Charge Carrier Activity on Single-Particle Photo(electro)catalysts: Toward Function in Solar Energy Conversion

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ABSTRACT: Understanding the fundamental properties of charge carriers on the surface of semiconductor photo(electro)catalysts is key to the rational design of efficient photo(electro)catalytic devices for sunlight-driven energy conversion. Here high spatial resolution information is always desirable because of the ubiquitous heterogeneity in semiconductor particles. In this Perspective, we review the latest advances in nanoscale imaging and quantitative analysis of charge carrier activities on individual semiconductor particles down to subparticle resolution, covering the approaches of single-molecule super-resolution fluorescence imaging, scanning electron microscopy, and photoluminescence microscopy. We further highlight direct, operando functional assessments of their performances toward the targeted photo(electro)catalytic processes through single- and subparticle photocurrent measurements. We also discuss the significance of establishing quantitative relations between the desired functions of photo(electro)catalysts and their surface charge carrier activities. These fundamental relations can provide guiding principles for rationally engineering photo(electro)catalytic systems, for example with cocatalysts, for a broad range of applications.

1. INTRODUCTION

Sunlight is the most abundant renewable energy resource; Nature has evolved sophisticated, efficient photosynthetic processes to harvest solar energy for the production of chemical energy.1,2 The quantity of solar energy irradiated on the earth’s surface is approximately $3 \times 10^{24}$ J per year, which is around $10^{4}$ times the global energy consumption annually, according to the U.S. Energy Information Administration. The past decade has witnessed dramatic increases in research efforts on solar energy utilization and concomitant decreases in the operating and capital costs of a variety of light-harvesting systems.3

Photo(electro)catalysis, a promising technology that can efficiently utilize the solar energy, has attracted widespread interest, both fundamentally and for a myriad of practical applications such as energy conversion,4–8 environmental remediation,9,10 and chemical transformation.11–17 Photo(electro)catalytic processes are effective in overcoming reaction energy barriers through taking advantage of the additional energy generated by photon absorption. Moreover, photo(electro)catalysis offers a direct means to access a diverse array of reaction pathways that are otherwise unattainable using nonphotochemical strategies. The often-cited advantages of photo(electro)catalytic processes include nontoxicity, low cost, high efficiency, and no secondary pollution.

Semiconductors are probably one of the most widely used light-harvesting materials for photo(electro)catalytic applications. Rationally engineered semiconducting materials have been demonstrated to exhibit simultaneously a number of prominent advantages for photo(electro)catalysis, such as enhanced chemical stability in liquid environments, strong catalytic performance toward targeted reactions, and suitable band gap energies for harvesting a significant portion of the solar spectrum.4,18–24 The primary processes in semiconductor-based photo(electro)catalysis consist of the absorption of light to generate charge carriers (i.e., electrons and holes), and the subsequent exploitation of photoexcited electrons and holes to trigger reduction and oxidation reactions, respectively. During photocatalysis, the build-in electrical field in the depletion layer separates the electron–hole pair; in a photoanode, holes drift to the semiconductor/liquid interface, whereas in a photocathode, electrons drift to the interface. Under photoelectrocatalytic conditions, an electrical bias is imposed on the semiconductor material, providing an additional driving force that, depending on the applied potential, drives one type of charge carrier to the semiconductor/liquid interface and the other type to be collected by the counter electrode. The key to enhancing the photo(electro)catalytic performance of semiconductors and ultimately realizing the intended applications resides in the understanding and tailoring of charge carrier reactions on the surfaces of these light-absorbing semiconducting materials. Because of the compositional, morphological, and architectural complexity of hierarchically constructed semiconductor-based photo(electro)catalytic systems, it is highly desired to elucidate the charge carrier behaviors at different structural levels, ranging from the macro-/mesoscopic level down to the single-/subparticle level. Characterization of charge carrier behaviors at the ensemble level (i.e., using bulk semiconductor films) can be performed using a variety of analytic techniques, such as photoluminescence spectroscopy, electrochemical impedance spectroscopy, surface photovoltage spectroscopy and intensity modulated photocurrent spectroscopy, to name a few.25,26

Recently, nanostructured semiconductor-based photo(electro)catalytic systems have been demonstrated to exhibit enhanced performance toward a broad range of emerging applications, compared with their unstructured counterparts that lack nanoscale features. The strong performance of these nanostructured catalytic systems stems mainly from a large surface to volume ratio that results in abundant active
adsorption sites and photo(electro)catalytic reaction sites, and a significantly shortened characteristic length scale for molecular diffusion and charge transport; the latter comes from the reduced particle size, the presence of interconnected porous networks, and the enhanced photon absorption efficiency because of a large number of light traveling paths. These advantageous features of a hierarchically constructed catalytic system are essentially governed by the properties of its nanosized building blocks (i.e., individual semiconductor nanoparticles); the overall performance of a judiciously devised, bulk material system can be modulated systematically by tuning the size, shape, and composition of individual nanoparticles. However, at the single-particle and subparticle level, the intrinsic and prevalent structural heterogeneity usually leads to particle-dependent, facet-dependent, and even single-surface-site-dependent catalytic properties, which are hidden from ensemble-averaged measurements. Hence it is challenging to use the conventional ensemble-level characterization techniques to study the charge carrier surface reactions on individual particles.

Moreover, for further performance improvement with the aim of developing efficient, robust, and economically viable photo(electro)catalytic systems, there is ubiquitous need for surface modification of semiconductor particles with other aid agents (such as plasmonic metals or cocatalysts), in order to increase light absorption efficiency, decrease electron–hole recombination, and enhance stability in humid or liquid environments. Notably, these modifications are usually performed at the nanoscale, thus leading to an increased structural complexity of each individual particle, which in turn exacerbates the heterogeneity issue. Hence it is even more difficult to decipher the charge carrier properties in these surface-modified semiconductor particles.

