Low-Dimensional Semiconductors in Artificial Photosynthesis: An Outlook for the Interactions between Particles/Quasiparticles

Hui Wang, Wenxiu Liu, Sen Jin, Xiaodong Zhang,* and Yi Xie*

ABSTRACT: By virtue of their intriguing electronic structures and excellent surface properties, low-dimensional semiconductors hold great promise in the field of solar-driven artificial photosynthesis. However, owing to promoted structural confinement and reduced Coulomb screening, remarkable interactions between particles/quasiparticles, including electrons, holes, phonons, and excitons, can be expected in low-dimensional semiconductors, which endow the systems with distinctive excited-state properties that are distinctly different from those in the bulk counterparts. Consequently, these interactions determine not only the mechanisms but also quantum yields of photosynthetic energy utilization. In this Outlook, we review recent advances in studying the unique interactions in low-dimensional semiconductor-based photocatalysts. By highlighting the relevance of different interactions to excited-state properties, we describe the impacts of the interactions on photosynthetic energy conversion. Furthermore, we summarize the regulation of these interactions for gaining optimized photosynthetic behaviors, where the relationships between these interactions and structural factors/external fields are elaborated. Additionally, the challenges and opportunities in studying the interaction-related photosynthesis are discussed.

1. INTRODUCTION

Photosynthesis, which plays a crucial role in balancing ecological cycles of materials and energy, displays an excellent prototypical model for converting solar energy to chemical energy. Inspired by this process, numerous efforts have been devoted to artificial photosynthesis for pursuing solar energy utilization for decades.1−9 Analogous to chloroplasts (in plants) or light-harvesting pigments (in some bacteria) in natural photosynthesis, catalysts in artificial photosynthesis act as a light antenna, and the transfer of energetic photoinduced species in catalysts toward substrate molecules is responsible for the relevant energy conversion. In terms of designing advanced photocatalysts, many light-harvesting materials have been proposed for their potentials in artificial photosynthesis, which can be mainly divided into two kinds: atomic/molecular systems (e.g., ions, organic species, metal complexes, etc.) and solid-state systems (mainly, noble metals and semiconductors). The two kinds of photocatalysts have their own merits and demerits in aspects like material source, molar extinction coefficient, surface property, chemical stability, biotoxicity, and so on. Besides, a major difference lies in their excited-state properties, where the different configurations and kinetics of photoinduced species result in quite distinct behaviors in certain photosynthetic reactions. Herein, exploring advanced photocatalysts for combining the advantages of both molecular and solid-state systems would be meaningful to the pursuit of plentiful solar-driven artificial photosynthesis.

Owing to their impressive surface and electronic structures, low-dimensional semiconductors have been attracting tremendous attention in the field of artificial photosynthesis.9−12 As compared to their bulk counterparts, low-dimensional semiconductors tend to possess smaller sizes and higher specific surface areas, which facilitates reactive-site exposure and structural modifications. In addition, low-dimensional semiconductors possess novel electronic structures, where structural confinement leads to tunable size-dependent excited-state properties. The most exciting feature is that low-dimensional semiconductors appear to display some molecule-like excited-state configurations and kinetics, due to the promoted interactions between particle/quasiparticles (e.g., electrons, holes, excitons, phonon, etc.) induced by reduced dimension and Coulomb screening.12 All these features make low-dimensional semiconductors excellent platforms combining the merits of both molecular and solid-state photocatalysts for achieving versatile photosynthetic energy utilization.

Received: April 30, 2020
Published: June 5, 2020
Although great achievements have been made in low-dimensional semiconductor-based photosynthesis, the limited understanding of the involved excited-state properties sets restrictions on the comprehensive optimization of photosynthetic performance. As compared to their bulk counterparts, low-dimensional semiconductors possess much more complicated excited-state properties linked to the interactions between particles/quasiparticles. Consequently, traditional viewpoints focusing on band structures and charge-carrier behaviors seem to be insufficient in depicting the whole profiles of photoexcitation processes in low-dimensional semiconductors. Over the past decade, benefiting from the developments in synthetic and characterization techniques, great progress has been made in studying the excited-state properties in low-dimensional semiconductors, which make the impacts of these interactions on photosynthetic behaviors accessible to researchers. In this Outlook, focusing on the intriguing interaction-dominated excited-state properties, we review recent advances in photosynthesis with low-dimensional semiconductors. We describe the interactions between different particles/quasiparticles in low-dimensional semiconductors, where their impacts on the excited-state properties and hence the photosynthetic behaviors are highlighted. Moreover, on the basis of the understanding, we summarize the strategies in optimizing the excited-state properties for achieving high-efficiency photosynthesis. Finally, we conclude the Outlook with a perspective on the challenges and opportunities in investigating the interaction-related photosynthesis of low-dimensional semiconductors.

As compared to their bulk counterparts, low-dimensional semiconductors possess much more complicated excited-state properties linked to the interactions between particles/quasiparticles.

2. EXCITED-STATE PROPERTIES IN LOW-DIMENSIONAL SEMICONDUCTORS

As for photosynthetic conversion of solar energy to chemical energy, the effective photoexcitation of catalysts is required. Upon illumination by light with suitable photon energy, reactive photoinduced species acting as energy carriers are generated in catalysts, followed by transferring toward substrate molecules. With regard to photosynthesis, excited-state properties such as excitation, relaxation, and recombination of these photoinduced species are vital to the relevant performance. However, owing to their solid-state features but strong confined structures, low-dimensional semicon conductors exhibit fairly unique electronic states that are different from those of molecular and bulk systems. In fact, this is the fundamental cause of the rich potential of low-dimensional semiconductors in photosynthesis. In this section, we carry out a brief discussion on the excited-state properties of low-dimensional semiconductors.

Due to their different chemical components and structures, molecular and solid-state photocatalysts possess different electronic configurations, which would lead to diverse photosynthetic behaviors. As for molecular catalysts, a discrete energy-level diagram based on molecular orbital theory is generally employed to describe the involved excited states (Figure 1a). Molecular orbital theory is a delocalized bonding approach, where electrons are deemed to interact with all nuclei, rather than the isolated nucleus in the system. That is, molecular orbitals, arising from the hybridization (namely, bonding and antibonding combinations) of atomic orbitals from every atom, distribute all over the molecular system, and the accommodation of electrons to these discrete (or quantized) molecular orbitals leads to energy reduction of the system. In consideration of the Coulomb and exchange interactions, the excited molecule can be regarded as a bound electron–hole state, or so-called molecular exciton.13 As for bulk semiconductor-based photocatalysts, excited-state properties are much more complicated as compared to those of molecular systems. Typically, band theory is used to depict the involved excited states (Figure 1b), and a periodic potential resulting from the periodic crystal structure is proposed to simplify the electronic behaviors. In fact, semiconductors can be considered as extended, strong-couple molecular systems, where an infinite number of frontier occupied and unoccupied molecular orbitals which are closely localized in energy space constitute their valence and conduction bands, respectively. The energy separation between these molecular orbitals (in the order of $10^{-22}–10^{-23}$ eV) is much smaller than the thermal energy (e.g., 26 meV at room temperature), which means that electronic transitions between these close-localization molecular orbitals can be easily provoked by exchanging energy between charge carriers and thermal vibrations.14 Band theory is only an approximation, and the complicated interactions between different species including charge carriers, and excitons, are fully considered. Different electronic structures can be expected so long as these interactions are considered. In fact, it is the major factor that is responsible for the characteristic excited-state properties of low-dimensional semiconductors.

