Ultrafast Dynamic Microscopy of Carrier and Exciton Transport

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Keywords
ultrafast imaging, pump-probe microscopy, charge mobility, exciton diffusion, interfacial charge transfer, solar cells

Abstract
We highlight the recent progress in ultrafast dynamic microscopy that combines ultrafast optical spectroscopy with microscopy approaches, focusing on the application transient absorption microscopy (TAM) to directly image energy and charge transport in solar energy harvesting and conversion systems. We discuss the principles, instrumentation, and resolutions of TAM. The simultaneous spatial, temporal, and excited-state-specific resolutions of TAM unraveled exciton and charge transport mechanisms that were previously obscured in conventional ultrafast spectroscopy measurements for systems such as organic solar cells, hybrid perovskite thin films, and molecular aggregates. We also discuss future directions to improve resolutions and to develop other ultrafast imaging contrasts beyond transient absorption.
INTRODUCTION

Effective energy transport over long distances and across interfaces remains the central challenge to achieving high efficiencies in solar energy harvesting and conversion systems (1). The frontier in solar energy research now lies in integrating nanostructured and molecular components across multiple length scales to create optimal devices. Over the past two decades, significant advances have been made in constructing the next generation of solar cells from low-dimensional nanomaterials (2–4), organic polymers and small molecules (2, 5), and hybrid organic–inorganic perovskites (6, 7). Compared with the traditional single-crystalline silicon solar cells, the new generation of solar cells generally have active layers that are polycrystalline and have heterogeneous interfaces; for instance, bulk heterojunction organic solar cells consist of ∼10-nm polycrystalline domains of conjugated polymer electron donors and fullerene acceptors (5).

After photoexcitation, the excited charge carriers or excitons created in the active layer of a solar cell need to migrate to the donor–acceptor interfaces or the electrodes for charge separation and collection. An exciton refers to the excited electron in the conduction band and the hole left behind in the valence band bound by the attractive Coulomb interaction between them. Charge and exciton diffusion length are important parameters that determine the efficiency of a solar cell. A major challenge to measuring charge and exciton transport in nanostructured solar energy harvesting systems is the need for both femtosecond time resolution and nanometer spatial resolution because of the short excited-state lifetime (as short as hundreds of femtoseconds) and diffusion lengths (on the order of hundreds of nanometers or shorter). Conventionally, the lifetimes of the excited electronic states are studied with ultrafast nonlinear optical spectroscopy tools by recording the response of the excited states in the time domain; the most commonly used technique is transient absorption (TA) spectroscopy (also known as pump–probe spectroscopy) (8–10). More recently, multidimensional coherent electronic spectroscopy has been developed to investigate coherent interactions between excited states and how these interactions modulate energy and charge transfer pathways (11–15). These ultrafast spectroscopic tools are indispensable for elucidating the timescales of charge and energy transfer processes in solar energy harvesting systems. However, they are carried out over primarily large ensembles of molecules and particles in the solution phase and thus provide little to no information about the spatial domain. At the other extreme, many microscopic techniques have been developed to characterize structure and morphology of the nanostructured solar energy harvesting systems with excellent atomic spatial resolution but with no temporal resolution (16, 17).

To obtain simultaneous spatial and temporal resolutions, researchers have combined ultrafast nonlinear spectroscopy with microscopy approaches, including optical microscopy (18, 19), electron microscopy (20–22), scanning tunneling microscopy (23–26), and scanning probe microscopy (27, 28). The fields to which ultrafast microscopy has been applied include biology and materials research (29–36). Although electron microscopy and scanning tunneling microscopy approaches have the potential to achieve atomic resolution, in general they have more stringent sample and instrumentation requirements, such as ultrahigh vacuum, making them less accessible than optical microscopy approaches. Readers interested in ultrafast electron microscopy are directed to other reviews (37, 38).

A full review of the current state of ultrafast microscopy is beyond the scope of this article. Here, we focus on the applications of all-optical transient absorption microscopy (TAM) in solar energy harvesting systems. Particularly relevant to the solar energy conversion systems are the capabilities to image spatially dependent dynamics and to track the transport of excited charge carriers and excitons directly in space and in time. Examples of the systems and the questions discussed in this review are given in Figure 1. This review is organized as follows. First, we
Single nanostructures

1–10s of nanometers

Nanoscale interfaces

10–100s of nanometers

Molecular and nanostructured assemblies

10–100s of nanometers

Semiconducting thin films

> 100s of nanometers

Structure-dependent dynamics

Environmental effects

Morphology-dependent charge transfer

interfacial exciton transport

Transport across interfaces

Exciton delocalization

Coherent/incoherent exciton transport

Singlet and triplet excitons

Charge and exciton diffusion

Grain boundaries

Hot carrier transport

Figure 1

Examples of the systems and the questions investigated by transient absorption microscopy as discussed in this review. Examples include (left to right) dynamics in single nanostructures, charge transfer/exciton transport at nanoscale interfaces, exciton transport in molecular and nanostructured assemblies, and charge carrier transport in semiconducting thin films.

introduce the TAM instrumentation and the factors that control the signal-to-noise ratio (S/N) and spatial resolution. Second, we review measurements of exciton and charge dynamics at the single-nanostructure level. Third, we discuss spatial mapping of morphology-dependent and interfacial charge/energy transfer in spatially heterogeneous systems. Last, we devote a significant part of this review to the unique capabilities of TAM to image different regimes of exciton and charge transport as well as transport across interfaces and boundaries.

BASIC PRINCIPLES OF TRANSIENT ABSORPTION MICROSCOPY

TAM is constructed by combining TA pump–probe spectroscopy with optical microscopy (18, 39, 40). In pump–probe experiments, a laser pulse (pump) excites the system into the excited state and a second delayed pulse (probe) is used to monitor the population of a particular excited electronic state. A mechanical delay stage is commonly used to control the delay time between the pump and probe pulses. Three types of signals can be observed in a pump–probe experiment: ground state bleach, stimulated emission, and photo-induced absorption (Figure 2a). These different types of signals can be selected by choosing different pump and probe frequencies. The TA signal measures pump-induced probe intensity that is proportional to population changes, as given by

$$\frac{\Delta I}{I} \propto (\Delta n_f - \Delta n_i),$$

where $n_i$ and $n_f$ are the occupations of the initial and final states, respectively. The decay of the signal reflects the depopulation dynamics of the excited states.

