JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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Cluster Size Effects in the Photocatalytic Hydrogen Evolution Reaction

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S *Supporting Information*

ABSTRACT: The photocatalytic water reduction reaction on CdS nanorods was studied as function of Pt cluster size. Maximum H_2 production is found for Pt_{46}. This effect is attributed to the size dependent electronic properties (e.g., LUMO) of the clusters with respect to the band edges of the semiconductor. This observation may be applicable for the study and interpretation of other systems and reactions, e.g. H_2O oxidation or CO_2 reduction.

Photocatalysis offers a large variety of possibilities for generating renewable chemicals from solar energy. Highly abundant materials, e.g. water or CO_2, may be used for storing energy in solar fuels such as hydrogen, methanol, or methane.[1−3] Recent advances in colloidal chemistry have fostered a renewed interest in hybrid cluster-decorated semiconductor nanoparticle systems, since they have been shown to photocatalytically generate hydrogen in the presence of a sacrificial hole scavenger. Furthermore, control of particle shape, size, and morphology enable control over their electronic and optical properties.[4−9] While the properties of the semiconductor can be tuned precisely by colloidal chemistry, this technique is limited with respect to atomic control of the cluster catalysts. Knowledge of the effect of cluster size with atomic precision is highly desirable, since it has been shown that, in particular, clusters smaller than 1 nm in diameter are active in the photocatalytic water reduction reaction on CdS nanorods.[7,10] In addition, for other reactions and systems (e.g., Au clusters on TiO_2) effects of the size of the metal particles on their photocatalytic activity is found.[11−13] Despite these observations and the surprising catalytic activity of very small metal clusters,[14−17] a photochemical study of cluster size effects with atomic precision is still missing. Recently, we have succeeded in studying the photocatalytic activity of the hydrogen evolution reaction on CdS nanorods decorated with Pt clusters as a function of cluster coverage.[18] In this work, we focus on the cluster size effects on an atomic level at fixed coverages and their impact on the photocatalytic activity of semiconductor/metal cluster systems. In particular, we show that there is an optimum cluster size for maximum hydrogen generation efficiency, as smaller and larger clusters exhibit lower hydrogen production rates. While we focus on the results and their discussion below, full experimental details are given in the Supporting Information [SI].

Figure 1 displays high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) micrographs for clusters of different sizes on the semiconductor nanorods. In all images the clusters are homogeneously distributed over the nanorods, and the size of the clusters in the various micrographs differ significantly from each other. Different clusters in the same image appear uniform in size, confirming the monodispersity of the sample due to size selection and soft-landing.[18−21] In detail, the vast majority of the clusters consist of only one mass. The projected areas for the various clusters range from about 0.5 nm^2 for Pt_8 to over 1.0 nm^2 for Pt_{68}. Note that small numbers of cluster dimers are observed originating either from cluster diffusion or heating by the electron beam (see statistics of clusters on bare TEM grids, Figure S2 in SI). All images were recorded with the same cluster coverage of 0.04 e nm^{-2}, which corresponds to around 23 clusters per nanorod (see SI for calibration). Since the samples were stored in air for several weeks between deposition and STEM measurements, the findings further demonstrate that monodispersity and size selection are preserved under ambient conditions. The photocatalytic activity of the semiconductor/metal cluster catalysts was evaluated by the amount of hydrogen generated. In this work we normalized the hydrogen production to the number of possible electron trapping sites leading to hydrogen evolution, which is the number of clusters per nanorod. For studying the effect of cluster size, all parameters were kept constant except the size of the clusters deposited. Semiconductor nanorods were taken from only one batch and the coverage of the clusters was always chosen to be 0.04 e nm^{-2}. Note that constant cluster coverage for all samples is crucial since the evolution of hydrogen strongly depends on the number of clusters per nanorod.[18] As reported for similar systems before, all samples showed a linear increase of the H_2 amount over time (see Figure S3 in SI). This

