Chapter 10
Engineering FRET-Based Solar Cells: 
Manipulation of Energy and Electron 
Transfer Processes in a Light Harvesting 
Assembly

Soumik Sarkar, Samim Sardar, Abhinandan Makhal, Joydeep Dutta, 
and Samir Kumar Pal

Abstract From the prevalent interest in the advancement of renewable energy 
sources, dye-sensitized solar cells (DSSCs) have emerged as one of the front 
running prospects due mainly to a constructive balance between cost and efficiency. 
In this chapter, we will review our works on the utility of using Förster resonance 
energy transfer (FRET) in the light harvesting dynamics of zinc oxide (ZnO)-based 
nanomaterials, which has recently shown promise for significant improvement in 
various aspects of photoelectrochemical cells. Firstly, we have used ZnO 
nanoparticles (NPs) and Oxazine 1 as model donor and acceptor, respectively, to 
investigate the key ultrafast process of FRET in the NP–dye system. The conse-
quency of the energy transfer on the performance of a model ZnO NP-based DSSC 
has also been explored by using well-known Ruthenium-based sensitzers N719 
atached to ZnO NPs offering as an intrinsic co-sensitizer. By using a picosecond-
resolved FRET technique, we have also demonstrated the role of the gold layer in 
reducing the photogenerated charge transfer from ZnO–Au nanocomposite to a model 
contaminant methylene blue (MB). Due to the formation of the Schottky barrier at 
the ZnO–Au interface and the higher optical absorptions of the ZnO–Au 
photocathodes arising from the surface plasmon absorption of the Au NPs, 
enhanced power-conversion efficiency was achieved compared to bare 
ZnO-based DSSCs. Finally, potential co-sensitization of extrinsic sensitizer CdTe 
quantum dots (QDs) in ZnO nanorod (NR)-based DSSCs has been established 
where we have shown two major pathways by which CdTe QDs may contribute 
to the net photocurrent in a DSSC: (1) a direct injection of charge carriers from QDs 

S. Sarkar · S. Sardar · A. Makhal · S.K. Pal (✉)
Department of Chemical, Biological and Macromolecular Sciences, S.N. Bose National Centre 
for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700 098, India
E-mail: skpal@bose.res.in

J. Dutta
Water Research Center, Sultan Qaboos University, PO Box 17, 123 Al-Khoudh, 
Sultanate of Oman

X. Wang and Z.M. Wang (eds.), High-Efficiency Solar Cells: Physics, Materials, 
and Devices, Springer Series in Materials Science 190, DOI 10.1007/978-3-319-01988-8_10, 
© Springer International Publishing Switzerland 2014
to ZnO semiconductor via photoinduced electron transfer (PET) and (2) an indirect excitation of the sensitizing dye N719 molecules by funneling harvested light via FRET. Based on these advantages, the short-circuit current density and the photocurrentivity of the QD-assembled DSSCs with distinct architectures are found to be much higher than DSSCs fabricated with N719 sensitizer only. As demonstrated, the multipath enhancement offered in this device architecture results in an increased and extended photo-response with respect to the individual materials employed. Further engineering of suitable donor acceptor pairs and optimization of charge separation in conjugated molecular blends has the potential to become a continuing avenue toward enhancing hybrid DSSC efficiencies.

1 Introduction

The promising dye-sensitized solar cell (DSSC) is a relatively new class of low-cost solar cells suitable for renewable electricity generation [1, 2]. It is based on the process of conversion of solar energy to electrical energy by employing sensitizers adsorbed on the surface of wide band gap n-type semiconductor metal oxide nanoparticles (NPs), typically TiO₂ [3], ZnO [4], SnO₂ [5], Nb₂O₅ [6], etc. During the operation, photons intercepted by sensitizers create electron–hole pairs that are rapidly separated at the NP surface; followed by electrons injected into the semiconductor NPs and holes leaving to the opposite side of the device by means of redox species (usually I⁻/I₃⁻) in an electrolyte in liquid [7] or solid state [8]. State-of-the-art TiO₂-based DSSCs using Ruthenium sensitizers, which primarily absorbs light in the region of 350–700 nm, offer power-conversion efficiency of only 11% [9] and it has been recognized that the key improvement of the efficiency of DSSCs is to increase their spectral absorption range. In a recent study, it has been estimated that a DSSC with power-conversion efficiency of 15% using I⁻/I₃⁻ redox couple must absorb ~80% of the solar spectrum from 350 to 900 nm [10]. Light absorption in DSSCs is determined by the molar extinction coefficient of the sensitizers, the surface coverage of the dye (dye molecules nm⁻²), and the total surface area of the oxide film [11]. The sensitizers have traditionally been made from ruthenium-based complexes (for example, N719, Z907) [9, 12] that have fairly broad absorption spectra (Δλ ≈ 350 nm) but low molar extinction coefficients (5,000–20,000 M⁻¹ cm⁻¹). Organic dyes have recently been developed with substantially higher molar extinction coefficients (50,000–200,000 M⁻¹ cm⁻¹), but they have very narrow spectral bandwidths (Δλ ≈ 250 nm) [13]. Dye cocktails lead to a broader absorption spectra [14], but because of the absence of dyes that absorb efficiently in the red part of the spectrum, generally a lower efficiency is achieved. As dyes with strong absorptivity do not typically exhibit broad absorption overlapping the solar spectra, this is one of the major pitfalls of using dyes as photosensitizers in solar cells [15]. In an attempt to achieve enhanced light absorption and to broaden the spectral response, co-sensitization of the semiconductor NPs (titania) by dyes with complementary absorption spectra, has recently been
demonstrated [16]. However, the limitations of available sites at the surface of semiconductor NPs for the co-sensitizing dyes constrain the total light absorbed in the solar cells.

To improve the possibility of enhanced light absorption, the use of Förster resonance energy transfer (FRET), also known as electronic energy transfer, has recently experienced widespread research interest of several groups [17–22] including ours [23–27]. The mechanism of FRET involves a donor in an excited electronic state, which may transfer its excitation energy to a nearby acceptor in a non-radiative fashion through a long-range dipole–dipole interaction [28]. The theory is based on the concept of treating an excited donor as an oscillating dipole that can undergo energy exchange with a second dipole having similar resonance frequency. In principle, if the fluorescence emission spectrum of the donor molecule overlaps the absorption spectrum of an acceptor molecule, and the two are within a minimal distance (1–10 nm) from one another, the donor can directly transfer its excitation energy to the acceptor via exchange of a virtual photon. It is evident from the recent literatures that FRET serves as a popular signal transduction mechanism to develop bio-sensing systems and bioassays for proteins, peptides, nucleic acids, and small molecules [29–33]. FRET-based quantum dot (QD) pH sensors have been made [34], and electrical control of FRET in QDs has been demonstrated [35]. FRET in organic molecules has been used to study conformational changes in DNA [36] and to detect DNA with high sensitivity [37]. It has also been used in solar concentrators [38] and to improve quantum yields in organic light-emitting devices [39, 40]. Most importantly, FRET shows promise toward efficient solar energy conversion by using inexpensive and engineered fabrication processes in both QD-sensitized solar cells (QDSSCs) and DSSCs. In QDSSCs, the use of QDs as light harvesters has stimulated a lot of interests because of its higher extinction coefficient compared to conventional dyes [41] for efficient light energy conversion [42–45]. Because of the size quantization property, the optical and electronic properties of the semiconductor QDs can be engineered to further tune the response of QDSSCs [46–48]. In addition, QDs open up new possibilities for the utilization of hot electrons [49] or multiple charge carrier generation with a single photon [50]. Multiple-carrier generation in PbSe nanocrystals has shown that two or more excitons can be generated with a single photon of energy greater than the band gap [51]. The performance of a QDSSC is currently limited by several factors, including a limited choice of electrolytes with which QDs are chemically compatible, insufficient passivation of recombination channels (usually attributed to surface traps), and limited QD-loading capacities [52]. Recent studies have shown that it is possible to stabilize CdS QD-based DSSCs by coating the QD-sensitized nanoporous electrodes with a thin amorphous TiO$_2$ layer, which enables the use of various QD sensitizers in the presence of iodine-based electrolytes [53]. Utilizing two sensitizing layers of sensitizers N719 and CdS QDs separated by an amorphous titanium dioxide (TiO$_2$) layer, a significant increase in cell efficiency compared to a QD monolayer cell has been reported [54]. In a more recent study, Etgar et al. have used a cobalt complex (Co$^{2+}$/Co$^{3+}$) as an electrolyte in the solar cells, which permits
direct contact between the QDs and the electrolyte [17]. Choi et al. have recently
demonstrated the coupling of semiconductor nanocrystal and a red-NIR organic dye
with complementary spectral absorption in the visible region [55]. Alternatively,
the employment of FRET from covalently linked energy donor molecules to the
semiconductor (titania) surface-attached sensizers has been demonstrated in the
literature [56], where higher excitation transfer efficiency (>89 %) between
attached dye molecules followed by a subsequent improvement in the device
external quantum efficiency of 5–10 % between 400 and 500 nm spectral range
has been reported. The overall enhancement of power conversion efficiency of
the DSSC was still low (<9 %), which was argued to arise because of an increase
in the open-circuit voltage ($V_{oc}$) rather than because of an increase in the
short-circuit photocurrent density ($J_{sc}$). Recently, it has been demonstrated that
unattached, highly-luminescent chromophores inside a liquid electrolyte can absorb
high-energy photons and can efficiently transfer the energy to the anchored near-
infrared sensitizer leading to an increase in optical absorption efficiency [15].
In another work, enhancement in photovoltaic device performance has been
reported using long-range resonant energy transfer from a dissolved luminescent
dopant confined in the interwire spaces of a nanowire array electrode to an acceptor
species confined at the surface of the nanowires [20].