A typical TAM setup is illustrated in Figure 2b. The collinear and copropagating pump and probe beams are focused by an optical microscope objective. After the sample, either the transmission or the reflection of the probe is detected. There are two modes of imaging for TAM. For morphological imaging, the pump and probe beams are always overlapped in space and images can be acquired by either raster scanning the sample with a piezo stage or scanning the beams with scanning mirrors (path 1 in Figure 2b). In contrast to the conventional TA measurements, in which spectroscopic information represents a spatial average over the typically weakly focused
Figure 2
Working principle of TAM. (a) Energy diagram demonstrating different imaging contrasts used in TAM: ground state bleach, stimulated emission, and photoinduced absorption. The pump is represented by the blue arrow; the probe is represented by the orange arrow. (b) Schematic representation of a TAM setup. In path 1 (dashed gray line) the pump and probe beams are scanned together in space and the spatially dependent dynamics are imaged. In path 2 (blue line) only the probe beam is scanned to construct images of the excited state population. Abbreviations: AOM, acoustic-optical modulator; APD, avalanche photodiode; BS, beam splitter; OPA, optical parametric amplifier; TAM, transient absorption microscopy.

probe beam, the use of a tightly focusing microscope objective allows for locating nanostructures or a sample area of interest with diffraction-limited resolution. In addition, TAM also allows for the spatial control of the pump and probe beams, leading to a second mode of imaging. When the pump and probe beams are spatially scanned relative to each other, exciton and charge transport can be imaged directly. As indicated by path 2 of Figure 2, the pump beam is fixed and the probe is scanned by Galvo mirrors. The use of spatially separated TAM to image transport is one focus area of this review.

Signal generated from a single molecule, a single nanoparticle, or the sample volume interrogated in the tightly focused beams in TAM is much smaller than that from conventional TA spectroscopy (41). The pump-induced change in the probe intensity was estimated to be $10^{-7}$–$10^{-6}$
from the typical absorption cross section $10^{-16}$–$10^{-15}$ cm$^2$ of a single molecule (32, 42). Therefore, TAM requires a S/N higher than that for traditional TA spectroscopy. There are two main sources of noise in these experiments: laser fluctuation noise and electronic noise from the detection system such as detectors and lock-in amplifiers. Noise due to the fluctuation of laser intensity can be effectively eliminated by way of heterodyne lock-in detection with megahertz modulation (29, 42), where the intensity of the pump beam (or additional local oscillator) is modulated by an acoustic-optical modulator or an electro-optical modulator. Subsequently, a lock-in amplifier referenced to this modulation frequency can sensitively extract the pump-induced change in the probe. The fluctuation of laser intensity ($1/f$ noise) usually occurs at direct current frequencies as low as 10 kHz. When the modulation is in the megahertz range, the laser intensity noise nears the quantum shot noise limit (18). Therefore, TAM usually uses high-repetition-rate (greater than megahertz) lasers with a single-wavelength probe for the highest possible S/N, detecting $\Delta I/I$ on the order of $10^{-7}$ for pump–probe spectroscopy and single-molecule sensitivity (42). TAM with a broadband white-light probe and kilohertz laser sources has also been reported (43–46) but usually with a lower S/N with a detection limit of $\sim 10^{-4}$. The incorporation of a balanced detector can also be useful for suppressing the common-mode laser intensity noise with a reference pulse (47, 48).

Van Dijk et al. (49) used as an alternative approach to high-speed modulation a birefringent crystal to create perpendicularly polarized signal and reference beams in a common path interferometer, which detected dynamics in single gold nanoparticles with diameters as small as 10 nm. Utilizing background-free photoluminescence (PL) detection is another strategy to increase sensitivity. Recently, a pump–probe measurement of a single molecule at room temperature was achieved with 25-fs temporal resolution by use of a three-pulse scheme with PL detection (19, 50).

The spatial resolution for resolving features for morphological TAM imaging with far-field excitation and collection as shown in Figure 2 has a diffraction limit of $\sim \lambda/2$. A superresolution approach based on stimulated emission depletion improves spatial resolution by a factor of $\sim 2$ (51–53). For these measurements, a third doughnut-shaped laser beam was added to the optical path. A different superresolution approach, demonstrated by Massaro et al. (54), incorporated a focused diffraction-limited probe field with a spatially modulated pump excitation. Near-field TAM with subdiffraction-limited spatial resolution has also been demonstrated (55–59). In addition to near-field optical excitation and detection, time-resolved photoinduced force microscopy recorded the local force between an atomically sharp atomic force microscopy (AFM) tip and the photo-excited sample (27). A spatial resolution of $\sim 10$ nm, far below the diffraction limit, was reported (27). In addition, the force-detected signal follows the same time evolution (dynamics) as the optical detection (28). Another approach is to combine electronic detection with optical excitation in photoemission electron microscopy, imaging the lateral distribution of photoemitted electrons, which is not limited by diffraction limit (36, 60, 61).

The TAM modality to image carrier and exciton transport is achieved by scanning the pump and probe beams relative to each other. The relative change in probe transmission or reflection ($\Delta T$ or $\Delta R$) induced by the pump is recorded at different pump–probe displacements to create images. Thus, time-dependent carrier and exciton density images can be generated. For quantification of carrier and exciton transport rates and distances, the TAM results can be modeled to extract population in both temporal and spatial domains (62). The initial population $n(x, y, 0)$ injected by the pump could be approximated to a Gaussian distribution,

$$n(x, y, 0) = N \exp \left[ -\frac{(x-x_0)^2}{2\sigma_{x,0}^2} - \frac{(y-y_0)^2}{2\sigma_{y,0}^2} \right].$$
If the transport is diffusive, exciton and charge populations as a function of space and time can be described by a differential equation that includes both the diffusion out of the initial volume and population decay, which is given by

$$\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} - \frac{n(x,t)}{\tau},$$  \hspace{1cm} (2)

where $D$ is the diffusion constant and $\tau$ is the lifetime. The solution to Equation 2 dictates that exciton density at any later delay time ($t$) is also Gaussian and can be described as

$$\langle n(x,y,t)\rangle = N \exp \left[ -\frac{(x-x_0)^2}{2\sigma_{x,t}^2} - \frac{(y-y_0)^2}{2\sigma_{y,t}^2} \right].$$  \hspace{1cm} (3)