Received: June 17, 2013
Published: August 20, 2013

dx.doi.org/10.1021/ja406070q | *J. Am. Chem. Soc.* 2013, 135, 13262−13265

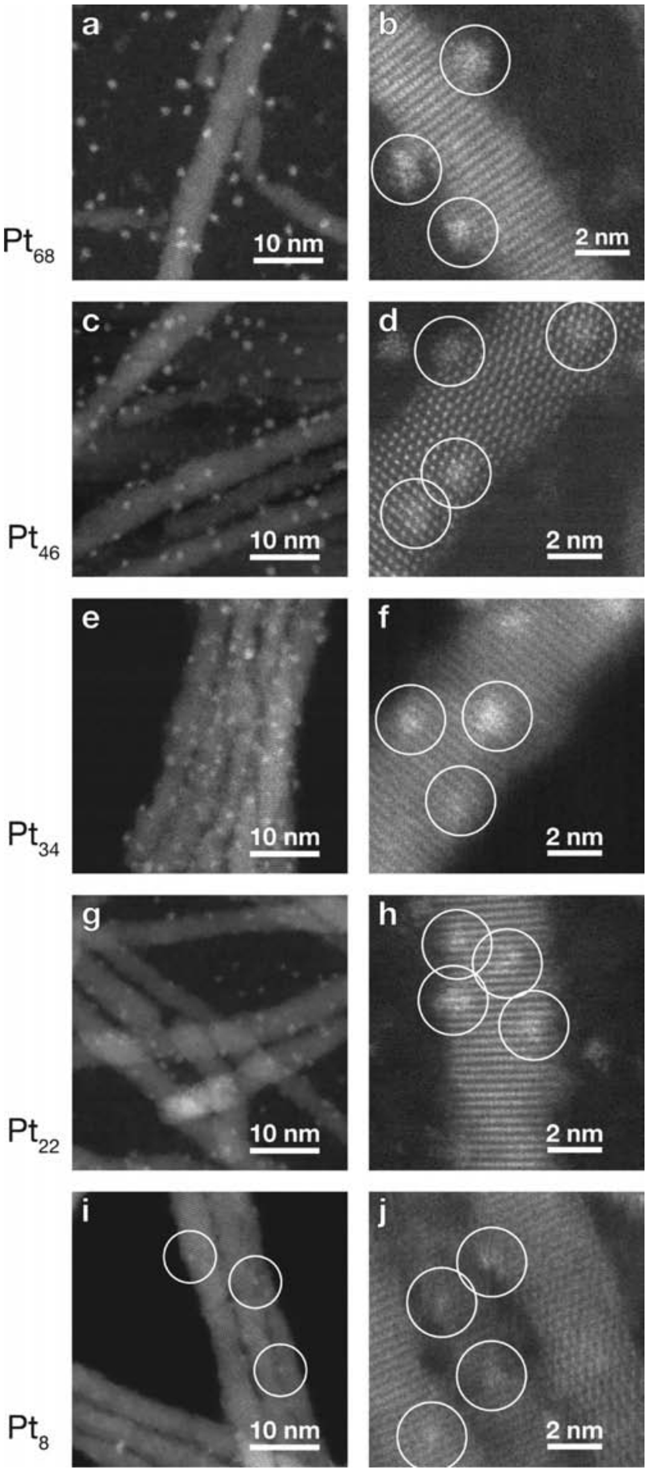

Figure 1. HAADF-STEM micrographs of different Pt cluster sizes with similar coverage deposited onto CdS nanorod thin films. For all samples the clusters are homogeneously distributed over the CdS nanorods. Clusters within the same micrograph are similar in size, but they differ significantly when comparing clusters of different sizes, as expected from soft-landing conditions. Monodispersity of the clusters is preserved even at ambient conditions, since the clusters were stored several weeks in air after deposition and prior to the TEM measurements. The micrographs serve for obtaining an average number of clusters per nanorod, about 23 clusters per rod for the samples presented.

is a clear indication that the catalysts were stable over the course of the experiments. Triethanolamine (10 vol % - a common chemical and concentration, see SI) was added as a sacrificial hole scavenger, ensuring that the holes were removed quickly from the catalyst, thus preventing the semiconductor from decomposition.[7]

The average production rate of H_2 per hour was calculated from the individual samples and plotted versus cluster size (see Figure 2; the individual data points of the measurements are given in the SI in Figure S2). Pt$_8$ and Pt$_{22}$ clusters show hydrogen productions below 1‰ h^{-1}, and an increase above 1‰ h^{-1} is observed for Pt$_{34}$. The H_2 production rate further increases over 1.5‰ h^{-1} for Pt$_{46}$ and then decreases again for Pt$_{68}$. For the measured cluster sizes, Pt$_{46}$ is the most active. This trend is even more pronounced when the monolayer quantum efficiency (ML QE) is used for assessing the activity of the photocatalytic system, taking into account that clusters, due to the deposition method applied, only cover the upper-most layer of the nanorods. Thus, hydrogen is only generated in this region of the sample.[18]

