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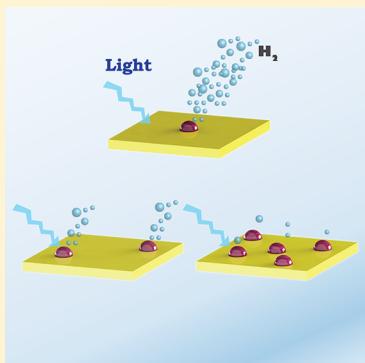
## Less Is More: The Case of Metal Cocatalysts

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### Supporting Information

**ABSTRACT:** We provide evidence that for a multielectron reaction such as hydrogen reduction, the photocatalyst design should include only a single cocatalytic site per each segment of the semiconductor capable of light excitation. This is to ensure that intermediates are formed at close proximity. These findings are demonstrated by evaluating the efficiency for hydrogen production over a nanoparticle-based photocatalyst consisting of Pt-decorated CdSe@CdS rods. Rods decorated with a single Pt catalyst were found to be the most active for hydrogen production, with QE of 27%, while rods having two reduction sites reached QE of only 18% and rods with multiple sites showed very low activity. The advantage of using a single catalytic site became negligible when the rods were employed in catalyzing a single electron reaction. We believe the implications of this finding are of significance for the proper design of photocatalysts aimed at solar-to-fuel energy conversion.



The solar-driven photocatalytic splitting of water into hydrogen and oxygen is a potential source of clean and renewable fuels;<sup>1,2</sup> however, four decades of global research have proven this multistep reaction to be highly challenging. Systems that are sufficiently stable and efficient for practical use have not yet been realized. Perhaps it can be attributed, in part, to the fact that this redox reaction involves the injection of multiple photoinduced charges.

Semiconductor photocatalysts are often loaded with metallic cocatalysts that both promote charge separation and act as an active site for hydrogen reduction.<sup>3,4</sup> These cocatalysts play an essential role in reactions such as water splitting, as they offer lower activation potentials for hydrogen evolution and greatly enhance the photocatalytic activity.

In light of the cocatalyst significance and motivated by cost reduction considerations (cocatalysts are typically noble metals), numerous efforts have been put into assessing the optimal metal cocatalyst quantity. This is mostly done by reporting performance per mass of the metal decorating the photocatalyst. However, this metric fails to decouple the number of metal sites and the average size of those sites.

Here we show that for a multi-electron reaction such as hydrogen reduction it is the number of cocatalytic sites per unit of light excitation (i.e., segment of the semiconductor that can absorb light and generate charge carriers) that requires optimization rather than the total mass of the cocatalyst.

The first step in hydrogen evolution is the bonding of hydrogen to the catalyst  $H^+ + e^- + * \rightarrow H^*$ , where  $*$  denotes a site on the surface able to bind to hydrogen. The second step is the release of molecular hydrogen through one of the two processes:  $2H^* \rightarrow H_2 + 2^*$  or  $H^+ + e^- + H^* \rightarrow H_2 + *$ .<sup>5,6</sup> Hence, the two electrons generated in the photocatalyst must be transferred to the same cocatalyst site, so that the two  $H^*$

will be formed at close proximity and will readily find each other.

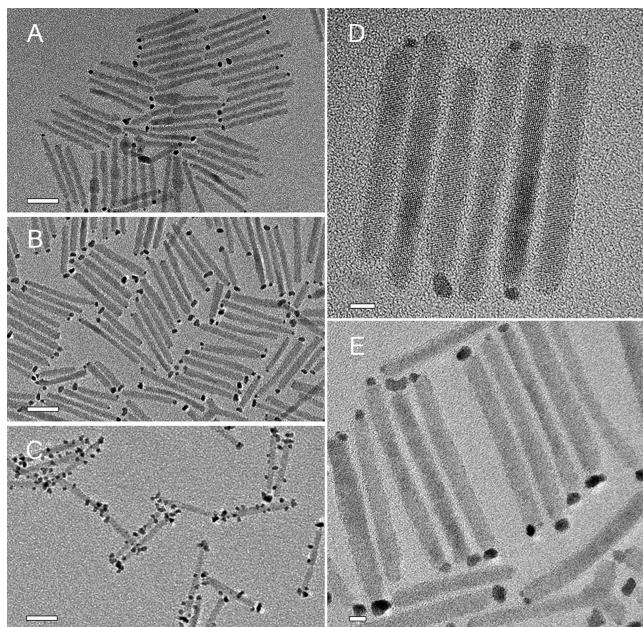
To test this hypothesis we employ a well-controlled nanoparticle-based artificial system for catalyzing the reduction half reaction.<sup>7</sup> The light absorption and excitation unit consists of a cadmium selenide (CdSe) quantum dot embedded asymmetrically within a cadmium sulfide (CdS) quantum rod.<sup>8–11</sup> This structure has been widely studied optically<sup>12–14</sup> and photocatalytically<sup>15–20</sup> and is well-characterized. Platinum (Pt) cocatalysts were grown onto CdS nanorods,<sup>21</sup> forming single (S–Pt), double (D–Pt), or multiple (M–Pt) reduction sites per photocatalyst, as can be seen in Figure 1. The Pt nanoparticle size ranges between 0.5 nm and up to 3 nm; hence we consider each Pt nanoparticle as a single site for hydrogen production.