The ultimate metric for evaluating the performance of photo(electro)catalysts is how well they function for the intended applications. Such functional evaluation should be performed by direct quantification of the key parameters that dictate the catalytic efficacy for the application of interest, for example the amount of $\text{H}_2$ and $\text{O}_2$ evolved, and/or the quantity of electrical energy generated. Fundamental studies on the charge carrier behaviors of photo(electro)catalysts are truly useful only when these fundamental properties gained can be directly related to the functional assessment of these catalysts. The intrinsic heterogeneity present in nanoscale catalytic systems makes their accurate functional assessment and faithful performance interpretation an even bigger challenge. For example, the ensemble-averaged activity could be dominated by a small population of highly active catalyst particles. In another case, the photoelectrochemical energy conversion efficiency of a device composed of individual silicon nanowires has been shown to be limited by those individual nanowires with the worst performance. Furthermore, it is technologically challenging to perform functional evaluation on individual particles or small structural features; for instance, it is difficult to measure the quantity of gas evolved or the electricity generated at a single-particle and subparticle level.

Therefore, it is of paramount importance to study the charge carrier activities of photo(electro)catalysts and evaluate their functions at the highest spatial resolution possible, i.e., at the single-particle, and preferably, subparticle level, due to the prevalence of heterogeneity related to (i) the inevitable structural variations among individual catalytic particles, (ii) the increased morphological/architectural complexity in catalysts upon surface modifications, and (iii) the convoluted functional contributions from individual nanoscale building blocks in a realistic bulk catalytic system. In this Perspective, first, we review in Section 2 the latest developments on nanoscale imaging of charge carrier activities on single semiconductor particles, highlighting the progress made toward differentiating the variation of catalytic properties across different crystal facets of a single particle, different locations relative to the loaded plasmonic nanostructures, and different sites within the same crystal facet. Next, in Section 3, we provide an account of recent advances that have demonstrated direct, quantitative, in situ functional evaluation of photo-(electro)electrodes toward the targeted chemical processes at a single-particle and subparticle level. Last, in Section 4, we conclude this review with a discussion on the significance of establishing relationships between the desired functions of photocatalysts and the fundamental underlying charge carrier behaviors, offering insights into how to improve catalytic performance by leveraging the underpinning knowledge of charge carrier activities distilled from fundamental, mechanistic investigations. Interested readers are referred to other recent reviews that focus on different aspects of photo(electro)catalytic applications.

2. NANO SCALE IMAGING OF CHARGE CARRIER ACTIVITY ON SINGLE SEMICONDUCTOR PARTICLES

Here we discuss the latest work in imaging the activities of charge carriers on single semiconductor particles down to nanometer spatial resolution. These studies provide direct spatial differentiation on a single particle among different surface facets, different locations relative to loaded plasmonic nanoparticles, and different sites within a single surface facet. A number of approaches have been employed. Among them, single-molecule fluorescence microscopy coupled with fluorogenic probe reactions, directly measures the charge carrier surface activity on individual nanoparticles; it is quantitative, with single reaction temporal resolution and nanometer spatial resolution, and can be carried out in real time under operando conditions. However, the high sensitivity of single-molecule fluorescence microscopy comes with the expense of temporal resolution; ultrafast processes with time scales less than microseconds are difficult to probe by this technique. Electron microscopy is another nanometer-resolution approach: it can image surface charge carrier activities directly using appropriate deposition reactions as probes, but can only be performed ex situ and is not quantitative. Photoluminescence microscopy is capable of imaging charge carrier properties, and can be performed in real time under operando conditions, but only has diffraction-limited resolution (≈300 nm) and cannot probe a specific type of surface charge carrier. All these approaches, although capable of obtaining many insights into charge carrier activities, cannot directly assess the function of the semiconductors (for water splitting or oxygen reduction, for example); this general limitation will be addressed in Section 3 later.

2.1. Facet-Dependent Charge Carrier Activities on Single-Particle Photo(electro)catalysts. Tachikawa and co-workers used single-molecule fluorescence spectroscopy to investigate the facet dependence of photocatalytic activity on TiO$_2$ anatase crystals, which have a plate-like morphology with dimension of $\sim 4 \mu m \times 4 \mu m \times 1 \mu m$ (Figure 1A). They used an ultraviolet (UV) light (365 nm) to excite the charge carriers upon surface modifications, and (iii) the convoluted functional contributions from individual nanoscale building blocks in a realistic bulk catalytic system. In this Perspective, first, we review in Section 2 the latest developments on nanoscale imaging of charge carrier activities on single semiconductor particles, highlighting the progress made toward differentiating the variation of catalytic properties across different crystal facets of a single particle, different locations relative to the loaded plasmonic nanostructures, and different sites within the same crystal facet. Next, in Section 3, we provide an account of recent advances that have demonstrated direct, quantitative, in situ functional evaluation of photo-(electro)electrodes toward the targeted chemical processes at a single-particle and subparticle level. Last, in Section 4, we conclude this review with a discussion on the significance of establishing relationships between the desired functions of photocatalysts and the fundamental underlying charge carrier behaviors, offering insights into how to improve catalytic performance by leveraging the underpinning knowledge of charge carrier activities distilled from fundamental, mechanistic investigations. Interested readers are referred to other recent reviews that focus on different aspects of photo(electro)catalytic applications. Here we discuss the latest work in imaging the activities of charge carriers on single semiconductor particles down to nanometer spatial resolution. These studies provide direct spatial differentiation on a single particle among different surface facets, different locations relative to loaded plasmonic nanoparticles, and different sites within a single surface facet. A number of approaches have been employed. Among them, single-molecule fluorescence microscopy coupled with fluorogenic probe reactions, directly measures the charge carrier surface activity on individual nanoparticles; it is quantitative, with single reaction temporal resolution and nanometer spatial resolution, and can be carried out in real time under operando conditions. However, the high sensitivity of single-molecule fluorescence microscopy comes with the expense of temporal resolution; ultrafast processes with time scales less than microseconds are difficult to probe by this technique. Electron microscopy is another nanometer-resolution approach: it can image surface charge carrier activities directly using appropriate deposition reactions as probes, but can only be performed ex situ and is not quantitative. Photoluminescence microscopy is capable of imaging charge carrier properties, and can be performed in real time under operando conditions, but only has diffraction-limited resolution (≈300 nm) and cannot probe a specific type of surface charge carrier. All these approaches, although capable of obtaining many insights into charge carrier activities, cannot directly assess the function of the semiconductors (for water splitting or oxygen reduction, for example); this general limitation will be addressed in Section 3 later.
carriers in these crystals and probed the photogenerated electrons on the basal {001} and lateral {101} facets using a nitro-functionalized BODIPY dye (DN-BODIPY) (Figure 1A). The photocatalytic reduction of DN-BODIPY generates a fluorescent product molecule, an amine-functionalized BODIPY (HN-BODIPY), whose fluorescence was detected using a 488 nm laser over the course of the experiment. By localizing the positions of the individual reaction products, they observed more reaction products on the lateral {101} facet, reflecting its higher reduction activity than that of the basal {001} facet (Figure 1B).