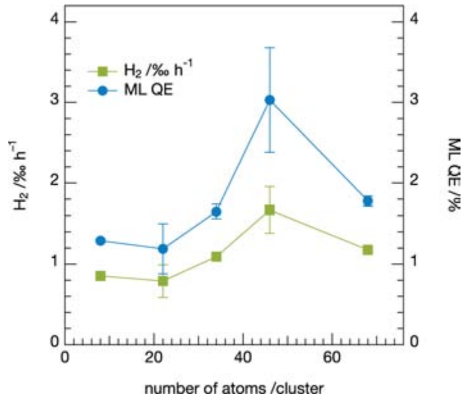

Figure 2. Photocatalytic activity of the CdS nanorods decorated with size-selected Pt clusters as a function of cluster size. The average H_2 production rate clearly changes with the size of the clusters deposited. While a value below 1‰ h^{-1} is obtained for smaller clusters (Pt$_8$ and Pt$_{22}$), this value increases to over 1‰ h^{-1} for Pt$_{34}$. After having reached a maximum H_2 production rate for Pt$_{46}$, the H_2 production rate drops again for larger clusters of Pt$_{68}$. This trend is even more pronounced for the monolayer quantum efficiency (ML QE) of the cluster−semiconductor catalysts, which takes into account that just the uppermost layer of the CdS nanorod film is covered with clusters.

Accounting for this effect, the ML QE of the nanorod substrates can be directly compared with the regular QE of e.g. colloidal nanoparticle systems (see SI).

When discussing the photocatalytic activity of the cluster−semiconductor system as function of cluster size, two conclusions can be drawn. First, a clear cluster size effect is found, which demonstrates that the number of atoms in the cluster is crucial for its photocatalytic activity. Second, for the measured data points a maximum in activity is observed for Pt$_{46}$. It is well illustrated that, in this size range, cluster properties, like chemical and catalytic activity, energy levels, or the ionization potentials and electron affinities strongly vary with cluster size.[22] These quantum size effects are particularly strong for clusters with a few tens of atoms, but clear variations of such observables diminish for larger clusters, and a rather smooth dependency on size is observed.[23] For the reduction of H^+ ions to molecular hydrogen two electrons are required. In an initial step, photons with energy higher than the band gap of the semiconductor generate electron/hole pairs. While the holes are consumed by the sacrificial scavenger molecules, the electrons are trapped at the Pt-clusters. In a subsequent electron transfer step, protons are reduced to molecular hydrogen at the cluster surface. To discuss the observed size-dependent hydrogen production rate for each of the above-mentioned steps the influence of cluster size must be identified. The generation of the charge carriers is obviously not cluster-size dependent. In our system the bulk recombination is reduced by the use of nanoscale semiconductor rods. The trapping of the electrons, however, is strongly related to cluster size as unoccupied electronic states below the lower edge of the conduction band favor the charge density in the cluster. Similarly, the electron transfer to the hydrogen atom is also dependent on the position of the clusters' LUMO, which must lie above the hydrogen reduction potential. While these are purely thermodynamic arguments, the actual formation of molecular hydrogen may also be influenced by reaction kinetics. Here the activation energies are clearly influenced by the cluster properties as e.g. the adsorption geometry of the reactants, the character of the transition state, or the thermal and charge-dependent fluxionality of the cluster upon reaction. While such effects will indeed contribute to the hydrogen generation kinetics, it is generally believed that the competition between charge carrier separation and recombination is crucial for the efficiency of the overall process.[24] To interpret these complex reaction steps, we therefore focus solely on the thermodynamics of this key step and propose the following simplified model of the electron transport that is illustrated in Figure 3.

For the H^+ reduction to take place, the electron must be transferred to a hydrogen ion in two steps, first from the semiconductor to the cluster and then from the clusters to the protons.[25] For the actual formation of molecular hydrogen, two electrons have to be transferred successively to the protons.[26] Thus, the suggested model is treating both reduction steps discretely (i.e., not considering a concerted two-electron reduction).[27] For both electron transfer steps opposing effects for the optimal position of the cluster's LUMO play an important role for the efficiency of the H_2 production. On one hand, an efficient trapping of the electron at the cluster is achieved if its LUMO is low in energy compared to the lower edge of the conduction band of the semiconductor. On the other hand, an electron transfer to the hydrogen is only possible if the LUMO is above the reduction potential of H^+/H_2.

