

Understanding the Photoelectrochemical Behavior of Metal Nanoclusters: A Perspective

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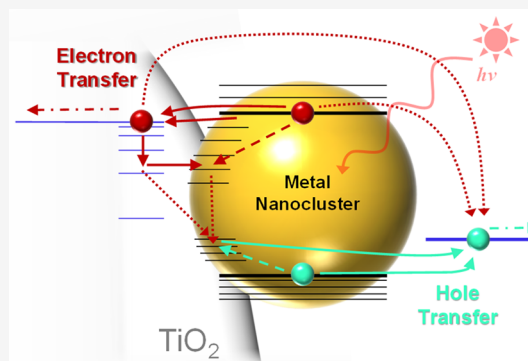
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ABSTRACT: Since the invention of metal nanocluster (NC)-based photoelectrochemical (PEC) devices, limited progress has been made in this area due to various intricacies associated with this new class of photoactive nanomaterials. Recent research has shown that NC–TiO₂ photoelectrodes possess charge separation and transfer complexities that are not seen in dye–TiO₂ or quantum dot–TiO₂ photoelectrodes. Even the degradation mechanism of NC-based photoelectrodes has a multitude of complexities, such that the degradation of NCs can have a silver lining of introducing plasmons to enhance charge separation in NC–TiO₂ photoelectrodes. Therefore, NC-based photoelectrodes require a comprehensive overview from a photoelectrochemistry perspective to better understand these systems. In this Perspective, we provide a review of recent progress in understanding the degradation and charge transfer mechanisms of NC–TiO₂ photoelectrodes. We also provide an overview of the various methodologies to control the properties of NCs for PEC applications and how these variables have been utilized to improve NC-based PEC device performance. Finally, we discuss the future of NC-based PEC devices and highlight the immense research opportunities present in this field.



1. INTRODUCTION

Metal nanoclusters (NCs) lie in the gray area between the realms of molecules and nanoparticles or nanocrystals.^{1,2} Molecules possess a discrete electronic structure, and metal nanoparticles (NPs) are capable of surface plasmon resonance (SPR) but still have continuous electronic structures like bulk metals.³ However, when formed into extremely small particles less than 2 nm, the quantum confinement of NCs becomes so strong that a discrete electronic structure appears.^{4,5} The continuous band structure is split into discrete highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels; in the case of Au, this transition has been found to occur at around ~200 Au atoms.^{6,7} Hence, metal NCs possess a molecule-like discrete electronic structure and are composed of a precise number of metal atoms and ligands.⁸ However, unlike molecules, NCs can also form type II heterostructures with wide band gap semiconductors similar to quantum dots (QDs).^{9,10} Therefore, metal NCs are considered neither NPs nor molecules. Hence, most authors refer to them as molecule-like structures.

Metal NCs provide exciting new opportunities for various applications, which stem from the fact that the properties of NCs can be tuned with a wide variety of variables.¹¹ Moreover, NCs possess many unique aspects that do not exist in traditional sensitizers, such as dyes or QDs.^{9,12–14} The bandgap of QDs is proportional to their size;^{15,16} hence, the size of the NCs seems to be an obvious variable in controlling

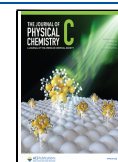
the optoelectronic properties of the NCs.¹⁷ Although NCs do show a size dependency of the HOMO–LUMO (HL) gap and excited-state properties (as early research has suggested), this dependency is short-ranged and cannot be generalized.^{18,19} In general, NCs do not follow the scaling law; therefore, their properties show more significant dependency on structure than size. For example, the synthesis of an Au NC with a body-centered cubic (*bcc*) structure instead of a hexagonal close-packed (*hcp*) structure can increase the excited-state lifetime by 3 orders of magnitude.^{20–22}

The doping of NCs is perhaps the easiest variable to control for tuning NCs for photoelectrochemical (PEC) applications.^{23–26} Doping NCs, even with a single heteroatom, can cause a dramatic shift in their properties.^{27,28} The introduction of a single Ag atom into Au₁₈(SR)₁₄ increases its extinction coefficient, photoluminescence (PL) lifetime, and recombination resistance.²⁹ Doping is also significant for PEC from a design perspective because dye–TiO₂ photoelectrodes usually require a cocatalyst for effective PEC applications. However,

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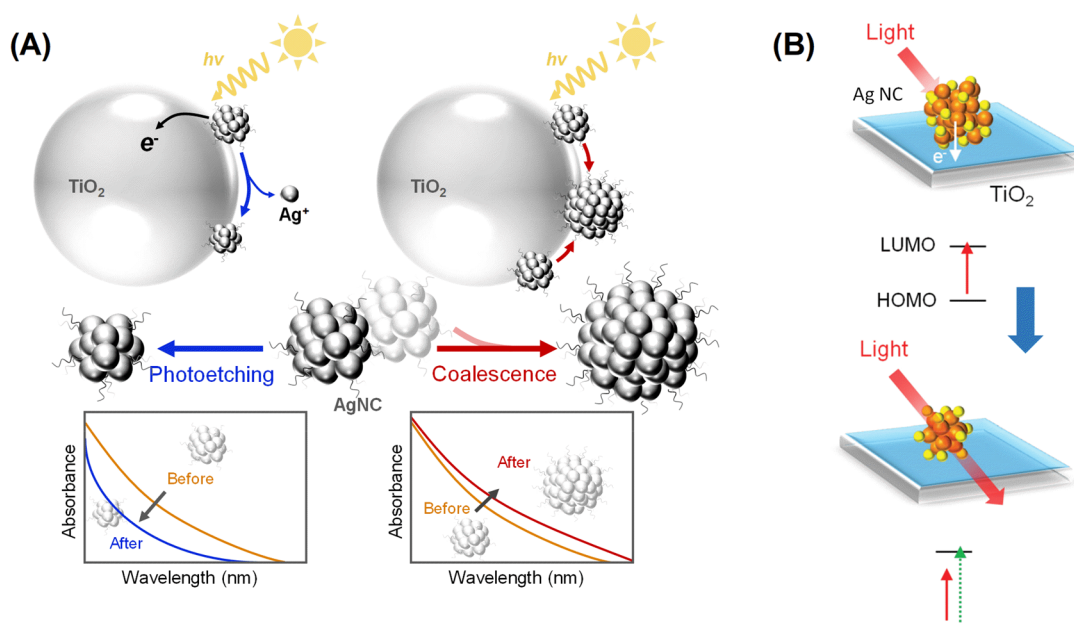


Figure 1. (A) Schematic representation of photoinduced etching and the transformation to nanoparticles and the resulting change in the UV-vis absorption spectra. Adapted from ref 14. Copyright 2019 American Chemical Society. (B) Schematic illustration of the interaction of light with NCs before and after photoetching. Adapted with permission from ref 61. Copyright 2015 Royal Society of Chemistry.

doping NCs with suitable heteroatoms can tune their catalytic ability toward the desired reaction and eliminate the need for a cocatalyst. For example, Choi et al.³⁰ introduced a Pt atom into Au₂₅(SR)₁₈ and Au₃₈(SR)₂₄ cores and showed that their catalytic activity in the hydrogen evolution reaction was significantly improved. This was attributed to the reduced Gibbs free energy for H₂ binding with the doped NCs. Ag-doping of Au₂₅(SR)₁₈ NCs can also improve their oxygen reduction reaction activity.³¹ Catalytic activities of NCs for various reactions have been well summarized in a recent review article.³²

Ligand engineering is another NC property control variable, which can be employed in two different ways:^{33–37} either (i) by controlling the metal-binding functional group in the ligand,³⁸ typically thiols or selenol, or (ii) by controlling the organic chain length of the ligand.^{33,39} Similar to doping, ligand engineering does not change the structure of the NCs, but it can still significantly tune their properties for a specific purpose. Kurashige et al.^{38,40} showed that replacing the thiol group with selenol can improve the stability of NCs. Co-protecting the NCs with negatively and positively charged ligands can produce additional absorption peaks via surface charge anisotropy.³³ Moreover, the introduction of electron-rich functional groups in the ligand chain can also enhance the PL of thiol-protected NCs.³⁹ Virtually, all the progress in the use of NCs for PEC devices can be attributed to the advent of glutathione (GSH)-protected NCs.^{11,41} GSH contains two carboxylic functional groups, and GSH-protected NCs are water-soluble, making it possible to load a large number of NCs on a TiO₂ surface via pH-assisted adsorption.^{42,43} GSH-protected NCs also possess very high photochemical stability compared to organosoluble NCs.

