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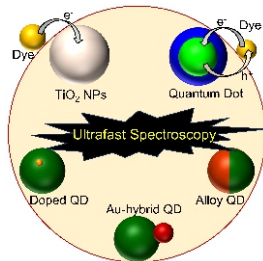
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सौर सेल पदार्थों पर अल्ट्राफास्ट स्पेक्ट्रमिकी यात्रा की कहानी

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उन्नत सामग्रियों में
अल्ट्राफास्ट सस्पेक्ट्रमिकी

सारांश

अर्धचालक नैनोपार्टिकल्स एवं क्वांटम डॉट्स (क्यूडी) पर हमारी परादूत स्पेक्ट्रमिकी यात्रा का रोडमैप 1998-2017 की अवधि में तैयार हुआ। इस दौरान, हमने TiO_2 नैनोकणों में इंटरफेसियल इलेक्ट्रॉन स्थानांतरण प्रक्रियाओं और डाई सेंसिटाइज्ड सोलर सेल अनुप्रयोगों के लिए विशेष रूप से डिजाइन किए गए डाई अणुओं के बारे में महत्वपूर्ण जानकारी प्रदान की। कई विशेष रूप से डिजाइन किए गए QD/अणु संयोजन में अल्ट्राफास्ट हॉट और थर्मलाइज्ड इलेक्ट्रॉन और होल ट्रांसफर डायनेमिक्स का मूल्यांकन किया गया है।Mn- और Cu-डोपिंग, Auहाइब्रिड और मिश्रधातु क्यूडी सहित कई उन्नत कार्यात्मक क्यूडी की परादूत वाहक विश्रांति गतिकी पर हमारी मौलिक समझ का वर्णन किया गया है जो सौर सेल दक्षता के साथ एक सीधा संबंध दर्शाता है।

मुख्य शब्दः परादूत स्पेक्ट्रमदर्शिकी, क्वांटम डॉट्स, नैनोपार्टिकल्स, इलेक्ट्रॉन एवं छिद्र स्थानांतरण, सौर सेल
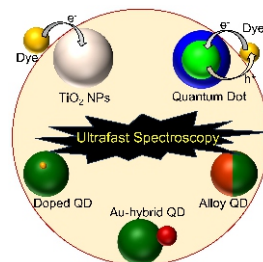
Spectroscopy in Advanced Materials

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A Tale of Ultrafast Spectroscopic Journey on Solar Cell Materials

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*Ultrafast Spectroscopy in
Advanced Materials*

ABSTRACT

The roadmap of our ultrafast spectroscopic journey on semiconductor nanoparticles and quantum dots (QDs) is described over the period of 1998–2017. Over this time, we provided significant insights into the interfacial electron transfer processes in TiO_2 nanoparticles and tailor designed dye molecules for dye sensitized solar cell applications. Ultrafast hot and thermalized electron and hole transfer dynamics in several tailor designed QD/molecule composite is summarized. Our fundamental understanding on the ultrafast carrier relaxation dynamics of several advanced functional QDs including Mn- and Cu-doping, Au-hybrids and alloy QDs is described which provides a direct correlation with the solar cell efficiency.

KEYWORDS: *Ultrafast spectroscopy, Quantum dots, Nanoparticles, Electron and hole transfer, Solar cell*

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Introduction

Semiconductor nanomaterials, including quantum dots (QDs) are of immense interest in the field of solar cells, light emitting diodes, photocatalysis etc. due to their easy solution processability and bandgap tunability [1]. To successfully utilize such tiny materials in certain devices, it is extremely important to understand the fundamentals of the exciton (bound electron-hole pair) relaxation-recombination dynamics within these materials which often falls in fast to ultrafast timescale [2]. In this regard, during our journey in BARC from 1998–2017, we have extensively investigated the ultrafast charge transfer dynamics in several oxide semiconductor and metal nanoparticles, and chalcogenide QDs, after sensitizing with a series of molecules. We also fabricated several chalcogenides QD-based heterostructures and investigated their ultrafast photophysical dynamics and showed that they have a direct correlation with the solar cell efficiency. In this article, we aim to summarize some of the key findings of our journey in BARC from 1998–2017 which includes 13 PhD thesis and 121 peer-review research publications (Fig.1).