The diffusion constant $D$ along one direction is then given by

$$D_{x(t)} = \frac{\sigma_{x(t),t}^2 - \sigma_{x(t),0}^2}{2t}. \hspace{1cm} (4)$$

The solution for $D$ is not dependent on exciton lifetime $\tau$. The average distance that excitons or charge travels in time $t$ is defined as $L$ and is given by

$$L_{x(t)} = \sigma_{x(t),t}^2 - \sigma_{x(t),0}^2. \hspace{1cm} (5)$$

It is important to understand how annihilation or higher-order processes impacted the spatial distribution of the charge or excitons. Because the density is higher at the center of the spot than at the edge, leading to faster decay due to annihilation, annihilation could lead to artificial broadening of $\sigma$ and error in measuring $D$ (62). Performing pump-fluence-dependent measurements is necessary to correctly account for both exciton diffusion and exciton–exciton annihilations.

The precision in determining the exciton propagation distance $L$ is dictated by the smallest measurable change in the population profiles and not directly by the diffraction limit (63). From Equation 5, we can perform a sensitivity analysis to find that the uncertainty in determining the transport length along one direction is given by

$$\Delta L = \sqrt{\frac{\sigma_{x(t),t}^2}{\sigma_{x(t),0}^2} (\Delta \sigma_t)^2 + \frac{\sigma_{x(t),0}^2}{\sigma_{x(t),0}^2} (\Delta \sigma_0)^2} = \sqrt{\Delta \sigma_t^2 + \left(\frac{\sigma_0}{\tau}\right)^2 (\Delta \sigma_0^2 - \Delta \sigma_t^2)}. \hspace{1cm} (6)$$

Equation 6 shows that $\Delta L$ comes from the errors of the Gaussian variances measured at different times ($\Delta \sigma_t$ and $\Delta \sigma_0$), as well as the ratio between the beam size and the transport length ($\frac{\sigma}{\tau}$). Both $\Delta \sigma_t$ and $\Delta \sigma_0$ are determined by the S/N of the experiments, and using a smaller beam size will reduce $\left(\frac{\sigma_0}{\tau}\right)^2$. Therefore, both improving S/N and reducing beam size can improve the resolution in imaging transport. For the examples in this review that use diffraction-limited far-field excitation, the resolution limit is $\sim 50$ nm (62, 64, 65). By introducing a third stimulated emission depletion beam to effectively reduce the pump beam size, Penwell et al. (52) have improved the resolution to $\sim 10$ nm.

An alternative to scanning the probe beam to acquire transport imaging is the use of a focused pump beam and a defocused wide-field probe beam. Delor et al. (66) have recently demonstrated wide-field interferometric scattering microscopy to image charge transport, which involves interferometrically detecting elastically scattered light from sample features due to local variations in polarizability. Guo et al. (67) reported wide-field TAM using an array of pump laser beams generated with diffractive optics that was capable of performing 41 parallel TA experiments. The use of both approaches can significantly reduce data acquisition time.
PROBING CARRIER AND EXCITON DYNAMICS AT THE SINGLE-NANOSTRUCTURE LEVEL

A unifying theme for low-dimensional nanostructures is that size, shape, and structure are critical for determining properties. Because traditional ensemble measurements are integrated over a large number of structures, the information about how the dynamics are affected by differences in structure and the local environment is lost for low-dimensional nanostructures. In contrast to a PL-based image, TAM using absorption as an imaging contrast is a universal tool for providing dynamics and spectroscopic information at the single-nanostructure level (41, 68–71). The development of single-particle pump–probe measurements was pioneered by Orrit (49), Okamoto (56), Vallée (72), and colleagues. TAM has revealed energy relaxation pathways in many low-dimensional nanostructures, including plasmonic nanoparticles (49, 56, 72–74), semiconducting nanowires (75–78), single-walled carbon nanotubes (79–81), graphene (31, 34, 51, 58, 82, 83), and two-dimensional (2D) semiconductors (84, 85).

Staleva & Hartland (86) overcame sample inhomogeneity by conducting experiments on single silver nanocubes. TA traces of a single particle and ensemble particles are compared in Figure 3a,b, showing more pronounced modulation and a much longer damping time for the single particles than for the ensemble particles. Damping time differed considerably from particle to particle owing to the heterogeneity of their local environments (86). Another example that demonstrates the importance of single-particle measurements is single-walled carbon nanotubes, where multiple chiralities of both semiconducting and metallic tube types coexist in the as-produced samples (87). By correlating TAM to AFM and Raman spectroscopy, Gao et al. (80, 81) imaged individual chirality-assigned suspended carbon nanotubes (Figure 3). TA spectra of the same nanotube supported by the substrate versus freely suspended were obtained by recording TA images at different probe wavelengths (Figure 3c). The results showed an ∼40-meV red-shift of the lowest exciton transition when supported on a glass substrate, which was attributed to dielectric screening effects.

How the local environment modulates excited-state relaxation pathways has also been investigated at the single-nanostructure level. Grumstrup et al. (78) studied the impact of strain on carrier recombination rates in single silicon nanowires on a stretched poly(dimethylsiloxane) (PDMS) substrate. When the PDMS substrate was relaxed and the nanowire adopted a bent configuration, the rate of electron-hole recombination increased by sixfold compared with that of the strained nanowire. For semiconducting cadmium telluride nanowires, Lo et al. (76) demonstrated that carrier trapping dynamics varied significantly from wire to wire owing to differences in the energetics or density of surface trap sites. Gao et al. (83) investigated the role of substrate in carrier cooling dynamics of graphene, showing that the interactions between the excited charge carriers and the surface optical phonon modes of the glass substrate functioned as an additional relaxation channel for supported graphene.