The general role of the sensitizer is to extend the absorption capacity of wide bandgap semiconductors to the visible and near-infrared regions of the solar spectrum.⁴⁴ Dye molecules and QDs are two classes of sensitizers that have been researched extensively; however, the performance improve-

ments of PEC devices based on these classes of sensitizers have plateaued.⁴⁵ Therefore, NCs provide new opportunities to design new PEC devices for effective light harvesting. The NC-based PEC solar cell device was invented in 2010, but it showed a limited performance output.⁴⁶ Later, the Kamat group⁴⁷ demonstrated a power conversion efficiency (PCE) of 2.3% with GSH-stabilized NCs and introduced the term “metal-cluster-sensitized solar cells (MCSSCs)”. Our group studied the size-dependent PCE of GSH-protected Au NCs and demonstrated a PCE of 3.80%.⁴⁸ Recently, a PCE of 4.22% has also been achieved with Ag-doped Au₁₈(SR)₁₄ NCs as a sensitizer.²⁹ However, progress in the field of NCs for light harvesting has been slow compared to other technologies such as perovskite solar cells.⁴⁹ This can be attributed to the difficulty in fabricating stable devices and the lack of a mechanistic understanding of the behavior of NCs in such devices.

As was discovered recently, the hole transfer mechanism from NC–TiO₂ photoelectrodes is also complicated due to various unforeseen processes at the NC–TiO₂ interface.^{13,50} Adsorption of NCs on TiO₂ creates a large number of surface states that can enhance recombination.⁹ Moreover, the hole transfer mechanism in NC–TiO₂ photoelectrodes was found to be size and electrolyte dependent.^{13,50} The degradation mechanism in NCs is also not straightforward; they can either decompose or coalesce into NPs, which can introduce plasmon-induced mechanisms.^{51,52} Even more interestingly, the adsorption mode of NCs with TiO₂ appears to play a dramatic role in the recombination behavior and hysteresis in MCSSCs.¹² All these observations require a fresh look at the field of NC research. In this Perspective, we have reviewed recent progress in understanding NC-based PEC devices’ charge transfer processes and degradation mechanisms. We have also reviewed the literature about controlling the optoelectronic properties of NCs and how those controls have been utilized to design PEC devices.

2. PHOTO-INDUCED TRANSFORMATION AND ETCHING

The interactions of NCs with light lead to various phenomena that need to be understood to effectively use NCs for PEC applications. When NCs are excited by photon absorption in the solution phase, they dissipate that energy via radiative or nonradiative recombination.^{53–56} However, NCs are primarily used as sensitizers in photoelectrochemistry to broaden the absorption capacity of wide bandgap semiconductors such as TiO₂. This configuration leads to two interesting phenomena to dissipate the absorbed energy: photoinduced transformation to NPs and etching (Figure 1A).^{9,14,57–60}

The primary purpose of an efficient sensitizer is to absorb light and create excitons with long lifetimes for charge separation. After the NCs absorb the photon, an exciton is generated, which consists of an electron–hole pair. Electrons reside at the LUMO level, and holes reside at the HOMO level. The electron is then transferred to the TiO₂ conduction band, and the hole needs to be transferred to the electrolyte to regenerate the NCs. Electron and hole transfer efficiencies depend on various factors, which will be discussed later. If the hole transfer is not efficient, it can lead to the accumulation of positive charges in the NCs. The accumulated charge can cause the oxidation of NCs and create metallic ions, which leads to a decrease in the size of the NCs; this process is called photoinduced etching.^{14,61} As the absorption edge of NCs is usually directly proportional to the size of the NCs, a decrease in the size of the NCs helps them circumvent the absorption of incident light. For example, if NCs are irradiated with light of wavelength λ , the etching process will continue until the NC sizes decrease to the extent when NCs can no longer absorb light of the wavelength λ (Figure 1B). UV–vis absorption spectroscopy can easily identify this mechanism because the etching of NCs decreases the absorption edge of the NCs (Figure 1A).

In the absence of effective hole transfer from NCs, another mechanism also appeared that can help NCs dissipate the absorbed energy. Light irradiation also causes photoinduced diffusion of NCs on the TiO₂ surface. This process can lead to the coalescence of NCs into larger NPs. The growth of NCs into larger NCs and eventually to the NP realm destroys their discrete electronic structure. The disappearance of discrete electronic structures also causes the appearance of SPR absorption. Therefore, larger NPs can dissipate the absorbed energy as phonons without the need for charge transfer. Thus, the effective removal of holes from NCs is crucial for their long-term stability. This mechanism can also be detected by UV–vis absorption spectroscopy as an increase in the absorption of the photoelectrodes and the appearance of a surface plasmon peak (Figure 1A). Transmission electron microscopy can also be used to observe the formation of larger NPs.

Which NC degradation mechanism will be present depends on the structure of the NC photoelectrode. Kogo et al.⁶¹ observed that shining a 760 nm light on the Ag NCs supported on a TiO₂ crystal caused the etching of the NCs. The etching of NCs continued until the absorption edge of the NCs shifted to a shorter wavelength than 760 nm. However, Khan et al.⁹ observed that Au NCs transformed to larger NPs upon light exposure. Abbas et al.¹⁴ also observed that Ag NCs coalesce into larger NPs under irradiation. Therefore, it is important to identify the factors that could lead to the occurrence of certain

NC degradation mechanisms. Two possible reasons for this exist. First, it could be due to the type of exposed light. If a monochromatic light of a single wavelength is used, the etching process is a viable option to prevent the buildup of positive charges in the NCs. All light-induced processes would cease once the NC size has been reduced to the point that they lose the ability to absorb an irradiated photon. However, under exposure to a continuum of light (e.g., simulated solar spectrum), the etching process would only stop if NCs disappeared completely.

Another process that needs to be considered is the photoinduced diffusion of NCs. NCs experience photoinduced diffusion upon exposure to light. If they can get together, then they can merge into larger NPs and dissipate the incident energy via SPR. So far, the etching of NCs has been observed on a single crystal TiO₂ substrate, and the formation of NPs has been observed on a mesoporous TiO₂ substrate. We believe that distances among the NCs may play a key role. On a mesoporous TiO₂ substrate, a large number of NCs are adsorbed with an average distance of ~ 10 nm. Therefore, NCs would be able to get together and form larger particles via light-induced diffusion. However, the distance between NCs on a single crystal substrate is usually much larger (~ 200 nm). On a single crystal substrate, NCs would also experience light-induced diffusion; however, they undergo the oxidation process before the NCs could merge and form larger particles. Once their size has reduced to the point that they do not absorb the incident light, the light-induced diffusion stops. Hence, the etching mechanism is observed as the degradation process.

The transformation of NCs into plasmonic NPs has enormous implications for PEC performance. At first glance, the transformation process can be considered a photocurrent degradation mechanism. As the number of NPs on the oxide electrode surface increases, the number of NCs is reduced, resulting in a loss of photocurrent. However, plasmonic NPs can also positively impact charge separation processes. Surface plasmon enhanced charge separation is a well-documented process.^{52,62–65} Therefore, the presence of a certain number of NPs could be beneficial. However, NPs could also act as recombination centers. Consequently, a continuous and unhindered photoinduced growth of NCs to NPs is detrimental. Hence, a balance between the number of NPs and NCs on the oxide semiconductor surface is critical to achieve improved performance. In the Au₂₅–TiO₂ photoelectrode, an SPR-enhanced photocurrent has already been achieved.⁹ The impact of plasmonic NPs on charge separation will be discussed in more detail in the latter part of this Perspective.

It has also been observed that Ag NCs transform into NPs more rapidly than Au NCs.⁶⁶ However, is the transformation process size dependent? If yes, is it only due to the hole transfer ability of the NCs or is it also related to the thermodynamic stability of the NCs? All these questions remain unanswered, and further research is underway in our laboratory to answer these questions.