They further determined the substrate concentration dependence of the specific photoreduction rate of the two types of facets (Figure 1C). Both show classical Langmuir–Hinshelwood saturation kinetics.54 The lateral {101} facet shows a higher saturation level (~4 times), further supporting its higher reduction activity. Moreover, it also has a larger adsorption equilibrium constant for the substrate (i.e., $K^{[101]} > K^{[001]}$). They attributed the higher reduction activity of the lateral {101} facet to the presence of defect sites or oxygen vacancies. On the other hand, the higher reduction activity could also be due to a larger population of electrons on the lateral {101} facet, which acts as an “electron reservoir” during the photogeneration process. Density functional theory (DFT) calculations55 predicted that the conduction band edge of the lateral {101} facet is slightly lower in energy than that of the basal {001} facet in anatase TiO$_2$, leading to a preferential electron flow toward the lateral {101} facet.

Moreover, using a fluorescent dye (4-aminophenyl BODIPY, i.e., H$_2$N-BODIPY) that probes the photogenerated holes, Majima and co-workers further observed that the basal {001} facet is more active for oxidative reactions, suggesting a preferential population of photogenerated holes at the basal facets, different from the behavior of electrons, which preferentially populate the lateral {101} facets. This difference in preference suggests a natural spatial separation of photogenerated electrons and holes toward different facets on a single anatase TiO$_2$ crystal, which is expected to reduce the recombination probability, leading to enhanced photocatalytic activity.

Li and co-workers studied the electron and hole activities on different facets of monoclinic decahedral-shaped bismuth vanadate (BiVO$_4$) microcrystals (a few microns wide and ~1 μm high in dimension) by monitoring the photocatalytic deposition of metal or metal oxide via scanning electron microscopy (SEM).47 They mixed a series of metal ion precursors (e.g., PtCl$_4^{2-}$, Ag$^+$, HAuCl$_4^−$, Pb$_2^+$, and Mn$^{2+}$) individually with BiVO$_4$ crystals and irradiated them using a Xe lamp ($\lambda > 420$ nm). The presence of PtCl$_4^{2-}$, Ag$^+$, or HAuCl$_4^−$ ions led to the formation of photooxidized metallic nanoparticles (confirmed via X-ray photoelectron spectroscopy) preferentially on the basal {010} facets (Figure 2A). In contrast, the presence of Pb$_2^+$ or Mn$^{2+}$ ions led to the formation of photooxidized PbO$_2$ and MnO$_x$ ($x = 1.5–2$) particles preferentially on the lateral {110} facets (Figure 2B).

They proposed that the preferential formations of the photooxidized metal nanoparticles on the basal {010} facets and of the photooxidized metal oxide particles on the lateral {110} facets reflect the more availabilities of electrons and holes on the {010} and {110} facets, respectively. In other words, facets have distinct preferences for different charge carriers (the possibility that different metal ion precursors adsorb preferentially was ruled out by changing precursor charges and isolectric point measurements of the facets). Using DFT calculations, they further showed that the conduction band edge of the lateral {110} facets is ~0.37 eV higher in energy than that of the basal {010} facet, while the valence band edge of the lateral {110} facet is also higher (by ~0.42 eV). These energy differences result in an electron flow from the lateral {110} facets to the basal {010} facets and a concurrent hole flow in the opposite direction upon light excitation, giving rise to charge separation toward different facets.

The facet-selective photodeposition of metals or metal oxides was also observed when a mixture of precursors were used (Figure 2C and D). Li and co-workers envisioned that the presence of both metals and metal oxides on different surface facets would facilitate charge carrier separation on the same crystal (e.g., Ag/MnO$_x$/BiVO$_4$ and Pt/PbO$_2$/BiVO$_4$). When used for photocatalytic water oxidation, these modified BiVO$_4$ crystals indeed showed higher O$_2$ evolution activities, presumably due to enhanced charge separation, than those BiVO$_4$ crystals on which the metal and metal oxide cocatalysts were deposited randomly via impregnation (Figure 2E).

In a related study earlier than Li et al., Majima’s group performed photodeposition of Pt and Au nanoparticles on TiO$_2$ mesocrystals and observed preferential deposition on the lateral anatase {101} facets.48 Chamtouri et al.49 extended a similar approach to study the solvent effect on photodeposition of metals on the {001} and {101} facets of TiO$_2$ anatase microcrystals that were used by Majima et al.

Using single-particle spectroelectrochemistry, Tachikawa and co-workers measured the single-particle photoluminescence (PL) of the same type of BiVO$_4$ microcrystals on an electrode in an electrolyte environment across a range of electrochemical potentials (Figure 3A).53 Under 405 nm laser excitation, the PL of these BiVO$_4$ crystals peaks at ~670 nm and results from the radiative recombination of conduction-band electrons and holes.
trapped at electronic states within the bandgap (i.e., trap states). These crystals (a few micrometers wide and ~1 μm high in dimension) are also much larger than the diffraction-limited resolution so that the PL could be resolved between the lateral {110} and basal {010} facets within a single particle under wide-field illumination and imaging conditions (Figure 3B). A positive potential of 2.05 V increases the number of holes at the trap states, which can recombine with conduction band electrons radiatively, resulting in an enhanced PL intensity. At a negative potential of −0.45 V, no holes at the trap states are available, and thus their radiative recombination with the conduction band electrodes is disrupted, leading to the PL quenching. At such a negative potential, the nonradiative recombination between the valence band holes and conduction band electrons should be the dominant process.

