An Excitonic Perspective on Low-Dimensional Semiconductors for Photocatalysis

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ABSTRACT: Low-dimensional semiconductors provide a marvelous platform for pursuing versatile photocatalytic solar energy conversion. Compared with the bulk counterparts, low-dimensional semiconductors possess notable Coulomb-interaction-mediated excitonic effects arising from the reduced dielectric screening. As a consequence, excitons or bound electron—hole pairs, together with charge carriers, serve as the primary photoinduced energetic species. In terms of photocatalysis, exciton-based energy transfer establishes distinctly different mechanisms for energy utilization beyond the traditional carrier-based charge transfer. Moreover, owing to the relationships between excitons and charge carriers, excitonic effects play a crucial role in determining quantum yields of both exciton- and carrier-triggered photocatalytic reactions. The above unique features enable optimized low-dimensional semiconductor-based photocatalysis to be achieved by non-trivial excitonic regulation. In this Perspective, we attempt to provide an overview of the impacts of excitonic effects on low-dimensional semiconductor-based photocatalytic energy conversion. We discuss the interplay between the excitonic and charge-carrier aspects in low-dimensional semiconductors and highlight the necessity of evaluating excitonic effects when dealing with both exciton- and carrier-triggered photocatalysts. We conclude the Perspective with an eye toward the future challenges in the field.

■ INTRODUCTION

Ever since the discovery of water photolysis on TiO₂ photoelectrode by Fujishima,¹ semiconductor-based photocatalysis has triggered broad interest due to its promising prospect of achieving large-scale solar energy conversion. As a crucial precondition of high-efficiency photocatalysis, the design of semiconductors with optimized electronic and surface properties is of great importance.²⁻⁴ Over the past decades, the development of nanomaterials and nanotechnology has opened up a hopeful avenue for pursuing advanced photocatalysts, and semiconductors with certain low-dimensional morphologies, such as zero-dimensional nanocrvstals and nanodots, one-dimensional nanotubes and nanowires, and two-dimensional nanosheets, have been widely employed in photocatalytic research.^{5–10} By virtue of their small sizes and broken symmetries, low-dimensional semiconductors exhibit significant advantages in electronic and surface properties, as compared with their bulk counterparts, which can give impetus to the pursuit of diverse photocatalytic energy exploitation. In comparison with their bulk counterparts, low-dimensional semiconductors possess reduced dielectric screening due to the limited dimensionalities.^{11,12} That means the Coulomb interactions between charged species (i.e., electrons and holes), which can be usually ignored in bulk semiconductors, might be rather robust in the low-dimensional ones. As a consequence, excitonic effects arising from the electrostatic interactions between photoinduced electrons and holes would lead to some non-trivial photoexcitation processes in lowdimensional semiconductors, which might be out of accord with the traditional excitation scenarios based on energy band theory.^{13–15} For instance, one of the most remarkable incompatibilities is the formation of excitons or bound electron—hole pairs during photoexcitation. Such electrically neutral photoinduced species not only determine the yields of charged carriers but also establish alternative mechanisms for energy transport and utilization. In fact, it has been demonstrated that excitonic effects play crucial roles in the photoexcitation applications of low-dimensional semiconductors such as photoluminescence, photodiodes, and photovoltaics.^{16–18}

However, in terms of photocatalysis, the importance of excitonic effects has not been fully realized due to several subjective or objective factors. A major reason for the neglect of excitonic effects in the field of photocatalysis is that most of the established photocatalytic reactions involve the oxidation or reduction of substrate molecules (e.g., water splitting, carbon dioxide reduction, nitrogen fixation), in which charge-carrier behaviors are considered to be directly responsible for the redox processes.¹⁹ In this case, the excitonic aspect of photoexcitation processes appears to be irrelevant to catalytic

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Figure 1. Schematic illustration of (a) band structures and exciton energy levels and (b) the impacts on optical response in low-dimensional semiconductors. Panel b reproduced with permission from ref 31. Copyright 2017 Nature Publishing Group.

performance. Another factor limiting the disclosure of the excitonic aspect in low-dimensional semiconductor-based photocatalysis lies in the difficulties in characterizing excitonic properties. In contrast to the mature electrical and optical techniques for characterizing charge-carrier properties, there are quite limited methods for interrogating excitonic properties due to the complicated spin/orbital/valley degrees of freedom.²⁰⁻²² Such limited methods usually depend on the test environments, which would be inapplicable under photocatalytic conditions. Besides, the complexities of photocatalysis also hinder the investigation of the impacts of excitonic effects. Since factors including both electronic and surface properties determine the performance, the advantages of low-dimensional systems in terms of these factors make it challenging to figure out the individual impacts of excitonic effects. Despite all these difficulties, the objective existence of excitonic effects in lowdimensional semiconductors must be considered when dealing with photocatalytic processes. Uncovering the impacts of excitonic effects on low-dimensional semiconductor-based photocatalysis will not only give insights into photocatalytic mechanisms but also pave new avenues for pursuing optimized solar energy utilization.

Recently, benefiting from the progress in both experimentally and theoretically exploring the relevant photoexcitation processes, considerable achievements have been made in investigating and regulating the excitonic properties of lowdimensional semiconductor-based photocatalysts, which establish a comprehensive understanding of photocatalytic processes. In this Perspective, we focus our attention on excitonic effects in low-dimensional semiconductors and aim to provide an overview of their impacts on the relevant photocatalytic applications. By describing the whole excitedstate profile, we highlight the unique photoexcitation properties induced by excitonic effects in low-dimensional semiconductors and emphasize the interplay between excitonic and charge-carrier processes. In addition, we summarize the effects of different excitonic behaviors such as dissociation, annihilation, and cooling on solar energy utilization in different photocatalytic reactions and discuss the key factors affecting the efficiency and selectivity of these reactions. Furthermore, we systematically review recent advances in excitonic regulation in low-dimensional photocatalysts and present the intrinsic mechanisms of these optimization strategies for regulating different excitonic behaviors. We conclude with a perspective on the challenges in the further exploration of excitonic effects in low-dimensional semiconductor-based photocatalysts.