3. CORE ENGINEERING

Structurally, NCs have two important components that can be used to control their electronic structure and excited-state behavior: surface ligand–metal motifs and a metallic core. Changes in surface ligands have been widely used to tune the optoelectronic properties of NCs.^{34–36} However, the core

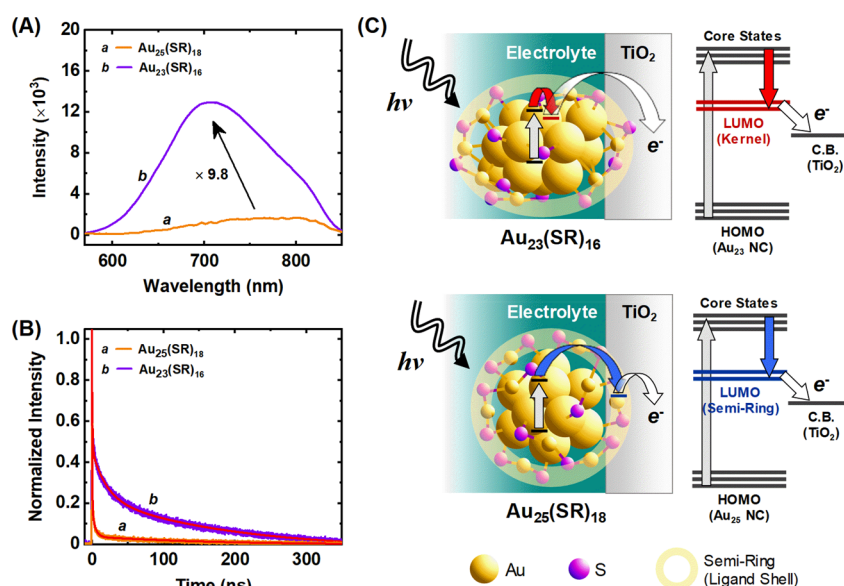


Figure 2. (A) Steady-state PL intensity and (B) PL lifetimes of $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Au}_{23}(\text{SR})_{16}$ NCs. (C) Illustration of excited-state decay pathways in $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Au}_{23}(\text{SR})_{16}$ NCs. Adapted from ref 72. Copyright 2021 American Chemical Society.

restructuring of the NCs also impacts the optoelectronic behavior of the NCs. Therefore, unlike large NPs, NCs typically do not follow the scaling law because the properties of the NCs can be significantly influenced by changes in the core structure.⁶⁷ The observation of subnanosecond to microsecond long excited-state lifetimes has been attributed to the core structure of the NCs.²² In some Au NCs, the core structure consists of an arrangement of Au_4 tetrahedrons that can be arranged into face-centered cubic (*fcc*), *bcc*, or *hcp* structures.^{68–70} The *bcc* core structure of Au NCs can produce an excited-state lifetime of several microseconds, but excited electrons decay to the ground state within ~ 1 ns in an *hcp* core.²² In these NCs, the charge transfer processes are mostly centered at the core of the NCs. However, in NCs that do not exhibit these structures, the excited-state behavior is dictated by the ligand-to-metal charge transfer process.^{19,71} Even in those NCs, the core can be tuned to achieve a desired excited-state behavior from NCs.

Our group demonstrated this behavior on $\text{Au}_{25}(\text{SR})_{18}$ NCs as a model system.⁷² We used a simple chemical etching process to transform $\text{Au}_{25}(\text{SR})_{18}$ to $\text{Au}_{23}(\text{SR})_{16}$ NCs. This process removed two Au atoms from the oligomer shell and restructured the core from an Au_{13} icosahedron to an Au_{15} cuboctahedron. $\text{Au}_{23}(\text{SR})_{16}$ displayed almost ten times higher PL than $\text{Au}_{25}(\text{SR})_{18}$ due to this simple change in core structure (Figure 2A). The increased PL intensity was also reflected in the prolonged PL lifetime of $\text{Au}_{23}(\text{SR})_{16}$ to 221 ns compared to 47.5 ns of $\text{Au}_{25}(\text{SR})_{18}$ (Figure 2B). The change in core structure influenced the recombination mechanism of $\text{Au}_{23}(\text{SR})_{16}$ at a fundamental level. In $\text{Au}_{25}(\text{SR})_{18}$ NCs, the PL mechanism is ascribed to ligand-to-metal charge transfer (Figure 2C).^{54,73} Hence, the Au(I)-ligand shell dictates the PL of the behavior of $\text{Au}_{25}(\text{SR})_{18}$ NCs, and the long-lived triplet state that acts as a reservoir for PL is located at the ligand shell. In $\text{Au}_{23}(\text{SR})_{16}$ NCs, however, the recombination pathways are solely centered at the Au_{15} kernel, and the ligand shell does not play a significant role.⁷⁴ Furthermore, in $\text{Au}_{25}(\text{SR})_{18}$ NCs, the core is usually the center of the high nonradiative recombination rate. However, the change of the Au_{13}

icosahedron to the Au_{15} cuboctahedron reduced the core relaxation in $\text{Au}_{23}(\text{SR})_{16}$.⁷² The reduced vibrational freedom decreased the nonradiative recombination that was predominant in $\text{Au}_{25}(\text{SR})_{18}$ and thus enhanced the PL of $\text{Au}_{23}(\text{SR})_{16}$.

However, the purpose of NCs in PEC applications is to achieve higher photocurrent, which requires efficient charge injection into the oxide film. Therefore, a high PL may not necessarily bear fruit in a PEC device. In a typical PEC device, NCs are attached to the mesoporous TiO_2 surface to be used as a photoelectrode. In $\text{Au}_{23}(\text{SR})_{16}$, the PL was centered at the core of the NCs. Hence, the long-lived excited states are located in the core of the NCs, farther away from the NC surface, which is usually attached to the oxide surface. This increased distance between the TiO_2 surface and long-lived excited states of $\text{Au}_{23}(\text{SR})_{16}$ did not increase the charge injection significantly compared to $\text{Au}_{25}(\text{SR})_{18}$. Nonetheless, when an Au_{23} - TiO_2 photoelectrode was used in solar cell applications, the PCE increased from 2.42% to 3.67%. Au_{23} -sensitized solar cells (Au_{23} -SSCs) showed a considerable increase in both the short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}). This increased PEC performance was mainly attributed to the recombination behavior of the Au_{23} - TiO_2 photoelectrodes. The attachment of $\text{Au}_{23}(\text{SR})_{16}$ to the TiO_2 surface produced greater band bending compared to Au_{25} - TiO_2 , which reduced the electron recombination with the NCs. Moreover, the β parameter used to identify the recombination pathways in the sensitized solar cells was 0.58 in the Au_{23} -SSCs compared to 0.39 in the Au_{25} -SSCs. In the β recombination model, a value of 0.5–0.7 signifies the minimal role of the sensitizer in the recombination.⁷⁵ A value lower than 0.5 shows that the sensitizer plays an active role in the recombination.⁷⁶ Therefore, while the charge injection for Au_{23} -SSC was similar to that for Au_{25} -SSC, the direct recombination with NCs was significantly reduced, which increased the PEC performance. These results highlight that core restructuring is an important tool for optical applications as well as optoelectronic applications of the NCs.