Although most of the reported works on DSSCs are based on TiO$_2$ porous thin
films, various nanostructures of ZnO have also been used for DSSC fabrication [8,
57, 58]. The advantages of using ZnO over TiO$_2$ are its direct wide band gap
(3.37 eV), higher exciton binding energy (60 meV) compared to TiO$_2$ (4 meV) [59,
60], and higher electron mobility (200 cm$^2$ V$^{-1}$ s$^{-1}$) over TiO$_2$ (30 cm$^2$ V$^{-1}$ s$^{-1}$),
while the conduction band edges of both materials are located at approximately the
same level [61]. This unique combination of properties opens, in principle, wide
possibilities of using ZnO in DSSC fabrication. An irreversible electron injection
from organic molecules into the conduction band of ZnO semiconductor was first
experimentally evidenced by H. Tributsch and M. Calvin [62]. Nowadays, this
efficient electron transporting material shows promises in various technologies
similar to DSSCs, such as inverted polymer solar cells [63, 64], QDSSCs [65,
66], and hybrid light-emitting diodes [67]. Another advantage of using ZnO over
TiO$_2$ is different morphologies such as nanoparticles [68, 69], hierarchical
aggregates [70, 71], porous films [72], nanosheets [73], nanowires [8, 74], tetrapods
[75], hollow tubes [76] can be prepared with relative ease. A large range of
fabrication procedures is available for ZnO nanostructures, such as sol–gel pro-
cesses [77, 78], chemical bath deposition, including hydrothermal [74], electrode-
position [72], spray pyrolysis [71], polyl hydrolysis [79], chemical vapor
deposition [80], etc. However, the efficiency of DSSCs based on ZnO
nanostructures is still very low (7.5 %) [71]. One of the possibilities to enhance
the efficiency of ZnO-based DSSC is the enhancement of the light absorbing ability
of the DSSC. It has to be noted that ZnO can absorb high-energy photons
(>3.37 eV) and offers photoluminescence (PL) in the visible region (2.25 eV)
[27, 81]. Careful use of the defect mediated ZnO PL for the excitation of the surface
adsorbed sensitizer, in order to enhance the overall efficiency of the ZnO-based DSSC will be discussed. We also approached to fabricate the composite nanocluster-based DSSCs where Au NPs have been employed to facilitate efficient charge separation, thus serving as a Schottky-barrier for reducing the rate of electron-hole recombination. In another study, we have demonstrated that size tunable CdTe QDs capped with 3-mercaptopropionic acid (MPA), assembled in an N719-sensitized solar cell, can absorb visible-light in the gaps, where sensitizer N719 has lower absorption or does not absorb any light. In this design, QDs serve as a co-sensitizer that can directly transfer electrons to ZnO NRs. Moreover, the QDs, those are not in a direct attachment to the ZnO NR surface, funnel the absorbed energy to nearby dye molecules via FRET rather than contributing directly as sensitizer. By using steady-state and picosecond-resolved fluorescence spectroscopy, we have demonstrated that PL from QDs can be useful to excite the sensitizer molecules for an enhanced light absorption. The consequence of QD-mediated electron and energy-harvesting processes on the overall performance of a model QD-assembled DSSC will also be discussed in the following sections.

2 Materials and Methods

2.1 Preparation of ZnO Nanoparticles (NPs) and ZnO–Au Nanocomposites (NCs)

In order to synthesize colloidal solution of ZnO NPs, zinc acetate dihydrate, Zn(CH₃COO)₂·2H₂O (Merck) was used as starting material. ZnO NP colloidal solution in ethanol was synthesized by following our earlier reports [81–83]. Briefly, a 20 ml 4 mM zinc acetate solution was prepared in ethanol (Merck) followed by a dilution up to 50% by adding another 20 ml fresh ethanol to the solution. Then 20 ml of 4 mM NaOH solution in ethanol was added to it under constant stirring. The reaction beaker was then kept in a preheated water bath at 60 °C for 2 h to hydrolyze, after which a transparent ZnO NP colloid was obtained. Next, ZnO–Au NC colloid was prepared by in situ synthesis of Au NPs on the surface of the ZnO NPs. 5 ml of 1 mM chloroauroic acid, HAuCl₄·H₂O (Sigma) ethanolic solution was slowly added to as-synthesized ZnO NP colloid under constant stirring at 25 °C. The stirring was continued for 15 min. Then 7 ml of 5 mM sodium borohydride, NaBH₄ (Sigma), in ethanol solution was added drop-wise to the solution in order to reduce gold chloride to Au NPs. Immediately after adding NaBH₄, the solution became red from pale yellow indicating the formation of the Au NPs in the ZnO NP colloid. The weight ratio between ZnO and Au after the preparation process was found to be 1.3:1. The colloidal solutions of ZnO NPs and ZnO–Au NCs were used to perform all the spectroscopic studies.
2.2 Preparation of ZnO Nanorods (NRs)

The most widely used fabrication method to obtain vertically-aligned ZnO nanostructures is the hydrothermal method [84]. First, FTO substrates were cleaned ultrasonically with soap water, acetone, ethanol, and deionized (DI) water. 15 mM of zinc acetate dihydrate was dissolved in 10 mL of DI water, which was sprayed on top of the clean FTO substrates (from a distance of 25 cm) at a rate of 1 mL min⁻¹. The substrates were preheated to 420 °C on a hot-plate before spraying. After spraying 10 mL completely, the substrates were allowed to cool to room temperature followed by annealing in air at 300 °C for 5 h. The ZnO NPs seeded FTO substrates were then placed in a sealed chemical bath containing equimolar concentration of zinc nitrate hexahydrate and hexamethylenetetramine (20 mM) at 95 °C for 20 h. This leads to the growth of ZnO NRs of length ca. 3–4 μm, diameter 100–200 nm. The ZnO NRs coated substrates were then retracted from the chemical bath, were rinsed several times with DI water, and were annealed at 350 °C for 60 min to remove any organic impurities prior to further use.

2.3 Preparation of 3-MPA Capped CdTe QDs

Several synthetic routes to CdTe QDs have been reported [85–90]. In this study, 0.12 mol of CdCl₂ was dissolved in deionized (DI) water. To this solution 0.024 mol of tri-sodium citrate dihydrate, 0.03 mol of Na₂TeO₃, 0.011 mol of 3-MPA, and 0.086 mol of NaBH₄ were added successively and were stirred to make the stock solution for CdTe QD synthesis. This stock solution was refluxed for 7, 20, and 30 min in a commercial Panasonic microwave oven (low-power mode) to synthesize 440, 500, and 550 nm absorption peak QDs, respectively. The QDs with 610 nm absorption peak were synthesized by refluxing the stock solution in a commercial oven at 106 °C for 9 h. As-prepared QDs, without any further purification, were used in the fabrication of ZnO NR-based DSSCs.

2.4 Fabrication of ZnO-Based DSSCs

The ZnO NP-based photoelectrodes were prepared by in situ synthesis of ZnO NPs on commercial fluorinated tin oxide (FTO) glass substrates (Asahi, Japan) using a simple hydrothermal process [84]. CdTe QD-decorated photoelectrodes (PEs) were fabricated by dipping the ZnO NR coated FTO (as discussed in Sect. 2.2) into CdTe colloid at 60 °C for 3 h. The photoelectrodes were removed, were washed with ethanol, and were annealed at 165 °C for 1 h. This cycle was repeated three times to obtain a uniform layer of CdTe particles on the ZnO surface. For co-sensitizing the photoelectrodes with N719 dye, the as-prepared CdTe QD coated PEs were dipped
into a 0.5 mM dye N719 in ethanol solution for 24 h in dark at room temperature. After 24 h, the substrates were withdrawn from the dye solution and were rinsed with ethanol several times in order to remove the excess dye on the film surface. We define this geometry of the sample as ZnO-QD-N719. In another architecture, we have dipped the ZnO NR with N719 first, and then PEs were coated with CdTe QDs (ZnO-N719-QD architecture). The same procedures were followed to prepare the substrates for the time-resolved measurements, only by replacing FTO plates with quartz. The photoelectrodes sensitized with N719 only (control) were fabricated by dipping ZnO photoelectrodes directly into 0.5 mM dye solution for 24 h following a similar procedure as described above. The photoelectrodes were then dried in dark at room temperature in a controlled humidity chamber (40 % humidity) for 2 h. A thin layer of Pt catalyst deposited on the FTO substrates was used as a counter electrode to assemble the DSSC. The counter electrodes were prepared by dropping 10 μL of 5 mM chloroplatinic acid (H₂PtCl₆·H₂O) solution in isopropanol on FTO substrates followed by the thermal decomposition of the H₂PtCl₆·H₂O to Pt NPs at 385 °C for 30 min. A single layer of Surlyn 1702 (50 μm thickness) from Dupont was placed between the two electrodes, and the device was sealed. The liquid electrolyte composed of the 0.5 M LiI, 0.05 M I₂, and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile (ACN) was then filled in the cell using capillary force through small holes drilled on the counter electrode. Finally, the holes in the counter electrode were sealed to prevent the electrolyte from leaking. It is to be noted that, QDs are relatively less stable in iodine-based electrolyte [91], and in the technological applications of QD-decorated solar cells selection of other iodine-free electrolytes would be more appreciated. The characteristics of the solar cells reported here were recorded immediately after filling in the electrolyte in the sandwich structure in order to minimize losses due to corrosion of the CdTe QDs [48].

