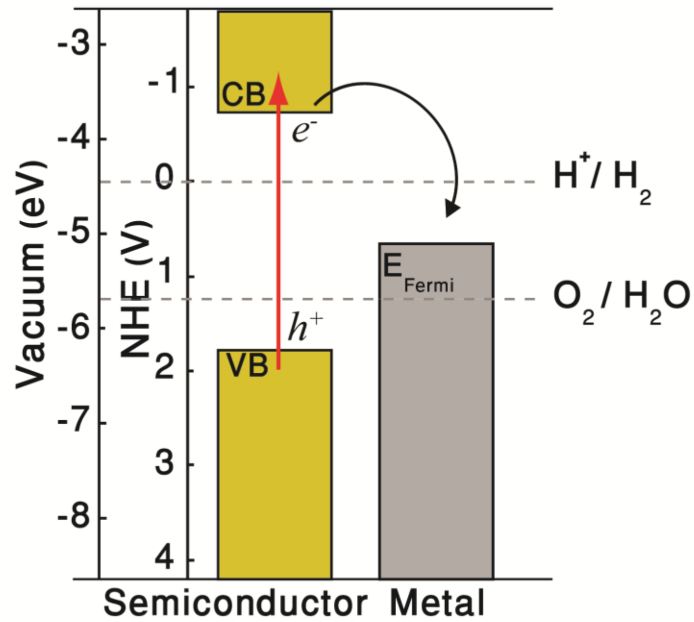
Z. Wu et al, J. Mater. Chem. A, 2, 14571–14576, (2014)



- Compatible for most applications where fossil fuels are used.

Photocatalytic Hydrogen Production



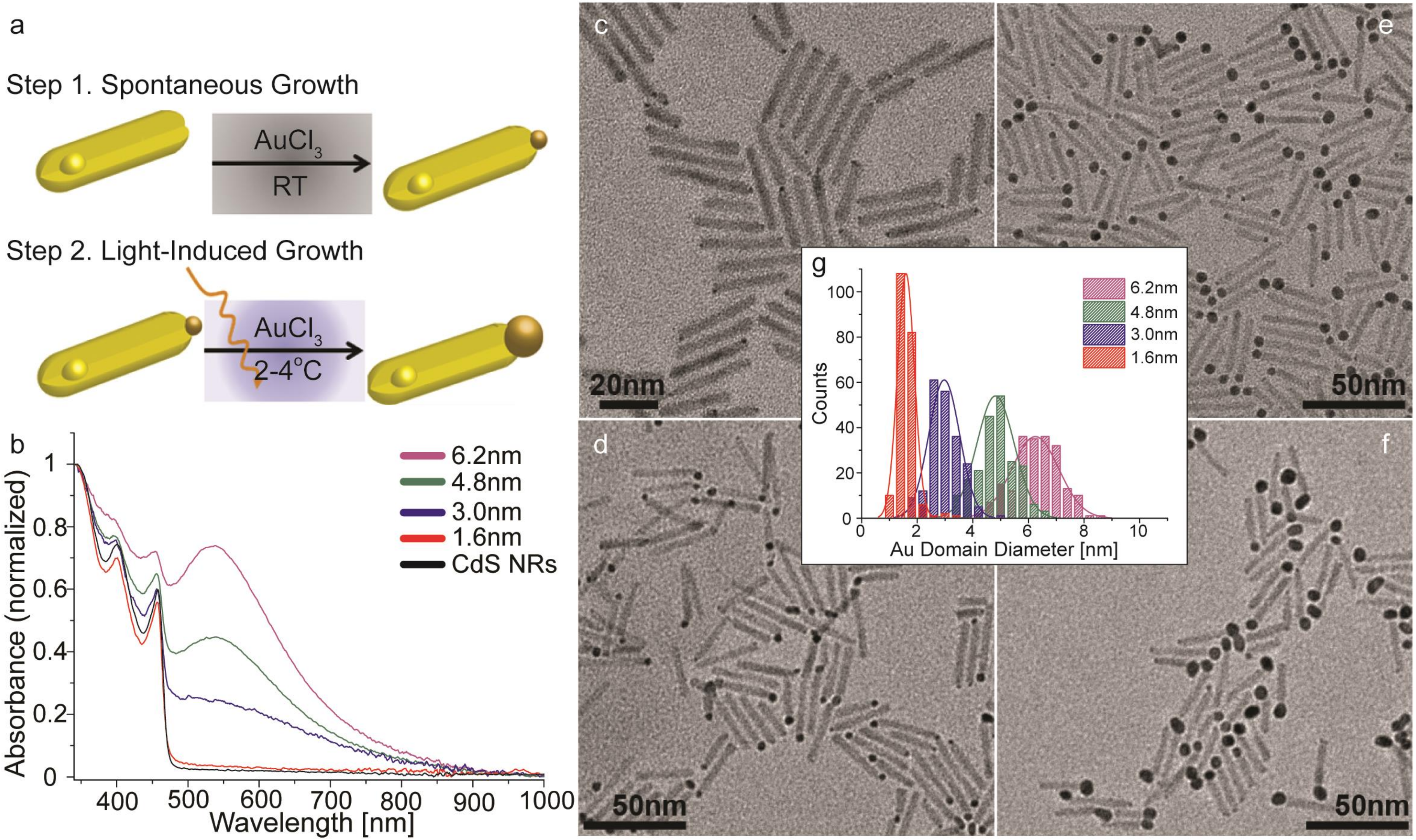


Reduction: $4H_2O_{(l)} + 4e^- \rightarrow 2H_{2(g)} + 4OH^-{}_{(aq)}$

Oxidation: $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+ + 4e^-$

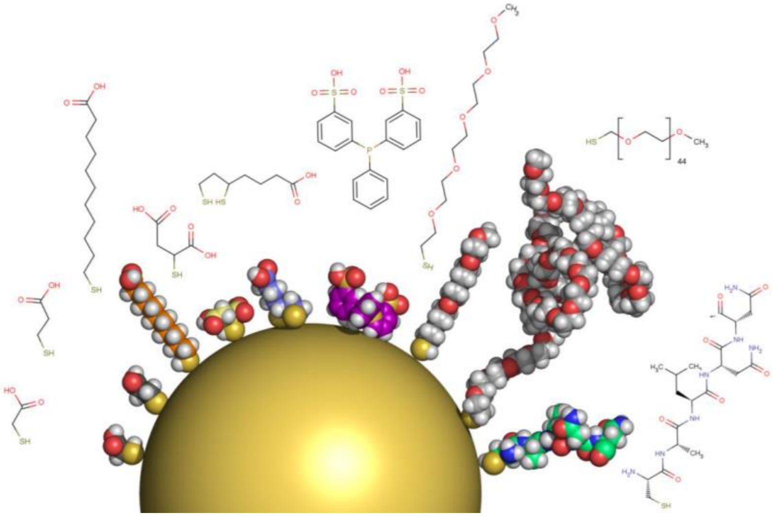
Total Reaction: $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$