As compared to their bulk counterparts, low-dimensional semiconductors possess remarkably promoted interactions between different species due to promoted structural confinement and reduced dielectric screening. These interactions endow low-dimensional systems with nontrivial excited-state properties that could hardly be observed in bulk systems. For instance, owing to size/dimension reduction, quantum confinement effects can greatly impact the band structures of...
low-dimensional semiconductors. That is, the hybridization of a finite number of atomic orbitals in low-dimensional semiconductors leads to a finite density of states, which thus gives rise to discrete energy levels and blue-shifted band gaps. Besides, the reduced dimension also leads to limited electronic screening in low-dimensional systems, thus resulting in promoted Coulomb interactions between electrons that can greatly impact the band structures.\textsuperscript{15–18} As a typical result, size-/thickness-dependent band structures can be widely observed in low-dimensional semiconductors.\textsuperscript{17,18} Moreover, as for the symmetry breaking in low-dimensional semiconductors, the potential anisotropic dispersions of electronic structures can further promote electron–electron interactions in particular orientations, thus leading to some anisotropic electronic properties.\textsuperscript{18} In addition to the above band-structure changes, strong interactions between electrons also impact the other excited-state properties like transport behaviors and charge-carrier relaxations.\textsuperscript{19,20} Another remarkable feature in low-dimensional semiconductors is the promoted Coulomb interactions between photoinduced electrons and holes.\textsuperscript{21,22} In semiconductors, photoexcitation gives rise to the formation of electrons and holes in conduction and valence bands, respectively, whereas the typically high dielectric properties in bulk systems result in faint Coulomb interactions between these charged species. However, screening reduction effectively rouses such interactions and hence leads to robust excitonic effects in low-dimensional semiconductors (Figure 1c). As a consequence, excitons (or bound electron–hole pairs) can be expected in the systems. The energy difference between quasiparticle band gap and lowest excitonic energy level is called exciton binding energy ($E_b$), which can be used to evaluate the strength of excitonic effects. In addition, there are also other kinds of interactions such as electron–phonon, electron–exciton, and exciton–exciton interactions in low-dimensional semiconductors that can impact both the mechanism and efficiency of solar energy utilization (further discussion will be given later). All these interactions permit low-dimensional semiconductors to possess excited-state properties with both solid-state and molecular features, which pave the way for achieving diverse photosynthetic energy utilizations.

Figure 2. (a) Electron doping concentration-dependent band gap evolutions, where $E_{\text{con}}$ (red squares) and $E_g$ (blue dots) denote onset energy and quasiparticle band gap, respectively. (b) Top and side views of the square of the electron wave functions of the first bound excitons in monolayer black phosphorus. (c) Schematic illustration of the sub-band structures and (d) wavelength-dependent reactive oxygen species generation of two-dimensional black phosphorus. Panel a reproduced with permission from ref 26. Copyright 2017 American Physical Society. Panel b reproduced with permission from ref 18. Copyright 2014 American Physical Society. Panels c and d reproduced with permission from ref 29. Copyright 2018 American Chemical Society.
3. IMPACTS OF THE INTERACTIONS ON PHOTOSYNTHESIS

On the basis of the above discussion, it can be concluded that the abundant interactions between different species jointly dominate excited-state properties of low-dimensional semiconductors. Therefore, the clarification of the relationships between different interactions and photosynthetic behaviors is essential for gaining optimized photosynthetic energy utilization. In terms of semiconductor-based photosynthesis, band structures (including band gap and energy levels) and photoinduced species behaviors (e.g., intraband relaxation, radiative/nonradiative recombination, migration, etc.) are considered to be directly associated with the involved solar energy conversion. However, in view of the promoted interactions in low-dimensional semiconductors, traditional considerations focusing on charge-carrier properties for understanding and optimizing the involved photosynthetic behaviors would be finite. In this context, we can make connections between the promoted interactions and photosynthetic behaviors of low-dimensional semiconductors by figuring out the changes in band structures and photoinduced species behaviors.

3.1. Electron−Electron Interactions. Owing to reduced screening effects, promoted Coulomb interactions between electrons emerge in low-dimensional semiconductors. Given that electronic bands of semiconductors originate from the interplay of the electrons and nucleus, the promoted interactions between electrons lead to renormalized electronic energy levels and elevated quasiparticle band gaps. A characteristic change resulting from the promoted interactions is the size-/thickness-dependent band structures. For instance, layer-dependent band structures of two-dimensional transition metal dichalcogenides (TMDs) have been theoretically and experimentally demonstrated.\textsuperscript{23,24} Besides, the electron−electron interaction-induced band structure renormalization widely exists in these systems, and even low-concentration electron doping can lead to giant band gap reduction (Figure 2a).\textsuperscript{25,26} Since that band gap and band-edge energy levels determine the light-responsive region and charge-carrier redox capacity, respectively, the above features in low-dimensional semiconductors enable photosynthetic behaviors to be tuned by precise size/dimension control and chemical doping. Moreover, as for some low-dimensional semiconductors with unique structural factors, symmetry breaking and dimension reduction lead to anisotropic electronic band structures.\textsuperscript{18,27,28} This anisotropic feature can give rise to pretty distinctive photosynthetic behaviors. Taking two-dimensional black phosphorus as an example, both theoretical and experimental studies confirm the highly anisotropic optical responses in the system, where the quasi-one-dimensional dispersions of electronic structures associated with the anisotropic in-plane crystal structure are crucial (Figure 2b).\textsuperscript{18,27,28} The extraordinary band dispersions and strong electron−electron interactions induce pronounced self-energy corrections, which are responsible for the enlarged band gap and the presence of van Hove singularities. The van Hove singularities lead to nontrivial subband structures and therefore excitation-energy-dependent optical response in this two-dimensional system. Our group...