EXCITONIC EFFECTS IN LOW-DIMENSIONAL SEMICONDUCTORS

Owing to the negligible excitonic effects in most bulk semiconductors, the thermodynamics and kinetics of photoinduced charge carriers are deemed to dominate the involved photoexcitation processes and hence the photocatalytic behaviors. Traditionally, the classical energy band model is employed to depict the photoexcitation scenarios of semiconductor-based photocatalysts.^{2,3} In brief, the effective excitation of semiconductors under suitable illumination (whose photon energy should be larger than the band gap of semiconductors) leads to the generation of hot electrons and holes in conduction and valence bands, respectively. Followed by scattering-mediated intra-band cooling processes, metastable band-edge carriers are formed. These energetic species would either decay via radiative/nonradiative pathways or boost charge-transfer reactions on the surface of catalysts. According to the model, there are several factors determining the relevant photocatalytic behaviors. For instance, band structures impact the light absorption properties and redox potentials of band-edge carriers, while charge-carrier behaviors like intra-band cooling, recombination, and transport are responsible for quantum yields. On the basis of the energy band model, the regulation of band structures and chargecarrier behaviors has always been considered to be effective for optimizing photocatalytic energy utilization.^{23,24}

The energy band model provides a simplified and intuitive understanding of the photoexcitation scenarios involved in semiconductors, whereas its establishment is based on an important premise: that the interactions between photoinduced electrons and holes can be ignored. In fact, that is why the energy band model might be not applicable for fully depicting the photoexcitation scenarios in low-dimensional systems. Because of dielectric confinement effects, excitonic effects originating from the Coulomb interactions between electrons and holes can be significantly promoted in lowdimensional semiconductors, which would endow the systems with distinct photoexcitation scenarios. The most remarkable feature induced by excitonic effects is the generation of different photoinduced species. In contrast to free (to be accurate, almost free) charge carriers in photoexcited bulk semiconductors, electrons and holes in photoexcited lowdimensional ones might be correlated, owing to the promoted Coulomb interactions.^{11,12} Such correlations would lead to the formation of excitons or bound electron-hole pairs. It is worth noting that an exciton is different from the usually mentioned "electron-hole pair" in photocatalytic research. The expression



Figure 2. (a) Schematic illustration of Zeeman splitting of different spin-state excitons under a magnetic field. The impacts of spin-orbit coupling on (b) band structures and excitonic properties and (c) the polarization properties of photoluminescence in two-dimensional $Mo_{(1-x)}W_xSe_2$ solid solutions. (d) Magnetic field-dependent emissions and (e) the corresponding splitting energies of spin-singlet and -triplet states. Panels b and c reproduced with permission from ref 56. Copyright 2015 Nature Publishing Group. Panels d and e reproduced with permission from ref 60. Copyright 2020 American Chemical Society.

"electron—hole pair" is typical used to emphasize the geminate generation of an electron in the conduction band and a hole in the valence band excited by a single photon, and the generated "electron—hole pair" is uncorrelated. In fact, there are several significant differences between the exciton and uncorrelated "electron—hole pair", which also determine the characterizations of excitonic aspect.

Difference in Energy Level. As compared to the uncorrelated case, an exciton formed by a pair of band-edge charge carriers (i.e., an electron at the conduction band minimum and a hole at the valence band maximum) possesses a lower energy. This is a result of energy release during the bound process, and the energy difference is the so-called exciton binding energy (E_b). As for Wannier–Mott excitons (a kind of weak-binding excitons), the excitonic energy levels can be described according to the Rydberg equation:

$$E_n = E_{\rm g} - \frac{\mu e^4}{2h^2 \epsilon^2 n^2}$$

where E_n and E_g denote exciton energy levels and band gap, respectively, *n* is the principal quantum number, μ is the reduced mass of the electron and hole, and ϵ is the relative permittivity. Accordingly, a series of exciton energy levels can be expected (Figure 1a). Note that the above equation corresponds to the situation in three-dimensional systems, and the screened Coulomb potential should also be considered in low-dimensional ones. As an important parameter, E_b can be used to evaluate the strength of excitonic effects or the thermal stability of excitons. Once E_b is larger than the ambient thermal energy of k_BT (k_B , Boltzmann constant; *T*, ambient temperature), a desirable exciton stability can be expected. Traditionally, the critical value of 26 meV is used to determine intrinsic excitonic strength at room temperature.²⁵ Certainly, there are also some extrinsic factors like surrounding polarization and energetic disorder that can impact the stability of excitons, which are crucial to the corresponding excitonic regulation (see details below). Some bulk systems can also possess large $E_{\rm b}$, which could be linked to various factors like valence-electron localization, defects, and confined structures.²⁶⁻²⁸ As for low-dimensional semiconductors, the value of $E_{\rm b}$ varies from several meV to several hundred meV, depending on crystal/electronic structures or even surrounding environments.²⁹⁻³² The fact that many low-dimensional semiconductors exhibit size- or thickness-dependent $E_{\rm b}$ greatly enriches the relevant photocatalytic applications, since both energy level and quantum yield of excitons can be controlled by structural regulation.³³⁻

Benefiting from such an energy difference, spectroscopic techniques including photoluminescence spectroscopy and absorption spectroscopy can be applied for characterizing excitonic properties in low-dimensional semiconductors.^{37,38} Taking absorption spectroscopy as an example, the potential excitonic transitions would result in different spectral line shapes. Quasiparticle band gap (E_g) corresponds to the threshold of interband transitions (that is, from valence band maximum to conduction band minimum) leading to the formation of uncorrelated electron-hole pairs, while optical band gap (E_{opt}) is estimated from the threshold of the absorption spectrum. Generally speaking, the values of E_g and E_{opt} in semiconductors with faint excitonic effects are almost equivalent. However, as for low-dimensional semiconductors, the presence of excitonic absorption might lead to two possible

scenarios: for excitonic transitions with small oscillator strengths, weak sub-band absorption or tailed absorption could be observed;^{39,40} for excitonic transitions with large oscillator strengths, the result from absorption spectral analysis (i.e., E_{opt}) would be the energy levels of the corresponding excitonic states.^{41,42} To go further, the identification of quasiparticle band gaps in low-dimensional semiconductors usually involves techniques like photoconductivity spectroscopy and scanning tunneling spectroscopy.^{43,44} It should be pointed out that the intrinsic excitonic transitions ought to result in a series of sharp peaks in the absorption spectrum corresponding to the discrete exciton energy levels (Figure 1b),³¹ whereas phonon-induced spectral broadening in assembled samples usually gives rise to consecutive spectral lines at room temperature.

It is noteworthy that there is also photoinduced generation of free charge carriers in low-dimensional semiconductors with strong excitonic effects. Under certain conditions, the concentration ratio of excitons to free charge carriers can be described by the Saha–Langmuir equation:

$$\frac{x^2}{1-x} = \frac{1}{n} \left(\frac{2\pi\mu k_{\rm B}T}{h^2}\right)^{3/2} {\rm e}^{-E_{\rm b}/k_{\rm B}T}$$

where x denotes the ratio of free charge carriers to the whole particles (i.e., free charge carriers and excitons), n is the total number of energetic particles, and μ is the reduced mass of the exciton.^{45,46} According to this equation, it is clear that, at a certain temperature and excitation density, the ratio of excitons to charge carriers is mainly determined by $E_{\rm b}$ of the material. The co-existence of excitons and charge carriers endows lowdimensional semiconductors with quite intriguing photoexcitation processes, and the excitonic and charge-carrier behaviors should be comprehensively considered when dealing with the relevant photocatalysis.

