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Dye-sensitized solar cells: Atomic scale investigation of interface structure and dynamics*

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Recent progress in dye-sensitized solar cells (DSC) research is reviewed, focusing on atomic-scale investigations of the interface electronic structures and dynamical processes, including the structure of dye adsorption onto TiO_2 , ultrafast electron injection, hot-electron injection, multiple-exciton generation, and electron-hole recombination. Advanced experimental techniques and theoretical approaches are briefly summarized, and then progressive achievements in photovoltaic device optimization based on insights from atomic scale investigations are introduced. Finally, some challenges and opportunities for further improvement of dye solar cells are presented.

Keywords: dye-sensitized solar cells, interface structure, absorption, electron injection, multiple-exciton generation, charge recombination

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1. Introduction

The first practical photovoltaic cell, based on a diffusive silicon p-n junction and reaching an efficiency of 6%, was developed in 1954 at Bell Laboratories by Daryl Chapin et al.^[1] Since then, solar cell technology has come into a new age. Dye-sensitized solar cells (DSC), one of the most promising third generation solar cell technologies, based on highly porous nanocrystalline titanium dioxide films and organic dyes, have drawn considerable technological interest for their potential to decrease manufacturing costs and for their demonstrated high energy conversion efficiency, since the seminal work by Grätzel et al. in 1991.^[2] The highest solarto-electricity power conversion efficiency (PCE) for molecular DSC is 13% under AM1.5G full sun irradiation, obtained by sensitization of modified zinc-porphyrin-based donor- π acceptor (D- π -A) dye in 2014.^[3] Wang *et al.* have achieved comparable efficiency of 12.8% at half irradiance of AM1.5G sunlight using metal-free all-organic dyes, which have a large molar absorption coefficient, are environmentally benign and cost less, compared with dyes containing heavy metals.^[4]

Typical DSCs at present consist of stacked layers of components, including a transparent conducting glass substrate, a transparent conducting layer, TiO_2 nanoparticles, dyes, an electrolyte, and a counter electrode covered with a sealing gasket, as shown in Fig. 1(a). Figure 1(b) shows the operation of a dye-sensitized solar cell, which starts with the photoexcitation of the sensitizer, where an electron is excited from the ground state to higher-energy excited states by photon ab-

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sorption. Then the excited electron jumps from the sensitizer molecule into the conduction band of the semiconductor, joining the formation of mobile electrons (and a dye cation). On one hand, titanium dioxide, acting as the electron-transport material, transports the injected electrons to the back conductive contact. On the other hand, the electrolyte, serving as the hole-transport material, reduces oxidized dyes and transports holes to the counter electrode.

In 1961, Shockley and Queisser calculated the maximum theoretical solar conversion efficiency of a solar cell using a single p–n junction to be 33.7% under standard AM1.5G solar irradiation, reached with a band gap of 1.37 eV, known as the Shockley–Queisser limit or detailed balance limit.^[5] According to the Shockley–Queisser limit, energies are lost in DSC mainly in the following four ways:

(i) Blackbody radiation, which is a type of electromagnetic radiation within or surrounding a solar cell that is in thermodynamic equilibrium with its environment, representing 7% of the available incoming solar energy.

(ii) Spectrum losses. Only photons with energy higher than the HOMO–LUMO (highest occupied molecular orbital– lowest unoccupied molecular orbital) band gap can be absorbed by the sensitizers in DSC, which means only ultraviolet and visible light will contribute to power production, whereas infrared, microwaves, and video waves will not.

(iii) Thermal relaxation, which includes two processes:1) electrons in the excited states of the chromophores easily jump back to the ground state if not rapidly injected into the

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 TiO_2 conduction band, 2) injected electrons in the semiconductor conduction band tend to thermally relax to the conduction band edge rapidly.

(iv) Radiative recombination. Electrons in the TiO_2 conduction band will recombine with holes in electrolyte and dyes if not efficiently transfer to the conducting contact, causing power loss by emitting photons.



Fig. 1. (a) General scheme of dye-sensitized solar cells. (b) Typical electronic dynamic processes in the dye-sensitized solar cells.

Among all the four main pathways causing loss of incoming energy, blackbody radiation is inevitable. Therefore, reducing spectrum losses, thermal relaxation, and radiative recombination are major ways to optimize dye-sensitized solar cells. In this review, we breakdown the energy conversion in DSC into the individual processes taking place at solar cell interfaces, including dye/TiO₂ interface optimization, dye absorption properties, electron injection, thermal relaxation, and electron–hole recombination. In Section 2, we mainly introduce experimental and theoretical methods to identify the precise interface structure of the dye/TiO₂ system, discussing the adsorption structures of organic chromophores on the semiconductor substrate, and presenting advanced methods to control the dye/TiO₂ binding configurations. In Section 3, the energy gap optimization to improve photon absorption is presented. Frequently used methods to reduce the solar spectrum losses, including co-sensitization of two sensitizers with complementary absorption spectra and using near infrared dyes, are discussed. In Section 4, we briefly introduce advanced experimental techniques and theoretical approaches to investigate the interface electron transfer dynamics, and factors influencing electron injection rates at the dye/TiO₂ interface. Hot-electron injection and multiple-exciton generation are presented in Section 5 as two efficient novel ways to reduce thermal relaxation losses. In Section 6, a short summary and future prospectives are given.