2.5 Characterization Methods

High-resolution transmission electron microscopy (HRTEM) experiments are performed by FEI (Technai S-twin) instrument operated at 200 kV. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6301F operated at 20 kV. Steady-state absorption and emission spectra were measured with a Shimadzu UV-2450 spectrophotometer and Jobin Yvon Fluoromax-3 fluorimeter, respectively. All the photoluminescence transients were taken using the picoseconds-resolved time-correlated single photon counting (TCSPC) technique. We used a commercially available picosecond diode laser-pumped (LifeSpec-ps) time-resolved fluorescence spectrophotometer from Edinburgh Instruments, UK. The picosecond excitation pulse from the picoquant diode laser was used at 375 nm with instrument response function (IRF) of 80 ps. A microchannel-plate-photomultiplier tube (MCP-PMT, Hamamatsu) was used to detect the photoluminescence from the sample after dispersion through a monochromator. For all transients the polarizer on the emission side was adjusted to be at 55° (magic angle) with respect to the polarization axis of...
the excitation beam. The observed fluorescence transients were fitted by using a
nonlinear least square fitting procedure to a function \( \hat{X}(t) = \int_0^\infty \hat{E}(t') R(t-t') dt' \)
comprising convolution of the IRF \((\hat{E}(t))\) with a sum of exponentials
\[
R(t) = \Lambda + \sum_{i=1}^N B_i e^{-t/\tau_i}
\]
with pre-exponential factors \((B_i)\), characteristic lifetimes \((\tau_i)\), and a background \((\Lambda)\). Relative concentration in a multi-exponential decay is
finally expressed as, \( c_i = \frac{B_i}{\sum B_i} \times 100 \). The average lifetime (amplitude-weighted) of a
multi-exponential decay [28] is expressed as \( \tau_{av} = \sum_{i=1}^N c_i \tau_i \).

In order to estimate FRET efficiency of the donor (ZnO) and hence to determine
distance of donor–acceptor pairs, we followed the methodology described in [46.2].
The Förster distance \((R_0)\) is given by,
\[
R_0 = 0.211 \times \left[ \kappa^2 n^{-3} Q_D J \right]^{\frac{1}{2}} \text{ (in Å)}
\]  
(10.1)

where, \( \kappa^2 \) is a factor describing the relative orientation in space of the transition
dipoles of the donor and acceptor. For donor and acceptors that randomize by
rotational diffusion prior to energy transfer, the magnitude of \( \kappa^2 \) is assumed to be
2/3. The refractive index \((n)\) of the medium is assumed to be 1.4. \( Q_D \), the integrated
quantum yield of the donor in the absence of acceptor are measured with respect to
a reference dye. For example, the \( Q_D \) value for the colloidal ZnO NPs was measured
to be \( 3.8 \times 10^{-3} \) by using Coumarin 500 as a reference. \( J \), the overlap integral,
which expresses the degree of spectral overlap between the donor emission and the
acceptor absorption, is given by,
\[
J = \frac{\int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda}
\]  
(10.2)

where, \( F_D(\lambda) \) is the fluorescence intensity of the donor in the wavelength range of \( \lambda \)
to \( \lambda + d\lambda \) and is dimensionless; \( \varepsilon_A(\lambda) \) is the extinction coefficient (in \( \text{M}^{-1} \text{cm}^{-1} \)) of
the acceptor at \( \lambda \). If \( \lambda \) is in nm, then \( J \) is in units of \( \text{M}^{-1} \text{cm}^{-1} \text{ nm}^4 \). The estimated
value of the overlap integral is \( 3.79 \times 10^{-6} \). Once the value of \( R_0 \) is known, the
donor–acceptor distance \((r_{DA})\) can be easily calculated using the formula,
\[
r_{DA}^2 = \frac{[R_0^2(1 - E)]}{E}
\]  
(10.3)

where \( E \) is the efficiency of energy transfer. The energy transfer efficiency is
measured using the relative fluorescence lifetime of the donor, in absence \((\tau_D)\) and
presence \((\tau_{DA})\) of the acceptor.
\[ E = 1 - \frac{\tau_{DA}}{\tau_D} \]  

(10.4)

We are also interested to obtain the thickness of the surface layer emitting visible light by using a simple model [92]. In order to obtain the below band gap (BBG) (550 nm, i.e., 2.25 eV) and near band edge (NBE) (365 nm, i.e., 3.39 eV) emission of the ZnO NPs, we have excited the sample with 320 nm (3.87 eV) light. The luminescence peak intensity ratio of the NBE to BBG emission for spherical particles of radius \( r \) and with a surface recombination layer of thickness \( t \), is given by [93],

\[ \frac{I_{\text{NBE}}}{I_{\text{BBG}}} = C \left( \frac{r^3}{3r(r-t)+r^3-1} \right) \]  

(10.5)

The constant \( C \), along with other quantities, contains the oscillator strengths, which in turn depend on the particle morphology. In order to calculate \( t \) from the above equation, we have taken the magnitude of \( C \) as 3.89 for small spherical particles [93] with radius \( r \approx 3 \) nm. In our system \( I_{\text{NBE}} \) (365 nm)/\( I_{\text{BBG}} \) (550 nm) \( \approx 0.853 \). Putting the values in (10.5), the thickness of the surface layer, \( t \), was found to be 1.30 nm. It represents an effective distance from the surface (effective diffusion length), within which the excited carriers recombine at the surface.

We have studied the complexation between ZnO NP with different concentrations of N719 dye. The ratio of the fluorescence intensity of the ZnO NP in the absence \( (I_0) \) and presence \( (I) \) of the quencher N719 was plotted in Fig. 10.5c, d by using Stern–Volmer equation [28],

\[ \frac{I_0}{I} \text{ or } \frac{\tau_0}{\tau} = 1 + K_{SV}[Q] \]  

(10.6)

where, \( I_0/I \) is the relative steady-state emission intensity, \( \tau_0/\tau \) is the relative excited state lifetime and \( K_{SV} \) is the Stern–Volmer constant.

In order to measure device performance, the incident photon-to-current conversion efficiency (IPCE) and photocurrent–voltage (\( J-V \)) characteristics were determined. The \( J-V \) characteristic measurements of the DSSCs were performed under AM1.5G sun irradiation (100 mW cm\(^{-2}\)) using 150 W small beam simulator (Sciecnetech, model SF150). The IPCE, defined as the number of electrons collected per incident photon, was evaluated from short-circuit photocurrent \( (J_{SC}) \) measurements at different wavelengths \( (\lambda) \), and the IPCE was calculated using (10.7),

\[ \text{IPCE} \% = \left[ 1.240 \times J_{SC} (\text{A/cm}^2) / \left[ \lambda (\text{nm}) \times P (\text{W/cm}^2) \right] \right] \times 100 \% \]  

(10.7)

where, \( P \) is the incident light power. The fill factor (FF) and power conversion efficiency (\( \eta \)) of the solar cells can be determined from (10.8) and (10.9),
\[ FF = \frac{V_M J_M}{V_{OC} J_{SC}} \]  
\[ \eta = \frac{V_{OC} J_{SC} FF}{P_{in}} \]  

where, \( V_M \) and \( J_M \) are the voltage and current density at the maximum power output, \( J_{SC} \) and \( V_{OC} \) are the short-circuit current and open-circuit voltage, respectively [94, 95]. At a fixed bias voltage of 5 V, the photoconductivity across the thickness of the thin films was measured by using FTO as one of the electrodes and a small (4 mm diameter) drop of mercury (Hg) on top of the film as a counter electrode. The light source (intensity 25 mW cm\(^{-2}\)) was turned ON and OFF every 20 s, and the obtained current values were continuously recorded using a programmable multimeter (Gwinstek GDM-396).

3 Results and Discussion

3.1 Dynamics of Light Harvesting in ZnO NPs [23]

In order to understand the key ultrafast processes associated to the dynamics of light-harvesting, we demonstrate our studies on the ultrafast energy transfer dynamics from ZnO NP to a well-known biological marker, Oxazine 1 (OX1). The cationic OX1 dye is supposed to bind at the surface of the n-type ZnO NP. The absorption and emission spectra of ZnO (energy donor) and OX1 (energy acceptor) are shown in Fig. 10.1. The broad emission peak of ZnO NPs centered at 550 nm is attributed to come from defect states at the surface [93, 96]. A. van Dijken et al. [97] proposed that the visible emission is due to the recombination of an electron from the conduction band with a deep electron trapping center of \( V_{O}^{+} \), which is considered as oxygen vacancy center. Alternatively, K. Vanheusden et al. [98] suggested that the recombinations of isolated \( V_{O}^{+} \) centers with photoexcited holes are responsible for the green emission. Because of the large surface-to-volume ratio of the ZnO NPs, efficient and fast trapping of photogenerated holes at surface sites are well speculated. However, the broad emission band can be decomposed into two components. The predominant emission energy is concentrated around the \( \lambda = 550 \) nm (2.25 eV) line while a smaller emission band occurs at around \( \lambda = 495 \) nm (2.50 eV). It has been reported that the emission center around 550 nm occurs from defect states near the surface layer (within a shell of \( t \)) while the shorter wavelength 495 nm emission occurs from defects near the bulk of the NPs [92, 93], which is located inside at a distance \( \approx t \) from the surface. As the size of the NP is increased, the relative contribution of the 495 nm emission increases. The absorption and emission spectra of the acceptor OX1 at the surface are also consistent with that reported in the literature [99].
Fig. 10.1 Normalized absorption (blue) and emission (green) spectra of ZnO NP with diameter of ~6 nm. Cascade harvesting of blue photon to red photon in the ZnO NP–OX1 complex is shown. The normalized absorption and emission of OX1 are shown.