CdS-Au Hybrid Size Controlled Synthesis

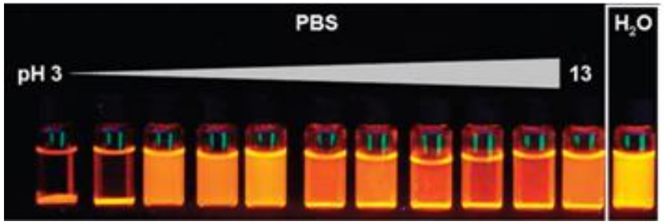


Ben-Shahar Y. et al. *Nat. Commun.*, **7** , 10416, (2016)

Surface Coating Effects

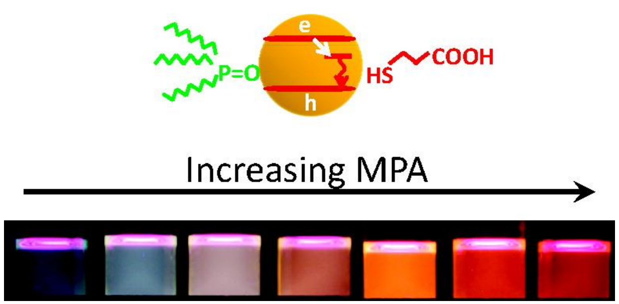


Provide Electro-Steric Stability



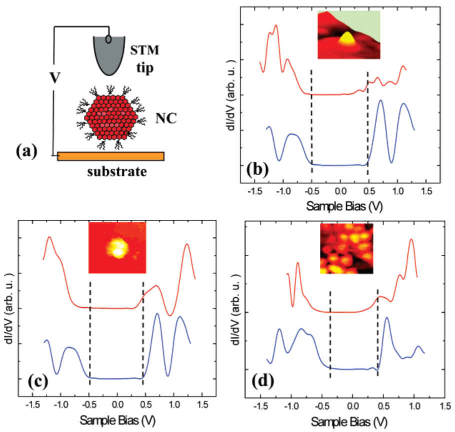
Lees E. E. et al. *ACS Nano*, 2009, *3* (5), 1121–1128

Tuning the Emission of CdSe QDs by Controlled Trap Enhancement



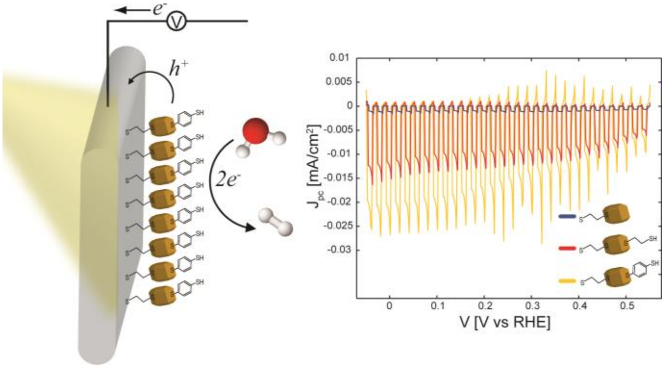
Kamat P. V. et al. *Langmuir* 2010, 26, 11272-11276

Tuning Energetic Levels in Nanocrystals QDs through Surface Manipulations



Tessler N. et al. *Nano Lett.*, 2008, 8(2), 678-684

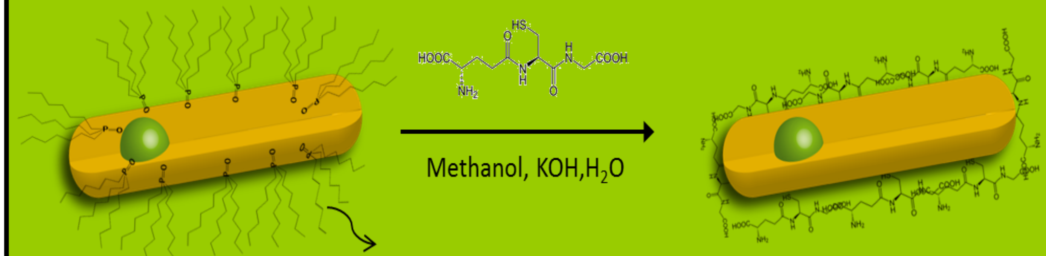
Effecting Photocurrents of Nanocrystals QDs-Based Photocathode



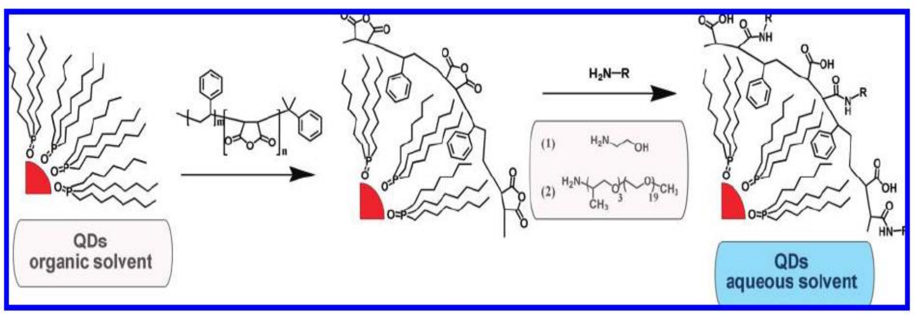
Ben-Shahar Y. et al. *J. Mater. Chem. A*, 2017, 5, 22255-22264.

Phase Transfer

L-Glutathione

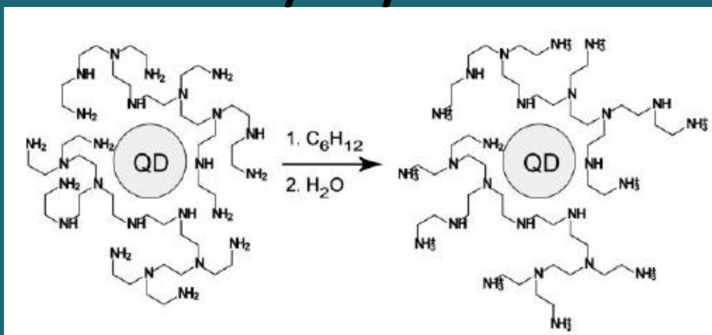


PSMA - Poly(styrene-co-maleic anhydride)



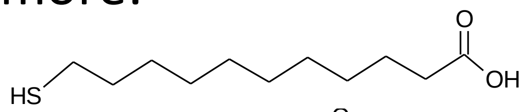
Lees E. E. et al., *ACS Nano*,2009, 3, 1121–1128

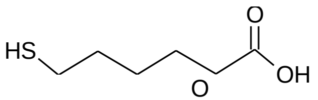
PEI - Polyethylenimine

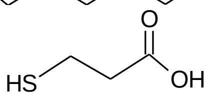


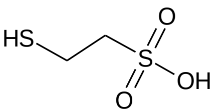
Nann, T. *Chem. Commun.*, 2005, 1735–1736

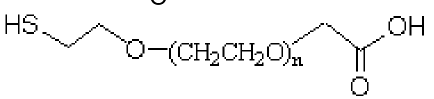
And more:

MUA 

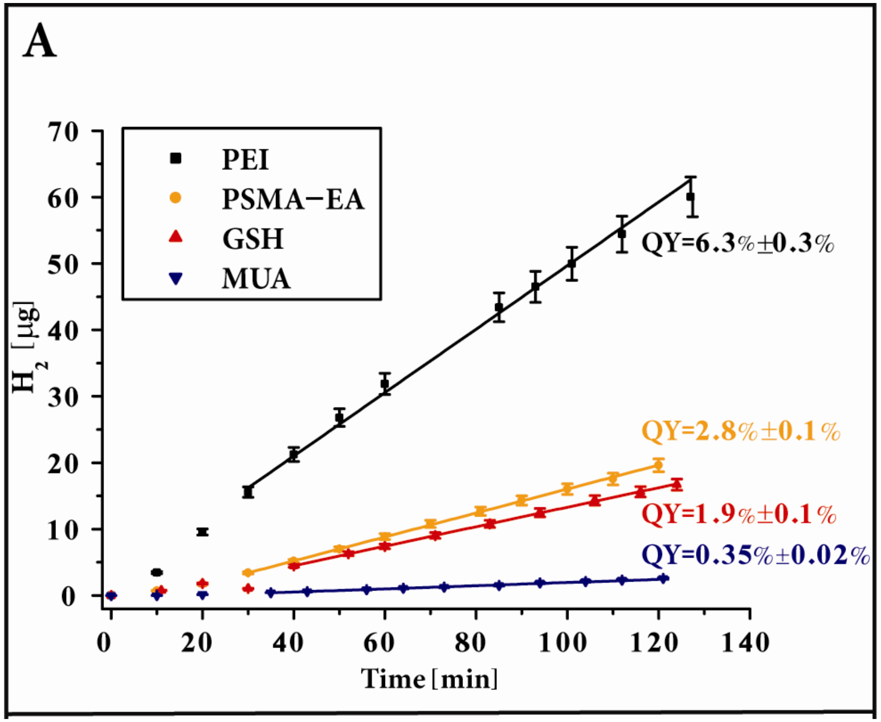
MHA 

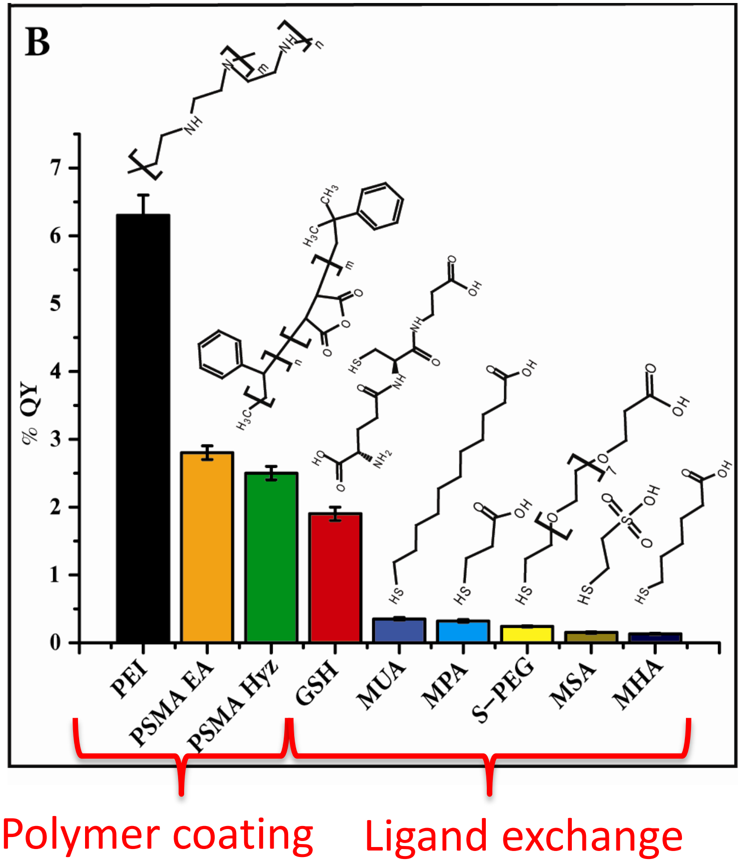
MPA 

MSA 

PEG 

Surface Coating Effect on Photocatalytic Hydrogen Production





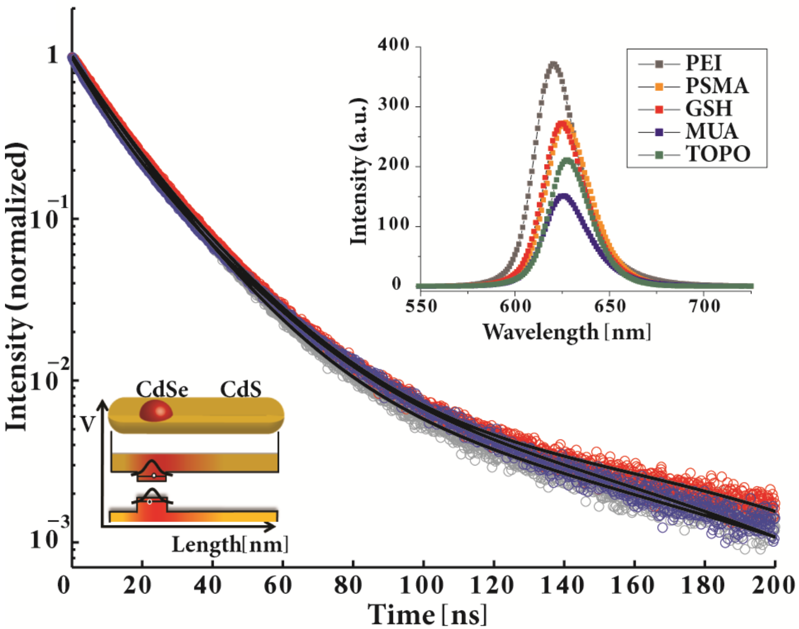
Apparent Quantum Yield

$$\%QY = \frac{n_e}{n_p} * 100\% = \frac{2n_{H_2}}{n_p} * 100\%$$

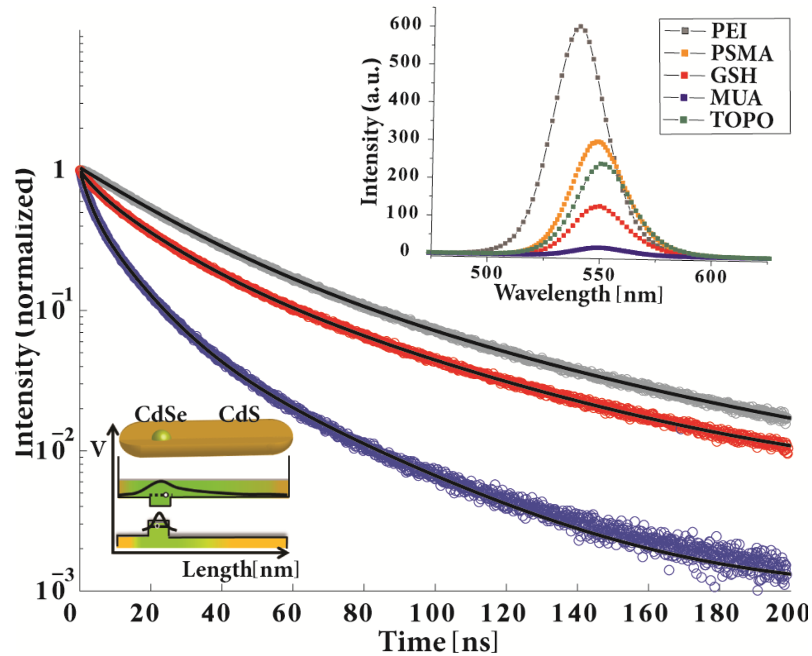
Ben-Shahar Y. et al. *Small,* 11 (4), 462-471, (2015).