2. Adsorption structure

2.1. Identification methods

In a DSC, dye adsorption is the first basic and important step for power production. Only when dye molecules bind effectively to the semiconductor substrate can the following processes such as electron injection and charge transport proceed with high efficiency. Knowing the precise interface structures for dye adsorption onto TiO_2 is of crucial importance for further device optimization. Infra-red (IR) spectroscopy and Raman spectroscopy are the most widely used spectral techniques to investigate the adsorbed layer and anchoring modes in experiments.

IR spectroscopy is applied to determine the nature of the adsorption groups and the mode of their interaction with the substrate, the changes caused in the adsorbed molecule by the field of the TiO₂ substrate, and the nature of new chemical compounds and/or bonds formed upon adsorption.^[6] The theory of IR techniques shows that a molecule, as a whole, undergoes so-called vibrations, in which the amplitude of motion differs for different atoms, while all atoms vibrate at the same frequency. When the amplitude of one of the vibration modes is considerably greater than that of the others, it becomes the characteristic vibration of the particular bond or groups of atoms ($-CH_3$, $> CH_2$, $> CO^6$). Fourier transform infrared (FTIR) spectroscopy is a measurement technique to record infrared spectra, which is widely used in experiments to recognize the adsorption structure of dye on metal oxides with the help of the Deacon–Philips rule.^[7] Taking carboxylate dyes as an example, an important parameter Δv , which is defined as the frequency splitting of the asymmetric and symmetric vibrations of surface bound carboxylate, is measured. Two cases are compared: Δv for dyes in solid state, Δv (solid), and Δv for the adsorbed dyes, Δv (ads). If Δv (ads) $> \Delta v$ (solid), the dye molecule takes a monodentate binding mode; if $\Delta v(ads) < \Delta v(solid)$, the bidentate bridging mode is

more preferred; if $\Delta v(ads) \ll \Delta v(solid)$, the chelating mode is most likely to present.^[7]

However, IR spectroscopy is inactive in homonuclear diatomic molecules and complex molecules whose vibrational modes are weak in the IR spectrum, or apparently absent from it.^[8] Fortunately, Raman spectroscopy offers distinct advantages in detecting and analyzing molecules with inactive IR spectra. Moreover, Raman spectra can be employed to study materials in aqueous solution, a medium that transmits IR poorly.^[8] Therefore, sample preparation for Raman study is generally simpler than for IR measurements. The Raman technique relies on inelastic scattering, Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system under study.

Other methods, such as nuclear magnetic resonance (NMR),^[9] Auger electron spectroscopy (AES),^[10,11] high-

resolution electron energy loss spectroscopy (HREELS),^[12,13] ultra-violent photoelectron spectroscopy (UPS),^[14] X-ray photoelectron spectroscopy (XPS),^[15] the temperature programmed desorption technique (TPD),^[16] and thermal desorption spectroscopy (TDS),^[17] are also useful for identification of interface structures and can provide more information about the intricate dye/TiO₂ interface adsorption phenomenon. Theoretical methods often confirm the interface binding configurations by comparing binding energies of different adsorption structures.^[18]

2.2. Anchor groups

For the majority of metal complex dyes, a carboxyl group is employed as an effective anchor through which dyes bind onto TiO₂ surfaces. Experimental^[19,20] and theoretical analyses^[21] have revealed that N719 and derivatives bind onto anatase (101) via one to three carboxylic/carboxylate groups forming bidentate or monodentate binding structures for each group.



Fig. 2. (a) Different adsorption structures of the M0 model dyes binding on TiO₂ anatase (101) surface. First row: adsorption with Ti–N bonding. Second row: adsorption without Ti–N bonding.^[18] (b) Raman spectrum of Eosin Y adsorbed TiO₂ under different conditions: curve *a* in air, curve *b* in acetonitrile, curve *c* in pure water, and curve *d* in HCl aqueous solution at pH 3.^[28]