With the applied potential going more positive, they observed an enhanced PL, but the degree of enhancement differs on the lateral vs basal facets (Figure 3B, upper). With increasingly positive potentials, the PL enhancement of the lateral facets onsets at ~1.62 V vs RHE (i.e., $E_\text{onset}$), earlier than that (~1.7 V) for the basal facets (Figure 3C), indicating that the gap states where the photogenerated holes are trapped are easier to be depleted by the positive potential and thus higher in energy at the lateral facets than those at the basal facets. The amplitude of PL enhancement is also larger at the lateral facets, suggesting a higher density of these gap states there (Figure 3D). Both the higher energy and the higher density of these gap states on the lateral facets suggest a preference for the holes to reside there than on the basal facets. Using a fluorogenic oxidation reaction that probes surface holes (Figure 3E), they further imaged where the fluorescent reaction product would preferentially form on individual microcrystals. Significantly more products were detected at the lateral facets (Figure 3F), further supporting the more availability of surface holes here, consistent with the observations of Li and co-workers described above.47

With the applied potential going more negative, they observed PL quenching. The quenching is uniform across the lateral and basal facets (Figure 3B, lower) in contrast to the behavior of facet-dependent PL enhancement observed at
positive potentials. The same extent of negative-potential-induced PL quenching between the lateral and basal facets indicates that the conduction band edge is equivalent across these two types of facets and the photoexcited electrons are equally available across both facets. This observation differs from the conclusion by the Li group that photogenerated electrons are more available on the basal facet.47 These different conclusions might come from the difference in their experimental conditions: Tachikawa’s experiments were carried out with an electrode where the applied electrochemical potential may change the relative conduction band energies of the different facets, whereas Li’s experiments were carried out without electrochemical control over the potential of the semiconductor material but their depositions of metals and metal oxides could alter the intrinsic energy levels of the respective facets.

Xu, Alivisatos, and co-workers used single-molecule fluorescence microscopy to study the photocatalytic properties of Sb-doped TiO₂ anatase nanorods (Sb-TiO₂) of ∼3 nm in diameter and 90−150 nm in length (Figure 4A).56 Under 514 nm light excitation, the photogenerated holes and electrons react with surface adsorbed H₂O/OH⁻ and O₂ and produce hydroxyl radical and superoxide radical, respectively. (C) Total internal reflection fluorescence (TIRF) setup and fluorogenic probe reaction for single-molecule fluorescence imaging. (D−H) The time sequence of 2D histograms of every 2000 product molecules in 10² nm² bins. The yellow dashed lines indicate the upper and lower boundaries of the nanorod. Panels reproduced from reference 56. Copyright 2015, National Academy of Sciences.

Figure 4. Activity differences at side facets vs ends of Sb-TiO₂ nanorods. (A) Transmission electron microscopy (TEM) image of Sb-TiO₂ nanorods (∼125 nm length and ∼3 nm diameter). (B) Photogeneration of reactive radicals upon illumination of Sb-TiO₂ nanorods with 514 nm laser, in which hole and electron react with adsorbed H₂O/OH⁻ and O₂ and produce hydroxyl radical and superoxide radical, respectively. (C) Total internal reflection fluorescence (TIRF) setup and fluorogenic probe reaction for single-molecule fluorescence imaging. (D−H) The time sequence of 2D histograms of every 2000 product molecules in 10² nm² bins. The yellow dashed lines indicate the upper and lower boundaries of the nanorod. Panels reproduced from reference 56. Copyright 2015, National Academy of Sciences.

Figure 5. Surface electron activity and localization on Au/TiO₂ and TiO₂ particles. (A) SEM image of Au/TiO₂ particles. Blue arrows indicate the positions of gold nanoparticles on the TiO₂ particle. (B) Photocatalytic reduction reaction of DN-BODIPY derivatives to the corresponding fluorescent HN-BODIPY derivatives. (C−D) Locations of detected fluorescent products on a single TiO₂ (C) and 14 nm Au/TiO₂ (D) particle. The red circles in panel D are eye guides of clustering effects. (E) Overlaid SEM image of a Au/TiO₂ particle with corresponding detected reaction product locations. Red and blue circles surround the reactive sites and the gold nanoparticle, respectively. (F) Schematic illustration of proposed charge carrier excitation, separation, and transfer mechanisms for Au/TiO₂ systems under 365 nm (left scheme) or 488 nm (middle and right schemes) laser excitations. Panels A−E reproduced from references 59, 60. Copyrights 2011 and 2013, Royal Society and American Chemical Society. Panel F redrawn based on the work in reference 59.
probed by the molecule amplex red to generate the fluorescent product resorufin (Figure 4C), a fluorogenic reaction that was earlier used to study single metal nanoparticle catalysis; and the fluorescence of the product was induced by the same 514 nm laser.

They mapped the product locations on individual Sb-TiO2 nanorods over a period of many hours and observed that the spatial pattern of reactions changed over time (Figure 4D–H). At the beginning, more reactions were observed at the center of individual nanorods while much fewer were observed at the two ends (Figure 4D). Over time, more reactions were observed at the two ends, while fewer were observed at the center (Figure 4H).

Assuming that the surface active sites are low coordination surface sites, Xu, Alivisatos, and co-workers attributed the initial activity of the nanorod center to the presence of a higher structural defect density resulting from the seeded-growth mechanism of these nanorods, following the rationale of Zhou et al. in explaining the spatial reactivity patterns along the sides of single Au nanorods. For the two ends of the Sb-TiO2 nanorods, which in general have higher percentages of low-coordination corner and edge sites and are thus expected to have higher activity as well, they attributed their observed low initial activity to inhibition by some inert adsorbates. Why these adsorbates would only inhibit the low coordination sites at the ends but not at the nanorod center was unexplained, however.

They further attributed the activity decay of the nanorod center over time to either inhibition by catalytic products, or surface reconstruction that results in the loss of low coordination sites. The activity increase of the two ends over time was attributed to either desorption of those inert adsorbates, which made more surface sites available, or surface reconstruction that generated more low coordination sites at the ends over time. The latter is less likely, however, as surface reconstruction typically leads to more stable surfaces, i.e., higher coordination surface sites. Moreover, why the product inhibition does not occur at the nanorod ends was unexplained.