We examined the activity of the Pt-decorated CdSe@CdS rods toward hydrogen production. A typical sample contained  $\sim 6 \times 10^{14}$ , 50 nm long rods, with 2.3 nm seed size. Solutions of rods suspended in water with IPA (10% by volume) acting as a hole scavenger were placed in a homemade gastight reaction cell purged with argon (at a controlled and variable flow rate). The samples were then illuminated with a 455 nm LED adjusted to 50 mW (i.e., with a photon flux of  $1.1 \times 10^{17}$  photons). The evolving hydrogen was analyzed using an online gas chromatograph equipped with a thermal conductivity detector. The apparent quantum efficiency of the sample, which is defined as  $QE = 2N_{H_2}/N_{hv}$ , was determined by quantifying the amount of evolved hydrogen at a given photon flux. The results are presented in Figure 2.

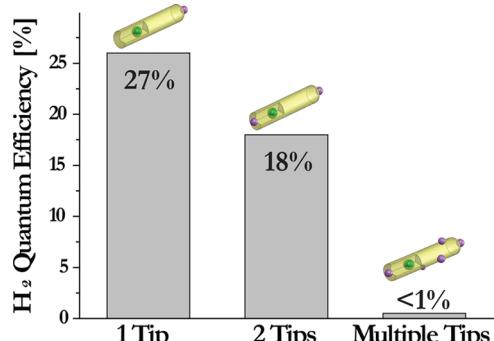
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**Figure 1.** TEM micrographs of CdSe@CdS nanorod photocatalysts with (A,D) single, (B,E) double, or (C) multiple Pt cocatalysts reduction sites. (a–c) bar = 25 nm; (e–d) bar = 5 nm.



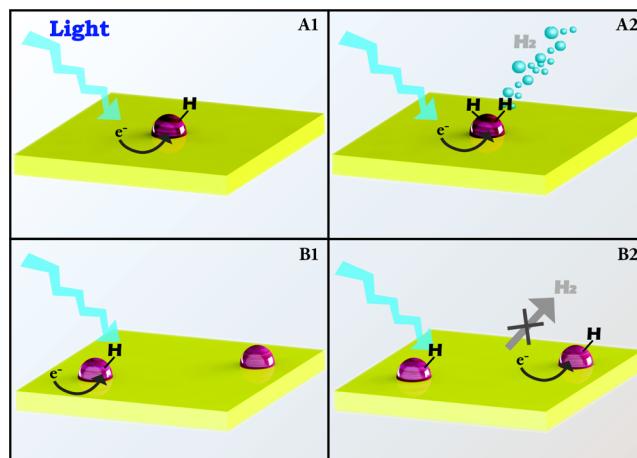
**Figure 2.** Photocatalytic quantum efficiency for the hydrogen reduction half reaction obtained with CdSe@CdS nanorod photocatalysts decorated with a single, double, or multiple Pt reduction sites.

Rods decorated with a single Pt catalyst were found to be the most active for hydrogen production, with QE of 27% (flow of  $1.5 \times 10^{16}$ ) hydrogen molecules per second), while rods having two reduction sites reached only QE of 18% and rods with multiple sites showed very low activity (QE under 1%). These results agree with our original hypothesis that was previously presented. With an apparent quantum yield of 27% these numbers indicate that about 25 hydrogen molecules are generated per second from a single rod. In other words, one hydrogen molecule is generated on a single rod every 40 ms. This results with a turnover frequency of 90 000 mol of hydrogen per 1 mol of catalysts per hour.

Similar trends in activity with CdSe rods were also reported by Bang et al.,<sup>22</sup> however, they attribute the difference in the reactivity to the geometrical effects of the Pt tips on CdSe nanorods, suggesting that the active area at the rod tip acts as the site for hole transfer, hence blocking it with a second Pt tip results in lower activity. The implications of their finding were thus limited only to photocatalysts with nanorod geometry. The conclusion that can be drawn from the hypothesis we

present here could be implemented in any photocatalyst system.

