Intermittent photocatalytic activity of single CdS nanoparticles

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Semiconductor photocatalysis holds promising keys to address various energy and environmental challenges. Most studies to date are based on ensemble analysis, which may mask critical photocatalytic kinetics in single nanocatalysts. Here we report a study of imaging photocatalytic hydrogen production of single CdS nanoparticles with a plasmonic microscopy in an *in operando* manner. Surprisingly, we find that the photocatalytic reaction switches on and off stochastically despite the fact that the illumination is kept constant. The on and off states follow truncated and full-scale power-law distributions in broad time scales spanning 3–4 orders of magnitude, respectively, which can be described with a statistical model involving stochastic reactions rates at multiple active sites. This phenomenon is analogous to fluorescence photoblinking, but the underlying mechanism is different. As individual nanocatalyst represents the elementary photocatalytic platform, the discovery of the intermittent nature of the photocatalysis provides insights into the fundamental photochemistry and photophysics of semiconductor nanomaterials, which is anticipated to substantially benefit broad application fields such as clean energy, pollution treatment, and chemical synthesis.

single-nanoparticle catalysis | intermittent activity | semiconductor photophysics | semiconductor photochemistry | surface plasmon resonance microscopy

Photocatalytic H₂ production based on semiconductor nanocatalysts is one of the most promising solutions for the energy crisis via solar-to-chemical energy conversion (1–3). In recent years, single-nanoparticle catalysis, which studies the catalytic activity at single-nanocatalyst level, has received great attention due to its unique strengths to understand the microscopic catalytic kinetics and mechanism (4–6). For semiconductor photocatalysts, single-nanoparticle photocatalysis is particularly interesting because of their comprehensive photophysical processes including photoinduced carrier generation, migration, and recombination. For example, the fluorescence photoblinking of individual semiconductor quantum dots has been a long-standing mystery since its discovery two decades ago (7), and its underlying mechanism remains an open question (8–10). When considering the fact that the photocatalytic activity of semiconductor nanomaterials is intrinsically associated with their photophysical processes, it naturally raises a question of whether the photocatalytic activity is also intermittent at single-nanoparticle level, or is it simply constant or monotonically decaying (due to photocorrosion and photopassivation), as one could intuitively predict.

This question has not been answered by the existing techniques for studying single-nanoparticle catalysis such as single-molecule fluorescence (4–6) and dark-field scattering (11–13). Although it is applicable to image individual dielectric nanoparticles with dark-field microscope (14), most studies so far have been focusing on plasmonic nanomaterials due to their relatively large scattering cross-section and the sensitive spectral dependence on the surrounding environment. Single-molecule fluorescence microscopy is one of the most adopted techniques in this field by monitoring the counts and locations of fluorescence bursts in a fluorogenic reaction, which indicate the

formation of fluorescent product molecules (15). Although powerful, fluorescence microscopy requires a fluorogenic model reaction and might compromise the nature of many important reactions where products are nonfluorescent (for example, photocatalytic H₂ production reactions). Besides, because it often takes tens of minutes to accumulate enough counts for statistical analysis, it has been mostly used to study the spatial heterogeneity at a cost of temporal resolution (4–6, 16). A previous study reported the inhibition and reappearance of photocatalytic activity of single Sb-doped TiO₂ nanorods as a result of the absorption and desorption of surface adsorbates (17). Analysis of the burst correlation times have also suggested the activity fluctuations of individual gold (5) and platinum (18) nanoparticles due to the dynamic surface restructuring of metal atoms. However, intermittent photochemical activity (i.e., stochastic blinking between ON and OFF states) of single semiconductor nanoparticles that is regulated by its intrinsic photophysical processes has been largely unexplored.