2.2. Charge Carrier Activity and Localization on Single Plasmonic-Metal/Semiconductor Heteronanostructure Particles. Plasmonic nanoparticles are often used to modify semiconductor particles to improve their photocatalytic properties. Majima and co-workers have used single-molecule super-resolution fluorescence imaging to investigate the photoreductive activities of Au nanoparticle modified anatase TiO2 particles (i.e., Au/TiO2) in comparison with the unmodified TiO2 nanoparticles. The anatase TiO2 particles are irregular in shape with size of ~100–200 nm; the Au nanoparticles used are ~5, 8, and 14 nm in size (Figure 5A). The fluorogenic probe reaction was the photocatalytic reduction of 3,4-dinitrophenyl-BODIPY (DN-BODIPY) sulfonate in Au-saturated aqueous or methanol solution (Figure 5B), similar to that in Figure 1A, which produces the fluorescent HN-BODIPY derivatives whose fluorescence was induced by a 488 nm laser. Methanol was used to scavenge the photogenerated holes in the reaction.

Using 365 nm light that can excite electrons across the bandgap of anatase TiO2, they observed that the photoreduced products are randomly distributed across the unmodified TiO2 particles (Figure 5C), indicating the photogenerated electrons are equally present on their surface sites. In contrast, on the Au/TiO2 particles, the detected photoreduced products tend to cluster spatially to subdiffraction limited regions of ~50 nm (Figure 5D), and the number of clusters scales with the average number of Au nanoparticles on each TiO2 particle. Majima and co-workers attributed this spatial clustering to the facile transfer of the photogenerated conduction band electrons on TiO2 to the Au nanoparticle (Figure 5F, left), on which most of the photoreductive probe reactions occur. Moreover, the overall photoreductive activity per TiO2 particle increases in the presence of Au nanoparticles likely because of the improved charge separation on these Au/TiO2 heteronanostructures as well as of the higher catalytic activity of Au particle surfaces. They further observed that smaller Au nanoparticles show higher activity for the photoreductive reactions; they rationalized it by the lower electron storage capacity of the smaller Au nanoparticles, which leads to faster interfacial electron transfer from the Au nanoparticles to the adsorbed reactants.

In the absence of the 365 nm light, the 488 nm laser that induces the product fluorescence cannot excite the TiO2 particles across the bandgap. Majima and co-workers did not observe significant photoreductive reactions on either TiO2 or Au particles, expectedly, but still detected reactions on Au/TiO2 particles, whereby the products there were clustered around Au nanoparticles (Figure 5E). As 488 nm can only cause sub-bandgap excitation of TiO2, which is typically inefficient, they rationalized that the observed photoreductive activity on Au/TiO2 particles should result from Au-plasmon enhanced photoexcitation on TiO2 that occur around the Au nanoparticle (Figure 5F, middle).

However, the photoexcited electrons from such Au-plasmon enhanced sub-bandgap photoexcitation of TiO2 should also be able to transfer to the Au nanoparticle, leading to charge separation as in the mechanism of Figure 5F left, and subsequently undergo reductive reactions more efficiently (Figure 5F, middle).

Alternatively, Majima et al. thought the 488 nm light could also excite the surface plasmon of Au nanoparticles, and the resulting hot electrons could transfer to the TiO2 particle, leading to photoreductive reactions around the Au nanoparticle (Figure 5F, right).

Fang, Vela, and co-workers performed a similar study of plasmonic metal–semiconductor heteronanostructures on Au-CdS nanorods, in which Au nanoparticles of 2–7 nm in size were grown at the two ends of CdS nanorods of ~178 nm in length and ~6 nm in diameter (Figure 6A). The fluorogenic oxidation of amplex red to resorufin was used as a probe reaction in their single-molecule imaging experiments (Figure 6B). Both H2O2 and O2 were present in their aqueous reaction solution. H2O2 can be oxidized by the photogenerated holes to produce hydroxyl radicals, which can oxidize amplex red to resorufin, effectively making this fluorogenic reaction a hole probe reaction. On the other hand, O2 can be reduced by the photogenerated electrons to become superoxide O2−, which can also oxidize amplex red to resorufin, effectively making this fluorogenic reaction an electron probe reaction. They were able to use the product residence time on the nanoparticle to differentiate these two reaction pathways in which the negatively charged resorufin molecules desorb more quickly on the reactive sites around photogenerated electrons than those reactive sites around photogenerated holes, even though the same probe molecule amplex red and the same fluorescent product molecule resorufin were involved in both pathways.

In the presence of a 532 nm laser, which excites the fluorescence of the reaction product resorufin as well as the surface plasmon of the Au nanoparticle, but cannot cause the
bandgap excitation of CdS, Fang et al. observed that both the hole-induced and electron-induced fluorescent reaction products tend to cluster at two separate locations (Figure 6C, lower), presumably at the two ends of individual Au-Cds nanorods, and the electron-induced reaction products are located closer to the middle of the nanorod. This observation supports the mechanism that upon exciting the Au nanoparticles, the holes stay on the Au nanoparticles while the electrons are transferred to the nearby sites of CdS nanorods, leading to charge separation (mechanism A; Figure 6C, upper). In contrast, in the presence of an additional 405 nm laser, which can cause bandgap excitation of CdS directly, the hole-induced reaction products are delocalized, while the electron-induced reactions are localized at the two ends (Figure 6D, lower) (the 532 nm laser is still present, as it is required to excite the product fluorescence and it also excites the Au nanoparticle plasmon). This observation reflects an opposite charge separation direction, in which the photogenerated electrons transfer to the Au particle and the holes accumulate on the CdS nanorod (mechanism B, Figure 6D, upper). These observations and mechanisms are consistent with those for the Au/TiO2 systems studied by Majima et al. (Figure S)\textsuperscript{59,60}.

