

Controlled Assembly of Hydrogenase-CdTe Nanocrystal Hybrids for Solar Hydrogen Production

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Supporting Information

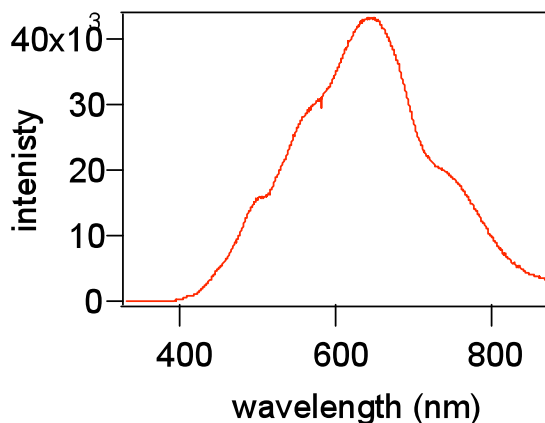


Figure S1. Emission spectrum of the white light illumination source.

Use of the Langmuir isotherm (and kinetic models)^{1, 2} is common for nanocrystals. It has been used for gold NC's and DNA in particular.³ Though the theory was originally derived for adsorption of gases to planar surfaces, its' use is not restricted to large surfaces, as the derivation concerns free surface cites, and the derivation does not include any assumptions about the relative number of surface sites vs. adsorbing molecules. The assumptions that are used in the derivation are:

1. Adsorption cannot proceed beyond a monolayer of coverage.
2. All surface sites are equivalent and can accommodate, at most, one adsorbed atom.
3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

The third assumption only holds for small gas phase molecules for which this equation was originally designed, but the equation is still considered useful for molecules in solution phase. This theory is preferable to protein-protein or protein-ligand models as they are designed to analyze transient adsorption complexes, rather than stable interactions.

Table S1. Fitted values for k_{OBS} and ΔI_{max} .

H ₂ ase (uM)	k_{OBS} (sec ⁻¹)	Error (95%)	ΔI_{max}	Error (95%)
3.74	0.00284	0.000087	314990	3350
2.80	0.00224	0.000058	296540	3130
1.87	0.00199	0.000053	229190	2730
0.75	0.00150	0.000051	192220	3430
0.38	0.00133	0.000047	132600	2630

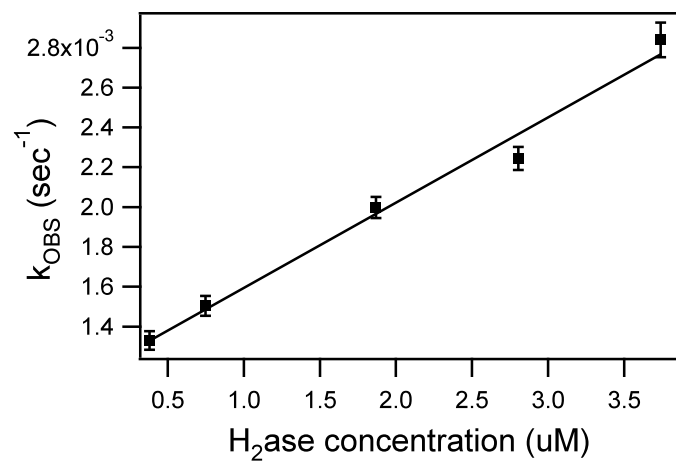


Figure S2. Plot of k_{OBS} vs. $\text{H}_2\text{ase concentration}$. Black line represents linear fit.

Derivation of eq. 8.

By definition

$$PLQE_{CdTe} = \frac{k_{RR}}{k_{RR} + k_{NR} + k_{ST}[T]}$$

Where [T] is the concentration of surface trap states in the nanocrystal.

For the samples containing inactive enzyme:

$$PLQE_{(I)} = \frac{k_{RR}}{k_{RR} + k_{NR} + k_{ST}[T']}$$

For the samples containing active enzyme

$$PLQE_{(A)} = \frac{k_{RR}}{k_{RR} + k_{NR} + k_{ST}[T'] + k_{ET}[H_2ase]}$$

Where [T'] is the concentration of trap states after adsorption of the H₂ase.

For a given detector/light source, PLQE \propto Emission Peak Area

So...

$$\frac{PLQE_{(I)}}{PLQE_{(A)}} = \frac{Area_{IA}}{Area_A} = \frac{k_{RR}(k_{RR} + k_{NR} + k_{ST}[T'] + k_{ET}[H_2ase])}{k_{RR}(k_{RR} + k_{NR} + k_{ST}[T'])}$$

$$\frac{Area_{(I)}}{Area_{(A)}} = \frac{k_{RR} + k_{NR} + k_{ST}[T']}{k_{RR} + k_{NR} + k_{ST}[T']} + \frac{k_{ET}[H_2ase]}{k_{RR} + k_{NR} + k_{ST}[T']}$$

$$\frac{Area_{(I)}}{Area_{(A)}} = 1 + \frac{k_{ET}[H_2ase]}{k_{RR} + k_{NR} + k_{ST}[T']}$$

Substituting:

$$k_{RR} + k_{NR} + k_{ST}[T'] = \frac{k_{RR}}{PLQE_{(I)}}$$

Gives the expression:

$$\frac{Area_{(I)}}{Area_{(A)}} = 1 + \frac{k_{ET}}{k_{RR}} * [H_2ase] * PLQE_{(I)}$$

$$\frac{k_{ET}}{k_{RR}} = \left(\frac{Area_{(I)}}{Area_{(A)}} - 1 \right) \frac{1}{[H_2ase] * PLQE_{(I)}}$$

However $PLQE_{(I)}$ is a function of H_2ase concentration:

$$PLQE_{(I)} = PLQE_{CdTe} * \frac{Area_{(I)}}{Area_{CdTe}} = PLQE_{H_2ase}$$

Where $PLQE_{H_2ase}$ is the PLQE of nc-CdTe- H_2ase for a specific $[H_2ase]$, and $PLQE_{CdTe}$ is the measured PLQE value of CdTe alone (17.5%).

This gives the final expression for eq. 8:

$$\frac{k_{ET}}{k_{RR}} = \left(\frac{Area_{(I)}}{Area_{(A)}} - 1 \right) \frac{1}{[H_2ase] * PLQE_{H_2ase}}$$

References:

1. Karpovich, D. S.; Blanchard, G. J., *Langmuir* **1994**, *10*, 3315-3322.
2. Langmuir, I., *J. Am. Chem. Soc.* **1918**, *40*, 1361.
3. Brown, K. A.; Park, S.; Hamad-Schifferli, K., *J. Phys. Chem. C* **2008**, *112*, 7517-7521.