Here we use a surface plasmon resonance microscopy (SPRM) to continuously monitor the H₂ production rate of individual CdS nanoparticles in an *in operando* manner, and report the discovery of intermittent photocatalytic activity of single CdS nanocatalyst. SPRM is an optical microscopy that we recently developed to image the local refractive index (RI) distribution with a temporal resolution up to microseconds and a spatial resolution around the diffraction limit (19–21). SPRM is capable of monitoring local H₂ concentration due to the large difference in the RI between H₂O and H₂. Instead of being constant or monotonically changing, it was surprisingly found that the photoinduced H₂ production rate of

Significance

Semiconductor photocatalysis holds promising keys to address various energy and environmental challenges. While conventional wisdom suggests a continuous photocatalytic reaction under constant light illumination, in the present article we report the discovery of intermittent photocatalytic activity at single CdS nanoparticle level. The observed intermittent photocatalysis is a photochemical consequence of its intrinsic photoexcitation processes. The latter is also responsible for the well-known fluorescence photoblinking of single-semiconductor quantum dots, a photophysical phenomenon that was discovered in the 1990s. The intermittent photocatalysis (a photochemical process) reported here could be an exciting complement of the beautiful picture of semiconductor photophysics and photochemistry, with significant implications in many application fields from clean energy to pollution treatment.

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Fig. 2. (A) Experimental SPRM image during hydrogen production (*Center*) reveals that the local RI reduction is confined in a volume smaller than the optical diffraction limit. This observation supports the nanobubble hypothesis by comparing with the simulated SPRM image for nanobubble (*Left*) or homogeneous diffusion hypothesis (*Right*). (Scale bar: 1 μm .) (*Lower*) Horizontal profiles of three images crossing the center are displayed (red: nanobubble, blue: experimental, black: supersaturation). (B) RI trajectory of a single CdS NP during electrochemical reduced H_2 evolution at a potential of $-400\text{ mV vs. Ag/Ag}_2\text{S}$. Each cycle, consisting of a gradual RI decrease and a rapid RI recovery, represents the growth and eclipse of a nanosized H_2 bubble. (C) The bubble lifetime follows Gaussian distribution rather than a power-law distribution. (D) The bubble lifetime becomes shorter when electrode potential scans toward more negative, indicating a faster H_2 evolution rate at higher overpotential. The lifetime vs. potential is fitted with a single-rate exponential curve.

nanoparticle, which was monitored continuously with SPRM. The change of the local RI over time was determined from the change in the average SPRM intensity of the tail region for each nanoparticle.

Surprisingly, we found that the photocatalytic production of hydrogen at each of seven CdS nanoparticles switched on and off stochastically even though the light illumination was constant. Two representative time traces showing this intermittent nature of photocatalytic reactions are plotted in Fig. 1B (red and blue curves) and more examples are given in [SI Appendix, Fig. S6](#). Zoom-in of the time trace for one CdS nanoparticle (NP2 from 3,460th to 3,750th s) reveals that the photocatalytic reaction was switched on and stayed ON for a certain time interval, and then switched off and stayed OFF for another time interval (see also [Movie S1](#)). As a control, the time trace of the local RI from a region where there was no CdS nanoparticle was also measured (black curve in Fig. 1B), which showed a flat line with no characteristic switching events. Note that the time traces for different CdS nanoparticles are uncorrelated, so ensemble average of a large number of nanoparticles would have washed out such intermittency. This observation underscores the need of single-nanoparticle studies to observe the intrinsic kinetics of the photocatalytic reactions. Similar intermittency was also observed on CdS nanoparticles with different crystal structures and shapes (nanorods), indicating that the intermittent nature of photocatalytic activity was a general phenomenon for various CdS nanomaterials regardless of their crystal structure and morphology ([SI Appendix, Fig. S7](#)). Please note that ~80% of over 300 individual CdS nanoparticles exhibited similar intermittent behaviors in tens of independent experiments within a typical recording time of 3 h.