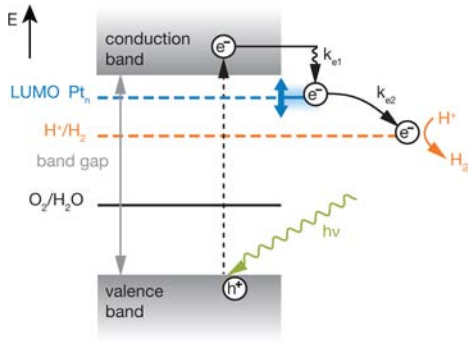

Figure 3. Reaction pathways for the photocatalytic H_2 evolution. Under illumination with a photon with an energy larger than the band gap, an electron/hole pair is created in the semiconductor. In order to form H_2, the electron has to be trapped efficiently at the cluster (k_{e1}), and then transferred to the H^+ atoms (k_{e2}). For the formation of H_2, two electrons have to be transferred to the protons. For an efficient trapping of the electron on the cluster, its LUMO has to be lower in energy than the lower edge of the conduction band of the semiconductor. Electron transfer from the cluster to H^+ is energetically favored, if the cluster's LUMO is higher in energy than the H^+ reduction potential. Therefore, H_2 evolution only takes place efficiently if the LUMO is positioned at an energy that is between the lower edge of the conduction band and the H^+/H_2 potential. An optimum position of the cluster's LUMO is governed by these opposing effects. Tuning the LUMO by cluster size, a maximum in the photocatalytic activity is achieved with a certain number of atoms.

Thus, the LUMO must be energetically in between the position of the lower edge of the conduction band and the reduction potential of H^+. This simple, purely thermodynamic model therefore predicts the possible existence of an optimal LUMO energy level of the catalyst.

The advantage of using small clusters for this photocatalytic process is the capability to tune the position of the electronic states, e.g. their LUMO, by changing cluster size.[28,29]

The observed size effects in Figure 2 may exactly reflect these properties. The maximum hydrogen evolution at Pt_{46} suggests that the position of its LUMO fulfills the aforementioned conditions best for all the measured cluster sizes. For the evaluation of our model, the position of a LUMO could be, in a first approximation, related to the gas-phase electron affinities. Whereas for alkali and coinage metals, electron affinities are indeed available from experimental studies over a considerably large size range,[30−32] for platinum, unfortunately, no such values are reported for our sizes. In order to obtain an accurate description of our system, gas-phase data may not be sufficient, as solvation and substrate interaction effects must be taken into account. The tuneability, however, is still present, as it has been illustrated that electron affinities can be correlated to macroscopic values, e.g. the reduction potential, by including solvation terms.[33] The foundation of the model we present has previously been reported,[34] and we extend this by including the tuneability of the clusters' electronic structures. The model is quite general and should be applicable to other reactions, e.g. CO_2 reduction, H_2O oxidation. The knowledge of electron affinities or ionization potentials of the clusters on the surface of a semiconductor may allow the prediction of the cluster efficiency during photocatalysis. In addition, the experimental method presented here, is applicable for elucidating size effects in other (photo)catalytic systems.

In conclusion, we present for the first time a study of cluster size effects on an atomic scale in the photocatalytic water reduction reaction. This was possible, as all parameters (size and composition of the CdS nanorods, type and concentration of the hole scavenger, as well as the cluster coverage) except the cluster size were kept constant. The maximum hydrogen production rate was found for Pt_{46}, indicating a clear size effect within the studied sizes. The size effect is interpreted via two electron transfer steps: first from the semiconductor to the cluster and second from the cluster to the hydrogen atom. The model suggests an optimum energetic position of the cluster's LUMO for a given photocatalytic system. The LUMO of Pt_{46} appears to be best situated out of all the cluster sizes measured for the H_2 production on Pt-decorated CdS nanorods. The model and the experimental approach presented is generally applicable and allows for studying size effects in other photocatalytic systems as well as for obtaining a deeper understanding of how to improve the efficiency of the cluster catalyst on a fundamental basis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further experimental details and procedures, characterization and measurement data as well as some additional background information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support by the DFG through the Nanosystems Initiative Munich (NIM) and LMUexcellent, by the Bavarian State Ministry of Sciences, Research and the Arts through Solar Technologies Go Hybrid, by the BMBF and an ERC Advanced Grant (ERC-2009-AdG 246645-ASC3) is gratefully acknowledged. F.F.S. thanks the 'European Graduate School for Sustainable Energy Technology, The molecular approach' and the 'TUM Graduate School' for support.

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