Difference in Spin Configuration. The spin degrees of freedom of excitons and uncorrelated "electron-hole pairs" are also different. As a fundamental property of elementary particles, spins are related to their intrinsic angular momentums, the quantum numbers of which are described by $\pm 1/2$. The sign (\pm) refers to the presence of two opposite directions (in a nutshell, spin upward or downward) of an electron under a magnetic field. In an uncorrelated "electronhole pair", the electron and hole spins are uncoupled, and they appear to precess independently under a magnetic field. Therefore, no obvious spin-dependent photophysical behaviors would be involved during excitation. In comparison, excitons as bound pairs possess distinctly different spin (to be exact, pseudo-spin) configurations, as a consequence of strong coupling between electron and hole spins. In detail, spin configurations of excitons can be described by the total angular momentum originating from the combination of the electron and hole spins. According to molecular orbital model, the antiparallel and parallel alignments of electron and hole spins give rise to total spin angular momentums of 0 and 1, respectively, and thus correspond to singlet- and triplet-state excitons. The use of "singlet" and "triplet" represents the numbers of possible spin wave functions, which can be verified by exciton fine structures (i.e., Zeeman splitting; Figure 2a) determined by spectroscopic measurements in a magnetic field.

The above understandings based on molecular orbital theory simplify the spin configurations of excitons and have been employed mainly to describe the corresponding scenarios in systems like polymeric/organic and carbon-/silicon-based semiconductors. $^{47-50}$ However, the applicability of these understandings in depicting the spin configurations in some semiconductors, especially the inorganic ones, is quite limited. One of the major reasons for such limitations is that there are some other degrees of freedom that are strongly coupled with exciton spins, which make it difficult to provide individual analyses on spin configurations of the involved excitonic states. A typical example is the presence of the relativistic interactions between spin and orbital degrees of freedom in semiconductors.^{51–53} Because an exciton in semiconductors is, in essence, an electron in the conduction band and a hole in the valence band, bound by the Coulomb interactions, the structures of conduction and valence bands inevitably impact spin degrees of freedom of the formed exciton. Considering that the bands of semiconductors originate from the hybridization of discrete atomic levels, the degenerate feature of these atomic levels should be considered when dealing with spin configuration of exciton states. Compared to heavy-atomfree semiconductors, including polymeric/organic and carbon-/silicon-based, the inorganic ones usually possess much stronger spin-orbit coupling, which executes an additional effect on lifting the orbital degeneracies, thus leading to spinorbit splitting of band-edge energy levels (mostly the valence band-edge energy level due to its orbital compositions).⁵⁴ Such a feature enables the observation of band-edge exciton fine structures in spectral (such as absorption and emission spectra) lines and unique responses to magnetic field or polarized light.^{55,56} For instance, Urbaszek and co-workers demonstrated the feasibility of spin-orbit engineering in twodimensional $Mo_{(1-x)}W_xSe_2$ solid solutions. By changing the ratio of Mo:W, they successfully regulated the spin-orbit splitting over a wide range, and hence the populations of dark and bright excitons (Figure 2b,c).⁵⁶ Moreover, the unique electronic structures and symmetry breaking in some lowdimensional semiconductors can give rise to much more complicated exciton spin degrees of freedom. For instance, due to inversion symmetry breaking and spin-orbit coupling, the coupling between spin and valley degrees of freedom can be observed in some transition metal dichalcogenide monolayers (such as MoS₂, MoSe₂, WS₂, WSe₂, etc.) and has been demonstrated to play a crucial role in both the involved spin and valley relaxations.⁵⁷⁻⁶⁰ Recently, Wang et al. reported valley-Zeeman splitting of interlayer excitons in WSe₂/MoS₂ van der Waals heterojunctions and observed the different splitting features of singlet and triplet excitons (Figure 2d,e).⁶⁰ The observation of the splitting of singlet excitons under a magnetic field is because of the coupling between the spin and valley. In addition to the above-mentioned coupling between the spin and different degrees of freedom, the robust exchange interactions between electrons and holes further complicate the identification of exciton spins in low-dimensional systems.^{61,62} That is, electron-hole exchange interactions can lead to effective mixing of electron and hole spin momentum states and hence the formation of so-called optically dark excitons, which greatly impacts both excitation and relaxation of excitons. In general, excitonic states within these semiconductors appear to exhibit "ill-defined" spin configurations. These features, on the one hand, open up possibilities for pursuing spin-dependent photoexcitation processes (as well as photocatalytic behaviors) and, on the other hand, set up obstacles to the accurate characterizations of spin-related excited-state properties. In view of the complicated



Figure 3. (a) Schematic illustration of Förster and plasmon-induced resonance energy transfer. (b) Distance-dependent PIRET enhancements and (c) LSPR absorption-dependent enhancements in photocatalysis and transient absorption in Au@SiO₂@Cu₂O heterostructures. (d) Dexter energy transfer for ${}^{1}O_{2}$ generation in a CdSe/PCA system. Panels a, b, and c reproduced with permission from ref 71. Copyright 2015 Nature Publishing Group. Panel d reproduced with permission from ref 80. Copyright 2018 Nature Publishing Group.

spin degrees of freedom, systematic spectroscopic measurements under certain conditions such as different temperatures, electric and magnetic fields, excitation power densities and polarizations, and even surroundings are necessary.

Other Differences. Aside from the differences in spin configuration and energy gap, there are also some other unique features in excitonic aspects in semiconductors. For instance, as bound states of electron and hole, excitons are electrically neutral. Such a feature suggests that excitons do not make contributions to conductivity and would exhibit different responses to the built-in or extrinsic electric fields as compared with the charged photoinduced carriers. In fact, it is exactly the different charged conditions that ensure the distinction of quasiparticle and optical band gaps of low-dimensional materials on the basis of photoconductivity measurements.⁴³ Another feature lies in the interactions or couplings between electronic and/or vibrational energy states, the strength of which can be used to picture the distribution forms or sizes of excitons.^{63,64} In brief, strong electronic couplings (describing the transitions between two electronic states) would lead to delocalized excitons, while strong coupling between electronic and vibrational energy states would lead to small-sized, localized excitons. These couplings determine not only energy transport mechanisms but also exciton dynamics in semiconductors.

The above characteristics suggest that excitonic effects will establish an additional aspect, beyond the traditional chargecarrier one, of photoexcitation processes in low-dimensional semiconductors, and the co-existence of excitons and charge carriers could have some intriguing impacts on photocatalytic behaviors.

IMPACTS OF EXCITONIC EFFECTS ON PHOTOCATALYTIC BEHAVIORS

With respect to semiconductor-based photocatalysis, properties including excitation, relaxation, transport (in catalysts), and transfer (between catalysts and substrate molecules) of energetic photoinduced species are generally deemed to determine the involved photocatalytic behaviors. As for lowdimensional semiconductors, excitons and charge carriers jointly act as the dominant energetic photoinduced species, and the differences and dependence between the two species inevitably impact photocatalytic behaviors. Therefore, it is necessary to provide comprehensive considerations on both the excitonic and charge-carrier aspects when handling the relevant photocatalysis. In this section, focusing on the relationships between the excitonic and charge-carrier aspects, we attempt to clarify the impacts of excitonic effects on lowdimensional semiconductor-based photocatalysis as follows.