2.3. Intrafacet Spatial Correlation of Holes and Electrons on Single-Particle Photoelectrodes. While the earlier single-molecule fluorescence imaging studies in Sections 2.1 and 2.2 focused on charge carrier activities on photocatalyst surfaces in the absence of electrochemical control, our group examined the photoelectrocatalytic processes on TiO2 nanorods under photoelectrochemical water oxidation conditions.\textsuperscript{62} These nanorods are 127 ± 27 nm in width and 1735 ± 437 nm in length, and are single crystals with well-defined \{100\} side facets (Figure 7A).\textsuperscript{62,63} We dispersed them on a transparent ITO working electrode in a microfluidic photoelectrochemical cell (Figure 7B) and used them as photoanodes to oxidize water under an applied electrochemical potential and 375 nm laser excitation, which excites charge carriers across TiO2’s bandgap. To probe the charge carrier reactions on the TiO2 surface, we doped the electrolyte solution with a low concentration of the fluorogenic redox-selective probe molecule amplex red or resazurin (Figure 7C). Under oxygen-free conditions, amplex red selectively probes hole-induced oxidation reactions; resazurin selectively probes electron-induced reduction reactions. Both reactions produce the fluorescent molecule resorufin, whose fluorescence was induced by a 532 nm laser, and imaged at the single-molecule level (Figure 7B).

Under steady-state photoelectrochemical water oxidation conditions, where the photoanodic current is dominated by water oxidation, we mapped the hole-induced and electron-induced reactions on individual TiO2 nanorods at nanometer precision across a range of electrochemical potentials (Figure 7D). Strikingly, we found that the reaction rates are nonuniform along the length of each nanorod: some nanorods exhibit hotspots of activity while others exhibit more delocalized reaction distributions, even though the same \{100\} crystal facets span the entire length (Figure 7A). These nonuniform activities indicate that the higher activity sites are not the \{100\} facet sites but probably regions with surface structural defects or impurity metal atoms, which are discernible by electron microscopy and elemental analysis, respectively.\textsuperscript{62}

Surprisingly, we found that there is a strong spatial correlation between hole- and electron-induced reactions on each nanorod (Figure 7E): wherever more hole-induced reactions were observed at more positive potentials, more electron-induced reactions were also observed at more negative potentials (Figure 7D), indicating that holes and electrons tend to reach and react at the same surface sites within a given nanorod facet and there is no significant lateral charge separation. With increasingly positive potentials, hole-induced reaction rates increase while electron-induced reaction rates decrease, as expected (Figure 7F). Interestingly, even at sufficiently positive potentials where there is a significant anodic current (>−0.3 V vs Ag/AgCl electrode; see later), the electron-induced surface reactions are still detectable, reporting the photogenerated electrons that escape from being collected by the ITO electrode and participate instead in surface reactions (i.e., surface recombination).

The potential dependences of hole-induced and electron-induced reaction rates allowed us to extract two effective rate constants \(k_h\) and \(k_e\) that reflect the local hole and electron activities on TiO2 nanorod surfaces, respectively. \(k_h\) of any nanorod spot is strongly correlated with its \(k_e\), further supporting that photogenerated holes and electrons prefer to reach and react at the same sites (Figure 7G). This spatial correlation of hole and electron reactions reflects a dual oxidation−reduction activity for the surface active sites and has functional implications for the underlying photoelectrochemical water oxidation processes (see Section 3.2 later).
Figure 7. Hole and electron activity mapping within the same facets of single TiO₂ nanorods under photoelectrochemical water oxidation. (A) TEM image (top) and cartoon (bottom) of a nanorod. (B) Experimental setup for wide-field single-molecule fluorescence imaging of photoelectrocatalysis via two-laser total internal reflection excitation, or for subnanorod photocurrent measurements via focused laser excitation, in a three-electrode microfluidic photoelectrochemical cell. (C) Redox-selective fluorogenic reactions. (D) Two-dimensional histogram (40 nm × 40 nm pixels) of all individual resorufin product molecules generated from hole-induced amplex red oxidation reactions at $E \geq -0.3$ V vs Ag/AgCl electrode (left) and electron-induced resazurin reduction reactions at $E \leq -0.4$ V (right) on a single TiO₂ nanorod. Solid white line: nanorod structural contour from SEM. Dashed white circles: focused 375 nm laser spots for photocurrent measurements and OEC deposition. Scale bar = 400 nm. (E) Pixel-to-pixel correlation (red dots) between the two-dimensional histograms of hole- and electron-induced surface reactions in D for the whole nanorod with a cross-correlation coefficient of $\rho = 0.84 \pm 0.01$. Black squares: binned and averaged data. Black line: linear fit. (F) Potential dependences of the specific hole-induced amplex red oxidation rate $V_{AR}$ (square symbols) and the specific electron-induced resazurin reduction rate $V_{RZ}$ (triangle symbols) at spots S1 and S2 on the nanorods in panel D. Solid lines: fits of theoretical modeling.62 (G) Correlation between the effective hole activity and electron activity rate constants, $k_h$ and $k_e$, for many nanorod spots (dots), with cross-correlation coefficients $\rho(k_h, k_e) = 0.75 \pm 0.03$. Solid triangles: binned and averaged data. Lines: linear fits. Panels reproduced from reference 62. Copyright 2016, Nature Publishing Group.