Figure 3. (a) Schematic illustration of energy-transfer-initiated intermolecular [2 + 2] cycloadditions, and (b) exciton decay dynamics in CdSe quantum dots with the additional 4-vinylbenzoic acid. Schematic illustrations of (c) P-type delayed fluorescence originating from TTA in polymeric carbon nitride and (d) biexciton-based energy transfer from excited CdSe/ZnS nanocrystals to surface acceptor dyes. Panels a and b reproduced with permission from ref \textsuperscript{32}. Copyright 2019 Nature Publishing Group. Panel c reproduced with permission from ref \textsuperscript{40}. Copyright 2017 Royal Society of Chemistry. Panel d reproduced with permission from ref \textsuperscript{42}. Copyright 2016 American Chemical Society.
recently demonstrated that the nontrivial sub-band structures in two-dimensional black phosphorus enable optically switchable photocatalytic oxygen activation, where visible- and ultraviolet-light illuminations lead to the selective generations of singlet oxygen and hydroxyl radical, respectively (Figure 2c,d).39

3.2. Electron–Hole Interactions. Induced by the promoted interactions between photoinduced electrons and holes, excitonic effects could be prominent and general in low-dimensional semiconductors. As a result, excitons will be dominating photoinduced species that coexist with charge carriers (that is, electrons and holes). The excitonic aspect of photoexcitation processes is inseparable from the widely investigated charge-carrier aspect, which has quite subtle impacts on low-dimensional semiconductor-based photosynthesis.

Exciton-based energy transfer can afford an alternative pathway for solar energy utilization, beyond the traditional carrier-based charge transfer.13,30,31 Undergoing exchange interactions or dipole–dipole coupling, excitons can resonantly transfer from photocatalysts to substrate molecules, in which the matches of both energy levels and spin multiplicities between the relevant excitonic states are required. In terms of most photosynthetic reactions, bond breaking/making via carrier-based charge transfer is more preferable to obtaining excited states of substrate molecules via exciton-based energy transfer. However, as for some special substrate molecules like oxygen and some organic molecules, exciton-based energy transfer might be much more facile, and the formation of molecular excited states with certain spin multiplicities can give rise to some intriguing behaviors. Recently, several exciting works have been done in exploring exciton-based energy-transfer-initiated photosynthesis in low-dimensional semiconductors.29,32–34 For instance, Jiang et al. reported photocatalytic intermolecular [2 + 2] cycloadditions triggered by triplet exciton-based energy transfer from CdSe quantum-dot-based photocatalysts (Figure 3a).32 Taking advantage of the tunable, triplet-like excitonic states, they regulated the involved triplet energy levels by controlling the size of CdSe quantum dots. Benefiting from these, CdSe quantum dots exhibited an excellent performance, both regioselectivity and diastereoselectivity, in photocatalytic intermolecular [2 + 2] of 4-vinylbenzoic acid derivatives. Using transient absorption spectroscopy, they deduced that triplet exciton-based energy transfer, rather than carrier-based charge transfer, between CdSe quantum dots and 4-vinylbenzoic acid occurred on the surface (Figure 3b). As compared to the above deduction, Castellano and co-workers have demonstrated that direct triplet exciton-based energy transfer between low-dimensional inorganic semiconductors and organic molecules is feasible, just like that in the molecular donor/acceptor system.35

Excitonic effects determine the photosynthetic efficiencies of redox-initiated reactions like water splitting, carbon dioxide reduction, nitrogen fixation, and so on.52,28,36 Since that excitonic aspect acts as an opposite of the charge-carrier aspect, excitonic and charge-carrier aspects are interrelated, and the concentrations of exciton and charge carrier are correlative. These features can be understood as follows: on one hand, the strength of excitonic effects (i.e., exciton binding energy, $E_b$) inherently dominates the concentrations of excitons and charge carriers, where a large $E_b$ means an unfavorable redox-initiated photosynthesis; on the other hand, given that excitons are essential bound electron–hole pairs, desirable charge-carrier concentrations can be expected by promoting the dissociation of excitons. Based on these understandings, it is rational to consider that reducing exciton binding energy and promoting excitonic dissociation are necessary in gaining high-efficiency redox-initiated photosynthesis. We will provide detailed discussions on the relevant excitonic regulations in the next section.

Besides, excitonic effects also impact the light absorption properties. That is, as for low-dimensional semiconductors with large exciton binding energies, promoted electron–hole interactions would lead to exciton absorption, which constitutes a remarkable part of the overall light absorption. Exciton absorption enables sub-band-gap excitation to be achieved in low-dimensional semiconductors. With regard to photosynthesis, the sub-band-gap exciton absorption would facilitate solar energy utilization. However, because of the factors like spin and valley degrees of freedom, exciton absorption in some systems tends to be low-coefficient as compared to interband absorption, and brightening these excitonic states would be advantageous to photosynthetic applications. In addition, as for some semiconductors with large exciton absorption coefficients, exciton absorption would dominate the optical spectral lines. In that case, the band gap estimated from the absorption spectrum (that is, optical band gap) is in fact the energy level of the excitonic state, rather than the energy gap between conduction- and valence-band edges (that is, quasiparticle band gap). There are several effective techniques to determine quasiparticle band gap.37–39 For instance, photoconductivity measurements have been widely employed for gaining the quasiparticle band gap, on the basis of the electrically neutral feature of the exciton.37 Other techniques like photoluminescence excitation spectroscopy and scanning tunneling spectroscopy39 have also been demonstrated to be feasible for extracting the quasiparticle band gap. Combined with some other band-structure characterization (like angle-resolved photoemission spectroscopy and ultraviolet photoelectron spectroscopy), quasiparticle band alignment can be deduced. However, it is worth noting that the determination of quasiparticle band structures in low-dimensional semiconductor-based photocatalysts would still be challenging, due to the fact that the band structure determined by the interactions between particles/quasiparticles can be significantly modified by the surrounding environments (detailed discussion will be given in Section 4.1).

3.3. Quasiparticle-Involved Interactions. The interactions between quasiparticles (such as exciton and phonon) should also be considered when dealing with low-dimensional semiconductor-based photosynthesis.

In comparison with the above-discussed excitonic effects induced by two-particle electron–hole interactions, there are some high-order interactions originating from Coulomb interactions among three or more photoinduced charge carriers. A typical characteristic is the presence of the interactions between two excitons, which embodies impacts on photosynthesis in a variety of ways. For instance, exciton–exciton annihilation, a nonradiative decay process originating from the inelastic collisions between two low-lying excitons, leads to the formation of a high-lying exciton: exciton–exciton annihilation can result in fast depopulation of photoinduced species that is undoubtedly detrimental to photosynthetic energy utilization. Also, they can lead to the generation of high-lying hot excitons, which presents a potential pathway for utilizing low-energy photons.40,41 For instance, by combining
transient absorption and photoluminescence measurements, we have demonstrated the presence of triplet-triplet annihilation (TTA) in polymeric carbon nitride (Figure 3c), which is the major restriction of the efficiencies of both exciton- and charge-carrier-based photosynthetic reactions.  