SPATIAL MAPPING OF ENERGY AND CHARGE TRANSFER DYNAMICS

A main feature of TAM is its ability to image morphology-dependent dynamics in spatially heterogeneous systems. For such measurements, the pump and probe beams always overlap in space (path 1 in Figure 2). For solar energy harvesting systems, TAM offers a distinct advantage over PL-based techniques because the signal is based on absorption, so that emissive singlet excitons, nonemissive triplet excitons, and separated charges can be monitored. TAM has been applied to image spatially dependent charge and exciton dynamics in organic solar cell active layers (43, 88, 89), organic semiconducting thin films (44, 45, 90), polycrystalline perovskite thin films (45, 46, 91–94), 2D heterostructures (95, 96), and plasmonic nanocavities (97).
For organic solar cells, the packing of the molecules and phase segregation of different compositions play a critical role in charge separation (5). Wong et al. (89) and Grancini et al. (43) demonstrated morphology-dependent TAM measurement in prototypical poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) blends for bulk heterojunction solar cells, showing PCBM-rich and P3HT-rich domains exhibit different dynamics. Such heterogeneity in charge and exciton dynamics suggested that information obtained in ensemble measurements by integrating over microscopically inhomogeneous areas could be misleading. Wong et al. (90) performed TAM with a white-light probe to map spatially resolved TA spectra in solution-cast thin films of singlet fission in 13-bis(triisopropylylsilyl)pentacene (TIPS-pentacene). These measurements revealed that the grain boundaries were composed of...
randomly packed nanocrystallites and had TA spectra different from those of the grain interior regions. Schnedermann et al. (45) performed TAM with a sub-10-fs pump and a white-light probe pulse, revealing spatial heterogeneity in impulsive stimulated Raman scattering spectra of TIPS-tetracene thin films.

Spatially and spectrally resolved TAM measurements have also been carried out in hybrid organic–inorganic polycrystalline perovskite thin films. Semiconducting lead halide perovskites, such as CH$_3$NH$_3$PbI$_3$, have recently attracted significant research interest, motivated largely by the rapid rise in efficiency of solar cells, achieving above 22% (6, 98). Because hybrid polycrystalline perovskite thin films used in solar cells are commonly grown by low-temperature solution processes, the formation of grain boundaries with trap states is inevitable. Simpson et al. (91, 92) used correlated TAM and PL microscopy to spatially map the distribution of trap states. Schnedermann et al. (45) reported that TA spectra exhibit large spectral variations as a function of space for hybrid perovskite thin films, indicating a significant underlying structural inhomogeneity even within the grain. Similarly, Nah et al. (46) demonstrated that, within single grains of CH$_3$NH$_3$PbI$_3$, strong spatial heterogeneities at the nanometer length scale were present and associated with simultaneous free-carrier and exciton populations. In another work by Nah et al. (93), TAM identified sub-bandgap states that were completely averaged away in ensemble measurements.

TAM also allows for detailed spatial investigation of charge and energy transfer dynamics at nanoscale interfaces. Two-dimensional heterostructures based on atomically thin and van der Waals layers, such as graphene and transition metal dichalcogenides (for instance, MoS$_2$ and WS$_2$), provide model systems for understanding charge separation at the nanoscale (99). Recently, Yuan et al. (96) examined charge transfer at the interface of the graphene layer and the single-layer and bilayer WS$_2$ (Figure 4a) using correlated TAM and AFM. The AFM image (Figure 4b) shows

**Figure 4**
Interlayer-coupling-dependent charge transfer from WS$_2$ to graphene. Good contact between the graphene and the WS$_2$ layers occurs in area 1 and poor contact in area 2. (a) Atomic models of 1L-WS$_2$/graphene and 2L-WS$_2$/graphene interfaces with aligned layers. (b) AFM height image of the 2L-WS$_2$/graphene heterostructure. (c) Correlated TAM image of the 2L-WS$_2$/G heterostructure measured at 0 ps probing the A-exciton resonance. The pump photon energy is 3.14 eV, the probe photon energy is 1.99 eV, and the pump fluence is $\sim$2 µJ cm$^{-2}$. (d) TAM image of the 2L-WS$_2$/graphene heterostructure measured at 2 ps with the same experimental conditions as panel c. (e) Normalized transient dynamics of the heterostructure in areas 1 and 2 as marked and of a control 2L-WS$_2$ layer. The solid lines are the fitting curves, with exponential decays convoluted with the experimental response function. Scale bars = 1 µm. Abbreviations: 1L, single layer; 2L, bilayer; AFM, atomic force microscopy; norm, normalized; TAM, transient absorption microscopy. Figure adapted from Reference 96 with permission from AAAS.
significant spatial heterogeneity in the contact between the bilayer WS$_2$ and the graphene layer, with a strong coupling area 1 and a weak coupling area 2. TAM images at different delay times (Figure 4c,d) and spatially dependent dynamics (Figure 4e) showed that better interlayer coupling led to faster charge transfer from WS$_2$ to graphene. Notably, the interlayer coupling also resulted in new interlayer charge transfer transitions that promote electrons from graphene to WS$_2$ and allow photo-carrier generation by excitation as low as 0.8 eV, below the WS$_2$ bandgap, which is promising for photovoltaic applications (96). Another example of energy transfer at the nanoscale imaged by TAM was presented by Deeb et al. (97), who directly visualized the energy transfer dynamics between 2D arrays of plasmonic gold bowtie nanocavities and dye molecules. By correlating ultrafast microscopy and far-field light emission, they found that bowtie nanoparticles acted as isolated cavities when the diffractive modes of the array did not couple to the plasmonic gap mode. These results demonstrated how ultrafast microscopy could provide insight into the mechanism for nanolasers.

IMAGING MORPHOLOGY-DEPENDENT CHARGE TRANSPORT

By spatially separating the pump and probe beams, TAM provides a new way to directly image charge carrier transport, visualizing how quickly electrons or holes can move in a material. Carrier mobility is conventionally measured by electrical methods using the Hall effect or field effects (100). These electrical methods rely on forming contacts and the results generally reflect spatial and time-averaged mobilities. Noncontact optical techniques, most notably terahertz spectroscopy, have also been used to obtain carrier mobility of nanostructures and thin films (101–103). Although terahertz spectroscopy can be coupled to ultrafast laser excitation to study time-dependent transport behaviors, it does not provide spatial resolution. Compared with these more established techniques, TAM is a contact-free and noninvasive method that provides two significant advantages: (a) the ability to directly address morphological and structural factors such as nanostructure size and shape, substrate, and grain boundaries; and (b) the ability to provide information about both spatial and temporal domains that allows for differentiating different transport regimes.