One of our early works on the interfacial electron transfer dynamics was reported in surface modified TiO$_2$ nanoparticles sensitized by the molecule Alizarin (Fig.2a, b) [3]. Ultrafast electron injection from the Alizarin molecule to TiO$_2$ has been confirmed by direct detection of the electron in the conduction band of TiO$_2$, as well as the corresponding Alizarin cation, along with the bleaching of the dye molecule. The back electron transfer (BET) dynamics is found to be slower on the surface modified TiO$_2$ than the unmodified one, which has been explained on the basis of electron transfer in the Marcus inverted region. Similar interfacial electron transfer and BET dynamics has been demonstrated extensively involving TiO$_2$ and ZrO$_2$ nanoparticles and several molecules [4]. We provided detailed insight into the electron injection dynamics of intramolecular charge transfer and twisted intramolecular charge transfer (TICT) states of coumarin molecules to TiO$_2$ NPs
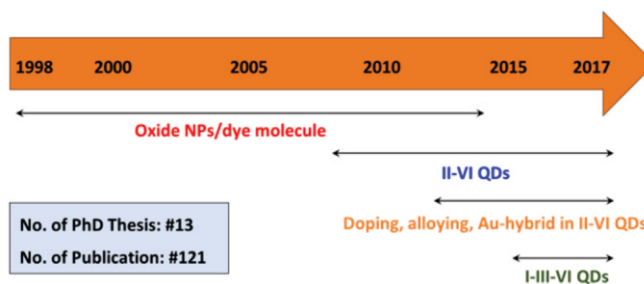

Fig.1: Timeline showing our progress in different fields over the two decades in BARC.

(Fig.2c, d) [5-6]. Our result provides information on the extremely slow BET process in the TiO$_2$/coumarin system involving TICT states, being TICT is a charge separated state, and could serve as a very good system for the dye sensitised solar cells (DSSC).

We demonstrated the kinetic model of the exciton decay of porphyrin J and H-aggregates which are suitable for light harvesting antenna due to their wide range of coverage of the solar energy spectrum [7-8]. Further, we showed that these aggregates form complexes with TiO$_2$ NPs and improve the photoinduced charge separation (Fig.2e, f). We attributed higher yield of the charge separation is due to exciton-coupled charge transfer dynamics in porphyrin aggregates and their complexes with TiO$_2$ NPs. We further demonstrated the ultrafast interfacial charge transfer and BET dynamics to TiO$_2$ and ZrO$_2$ nanoparticles involving several tailor made catechol and resorcinol Ru- and Os-porphyrin based dye and BODIPY molecules [9-11]. Our result suggests that although strong catechol coupling may be favourable for interfacial electron injection to TiO$_2$ NPs in <100 fs timescale, the stronger coupling reduces the spatial separation between TiO$_2$ and the dye, causing faster BET reactions compared to the corresponding resorcinol derivatives, where slower BET is
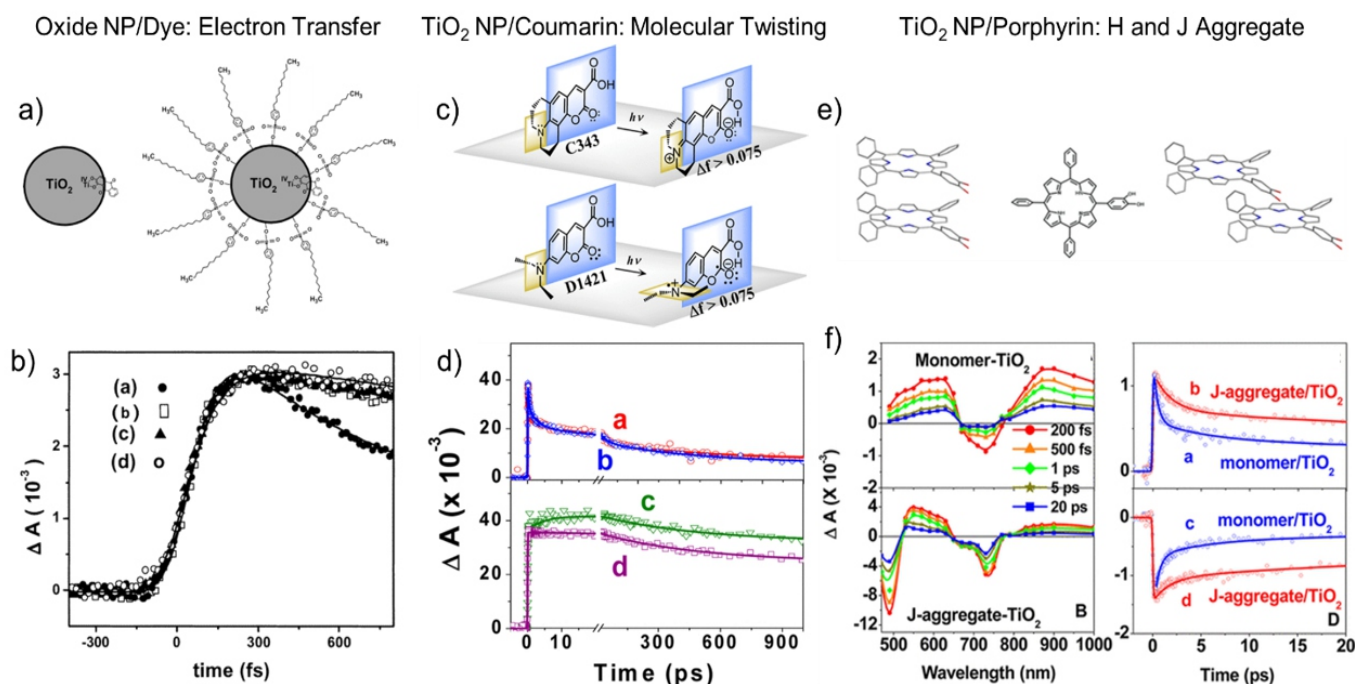