Energy Utilization Mechanisms. Photocatalytic energy utilization is mainly implemented by the transport and transfer of energetic photoinduced species. Traditionally, the charge transfer mechanism is deemed to be prevalent in semiconductor-based photocatalysis, and the match between bandedge energy levels and redox potentials in the systems is important.⁴ However, since excitons also act as dominant energetic photoinduced species, the transport and transfer of excitons would account for a considerable portion of energy utilization involved in low-dimensional semiconductor-based photocatalytic systems. There are two primary mechanisms for exciton-based energy utilization: Förster and Dexter energy transfer mechanisms. Mediated by dipole-dipole coupling between different excitonic states, Förster energy transfer enables the long-range (on the scale of 10 nm) hopping of excitons in donor/acceptor systems.⁶⁵⁻⁶⁸ Accordingly, an

overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor is necessary (that is, energy-level match; in fact, Förster energy transfer is a nonradiative process and does not involve the emission and reabsorption of photons). The efficiency of Förster energy transfer exhibits a significant dependence on the inverse sixth power of the distance between the donor and the acceptor, which could be identified according to spectroscopic analyses. In terms of photocatalysis, the most typical application of Förster energy transfer is a sensitization process for promoting light harvesting of the systems.⁶⁸ Förster energy transfer has been considered to occur mainly between singlet excitonic states, whereas there are several recent research reports demonstrating feasible transfer between singlet and triplet states induced by strong spin-orbit coupling, which establish a potential pathway to the achievement of spin-flip transitions.^{69,70} Although Förster energy transfer establishes an alternative pathway for light harvesting, the feature of redshifted energy utilization would hinder its application in the field of photocatalysis. A similar dipole-dipole couplingmediated energy transfer has been proposed for overcoming this issue. Plasmon-induced resonance energy transfer (PIRET) enables the non-radiative transfer of plasmonic energy toward the blue direction (Figure 3a).^{71,72} Taking Au@ SiO₂@Cu₂O heterostructures as an example, Wu and coworkers identified the inverse symmetry between distance dependences of PIRET and the localized surface plasmon resonance (LSPR) absorption-dependent photocatalytic enhancement (Figure 3b,c). They suggested that energy transfer between a semiconductor and a plasmon was governed by their relative dipole moments and the dephasing times of the plasmon.

Dexter energy transfer represents another typical excitonbased mechanism for solar energy utilization. As compared with Förster energy transfer, Dexter energy transfer is mediated by exchange interactions, in which electronic couplings between both valence and conduction bands of the acceptor and donor are necessary.^{73–75} That means, in addition to the spectral overlap, a wave function overlap between acceptor and donor is also required in the Dexter case. Due to this feature, Dexter energy transfer usually occurs within 1 nm, with a transfer rate exhibiting exponential distance dependence. As for photocatalysis, Dexter energy transfer possesses a much more direct influence than the Förster case: the Dexter coupling mechanism is more feasible to boost energy transfer between excitonic states with different spin multiplicities, which would overcome the spin forbidden in direct transitions. As such, triplet excited states of acceptors can be generated and hence facilitate some unique reactions. A typical example is the photocatalytic singlet oxygen $({}^{1}O_{2})$ generation.⁷⁶⁻⁷⁸ Despite a quite small energy gap (~0.98 eV) between its lowest singlet and ground (triplet) states, direct excitation for ¹O₂ generation is forbidden due to the spin conservation rule. Traditionally, two sequential charge transfer processes are deemed to be accountable for semiconductor-based photocatalytic ${}^{1}O_{2}$ generation, where superoxide radical $(O_2^{\bullet-})$ acts as an intermediate.⁷⁹ However, it seems that these diffusioncontrolled processes would be impracticable to explain the high-yield $^{1}O_{2}$ generation or $O_{2}^{\bullet-}$ -lacking characteristics in some systems, where Dexter energy transfer would take responsibility. Note that molecular co-catalysts are usually used for ${}^{1}O_{2}$ generation (Figure 3d)⁸⁰ due to the ill-defined spin configurations in semiconductors. Beyond ¹O₂ generation,

there are several other types of photocatalytic reactions undergoing exciton-based energy transfer mechanisms, such as isomerization of alkenes and [2+2] cycloadditions.^{81,82} In fact, energy-transfer-initiated photocatalysis has been attracting considerable attention over the past decade, in which molecular photocatalysts are typically involved.^{83–86} However, owing to the differences in factors like energy levels, surface structures, and the interactions between particles/quasiparticles, low-dimensional semiconductors tend to possess some unique features as compared with the molecular counterparts. These unique features, on the one hand, complicate the scenarios of energy transfer in low-dimensional systems; on the other hand, they endow the systems with rich possibilities for optimizing the corresponding photocatalytic behaviors.

Although usually sketched as a process involving the net transfer of both electron and hole, Dexter energy transfer is different from two sequential charge transfer processes (such as charge-transfer-mediated ¹O₂ generation). Several exciting works have been done which highlighted that factors like donor-acceptor distance and bridge structure greatly dominate the real processes occurring therein.^{87,88} Overall, as compared with a carrier-based charge transfer mechanism, an exciton-based energy transfer mechanism is usually limited in directly driving semiconductor-based photocatalysis. The main reasons lie in two factors: the energy transfer process requires harsher terms, such as spectral and wave function overlaps, than the charge transfer process; as for a substrate molecule, the generation of its excitonic excited states requires higher energy than the generation of the corresponding redox products (usually half-reactions). In addition, there is a special kind of Dexter energy transfer process, exciton-exciton annihilation (EEA).⁸⁹⁻⁹¹ Originating from the collision between two low-lying excitons, EEA leads to the transition of one exciton to its high-lying excitons and the annihilation of the other exciton. As such, EEA would impact photocatalytic solar energy utilization: on the one hand, it is harmful to the accumulation of energetic photoinduced species; on the other hand, it establishes a feasible pathway for generating high-lying photoinduced species by low-energy photons (detailed discussions will be given later).

Photocatalytic Quantum Efficiency. Aside from the above differences in mechanisms for energy utilization, there are also obvious dependence and interplay between the excitonic and charge-carrier aspects which can greatly impact the photocatalytic quantum efficiency. Owing to the coexistence of the excitonic and charge-carrier aspects in lowdimensional semiconductors, the efficiencies of energy-transfer- and charge-transfer-mediated photocatalytic reactions would be closely related. This is because, according to the Saha-Langmuir equation, the concentration ratio of excitons to free charge carriers under certain conditions (i.e., temperature and photoexcitation density) is mainly determined by $E_{\rm b}$ (Figure 4a), and consequently, the efficiencies of photocatalytic reactions undergoing exciton- and carrier-triggered mechanisms would be interrelated. This dependence between the generations of exciton and charge carrier represents an important intrinsic factor determining both efficiency and selectivity of photocatalytic reactions. A typical example is the intrinsic faint performance of low-dimensional semiconductors in carrier-triggered photocatalytic reactions, arising from the low-concentration charge carriers linked to strong excitonic effects. Moreover, as depicted by the Saha-Langmuir



Figure 4. (a) Schematic illustration of the interplay between the excitonic and charge-carrier aspects in polymeric carbon nitride. Heavy-atom effects on (b) photocatalytic hydrogen generation, (c) $O_2^{\bullet-}$ production, and (d) 1O_2 generation from polymeric carbon nitride. Panels b, c, and d reproduced with permission from ref 92. Copyright 2017 Royal Society of Chemistry.