The early demonstrations of TAM imaging of carrier transport were carried out on single metallic, semiconducting nanowires. Lo et al. (104) visualized the transport of surface-propagating plasmon at the micrometer length scale in single gold nanowires. These experiments also show that scanning the probe beam over a 10-µm range at the sample does not introduce a significant time delay between the pump and probe. In such single-particle measurements, the role of the environment such as the substrate can be readily probed. For instance, how the surface-propagating plasmon mode is coupled to the substrate was visualized by Johns et al. (74). Carrier migration in single semiconducting silicon nanowires was imaged by Gabriel et al. (105) and Grumstrup et al. (77, 78), who determined a diffusion constant of 6–10 cm$^2$ s$^{-1}$ by modeling their data to a diffusion model. Because the measurements directly provide time-dependent spatial distribution of carriers, the migration of mobile free carriers can be differentiated from that of less mobile trapped carriers (105).

Motivated by the long-range carrier transport in hybrid perovskite solar cells (106), a few groups have used TAM to image carrier transport in single-crystalline and polycrystalline hybrid lead halide perovskites. Guo et al. (62) measured carrier transport in polycrystalline CH$_3$NH$_3$PbI$_3$ thin films by using excited-state absorption of the carrier as an imaging contrast (Figure 5). When the TAM results were fitted to the broadening of Gaussian profiles as a function of pump–probe delay time using Equation 3 (Figure 5), carrier transport was diffusive, with a diffusion constant $D$ of $\sim$0.1 cm$^2$ s$^{-1}$. Measurements from wide-field TAM with diffractive optics reported diffusion...
Figure 5
Two-dimensional transient absorption microscopy imaging of carrier transport in perovskite. (a) Two-dimensional imaging of the carrier density profile in CH$_3$NH$_3$PbI$_3$ at different pump–probe delay times. For delay times greater than 1 ps, the signal maximum in each image was normalized to the signal maximum at 1 ps. Scale bar = 300 nm. (b) Scans of excited-state density profiles projected along one dimension. The profiles are fitted with Gaussian functions. (c) Diffusion coefficients obtained through fitting the variances of Gaussian profiles; measurements have been performed on four different sample areas. Abbreviations: ΔT, differential transmission; norm, normalized. Figure adapted from Reference 62 with permission from Macmillan Publishers Limited.

Coefficients between 0.01 and 0.20 cm$^2$ s$^{-1}$ (67). Hill et al. (107) reported carrier diffusion constants on the order of 1–2 cm$^2$ s$^{-1}$ for single-crystalline nanoflakes, higher than that for polycrystalline thin films, suggesting grain boundaries slow carrier transport. In these TAM measurements, carrier diffusion constant $D$ is measured, which can be related to carrier mobility with the Einstein relation

$$D = \frac{\mu kT}{q},$$

where $\mu$ is the carrier mobility, $q$ is the carrier charge. Carrier mobility of 4–80 cm$^2$ s$^{-1}$ V$^{-1}$ is deduced from the TAM measurements, consistent with the values reported from methods using the Hall effect (108) and from terahertz measurements (102).

Carrier transport across grain boundaries is an important process for defining efficiency of solar cells based on polycrystalline semiconducting thin films. Carrier transport across grain
Figure 6
Carrier transport across grain boundaries in a polycrystalline CH$_3$NH$_3$PbI$_3$ thin film. (a) Morphological TAM images of the perovskite thin film taken at a 10-ps time delay between the pump (630 nm) and probe (755 nm) wavelengths. The pump location is indicated by the dashed circle. (b–d) TAM images of carrier transport at (b) 10-ps, (c) 2.5-ns, and (d) 5-ns time delays. The arrows in panels c and d denote fast and slow transport directions. Scale bars = 1 µm. Abbreviations: ΔT, differential transmission; norm, normalized; TAM, transient absorption spectroscopy. Figure adapted with permission from Reference 94; copyright 2018 American Chemical Society.

boundaries in polycrystalline thin films can be uniquely addressed by TAM, as recently demonstrated by Snaider et al. (94) and Deloro et al. (66) on CH$_3$NH$_3$PbI$_3$ thin films. By selectively imaging the sub-bandgap states, Snaider et al. (94) showed that lateral carrier transport was slowed down by the grain boundaries. Carrier diffusion constant is reduced by the grain boundaries only by a factor of ~2 for micrometer-sized grain samples (94). For grain sizes on the order of ~200 nm, carrier transport over multiple grains within a time window of 5 ns has been observed (94) (Figure 6). Therefore, the long carrier lifetimes allowed for efficient transport across the grain boundaries, despite the reduced diffusion constants (94). Collectively, these TAM measurements (62, 66, 67, 94, 107) shed light on the factors contributing to long-range carrier transport in hybrid perovskite solar cells. Specifically, although the carrier diffusion constant is modest compared with that of conventional semiconductors such as silicon, long-range carrier transport can be achieved in polycrystalline thin films with a long carrier lifetime that is robust against defects and grain boundaries.

NONEQUILIBRIUM CARRIER TRANSPORT

Hot (nonequilibrium) carrier thermalization is one of the major sources of efficiency loss in solar cells (109). Such loss can be reverted if the hot carriers can be harvested before they equilibrate with the lattice and the ultimate thermodynamic limit on conversion efficiency can be increased from the Shockley–Queisser limit of 33% to approximately 66% (110). If the hot carriers are to be harvested, they must be able to migrate to the electrodes before they reach thermal
equilibrium with the lattice. Our understanding of hot carrier transport in semiconductors remains elusive because it is highly complex, involving both relatively short-lived nonequilibrium electron and phonon populations. Experimentally, direct measurements are challenging because simultaneously high temporal and spatial resolutions are required.