For a photocatalyst with a single reduction site, the release of a hydrogen molecule will correlate to the absorption of two photons, yet for a photocatalyst decorated with two metal sites this is more complicated. While the Pt tips are serving as independent H<sub>2</sub> evolution sites, they share the same segment of the semiconductor that can absorb light and generate charge carriers. After H<sup>\*</sup> has been successfully created at one site, a photoinduced electron that is generated by a photon absorption event might be transferred to the second site. This will result in two H<sup>\*</sup> atoms that cannot combine to release as a hydrogen molecule, as illustrated in Figure 3. The system must wait for

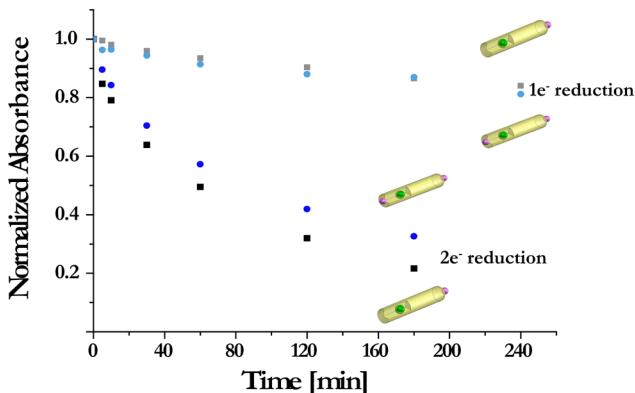


**Figure 3.** Illustration demonstrating the formation of hydrogen on a single (A) or a double (B) metal catalyst. In A2, a hydrogen molecule is released from a photocatalyst with a single reduction site. In B2, after H<sup>\*</sup> has been successfully created at one site, a photoinduced electron that is generated by a photon absorption event is transferred to the second site. The two hydrogen atoms are bound to different catalyst sites and as a result cannot recombine and release a hydrogen molecule. The improved activity of a single cocatalyst site structure is related to its ability to host the two required electrons, and resulting intermediates, simultaneously at close proximity.

yet another successful photon absorption. In this situation the reduction intermediate is forced to wait an extended duration of time before the reaction can be completed.

This new requirement for three photons instead of two might result in lower activity, depending on the long-lived stability of the intermediate. While operating at higher photon flux is expected to shorten this time frame, the rate-limiting step here was the absorption of light by the semiconductor. Increasing the photon flux only resulted with a decrease in the apparent quantum efficiency. The activity is expected to range from two-thirds to 80% of that obtained from the photocatalyst decorated with a single site. The activity will reflect the tendency of the electron to favor the second site. Here the obtained efficiency for hydrogen production implies a dominant preference of the electron toward the nonprotonated site. This might be related to Coulomb repulsion despite utilization of the electron for the reduction reaction.<sup>23</sup> The improved activity of a single cocatalyst site structure is related to its ability to host the two required electrons, and resulting intermediates, simultaneously at close proximity. It is important, however, to note here that this will be valid only for a multielectron reaction.

To further confirm our hypothesis and interpretation of the results for the hydrogen production, we examined the activity through a series of dye reduction reactions. With a characteristic peak at  $\sim 667$  nm that is lost with the reduced form, methylene blue is a highly examined redox indicator. Its reduction reaction requires two electrons, similar to the hydrogen reduction reaction. Monitoring the dye's characteristic peak in the absorption spectra over the time trajectories of a reduction reaction allows for assessment of activity kinetics. Indeed, the activity toward methylene blue reduction was found to be considerably higher for rods decorated with a single Pt catalyst (black squares in Figure 4) compared with rods having two reduction sites (blue dots in Figure 4). This is consistent with the activity trends observed for hydrogen.



**Figure 4.** Photocatalytic activity obtained with CdSe@CdS nanorod photocatalysts decorated with a single (squares) or double (circles) Pt reduction catalyst sites, toward single- and two-electron reduction reactions.

In contrast, rhodamine 6G (R6G) has a characteristic peak at  $\sim 530$  nm that is lost after a single electron reduction reaction. Here the activities toward the dye reduction, for both rods decorated with a single or double Pt catalyst, were found to be comparable (gray squares and light-blue dots in Figure 4). The similarities in activity toward the reduction of R6G were expected. According to our model, the advantage of using a single catalytic site becomes redundant when it comes to catalyzing a single-electron reaction.

Our results confirm that when dealing with multielectron reactions, the morphology of the photocatalyst should include only a single cocatalyst per excitation unit to ensure that all intermediates are formed on the same catalytic site. The advantage of utilizing a single catalyst should become more pronounced in correlation with the number of electrons that are involved in the process. Thus, this finding should be critical for the proper design of photocatalysts aimed at water oxidation.<sup>24,25</sup> We believe the implications of this finding are of significance for our ability to maximize the potential of any catalytic system, so that we can realize an efficient photocatalyst for genuine solar-to-fuel energy conversion.

## ASSOCIATED CONTENT

### Supporting Information

Detailed description of the typical preparation of the different Pt-decorated CdSe@CdS nanorods and techniques used in characterization of these particles. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.5b00872.

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### Notes

The authors declare no competing financial interest.

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