Surface Coating Effect on PL and Lifetime of CdSe@CdS Nanorods

Type I



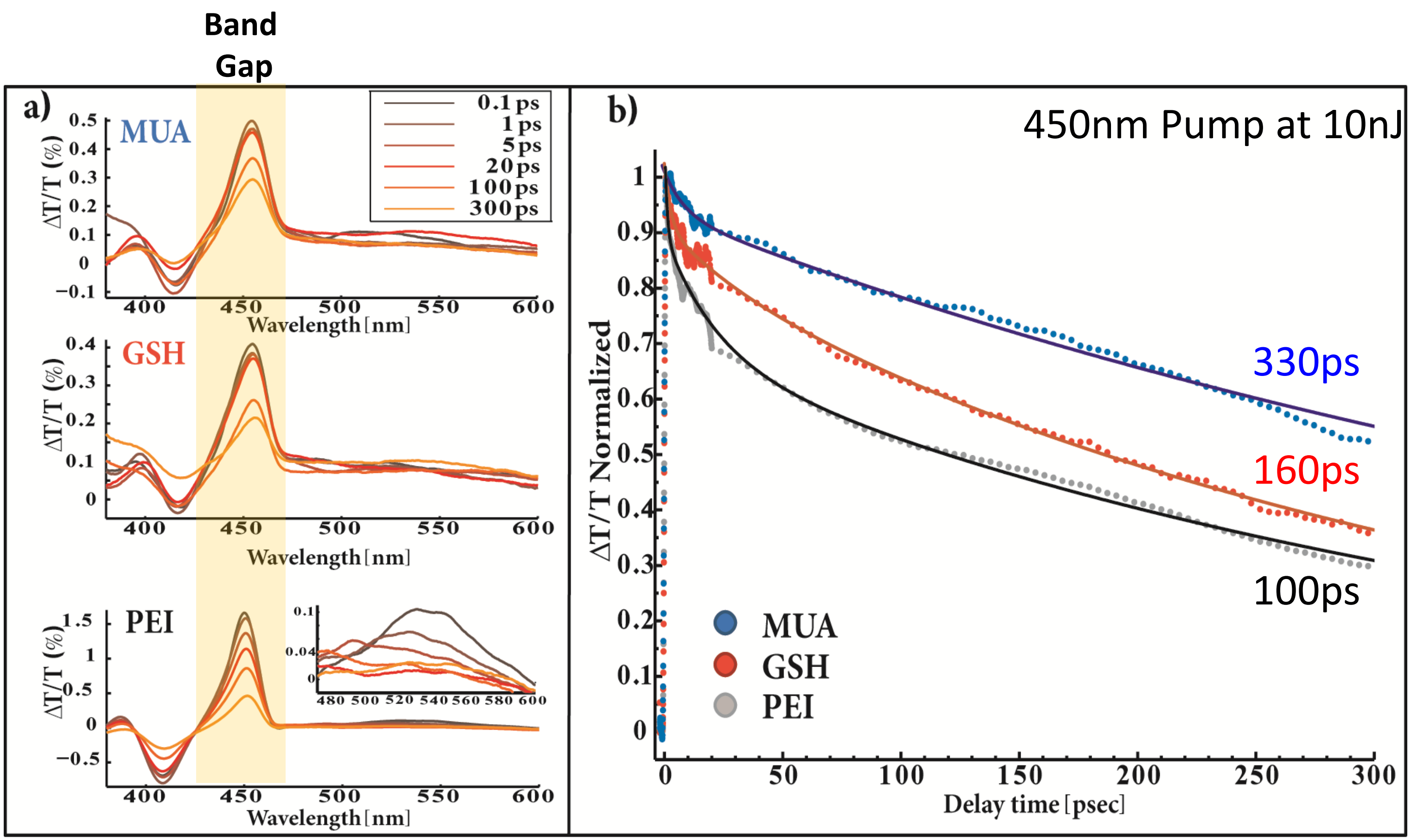
Quasi Type II



$\tau_{1/e}$	PEI [ns]	GSH [ns]	MUA [ns]
Type I	14	12	12
Quasi Type II	31	19	7

Ben-Shahar Y. et al. *Small,* 11 (4), 462-471, (2015).