The consistency of the spectral pattern of the acceptor OX1 with the other studies clearly rules out the possibility of any damage of the OX1 molecule at the ZnO surface. The spectral overlap of the ZnO emission spectrum with that of the OX1 absorption spectrum is shown in Fig. 10.2a. The faster excited state lifetime of the ZnO–OX1 adduct with respect to that of the free ZnO NPs is clearly noticeable from Fig. 10.2b. The baseline upliftment comes from the long lifetime component, which is not ending in our experimental time window.

The detailed spectroscopic and fitting parameters of the fluorescence decays are represented in Table 10.1. From the average lifetime calculation for the ZnO–OX1 complex, we obtain the effective distance between the donor and the acceptor, $r_{DA} \approx 1.58$ nm, using (10.3) and (10.4). It is noted that $r_{DA}$ is much smaller than the radius of the NP (~3 nm; inset Fig. 10.2b) and is comparable to the thickness $t$ of the surface layer of the NPs, i.e., $r > r_{DA} \approx t$. In the case of organic acceptor molecules at the surface of a semiconductor QD (CdSe) donor, the overall donor–acceptor distance is reported to be nearly equal (or larger) to the radius of the donor quantum dot [100]. The relatively shorter donor–acceptor distance in the case of ZnO–OX1 system compared to other systems [100] can be rationalized from the fact that the origin of the PL peaking at 550 nm is essentially from the surface layer of approximate thickness 1.3 nm of the ZnO NPs.

In order to compare the FRET efficiency from other emission centers (Scheme 10.1) of ZnO NPs, we have also studied the energy transfer dynamics at $\lambda_{em} = 495$ nm. The relative dynamical quenching of the ZnO–OX1 system with
Fig. 10.2 (a) Steady-state absorption spectra of OX1 (red) and emission spectra of ZnO NP (blue) are shown. An overlapping zone between emission of ZnO NP and absorption of acceptor OX1 is indicated as a green shaded zone. The picosecond-resolved fluorescence transients of ZnO NP, in absence (blue) and in presence of acceptor OX1 (red) (excitation at 375 nm) collected at (b) 550 nm and (c) 495 nm, are shown. Inset of the figure (b) shows the HRTEM image of ZnO NPs.
Table 10.1  Picosecond-resolved luminescence transients of various samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$\tau_{av}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NP (550 nm)</td>
<td>47.6 ± 0.8 (40 %)</td>
<td>3.79 ± 0.19 (23 %)</td>
<td>0.281 ± 0.003 (37 %)</td>
<td>20.32</td>
</tr>
<tr>
<td>ZnO NP–OX1 (550 nm)</td>
<td>19.0 ± 0.7 (1.4 %)</td>
<td>2.80 ± 0.02 (33.3 %)</td>
<td>0.259 ± 0.005 (65.3 %)</td>
<td>1.37</td>
</tr>
<tr>
<td>ZnO NP (495 nm)</td>
<td>35.1 ± 0.9 (30 %)</td>
<td>2.48 ± 0.15 (30 %)</td>
<td>0.089 ± 0.009 (40 %)</td>
<td>11.29</td>
</tr>
<tr>
<td>ZnO NP–OX1 (495 nm)</td>
<td>32.5 ± 0.4 (10 %)</td>
<td>2.32 ± 0.02 (36 %)</td>
<td>0.148 ± 0.006 (54 %)</td>
<td>4.17</td>
</tr>
<tr>
<td>ZnO NR (495 nm)</td>
<td>10.4 ± 0.1 (6.3 %)</td>
<td>2.44 ± 0.02 (28.2 %)</td>
<td>0.159 ± 0.004 (65.5 %)</td>
<td>1.45</td>
</tr>
<tr>
<td>ZnO rod–OX1 (495 nm)</td>
<td>8.454 ± 0.06 (5.1 %)</td>
<td>1.52 ± 0.01 (21.0 %)</td>
<td>0.087 ± 0.003 (73.9 %)</td>
<td>0.82</td>
</tr>
<tr>
<td>OX1 in EtOH (665 nm)</td>
<td>0.693 ± 0.001 (100 %)</td>
<td>–</td>
<td>–</td>
<td>0.69</td>
</tr>
<tr>
<td>ZnO NP–OX1 (665 nm)</td>
<td>0.867 ± 0.002 (100 %)</td>
<td>–</td>
<td>–</td>
<td>0.87</td>
</tr>
</tbody>
</table>

The emission from ZnO NPs (emission at 495 and 550 nm) was detected with 375 nm excitation. The emission of the acceptor OX1 in ethanol and at ZnO surface (emission at 665 nm) was detected with 633 nm laser excitation. Numbers in the parentheses indicate relative weightage.
Scheme 10.1  Schematic diagram of ZnO NP-oxazine 1 nanocomposite depicting the FRET dynamics from different oxygen vacancy centers (V_{O}^{+}/V_{O}^{2+}, V_{O}^{3+}/V_{O}^{3+}) of ZnO NPs to oxazine 1 molecules. Singly charged oxygen vacancy center (V_{O}^{+}), present in the surface depletion region, captures a hole to generate V_{O}^{3+} center, leading to an emission in with a peak in the vicinity of 2.25 eV (550 nm). In absence of depletion region V_{O}^{+} becomes neutral center (V_{O}^{+}) by capturing one electron from the conduction band, which is responsible for an emission at 2.50 eV (495 nm). Typical FRET distances from different energy states of ZnO NPs to surface adsorbed oxazine 1 are also shown. The band gap excitation (3.87 eV, i.e., 320 nm) is shown by curved arrows.

respect to free ZnO at 495 nm is shown in Fig. 10.2e. The relevant data are also given in Table 10.1. From the average lifetime data and using (10.3) and (10.4) we obtain for the 495 nm emission r_{DA} = 2.25 nm, which is much larger than that observed at 550 nm. In this case r = r_{DA} > r clearly indicating that the emission at 495 nm is from defect sites located within the bulk of the NPs. The efficiency of the FRET (E) as obtained from (10.4) is found to be the highest for 550 nm line (93 %) and much smaller (63 %) for the 495 nm line.

We have extended our studies on the attachment of the oxazine 1 molecules at the surface of the ZnO NRs. The NRs are very important components for the state-of-the-art ZnO-based DSSCs [101]. The morphology of ZnO NR was characterized by SEM. A typical SEM image of ZnO NR (Figure 10.3b inset) shows 400 nm long and 40 nm wide NR growths. The NRs are found to offer photoluminescence peaking at 495 nm. The spectral characteristic is consistent with the fact that the emission is dominated by the bulk state of the semiconductor [93, 102]. As shown
in Fig. 10.3b, the fluorescence quenching of the ZnO NR-OX1 adduct offers insignificantly small quenching with efficiency 44% compared to that of the free NRs in the bulk ethanol. No attempt has been made to estimate donor–acceptor distance in the case of NR-OX1 adduct because of the inadequate quantum yield of the ZnO NRs. We also considered the possibility of electron transfer from the ZnO surface to a well-known electron acceptor OX1 [99]. It has been demonstrated that the molecule offers an ultrafast fluorescence decay following an electron transfer reaction [103]. However, from Fig. 10.3a it is evident that the fluorescence decay of OX1 at the ZnO surface is slightly longer than that in the bulk ethanol.

The observation clearly rules out the possibility of any kind of electron transfer reaction in the quenching process of the ZnO NPs. Furthermore, a slight lengthening of the excited state lifetime of the acceptor molecule OX1 confirms its proximity to ZnO surface, which makes OX1 molecule more restricted. The overall picture that evolved from our studies is summarized in Scheme 10.1.
3.2 Role of Resonance Energy Transfer in Light Harvesting of Zinc Oxide-Based Dye Sensitized Solar Cells [24]

After a detailed understanding of the defect states in ZnO NPs, the effect of the ZnO-mediated light harvesting process on the overall efficiency of a model DSSC has also been demonstrated. We have explored the FRET dynamics from ZnO semiconductor NPs to surface adsorbed N719 sensitizers. By using steady-state and picosecond-resolved fluorescence spectroscopy, we have demonstrated that PL from ZnO NPs can be used to excite the sensitizer molecules for the enhancement of light absorption possibility. The study also reveals that physical migration of the photoinduced charge from the ZnO NPs to the SD molecules is insignificantly small in the de-excitation of the semiconductor NPs. The effect of the ZnO-mediated light harvesting process on the overall efficiency of a model DSSC has also been demonstrated.