For all-organic dyes, cyanoacrylic group^[22,23] and phosphoric acid group^[24,25] are commonly used as binding units. Phosphoric acid groups are known to adsorb strongly to most metal oxides and to adsorb on the TiO₂ surface via a bidentate binding of phosphonate to Ti(IV) ions by *in situ* internal reflection infrared spectroscopy.^[25] Cyanoacrylic acid groups are mostly used as anchoring moiety in all-organic donor- π -bridge acceptor dyes, combining the electron withdrawing properties of the cyano-unit with the binding motif of the carboxylic group.^[22,23] However, controversy exists concerning the adsorption configurations of cyanoacrylic dyes. It is widely assumed intuitively that all-organic cyanoacrylic dyes also bind the TiO₂ surface through their carboxylic group, similar to N719. In 2007, Johansson *et al.* revealed that L2 dye adsorbed onto TiO₂ surface with a dominating orientation that the diphenylaniline donor moiety jutted out from the surface.^[26] In 2012, Jiao *et al.* proposed a tridentate anchoring site of all-organic cyanoacrylic dye featuring Ti–N bonding in DSC based on first-principles molecular dynamics and realtime time-dependent density functional theory.^[18] The cyano group not only acts as an electron-drawing acceptor but also directly binds onto TiO₂ and contributes to interface stability. As shown in Fig. 2(a), numerous adsorption configurations of model cyanoacrylic M0 dye on prototypical TiO₂ anatase (101) surface are considered. Extensive energetic, vibrational recognition, and electronic data reveal that Ic is the most stable configuration with optimal energy alignment to minimize kinetic redundancy and presents ultrafast photoelectron injection dynamics with a high yield. In a recent work, a novel acyloin anchor group is found to strongly bind to TiO₂ semiconductors and enable efficient electron injection into the substrate.^[27] However, the detailed interface configuration is still unknown.

2.3. Manipulation of interface adsorption structures

With solid and comprehensive characterization of the dye/TiO₂ interface geometry, a complete understanding of the working mechanism of DSC and details about interface electronic structure and dynamics can be achieved. De Angelis *et al.* investigated the adsorption configuration of the most popular Ru-complex N719 dye on TiO₂ and showed that the dipole moment orientation of different sensitizers results from their binding configurations, the variation of which can lead to a shift in the TiO₂ conduction band edge (CBE) as large as 0.61 eV, introducing a larger open circuit voltage (V_{oc}).^[21] Jiao *et al.* studied the adsorption configuration of allorganic cyanoacrylic dyes and found that the interface adsorption, which improves short circuit current (J_{SC}).^[18]

Interface binding configurations do have a critical influence on DSC performance. However, precise control of the binding structure of dyes onto nanocrystalline TiO₂ surface to optimize the device efficiency remains a big challenge. In 2013, Zhang et al. successfully manipulated the adsorption structure of Eosin Y dyes on TiO₂ substrate by changing the PH value of the organic electrolyte.^[28] Figure 2(b) shows the Raman spectra of EY/TiO2 measured under different electrolyte conditions. By adding a small fraction of water into the electrolyte, the pKa value of EosinY carboxyl becomes lower than the pH value of the P25 TiO₂ system, the hydrogen atom of the carboxyl group dissociates and transfers to the solution or to the TiO₂ surface, leading to an interface structure transition from a hydrogen bonded monodentate to a bidentate bridging configuration, and enhancing the energy conversion efficiency of the corresponding fabricated photovoltaic device. This work has established a direct link between microscopic interface adsorption structures and macroscopic photovoltaic performance, and has highlighted a new way to optimize DSC efficiency by manipulating interface binding configurations.

3. Absorption property

Photon absorption by chromophores is the first step in the sequence of processes for energy production in DSC. The optical absorption property of the sensitizer directly determines how much solar energy can be converted into electricity at most. Shockley and Queisser calculated that an ideal absorption threshold energy to absorb photons and produce energy most efficiently would be in the range 1.3 eV–1.4 eV (roughly 940 nm–890 nm),^[5] which is readily met by bulk semiconductors that have a direct allowed optical transition at the appropriate band gap energy. However, molecular absorbers always have absorption onsets much higher than the calculated optimum 1.3 eV–1.4 eV. For example, N719, the most commonly used ruthenium bipyridine dye, has an absorption onset at ~ 1.65 eV (750 nm), significantly higher than the ideal threshold.^[29]

In recent years, tremendous developments have been made in engineering novel fabrication structures and dyes to improve the corresponding light harvesting property. One way to broaden the absorption spectrum is co-sensitization, using two dyes with complementary absorbance.^[3,4,30] For instance, the high DSC power conversion efficiency of over 12% was achieved by using modified Zn-porphyrin dye YD2-o-C8 coadsorbed with metal-free dye Y123 (see Figs. 3(a) and 3(b)) by Grätzel et al.^[30] As evidenced by the Incident Photonto-electron Conversion Efficiency (IPCE) spectra shown in Fig. 3(b), Zn-porphyrin dye YD2-o-C8 lacks absorption in the range 480 nm-630 nm. This dip in the green spectral region can be compensated by dye Y123, which possesses a strong absorption capacity around 532 nm. In 2013, Wang et al. achieved over 11% efficiency using a device made via cografting of metal-free all-organic dye C258 or C259 with dye C239, which has advantages of non-toxicity, easy synthesis, low cost, and high extinction coefficients compared with the metal-based dyes.^[4]