equation, the balance of excitons and free charge carriers can be influenced by extrinsic factors like photoexcitation density and temperature, and hence the performance of exciton- or carrier-triggered reactions can be selectively regulated by modifying these extrinsic factors. Another example illuminating the impact of the dependence between the excitonic and charge-carrier aspects is the photocatalytic behaviors dominated by triplet-triplet annihilation in polymeric carbon nitride.⁹² Triplet-triplet annihilation can lead to the consumption of one exciton per collision, which inevitably limits the performances of exciton-triggered photocatalytic reactions. However, we identified that the addition of bromine atoms would lead to simultaneous reduction in photocatalytic efficiencies of both carrier- and exciton-triggered reactions (that is, hydrogen generation/ $O_2^{\bullet-}$ production and 1O_2 generation; Figure 4b-d). This can be understood as follows: heavy-atom effects induced by bromine lead to enhanced intersystem crossing rates and hence promoted triplet exciton generation; accelerated exciton consumption induced by promoted triplet-triplet annihilation results in faint excitontriggered photocatalytic reactions, while the shifted concentration equilibrium between exciton and charge carrier is responsible for the reduced carrier-triggered photocatalytic performance.

Considering that the essential constituents of excitons are electrons and holes, excitons and charge carriers can interconvert into each other. The significance of this term is different from that of the above-mentioned one. As discussed in the above paragraph, the certain concentration ratio of excitons to charge carriers determined by $E_{\rm b}$ represents the reversible thermodynamic equilibrium between excitons and free charge carriers (that is, band-edge electrons and holes), while the conversion between excitons and charge carriers mentioned in this paragraph mainly refers to a non-equilibrium phenomenon. An explanatory example is the pursuit of chargecarrier accumulation by boosting exciton dissociation.⁹³⁻⁹⁵ It has been demonstrated that structural factors like heterojunctions and vacancies can provide energetic disorder for initiating exciton dissociation into charge carriers. However, such exciton dissociation is a non-equilibrium process, where

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irreversible energy loss leads to the formation of low-energy charge carriers trapped by other components or defects in the systems. In other words, these generated charge carriers are no longer the corresponding band-edge electrons and holes, but they can hardly go back to bound states. An opposite phenomenon to exciton dissociation is the formation of trapped excitons at defect sites, which can even occur in semiconductors with faint excitonic effects.^{96,97} These trapped excitons are usually strongly localized with large trapping energies and can seldom turn back to free charge carriers, which can notably impact photocatalysis-related properties like charge-carrier transport.²⁷ As for photocatalysis, the irreversible interconversions between excitons and charge-carriers would promise that high-efficiency and -selectivity photocatalysis could be achieved.

Moreover, excitonic effects can impact the efficiency of solar energy harvesting in low-dimensional semiconductors. As an important factor in photocatalysis, the light absorption property of a catalyst determines the available light region. From a charge-carrier perspective, band-structure modifications for optimizing light absorption of semiconductor-based photocatalysts have been attracting tremendous attention. However, excitonic effects can notably impact the light absorption properties of low-dimensional semiconductors. Formed by the correlations between the conduction and valence band states, excitonic states exhibit energy levels that are traditionally lower than those between band-edge states, due to the release of partial energy during the correlation processes. Thus, the feasible excitation of excitonic states enables the extension of the light absorption regions of photocatalysts. However, there are two points that need to be noted: oscillator strengths of excitonic transitions (including excitation and relaxation) strongly depend on the couplings between different degrees of freedom, and hence excitonic absorption coefficients can be quite diverse in different semiconductors;³⁸⁻⁴¹ the excitation of excitonic states linked to sub-band gap absorption leads to the formation of excitons, rather than uncorrelated charge carriers, and thus searching strategies for boosting exciton dissociation would be necessary in pursuit of charge-carrier generation. In addition to direct excitonic absorption, EEA can also provide potential pathways for realizing broadband light harvesting in hybrid systems (e.g., semiconductor/molecule and semiconductor/semiconductor systems).^{98–100} EEA originates from the collision between two low-lying excitons, during which the transfer of energy and momentum from one to the other leads to the formation of a high-lying exciton (also known as a hot exciton). The generated hot exciton can either relax to a low-lying state again or transfer to another component of hybrid systems. The latter situation exemplifies the use of low-energy photons for gaining high-energy excitons. According to the above description, it is clearly to see that, unlike direct excitonic absorption for broadening the intrinsic light absorption ranges of semiconductors, EEA-based light harvesting mainly depends on electronic couplings between different components in hybrid systems.⁷³ Such couplings are crucial to the timely transfer of hot or high-lying excitons before their cooling.

Overall, the unique characteristics of excitons provide lowdimensional semiconductors with non-trivial mechanisms for photocatalytic solar energy utilization, while the interplay between the excitonic and charge-carrier aspects further diversifies photocatalytic behaviors in these systems. In this case, it is rational to regulate the excitonic aspect of low-



Figure 5. (a) Layer-number-dependent E_b in two-dimensional black phosphorus. (b) Electron spin resonance (ESR) trapping tests for detecting ${}^{1}O_2$ generation. (c) Schematic illustration of how CdS quantum dots photosensitize Pd-based Heck coupling between styrene and iodocyclohexane. (d) Absorption spectrum of the Pd(II)CH₂TMS(Xantphos)I and emission spectra of different photosensitizers. Panel a reproduced with permission from ref 102. Copyright 2018 American Association for the Advancement of Science. Panel b reproduced with permission from ref 103. Copyright 2015 American Chemical Society. Panels c and d reproduced with permission from ref 104. Copyright 2020 American Chemical Society.

dimensional semiconductors in pursuit of optimized and versatile photocatalytic reactions.

EXCITONIC REGULATION IN LOW-DIMENSIONAL PHOTOCATALYSTS

On the basis of the above discussions, it can be seen that the excitonic aspect serves as an integral part of the photoexcitation processes in low-dimensional semiconductors and greatly impacts the relevant photocatalytic performance. Therefore, searching effective strategies for regulating excitonic properties is necessary for the pursuit of optimized photocatalytic reactions, regardless of whether they are exciton- or carrier-triggered ones. In this section, we provide a summary of recent progress in regulating the excitonic properties in lowdimensional photocatalysts.

Exciton-Binding-Energy and Exciton-Energy-Gap Regulation. With respect to exciton-triggered reactions, photocatalytic performance is typically linked to E_b and exciton energy gap. The former determines exciton concentrations in catalysts, while the latter partially determines the feasibility of energy transfer from catalysts to substrates. As for low-dimensional semiconductors, the two factors are closely related and tend to be modified simultaneously.