The HRTEM image of the ZnO NPs is shown in Fig. 10.4a and a predominance of NPs with diameters of 6–7 nm were found in the synthesized colloids (inset of Fig. 10.4a). Figure 10.4b shows the UV–Vis absorption spectra of ZnO NP and dye N719. The PL spectrum of the ZnO NPs upon excitation with 375 nm is also shown in the figure. Significant spectral overlap of the ZnO PL spectrum with that of the absorption of N719 justifies the possibility of energy transfer from ZnO to the N719 dye molecules. In order to investigate the complexation of ZnO NPs with the sensitizer N719, we have studied the steady-state PL of the ZnO NPs in the presence of various concentrations of N719 as shown in Fig. 10.5a.

We have studied the PL transients at 550 nm (excitation at 375 nm) (Table 10.2) in the absence and presence of N719 dyes, as shown in Fig. 10.5b. The PL quenching, as evident from the steady-state and time-resolved PL studies, shows the affinity of the N719 dyes with the ZnO NPs. Detailed Stern–Volmer (S–V) analysis on the quenching of the ZnO PL (as shown in Fig. 10.5a, c) reveals the S–V constants to be $K_{SV}$ (steady state) = $1.14 \times 10^7$ M$^{-1}$ S$^{-1}$ and $K_{SV}$ (time resolved) = $0.87 \times 10^7$ M$^{-1}$ S$^{-1}$, respectively. The similarity of $K_{SV}$ constants from steady-state and time-resolved measurements indicate the ZnO PL quenching to be dynamic in nature. In other words, the possibility of formation of non-fluorescent ZnO–N719 complex in the ground state is found to be negligibly small.

The dynamic nature of the PL quenching of ZnO NPs upon complexation with N719 is further justified from the FRET from donor ZnO to the surface adsorbed sensitizer N719. The overall FRET efficiency is found to be 74%. In this case the spectral overlap integral, $J$ (10.2) and the Förster distance ($R_0$) are found to be $6.597 \times 10^{14}$ and 1.84 nm, respectively. From FRET dynamics, it has to be noted that the effective distance ($r_{DA}$) between the donor (ZnO NP) and the acceptor (N719) is 1.54 nm, which is much lower than that of the average radii of the NPs (~3 nm). In a FRET study [104] on cadmium selenide (CdSe) QD (donor) and a surface adsorbed organic dye (ethidium bromide; acceptor), the donor–acceptor distance was found to be close to the radius of the quantum dot. The relatively shorter donor–acceptor distance compared to the radius of the ZnO nanocrystallites
in the present study, can be rationalized from the fact that the origin of the PL peaking at 550 nm essentially arises from the crystallites exposed in the surface of ZnO NPs. It is important to note that the thickness of the surface layer (t) obtained from calculation (10.5) is found to be 1.30 nm, which is comparable to the effective distance between the donor and acceptor calculated from FRET study. The observation is consistent with the fact that there is a surface region from where the defect related emission occurs.

In order to investigate the effect of light harvesting of high energy photons by the host ZnO semiconductor in a model DSSC, we have studied the photocurrent–voltage (J–V) characteristics as shown in Fig. 10.6a. The J–V characteristics of the solar cells were measured in two different experimental conditions. Firstly, we have excited the cells with whole solar spectrum (circle-line presentation in Fig. 10.6). Secondly, we used a yellow filter to block the solar spectra below 400 nm (high energy photons) as shown in a square-line presentation in Fig. 10.6a. The total light power in both the cases was very carefully maintained.

Fig. 10.4 (a) HRTEM image showing ZnO NPs with ~3 nm radius. Inset shows the size distribution of the ZnO NPs. (b) Steady-state absorption spectra of ZnO NP (blue), N719 (red) and emission spectra of ZnO NP (green) are shown. An overlapping zone between emission of ZnO NP and absorption of acceptor N719 is indicated as a red shaded zone.
Fig. 10.5  (a) Steady-state emission intensity of ZnO NPs (excitation at 375 nm) in presence of increasing concentration of N719 dye relative to that of ZnO emission without N719. (b) The picosecond-resolved fluorescence transients of ZnO NP, in absence (blue) and in presence of acceptor N719 (red) (excitation at 375 nm) collected at 550 nm. Inset show the faster PL decay of ZnO NP in the presence of BQ. (c) Excited state lifetime of the PL emission of ZnO NPs (excitation at 375 nm) in the presence of increasing concentration of N719 dye relative to that of ZnO emission without N719 is shown.
Table 10.2 Picosecond-resolved luminescence transients of ZnO NPs in the presence and absence of N719

<table>
<thead>
<tr>
<th>Sample</th>
<th>( t_1 ) (ns)</th>
<th>( t_2 ) (ns)</th>
<th>( t_3 ) (ns)</th>
<th>( t_{avg} ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NP (bare)</td>
<td>47.6 (41 %)</td>
<td>3.78 (23 %)</td>
<td>0.280 (36 %)</td>
<td>20.32</td>
</tr>
<tr>
<td>ZnO NP + N719</td>
<td>29.1 (12 %)</td>
<td>3.86 (38 %)</td>
<td>0.344 (50 %)</td>
<td>5.25</td>
</tr>
<tr>
<td>ZnO NP + BQ</td>
<td>30.2 (6 %)</td>
<td>1.93 (18 %)</td>
<td>0.187 (76 %)</td>
<td>2.20</td>
</tr>
</tbody>
</table>

The emission from ZnO NPs (emission at 550 nm) was detected with 375 nm laser excitation. Numbers in the parentheses indicate relative weightage.

Fig. 10.6 J-V curves of (a) ZnO NP and (b) TiO₂ NP-based DSSCs in the presence and absence of UV at 100 mW cm⁻². The open circuit voltage \( V_{OC} \) and short-circuit current density \( J_{SC} \) values are found to be much higher when the device performance was measured under whole solar spectrum. Upon the use of the optical filter, a sharp decrease in current from 1,190 to 668 µA cm⁻² was observed. In retrospect, compared to 44 % change in the short circuit current, \( V_{OC} \) reduced marginally by 6.7 % while fill factor (FF) reduced only by around 11.8 % (Table 10.3). As shown in Fig. 10.4b the sensitizer N719 absorbs very little in the UV region (below 400 nm) of the solar spectrum. Thus it is expected that the efficiency of the solar cell will not be affected much on the presence of high energy photons due to the absence of
noticeable optical absorption in the dye at lower wavelengths (below 400 nm). This observation clearly demonstrates that ZnO DSSCs can harvest high energy photons as well. High energy photons were found to have a minimum effect on the solar cell performance of TiO₂-based solar cells fabricated with the same sensitizer (Fig. 10.6b). These observations (Fig. 10.6a, Table 10.3) reveal that the efficiency of ZnO-based DSSC increases by 118% if the UV portion of the AM1.5 spectra is employed, which was compared to a marginal 9% increase in efficiency in the case of TiO₂-based DSSCs. It is clear that harvesting of high energy photons in the case of TiO₂-based DSSCs does not contribute appreciably to the enhancement of the device efficiency. It is worth noting that the efficiency obtained from the model DSSC using NPs is lower compared to the maximum efficiency reported where NR has been taken in order to provide higher surface area and better charge transport.

It has to be noted that N719 is a redox active organic dye [20]. In this regard the PL quenching of the ZnO NPs upon adsorption of the dye may be associated with excited state electron transfer from ZnO to the N719 dye molecule. In order to investigate the electron transfer dynamics from the ZnO NPs upon excitation, we have studied the complexation of the NPs with an organic molecule, benzoquinone (BQ), which is well known as an electron acceptor [105] and efficiently accepts excited electrons from the surface of semiconductor quantum dots [106].

From our studies the quenching of the PL intensity of ZnO NPs upon complexation with BQ is evident. As shown in the inset of Fig. 10.5b, a very sharp decay in fluorescence at 550 nm in the presence of the electron acceptor is indicative of the fast transfer of excited electrons from the conduction band of the ZnO NPs into the LUMO of BQ molecules. The ZnO–BQ system exhibited a faster initial decay with a time period of 0.187 ns with a majority (76%) of the excited electrons following this path (Table 10.2). The faster decay in presence of BQ as compared to N719 at the same excitation of 375 nm may be indicative of energy transfer from the ZnO donor NPs to the N719 acceptor molecules rather than transfer of electrons. In the case of pure ZnO in ethanol (Fig. 10.5b), the excited state lifetime (κex = 0) of ZnO NPs is 20.32 ns, which yields a radiative rate constant of 4.92 × 10⁵ s⁻¹. Upon the addition of N719 and BQ in separate ZnO NP solution, the average lifetimes were found to reduce to 5.25 and 2.20 ns, with rate constants of 1.90 × 10⁸ and 4.55 × 10⁶ M⁻¹ s⁻¹, respectively. We have calculated electron transfer rate, which is directly reflected in the non-radiative rate constants (κnr). The calculated κnr values were found to be 1.41 × 10⁸ and 4.06 × 10⁶ M⁻¹ s⁻¹ for the ZnO–N719

---

### Table 10.3 Device performance of the DSSCs with ZnO and TiO₂ NPs

<table>
<thead>
<tr>
<th>Device with N719</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (μA cm⁻²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NP (with UV)</td>
<td>0.45</td>
<td>1190.00</td>
<td>44.66</td>
<td>0.24</td>
</tr>
<tr>
<td>ZnO NP (without UV)</td>
<td>0.42</td>
<td>668.00</td>
<td>39.39</td>
<td>0.11</td>
</tr>
<tr>
<td>TiO₂ NP (with UV)</td>
<td>0.77</td>
<td>6760.00</td>
<td>46.30</td>
<td>2.41</td>
</tr>
<tr>
<td>TiO₂ NP (without UV)</td>
<td>0.77</td>
<td>6086.67</td>
<td>47.15</td>
<td>2.21</td>
</tr>
</tbody>
</table>

*Short circuit photocurrent densities (J<sub>sc</sub>), open-circuit voltage (V<sub>oc</sub>), fill factor (FF), and efficiency (η) (see (10.8) and (10.9)).*
and ZnO–BQ systems, respectively. From the above $k_{rt}$ values, we can conclude that the electron transfer rate, in case of ZnO–BQ composite, is threefold higher compared to the energy transfer in ZnO–N719 system. In the case of electron transfer from excited state ZnO NPs to N719, the short-circuit current of the ZnO NP-based DSSC is expected to be reduced. However, as shown in Fig. 10.6, the efficiency of the DSSCs in the presence of UV light (i.e., when the ZnO NPs were excited) is increased. Charge conservation clearly rules out any possibility of back electron transfer from ZnO NPs to the sensitizer N719. The overall picture that is evident from our studies is represented in Scheme 10.2.