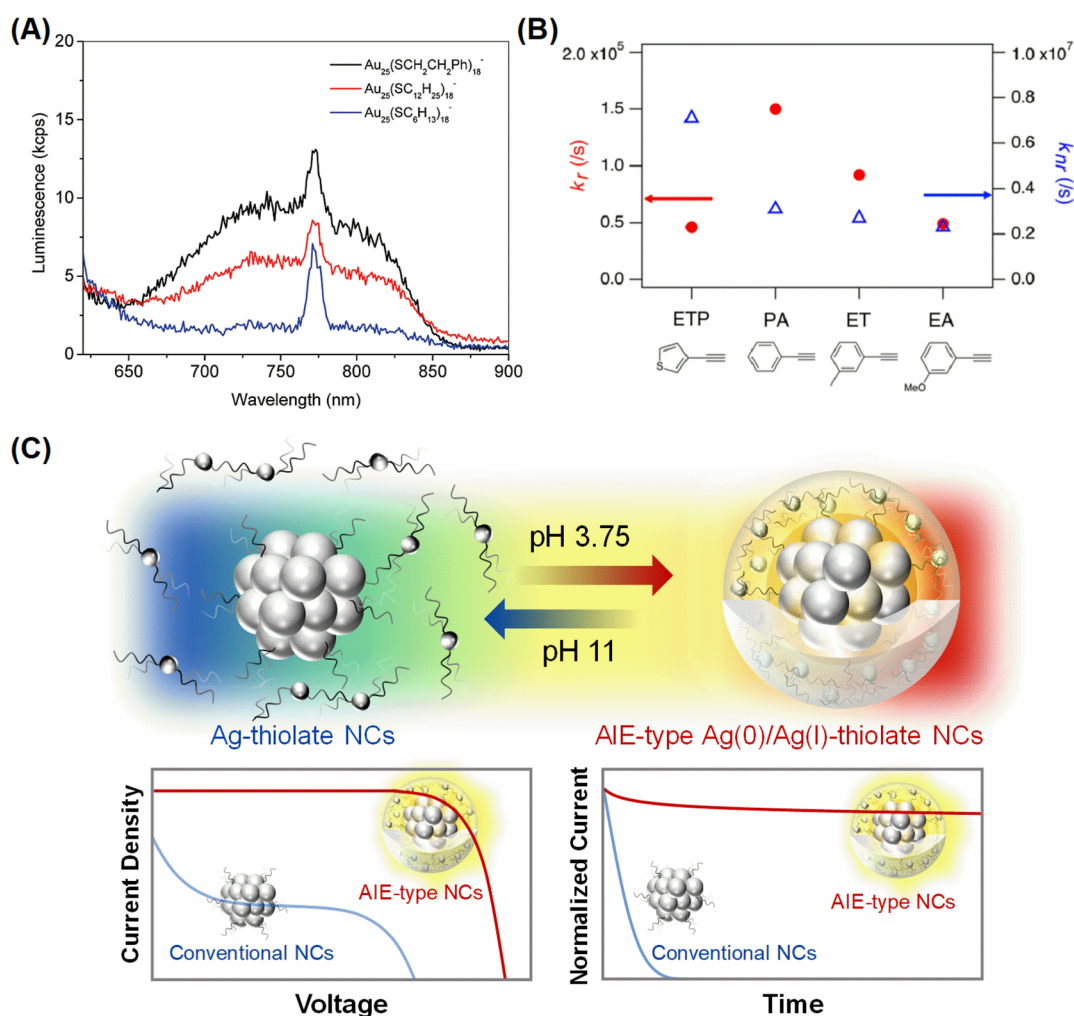


Figure 3. (A) Steady-state PL intensity of $\text{Au}_{25}(\text{SR})_{18}$ NCs protected with various ligands. Adapted from ref 39. Copyright 2010 American Chemical Society. (B) Radiative (k_r) and nonradiative (k_{nr}) recombination of $\text{Au}_{22}(\text{C}\equiv\text{CR})_{18}$ NCs protected with various ligands. Adapted from ref 83. Copyright 2019 American Chemical Society. (C) Schematic illustration of current–voltage (J – V) curves and stability of MCSSCs based on conventional and AIE-type core–shell Ag NCs. Adapted from ref 87. Copyright 2019 American Chemical Society.

4. LIGAND ENGINEERING

Ligands play an indispensable role in the determination of the optical and optoelectronic properties of the NCs. Ligands both protect the NCs and actively participate in the determination of the electronic structure of the NCs.^{5,40,77–79} For example, the sulfur atoms in thiolated NCs contribute significantly to the HOMO and LUMO.^{80,81} Moreover, the ligand-to-metal charge transfer is usually the dominant mechanism for the PL of most NCs.^{54,71,82} The triplet states responsible for the long lifetime of the NCs are also situated in the oligomer shell. Hence, NCs are more similar to organometallic molecules than QDs with respect to their electronic structure. Wu and Jin³⁹ systematically showed the effect of ligands on the PL of thiolated $\text{Au}_{25}(\text{SR})_{18}$ NCs. The PL of Au NCs depends on the electron-donating ability of the protecting ligand (Figure 3A). Therefore, electron-rich functional groups in the ligand chain increased the PL of the NCs. The electron donation of ligands can also be enhanced if the core of the NCs has a positive charge. Ito et al.⁸³ also showed that tuning the ligand functional groups is a key to enhancing the PL of the NCs (Figure 3B). The nonradiative recombination in NCs can be suppressed by reducing the relaxation in the oligomer shell.⁸⁴ Pyo et al.⁵⁶ achieved a quantum yield of 60% via rigidification

of the oligomer shell of the $\text{Au}_{22}(\text{SR})_{18}$ NCs by tetraoctylammonium cation wrapping.

As stated before, the excited-state lifetime of NCs depends strongly on the protecting ligand. Moreover, long excited-state lifetimes are essential for the efficient use of NCs in light harvesting applications. Hence, ligands also play a crucial role in successfully utilizing NCs in PEC applications. This is the reason why almost all publications on NC utilization in PEC applications make use of GSH-protected NCs.^{11,41,46,85,86} This is mainly because of their exceptional photochemical stability and long excited-state lifetimes.⁷¹ While the GSH-protected Au NCs display good stability in corrosive I^-/I_3^- redox environments, GSH-protected Ag NCs decompose readily, even in mild $\text{Co}^{2+}/\text{Co}^{3+}$ redox environments (Figure 3C).^{48,87,88} Iodide is very corrosive to gold. Therefore, GSH-protected Au NCs that can withstand the I^-/I_3^- redox environment is extraordinary. However, the GSH shell was unable to protect Ag NCs even from the $\text{Co}^{2+}/\text{Co}^{3+}$ redox couple. Therefore, a thicker shell was required to isolate the Ag atoms from the redox environment. Hence, Ag(I)-thiolate oligomers were condensed onto the Ag NC by pH manipulation to form a core–shell structure (Figure 3C). These Ag(0)/Ag(I)-thiolate

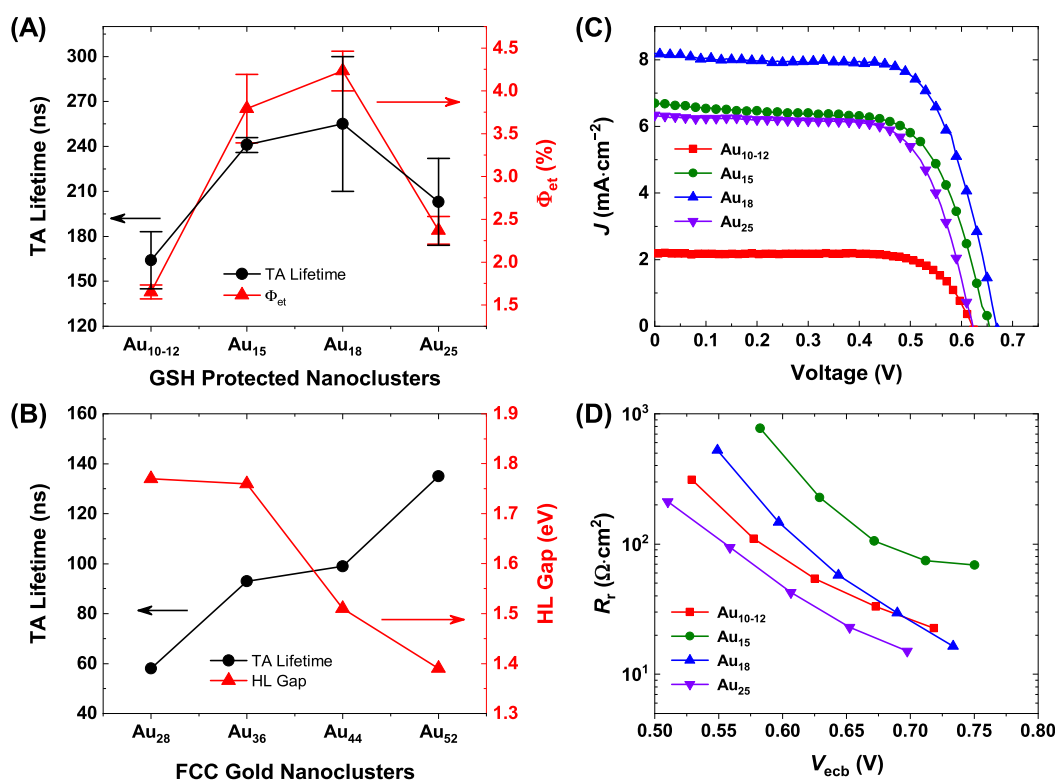


Figure 4. (A) Transient absorption (TA) excited-state lifetimes and charge transfer efficiencies (Φ_{et}) of Au_{10-12} , Au_{15} , Au_{18} , and Au_{25} NCs. Adapted from ref 19. Copyright 2014 American Chemical Society. (B) TA lifetimes and HL gap of various *fcc* Au NCs. Adapted from ref 69. Copyright 2017 American Chemical Society. (C) Current–voltage (J – V) curves and (D) recombination resistance (R_r) of MCSSCs based on Au_{10-12} , Au_{15} , Au_{18} , and Au_{25} NCs. Adapted from ref 48. Copyright 2016 American Chemical Society.

core–shell structures significantly improved the stability of the Ag NCs in solar cells.⁸⁷