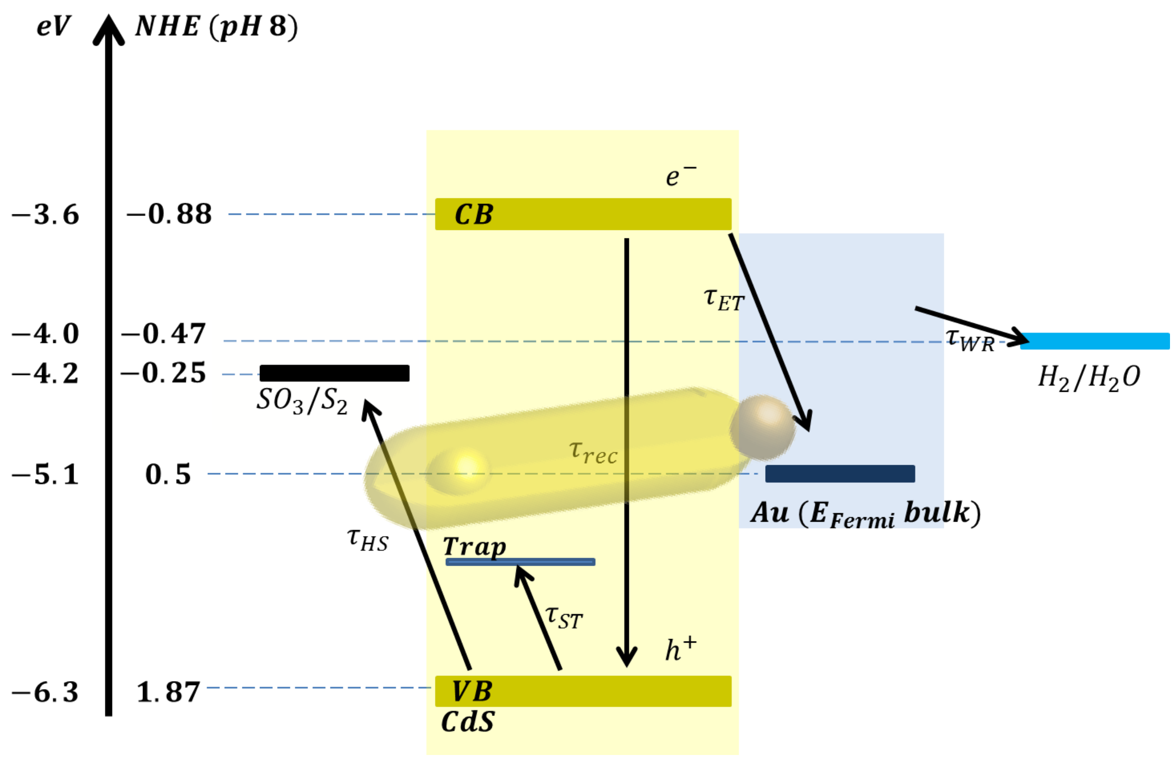
CdS-Au HNPs– Charge Transfer Dynamics



Fastest charge transfer dynamics is seen in the case of the PEI coated HNPs, slower with GSH, and the slowest with MUA passivated HNPs

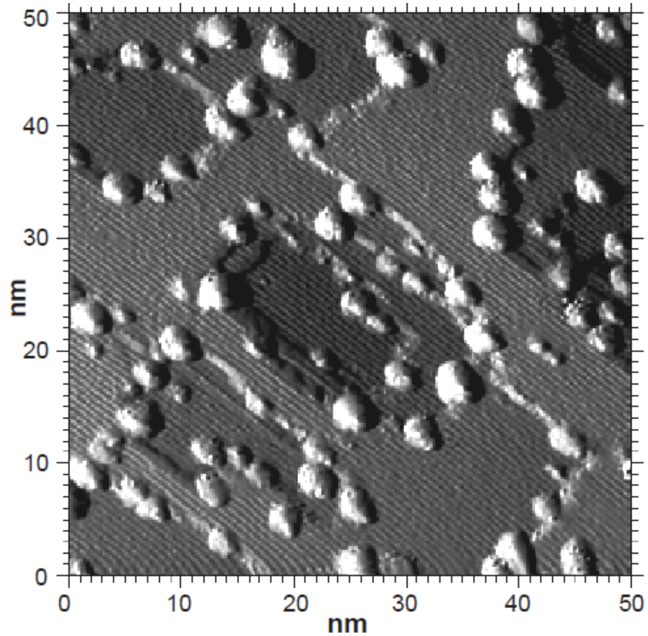
Ben-Shahar Y. et al. *Small,* 11 (4), 462-471, (2015).

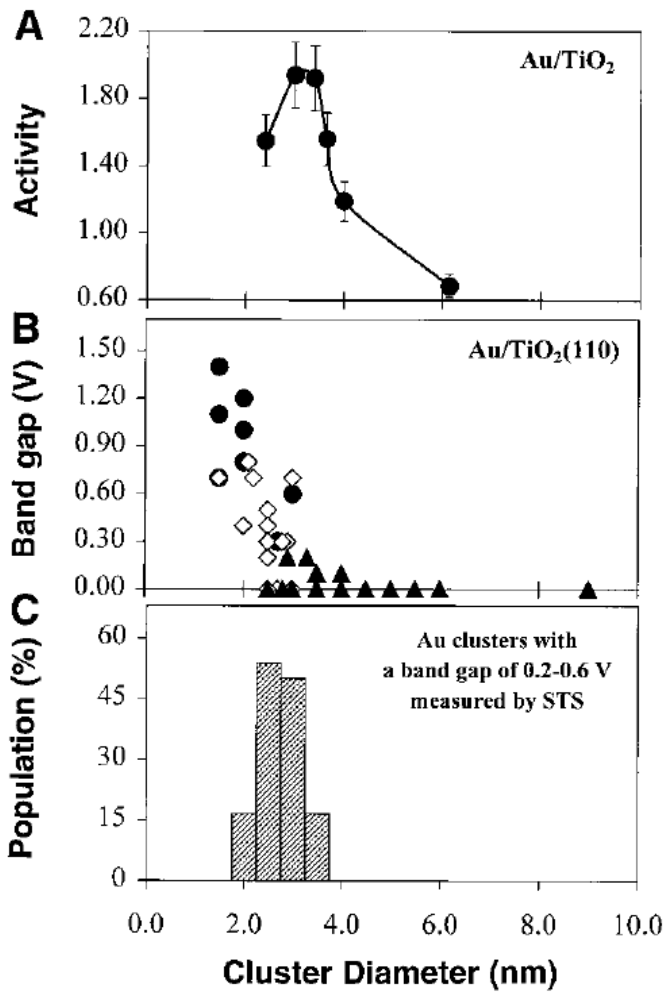
Mechanism – Energy Band Alignment



Improved surface passivation of the particle surface, leads to decrease in the available hole trapping sites. Trapping of holes leads also to slower electron transfer due to the electron - trapped hole coulomb interactions. To avoid this loss route through surface trapping, surface defects must be passivated.