3.3 **Photoselective Excited State Dynamics in ZnO–Au Nanocomposites and Their Implications in Photocatalysis and Dye-Sensitized Solar Cells** [25]

In this section, we aimed to elucidate the mechanism of pronounced intrinsic emission from colloidal ZnO and ZnO–Au NCs upon above band-edge and below band-gap excitation. To probe the correlation between dynamics of photon-generated carrier trapping at the defect sites and kinetics of charge migration from ZnO and ZnO–Au semiconductors, methylene blue (MB) degradation was examined using UV light and optical filters. Photostability and luminescence studies from a ZnO–Au NC colloidal dispersion reveal FRET dynamics from donor semiconductor to gold acceptor. Finally, we have designed a model DSSC-based on ZnO NPs, which leads to an increase in short-circuit photo-current ($J_{SC}$) and improved overall efficiency ($\eta$) in the presence of Au NPs. The reason behind the giant improvement in efficiency is also clarified by photoconductivity measurements of the ZnO NP and ZnO–Au NC thin films.

The structure, crystalline phase, size, and morphology of ZnO NPs and ZnO–Au NCs were determined (with TEM). Representative HRTEM images of the ZnO–Au NCs are illustrated in Fig. 10.7a, where the measured average diameters are 6 nm and 8 nm for ZnO and Au NPs, respectively. From TEM observation it was found that, the ZnO–Au NCs are fairly monodisperse and their shapes are different from that of the spherical ZnO NPs due to the incorporation of Au components. The higher contrast of Au observed in the TEM image is due to the higher electron density of metallic Au compared to semiconductor ZnO. The relevant TEM images are shown in Fig. 10.8a–c. After the synthesis of ZnO–Au NCs, the Zn–Au weight ratio was calculated by using a field emission-type scanning electron microscope (FEI-SEM; Quanta 200). From EDAX analysis it was found to be 1.3:1 as shown in the table below.

The visible absorption spectrum of gold grown onto the ZnO NPs was clearly characterized by the plasmon resonance peak of Au NPs. Figure 10.7b shows the absorption spectra of the ZnO–Au NCs and pure ZnO NPs. It is generally believed that the band-edge absorption of semiconductor in the quantum-confined size
Scheme 10.2. It represents a model DSSC based on the ZnO NPs, which contain sufficient defect states, namely, oxygen vacancy centers near surface depletion region. The system consists of a fluorinated tin oxide (FTO) on which semiconductor ZnO NP (gray big circle) is fabricated. The sensitizer dye N719 (small yellow circle) is bound to ZnO NP by surface adsorption. The entire structure is immersed in a liquid redox electrolyte (I\textsubscript{3}/I\textsubscript{2}). In regular DSSC, light is directly absorbed by the sensitizer, exciting an electron from HOMO to LUMO level. In the proposed configuration that contains a semiconductor having appreciable amount of defect states, an additional “indirect excitation” of N719 is introduced by using the sensitivity of FRET. In the FRET-based cell, the semiconductor NP is found to be excited in the presence of UV light, by which, an electron is promoted from the valance band to the conduction band, followed by energy transfer from excited states of semiconductor to N719 molecules via FRET. Thereafter, charge separation occurs exactly as it does in regular DSSCs and electron is injected from the excited state of the dye into the conduction band of the semiconductor electrode and the electron is thus transported to the charge collector. In presence of a UV cut-filter the FRET-based cell performs like a regular DSSC as no energy transfer from ZnO NP to N719 takes place due to the absence of UV light.
regime (≤7 nm) is dependent on the particle size [107]. There is no distinct variation in absorption characteristics in the range 300–420 nm, which implies that no apparent growth of ZnO NPs occurred during the formation of Au on ZnO NPs. An SP band, resulting from Au in the ZnO–Au NCs, centered at ~525 nm can also be observed in the NC (Fig. 10.7b). In Fig. 10.9a we have plotted the excitation spectra of bare ZnO NPs and ZnO–Au NCs monitored at the emission peaks (368 nm and 550 nm, respectively). The room temperature PL spectra of both the bare ZnO NPs and ZnO–Au NCs (Fig. 10.9b) are composed of one broad emission band upon excitation below the band-gap ($\lambda_{ex} = 375$ nm) and two emission bands upon excitation above the band-edge ($\lambda_{ex} = 320$ nm). The narrow UV band centered at 368 nm is due to exciton recombination. Analysis of the broad emission observed in our sample in the blue-green region shows that it is composed of two emission bands (shown as dotted lines in Fig. 10.9b (inset)), which are marked as P1 and P2 [96]. The characteristics of each emission band depend upon whether it arises from a doubly charged vacancy center $V_O^{2+}$ (P2) or a singly charged vacancy center $V_O^+$ (P1). The $V_O^{2+}$ center, created by capture of a hole by the $V_O^+$ center in
a depletion region, leads to the P2 emission line. The singly charged center (V$^{+}$) in
the absence of a depletion region turns into a neutral center (V$^{0}$) upon the capture
of an electron (n-type ZnO) from the conduction band, which then recombines with
a hole in the valence band giving rise to the P1 emission [93]. The spectral content
of the blue-green band is determined by the relative weight of the two overlapping
emission peaks.

As shown in Fig. 10.9b, when excitation below the band-gap ($\lambda_{ex} = 375$ nm)
was used, the defect-related emission is suppressed in the presence of Au NPs.
Herein, we propose FRET from donor ZnO NP to Au acceptor, which is responsible
for the observed suppression of emission bands.

The spectral overlap of the ZnO emission spectrum with that of the Au absorp-
tion spectrum is shown in Fig. 10.10a. The faster excited state lifetime of the

![Figure 10.8](image-url)

**Fig. 10.8** (a) HRTEM image of bare ZnO NPs. (b) TEM image of bare ZnO NPs (inset shows particle size distribution of ZnO NPs). (c) TEM image of ZnO–Au NCs (inset shows particle size distribution of Au NPs attached to ZnO NPs). Table (left) shows EDAX analysis of ZnO–Au NCs by using a field emission-type SEM. Table (right) shows picosecond-resolved luminescence transients of ZnO NPs in the presence and absence of Au NPs. The numbers in the parentheses indicate relative weightage. (d) The emissions from ZnO NPs and ZnO–Au NCs (probing at 520 nm) were detected with a 300 nm laser excitation.
Fig. 10.9 (a) Excitation spectra of ZnO NPs (blue) and ZnO–Au NCs (red) monitored at 368 and 550 nm. (b) Steady-state emission spectra of ZnO NPs (blue) and ZnO–Au NCs (red) are shown (excitation at 320 and 375 nm). The inset shows that the defect related green emission is composed of two bands, P1 and P2.

ZnO–Au NC with respect to that of the free ZnO NP is clearly noticeable from Fig. 10.10b. Details of the spectroscopic parameters and the fitting parameters of the fluorescence decays are tabulated in Table 10.4. In order to estimate FRET efficiency of the donor (ZnO) and hence to determine distances of donor–acceptor pairs, we followed the methodology described in chapter 13 of reference [28]. In this case the spectral overlap integral, \( J (10.2) \) is found to be \( 2.82 \times 10^{16} \).

From the average lifetime calculation for the ZnO–Au NC, we obtain the effective distance between the donor and the acceptor, \( r_{DA} \approx 2.55 \) nm, using (10.3) and (10.4). It is to be noted that the smaller value of \( r_{DA} \) compared to the radius of the ZnO NPs (\( \sim 3 \) nm; Fig. 10.7a) can be rationalized from the fact that the origin of the PL peaking at 550 nm arises essentially from surface defects in the ZnO NPs [23]. Moreover, comparing the PL spectra of bare ZnO NPs and ZnO–Au NCs upon excitation above the band-edge, it was observed that the emission due to excitonic recombination is suppressed, while the defect-related emission is red shifted in the presence of Au NPs. In this respect, we have shown that the energy
Fig. 10.10  (a) SP band of Au NPs and emission spectra of ZnO NPs are shown. An overlapping zone between emission of ZnO NPs and absorption of acceptor Au is indicated as a gray shaded zone. (b) The picosecond-resolved fluorescence transients of ZnO NPs, in the absence (blue) and presence of acceptor Au (red) (excitation at 575 nm) collected at 550 nm.