Fig.2: a, b) Schematic of TiO$_2$ NPs without and with alizarin molecule, and corresponding ultrafast transients (in different solvent for the nanocomposite in b-d) respectively [3]. c, d) Molecular structure of two coumarin (C343 and D1421) and corresponding transients in upper and lower panel respectively. Reproduced from J. Phys. Chem. C 2014, 118 (20), 10661-10669. e) Molecular structure of the porphyrin monomer and H and J aggregates, and f) transient absorption spectra of the monomer and J aggregates in the presence of TiO$_2$, and corresponding transients, respectively [7].

observed. We proposed that such slowing down of the BET processes may lead to significant boosting of the solar cell performance in the DSSC devices made with resorcinol derivatives. We also demonstrated electron transfer and proton-coupled electron transfer reactions in Ru-polypyridyl complexes where water plays an important role [12].

Following demonstration of the ultrafast interfacial processes in a variety of oxide semiconductor NPs and dye molecules for their proper utilization in DSSCs, we turned our attention to work on the emerging chalcogenide quantum dots (QDs) in 2009. We prepared several thiol capped water soluble MX QDs where M = Cd, Zn and X = S, Se, Te, and their core/shell heterostructures, and investigated their ultrafast charge carrier dynamics [13]. The cooling and population dynamics of mercaptopropionic acid capped CdTe QDs in different quantized states of the charge carriers were monitored by following the growth kinetics of the bleach at different excitonic positions upon above bandgap excitation with a 400 nm femtosecond pump pulse. The carrier cooling time to the second and first excitonic state was measured to be 150 fs and 500 fs respectively, which increases with increasing the size of the CdTe QDs, and has a strong dependence on the defect states [13]. Electron and hole cooling time of the first excitonic state of CdTe QDs was determined using electron and hole quencher and measured to 700 fs and 150 fs respectively. Electron and hole trapping dynamics were also measured to in the range of 1 ps. We further compared the ultrafast charge transfer dynamics of the CdTe QDs with type-II CdTe/CdS core/shell QDs [14]. In the type-II CdTe/CdS core/shell, the electron is transferred to the CdS shell while the hole is localized in the CdTe core due to their band alignment. Using a femtosecond transient absorption study, we corroborated the above ultrafast processes in the core/shell QDs using individual electron and hole quencher molecules. Importantly,

we observed slow carrier relaxation to the band edge states and increased carrier lifetime due to charge separation which may have profound usage of these materials in photovoltaics. We further extend our idea on increased charge separation of CdTe QDs upon decoration with graphene where extremely longer charge recombination time (>1 ns) was observed, as compared to ~50 ps in CdTe QDs (Fig.3a, b). The observation reflects efficient charge separation on the graphene surface and can serve as an efficient quantum dot solar cell (QDSC) material [15].