The time durations of ON and OFF states of the photocatalytic reactions are marked by red and black dots in Fig. 1B (*Bottom*), respectively, showing stochastic distributions over time scales spanning from 0.16 s (the temporal resolution in the present work) to hundreds of seconds. Statistical analysis (26) of the individual switching events for different nanoparticles shows that the OFF state follows a full-scale power-law distribution, and the ON state can be fitted with a truncated power-law distribution (solid curves in Fig. 1C and *SI Appendix, Figs. S6 and S8*). The two distributions can be expressed as

$$p(t_{\text{off}}) = C \cdot t_{\text{off}}^{-\alpha_{\text{off}}}$$

$$p(t_{\text{on}}) = \begin{cases} C \cdot (k_{\text{cutoff}} t_{\text{on}})^{-\alpha_{\text{on}}} & \text{for } t_{\text{on}} \geq 1/k_{\text{cutoff}} \\ C \cdot \exp(-\alpha_{\text{on}}(k_{\text{cutoff}} t_{\text{on}} - 1)) & \text{for } t_{\text{on}} < 1/k_{\text{cutoff}} \end{cases},$$

respectively, where $p(t_{\text{on}})$ is the probability density of a certain on-event duration time (t_{on}), C is a constant, α_{on} is the power-law coefficient of ON events, and k_{cutoff} is the truncation factor. Note that the above functions are widely used to analyze fluorescence photoblinking (26) and many other stochastic processes in physical (27) and social sciences (28). A truncated power-law distribution indicates any process faster than k_{cutoff} is prohibited while processes slower than k_{cutoff} are stochastically distributed (27).

Control experiments were performed to show that the measured switching of the local RI was indeed due to the intermittent hydrogen production. First, the local RI did not change when the nanoparticles were not illuminated with light, or illuminated with red light ($\lambda > 600$ nm, *SI Appendix, Fig. S9*). Second, when replacing $\text{S}^{2-}/\text{SO}_3^{2-}$ with HPO_4^{2-} in the solution, no switching in the local RI was detected (*SI Appendix, Fig. S9*), which was expected because $\text{S}^{2-}/\text{SO}_3^{2-}$ was known to facilitate photocatalytic hydrogen production (3, 29). These results also demonstrated that the photothermal effect was not responsible for the intermittent photocatalytic activity because it would be independent of electrolytes. The illumination of blue light was found to increase the local temperature around single nanoparticles by 0.1 °C as determined by a photothermal conversion approach (30) (*SI Appendix, Fig. S10*), suggesting a small thermal disturbance to the local reaction. Third, the position of individual CdS nanoparticles did not move at all over the entire experiment (hundreds of switching events in 2 h), indicating Brownian motion of the nanoparticle was negligible. Fourth, CdS nanoparticles exhibited excellent photostability in the presence of $\text{S}^{2-}/\text{SO}_3^{2-}$ without the sign of photocorrosion (*SI Appendix, Fig. S11*). Besides, an irreversible photocorrosion process was anticipated to display a monotonic change in the SPR intensity (*SI Appendix, Fig. S9*) rather than switching between two states. Finally, the RI changes due to interfacial processes, such as the adsorption and

Fig. 4. (A) Probability density of ON events in the presence of 500 (magenta) and 200 (black) mM Na₂S. (B) Probability density of ON events under the blue-light power density of 14 (blue), 9 (magenta), and 6 (black) mW·mm⁻². (C) Correlation between k_{cutoff} (extracted from the probability density curves in A and B) and bulk H₂ production rate (measured from conventional photocatalysis experiment using ensemble materials). (D) Calculated truncated power-law distributions by adjusting the maximum rate k_{cutoff} in a multiple-rate stochastic process.

The exponential dependence of the ON-state duration time with the overpotential (Fig. 2D, Inset) demonstrates that the bubble lifetime is regulated by hydrogen production rate.