TAM with femtosecond temporal resolution that is in theory limited only by laser pulse duration can directly address the nonequilibrium transport regimes that are not accessible by time-averaged steady-state techniques. Recently, Guo et al. (111) demonstrated this capability by imaging hot carrier transport in polycrystalline CH$_3$NH$_3$PbI$_3$ thin films using TAM, visualizing three distinct transport regimes (Figure 7). In these experiments, hot carriers were selectively monitored with a photoinduced absorption band resulting from bandgap renormalization by hot carriers. Quasi-ballistic transport up to 230 nm within the pulse width of $\sim 300$ fs was observed. The nonequilibrium transport persisted over tens of picoseconds and $\sim 600$ nm before reaching the diffusive transport limit when the carriers were in thermal equilibrium with the lattice. Ruzicka et al. (82) presented hot carrier transport in graphene imaged by TAM, resulting in a diffusion constant as high as $10^4$ cm$^2$ s$^{-1}$ for a carrier temperature of 3,600 K. Consistent with these TAM

![Figure 7](https://www.annualreviews.org/static/image/ultrafast-microscopy-of-energy-transport/261.png)

**Figure 7**

Transient absorption microscopy images probing at 1.58 eV with two pump photon energies—(a) 3.14 eV and (b) 1.97 eV—at different pump–probe delay times. Scale bars = 1 $\mu$m. (c) Hot carrier distribution at a 0-ps delay for 3.14-eV excitation over a radial distance obtained by averaging all angles compared to the IRF. Solid lines are Gaussian fits. Abbreviations: $\Delta T$, differential transmission; IRF, instrument response function; norm, normalized. Figure adapted from Reference 111 with permission from AAAS.
measurements, Liao et al. (22) used ultrafast electron microscopy to visualize enhanced hot carrier diffusion in amorphous silicon immediately after photoexcitation.

**EXCITON TRANSPORT**

The optical properties of many nanostructured and organic materials desirable for solar energy harvesting are dictated by excitons (i.e., bound electron–hole pairs) (112, 113), whose large oscillator strength leads to efficient light absorption. Examples of these excitonic materials include conjugated polymers, molecular aggregates, carbon nanotubes, and quantum dots (QDs). The energy levels of an exciton are analogous to those of the hydrogen atom, in which the hole plays the role of the proton. Because dielectric screening reduces Coulomb interaction in the materials, the exciton binding energy is orders of magnitudes smaller than the 13.6-eV binding energy (Rydberg energy) in atomic hydrogen, typically in the range of a few hundred millielectron volts. Depending on the strength of the binding energy, excitons can be roughly grouped into two types, Wannier and Frenkel. For bulk inorganic semiconductors, the high dielectric constants lead to small binding energies on the order of 10 meV and delocalized Wannier excitons with radii larger than the lattice spacings. Frenkel excitons with larger binding energies of hundreds of millielectron volts are prevalent in low dielectric organic materials, with sizes that approximate the size of the molecular unit. Because the physical size of the nanostructures could be smaller than the size of the exciton, excitons in low-dimensional materials might be hybrids of the Wannier and Frenkel types.

Because the excitons generated by photoexcitation must be able to reach an interface with the electron acceptors for charge separation, exciton diffusion length is an important material parameter (114, 115). Excitons do not have net charges; thus, their transport cannot be measured by electrical methods. Previously, exciton diffusion had been characterized indirectly primarily by PL quenching (116). However, the results of these experiments could be incongruous owing to the inhomogeneity at the interface with the quenchers, leading to inconsistency in the measured diffusion lengths. More importantly, these measurements did not test the fundamental assumptions of exciton transport and therefore did not provide significant insights into mechanisms. More direct measurements such as PL microscopy were used to image the extent of exciton transport in ordered and disordered molecular solids and molecular aggregates (63, 117, 118). A major drawback of PL-based techniques is that the time resolution is usually limited to the order of ~100 ps, which might not be sufficient to unravel fast energy transfer processes. In addition, nonemissive species such as triplet excitons and free carriers cannot be imaged directly. More recently, several groups have demonstrated TAM as a new tool for directly imaging exciton transport (52, 64, 65, 119–121). As discussed below, the simultaneously high spatial and temporal resolutions of TAM allow for direct examination of the underlying mechanisms to provide design principles for molecular based light-harvesting materials.

Exciton transport of tightly bound excitons in single-layer 2D transition metal dichalcogenides has been investigated by TAM (119, 121), highlighting the importance of the dielectric environment. Because the interlayer coupling is relatively weak, the electrons and holes are confined in the layer plane and excitons dominate the optical properties of these materials, with large exciton binding energy ranging from 0.3 to 0.7 eV for the monolayers (122). These 2D excitons are not strictly Wannier or Frenkel but in the intermediate regime owing to the nature of the Coulomb interaction between electrons and holes in two dimensions. The dielectric function of the monolayer is large enough to allow for the spatial extent of the wave function to extend over a few nanometers in the layer, and poor screening in the vacuum or dielectric environment outside the layer allows for large (~0.4 eV) binding energies (123). At the single-layer limit, the excitons
are subjected to interfacial Coulomb scattering by charge impurities and remote scattering from phonons of the substrate in addition to intrinsic phonon scattering. Shi et al. (84) elucidated exciton dynamics in suspended and substrate-supported single-layer WS$_2$. The trapping of excitons at the picosecond timescale by surface trap states suggested the importance of controlling the surface properties of 2D semiconductors along with their dimensions. Therefore, it is expected that substrate and surface defects play an important role in exciton dynamics and transport. Yuan et al. (121) determined the exciton diffusion constant of mechanically exfoliated single-layer WS$_2$ to be $2.0 \pm 0.4$ cm$^2$ s$^{-1}$. Exciton motion in the chemical vapor deposition grown in single-layer WS$_2$ was more than one order of magnitude slower, with a diffusion constant of $0.1 \pm 0.04$ cm$^2$ s$^{-1}$, consistent with higher defect concentration (121).

TAM has also been applied to image singlet and triplet Frenkel excitons in organic materials. Wan et al. (65) and Zhu et al. (120) showcased the unique capability of TAM to image both bright singlet and dark triplet exciton transport by tracking their population using excited-state absorption in singlet fission occurring in single acene crystals (Figure 8). Singlet fission is a light downconversion process in certain organic semiconductors that splits a singlet (spin 0) exciton into two triplet (spin 1) excitons, each with roughly half of the singlet energy, which generates one extra electron–hole pair per photon absorbed, promising to increase solar cell efficiency beyond the Shockley–Queisser limit (124). However, the small diffusion constant of the triplet excitons could hinder long-range transport and the thickness limited by triplet diffusion length might not be sufficient for light absorption. Using TAM, Wan et al. (65) and Zhu et al. (120) uncovered a new exciton transport mechanism; specifically, the interchange between bright (singlet) and dark (triplet) populations led to a cooperative transport mechanism in singlet fission materials. The migration of the slow-moving triplet excitons can be enhanced by that of the mobile singlet excitons, leading to triplet transport over hundreds of nanometers at a nanosecond timescale, which is much shorter than the previously expected microsecond timescale and beneficial for solar cell applications.