We then extend our idea on charge separation in several tailor made QDs and QD core/shell systems by sensitizing them with a large number of organic and inorganic molecules, which often form strong charge transfer (CT) complexes. For example, one of our early works in this direction was reported in CdS QDs/ 4´, 5´-dibromofluorescein (DBF) nanocomposite, followed by strong ground state CT complex formation [16]. The strong CT complex formation in <100 fs timescale results in efficient interfacial hole and electron transfer processes from one component to another in the nanocomposite (Fig.3c, d). Here, the nanocomposite forms a type-II like structure, in which the photoexcited CdS QDs can transfer the hole to the DBF molecule in 800 fs, while the photoexcited DBF can transfer electrons to the CdS domain in 100 fs timescale which we have revealed by ultrafast experiments. Strong CT complex formation is also observed in CdSe QDs and CdSe based type-I and type-II core-shell NCs and aurin tricarboxylic acid (ATC) nanocomposite where the effect of shell materials on the CT process has been described [17]. While the electron injection dynamics was observed in <150 fs in all three cases, the hole transfer process has been found to be facilitated in CdSe/CdTe type-II structure (~3 ps) and it is retarded in CdSe/ZnS type-I structure (~6 ps) due to their electronic band alignment. We further provided important information about the hot carrier
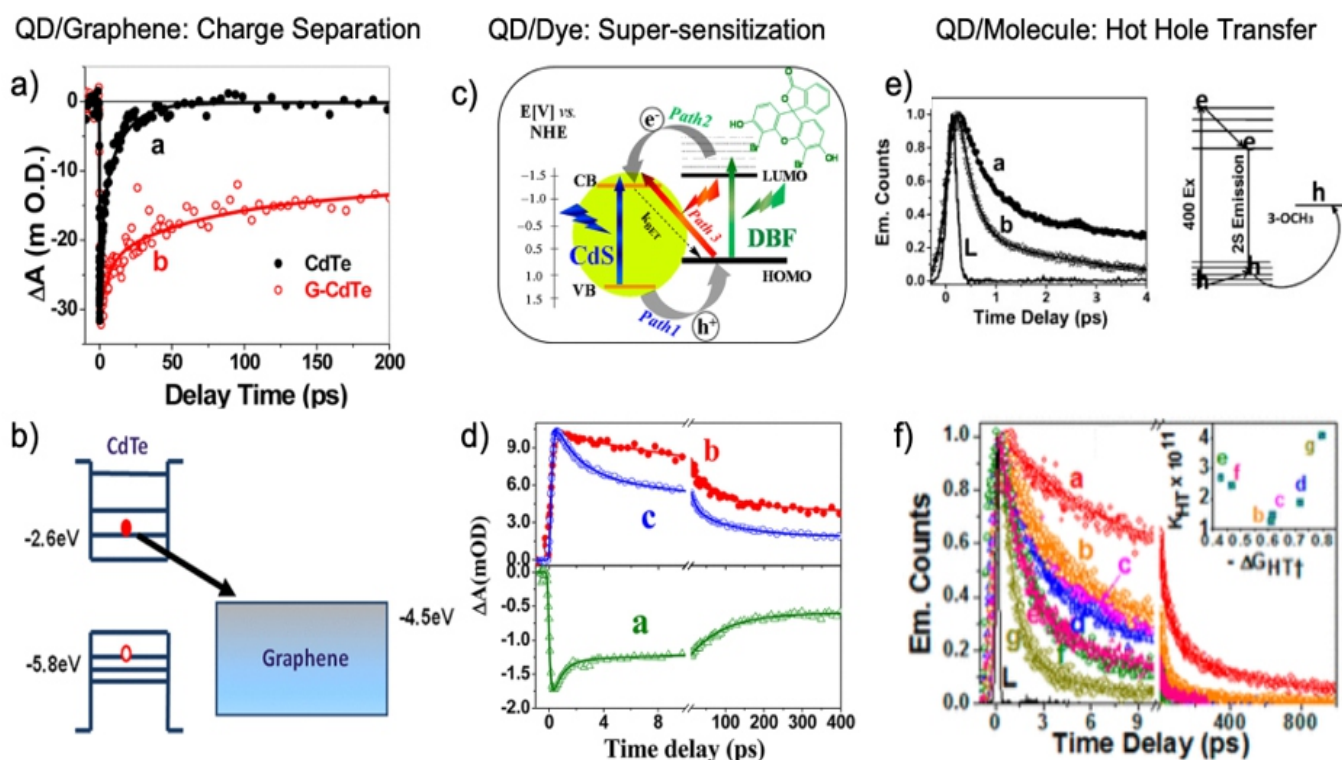