Then, we highlighted that hot excitons induced by TTA can be resonantly transferred to molecular ketones, thereby leading to promoted photosynthetic molecular oxygen activation under visible illumination. In addition to exciton-exciton annihilation, the interactions between excitons might lead to the formation of high-order quasiparticles like the biexciton. Although these quasiparticles have been deemed to be short-lived, their abundant dipole moments permit considerable energy transfer to the single-exciton (Figure 3d). Traditionally, high-order interactions closely depend on the concentrations of photoinduced species, and high-density illumination would be beneficial.

Electron-phonon interactions represent another kind of quasiparticle-involved interactions. The interactions between electronic and vibrational subsystems are intrinsic characteristics of semiconductors, which determine the transitions between diastereoisomers of semiconductors, and the corresponding modifications have been the focus of photosynthetic research. With regard to low-dimensional semiconductors, band structures are closely associated with different interactions, and this feature opens up new possibilities of extending light harvesting. Although numerous optimization strategies including defect/distortion engineering, solid solution construction, and heterostructure introduction have been proposed, the consideration of the interactions between particles in low-dimensional semiconductors would provide some different viewpoints. For instance, given that Coulomb interactions between these charged species are related to dielectric screening, band gap modulation would be proceeded by extrinsically or intrinsically engineering the dielectric properties. In this respect, Raja et al. reported band gap modulation of two-dimensional TMDC nanosheets by tuning the surrounding dielectric environment. They constructed heterostructures between TMDCs and graphene/h-BN nanosheets for achieving dielectric environment regulation. The band gaps of TMDC nanosheets exhibited high sensitivities to nanoscale dielectric change, resulting in significant band gap reduction of several hundred meV (Figure 4a,b). Ryoo et al. demonstrated that a high dielectric environment leads to the opposite shifts of conduction- and valence-band edges that are responsible for the reduction of quasiparticle band gaps. Beyond heterojunctions, chemical doping has also been demonstrated to impact band structures undergoing a Coulomb-interaction engineering mechanism. Moreover, using angle-resolved photoemission/optical spectroscopies and first-principles calculations, Waldecker et al. demonstrated the rigid shifts of valence and conduction bands under dielectric environments, which could be related to the spatial structure of the changes in the Coulomb potential. Such a feature endows dielectric environment-controlled strategies with extensive prospects in the field of photosynthesis. These findings hint that the impacts of traditional optimization strategies on excited-state properties of low-dimensional semiconductor-based photocatalysts should be reassessed. In fact, similar regulations have been unconsciously proceeded in many photocatalysts. For instance, Yang and co-workers have theoretically investigated the impact of buckled geometry on optical properties of g-C3N4 in which they highlighted that the changes in optical absorption would be crucial to photocatalytic water splitting. According to many-body Green’s function-based quasiparticle energy calculations, they suggested that buckled structures lead to a slight increase in quasiparticle band gap but significant reduction in optical band gap linked to first bright excitonic energy, which would be responsible for the visible-light response of g-C3N4. Besides, they reported that even water adsorption can lead to a degree of reduction in excitonic energy, which also facilitates light absorption of the system.

The regulation of high-order interactions typifies another direction in extending light absorption. A prime example is by taking advantage of the TTA-based upconversion process in hybrid photocatalyst systems. TTA enables high-lying (or hot) singlet excitons to be generated by the collisions between triplet excitons, and the utilization of high-lying effective light absorption. In view of the fact that visible and infrared light make up the majority of solar radiation, it is rational to maximize photosynthetic energy utilization by extending the light response of semiconductor-based catalysts to the visible and infrared regions.

Band structures determine light absorption properties of semiconductors, and the corresponding modifications have been the focus of photosynthetic research. With regard to low-dimensional semiconductors, band structures are closely associated with different interactions, and this feature opens up new possibilities of extending light harvesting. Although numerous optimization strategies including defect/distortion engineering, solid solution construction, and heterostructure introduction have been proposed, the consideration of the interactions between particles in low-dimensional semiconductors would provide some different viewpoints. For instance, given that Coulomb interactions between these charged species are related to dielectric screening, band gap modulation would be proceeded by extrinsically or intrinsically engineering the dielectric properties. In this respect, Raja et al. reported band gap modulation of two-dimensional TMDC nanosheets by tuning the surrounding dielectric environment. They constructed heterostructures between TMDCs and graphene/h-BN nanosheets for achieving dielectric environment regulation. The band gaps of TMDC nanosheets exhibited high sensitivities to nanoscale dielectric change, resulting in significant band gap reduction of several hundred meV (Figure 4a,b). Ryoo et al. demonstrated that a high dielectric environment leads to the opposite shifts of conduction- and valence-band edges that are responsible for the reduction of quasiparticle band gaps. Beyond heterojunctions, chemical doping has also been demonstrated to impact band structures undergoing a Coulomb-interaction engineering mechanism. Moreover, using angle-resolved photoemission/optical spectroscopies and first-principles calculations, Waldecker et al. demonstrated the rigid shifts of valence and conduction bands under dielectric environments, which could be related to the spatial structure of the changes in the Coulomb potential. Such a feature endows dielectric environment-controlled strategies with extensive prospects in the field of photosynthesis. These findings hint that the impacts of traditional optimization strategies on excited-state properties of low-dimensional semiconductor-based photocatalysts should be reassessed. In fact, similar regulations have been unconsciously proceeded in many photocatalysts. For instance, Yang and co-workers have theoretically investigated the impact of buckled geometry on optical properties of g-C3N4 in which they highlighted that the changes in optical absorption would be crucial to photocatalytic water splitting. According to many-body Green’s function-based quasiparticle energy calculations, they suggested that buckled structures lead to a slight increase in quasiparticle band gap but significant reduction in optical band gap linked to first bright excitonic energy, which would be responsible for the visible-light response of g-C3N4. Besides, they reported that even water adsorption can lead to a degree of reduction in excitonic energy, which also facilitates light absorption of the system.