In contrast to molecular catalysts with permanent excitonic properties, low-dimensional semiconductors possess much more flexible and tunable excitonic properties, and several effective strategies have been established for the corresponding optimizations. Since excitonic effects arise from the Coulomb interactions, it is rational to optimize the two factors by regulating the electronic screening. For instance, it is well known that dielectric screening in low-dimensional semiconductors exhibits a prominent dependence on size and/or thickness. Accordingly, E_b and exciton energy gap can be effectively optimized by controlling the size and/or thickness of catalysts. Taking layered black phosphorus as an example, it has been theoretically and experimentally demonstrated that the involved $E_{\rm b}$ and exciton energy gap display significant layer-number dependence (Figure 5a), which endows black phosphorus with a tunable band gap spanning over a wide range (from 0.3 eV in bulk to 1.5 eV in monolayer).^{101,102} Inspired by this feature, we speculated that black phosphorus nanosheets could be used as an efficient visible-light photo-catalyst for ${}^{1}O_{2}$ generation. 103 To this end, we have prepared few-layer black phosphorus via water-assisted exfoliation. Due to the modified excitonic effects induced by reduced dimensionality, few-layer black phosphorus exhibits a wide absorption spectrum covering the visible and near-infrared regions. Photocatalytic measurements verified the excellent visible-light-driven ¹O₂ generation in few-layer black phosphorus (Figure 5b), showing a quantum yield of ~0.91 at 530 nm excitation. Benefiting from the high ¹O₂ generation, few-layer black phosphorus could be used in boosting reactions like Diels-Alder cycloadditions and ene reactions. Recently, Weiss's group reported the use of CdS quantum dots as sensitizers for boosting transition-metal photocatalytic Heck coupling, in which triplet-exciton-based energy transfer from CdS quantum dots to intermediate transition-metal complexes was crucial.¹⁰⁴ Taking Pd-based photocatalysis for Heck coupling between styrene and iodocyclohexane as a prototype, they demonstrated that, in addition to the direct excitation of Pd-based photocatalyst, the excitation of CdS quantum dots plays a crucial role in accessing high-reactivity and -selectivity



Figure 6. Transient absorption kinetic traces (taken at 450 nm) under (a) 315 and (b) 360 nm excitations. (c) Schematic illustration of the energy-transfer scenarios in polymeric carbon nitride/ketone systems. (d) ESR trapping tests for detecting ${}^{1}O_{2}$ generation in different samples. Reproduced with permission from ref 110. Copyright 2020 Wiley-VCH.

Heck coupling (Figure 5c). Using radical-trapping control tests and transient absorption/photoluminescence measurements, they identified that the triplet-triplet energy transfer between CdS quantum dots and Pd(II) intermediate results in the formation of a Pd(I) intermediate. This process drives the reaction toward the Heck product rather than the cyclohexene byproduct. By regulating exciton energy gap via size control, they maximized the spectral overlap between the emission of CdS quantum dots and the absorption of Pd(II) intermediate, enabling optimized photocatalytic performance to be achieved in the 2.4-nm-radius case (Figure 5d). Beyond the above sizeand thickness-control strategies, the construction of heterojunction structures has also been confirmed to be effective in regulating $E_{\rm b}$ and exciton energy gaps. Compared to the bare counterparts, low-dimensional semiconductors in heterojunction structures are, in fact, surrounded by some other components with different dielectric properties. Several recent works have demonstrated that the differences in dielectric environments would result in changes in the strengths of the Coulomb interactions between electrons and holes, thus giving rise to modified $E_{\rm b}$ and exciton energy gaps.^{31,32,105} In this regard, it is rational to provide comprehensive assessments on low-dimensional semiconductor-based photocatalysis, since the local dielectric environments (including but not limited to heterojunctions and solvent environments) lead to inevitable changes in excitonic properties.

Exciton-Spin-State Regulation. Another important factor determining exciton-triggered photocatalytic performance is spin configuration. As depicted above, spin configuration as an intrinsic degree of freedom of excitons determines not only energy transfer mechanisms but also photocatalytic efficiencies. Consequently, spin-state relaxation should be considered when dealing with low-dimensional semiconductor-based photocatalysis.

In terms of spin-state relaxation in photocatalysis, one of the most important tasks is to optimize the generation of triplet excitons. Due to their unity-spin and long-lived features, triplet excitons are usually involved in exciton-triggered reactions. According to the spin conservation rule, triplet excitons are mainly generated by the spin-state relaxation of singlet excitons undergoing a spin-flip process termed intersystem crossing rather than by direct excitation. However, as for metal-free semiconductors, the intersystem crossing rates are typically low due to their weak spin-orbit coupling, thereby leading to faint triplet exciton generation.¹⁰⁶⁻¹⁰⁸ Taking polymeric carbon nitride as an example, we have managed to optimize spin-state relaxation for triplet exciton harvesting by different strategies.^{92,109,110} For instance, we have demonstrated that the incorporation of carbonyl groups can effectively promote spinstate relaxation in the systems.¹⁰⁹ According to spectroscopic analyses, we identified that, as compared with the pristine counterparts, the oxidized carbon nitride containing carbonyl groups exhibited promoted spin-orbit coupling and reduced singlet-triplet energy gap, thereby giving rise to significant promotion in the intersystem crossing rate and hence the triplet exciton generation. Such optimizations endow the oxidized carbon nitride with excellent performance in excitontriggered photocatalytic ${}^1\mathrm{O}_2$ generation. In addition to the modification on intrinsic intersystem crossing rate in polymeric carbon nitride, we recently demonstrated that the extrinsic introduction of molecules with suitable electronic configurations can also lead to apparent promotion in triplet exciton generation involved therein.¹¹⁰ According to the opposite evolution in transient absorption kinetics under different excitations in a polymeric carbon nitride/acetone system (Figure 6a,b), we highlighted that excited states with mixed $\pi\pi^*/n\pi^*$ configurations in aliphatic ketones enable intriguing exciton-based energy transfer processes in the system: hotexciton-based energy transfer from polymeric carbon nitride to ketones and triplet-exciton-based energy transfer from acetone to polymeric carbon nitride (Figure 6c). Benefiting from the two opposite energy transfer processes, polymeric carbon



Figure 7. (a) Band-edge charge densities of BiOBr model with an oxygen vacancy. (b) Transient absorption kinetic traces of BiOBr and BiOBr-OV samples. (c) Schematic illustration of oxygen-vacancy-mediated exciton dissociation in BiOBr system. (d) Schematic illustration of exciton dissociation and charge-carrier transport in semicrystalline carbon nitride. (e) Steady-state and time-resolved fluorescence spectra and (f) Mott–Schottky plots of pristine and semicrystalline carbon nitride. Panels a, b, and c reproduced with permission from ref 111. Copyright 2018 American Chemical Society. Panels d, e, and f reproduced with permission from ref 117. Copyright 2017 American Chemical Society.

nitride exhibited promoted triplet exciton harvesting in appearance, and as a consequence, ketones could serve as co-catalysts for boosting exciton-triggered photocatalytic reactions (Figure 6d). Beyond the above-mentioned strategies, there are some other methods for promoting intersystem crossing rates such as heavy-atom incorporation and donor– acceptor construction.