Although co-sensitization yields high efficiency in DSC, the fabrication and optimization of these devices can be laborious and technically challenging. The development of a single sensitizer with a panchromatic light harvesting character remains a main objective in the realization of the ultimate PCEs with standard device fabrication protocols. Most recently, the new dye SM315, incorporating the proquinoidal benzothiadiazole (BTD) unit into a prototypical structure of D- π -A porphyrins, is reported to achieve unprecedented energy efficiency of 13% at full sun illumination without the requirement of a co-sensitizer. The utility of an electron-deficient BTD-functionalized anchor significantly broadens the Soret and Q-band absorbance of porphyrins, yields impressively high light harvesting across the whole visible wavelength range, resulting in an improved J_{SC} .^[3]



Fig. 3. (a) Chemical structures of porphyrin dye YD2-o-C8 and all-organic dye Y123. (b) Spectral response of the IPCE for YD2-o-C8 (red dots), Y123 (blue triangles), and YD2-o-C8/Y123 cosensitized nanocrystalline TiO₂ films (black squares).^[30] (c) Chemical structures of dye Y1 and derivatives. (d) Absorption spectra of dye Y1 and derivatives. The grey dashed line is the experimental curve for Y1.^[32]

Additionally, another way to improve the sensitizer's light harvesting property is to adjust the dye's absorption in the near-IR range of solar irradiance, for example, by replacing the dye's donor with stronger electron attributors such as the ullazine group,^[22] or by employing electron-rich π linkers.^[30,31] Jiao *et al.* designed a series of donor- π -acceptor dyes (Y1 and derivatives, see Fig. 3(c)) with paraquinoid rings as π -conjugation moiety as sensitizers in DSC.^[32] The introduced paraquinoid rings drastically shift the optical response from violet-blue to near-infrared and significantly enhance photoabsorption of the chromophore, compared with the small changes in the absorption spectrum of donor- π -acceptor dyes with the phenyl group as the π -bridging unit (see Fig. 3(d)). In addition, real time excited state electron dynamics simulations based on time-dependent density functional theory indicate that these paraquinoid conjugation dyes maintain high thermal stability when adsorbed on the TiO₂ surface and ultrafast electron-hole separation at ambient temperature. The simple but effective infrared dye Y1b2 is predicted to reach a high energy conversion efficiency close to 20% in ideal theoretical conditions.^[31]

4. Electron injection

After photo-excitation, the electron-hole separation, integral to the functioning of the cell, occurs by electron transfers from the photo-excited chromophore into the conduction band of the nanocrystalline semiconductor, in a time ranging from subpicoseconds^[33–35] to tens of picoseconds^[36] and even nanoseconds. Efficient electron injection is fundamental for DSC operation, and directly determines the short circuit current of the photovoltaic device. Electrons in excited states after photo-excitation, if not rapidly injected, easily lose the absorbed photon energy as heat through electron-phonon scattering and subsequent phonon dissipation thus generating (thermal) loss in efficiency. Therefore, it is of crucial importance to fully understand the interface electron transfer dynamics both experimentally and theoretically for further development of the nanoparticle-based device.

4.1. Experimental techniques measuring interface electronic dynamics

Ultrafast laser spectroscopy, which works by measuring the excited state dynamics of the sensitizer through transient absorption or fluorescence decay, is most popularly used in measuring electronic dynamics between semiconductor nanoparticles and dye sensitizers. Transient absorption spectroscopy, also known as flash spectroscopy, uses an excitation (or pump) pulse (promoting a fraction of the molecules to their electronically excited state), a weak probe pulse with low intensity to avoid multiphoton/multistep processes and a delay τ with respect to the pump pulse to record information on the interfacial dynamic processes by calculating the difference absorption spectrum (ΔA) between the absorption spectrum of the excited sample and the absorption spectrum of the sample in the ground state.

As most transient absorption studies in the visible and near-IR region are hindered by spectral overlap of absorption in various electronic states, such as the excited states, cationic state, and ground state, as well as stimulated emission, there have been many conflicting reports of electron transfer (ET) rates. Femtosecond mid-IR spectroscopy^[37] can directly study the electronic dynamics at the adsorbate/semiconductor interface systematically by measuring IR absorption consisting of free carrier absorption, intraband transitions between different valleys (or subbands) within the conduction or the valence bands, and trap states absorption. Since the IR absorption of electrons are direct evidence for the arrival of electrons inside semiconductors, they provide an unambiguous spectroscopic probe for studying interfacial electron transfer between the semiconductor and adsorbates.

The time-correlated single photon counting (TC-SPC) technique^[38] is also an ideal method which allows multiwavelength imaging in conjunction with a laser scanning microscope and a pulsed excitation source to investigate the excited state lifetime of electrons at an interface. The TC-SPC technique is based on a four-dimensional histogramming process that records the photon density over the time of the fluorescence decay, the *x*-*y* coordinates of the scanning area, and the wavelength, which has advantages of ultra-high time resolution (25-ps full-width at half-maximum), ultra-high sensitivity (down to the single photon level) and a perfect signalto-noise ratio. It can accurately describe the electron transfer processes between the sensitizers and the TiO₂ substrate.