The regulation of high-order interactions typifies another direction in extending light absorption. A prime example is by taking advantage of the TTA-based upconversion process in hybrid photocatalyst systems. TTA enables high-lying (or hot) singlet excitons to be generated by the collisions between triplet excitons, and the utilization of high-lying

4.2. Regulating Exciton−Exciton Interactions.

In view of the abundant impacts induced by the strong interactions in low-dimensional semiconductors, the appropriate regulation of these interactions will be beneficial for gaining advanced photosynthetic energy utilizations. In this section, we summarize recent advances in the regulation of these interactions for optimizing photosynthesis-related excited-state properties in low-dimensional semiconductors.
singlet excitons before their cooling down would bring about rich possibilities for utilizing low-energy photons. For instance, we have proposed the utilization of ketones as molecular cocatalysts to promote the visible-light response of polymeric carbon nitride. Polymeric carbon nitride here was used as the TTA medium for its robust interactions. According to spectral analyses, we demonstrated that the promoted visible-light response can be related to two factors: the sub-picosecond internal conversion (that is, cooling down of hot excitons) in polymeric carbon nitride and the near-unity intersystem crossing (ISC) efficiency in ketones. Benefitting from these features, two exciton-based energy transfer processes in opposite directions were established: the transfer of hot excitons from polymeric carbon nitride to acetone and the transfer of the triplet exciton from acetone to polymeric carbon nitride (Figure 4c). The resulting triplet exciton harvesting under visible light illumination promotes photocatalytic singlet oxygen generation (Figure 4d). It is worth noting that quantum yields of these TTA-based photosynthetic processes are usually low under solar irradiation, on account of the photoinduced species concentration-dependent feature of high-order interactions.

4.2. Charge-Carrier Accumulation. Beyond extensive light harvesting, effective accumulation of charge carriers is also an essential prerequisite of redox-initiated photosynthetic reactions. Traditional research mainly focuses on optimizing the charge-separation feature of semiconductor-based photocatalysts. However, as for low-dimensional semiconductors, charge-carrier accumulation is often governed by the interaction-related factors like excitonic effects and non-radiative decays, and consequently, the regulation of these factors should be the crux of photosynthetic research. Given the promoted excitonic effects, excitons and charge carriers jointly constitute the dominant photoinduced species in low-dimensional semiconductors. As a consequence, dissociating excitons consisting of bound electrons and holes into free charge carriers would establish an additional pathway for elevating charge-carrier accumulation. In general, energetic disorders, which can provide a reduced free energy barrier and enhanced thermodynamic driving force, are deemed to facilitate exciton dissociation. Hence, structural factors like vacancy, heterojunction interface, and lattice distortion are generally employed for boosting exciton dissociation in low-dimensional semiconductors. For instance, we have managed to promote charge-carrier accumulation in BiOBr nanoplates by engineering exciton dissociation via oxygen vacancy introduction. According to theoretical simulations, we highlighted that band-edge charge density distributions around the oxygen vacancy are notably delocalized, implying the potential instability of excitons (Figure 5a). Spectral analyses indicated the reduced exciton concentration (Figure 5b) and promoted charge-carrier concentrations induced by oxygen vacancies. Benefitting from these features, the defective BiOBr sample exhibited an excellent performance in redox-initiated photocatalytic superoxide radical generation (Figure 5c). It should be emphasized that exciton dissociation is different from charge separation, and partially dissociated charge-transfer intermediate states driven by electron–phonon coupling-mediated energy dissipation are initially formed before the occurrence of charge separation (Figure 5d).
Furthermore, nonradiative decays, which are induced by the interactions like electron–phonon interactions and exciton–exciton annihilation, are also detrimental to charge-carrier accumulation. For instance, electron–phonon interactions can set up an important nonradiative pathway for relaxing energy from electronic to vibrational subsystems. In this regard, suppressing these interactions, which has been unintentionally achieved in some systems, would favor charge-carrier accumulation. For instance, the construction of core–shell structures has been employed for optimizing aspects including light harvesting and charge separation, whereas the regulation of electron–phonon interactions has proceeded simultaneously. Woggon and co-workers have recently investigated the impact of CdS shell thickness on nonradiative decays of the CdSe core. Using temperature-dependent photoluminescence measurements, they highlighted that, in addition to the promoted surface-defect passivation, the increase of shell thickness can effectively reduce electron–phonon coupling in the CdSe core, thus leading to prominent suppression in nonradiative decays. Also, some other structures like heterojunction and doping have been demonstrated to be feasible in regulating electron–phonon coupling in low-dimensional semiconductors. As for the regulation of exciton–exciton annihilation, optimization strategies including dimension control, defect engineering, and heterojunction construction have been proposed. For instance, focusing on polymeric carbon nitride with intrinsically weak SOC and large $\Delta E_{ST}$, we demonstrated that ISC rate can be effectively promoted by incorporating carbonyl groups into the polymeric networks. The incorporation of carbonyl groups leads to simultaneous optimization of SOC and $\Delta E_{ST}$: on one hand, carbonyl groups enhance the SOC, and on the other hand, they decrease $\Delta E_{ST}$, thereby promoting ISC.

4.3. Spin-Relaxation Optimization. Spin degrees of freedom constitute an important aspect in electronic excitation of low-dimensional semiconductors, which can also impact photosynthetic performance. As is well-known, long-lived triplet excitons are usually required in triggering energy-transfer-mediated reactions. However, owing to spin conservation, triplet-exciton generation via the direct photoexcitation of ground states (mostly, singlet multiplicity) is forbidden. Triplet-exciton generation usually involves the spin relaxation of singlet excitons, undergoing a nonradiative process called intersystem crossing (ISC) for achieving spin flips. Accordingly, the key of high-efficiency triplet exciton generation lies in ISC regulation. Driven by the coupling between two states with different multiplicities, the ISC rate is determined by two factors of semiconductors: spin–orbit coupling (SOC) and singlet–triplet energy gap ($\Delta E_{ST}$). Given that strong SOC and small $\Delta E_{ST}$ favor ISC, great efforts have been devoted to the corresponding optimizations. For instance, focusing on polymeric carbon nitride with intrinsically weak SOC and large $\Delta E_{ST}$, we have demonstrated that ISC rate can be effectively promoted by incorporating carbonyl groups into the polymeric networks. The incorporation of carbonyl groups leads to simultaneous optimization of SOC and $\Delta E_{ST}$: on one hand, carbonyl groups enhance the SOC, and on the other hand, they decrease $\Delta E_{ST}$, thereby promoting ISC.
respectively (Figure 6). By using dynamic spectral measurements, we identified triplet alizarin and ground-state hybrid complexes, molecules could lead to the formation of similar charge-selective excitations of CdS quantum dots and alizarin. They observed that the spin-controlled charge recombination pathways across the interface of CdS quantum dot/alizarin. They highlighted their impacts on bond dissociation processes. In view of these results, the potential impacts of spin relaxation on photosynthesis in low-dimensional semiconductors should be widely recognized.