We further studied the correlation between k_{cutoff} and the bulk hydrogen production rate by varying the concentration of S²⁻ ([S²⁻]) and the power density of blue-light illumination; both are confirmed to be relevant to the hydrogen production rate (SI Appendix, Fig. S16) (3). When [S²⁻] was reduced from 500 to 200 mM, intermittent photocatalysis remained but the ON-state duration increased significantly (SI Appendix, Fig. S17). Statistical analysis of the ON-state duration reveals a sixfold decrease in k_{cutoff} associated with the reduction of [S²⁻] and a significant shift of the truncation toward a longer time scale (Fig. 4A). A similar analysis shows that k_{cutoff} decreases with illumination power density (Fig. 4B). Plotting k_{cutoff} vs. hydrogen production rate shows a linear relationship (Fig. 4C), suggesting that k_{cutoff} reflects the photochemical reaction rate of single CdS nanoparticles. We also examined the effect of [S²⁻] and illumination power density on the OFF-state duration distribution, and full-scale power-law distributions remained in all cases (SI Appendix, Fig. S18).

In addition to the ON/OFF event time, the growth rate of nanobubble is also able to quantify the H₂ generation rate associated with single nanoparticles (SI Appendix, Fig. S17B). If we compare the growth rates of nanobubble in different ON events under the same conditions, they are also stochastic and vary by up to 10× (SI Appendix, Fig. S17C). When increasing the apparent photochemical reaction rate, growth rates of nanobubble also increase. We chose ON/OFF event time instead of growth rate in power-law analysis, because the reliable curve fitting for growth

rate required significantly more data points and it tended to induce uncertainties when the signal/noise ratio was not good enough.

A similar power-law distribution has been observed in fluorescence photoblinking of single quantum dot, which has been attributed to photoionization and multiple rates during carrier recombination (8, 10). These processes may also contribute to the intermittent photocatalytic activity of single CdS nanoparticles observed here because of the intrinsic connection between the photochemical reactions and the photophysical processes. For example, previous studies have suggested that the interfacial electron transfer activity of semiconductor nanoparticles was modulated by the fluorescence photoblinking dynamics (33). The absence of power-law distribution in electrochemical reduction of hydrogen further supports this point, as photophysical processes are solely involved in the photocatalysis but not in the electrochemical reduction. When looking at the photochemical reactions at single CdS nanoparticles, multiple reaction sites could exist simultaneously on the nanoparticle surface, resulting in a stochastic distribution of the reaction energy barriers at each active site due to the heterogeneous coordination states and dangling bonds (34, 35). Therefore, the photophysical processes as well as multiple interfacial electron transfer rates are believed to be the key for the observed power-law distribution. While general power-law distributions of ON/OFF events are attributed to the intermittent photophysical processes, the truncation (k_{cutoff}) is a consequence of the interfacial photochemical reactions, because such truncation is a unique distribution that has been rarely observed in fluorescence photoblinking. Therefore, it reflects the reaction rate at the single-nanoparticle level (Fig. 4C). The existence of multiple reaction sites was also supported by two experimental observations. First, multiple nanobubble generation sites were often found for CdS nanorods (SI Appendix, Fig. S7 E–H). Second, multiple states rather than two states existed on the projection of SPR trajectory curves on the intensity axes (SI Appendix, Fig. S20 and Fig. 5). We attributed this feature to the different locations (vertical distances to the substrate) and different sizes of the nanobubbles as a result of the multiple reactive sites. SPRM signal of a bubble sensitively relies on the vertical distance and the size. Note that the varied SPRM intensity does not affect the power-law analysis which relies on the duration time of ON/OFF events, rather than its intensity.

To further support the above analysis, we simulated the probability density of ON-state durations with a stochastic model

Fig. 5. Zoom-in of the projection histograms of the corresponding SPR intensity of NP1 (A) and NP2 (B) reveal the existence of multiple states (multiple ON and single OFF) rather than two states (single ON and single OFF).