4.2. Theoretical approaches describing interface electronic dynamics

Empirical theoretical approaches, which are mainly based on optimized structural features, ground-state molecular dynamics simulations, and/or with empirical kinetic parameters (such as assuming an exponential decay of ET rate as a function of dye length^[39] and constant electron-phonon coupling strength^[40]), have been commonly employed to deal with the critical electron transfer process at the dye/TiO2 interface. For instance, Persson et al. studied the influence of anchor-cumspacer groups on electron transfer time by approximating the effective electronic coupling strength with the calculated band width for heterogeneous electron transfer interactions based on ground-state DFT calculations.^[41] Abuabara et al. successfully investigated the influence of temperature changes on electron injection at the dye/TiO2 interface using ground-state molecular dynamics and studied the electron transfer process using an extended Hükel Hamiltonian.^[42] Prezhdo et al. reproduced the injection dynamics of model chromophores with atomistic details, using ground state molecular dynamic simulation and time domain non-adiabatic trajectory surface hopping based on ground-state trajectories.^[43] Li et al. studied electron transfer from perylene derivatives into the anatase TiO₂ (101) surface using density functional theory (DFT) and a Fock matrix partitioning method.^[44] Jones et al. could rapidly predict the injection rate in DSC by partitioning the system into molecular and semiconductor subsystems and computing the retarded Green function.^[45]

However, there are some problems associated with these empirical models:

i) The excited state potential energy surfaces (PES), which differ from ground state PES, are missing in these simulations, thus the electronic properties in excited states cannot be addressed adequately.

ii) The electronic couplings at the interface, which is subject to the molecular details of the dyes and the configurations of their dynamic bindings to TiO_2 , cannot be described precisely, thus the time scales obtained therein are questionable.

Real-time time-dependent density functional theory (TDDFT),^[46] which quantum mechanically evolves the wavefunctions of excited electron–hole pairs at the dye/TiO₂ interface based on the excited state Hamiltonian, has been used to describe the interfacial electronic dynamics and demonstrated to be especially adequate to treat the interface electronic dynamics and to yield consistency with experiments by Meng *et al.*^[18,35,47–51] This TDDFT approach has advantages over the previous methods in several aspects:

(I) Very efficient atomic orbital basis sets are adopted, which are small in size and fast in performance.

(II) Either a periodic system or a finite-sized supercell with a large vacuum space can be treated without heavy calculation cost.

(III) Real time excited state trajectories with manyelectron density self-consistently propagating at every electronic and ionic step, and forces calculated from mean-field theory are achieved.

Therefore, both experimental and theoretical methods offer promising ways to investigate the interface electron transfer dynamics in chromophore/semiconductor systems, allowing a systematic study of the dependence of ET rates on the specific properties of the adsorbates, semiconductors, and the solvent environments.

4.3. Factors affecting electron injection

4.3.1. Bridging length

According to Marcus theory,^[51,52] the electron injection rate is strongly dependent on the electronic coupling strength and driving force between the sensitizer and the semiconductor substrate. The electronic coupling strength between molecular excited states and TiO₂ can be modified through changing the bridging length between the adsorbates and the binding group. Lian *et al.* explored the influence of the bridge length on interfacial ET rates by measuring ultrafast electron injection into TiO₂ from a rhenium complex with n = 0-5methylene spacers inserted between the bipyridine rings and the carboxylate anchoring groups using femtosecond infrared spectroscopy.^[53] They found that the injection rate decreases exponentially with increasing the number of spacers.

4.3.2. Anchoring group

In addition to the bridge length, variation of the binding groups is another factor that affects the coupling. In 2007, Lian et al. investigated the effects of anchoring groups on electron injection by comparing the ET rate from a ReC1 complex to metal oxides (TiO₂, SnO₂, ZnO) through carboxylate and phosphonate groups.^[54] Faster injection dynamics was observed from phosphonate based chromophores, which leads to a stronger electronic coupling between the bipyridine ligand and metal center than the carboxylate group. Recently, Bartelt et al. synthetized a series of semi-squarylium dyes with a novel acyloin anchor group and investigated the electron injection properties of these dyes using a combination of ultrafast and photoemission spectroscopy.^[27] They found this acyloin anchor group shows stronger electronic coupling with the substrate and facilitates ultrafast electron injection into TiO₂ compared with a carboxylic acid anchored indoline dye D131. More directly, we have calculated the injection rates of two dyes D404 (with cyanoacrylic acid anchor moiety) and SY404 (with acyloin anchor group) sharing the same donor, using real-time excited states TDDFT simulation. From Fig. 4 we can see that, at time t = 0, electrons have a dominant distribution on the sensitizers, so the energy difference between the molecular LUMO level and the TiO₂ conduction band minimum drives electrons to inject efficiently into the substrate with a lifetime of 33 fs for dye SY404 and 60 fs for dye D404. Apparently, SY404 dye with an acyloin anchor possesses faster electron injection dynamics due to the stronger electronic coupling with the TiO₂ substrate.