5. CONCLUSIONS AND OUTLOOK

Low-dimensional semiconductors exhibit great prospects in the field of artificial photosynthesis. However, the significant interactions between particles/quasiparticles induced by promoted structural confinement and reduced dielectric screening endow low-dimensional semiconductors with pretty different excited-state scenarios, as compared to those in the bulk counterparts. Therefore, it is essential to clarify the impacts of these interactions on the relevant solar energy utilization. In this Outlook, we summarize recent progress in investigating the interactions in low-dimensional semiconductors, where the impacts of different interactions on photosynthetic energy conversion are highlighted. According to our descriptions, it is clear to see that the regulation of these interactions, whether intentionally or unconsciously, has been realized in many optimization attempts, thus enabling diverse photosynthetic applications to be obtained in these low-dimensional systems.

Despite all the above achievements, the crucial roles of these interactions in photosynthesis of low-dimensional semiconductors are not yet fully recognized. One of the primary reasons is the difficulties in characterizing the excited-state properties linked to these interactions. The interactions between different particles/quasiparticles lead to many possible variables in excited-state properties, whereas the separate consideration of these variables as well as their impacts on photosynthesis are biased. For gaining insights into the interaction-dominated excited-state properties, advanced spectroscopic techniques (e.g., photoluminescence, transient absorption, and vibrational spectroscopies) and systematic

![Figure 6. Transient absorption kinetics of different species for CdS quantum dots/alizarin under (a) 600 nm and (b) 400 nm excitation. (c, d) Corresponding illustrations of the spin-controlled charge-recombination pathways. Reproduced with permission from ref 77. Copyright 2020 American Chemical Society.]
controlled experiments (e.g., temperature-dependent, excitation-wavelength-dependent, and pump-fluence-dependent tests) are required. Another challenge lies in the complicated structures of low-dimensional semiconductors. To date, the accurate characterizations of the relevant crystal structures remain difficult, and even a slight change in structures can lead to giant modifications of these interactions, which make it difficult to establish conclusive relationships between the structures and interactions. In this regard, constructing representative low-dimensional semiconductors with precise structural factors is necessary. Moreover, there are difficulties in investigating the interactions under photosynthetic reaction conditions. According to the above review, it can be seen that reaction factors like solvent environment, illumination, and substrate-molecule adsorption appear to bring about changes in the interactions as well as the involved energy conversion. In view of these features, future attempts should be focused on developing in situ characterization techniques for investigating the evolution of the interaction-dominated excited-state behaviors under the reaction conditions.

The interactions between different particles lead to many possible variables in excited-state properties, whereas the separate consideration of these variables as well as their impacts on photosynthesis are biased.

Taken together, the interactions between particles/quasi-particles in low-dimensional semiconductors open up tremendous possibilities in photosynthetic applications. The evaluation of the impacts of these interactions not only establishes a brand new understanding of the involved catalytic mechanisms but also paves the way for gaining comprehensively optimized solar energy utilization.

AUTHOR INFORMATION

Corresponding Authors
Xiaodong Zhang – Hefei National Laboratory for Physical Sciences at the Microscale, CAS Centre for Excellence in Nanoscience, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China; Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui 230031, P. R. China; orcid.org/0000-0002-8288-035X; Email: zbsdixd@ustc.edu.cn

Yi Xie – Hefei National Laboratory for Physical Sciences at the Microscale, CAS Centre for Excellence in Nanoscience, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China; Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui 230031, P. R. China; orcid.org/0000-0002-1416-5557; Email: yxie@ustc.edu.cn

Authors
Hui Wang – Hefei National Laboratory for Physical Sciences at the Microscale, CAS Centre for Excellence in Nanoscience, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China; Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui 230031, P. R. China

Wenxiu Liu – Hefei National Laboratory for Physical Sciences at the Microscale, CAS Centre for Excellence in Nanoscience, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Sen Jin – Hefei National Laboratory for Physical Sciences at the Microscale, CAS Centre for Excellence in Nanoscience, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acssentsci.0c00540

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (2017YFA0207301, 2019YFA0210004), the National Natural Science Foundation of China (21922509, 21905262, 21809074), the Strategic Priority Research Program of Chinese Academy of Sciences (XDB36000000), the Youth Innovation Promotion Association of CAS (2017493), the Young Elite Scientist Sponsorship Program by CAST, and the Key Research Program of Frontier Sciences (QYZDY-SSW-SLH011).

REFERENCES

(1) Karkas, M. D.; Verho, O.; Johnston, E. V.; Akermark, B. Artificial Photosynthesis: Molecular Systems for Catalytic Water Oxidation. Chem. Rev. 2014, 114 (24), 11863–12001.

(2) Bard, A. J.; Fox, M. A. Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen. Acc. Chem. Res. 1995, 28 (3), 141–145.

(3) Shaw, M. H.; Twilton, J.; Macmillan, D. W. C. Photoredox catalysis in organic chemistry. J. Org. Chem. 2016, 81 (16), 6898–6926.

(4) Tachibana, Y.; Vayssieres, L.; Durrant, J. R. Artificial photosynthesis for solar water-splitting. Nat. Photonics 2012, 6 (8), S11–S18.

(5) Marzo, L.; Pagire, S. K.; Reiser, O. J.; König, B. Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? Angew. Chem., Int. Ed. 2018, 57, 10034–10072.

(6) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. Science 2014, 343 (6174), 1239176–1239176.

(7) Kudo, A.; Miseki, Y. Heterogeneous Photocatalyst Materials for Water Splitting. Chem. Soc. Rev. 2009, 38 (1), 253–278.

(8) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-Based Photocatalytic Hydrogen Generation. Chem. Rev. 2010, 110 (11), 6503–6570.

(9) Xiang, Q.; Yu, J.; Jaroniec, M. Graphene-Based Semiconductor Photocatalysts. Chem. Soc. Rev. 2012, 41 (2), 782–796.

(10) Osterloh, F. E. Inorganic Nanostructures for Photoelectrochemical and Photocatalytic Water Splitting. Chem. Soc. Rev. 2013, 42 (6), 2294–2320.

(11) Voiry, D.; Shin, H. S.; Loh, K. P.; Chhowalla, M. Low-Dimensional Catalysts for Hydrogen Evolution and CO2 Reduction. Nat. Rev. Chem. 2018, 2, 0105.

(12) Wang, H.; Zhang, X.; Xie, Y. Recent Progress in Ultrathin Two-Dimensional Semiconductors for Photocatalysis. Mater. Sci. Eng., R 2018, 130, 1–39.

(13) May, V.; Kühn, O. Charge and Energy Transfer Dynamics in Molecular Systems, 3rd ed.; Wiley-VCH, 2011.

(14) Schwentner, N.; Koch, E.-E.; Jortner, J. Electronic Excitations in Condensed Rare Gases; Springer-Verlag: Berlin, 1985.

(15) Yang, L.; Park, C.; Son, Y.; Cohen, M. L.; Louie, S. G. Quasiparticle Energies and Band Gaps in Graphene Nanoribbons. Phys. Rev. Lett. 2007, 99 (18), 186801.