In molecular or nanostructured assemblies, the electronic interaction between the components dictates the exciton transport within the assemblies. At the weak interaction limit, excitons migrate incoherently via hopping between individual components using Förster resonant energy transfer (FRET). Yoon et al. (125) presented a direct measurement of exciton diffusion in highly ordered CdSe QD superlattices where the interactions between QDs were weak owing to large inter-dot distance. Exciton motion was diffusive, with an exciton diffusion coefficient of $(2.5 \pm 0.2) \times 10^{-2}$ cm$^2$ s$^{-1}$ for superlattices constructed from 3.6-nm CdSe QDs with a center-to-center distance of 6.7 nm. The measured exciton diffusion constant is in good agreement with FRET theory.

Exciton transport is less well understood in the intermediate coupling regime, where many molecular aggregates and photosynthetic antennas belong (12). In this regime, exciton transport cannot be described by incoherently hopping between individual chromophores via FRET. Excitons are delocalized over part of the system, and the exciton delocalization (coherent) length is defined by the competition between intermolecular coupling strength and disorder. Transport has mixed coherent and incoherent characteristics. For instance, Hildner et al. (19) used single complex ultrafast spectroscopy to demonstrate quantum coherent energy transfer within individual light-harvesting complexes of a purple bacterium, where strong intermolecular coupling resulted in delocalized excitons. They found that quantum coherences between electronically coupled energy eigenstates of different chromophores persist for at least 400 fs (19). With each delocalized segment the excitation energy propagates ballistically, compared with the diffusive hopping described by FRET, as schematically shown in Figure 9a. Wan et al. (64) have imaged the transport of delocalized excitons in porphyrin aggregates that mimic photosynthetic antennas (Figure 9). TAM measurements provided exciton diffusion constants of 3–6 cm$^2$ s$^{-1}$ for these aggregates, which were three to five times higher than a theoretical lower bound for pure incoherent
Figure 8

Triplet and singlet exciton propagation in a single tetracene crystal. (a) TAM images in the a-b plane pumped at 470 nm (300 fs pulse−1) with probe wavelength and polarization to select triplet excitons at different pump–probe delays. Color scale represents the intensity of ΔT of the probe beam. The images show the spatial distribution of the ΔT signal measured at pump–probe delay times as labeled. (b) Images of singlet excitons at different pump–probe delays. (c,d) Cross sections of the TAM images fitted with Gaussian functions from panels a and b, respectively, with the maximum ΔT signal normalized. Scale bars = 1 μm. Abbreviations: ΔT, differential transmission; TAM, transient absorption microscopy. Figure adapted from Reference 65 with permission from Macmillan Publishers Limited.

hopping. Simulation showed that the states crucial for exciton transport are delocalized over as few as 10 molecules, suggesting that coherent effects play a role despite relatively weak delocalization (64).

For disordered organic materials such as conjugated polymer thin films, exciton transport occurs over a much shorter range (on the order of 10 nm). Therefore, further enhancement in spatial resolution is desirable for exciton transport. Penwell et al. (52) measured a migration length of 16 nm in poly[2,5-di(hexyloxy)cyanoterephthalyldiene] conjugated polymer films by combining stimulated emission depletion microscopy with gated fluorescence detection (Figure 10).
Figure 9
TAM imaging of coherent exciton transport in tubular molecular aggregates. (a) Schematic illustration of coherent transport in molecular aggregates. Each section represents the coherent length. (b) AFM height image of the tubular porphyrin nanotubes deposited on a glass substrate. Scale bar = 500 nm. (c) TAM images of exciton propagation at different pump–probe delay times for the bundle of nanotubes. The color scale represents the intensity of the $\Delta T$ of the probe beam at 0 ps. For 3 and 15 ps, $\Delta T$ is plotted on scales relative to the one at 0 ps, with the multiplication factor as labeled. The images show the spatial distribution of the $\Delta T$ signal measured at pump–probe delay times as labeled. The pump intensity was 4.1 µJ cm$^{-2}$. Scale bar = 0.5 µm. (d) Cross sections of the TAM images along the long axis fitted with Gaussian functions at different delay times, with the maximum $\Delta T$ signal normalized to unity. (e) $\sigma^2_t - \sigma^2_0$ as a function of pump–probe delay time (symbols), with a linear fit to Equation 4 (red line), which yields a diffusion constant of 6.4 ± 0.2 cm$^2$ s$^{-1}$. Error bars of $\sigma^2_t - \sigma^2_0$ are the standard errors estimated from Gaussian fitting to the spatial intensity distributions. Abbreviations: $\Delta T$, differential transmission; AFM, atomic force microscopy; TAM, transient absorption microscopy; TTPS₄, tetrasodiummeso-tetra(sulfonatophenyl)porphine. Figure adapted with permission from Reference 64; copyright 2017 American Chemical Society.
Migration in these films was essentially diffusive because intrinsic chromophore energetic disorder is comparable to chromophore inhomogeneous broadening.

**CHARGE AND EXCITON TRANSPORT ACROSS INTERFACES**

Transport across heterointerfaces plays a key role in light-to-electricity conversion using organic and nanostructured materials (126). The detailed mechanism for charge separation at the donor–acceptor interface in organic solar cells remains unknown. After electron transfer from the electron donor materials to the electron acceptor materials, spatially separated charge transfer (CT) excitons are formed across the interface (13, 126, 127). Owing to the low dielectric constant of organic materials, the CT excitons still possess large exciton binding energy (on the order of 100 meV) (126). How the electrons and holes escape the large interfacial Coulomb potential is under intense debate. CT exciton diffusion has been proposed as a mechanism for the electrons and holes to achieve charge separation (127). As discussed below, TAM has the unique ability to visualize how charges and excitons transport across interfaces, which has been poorly understood owing to the lack of direct characterization tools.