5. SIZE CONTROL

Excited-state dynamics have a complicated relationship with the size of the NCs.^{19,69} Usually, an increase in the NC size decreases its HL gap, and it reduces its excited-state lifetime.¹⁹ However, NCs do not strictly follow the scaling law, especially when NCs consist of 50 or fewer metallic atoms.^{18,70} The Kamat group carried out one of the first studies about the excited-state dynamics of the NCs.^{19,71} They studied the excited-state behavior of four GSH-stabilized, water-soluble NCs and found a correlation between the size and excited-state lifetime (Figure 4A). Interestingly, the excited-state lifetime of the NCs with a core showed a short and a long component, but homoleptic NCs (which do not have a metallic core) did not show any short relaxation.⁸⁹ Therefore, the short lifetime component was linked to the relaxation within the core, and the long component was attributed to the ligand-to-metal charge transfer. Kwak et al.⁹⁰ also found that NCs with a wider HL gap showed longer excited-state lifetimes. This is in sharp contrast to the QDs, which show a decrease in the lifetime when they are formed into smaller sizes.^{91,92} Hence, QDs with large bandgaps show faster excited-state decay. This is mainly attributed to the larger number of surface states in smaller QDs due to the high surface area. However, recent studies suggest that NCs have only a weak correlation with size and excited-state lifetimes.⁶⁷ It is hard to make a simple correlation between the NC's size and excited-state lifetime due to the huge variation in the lifetime of NCs caused by structural

varieties. For example, in *fcc* structured Au NCs, an increase in size increases their excited-state lifetime (Figure 4B).⁶⁹

The complicated relationship between NC size and optoelectronic properties is also reflected in the solar cell performance of MCSSCs. Abbas et al.⁴⁸ studied the effect of NC size on solar cell performance with $\text{Au}_{10-12}(\text{SR})_{10-12}$, $\text{Au}_{15}(\text{SR})_{13}$, $\text{Au}_{18}(\text{SR})_{14}$, and $\text{Au}_{25}(\text{SR})_{18}$ NCs. These four NCs seemed to follow the scaling law, as the size increase was associated with a decrease in the HL gap. Among these four NCs, $\text{Au}_{18}(\text{SR})_{14}$ was the best sensitizer (Figure 4C). It showed the highest PCE of 3.80%. However, an increase in the size beyond $\text{Au}_{18}(\text{SR})_{14}$ decreased the PCE to 2.81% due to the high recombination rate in $\text{Au}_{25}(\text{SR})_{18}$ (Figure 4D). However, recent studies have indicated that the PCE performance of NCs correlates more with structure than size. For example, $\text{Au}_{22}(\text{SR})_{18}$ is larger than $\text{Au}_{18}(\text{SR})_{14}$ and has a wider HL gap.¹² $\text{Au}_{23}(\text{SR})_{16}$ NCs have also been reported to possess a PCE of 3.67% and a long PL lifetime.⁷² Even in PEC devices, Au NCs have shown hole transfer mechanisms that depend on size, but more research is needed to fill the gap and understand the size, structure, and excited-state correlations in working PEC devices.^{13,50}

6. SLUGGISH REGENERATION

Although NCs of other elements have been prepared, Ag and Au NCs are the main candidates for PEC applications due to their photochemical stability. However, the stability of NCs for PEC applications still requires much attention. As discussed earlier, NCs can either degrade via complete oxidation into ions or transform into NPs. Besides chemical corrosion by the electrolytes, sluggish regeneration by hole transfer to the

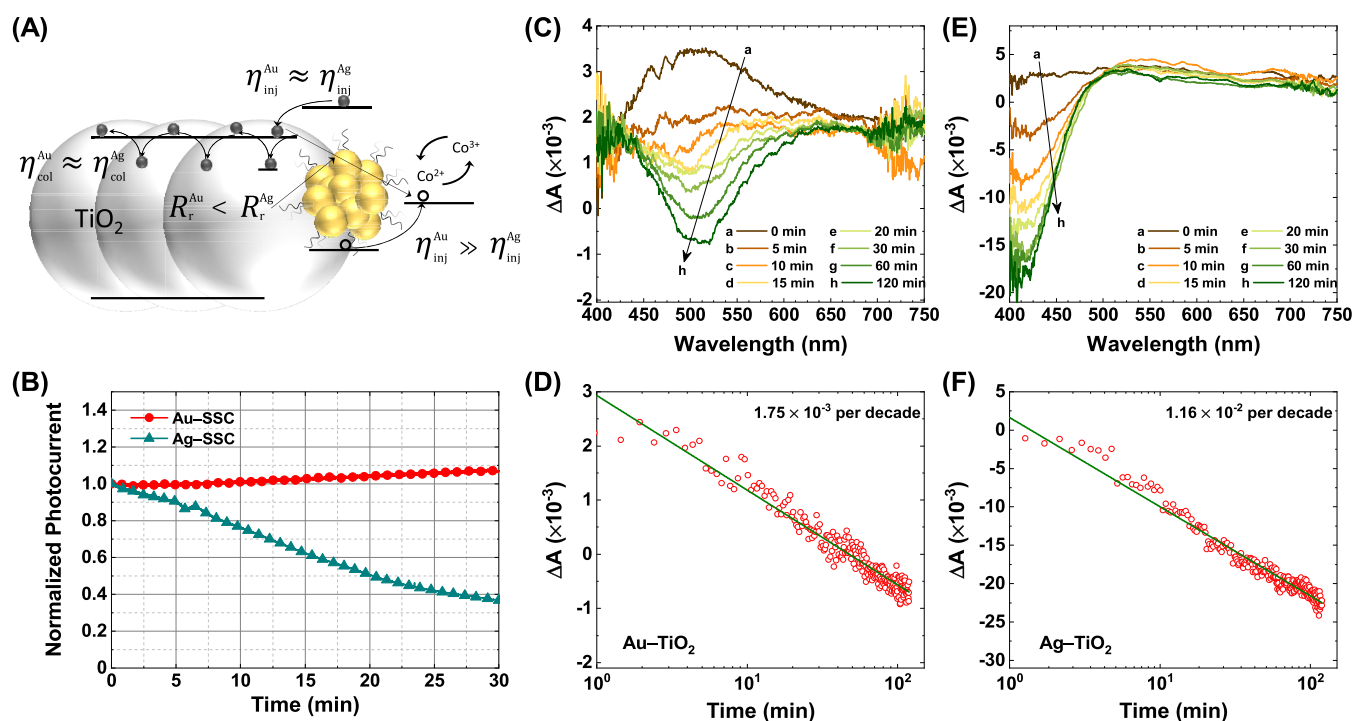


Figure 5. (A) Comparison of various mechanistic processes in photocurrent generation in Au-SSC and Ag-SSC. (B) Photocurrent stability of Au-SSC and Ag-SSC. (C, E) Transient absorption spectra and (D, F) growth of bleaching signals of Au-TiO₂ and Ag-TiO₂ photoelectrodes, respectively. Adapted from ref 66. Copyright 2020 American Chemical Society.

electrolyte is the major reason for NC degradation. Both Au and Ag NCs suffer from inefficient hole transfer to the electrolyte. However, this problem is more profound in Ag NCs.

There are four major components to photocurrent generation in photoelectrodes that include light harvesting, charge injection, regeneration, and charge collection efficiencies.⁹³ Abbas et al.⁶⁶ used Ag and Au NCs of similar light harvesting, charge injection, and charge collection efficiencies to discern the effect of NC regeneration on the solar cell device performance (Figure 5A). Interestingly, there was a significant difference in the regeneration efficiency of Ag and Au NCs, which was also reflected in the device stability. When a photon is absorbed and an exciton is created, the electron from the LUMO of NC is injected into the TiO₂ conduction band, and the hole is left in the HOMO of the NC. The hole from the NC needs to be transferred to the electrolyte to regenerate the neutral state of the NC. The HOMO typically has the highest contribution from the metallic atoms in the core of the NCs.⁹⁴ Therefore, oxidation of the NC core occurs if the hole is not transferred effectively to the electrolyte. Hence, oxidation of the NCs combined with the photoinduced diffusion led to the formation of large plasmonic NPs on the TiO₂ surface. Due to the slow regeneration, Ag-SSC can degrade to 40% of the initial current within 30 min, but Au-SSC can sustain prolonged operation in the Co²⁺/Co³⁺ redox environment (Figure 5B).

Therefore, different regeneration rates can lead to different rates of NP formation among Au and Ag NCs. This process has been observed by transient absorption spectroscopy (TAS) in Au-TiO₂ and Ag-TiO₂ photoelectrodes. In TAS, the SPR usually appears as a bleaching signal and molecular excited states appear as positive signals.^{95,96} The bleaching signals of Ag NPs and Au NPs are typically located at 520 and 460 nm,

respectively.^{96–98} However, their location can vary depending upon the shape and other characteristics of the NPs.⁹⁹ Continuous TAS measurements under continuous laser exposure showed a significant difference between the Au and Ag NCs (Figure 5C–F). An NP bleaching signal was observed in both NCs. However, the growth of the plasmonic signal was an order of magnitude higher in Ag-TiO₂ films than in Au-TiO₂. Therefore, sluggish regeneration is one of the major bottlenecks in Ag NCs, which limits their use in PEC applications.