(16) Hwang, E. H.; Sarma, S. D. Band-Gap Renormalization in Photoexcited Semiconductor Quantum-Wire Structures in the GW
Approximation. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1998, 58 (4), R1738.

(17) Brus, L. E. Electron–Electron and Electron–Hole Interactions in Small Semiconductor Crystallites: The Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* 1984, 80 (9), 4403–4409.

(18) Tran, V.; Soklaski, R.; Liang, Y.; Yang, L. Layer-Controlled Band Gap and Anisotropic Excitons in Few-Layer Black Phosphorus. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2014, 89 (23), 235319.

(19) Gold, A.; Ghazali, A. Analytical Results for Semiconductor Quantum-Well Wire: Plasmons, Shallow Impurity States, and Mobility. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1990, 41 (11), 7626–7640.

(20) Guyot-Sionnest, P.; Shim, M.; Matranga, C.; Hines, M. A. Intraband Relaxation in CdSe Quantum Dots. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1999, 60 (4), R2181.

(21) Efros, A. L.; Efros, A. L. Interband Absorption of Light in a Semiconductor Sphere. *Sov. Phys. Semicond.* 1982, 16, 772–775.

(22) Choi, J. H.; Cui, P.; Lan, H.; Zhang, Z. Linear Scaling of the Exciton Binding Energy versus the Band Gap of Two-Dimensional Materials. *Phys. Rev. Lett.* 2015, 115, 066403.

(23) Cheiwchanchamnangij, T.; Lambrecht, W. R. L. Quasiparticle Band Structure Calculation of Monolayer, Bilayer, and Bulk MoS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2012, 85 (20), 205302.

(24) Zhang, Y.; Chang, T.; Zhou, B.; Cui, Y.; Yan, H.; Liu, Z.; Schmitt, F.; Lee, J.; Moore, R. C.; Chen, Y. Direct Observation of the Transition from Indirect to Direct Bandgap in Atomically Thin Tipctal MoSe₂. *Nano. Technol. 2014, 9 (2), 111–115.

(25) Ugeda, M. M.; Bradley, A. J.; Shi, S.; Jornada, F. H. D.; Zhang, Y.; Qiu, D. Y.; Ruan, W.; Mo, S. K.; Hussain, Z.; Shen, Z. Giant Bandgap Renormalization and Excitonic Effects in a Monolayer Transition Metal Dichalcogenide Semiconductor. *Nat. Mater. 2014, 13 (12), 1091–1095.

(26) Yao, K.; Yan, A.; Kahn, S.; Sulsu, A.; Liang, Y.; Barnard, E. S.; Tongs, Z.; Zettl, A.; Borys, N. J.; Schuck, P. J. Optically Discriminating Carrier-Induced Quasiparticle Band Gap and Exciton Energy Renormalization in Monolayer Mo₇Se₇. *Phys. Rev. Lett. 2017, 119 (8), 087401.

(27) Niu, S.; Joe, G.; Zhao, H.; Zhou, Y.; Orvis, T.; Huyan, H.; Salman, J.; Mahalingam, K.; Urwin, B.; Wu, J. Giant Optical Anisotropy in a Quasi-One-Dimensional Crystal. *Nat. Photonics 2018, 12 (7), 392–396.

(28) Wang, X.; Jones, A. M.; Seyler, K. L.; Tran, V.; Jia, Y.; Zhao, H.; Wang, H.; Yang, L.; Xu, X.; Xie, F. Highly Anisotropic and Robust Excitons in Monolayer Black Phosphorus. *Nano. Technol. 2015, 10 (6), 517–521.

(29) Wang, H.; Jang, S.; Shao, W.; Zhang, X.; Chen, S.; Sun, X.; Zhang, Q.; Luo, Y.; Xie, Y. Optically Switchable Photocatalysis in Ultrathin Black Phosphorus Nanosheets. *J. Am. Chem. Soc. 2018, 140 (9), 3479–3482.

(30) Cnops, K.; Rand, B. P.; Cheyns, D.; Verreet, B.; Empl, M.; Hereemas, P. 8.4% Efficient Fullerene-Free Organic Solar Cells Exploiting Long-Range Exciton Energy Transfer. *Nat. Commun. 2014, 5 (1), 3406.

(31) Van Grondelle, R.; Novoderezhkin, V. I. Energy Transfer in Photosynthesis: Experimental Insights and Quantitative Models. *Phys. Chem. Chem. Phys.* 2006, 8 (7), 793–807.

(32) Jiang, Y.; Wang, C.; Rogers, C. R.; Kodaimati, M. S.; Weiss, E. A. Regio- and Diastereoselective Intermolecular [2 + 2] Cycloadditions Photocatalysed by Quantum Dots. *Nat. Chem. 2019, 11 (11), 1034–1040.

(33) Zhang, Z.; Rogers, C. R.; Weiss, E. A. Energy Transfer from CdS QDs to a Photogenerated Pd Complex Enhances the Rate and Selectivity of a Pd-Ptocatalysed Heck Reaction. *J. Am. Chem. Soc. 2020, 142 (1), 495–501.

(34) Lu, J.; Pattengale, B.; Liu, Q.; Yang, S.; Shi, W.; Li, S.; Huang, J.; Zhang, J. Donor–Acceptor Fluorophores for Energy-Transfer-Mediated Photocatalysis. *J. Am. Chem. Soc.* 2018, 140 (42), 13719–13725.
Activity. Enhancing Charge Carrier Separation to Improve Photocatalytic Semiconductor Photocatalysis.

Sub-Bandgap Photocatalysis.

Faraday Discuss. Donor L.; Tang, M. L.; Roberts, S. T. Achieving Spin-Triplet Exciton Nanoscale 2018 17478

Semiconductors through External Dielectric Screening. Wehling, T. O.; Heinz, T. F. Rigid Band Shifts in Two-Dimensional Koch, R. J.; Jozwiak, C.; Taniguchi, T.; Watanabe, K.; Rotenberg, E.; Wehling, T. O.; Heinz, T. F. Rigid Band Shifts in Two-Dimensional Semiconductors through External Dielectric Screening. Phys. Rev. Lett. 2019, 123 (20), 206403.

Sun, J.; Li, X.; Yang, J. The Roles of Buckled Geometry and Water Environment on the Excitonic Properties of Graphitic C3N4, Nanoscale 2018, 10 (8), 3738–3743.

Kim, J.; Kim, J. Encapsulated Triplet–Triplet Annihilation-Based Upconversion in the Aqueous Phase for Sub-Band-Gap Semiconductor Photocatalysis. J. Am. Chem. Soc. 2012, 134 (42), 17478–17481.