Fig.3: a, b) Ultrafast transients of CdTe QDs without and with graphene, and corresponding schematic of electron transfer [15]. c, d) Schematic of electron, hole transfer in the CdS QDs/DBF molecule super-sensitized system, and a few transients of the system, respectively [16]. e) Hot hole transfer dynamics of CdSe QDs in the presence of 3-methoxycatechol [18]. f) Hole transfer dynamics of CdSe QDs in the presence of different catechol derivatives [18].
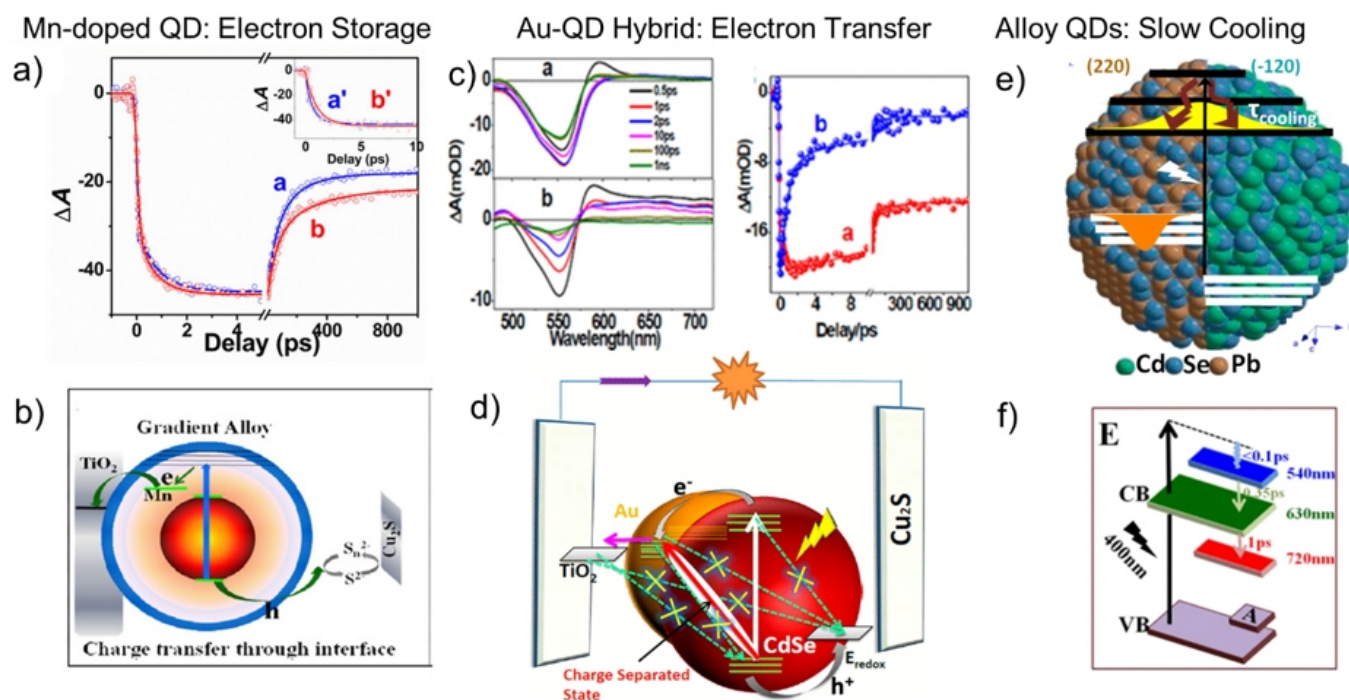
Mn-doped QD: Electron Storage

Au-QD Hybrid: Electron Transfer

Alloy QDs: Slow Cooling

Fig.4: a, b) Ultrafast transients of undoped and Mn-doped alloy QDs, and corresponding schematic of Mn-mediated electron transfer process, respectively [20]. c, d) Transient absorption spectra and kinetics of CdSe and Au-CdSe hybrids, and corresponding electron transfer to Au domain schematic, respectively [22]. e) Slow electron cooling process in the CdSe/PbSe Janus structure [24]. f) Slow carrier cooling process via intra bandgap donor-acceptor states in CuInS$_2$ QDs [25].