The importance of spin-state relaxation is also embodied in its impacts on photocatalytic quantum efficiencies. The effective accumulation of energetic photoinduced species (including excitons and charge carriers) in catalysts is essential for gaining high efficiency, whereas the correlations between excitons might afford robust non-radiative decays in many lowdimensional semiconductors. For instance, we have demonstrated that triplet-triplet annihilation establishes an important non-radiative decay in polymeric carbon nitride, and accordingly, excessive high-concentration triplet exciton is detrimental to the effectual accumulation of both excitons and charge carriers. In fact, it has been confirmed that the excessive improvement of intersystem crossing rates (for instance, by introducing heavy atoms) can lead to promoted consumption of energetic photoinduced species. To this issue, we have proposed that dimensionality control can effectively regulate the spin-state relaxation in the system.⁹² Owing to the promoted conjugated degrees induced by dimensionality reduction, two-dimensional polymeric carbon nitride exhibits reduced spin-orbit coupling and promoted singlet-triplet energy gap, as compared with the bulk counterpart. Benefiting from these changes, the intersystem crossing efficiency in twodimensional polymeric carbon nitride is only \sim 7% of that in bulk material. As such, suppressed triplet-triplet annihilation linked to the low-concentration triplet exciton can be expected in two-dimensional polymeric carbon nitride, as evidenced by its faint E-type delayed fluorescence. This result reveals the essence of the high efficiencies for both photocatalysis (linked

to charge-carrier concentration) and photoluminescence (mainly linked to singlet-exciton radiative decay) in twodimensional polymeric carbon nitride.

Exciton-toward-Charge-Carrier Regulation. Excitonic regulation should also be considered in pursuing optimized carrier-triggered photocatalytic reactions. According to the above discussions, it is clear that the dependence and interplay between the excitonic and charge-carrier aspects can afford additional access to the regulation of charge-carrier properties. As a matter of fact, the above-discussed dimensionality control for optimizing photoinduced species accumulation in twodimensional polymeric carbon nitride can also be useful for excitonic regulation for boosting carrier-triggered photocatalytic performance. In addition, there is another intuitive term, exciton dissociation, that is pertinent to this subject. Owing to the robust excitonic effects, low-dimensional semiconductors are likely to possess insufficient free chargecarrier generation, which undoubtedly sets restrictions on carrier-triggered photocatalysis. In this case, searching effective strategies to dissociate excitons into uncorrelated electrons and holes would be favorable. To overcome the energy barrier of exciton dissociation, energetic disorder associated with structural factors like heterojunctions and defects is typically required.^{93–95,111–115} For instance, focusing on the low chargecarrier concentration induced by strong excitonic effects in bismuth oxybromide (BiOBr), we recently proposed that effective exciton dissociation could be achieved by defect engineering.¹¹¹ Using first-principles calculations, we identified that the introduction of oxygen vacancy could significantly distort the distribution of band-edge charge density (Figure 7a), which hints at the reduced stability of excitons near the defective site. Photoluminescence and photoelectrochemical measurements confirmed that the defective sample displayed lower exciton concentration but higher charge-carrier concentration than the pristine sample. Further transient absorption

measurements highlighted that the oxygen vacancy would hold up an additional relaxation pathway, where the defectmediated trapping state enables significant promotion in recovery lifetime of photoinduced charge carriers (Figure 7b,c). There are many other structural factors that can induce exciton dissociation. For instance, noble metal particles are widely employed as co-catalysts for booming carrier-triggered water splitting, the positive role of which in providing reactive sites has been verified.¹¹⁶ However, as for low-dimensional semiconductors, the covert impacts of noble metal particles on exciton dissociation should be recognized. That is, the disordered energy landscape at the interface between photocatalyst and noble metal particles would provide additional driving force for promoting exciton dissociation.¹¹³ Similar phenomena can be widely observed in heterojunctions, where the types of energy band alignment and thermal vibrations are crucial. 114,115

Beyond heterojunctions, some single-component systems exhibit promoted excitonic dissociation.117-119 For instance, focusing on the insufficient charge-carrier generation in polymeric carbon nitride, we proposed that the introduction of order-disorder interfaces can promote charge-carrier concentration by boosting exciton dissociation (Figure 7d).¹¹⁷ According to theoretical simulations and spectral analyses, we identified that the ordered heptazine-based melon chains displayed lower HOMO and LUMO energy levels than the disordered ones. In this case, electrons and holes generated by exciton dissociation at the order-disorder interfaces would be selectively injected toward the ordered and disordered chains (to some extent, be trapped by different components of the system), respectively, while the high conjugated feature of the ordered chains would facilitate the transport of electrons. Steady-state and time-resolved photoluminescence spectra confirmed the low-concentration singlet exciton and accelerated exciton dissociation in semicrystalline carbon nitride (Figure 7e). Mott-Schottky measurements verified that semicrystalline carbon nitride exhibits ~7-fold increase in electron concentration as compared with the amorphous one (Figure 7f). Benefiting from this, semicrystalline carbon nitride displays promoted electron-triggered $O_2^{\bullet-}$ production but suppressed exciton-triggered ¹O₂ generation. Another classical example is the construction of donor-acceptor copolymers.^{118,119} Different from the traditional polymers consisting of single repeated units, donor-acceptor copolymers are comprised of at least two kinds of repeated units with different electronegativity properties. Owing to the alternate arrangement of electron-rich and -deficient units, electrons and holes in excitons would display spatially separated distribution, leading to the formation of bound charge transfer states that can be more easily dissociated into free charge carriers. As for inorganic semiconductors, some similar features can be observed. For instance, it has been demonstrated that, although with giant excitonic effects, BiOBr samples with (010)-facet exposure exhibit excellent performance in carriertriggered molecular oxygen activation.²⁸ Recent, Shi et al. identified that BiOBr with different facets exposure tend to exhibit subtle differences in band structures, which would lead to spatial separation of photogenerated charges in the system.¹²⁰ Therefore, it can be deduced that the facetdependent spatial charge separation can constantly shift the thermal balance from excitons to charge carriers, thus leading to promoted carrier-triggered reactions.

Furthermore, the unique symmetry-breaking features in lowdimensional semiconductors might lead to anisotropic electronic and optical properties, which would offer extrinsicfield access to regulating carrier-triggered photocatalysis. In this regard, two-dimensional black phosphorus-based photocatalysis represents a prototypical illustration.¹²¹ Arising from its unique crystal structure, two-dimensional black phosphorus exhibits remarkable band dispersions along the armchair direction. Such anisotropic band dispersions permit twodimensional black phosphorus some intriguing photophysical properties that are usually involved in one-dimensional materials. For instance, by using photoluminescence spectroscopy and femtosecond time-resolved transient absorption spectroscopy, we have verified the presence of sub-band structures that can be linked to van Hove singularities in twodimensional black phosphorus. Benefiting from this, the system exhibits notable excitation-energy-dependent photocatalytic behaviors: exciton-triggered ¹O₂ generation and carriertriggered hydroxyl radical production occurred under visibleand ultraviolet-light illumination, respectively. Note that excitonic effects dominate the photoexcitation properties of two-dimensional black phosphorus, whereas the energy levels or redox potentials of different energetic photoinduced species under certain illuminations are responsible for the optically switchable photocatalysis.