Zhu et al. (128) used heterostructures that integrated exfoliated WS$_2$ layers with tetracene thin films as a model system with 2D crystalline organic–inorganic interfaces (Figure 11a). They determined electron and hole transfer across the atomically sharp nano-interface to be rapid, with time constants of $\sim 2$ and $\sim 3$ ps, respectively. TAM measurements of exciton transport at these 2D interfaces, as shown in Figure 11, revealed the coexistence of delocalized and localized CT excitons, with diffusion constants of $\sim 1$ and $\sim 0.04$ cm$^2$ s$^{-1}$, respectively. These highly mobile CT excitons were proposed as key factor in driving efficient charge separation for photovoltaic applications at heterointerfaces.

TAM has also imaged charge transport at inorganic semiconducting interfaces. Gabriel et al. (129) used pump-probe microscopy to directly image the dynamics of photogenerated charge carriers in silicon nanowires encoded with p–n junctions along the growth axis. Their
Figure 11

(a) Schematic of the formation of CT excitons and the band alignment of the 1L-WS2/Tc heterostructure, showing the formation of a type II heterojunction. (b) TAM image of the 1L-WS2/Tc heterostructure taken with spatially overlapped pump and probe beams at 0 ps. Scale bar = 2 µm. (c) Exciton population profiles fitted with a sum of two Gaussian functions at different delay times, with the maximum ∆T signal normalized to unity for the 1L-WS2/Tc heterostructure along the line indicated in panel b. (d) Transport of two populations in the 1L-WS2/Tc heterostructure; σ1,0 and σ2,0 are extracted from panel c and plotted as a function of pump–probe delay time, with a linear fit to obtain diffusion constants. Abbreviations: ∆T, differential transmission; 1L, single layer; norm, normalized; TAM, transient absorption microscopy; Tc, tetracene. Figure adapted from Reference 128 with permission from AAAS.

results visualized charge separation as the carrier distribution reached the edges of the depletion region, leading to a persistent electron population in the n-type region (129). Man et al. (36) combined pump–probe microscopy with spectroscopic photoemission electron microscopy to image the motion of photoexcited electrons from high-energy to low-energy states in a type-II 2D InSe/GaAs heterostructure. Energy-resolved photoelectron images revealed an initial highly nonequilibrium distribution of photocarriers in space and energy, consequent formation of internal electric fields, bending of the semiconductor bands, and finally charge separation.

FUTURE DIRECTIONS AND OUTLOOK

As surveyed in this review, all-optical ultrafast dynamic microscopy provides new opportunities in imaging exciton and charge transport, elucidating previously obscured mechanisms in solar energy
harvesting systems. The potential of ultrafast dynamic microscopy in materials research is vast and is not limited to the topics discussed in this review. We conclude with a few future directions that could lead to broader applications of ultrafast dynamic microscopy.

Further improvement of spatial resolution is highly desirable, and there have been active developments on this front. The use of superresolution techniques such as stimulation depletion and structural illumination can improve spatial resolution by tens of nanometers (35, 51–53). Another development is nanofocusing strategies. Kravtsov et al. (130) used a three-dimensional conical gold tip to focus light to image the few-femtosecond coherent dynamics of plasmonic hotspots on a nanostructured gold surface with a spatial resolution of a few tens of nanometers. The challenge to implementing these subdiffraction-limited techniques is maintaining a high S/N so that they can be applied to a variety of systems.

Another area for improvement is developing imaging contrasts with high structural sensitivity such as Raman scattering and infrared absorption for the excited states. With the application of sophisticated pulse-shaping techniques, wide-field Fourier transform infrared (IR) microscopy and vibronic optical microscopy with temporal resolutions as good as 10 fs have been recently demonstrated (45, 131). Transport imaging could be achieved by spatially separating the pump and the IR or the Raman probe similar to the TAM measurements described in this review.

In many solar energy harvesting systems, the excited-state absorption spectra are highly congested, making it challenging to investigate the role of electronic couplings in energy transport. A solution is to combine optical microscopy with multidimensional spectroscopy that is capable of mapping electronic interactions between different excited states (12). Aeschlimann et al. (60) have demonstrated proof-of-concept coherent 2D nanoscopy. Four-wave mixing spectroscopy was coupled to photoemission electron microscopy to achieve a spatial resolution of 50 nm and local nanospectra from a corrugated silver surface were recorded (60). In an all-optical approach, a pulse-shaped and phase-locked pulse pair with PL detection has been used to detect coherent energy transfer pathways in a single photosynthetic antenna complex (19). The phase-locked pulse pair could be spatially separated from a probe pulse to directly measure the spatial extent of the coherent transport.

**SUMMARY POINTS**

1. High S/N is necessary to successfully implement TA pump–probe microscopy because signal generated from a single molecule, a single nanoparticle, or the sample volume interrogated in the tightly focused beams is much smaller than that from conventional TA.

2. For solar energy harvesting systems, TA as an imaging contrast offers a distinct advantage because emissive singlet excitons, nonemissive triplet excitons, and separated charges can be monitored.

3. By spatially separating the pump and probe beams, TAM provides a new way to image charge carrier and exciton transport with femtosecond temporal resolution and tens of nanometers spatial resolution and can directly address grain boundaries and interfaces.

4. With femtosecond temporal resolution, TAM can image different regimes of transport, such as nonequilibrium hot carrier transport and coherent exciton transport.
FUTURE ISSUES

1. The combination of ultrafast spectroscopy with superresolution and nano-focusing techniques is promising for achieving spatial resolution better than 10 nm.
2. Incorporating vibrational structural probes such as Raman scattering and infrared absorption will be crucial for elucidating the role of vibration in electronic energy transport.
3. Coherent ultrafast microscopy by coupling optical microscopy to multidimensional spectroscopy has the potential to directly map out energy transport pathways that involve multiple excited states.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

The authors acknowledge support from the US National Science Foundation (NSF) through grant NSF-CHE-1555005 for work on molecular excitons and through grant NSF-DMR-1507803 for work on hybrid perovskites, as well as support from the US Department of Energy through grant DE-SC0016356 for work on 2D materials.

LITERATURE CITED