Metal Co-Catalyst Size Effect on Photocatalysis with Hybrid Nanoparticles

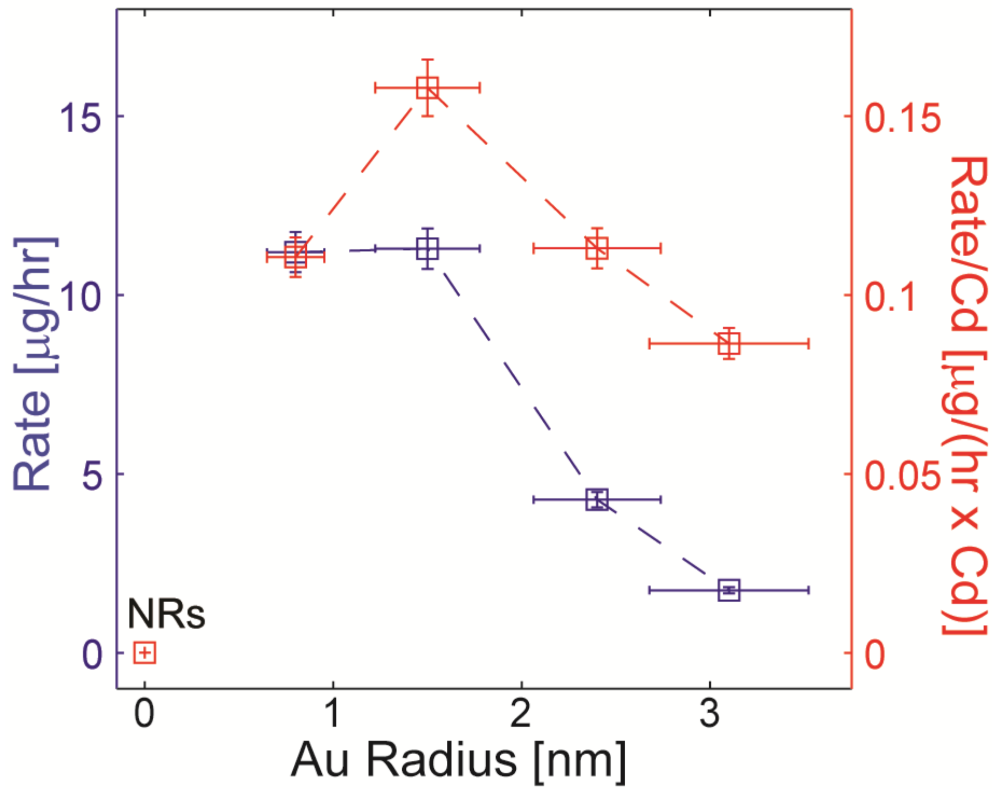




The size dependence of thermal catalysis on bare Au islands deposited on Titania, reveal sharp optimal catalytic performance for CO oxidation at island thickness of ~2 atomic layers corresponding to ~3nm. This is attributed to a metal to non-metal transition.

Valden, M., Lai, X. & Goodman, D.W. *Science* **281,** 1647-1650 (1998).

Metal Domain Size Effect on Photocatalytic Hydrogen Production
Actual vs. Normalized Production Rate

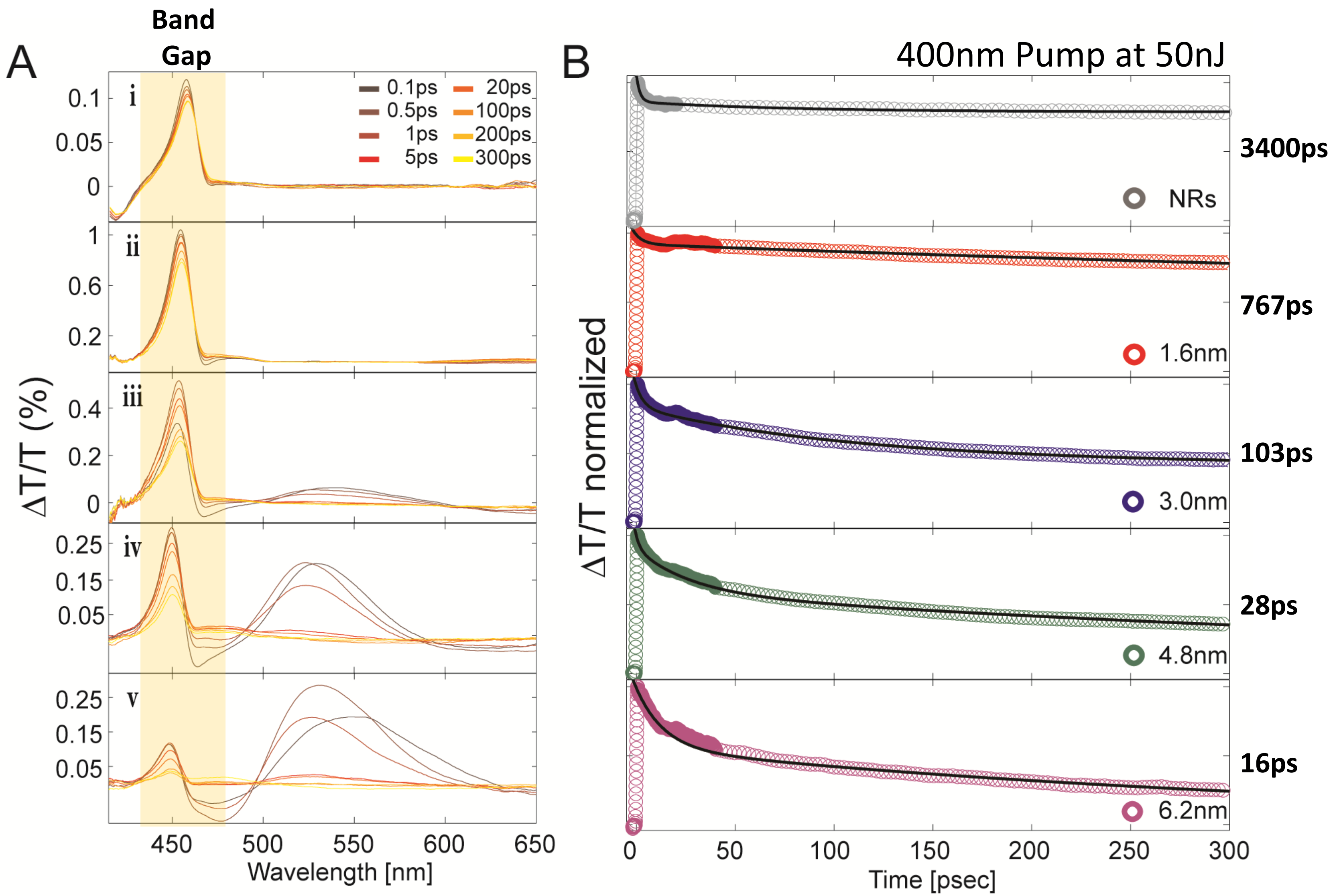


Cd^{+} ion concentrations of the different HNPs samples obtained by ICP-MS

	No Au	1.6nm	3.0nm	4.8nm	6.2nm
Avg. Cd [ppb]	196.9 (073%)	251.9 (1.21%)	177.9 (0.81%)	94.2 (1.18%)	50.4 (1.06%)

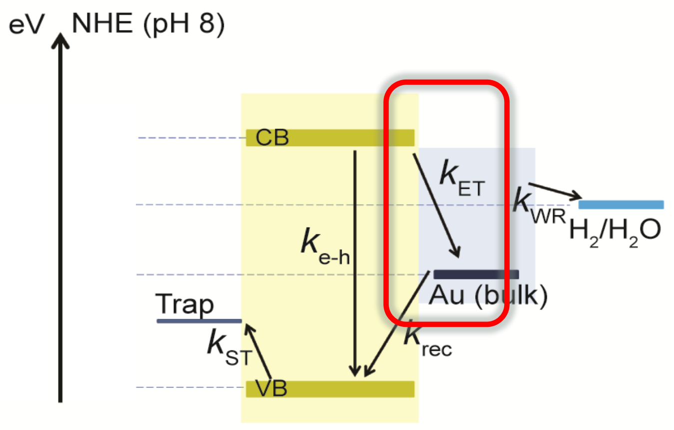
Ben-Shahar Y. *Nat. Commun.*, **7** , 10416, (2016)