Kwon, O. S.; Kim, J.; Cho, J. K.; Kim, J. Triplet–Triplet Annihilation Upconversion in CdS-Decorated SiO2 Nanoparticles for Sub-Bandgap Photocatalysis. ACS Appl. Mater. Interfaces 2015, 7 (1), 318–325.

Xia, P.; Raulerson, E. K.; Coleman, D.; Gerke, C. S.; Mangolini, L.; Tang, M. L.; Roberts, S. T. Achieving Spin-Triplet Exciton Transfer between Silicon and Molecular Acceptors for Photon Upconversion. Nat. Chem. 2020, 12 (2), 137–144.

Marschall, R. Semiconductor Composites: Strategies for Enhancing Charge Carrier Separation to Improve Photocatalytic Activity. Adv. Funct. Mater. 2014, 24 (17), 2421–2440.

Kelly, A. Exciton Dissociation and Charge Separation at Donor–Acceptor Interfaces from Quantum-Classical Dynamics Simulations. Faraday Discuss. 2020, 221, 547–563.

Shi, L.; Lee, C. K.; Willard, A. P. The Enhancement of Interfacial Exciton Dissociation by Energetic Disorder Is a Non-equilibrium Effect. ACS Cent. Sci. 2017, 3 (12), 1262–1270.

Wang, H.; Yong, D.; Chen, S.; Jiang, S.; Zhang, X.; Shao, W.; Zhang, Q.; Yan, W.; Pan, B.; Xie, Y. Oxygen-Vacancy-Mediated Exciton Dissociation in BiOBr for Boosting Charge-Carrier-Involved Molecular Oxygen Activation. J. Am. Chem. Soc. 2018, 140, 1760–176.

Melissen, S. T. A. G.; Bahri, T. L.; Steimann, S. N.; Sautet, P. Relationship between Carbon Nitride Structure and Exciton Binding Energies: A DFT Perspective. J. Phys. Chem. C 2015, 119 (45), 25188–25196.

Wang, H.; Sun, X.; Li, D.; Zhang, X.; Chen, S.; Shao, W.; Tian, Y.; Xie, Y. Boosting Hot-Electron Generation: Exciton Dissociation at the Order–Disorder Interfaces in Polymeric Photocatalysts. J. Am. Chem. Soc. 2017, 139 (6), 2468–2473.

Pan, C.; Xu, J.; Wang, Y.; Li, D.; Zhu, Y. Dramatic Activity of C3N4/BiPO4 Photocatalyst with Core/Shell Structure Formed by Self-Assembly. Adv. Funct. Mater. 2012, 22 (7), 1518–1524.

Wang, D.; Hisatomi, T.; Takata, T.; Pan, C.; Katayama, M.; Kubota, J.; Domen, K. Core/Shell Photocatalyst with Spatially Separated Co-catalysts for Efficient Reduction and Oxidation of Water. Angew. Chem., Int. Ed. 2013, 52 (43), 11252–11256.

Achtstein, A. W.; Marquardt, O.; Scott, R.; Ibrahim, M.; Riedl, T.; Prudnikau, A.; Antanovich, A.; Owshchimikov, N.; Lindner, J. K. N.; Artemyev, M. V. Impact of Shell Growth on Recombination Dynamics and Exciton–Phonon Interaction in CdSe–CdS Core–Shell Nanoplatelets. ACS Nano 2018, 12 (9), 9476–9483.

Jin, C.; Kim, J.; Suh, J.; Shi, Z.; Chen, B.; Fan, X.; Kam, M.; Watanabe, K.; Taniguchi, T.; Tongay, S. Interlayer Electron–Phonon Coupling in WS2/hBN Heterostructures. Nat. Phys. 2017, 13 (2), 127–131.

Attaccalite, C.; Wirtz, L.; Lazzeri, M.; Mauri, F.; Rubio, A. Doped Graphene as Tunable Electron–Phonon Coupling Material. Nano Lett. 2010, 10 (4), 1172–1176.

Lee, Y.; Ghimire, G.; Roy, S.; Kim, Y.; Seo, C.; Sood, A. K.; Jang, J. I.; Kim, J. Impeding Exciton–Exciton Annihilation in Monolayer WS2 by Laser Irradiation. ACS Photonics 2018, 5 (7), 2904–2911.

Hoshi, Y.; Kuroda, T.; Okada, M.; Moriya, R.; Masubuchi, S.; Watanabe, K.; Taniguchi, T.; Kitaura, R.; Machida, T. Suppression of Exciton–Exciton Annihilation in Tungsten Disulfide Monolayers Encapsulated by Hexagonal Boron Nitriles. Phys. Rev. B: Condens. Matter Mater. Phys. 2017, 95 (24), 241403.

Zhang, X.; Xie, X.; Wang, H.; Zhang, J.; Pan, B.; Xie, Y. Enhanced Photoresponsive Ultrathin Graphitic-phase C3N4 Nanosheets for Bioimaging. J. Am. Chem. Soc. 2013, 135 (1), 18–21.

Li, Y.; Jin, S.; Xu, X.; Wang, H.; Zhang, X. Excitonic effects on photophysical processes of polymeric carbon nitride. J. Appl. Phys. 2020, 127 (17), 170903.

Zhao, J.; Wu, W.; Sun, J.; Guo, S. Triplet Photosensitizers: From Molecular Design to Applications. Chem. Soc. Rev. 2013, 42 (12), 5323–5351.

Dias, F. B.; Bourdakos, K. N.; Jankus, V.; Moss, K. C.; Kamtekar, K. T.; Bhalla, V.; Santos, J.; Bryce, M. R.; Monksman, A. P. Triplet Harvesting with 100% Efficiency by Way of Thermally Activated Delayed Fluorescence in Charge Transfer OLED Emitters. Adv. Mater. 2013, 25 (27), 3707–3714.

Wang, H.; Jiang, S.; Chen, S.; Li, D.; Zhang, X.; Shao, W.; Sun, X.; Xie, J.; Zhao, Z.; Zhang, Q. Enhanced Singlet Oxygen Generation in Oxidized Graphitic Carbon Nitride for Organic Synthesis. Adv. Mater. 2016, 28 (32), 6940–6945.

Wang, J.; Ding, T.; Nie, C.; Wang, M.; Zhou, P.; Wu, K. Spin-Controlled Charge-Recombination Pathways across the Inorganic/Organic Interface. J. Am. Chem. Soc. 2020, 142 (10), 4723–4731.

Migani, A.; Blancafort, L. Excitonic Interfacial Proton-Coupled Electron Transfer Mechanism in the Photocatalytic Oxidation of Methanol to Formaldehyde on TiO2(110). J. Am. Chem. Soc. 2016, 138 (49), 16165–16173.