(hole) extraction from QDs to different molecular adsorbates using combination of femtosecond transient absorption and upconversion spectroscopy (Fig.3e, f) [18]. The hot hole dynamics was probed by monitoring higher exciton states which takes place in only 250 fs timescale, in comparison to the thermalized hole transfer timescale of 2-10 ps. Our results suggest electron donating moiety in these molecular adsorbates helps in boosting the hot hole extraction. Overall, the nanocomposites were claimed to be a super-sensitizer which can boost the QDSC efficiency drastically by simultaneous extraction of electrons and holes.

We then switched our research direction on ultrafast processes in Mn- and Cu-doped QDs, Au-hybrid QDs, and different alloy QDs and nanocrystals (Ncs), all of which show a direct relevance to the QDSC performance. In particular, Mn-doped CdSe QDs and related NCs were investigated, which show introduction of structural defects in the doped QDs than the undoped QDs, leading to ultrafast recombination [19]. However, upon functionalization with bromo-pyrogallol red (Br-PGR) molecule, which forms a strong CT complex, the Mn-state can act as an electron storage centre within the QDs. We propose such electron storage capacity of the Mn-dopant may boost the QDSC performance tremendously. In fact, by developing Mn doping in tailor designed alloyed QDs that supports a CT state within the material, we show such electron storage capacity can boost the solar cell efficiency from ~3.3 % to 4.5 % from undoped to Mn-doped QDs (Fig.4a, b) [20]. Along with Mn-doping in QDs, we also investigated ultrafast carrier dynamics in Au-hybrid CdSe Qds [21]. Our results show that both hot and thermalized electron transfer to Au domain takes place from the CdSe QDs in a timescale of 150 fs and 300 fs respectively which has a Au NP size dependence. We further show that the ultrafast electron transfer to Au-domain and subsequent slow charge recombination process has a direct consequence on enhancing the photocatalytic dye-degradation of rhodamine B, as well as enhancing the solar cell

efficiency from 3.4 % to 4.4 % (Fig.4c, d) [22].

We also developed different alloy QDs, which includes CdS$_x$Se$_{1-x}$, CdPb$_x$Se$_{1-x}$, Cd$_x$Zn$_{1-x}$S$_y$Se$_{1-y}$, CuInS$_2$, AgInS$_2$, etc., and studied the ultrafast exciton and carrier dynamics for improved QDSC efficiency. As compared to sub-ps carrier cooling in CdSe and CdS QDs, extremely slow electron cooling of ~8 ps is observed in the CdS$_{0.7}$Se$_{0.3}$ QDs, which is one of the slowest reported carrier cooling in QDs, due to efficient electron-hole decoupling [23]. We also explored the electronic cross-talk dynamics in CdSe/PbSe Janus NCs where too we observed slow electron cooling of 5 ps due to hole localization in the PbSe domain (Fig.4e) [24]. Importantly, sub-picosecond exciton and biexciton dynamics has been demonstrated in CuInS$_2$ and AgInS$_2$ QDs, where the sub-bandgap antisite states play a significant role (Fig.4f) [25]. All these slow electron cooling dynamics have a direct relevance to the final outcome of the QDSC efficiency which also we have demonstrated in some of the above systems.

In summary, in the above-mentioned time frame, we have contributed ultrafast interfacial charge transfer dynamics as well as sub-picosecond exciton and carrier dynamics in a wide range of materials, including oxide semiconductor nanoparticles, II-VI and I-III-VI chalcogenide QDs and corresponding doped, alloyed and core/shell QDs. Our understanding provides important fundamental insight into the ultrafast processes that may lead to design of higher efficient DSSCs and QDSCs. Overall, we believe we have contributed significantly to the development of several solar cell materials for photovoltaic applications via providing important insights into the ultrafast photophysical processes.

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