Fig. 4. The fraction of photo-excited electrons distributed onto TiO_2 substrate as a function of time after photo-excitation of dyes SY404 and D404 with different anchor groups, using real-time TDDFT simulation. Insets are chemical structures of dyes SY404 and D404. Dashed lines show exponential fittings of the injection dynamics.

4.3.3. Adsorption configuration

Moreover, even for the same sensitizer, different adsorption configurations result in different coupling strengths, leading to different interfacial electron injection. In Ref. [18], Jiao *et al.* report their study of how the adsorption structure impacts the ET lifetime at the dye/TiO₂ interface, using TDDFT

electron-ion dynamics simulation. Figure 5(a) shows the fraction of excited state photoelectron χ distributed onto TiO₂ substrate as a function of time after photo-excitation of systems with binding structures of Ic, IIb, IIc (corresponding to the configurations shown in Fig. 2(a)). All three cases exhibit ultrafast electron injection. At time t = 0, photo-excited electrons are mainly distributed in the excited states of chromophore and start to inject into the TiO₂ conduction band at approximately 16 fs in an exponential way, ultimately finishing at about 100 fs. Exponential fitting shows an injection lifetime of 64 fs for Ic, slightly slower than the injection time of IIb and IIc (59 fs). Although Ic shows slower injection dynamics, it has a larger quantum yield (equilibrium photoelectron fraction) after injection, 70% compared to 37% for IIb and IIc, which results from stronger electronic coupling at the interface in IIb and IIc configurations, leading to substantial state mixing between the dye LUMO and the TiO₂ conduction band.



Fig. 5. (a) Electron injection dynamics for adsorption configurations Ic, IIb, and IIc, from coupled electron–ion MD simulation based on realtime TDDFT. Dotted lines are fitted by an exponential function. (b) The fraction of photo-excited electrons distributed onto TiO_2 substrate as a function of time after photo-excitation of dye N1 with different driving forces, using real-time TDDFT simulation.

4.3.4. Driving force

Besides electronic coupling strength, another critical factor influencing the interfacial electron injection kinetics is the driving force, which is defined as the potential difference between the molecular excited states and the TiO_2 conduction band minimum. Recently we designed a system using model dye N1 as the sensitizer and TiO_2 anatase (101) surface as the substrate and investigated the photoelectron injection behaviors arising from different molecular excited states of the system using real-time excited state TDDFT simulation. At time t = 0, one electron is promoted from the HOMO to higher excited states (LUMO and LUMO + 2) of the organic dyes, indicating that the first excited state of an electron-hole pair is generated upon photo absorption. As shown in Fig. 4(b), excited electrons are completely injected into the CB of the TiO₂ substrate within a time scale of 87 fs from the LUMO + 2 excited state and 160 fs from the LUMO excited state of dye N1, while holes keep stable and confined within the dye molecules. Here the lifetime of the injection process is estimated by the time when 63.2% electrons are transferred from the sensitizer into the TiO₂ electrode. Apparently, electrons undergo a faster injection dynamics with a larger driving force. In fact, according to Marcus theory, the electron transfer rates are not directly dependent on driving force but depend on the activation energy, which is related to the sum of the driving force and reorganization energy. Here, as reorganization energies are the same for injections from different excited states of the same dye, the driving force directly determines the ET rates at the N1/TiO₂ interface.

5. Thermal relaxation

Although a larger driving force contributes to ultrafast electron injection, resulting in larger incident photon-toelectron conversion efficiency (IPCE), it also causes a large energy loss, because photon energies exceeding the threshold energy gap usually dissipate as heat and cannot be converted into electricity. In DSC, an electron is excited from the ground state to a higher excited state by photon absorption, and then injects into the conduction band of the semiconductor substrate, leaving an electron deficiency (hole) in the sensitizer. Those hot electrons generated with photon energy in excess of the HOMO–LUMO band gap quickly cool (within $\sim 1 \text{ ps}$) to the band edges through sequential emission of phonons after injection. Ross et al. have shown that a single-threshold quantum-utilizing device in which the excited carriers thermally equilibrate among themselves, but not with the environment, can convert solar energy with an efficiency as high as 66%.[55]

5.1. Hot electron injection

One way to utilize the hot carrier energy is to quickly transfer the hot electrons to the conducting contact before they cool. Hot carrier cooling rates depend upon the carrier's effective mass and the density of hot carriers (i.e. the absorbed light intensity). Quantization effects in the space charge layer dramatically slow down the thermal relaxation and enhance the transfer of hot electrons out of the semiconductor. When the carriers in the semiconductor (i.e., in semiconductor quantum wells, quantum wires, quantum dots, superlattices or nanostructures) are confined by potential barriers to regions of space that are smaller than or comparable to their de Broglie wavelength or to the Bohr radius of excitons in the semiconductor bulk, the relaxation dynamics can be markedly altered; specifically, the hot-carrier cooling rates may be remarkably reduced. William et al. successfully slowed down the hot electron relaxation by using colloidal PbSe quantum dots as sensitizers and 1,2-ethanedithiol (EDT) passivated nanocrystalline rutile TiO_2 substrate, and observed the hot electron transfer from the higher excited states of PbSe quantum dots to the TiO₂ substrate within 50 fs using optical second harmonic generation (SHG).^[56] Figure 6(a) shows the temperature-dependent decay of the pump-induced SHG signal. A substantial rise in SHG signal, which is consistent with the hot electron transfer from PbSe to TiO₂, is observed after photo-excitation on a time scale shorter than the laser pulse (50 fs). Then a decrease