PERSPECTIVE AND CHALLENGES

To summarize, excitonic effects as an intrinsic property tend to be rather robust in low-dimensional semiconductors. Accordingly, the excitonic aspect, together with the traditional chargecarrier aspect, constitutes the photoexcitation processes and thus makes a significant contribution to photocatalytic behaviors of low-dimensional semiconductors. Owing to the unique characteristics like energy levels and spin configurations of excitonic states, exciton-based energy transfer provides lowdimensional semiconductors with an alternative pathway, beyond the traditional carrier-based charge transfer, for realizing energy harvesting and utilization. Besides, since excitons are in essence bound pairs of electron and hole, the excitonic and charge-carrier aspects of photoexcitation processes tend to be interrelated. The dependence and interplay between the two aspects play crucial roles in the involved photocatalytic behaviors. All these features indicate that some non-trivial photocatalytic behaviors associated with excitonic effects can be sought in low-dimensional semiconductors. As a consequence, regulation of the excitonic aspect establishes rich possibilities for gaining optimized photocatalytic solar energy utilization triggered by either charge carriers or excitons. Recently, benefiting from the advances in characterizing the photophysical processes, a series of achievements has been made in understanding and regulating the excitonic aspect for versatile photocatalytic applications. However, the excitonic perspective on lowdimensional semiconductor-based photocatalysis is far from mature, and there are some crucial issues that need to be addressed in the future:

Enlightening the Fundamental Mechanisms of Exciton-Triggered Photocatalysis. As a supplement to the traditional carrier-based charge transfer, exciton-based energy transfer establishes an alternative pathway for achieving photocatalytic solar energy conversion. However, several recent works have demonstrated that the energy transfer between semiconductors and molecules would be much more

complicated than expected, and some conclusions even challenge the conventional knowledge. For instance, Hofmann et al. found that the energy transfer from perovskite nanocrystals to dye molecules does not depend on spectral overlap, and electron-phonon coupling might be responsible for this non-resonant energy transfer.¹²² Wu's group recently investigated the energy transfer in semiconductor/dye systems, for which they suggested that triplet energy transfer would be mediated by electron transfer rather than the traditional onestep mechanism.^{123,124} These findings reveal that excitontriggered photocatalysis might involve some quite non-trivial scenarios of energy transfer between low-dimensional semiconductor-based photocatalysts and substrate molecules. One of the most likely reasons for the above abnormal phenomena is that, as compared with the traditional molecular counterparts, low-dimensional semiconductor-based photocatalysts tend to possess much more complicated couplings between different degrees of freedom. These couplings determine both the transfer and the relaxation of energetic species (including charge carriers and excitons). In addition, the rich surface structures of low-dimensional semiconductors also confuse the unraveling of the involved photocatalytic energy transfer. As for most exciton-triggered photocatalysis, the transfer of triplet excitons via a Dexter energy transfer pathway is crucial. Accordingly, the bonding configurations between photocatalysts and molecules would determine the mechanisms and efficiencies of different energy transfers. In contrast to the limited bonding scenarios in the molecular case, much more diverse bonding configurations can be expected in the lowdimensional semiconductor case, due to the abundant surface structures. Moreover, it has demonstrated that the adsorption of molecules can impact the intrinsic electronic structures of semiconductors.⁸⁸ According to the above discussions, it can be concluded that detailed characterizations and analyses of the coupling-dominated excitonic properties in low-dimensional semiconductor-based and the interactions between photocatalysts and substrates are necessary for enlightening insights into the fundamental mechanisms of exciton-triggered photocatalysis.

Extending the Methods for Characterizing the Excitonic Properties in Low-Dimensional Photocatalysts. The characterization of excitonic properties in lowdimensional semiconductors involves much more complicated experimental and theoretical techniques, which inevitably hinders the comprehensive understanding of the impacts of excitonic effects on photocatalytic behaviors. For instance, the theoretical investigation of excitonic properties in lowdimensional semiconductors required many-body techniques,^{125,126} which is computationally demanding, thus undoubtedly limiting the corresponding investigations. In this respect, qualitative approaches for exploring the excitonic effects by using first-principles calculations based on density functional theory would be favorable. For instance, Dvorak investigated the relationships between excitonic effects and the localization of the Kohn-Sham eigenstates, in which the importance of the localization of band-edge states on the excitonic binding energies of semiconductors was highlighted.¹²⁷ This approach has been used for determining the excitonic properties of ionic systems like bismuth oxyhalides and zinc oxide.^{28,111,128} As for the experimental characterizations, the commonly available techniques are usually sensitive to the states and dispersions of low-dimensional materials, and monodispersed characteristics of these materials

and micro/nano technologies are typically required.^{56,60} However, the applicability of these techniques in the context of photocatalytic systems is limited. In this regard, it is necessary to develop systematic and convenient techniques and methods for characterizing the excitonic properties involved in low-dimensional semiconductors under reaction conditions. Recently, the wide employment of transient absorption in photocatalytic research enables a close watch of the involved excitonic properties, whereas accurate interpretations of the results are still challenging. Moreover, given that excitonic effects depend on the surrounding environments, it is necessary to evaluate the potential impacts of dynamic structural changes on excitonic properties. That is, investigating the adsorption, activation, and dissociation of substrate and/or solvent molecules on the surface of lowdimensional semiconductors and the corresponding impacts on excitonic properties is required. To this issue, developing real-time and in situ techniques for detecting the evolution of excitonic properties under reaction conditions would be helpful.

Enriching the Strategies for Excitonic Regulation in Low-Dimensional Photocatalysts. Up to the present, quite limited optimization strategies have been proposed for regulating the excitonic processes of low-dimensional semiconductor-based photocatalysts. In fact, as a consequence of the insufficient investigations of the impacts of excitonic effects on photocatalytic behaviors, a systematic theory for excitonic regulation in low-dimensional semiconductor-based photocatalysis remains lacking. As for enriching the strategies for excitonic regulation, a major challenge lies in clarifying the relationships between structural factors (like vacancies, doping atoms, heterojunctions, etc.) and excitonic properties. To this issue, the precise design of low-dimensional semiconductors with certain structural factors and the accurate characterization of excitonic properties are essential. In addition, the dependence and interplay between the excitonic and charge-carrier aspects also pose obstacles. That is, on the one hand, structural factors implement impacts on the two aspects simultaneously; on the other hand, there are dependences and conversions between the two aspects. Both characteristics make it ambiguous to distinguish the exact contribution of structural modifications to excitonic regulation. As a matter of fact, the traditional charge-carrier regulations in low-dimensional semiconductors should be re-considered, where the potential effects of structural modification on optimizing the excitonic properties should be estimated. To this issue, detailed control photocatalytic measurements and analyses are needed. For instance, the quenching of certain photoinduced species can be used to identify their exact functions. By figuring out the impacts of structural factors on excitonic properties, it would be possible to enrich the strategies for the selective optimizations of the excitonic and charge-carrier aspects and, hence, the performances of photocatalytic reactions triggered by different photoinduced species.

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Notes

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