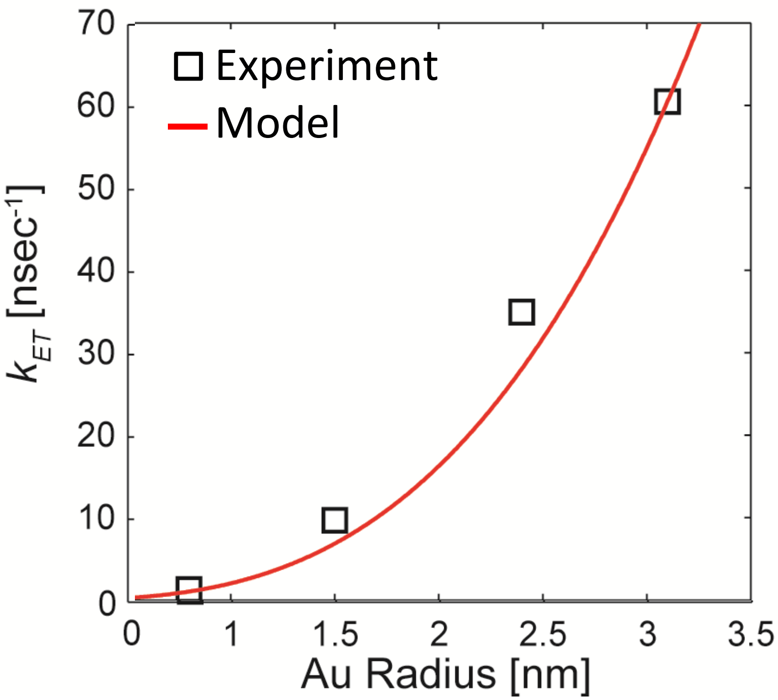
CdS-Au HNPs Different Metal Sizes– Charge Transfer Dynamics



Ben-Shahar Y. *Nat. Commun.*, **7** , 10416, (2016)

Charge Transfer Dynamics - Experimental vs. Model





Electron transfer dynamics –
Fermi Golden rule under consideration of the density of states of the metal

$$k_{ET} = \frac{4}{3\hbar} R^3 \left|t_{cf}\right|^2 \left(\frac{2m_e^*}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\varepsilon_c + \phi(R) + \varepsilon_F}$$

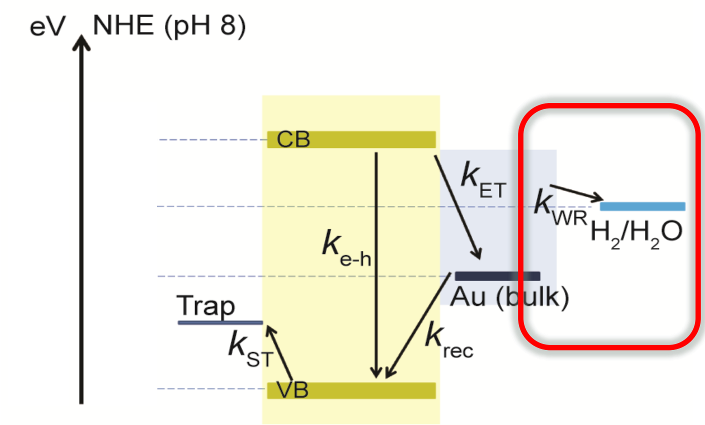
The work-function size dependency considered as:

$$\phi(R) = \phi_{bulk} - \frac{2\gamma v_M}{zFR}$$

Brus, L. E. et al, *Nano Lett.*, 2005, **5,** 131–135.

The electron charge transfer is strongly dependent on the density of states (R^3) and weakly on the work-function negative shifts due to decreased metal sizes ($\sqrt{\phi(R)}$).

Water Reduction – Electrochemical Kinetics

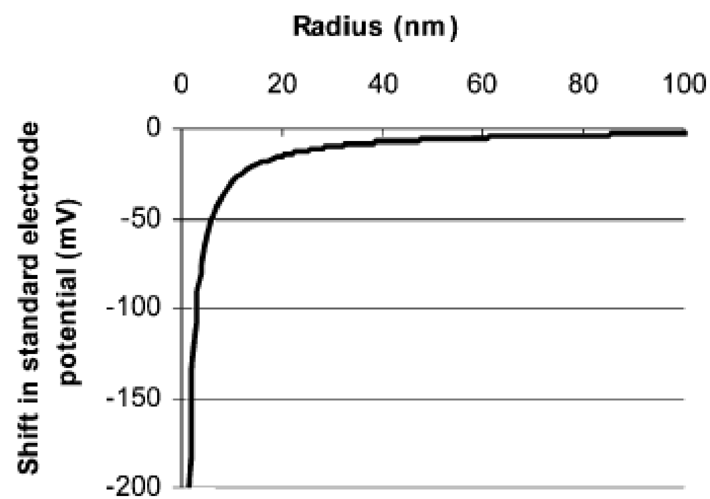


Water reduction surface reaction can be derived from the cathodic rate in the Butler-Volmer equation

$$k_{WR} = k_{WR}^{0} e^{-\frac{\alpha e F}{RT}(\phi(R) - \varepsilon_W)}$$

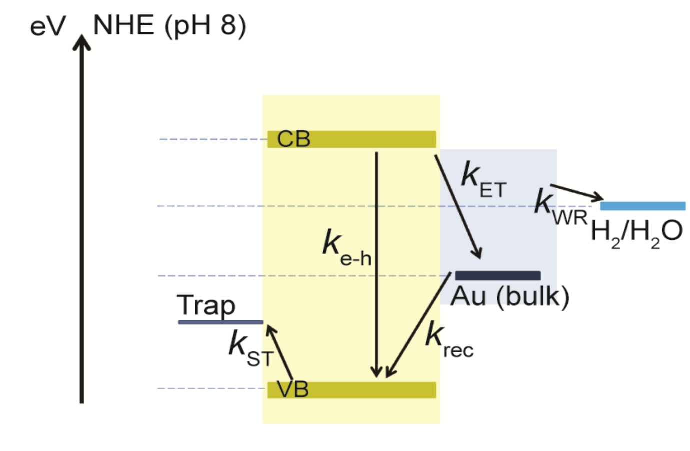
The anodic rate for the hydrogen oxidation (back reaction) can be neglected because the hydrogen concentration is small compared to the proton concentration.

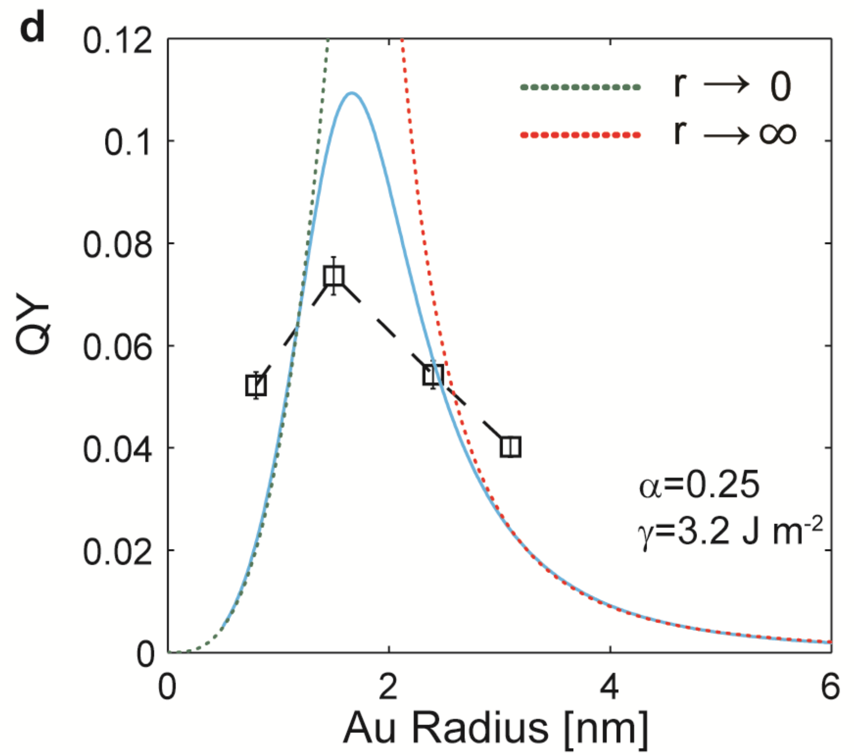
The reduction rate is strongly dependent on the work-function negative shifts due to decreased metal sizes.