**Table 10.4** Dynamics of picosecond-resolved luminescence transients of ZnO NPs in the presence and absence of Au NPs and the kinetics parameters for the photoselective degradation of methylene blue in the presence of ZnO and ZnO–Au nanocolloids.

<table>
<thead>
<tr>
<th>Time (ns)</th>
<th>Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>t1</td>
</tr>
<tr>
<td>ZnO NP  (bare)</td>
<td>47.58 (41 %)</td>
</tr>
<tr>
<td>ZnO–Au NC</td>
<td>33.34 (8 %)</td>
</tr>
</tbody>
</table>

Kinetics study \( y = A \exp(-kt) + \gamma_0 \)

<table>
<thead>
<tr>
<th>Samples and filters</th>
<th>k (sec(^{-1}))</th>
<th>A (%)</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO (420 HP)</td>
<td>1.055 \times 10^{-3}</td>
<td>2.66</td>
<td>0.96</td>
</tr>
<tr>
<td>ZnO–Au (420 HP)</td>
<td>1.388 \times 10^{-3}</td>
<td>2.78</td>
<td>0.93</td>
</tr>
<tr>
<td>ZnO (460 LP)</td>
<td>2.203 \times 10^{-3}</td>
<td>11.68</td>
<td>0.97</td>
</tr>
<tr>
<td>ZnO–Au (460 LP)</td>
<td>2.528 \times 10^{-3}</td>
<td>29.31</td>
<td>0.99</td>
</tr>
<tr>
<td>ZnO (320 HP-460 LP)</td>
<td>2.340 \times 10^{-3}</td>
<td>23.55</td>
<td>0.99</td>
</tr>
<tr>
<td>ZnO–Au (320 HP-460 LP)</td>
<td>2.287 \times 10^{-3}</td>
<td>19.65</td>
<td>0.99</td>
</tr>
</tbody>
</table>

*The emissions from ZnO NPs and ZnO–Au NCs (probing at 550 nm) were detected with a 375 nm laser excitation. Numbers in the parentheses indicate relative weightage.

*Kinetic constants (k), regression coefficients (R\(^2\)), and the percentages of photoselective degradation (A). Parentheses indicate the optical filters used in the study.*
is transferred from the Vo⁺ center to Au NPs, which leads to a reduction in the PL intensity at 520 nm. The energy transfer efficiency (E) is found to be ~19 % (Fig. 10.8d), which is much lower value compared to that of below band-gap excitation (E = ~85 %). In retrospect, excited electrons are preferentially trapped by Vₒ²⁺ center, which is originated by Vₒ⁺ center by capturing a hole. The formation of Vₒ²⁺ centers is more favorable upon band-edge excitation since the photogenerated holes have enough time to migrate during thermalization of highly excited electrons. This leads to more facile recombination of excited electrons via Vₒ²⁺ centers, and this recombination pathway is supported by the appreciable red shift observed in ZnO–Au NCs upon above band-edge excitation. However, the decrease in band-edge emission intensity in the presence of Au NPs is well understood, whereby, Au acts as a sink that can store and shuttle photogenerated electrons [108, 109]. As per our understanding, the optical activity of surface defect states in the overall emission of the semiconductor solely depends on the excitation wavelength.

It was reported by several researchers that in the presence of metal NPs in close proximity to semiconductor NPs, enhanced photocatalytic degradation of test solutions was observed. Thus we compared the role of a Au layer in promoting photogenerated charges in ZnO–Au and ZnO colloids by carrying out photo-reduction of a test contaminant (MB, purchased from Carlo Erba); MB is known to be an excellent probe for the study of interfacial electron transfer in colloidal semiconductor systems [81]. In general, the higher the charge migration from the surface of the ZnO semiconductor, the faster will be the degradation of the surface-attached MB. We have used a fiber-optic-based system for the measurement of light-induced chemical processes with spectroscopic precision. To demonstrate the sensitivity and usefulness of our designed system, we previously conducted a detailed study of the photodegradation of vitamin B2 (riboflavin) in aqueous phase [110]. In order to obtain different excitations we have used three different types of filters placed on a homemade UV bath (60 W; normally used for water purification). The optical filters, namely, 420 high pass (HP), 460 low pass (LP), and 320 high pass (HP), were chosen in order to achieve controlled and preferential excitation. The characteristics of the optical filters are shown in Fig. 10.11a, which clearly depicts that 420 HP (passes light above 420 nm) is only used for the SP excitation of Au NPs, 460 LP (passes light below 460 nm) is used for the above band-edge excitation of ZnO, and the combined use of 320 HP and 460 LP (passes light above 320 nm and below 460 nm) leads to preferential excitation of below band-gap excitation of ZnO. In Fig. 10.11b, the relative concentration ($C_n/C_0$) of MB in solution is plotted with respect to UV irradiation time, the results of which indicate the photodegradation of MB upon continued UV irradiation. It is to be noted that there was no obvious change in the concentration of MB stored in the dark for several hours (data are not shown here). Under selective UV radiation we have recorded the absorption peak of MB (at 655 nm) at 5 s intervals, using SPECTRA SUITE software supplied by Ocean Optics, and plotted it against the time of photolysis in a first-order exponential equation, and the kinetic parameters are represented in...
Table 10.4. The decrease in the absorbance at 655 nm implies the generation of the colorless photoproduct leuco-methylene blue (LMB). Note that in the present study we are interested in exploring the long-time photodegradation of MB (for several minutes). To compare the photodegradation of MB in the presence of ZnO NPs and ZnO–Au NCs with a 420 HP filter, it is clearly shown that no considerable change in absorbance peak at 655 nm takes place upon Au SP excitation. The photodegradation rates are found to be $1.055 \times 10^{-3}$ and $1.388 \times 10^{-3}$ s$^{-1}$, and the percentages of total photodegradation (i.e., the value of $A$ in the first-order kinetic equation shown in Table 10.4) are 2.66 and 2.78 for ZnO and ZnO–Au NCs, respectively. It reveals that electron transfer from Au NPs to MB is not allowed upon direct excitation of Au. Upon, replacing the 420 HP filter with a 460 LP filter, we observed an increase in the photodegradation rates in the presence of Au NPs ($k_{ZnO} = 2.203 \times 10^{-3}$ s$^{-1}$, $k_{ZnO-Au} = 2.258 \times 10^{-3}$ s$^{-1}$), and the percentage of photodegradation also improved from $A_{ZnO} = 11.68$ to $A_{ZnO-Au} = 29.31$. This is
attributed to improved charge separation in the presence of Au NPs, which also can store and shuttle excited electrons, thereby suppressing recombination. Such Au NP-stabilized ZnO NPs behave as more efficient electron accumulators (at the conduction band) than the bare oxide [111]. In retrospect, the photodegradation rate of MB was observed to decrease \( (k_{\text{ZnO}} = 2.34 \times 10^{-3}, k_{\text{ZnO-Au}} = 2.287 \times 10^{-3}) \), and the percentage of total photodegradation was found to be much lower \( (A_{\text{ZnO}} = 23.55, A_{\text{ZnO-Au}} = 19.65) \) in the presence of Au NPs when we used combined optical filters of 320 HP and 460 LP. This happens because excited electrons of ZnO can easily occupy the defect centers and resonantly transfer their energy to Au NPs via non-radiative processes (FRET, as previously discussed). As a consequence, in presence of Au, excited electrons are unable to migrate from the ZnO surface to perform the reduction of MB. Thus, it is important to note that the differences in rate constants are not significant, whereas considerable differences in the magnitude of total photodegradation are observed during above band-edge and below band-gap excitation of ZnO and ZnO–Au NCs. This is due to the fact that the total number of active electrons available for carrying out MB degradation is different for ZnO and ZnO–Au NCs for any particular excitation. Our study clearly demonstrates that the role of incorporated metal on semiconductor for facilitating redox reactions is solely dependent on the excitation of the semiconductor.

The efficient charge migration in metal-semiconductor NCs is expected to lead to improved DSSC performance of ZnO–Au NCs compared to bare ZnO [112]. Thus, we measured and directly compared the IPCE (using (10.7)) of ZnO and ZnO–Au-based DSSCs. Each of the two examined ZnO and ZnO–Au-based cells contained the same sensitizer dye N719 and I\(^{-}/I_3^-\) electrolyte, to allow for a fair comparison. The IPCE curves of the two cells are presented in Fig. 10.12a, which shows a broad spectral response in the range 440–600 nm. Significant enhancement in photocurrent generation is seen upon deposition of Au NPs on the ZnO electrodes. The enhancement in the photocurrent generation efficiency is indicative of the fact that the Au NPs assist in the charge separation within the nanostructured ZnO film as well as improve the interfacial charge transfer processes. Figure 10.12b shows the photocurrent–voltage (\( J–V \)) characteristics for solar cells, constructed using the bare ZnO NPs and ZnO–Au NCs. The short-circuit current density \( (J_{\text{SC}}) \) and the open-circuit voltage \( (V_{\text{OC}}) \) of the ZnO–Au NC-based DSSC were 261.87 \( \mu \text{A cm}^{-2} \) and 0.605 V, respectively, which are much higher than that of the bare ZnO-based DSSC \( (J_{\text{SC}} = 7.5 \mu\text{A cm}^{-2}, V_{\text{OC}} = 0.394 \text{ V}) \). The calculated values of FF and the overall power conversion efficiency of the ZnO-based DSSC were 30 % and 0.012 %, respectively, which are substantially improved in the presence of gold \( (\text{FF} = 53 \% \text{ and } \eta = 0.8 \%) \). Table 10.5 summarizes the measured and calculated values obtained from each \( J–V \) curve.