7. HETEROATOM DOPING

Metal NCs consist of a precise and small number of metallic atoms. Unlike QDs, doping the NCs even with a single heteroatom can dramatically change their properties.^{27,100–102} Moreover, dopant atoms can also be chosen to tune properties for a specific application. For example, Pt and Pd possess high catalytic abilities; therefore, doping the Au NCs with a single Pt or Pd atom significantly increases their catalytic abilities.^{23,30} Ag is usually a good candidate for improving the optical properties of NCs because an absence of Landau damping in Ag can be the source of a higher extinction coefficient in the doped NC.¹⁰³ As discussed in the previous section, Ag NCs suffer from severely low regeneration efficiency. However, Ag-SSCs do possess better recombination kinetics than Au-SSCs. Furthermore, Ag NCs typically have higher extinction coefficients than Au NCs. Therefore, the combination of the benefits of Au and Ag elements is an obvious path to improve the performance of NC-based PEC devices. Doping of Au NCs with Ag atoms can increase the extinction coefficient of the NCs but can also cause a blue shift in the absorption edge of the NCs due to a weaker relativistic effect in Ag compared to Au.^{25,31,104,105} Moreover, Ag atoms also have inherently low chemical stability. Therefore, fine-tuning of Ag content in Au

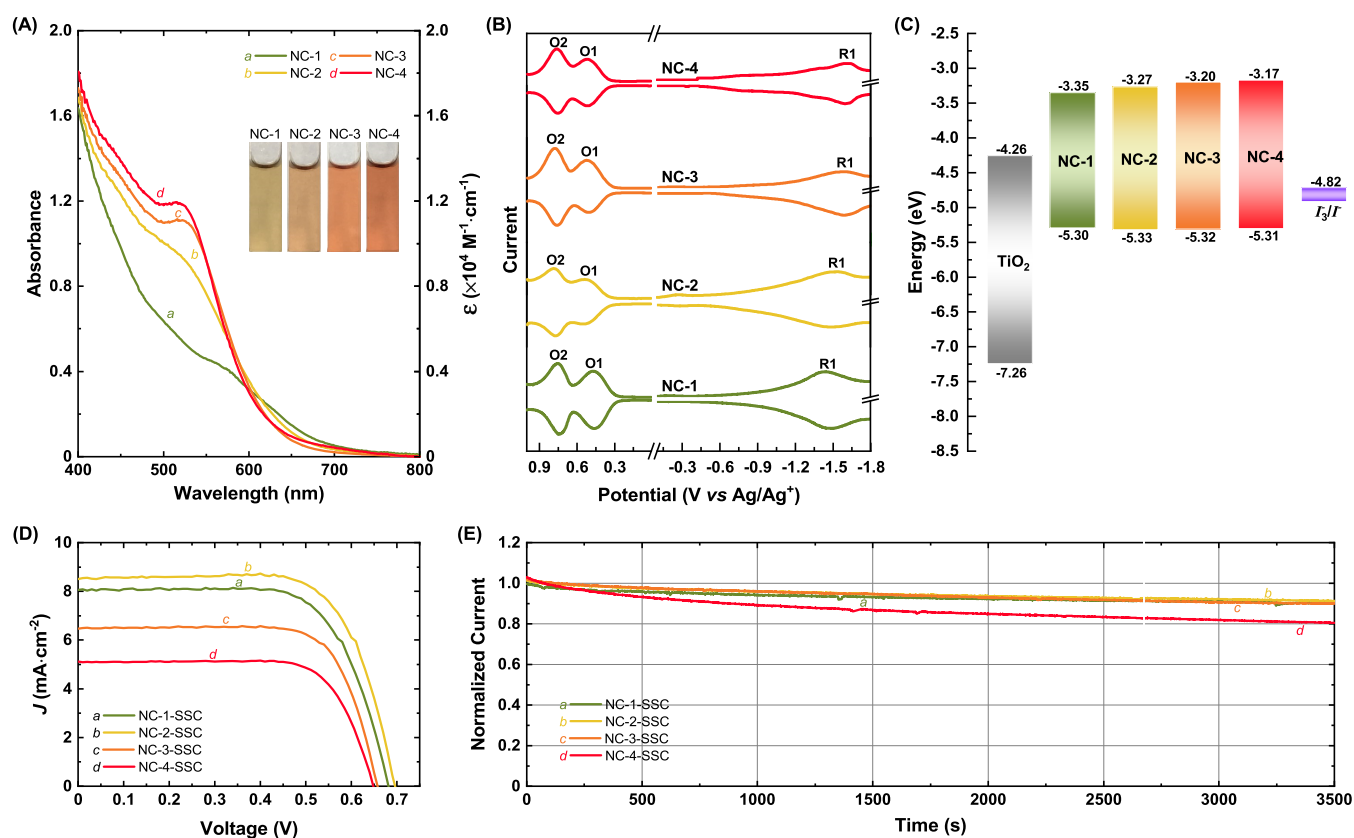


Figure 6. (A) UV-vis absorption spectra, (B) square wave voltammograms (SWVs), (C) HOMO-LUMO energy levels, (D) J - V curves, and (E) stability of NC-1 [$\text{Au}_{18}(\text{SR})_{14}$], NC-2 [$\text{Au}_{18-x}\text{Ag}_x(\text{SR})_{14}$, $x \leq 2$], NC-3 [$\text{Au}_{18-x}\text{Ag}_x(\text{SR})_{14}$, $x \leq 3$], and NC-4 [$\text{Au}_{18-x}\text{Ag}_x(\text{SR})_{14}$, $1 \leq x \leq 4$] NCs and their MCSSCs. Adapted with permission from ref 29. Copyright 2020 Royal Society of Chemistry.

NCs is required for an optimal performance increase of PEC devices.

Our group investigated the effect of Ag-doping on the solar performance of $\text{Au}_{18}(\text{SR})_{14}$ -based MCSSCs.²⁹ We systematically doped $\text{Au}_{18}(\text{SR})_{14}$ with up to four Ag atoms to study its impact on solar cell performance. As predicted by the theoretical study, the incorporation of Ag atoms increased the extinction coefficient of the $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ NCs (Figure 6A). Furthermore, the increase in the absorption was directly correlated with the number of Ag atoms introduced into the $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ structure. However, the absorption range was slightly reduced by Ag-doping because the absorption edge of the $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ NCs was blue-shifted due to a wider gap between the 4d and 5s electrons in the Ag atoms. Hence, the replacement of some of the Au atoms in the $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ structure increased the HL gap of the NCs (Figure 6B). Interestingly, this increase in the HL gap came mostly via a shift in the LUMO level (Figure 6C). The HOMO level did not significantly change due to the Ag-doping, but the LUMO level moved toward lower energy vs vacuum. In AgAu alloy clusters, the HOMO level originated from Au atoms and the LUMO, from Ag atoms.¹⁰⁶ Therefore, Ag-doping of Au NCs causes an increase in extinction coefficient and a decrease in the HL gap from the shift of the LUMO level.

When $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ NCs were used as a sensitizer, a PCE of 4.22% was achieved (Figure 6D), which is the highest reported PCE of MCSSCs to date. However, this PCE was achieved with $\text{AgAu}_{17}(\text{SR})_{14}$ NCs containing only a single Ag atom. The introduction of a higher number of Ag atoms led to a dramatic decrease in the photocurrent and photovoltage (and

consequently the PCE). This decrease was attributed to lower charge injection and lower recombination resistance. However, the stability results were more surprising. As Ag NCs suffer from severe photochemical stability issues, we expected that the stability of $\text{Au}_{18}(\text{SR})_{14}$ would decrease with the Ag-doping. This fact was confirmed for $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ NCs that contained four Ag atoms (Figure 6E). However, the incorporation of up to three Ag atoms in the $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ NCs did not cause a decrease in the stability. Instead, doping with a single Ag atom caused a slight increase in stability. This preservation of $\text{Ag}_x\text{Au}_{18-x}(\text{SR})_{14}$ NC stability was attributed to the location of the Ag atom. As the Ag atom was present in the core of the NC, it can avoid direct contact with the electrolyte, which can cause chemical corrosion of the NC. These observations have huge implications for developing NCs as optoelectronic materials for PEC applications because doping of Au NCs can provide higher absorption and lower recombination while maintaining the integrity of the NCs in long-term operations. However, this could only be achieved if Ag is doped in an appropriate amount and Ag atoms are incorporated into the core of the NCs. Moreover, it should be noted that only a limited amount of research is available on this subject. Further research could discover new mechanisms that can facilitate the improvement of PEC devices via heteroatomic doping of NCs.