3. FUNCTIONAL EVALUATION OF SINGLE-PARTICLE PHOTOCATHODES

The single-molecule single-particle imaging approaches discussed in Section 2 are powerful with regard to their nanometer spatial resolution, single-molecule sensitivity, and operando measurements. Nevertheless, these studies probe merely the charge carrier behaviors of the nanoscale photo(electro)catalysts, and do not target directly the chemical processes that the photo(electro)catalysts are meant for, for example, water oxidation, proton reduction, or oxidation of pollutants. The measured charge carrier activities on the surface of individual photo(electro)catalyst particles may or may not directly relate to their performance for the targeted functions. Therefore, quantitative evaluation of the functional performance of photo(electro)catalysts at the single- to subparticle level is necessary and remains a nontrivial task. Ensemble activity measurements of photo(electro)catalysts toward targeted chemical processes such as oxygen evolution and proton reduction reactions can effectively offer information on these catalysts’ function, but they lack the single- to subparticle level information (e.g., Figure 2E). Photoluminescence can be measured on single semiconductor particles (e.g., Figure 3) and be related to their photocatalytic activities but this relation is deduced via pre-established correlation, and thus photoluminescence is merely an indirect performance metric. Measuring the targeted reaction products such as O₂ and H₂ would be desired but remains a significant challenge at the single- or subparticle level under photo(electro)catalytic conditions. In principle, it is possible to correlate measurable single-particle-level optical signals (e.g., light scattering intensity with the quantity of gas evolved from a single catalyst particle, based on a predetermined calibration relation. However, it is more difficult to quantify the evolved gas at the subparticle level, which has yet to be achieved. More importantly, for photoelectrocatalytic processes, the photoelectrochemical current is the key metric that quantifies directly the overall performance of the semiconductor materials. Here we focus on two recent studies that have pushed the photoelectrochemical current measurements down to the single-particle and subparticle level under photoelectrochemical proton reduction and water oxidation conditions.

3.1. Photoelectrochemistry of Single Silicon Nanowire Photocathodes. To measure the photoelectrochemical current of individual semiconductor nanostructures, Yang and co-workers grew vertically aligned Si nanowires through a vapor–liquid–solid (VLS) method on a patterned device. Each nanowire (8–20 µm in length and 500–800 nm in diameter) stands on an isolated silicon electrode that is individually connected to external circuits for electrical measurements (Figure 8A). The Si nanowires were further decorated with Pt nanoparticles by impregnation in a solution of HF/K₂PtCl₆. The Pt nanoparticles act as a cocatalyst that facilitates the
The electron flux from the entire surface of each individual nanowire (i.e., Fluxwire) was quantified using the well-defined nanowire geometry and single-wire photocurrents. By examining many individual nanowires, they found that those with larger diameter and shorter length generate higher (>6 times) flux of electrons under one-sunlight illumination conditions, highlighting the importance of nanowire geometry in photoelectrochemical devices (Figure 8C). Reduced electron flux on a single nanowire could potentially alleviate the requirement on the turnover frequency of loaded catalysts, and thus decrease the overpotential. Moreover, they found that the photovoltage output of an ensemble array of nanowires is limited by individual nanowires with poor performance, suggesting the necessity of improving nanowire homogeneity within an array.

Because of the small size of the patterned electrodes, this device approach by Yang and co-workers has very low background currents, enabling sensitive measurements of photoelectrochemical currents down to the pA level. The patterned device also naturally provides a multiplexed measurement, as many nanowires are present, although the individual nanowires’ photoelectrochemical properties need to be measured one at a time. Besides photoelectrochemistry, electrochemical properties (i.e., without illumination) can be equally investigated. This approach lacks subparticle information, however, as the photoelectrochemical processes at all possible surface sites on each nanowire contribute to the measured current.

3.2. Subparticle Photoelectrochemical Current Mapping of TiO2 Nanorods. Building on our single-molecule fluorescence imaging of charge carrier reactions on single TiO2 nanorods, we have used a photocurrent microscopy approach to evaluate the catalytic performance of TiO2 nanorods toward photoelectrochemical water oxidation reactions down to the subparticle level. To do so, we focused a 375 nm laser to a diffraction-limited spot (~390 nm in diameter) on a single TiO2 nanorod to excite charge carriers locally while measuring the photoelectrochemical current through the entire ITO working electrode (Figure 7B). The current is dominated by the water oxidation reactions and should reflect the local performance of the illuminated spot of the TiO2 nanorod.

We further used the hole- and electron-induced reaction maps (Figure 7D) as a guide, so as to measure purposely the photoelectrochemical current at an activity hotspot or at a spot with low charge carrier surface activities. The photocurrent-vs-potential behavior differs on spots taken on the same nanorod (Figure 9A), immediately showing subnanorod photoelectrochemical behaviors. Using a modified Gärtnert–Butler model and a Reichman model, we were able to analyze the dependences on the applied potential of photocurrent, hole-induced amplex red oxidation rate, and electron-induced resazurin reduction rate (Figure 9A and Figure 7F). For each nanorod spot, this quantitative analysis allowed us to extract out \( \eta \), an absorbed-photon-to-current efficiency within the depletion layer, and \( E_{on,GR} \), the photocurrent onset potential predicted by the Gärtnert-Butler model, as well as \( k_{h} \) and \( k_{e} \), two effective rate constants that represent hole and electron surface catalytic efficiencies within each illuminated spot.
activities, respectively. Interestingly, $\eta$ of individual spots have no significant correlation with their $E_{on,GB}$ indicating that a higher efficiency site does not necessarily have a lower onset potential (Figure 9B). Expectedly, $\eta$ of individual nanorod spots are strongly correlated with their $k_h$ (Figure 9C), as water oxidation is mediated by surface holes. This correlation also validates that surface hole activities are effective indicators and perhaps determinants of the underlying water oxidation efficiencies.

Moreover, $k_h$ for each spot is also strongly correlated with its $k_e$ value (Figure 7G), further supporting the idea that photogenerated holes and electrons prefer to reach and react at the same sites. Importantly, the strong correlation between $\eta$ and surface hole and electron activities suggests that the nanorods exhibiting higher water oxidation efficiency effectively mediate both oxidation and reduction reactions (which of the two processes dominates depends on the applied potential), making these sites also more effective for surface recombination than the lower efficiency sites. We conjecture that this dual oxidation–reduction activity might be helpful for efficient redox cycling at the high efficiency sites during photoelectrochemical water oxidation (Figure 9D). Under continuous photoelectrochemical water oxidation, when the photogenerated holes migrate to the TiO$_2$ surface, the surface sites become oxidized. When the surface sites transfer the holes subsequently to adsorbed OH$^-$ or H$_2$O to oxidize them, surface sites themselves become reduced, resulting in a complete redox cycling. Therefore, sites that have dual oxidation–reduction activities would be more efficient for water oxidations. On the other hand, when some electrons diffuse to surfaces (i.e., not completely extracted away by the electrode), the same sites would be more capable of accepting the electrons to undergo the same redox cycle, but just in an opposite direction.