(27, 28) involving multiple active sites, each with a reaction rate (*SI Appendix*, Fig. S19). If assuming 100 active sites with rates uniformly distributed from 1×10^{-4} to 30 s^{-1} , the calculated probability density displays a full-scale power-law distribution ranging from 1,000 to 0.5 second (Fig. 4D, blue dots). In this case, k_{cutoff} is 30 s^{-1} . However, if reducing k_{cutoff} to 0.3 and 0.03 s^{-1} , truncated power-law distributions are predicted by the model (red and black dots), which reproduces key features of the experiments (Fig. 4A and B). The truncation point shifts toward longer time scale for the smaller k_{cutoff} , accompanying with lower probability densities in the plateau region and constant slopes in the linear region. The agreement between the multiple reaction rates model and the experimental data supports the hypothesis that multiple photochemical reaction rates stochastically distributed in a certain range with a maximal rate are responsible for the truncated power-law distribution of ON-state durations observed on single CdS nanoparticles. The active sites at atomic scale are attributed to the unsaturated Cd atoms with dangling bonds, as well as some big curvatures in the irregular CdS nanoparticles (contacts, edges, and caves). Further efforts are certainly required to comprehensively understand the structural basis of these active sites. Combining the SPRM technique proposed here and high-resolution electron microscopy is a promising way to achieve this goal in the future.

In summary, we report the intermittent photocatalytic activity of single CdS nanoparticles, and propose a multiple reaction sites model for the full-scale and truncated power-law distribution of ON and OFF events, respectively. As photoblinking is a general phenomenon for various types of semiconductor nanomaterials, the discovery of the intermittent photocatalysis opens a field of semiconductor-based photocatalysis and paves the way toward the rational design and discovery of photocatalysts with excellent efficiency by studying the photocatalysis at single-nanocatalyst level. From the photophysical point of view, the present work also connects the single-nanoparticle photophysics and photochemistry, offering another opportunity to clarify the mechanistic origin of the mysterious photoblinking of single-semiconductor nanomaterials.

Materials and Methods

Experimental Setups, Synthesis, and Characterizations of the CdS Nanoparticles.

The plasmonic microscopy setup was built on an inverted total internal reflection fluorescence microscope using gold-film-coated glass coverslip as the sensor chip. CdS nanoparticles (NPs) were synthesized according to the previous work (29). The resulting CdS NPs were uncapped (or capped with S^{2-}) to facilitate the photochemical reactions. CdS NPs with the cubic-phase were synthesized following a similar protocol as mentioned above, by switching the volume of Na_2S and $\text{Cd}(\text{OAc})_2$. The CdS nanorods were synthesized with a solvent thermal method. Dynamic light scattering, diffuse reflection UV-vis spectrum, X-ray powder diffraction, X-ray photoelectron spectroscopy, etc. were used to characterize CdS NPs. Please see *SI Appendix* for more details. All of the photochemical and electrochemical reactions were performed in aqueous solutions.

Power-Law Analysis. The power-law analysis of the SPRM trajectory curve was achieved with a self-developed MATLAB code using a threshold-based algorithm, which has been routinely adopted to analyze the blinking fluorescence trajectory. The ON/OFF event was differentiated by the amount of intensity fluctuation. A rapid decrease in the SPRM intensity (higher than a user-defined threshold) represents the beginning of an ON state, and a sharp increase represents the end of an ON state (and therefore the beginning of an OFF state). A detailed description on the MATLAB program is provided in *SI Appendix*, section 1.4. After collecting the duration times for a series of ON/OFF events, the probability density of each duration time was calculated with the following equation:

$$P(\tau_i) = \frac{2 \times \frac{N_{\tau,i}}{N_{\text{total}}}}{(\tau_{i+1} - \tau_i) + (\tau_i - \tau_{i-1})}$$

where $P(\tau_i)$ is the probability density of ON (OFF) event with duration time of τ_i , $N_{\tau,i}$ is the number of ON (OFF) event with duration time of τ_i , N_{total} is the total number of ON (OFF) events. The unit of $P(\tau_i)$ is s^{-1} .

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