8. NANOCUSTER OXIDE INTERFACE

TiO_2 is the most common substrate for building solar cells and PEC devices using NCs. One of the fascinating aspects of NCs is the NC- TiO_2 interface compared to QD- TiO_2 and dye-

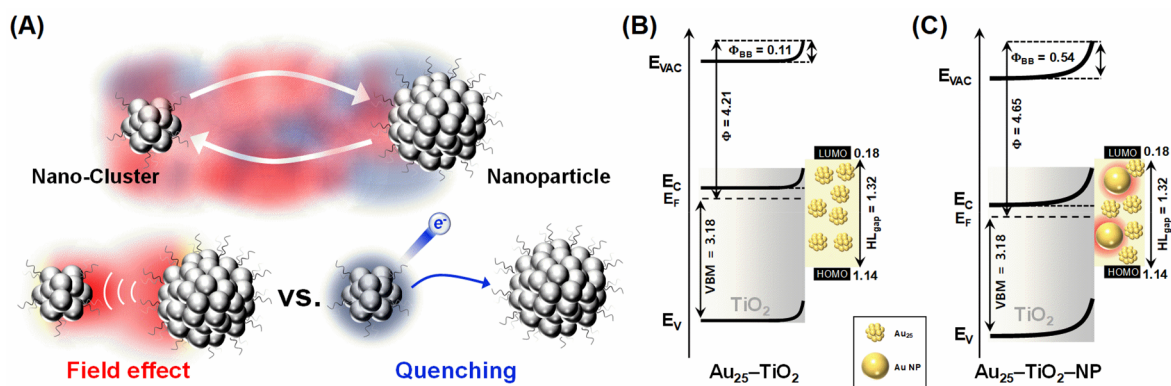


Figure 7. (A) Schematic illustration of quenching and charge separation enhancement by NPs in NC-NP-TiO₂ photoelectrodes. Adapted from ref 14. Copyright 2019 American Chemical Society. Band diagrams of (B) Au₂₅-TiO₂ and (C) Au₂₅-NP-TiO₂ photoelectrodes. Adapted from ref 9. Copyright 2021 American Chemical Society.

TiO₂ interfaces.⁴¹ NCs possess a discrete electronic structure similar to organic and organometallic compounds. However, similar to QDs,^{107–109} NCs can also form type II heterostructures with TiO₂ and act as small bandgap semiconductors.^{9,10,41,110} The band bending at the NC-TiO₂ interface that facilitates charge separation depends on the nature of the NCs. The presence of plasmonic NPs in combination with NCs is also important in that regard. However, the adsorption of the NC on the TiO₂ surface also adversely affects the interface by creating and activating many additional surface states. Therefore, the NC-TiO₂ interface requires a deeper look to understand its behavior in PEC devices because such unique aspects of the NC also bring several variables into play to control the charge separation and transfer dynamics in NC-TiO₂ photoelectrodes.

8.1. Charge Separation. NCs, despite their molecule-like discrete electronic structure, act as small bandgap semiconductors when adsorbed onto the TiO₂ surface and form a type II heterostructure. This is an important aspect because an upward band bending at the NC-TiO₂ interface forces the electrons to move away from the interface and reduces the recombination with the electrolyte and NCs. Wang et al.¹⁰ first reported this observation with Ag₄₄-TiO₂ photoelectrodes. The adsorption of Ag₄₄(SR)₃₀ NCs on TiO₂ caused an upward band bending of 0.7 eV. Since then, band bending has also been reported in Au₂₃-TiO₂ and Au₂₅-TiO₂ photoelectrodes.^{9,72} These results highlight the dual nature of NCs in that they act as molecules and small bandgap semiconductors. This property could be beneficial in the design of efficient light harvesting devices.

As discussed in Section 2, NCs can transform into plasmonic NPs upon irradiation. Although a continuous transformation of NCs to NPs would eventually lead to the loss of functionality in the PEC device, the presence of NPs in small numbers can also bring synergistic beneficial effects. One of these effects is the plasmon-enhanced charge separation. In the literature, however, reports of both beneficial and detrimental effects of the presence of NPs along with NCs exist (Figure 7A). Xiao et al.^{57,111} reported that NPs act as a mediator between NCs and TiO₂ to enhance charge separation. This mechanism can be observed as reduced PL intensity of the NCs due to rapid charge transfer between NCs and NPs. In contrast, our group reported a 3-fold increase in the PL and prolonged PL lifetime when NPs were present simultaneously with NCs.⁹ We attributed this behavior to the plasmonic field effect. In

addition, plasmonic NPs are electron reservoirs and can act as recombination centers. Using TAS, Abbas et al.¹⁴ reported that NPs can simultaneously enhance the charge separation and recombination in the NC-NP-TiO₂ photoelectrodes.

Along with the plasmonic PL enhancement effect and acting as recombination centers, NPs also profoundly affect the NC-TiO₂ interface structure (Figure 7B,C). For example, the Au₂₅-TiO₂ photoelectrode exhibited a band bending of 0.11 eV, which can be enhanced to 0.54 eV if some Au₂₅(SR)₁₈ NCs are transformed into NPs.⁹ Therefore, Au₂₅-NP-TiO₂ shows a dramatic increase in the charge separation compared to the Au₂₅-TiO₂ photoelectrode. Hence, from an interface perspective, the presence of NPs along with NCs is immensely beneficial. However, which mechanism will be present depends on the various factors; one such factor is the distance between the NCs and NPs. The quenching or recombination mechanism between the NC and NPs is usually active only in the 5 nm range.^{62,112,113} Therefore, NCs need to be in close proximity to NPs for effective quenching but plasmon-enhanced charge separation can occur up to 20 nm away from the NPs.^{114–117} Hence, NCs can benefit from increased charge separation without rapid self-recombination. This implies that a small number of NPs on the TiO₂ surface in combination with NCs could produce more efficient PEC devices. This assertion was demonstrated by our group recently, where we transformed some of the Au₂₅(SR)₁₈ NCs to NPs and revealed a significant enhancement in the photocurrent.⁹

8.2. Charge Transfer. Hole transfer is an important aspect of PEC reactions such as water oxidation.^{118,119} Unlike QDs, which tend to passivate the TiO₂ surface, the carboxylic groups that anchor the NCs on TiO₂ create additional surface states.⁹ Therefore, surface states play a crucial role in dictating the hole transfer behavior of the NC-TiO₂ photoelectrodes. Understanding the hole transfer mechanism is essential to developing methodologies to overcome limitations and improve the PEC performance. This point of view can be well understood by the example of α -Fe₃O₄. α -Fe₃O₄ requires a high overpotential for the onset of the photocurrent, which is attributed to the surface state charging.¹²⁰ The surface states need to be charged before the photocurrent is observed. These results have led to strategies that passivate the surface states and significantly reduce the onset overpotential.¹²¹

Abbas and Bang¹³ studied the size-dependent hole transfer mechanism in the NC-TiO₂ system consisting of Au₁₅(SR)₁₃,