Brus, L. E. et al, Nano Lett., 2005, 5, 131–135.

CdS-Au HNPs Size Effect– Combined Kinetic Model





The efficiency of this overall photocatalytic process is determent by the rate of the hydrogen generation H_2O/H_2 at infinite time.

$$QY_{H_2O/H_2}(t \to \infty) = \frac{k_{ET}k_{WR}}{(k_{WR}+k_{rec})-(k_{ET}+k_{ST}+k_{e-h})}$$

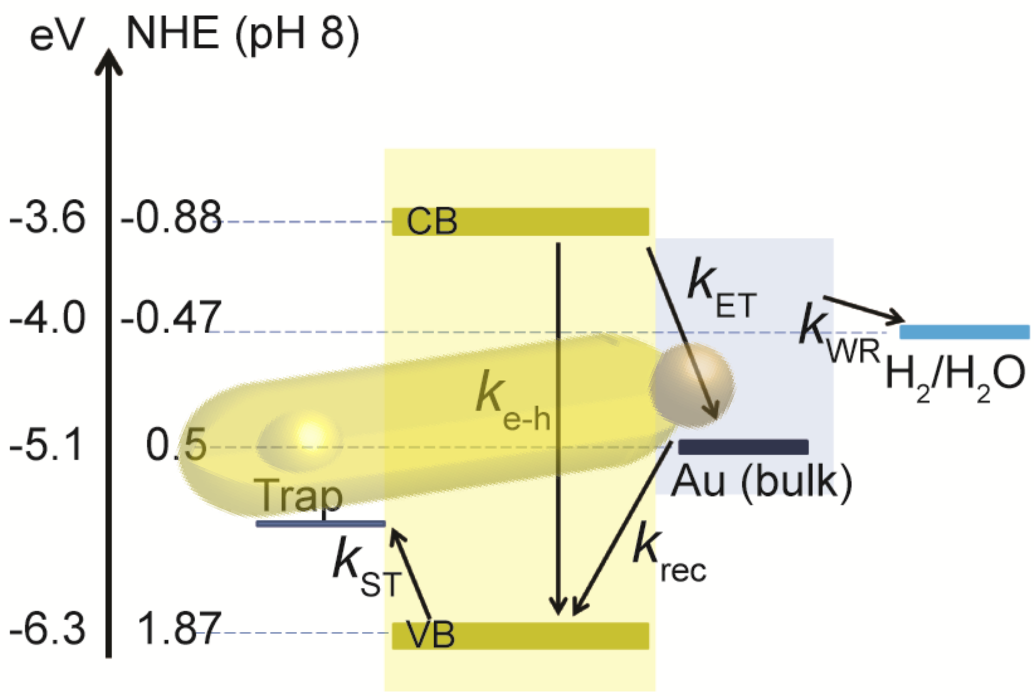
The behavior in 2 different Au tip size (*R*) limits:

$QY_{H_2O/H_2}(R \to 0) \sim \frac{k_{ET}}{k_{ST}} \ \alpha \ R^3$; $QY_{H_2O/H_2}(R \to \infty) \sim \frac{k_{WR}}{k_{rec}} \ \alpha \ \exp(R_0/R)$

Rate limited by electron transfer to Au ; *Rate limited by water reduction step*

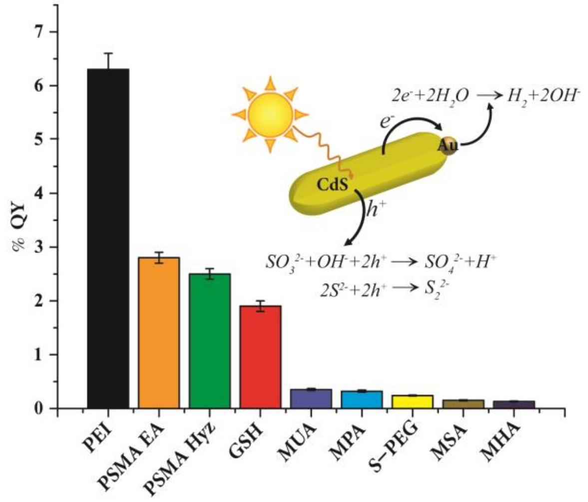
Y. Ben-Shahar et al. *Nat. Commun.*, **7** , 10416, (2016)

CdS-Au HNPs Size Effect– Kinetic Model; Energy Band Alignment

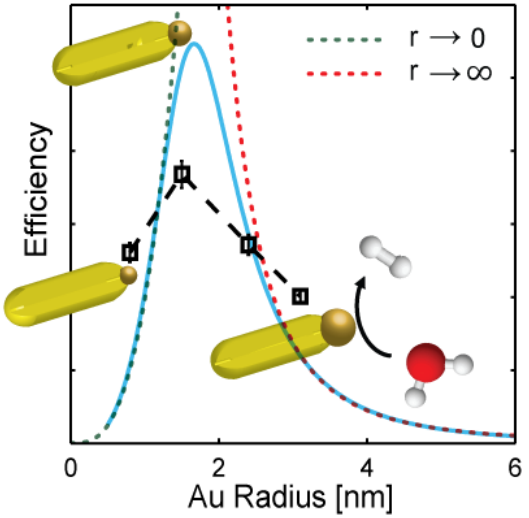


Non-monotonic behavior is seen due to competitive decay routes of the photo-excited electron, in the water reduction process.

Summary



Surface coating effect:
Polymer coating advantageous over thiolated alkyl-ligand exchange due to enhanced surface passivation.



Co-catalyst metal domain size effect:
Optimal metal domain size for efficient photocatalytic water reduction reaction, attributed to competing processes, charge transfer and catalytic reduction.

Acknowledgments

- **Prof. Uri Banin**
- Dr. Itzhak Shweky
- Dr. Nir Waiskopf
- All Banin lab members

POLIMI :
- Prof. Giulio Cerullo
- Prof. Francesco Scotongella

TAU/UC Berkeley:
- Prof. Eran Rabani

Funding:
Camber Scholarship
Ministry of Science and Technology, Israel
Laserlab EU