Fig. 6. (a) Temperature-dependent decay of the pump-induced SHG signal enhancement; the absolute intensity has been normalized for pump-induced change to better illustrate the temperature-dependent recovery rate. The bottom figure is the schematic representation of the interfacial electric field generated by separation of electrons and holes across the PbSe–TiO₂ interface.^[56] (b) APCE versus the incident photon energy divided by the quantum dot band gap energy (indicating the multiples of the band gap).^[57]

in the SHG signal caused by hot electron cooling is observed. The relaxation rate increases exponentially with temperature, resulting in a drastic decrease of the SHG signal.

5.2. Multiple-exciton generation

Another effective way to utilize the excess photon energy is multiple-exciton generation (MEG), which is the creation of two or more electron-hole pairs from one high energy photon by impact ionization. MEG happens on the condition that the rate of impact ionization is greater than the rate of electronic relaxation. MEG has been recognized for over 50 years in bulk semiconductors and observed in the photocurrent of bulk p-n junctions in Si, Ge, PbS, PbSe, PbTe, and InSb by impact ionization.^[58–64] However, the threshold photon energy for MEG (where the impact ionization rate is competitive with phonon scattering rates) in the bulk semiconductor is many multiples of the band gap, resulting in inefficient photovoltaic output. Fortunately, the impact ionization process has been found to be more efficient in semiconductor nanocrystals or quantum dots because the inverse Auger process of exciton multiplication is greatly enhanced due to quantum confinement effects. Matthew et al. were first to observe the MEG yields in colloidal Si nanocrystals in 2007, by using ultrafast transient absorption spectroscopy.^[64] They found the threshold photon energy for MEG in 9.5-nm diameter Si nanocrystals (effective band gap $E_{\rm g} = 1.20~{\rm eV}$) to be $2.4 \pm 0.1E_{\rm g}$ and find an exciton-production quantum yield of 2.6 ± 0.2 excitons per absorbed photon at 3.4 E_g . Parkinson et al. used a photoelectrochemical system composed of PbS quantum dots chemically bound to TiO₂ single crystals and demonstrated multiple-exciton collection (MEC) in experiment for the first time.^[57] Figure 5(b) shows the calculated absorbed photon-tocurrent efficiency (APCE) values as a function of the ratio of the excitation energy to the band gap of PbS quantum dots. Without the MEC process, the APCE values remain constant at $\sim 70\%$ for all sizes of quantum dots. The APCE values of a quantum dot with band gap $E_g = 0.94$ eV increase rapidly and exceed 100% at illumination energies larger than 2.7 times the nanocrystal band gap, indicating the presence of multipleexciton generation and collection processes. The strong electronic coupling and favorable energy alignment between PbS quantum dots and bulk TiO₂ promote the generation and quick collection of multiple excitons from higher excited states.

6. Electron-hole recombination

In addition to thermal relaxation, electron-hole recombination is another main loss of absorbed solar energy. Electrons injected into the TiO_2 conduction band easily lose energy by recombining with holes in the electrolyte and the oxidized sensitizers if not rapidly transported to the conducting contact, limiting the attainable energy conversion efficiency. Recombination with holes in the oxidized dyes and holes in the electrolyte acceptor species are intertwined together and difficult to separate in experiment. Generally, there are two ways to decrease the electron-hole recombination process in DSC: retarding the recombination with holes in the electrolyte and blocking the recombination with holes in the sensitizers.

In experiment, one could suppress the electron-hole recombination in the electrolyte by changing the size of electrolyte ions or adding additives. For instance, by replacing the traditional I^-/I_3^- redox couple with cobalt-complex electrolyte, electron recombination with holes in solution is dramatically reduced, increasing the electron collection efficiency of the device.^[3,4,30] As the size of the cobalt complex is larger than the I^-/I_3^- redox couple, it is difficult for cobalt complexes to contact the nanocrystal TiO₂ surface directly, hence retarding the charge recombination in the electrolyte. Adsorption of Li⁺ ions from the electrolyte on the semiconductor TiO₂ surface can also slow down both electron transport and charge recombination remarkably.^[66] Dai et al. found that upon introducing a special additive, tributyl phosphate (TBpp), to modify the dyed-TiO₂/electrolyte interface, the electron recombination at the dyed-TiO₂/electrolyte interface is restrained and the photovoltaic performance is enhanced by 40%.^[67] The TBpp parent molecule splits into several smaller fragments and forms four anchoring modes on the TiO₂ surface. The molecular cleavage of TBpp and adsorption of N719 assist each other on the sensitized TiO₂ surface, transforming the unstable N719 configuration into a stable N719 configuration, thus reducing N719 aggregation at the dye/TiO2 interface. Furthermore, these new fragments are multiply adsorbed on the non-sensitized TiO2 surface to form an insulating barrier layer. Therefore, the interface electron-hole recombination is retarded.