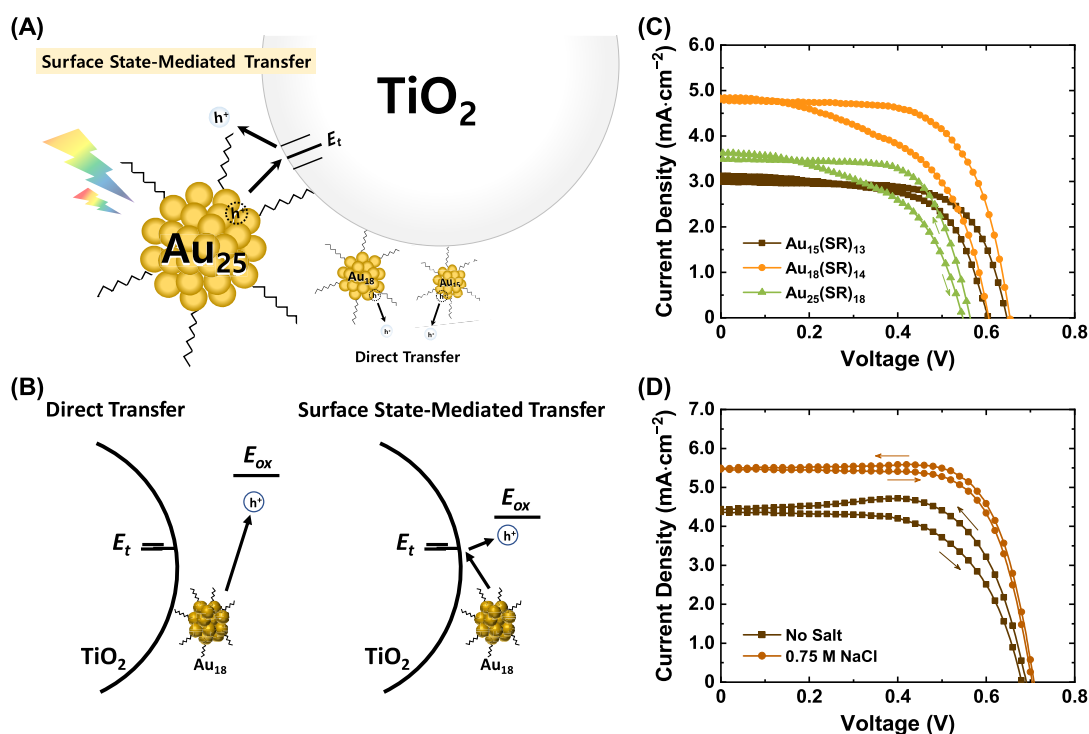


Figure 8. (A) Schematic illustration of the size-dependent hole transfer mechanism in the NC–TiO₂ photoelectrodes. Adapted from ref 13. Copyright 2020 American Chemical Society. (B) Schematic illustration of the electrolyte-dependent hole transfer mechanism in NC–TiO₂ photoelectrodes. Adapted from ref 50. Copyright 2022 American Chemical Society. (C) J – V hysteresis in Au₁₅(SR)₁₃, Au₁₈(SR)₁₄, and Au₂₅(SR)₁₈ NC-based MCSSCs. (D) Role of alkali ions on J – V hysteresis of the MCSSCs. Adapted from ref 12. Copyright 2020 American Chemical Society.

Au₁₈(SR)₁₄ and Au₂₅(SR)₁₈ NCs. Na₂SO₃ was employed as a hole scavenger. The hole scavenger was used to understand the hole transfer pathways without limiting the NC catalytic ability because it is also size dependent. As expected, Au₁₅–TiO₂ and Au₁₈–TiO₂ photoelectrodes exhibited a direct hole transfer via the HOMO level; however, Au₂₅–TiO₂ showed a surface state-assisted hole transfer (Figure 8A). This result is fascinating and unique because, although an effective hole scavenger was used, Au₂₅–TiO₂ displayed hole transfer via surface states. Furthermore, the direct hole transfer from the HOMO of Au₂₅(SR)₁₈ was so limited that, when ethylenediaminetetraacetic acid (EDTA) was used as a hole scavenger, the photocurrent of Au₂₅–TiO₂ fell below the unsensitized TiO₂ photoelectrode. Moreover, with EDTA, even the Au₁₈–TiO₂ photoelectrode displayed a surface state-assisted hole transfer mechanism (Figure 8B).⁵⁰ These results are critical in understanding the PEC devices because the surface state-assisted mechanism usually incurs higher losses due to the possibility of severe recombination because both holes and electrons can occupy the surface states. Therefore, the activation of the direct hole transfer in the NC–TiO₂ system could lead to enhanced photocurrents in the NC–TiO₂ PEC devices.

8.3. Hysteresis. Another exciting aspect of the NC–TiO₂ system is the severe hysteresis in some MCSSC devices. For example, highly purified GSH-protected NC-based MCSSCs show high hysteresis in the J – V curve scans (Figure 8C).¹² However, the addition of alkali ions during the adsorption of NCs on TiO₂ almost completely removes the hysteresis in those devices (Figure 8D). This behavior has been linked to the binding between the NC and TiO₂ surface. The presence of alkali ions during the adsorption of NCs helps them get closer to the TiO₂ surface and form stronger bonds.⁴² Alkali

ions help NCs form a chelating bond instead of an otherwise-formed ester-like bond. MCSSCs with alkali ion-assisted adsorption also show high recombination resistance, indicating a change in the charge separation at the NC–TiO₂ interface. These results suggest that the NC–TiO₂ interface needs to be studied in detail to fully understand the underlying mechanism for improving the NCs' performance in PEC applications.

9. SUMMARY AND OUTLOOK

Metal NCs have seen tremendous growth in the development of their synthesis protocols and understanding their structure and physical properties in recent years. Unfortunately, that growth has not been reflected in their use in light harvesting applications. One can ascribe this stagnation to the designation of NCs as a mere replacement of dyes to extend the absorption range of wide bandgap oxide semiconductors. As pointed out throughout this Perspective, NCs need to be treated independently from dyes and QDs because they possess unique aspects in terms of light harvesting applications. Therefore, NC–TiO₂ or generally NC–metal oxide photoelectrodes need to be decoupled into a separate category. Although the conception of metal NC-sensitized photoelectrodes took place over a decade ago, the progress in this field has been slow compared to other technologies such as perovskite solar cells.^{41,49,122} This could be partly attributed to wider attention being paid to the perovskite solar cells. However, in part, it can also be attributed to years of stagnant progress in the dye-sensitized solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSSCs) because MCSSCs have similar device structures to those devices. However, research has shown that NCs should not be treated merely as a separate class of sensitizers because they possess various attributes and mechanisms unseen in other sensi-

tizers.⁴¹ This misconception was also made with perovskite devices. Early research used perovskite merely as a sensitizer and even utilized liquid redox couples as electrolytes.^{123,124} However, later, it was discovered that solid-state device design is more suitable for perovskite-based solar devices. Even a TiO₂ film, which was used as electron transport media due to the device design borrowed from DSSCs and QDSSCs, was replaced with Al₂O₃ and SiO₂.^{125,126} Because the function of Al₂O₃ or the oxide layer was as a scaffolding layer, those design improvements can be credited for the rapid rise of perovskite solar cell performance. Therefore, the device design of NC-based solar cells also needs to be radically reviewed. Two noticeable design improvements that need to be tried are making a solid-state device and designing a new redox couple that is more suitable for NC-based devices. These developments could also open the door for organosoluble NCs and NCs that are unstable with the current redox couples. Hence, we believe the next breakthrough in the field of MCSSCs is very likely to come with improvements in device design.

The interface of the NC–TiO₂ photoelectrodes can be considered the leading contender for understanding the uniqueness of NCs compared to other sensitizers. The adsorption of the NCs on TiO₂ can create additional surface states that complicate recombination control. The presence of NCs on the TiO₂ surface also causes band bending that can be beneficial or detrimental for charge separation depending upon the direction of the band bending. The interfacial surface states can also be involved in the hole transfer mechanism in the PEC devices. The binding mode between the NCs and TiO₂ also seems to play a role in dictating the electron transfer between the NCs and TiO₂. The NC–TiO₂ interface also is the most probable cause for the severe hysteresis observed in some MCSSCs. Therefore, the NC–TiO₂ interface needs to be studied in greater detail to shine a light on these processes further and discover any unforeseen processes that may be present at this interface.

The degradation of the NC–TiO₂ photoelectrodes is another underappreciated aspect of this research area. The decomposition of NCs into metallic ions is an undesirable process; however, the transformation of the NC to NPs can be turned from a loss of functionality to an upgrade. Transformation of the NC to NPs brings two competing processes into the equation: quenching and SPR-enhanced charge separation. Recent research has shown that this transformation process can be harnessed in working devices to significantly boost PEC device photocurrent.⁹ However, more research is required to fully understand this process. Moreover, from a fundamental point of view, the formation of NPs followed by the photoinduced surface diffusion of NCs is an unexplored area. How this diffusion takes place and how it can be controlled are very interesting questions at the basic level that remained unanswered.

NCs have immense unrealized potential in PEC applications such as water splitting and CO₂ reduction. This conclusion stems from the fact that, apart from the light harvesting ability, NCs also possess catalytic abilities.^{32,127} Henceforth, the catalytic tuning of NCs has seen tremendous interest by researchers in recent years, and electrocatalysis by NCs has been demonstrated in various reactions.³² However, there have only been a few publications on the PEC application of the NCs. One of the reasons for this may be the difficulty of fabricating effective photoanodes with organosoluble NCs. Another reason could be the poor photochemical stability of

many NCs. However, as pointed out in this Perspective, the photochemical degradation of NCs could be avoided if holes from the NCs are transferred to the electrolyte effectively. This can be achieved if the catalytic abilities of the NCs are tuned for a specific reaction. This is an open area of research. Although immense research opportunities exist in this area, it has received little attention so far.

Therefore, we believe that metal NCs have the potential to grow exponentially for light harvesting applications. However, such growth can only be achieved if the working mechanisms of NC-based devices are analyzed on their own merit and can inspire radical new device designs and structures.

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Notes

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