Compared with the nanowire device approach in Figure 8, our photocurrent microscopy approach offers subparticle resolution, low cost (because no microfabrication is involved), and direct compatibility with optical microscopy, enabling direct measurements of surface charge carrier activities via fluorescence imaging experiments. However, the photocurrent measurements are very laborious, one spot at a time. Because of the large surface area of the ITO electrode, the background current is also very high, limiting the sensitivity to nA level at the moment. Using fabricated ITO microelectrodes could significantly increase the sensitivity, but the cost would increase.

4. IMPROVING PHOTOELECTRODE PERFORMANCE USING KNOWLEDGE OF CHARGE CARRIER SURFACE ACTIVITIES

The single-molecule single-particle level measurements of charge carrier activities on photo(electro)catalysts provide fundamental knowledge in understanding their properties for function. The ultimate goal of gaining this knowledge is of course to use it to guide the improvement of existing photo(electro)catalysts’ function or the design of new ones. For photoelectrocatalysts, one way to improve their function is to modify them with cocatalysts, such as oxygen evolution catalysts (OECs) for semiconductor photoanodes in photoelectrochemical water oxidation. However, because excess OEC material can hinder light absorption and decrease photoanode performance, its deposition needs to be carefully controlled. Yet it is unclear on what types of semiconductor surface sites OECs should be deposited to achieve optimal performance improvements, as various surface sites are present even on single crystals of semiconductors. This surface heterogeneity is more severe for nanostructured photoanodes that are desired materials because of their small charge carrier transport distances.

We have used the super-resolution maps (Figure 7D) of hole- and electron-induced reactions to guide the deposition of an OEC at charge carrier activity hotspots or low activity regions on single TiO$_2$ nanorod photoanodes. To achieve this site-selective deposition, we focused a 375 nm laser onto a target spot and deposited an amorphous cobalt-oxide-based OEC$^{72,73}$ photoelectrochemically (Figure 7B). The local generation of charge carriers results in the deposition of the OEC at the laser focus spot (Figure 10A). Subsequent photocurrent-vs-potential measurements at the deposition spots showed that expectedly, OEC deposition in general leads to an increase of photocurrent efficiency $\eta$ and a negative shift of the onset potential $E_{on,GB}$ across many individual nanorods (Figure 10B). At the individual spot level, the effect from OEC deposition varies significantly, however. For almost
all spots, the photocurrent efficiency $\eta$ increases (i.e., $\Delta \eta > 0$; Figure 10B). For $E_{\text{on,GB}}$, a minor but significant fraction (≈16%) show positive shifts (i.e., $\Delta E_{\text{on,GB}} > 0$; Figure 10B). For spots exhibiting the expected $\Delta E_{\text{on,GB}} < 0$, the magnitude of $\Delta E_{\text{on,GB}}$ is smaller for spots with larger $\Delta \eta$ (Figure 10B). Therefore, at the subnanorod level, photocurrent enhancement from OEC deposition on these nanorods are not necessarily accompanied by negative shifts in $E_{\text{on,GB}}$, and the magnitudes of their changes can be anticorrelated.

Most strikingly, we found that the relative (as well as absolute) changes in $\eta$ and $E_{\text{on,GB}}$ show strong negative correlations with their initial values before OEC was deposited. Spots with smaller initial $\eta$, characterized also by lower surface hole and electron activities, show larger enhancements (Figure 10C). Spots with more positive initial $E_{\text{on,GB}}$ exhibit larger negative shifts in $E_{\text{on,GB}}$ (Figure 10D). The negative correlations immediately identify the optimal sites for OEC deposition: for photocurrent enhancement, they are those with the lowest hole and electron activities, while for onset potential reduction, they are those with the most positive $E_{\text{on,GB}}$.

The identification of these optimal sites also highlighted the challenge of trying to engineer photoanodes with a minimal amount of catalyst. First, under typical photoelectrodeposition (or photodeposition) conditions, more catalyst material is deposited onto higher-activity sites (e.g., Figure 10E and references[67,77]) that show less OEC-induced photocurrent enhancement. Second, upon scanning the potential positively, their changes can be anticorrelated.

Despite these recent advances made toward single-particle photo(electro)catalysis discussed in this monograph, many research frontiers still await further development, for example, the realization of the rationalized photoanode modification with cocatalysts in Figure 10F at the bulk level or in actual functioning photoelectrochemical devices. It is also desired to develop cost-effective, scalable synthesis protocols and/or nanofabrication procedures that permit systematic interrogation of the relation between the photoelectrochemistry of nanoscale catalysts and their highly tunable chemical and morphological compositions. Moreover, the transient behavior of charge carrier activities at the subparticle level could be studied in principle by the techniques discussed in this Perspective, but has yet to be investigated in detail; such temporal information, when correlated to spatial information with nanometer precision, may offer additional insights into the fundamental mechanisms of important photoelectrocatalytic processes.

Another clear prospect for the future is the integration of all feasible high-resolution measurements and high-resolution manipulations to better modify photo(electro)catalysts with cocatalysts or plasmonic enhancers for applications. The many techniques and advances discussed in this Perspective should be strong foundations toward that.

5. CONCLUDING REMARK

The recent advances highlighted in this Perspective have pushed the quantitative measurements of charge carrier activities and functional performances of photo(electro)-catalysts down to nanometer spatial resolution, single-reaction temporal resolution, and under operating conditions. The fundamental knowledge gained also offered guiding principles to rationally engineer photoelectrodes for performance enhancements.

This Perspective also informs the advantages and disadvantages of different state-of-the-art techniques that have been employed to study charge carrier activity of single-particle photo(electro)catalysts. Electron microscopy offers high spatial resolution (<1 nm) but is an ex situ technique and does not provide quantitative information on the charge carrier behavior. Both single molecule microscopy and photoluminescence microscopy can be performed under operating conditions, but only the former offers subdiffraction-limit, nanometer spatial resolution. Single-particle photoelectrochemistry measurements and subparticle photocurrent mapping allow for direct functional evaluation, but need either elaborate device fabrication or laborious measurements.