On the other hand, making slight structural modifications to dye molecules can also slow down the charge recombination in oxidized dyes. Haid et al. decreased electron-hole recombination rates by a factor of about five through inserting a phenyl ring between the benzothiadiazole (BTDA) bridging unit and the cyanoacrylic acid acceptor.^[36] Ma et al. found that the fivefold change in the recombination rate comes mainly from the longer back electron transfer distance of the inserted dye, using quantum chemical simulations.^[49] As shown in Fig. 7, they used dye N1 and N2 as simplified models of dye 1 and dye 2 in Ref. [36] to investigate how small structural modifications significantly influence charge recombination. By the insertion of an additional phenyl ring close to the anchoring group, the electron-hole recombination rate is slowed down by a factor of about four (23 ps versus 6 ps). Charge transfer distance dependence was found to be the main factor for this significant difference in the recombination lifetime, by theoretical analysis.



Fig. 7. (a) Fraction of electrons transferred from the TiO_2 semiconductor substrate to the organic dyes N1 and N2 after excitation at the organic dye- TiO_2 interface. Dashed lines are results fitted by linear decay dynamics. The two insets show back electron transfer distances from the semiconductor TiO_2 to the sensitizers. (b) Fraction of electrons transferred from the TiO_2 semiconductor substrate to the organic dyes N3 and N4 after excitation at the organic dye- TiO_2 interface. Insets are chemical structures of N3 and N4. Dyes N3 and N4 are isomers with different dihedral angles between the donor moiety and the bridging unit (shown by numbers therein).

Besides the longer recombination distance, many people think that structural twisting of a donor- π -acceptor dye can break down the π -conjugation between the donor and acceptor and thus block electron back transfer to the sensitizer from the charge separated state. We have investigated the influence of structural twisting on the dye/TiO2 interface electron-hole recombination by calculating the recombination dynamics of two isomers dyes N3 and N4 adsorbed on the TiO_2 anatase (101) surface, based on real time excited state TDDFT. Figure 7(b) shows the evolution of the transfer of electrons back from the TiO₂ conduction band to the sensitizers. Two insets are the chemical structures of dyes N3 and N4. N3 and N4 share the same compositions but have $\sim 30^{\circ}$ difference in the dihedral angle between the donor moiety and bridging unit. Obviously, dyes N3 and N4 exhibit similar recombination dynamics, and the planar dye N4 even shows slower recombination dynamics. Therefore, structural torsion of organic dyes hardly affects the recombination process at the dye/TiO2 interface.

7. Conclusion and outlook

In this review, we briefly introduce the composition, working principles, and recent progress of dye-sensitized solar cell research, with a special focus on the atomistic-level information obtained from recent extensive investigations. Starting from the five critical factors affecting the solar cell efficiency: dye/TiO₂ interface structures, dye absorption properties, electron injection, thermal relaxation, and electron–hole recombination, we introduce the basic concepts of these factors and the roles they play in DSC, the advanced theoretical and experimental methodologies, the influence of these individual processes on overall DSC efficiency, past achievements and future opportunities for further improvements.

However, improving the DSC efficiency is a grand challenge which requires achieving more breakthroughs in fundamental concepts and employing the finest systematic engineering. There exists no universal method for chasing better photovoltaic performance in all cases. For instance, near IR dyes have better photon absorption, but their V_{OC} values are relatively low. Adding TBpp additives can slow down the electron-hole recombination at the TiO₂/electrolyte interface on one hand, but on the other hand, it also slows down electron transport rates in TiO₂ nanoparticles. MEG and MEC processes have been achieved only in quantum dot solar cells, but have not been available in organic DSC.

Clearly, the efficiency of DSCs is still far from the Shockley–Queisser limit for a single absorber, so great efforts should be made in narrowing this gap by more focused research and systematic methods. Several promising approaches can be taken to boost PCE efficiency further, for example, design of novel dyes with panchromatic absorption properties and large molar coefficient to significantly enhance light harvesting efficiency or design of dye structures to hinder the approach of redox species to the TiO2 surface, thereby lowering the rate of back electron transfer. In addition, fundamental research with precise characterization of the specific interface structures and dynamic processes is of crucial importance for future device optimization. Scanning tunneling microscopy and spectroscopy, for instance, have been demonstrated to be excellent tools for describing structural and electronic properties of various dye molecule geometries at the interface with single-molecule resolution.^[68] Non-contact atomic force microscopy with a functionalized tip might be effective in directly imaging dye adsorption on non-conductive substrates.^[69] More importantly, with extraordinary field enhancements under a sharp metal tip, detection of ultrafast electron dynamics for individual dye molecules or dye configurations might be possible. For realistic large-scale implementation, cost and stability are two other major preoccupations in DSC research.

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