We have also extended the photovoltaic measurements with ZnO NR and ZnO–Au NC solar cells with dye N719 and their \( J–V \) characteristics were measured under AM 1.5 illuminations, as shown in Table 10.6. In Fig. 10.13a, the best \( J–V \) characteristics obtained for both bare ZnO NR and ZnO–Au NC DSSCs are shown.
**Table 10.5** Device performance of the DSSCs with ZnO NP and ZnO–Au NC

<table>
<thead>
<tr>
<th>Device with N719</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (μA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO NP</td>
<td>0.394</td>
<td>7.5</td>
<td>44</td>
<td>0.012</td>
</tr>
<tr>
<td>ZnO–Au NC</td>
<td>0.605</td>
<td>261.87</td>
<td>53</td>
<td>0.8</td>
</tr>
</tbody>
</table>

*Short-circuit photocurrent densities ($J_{sc}$/cm$^2$), open-circuit voltage ($V_{oc}$), fill factor (FF), and efficiency ($\eta$) (see (10.8) and (10.9)).

**Table 10.6** J–V characteristics of the bare ZnO NR and ZnO–Au NC DSSCs, measured at 1 sun illumination (100 mW cm$^{-2}$)*

<table>
<thead>
<tr>
<th>J–V parameters</th>
<th>Bare ZnO NR DSSC</th>
<th>ZnO–Au NC DSSC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cell I</td>
<td>Cell II</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>$J_{sc}$ (mA cm$^{-2}$)</td>
<td>10.98</td>
<td>11.01</td>
</tr>
<tr>
<td>FF (%)</td>
<td>71.55</td>
<td>72.40</td>
</tr>
<tr>
<td>$\eta$ (%)</td>
<td>5.27</td>
<td>5.34</td>
</tr>
</tbody>
</table>

*The active area of all the DSSCs was maintained at 0.1 cm$^2$ during these experiments.
Fig. 10.13 (a) $I-V$ characteristics of the bare ZnO NR and ZnO–Au NC DSSC, measured at 1 sun (AM 1.5 G) illumination and (b) short circuit photocurrent density of the bare ZnO NR and ZnO–Au NC DSSCs measured at different incident wavelengths. The active area of all the DSSCs was maintained at 0.1 cm$^2$.

It was found that the photocurrent of the ZnO NR DSSC improved upon the incorporation of Au NPs in the ZnO NR photoelectrode. For the ZnO–Au NC DSSC, ~35% improvement in $J_{SC}$ (14.89 mA cm$^{-2}$) was obtained compared to the bare ZnO NR DSSC (11.01 mA cm$^{-2}$) and the overall power conversion efficiency improved from 5.34 to 6.49%. In Fig. 10.13b, the photocurrent response of bare ZnO NR and ZnO–Au NC-based DSSC measured at different incident wavelengths.
are shown. Due to the surface plasmon absorption of Au NPs, an improved photocurrent response was observed above 500 nm illumination in case of the ZnO–Au NC DSSC compared to the bare ZnO NR DSSC. The improved device performance observed in case of the ZnO–Au NC DSSC can also be attributed to the presence of the Schottky barrier at the ZnO–Au interface, which would block the back electron transfer from the CB of ZnO to the \( \Gamma^-/I^- \) redox electrolyte. In ZnO–Au NC system, due to the higher work function of ZnO (\( \Phi \approx 5.3 \) eV) compared to Au (\( \Phi \approx 5.1 \) eV), a Schottky barrier forms at the ZnO–Au interface. Upon light irradiation, the electrons from excited dye molecules are injected to the Au NPs embedded on the surface of ZnO NRs resulting in an electron accumulation in the Au NP. As a result, the Fermi energy level of the Au NPs is pushed closer to the CB of the ZnO and transfer of electrons from Au NPs to the CB of ZnO could occur to establish charge equilibrium in the system. Some of the electrons from dye can also directly injected to the CB of the ZnO. The formation of the Schottky barrier at the ZnO–Au NC system and the possible electron transfer path in ZnO–Au DSSC is schematically represented in Scheme 10.3 [112].

The photoconductivity measurement [113, 114] of the ZnO NP and ZnO–Au NC thin films were necessary in order to further understand the electron mobility (i.e., performance of the semiconductor) and charge transfer mechanism. Figure 10.14 shows the photocurrent response for the ZnO NP and ZnO–Au NC thin films, where an improved photocurrent was observed for the ZnO–Au NC thin film (~70 \( \mu \)A) under illuminated condition compared to the ZnO NP thin film (~1.5 \( \mu \)A).
This shows that the photogenerated electrons in ZnO NPs (from visible light absorption by the intermediate \( V_{O}^{+} \) center) are transferred to Au NPs, as mentioned earlier contributing in enhanced photocurrent of the ZnO–Au NC thin films compared to the ZnO NP. In case of the model DSSC shown here, a similar mechanism is responsible for the enhanced photocurrent observed (Fig. 10.12b) in the presence of Au NPs along with the ZnO NPs. Some of the injected electrons from the excited N719 dye to the CB of ZnO are captured by the intermediate defect sites of ZnO (\( V_{O}^{+} \)) resulting in poor photocurrent and fill factor of DSSC. However, in the presence of Au NPs in the ZnO thin film, we have observed higher photocurrent \( J_{SC} = 261.87 \ \mu A \ cm^{-2} \) and fill factor (FF = 53 %) compared to the ZnO NP DSSC \( J_{SC} = 7.5 \ \mu A \ cm^{-2} \) and FF = 44 %). Thus, it is noted that the ratios of improved photocurrent response (70:1.5) and short circuit current (261.9:7.5) for ZnO and ZnO–Au semiconductors are comparable. The improvement observed in the overall device performance is mainly due to increased conductivity by transferring the trapped electrons in \( V_{O}^{+} \) centers of ZnO to Au NPs, which then contribute to the photocurrent as well as the fill factor of the DSSC. It is worth noting that the efficiency obtained from the model DSSC with the use of NPs is lower than the maximum efficiency reported [115] with NRs, which were employed to provide higher surface area and better charge transport. The overall mechanistic explanation for the excitation-dependent recombination processes and the catalytic activity of Au NPs in the ZnO–Au NCs, as schematically shown in Scheme 10.4.
3.4 Dual-Sensitization via Electron and Energy Harvesting in CdTe QDs Decorated ZnO NR-Based DSSCs [26]

In this section, we will demonstrate the utilization of two sensitizers (one acting as energy donor while the other as an acceptor) by using the novel approach of FRET that can be very useful in order to achieve both broadening of optical absorption region in DSSCs as well as increasing the absolute loading of absorbing media on the semiconductor. We have explored that size tunable CdTe QDs capped with 3-mercaptopropionic acid (MPA), assembled in an N719-sensitized solar cell, can absorb visible light in the gaps where SD N719 has lower absorption or does not absorb any light. In this design, QDs serve as a co-sensitizer, which can directly transfer electrons to ZnO NRs. Moreover, the QDs that are not in a direct attachment to the ZnO NR surfaces harvest the absorbed energy to nearby dye molecules via FRET rather than contribute directly as sensitizers. By using steady-state and picosecond-resolved fluorescence spectroscopy, we have demonstrated that PL from QDs can be useful to excite the sensitizer dye molecule for an enhanced light absorption. The consequence of QD mediated electron and light-harvesting
processes on the overall performance of a model QD-assembled DSSC has also been demonstrated.

The morphological characterization by SEM (Fig. 10.15a) indicates the formation of arrays of ZnO NRs with a preferential growth direction along the polar facets in the [0002] direction of the ZnO hexagonal wurtzite crystal. The NRs growing perpendicular to the substrate are nearly uniform in length (≈3 μm) and possess a characteristic hexagonal cross section with diameter in the range of ≈180 nm. Inset Figure 10.15b–c show the TEM images of two distinctly different sizes of CdTe QDs (QD1 and QD2), which are found to be ≈4 ± 0.2 and ≈5 ± 0.4 nm in diameter. As shown in the insets of Fig. 10.15b–c, HRTEM image reveals the fringes of CdTe with a lattice spacing of 0.33 and 0.25 nm corresponding to (111) and (220) planes of cubic CdTe crystal, which are in good agreement with previous reports [116]. Both the absorption and PL spectra of CdTe QDs exhibit “quantum size effect,” as shown in Fig. 10.16. The tunable absorption bands of CdTe QDs can be so adjusted that they preferentially cover the “gaps” of sensitizer N719.
Fig. 10.16 (a) Normalized absorption spectra of the sensitizing dye N719 and 3-MPA-capped CdTe QDs with average diameters of 4 nm (QD1), 5 nm (QD2), 7 nm (QD3), and 9 nm (QD4). (b) Significant overlap between absorption spectra of N719 and photoluminescence (PL) spectra of four different-sized CdTe QDs is shown.

absorption, i.e., where sensitizer has none or very low extinction coefficient (Fig. 10.16a). As can be observed in Fig. 10.16b, there are significant overlaps between the optical absorption of sensitizer N719 and the emission bands of CdTe QDs, which is one of the foremost criteria for FRET dynamics. As shown in Fig. 10.17, upon 375 nm laser excitation, strong emissions of CdTe QDs (deposited on a quartz plate) were suppressed in the presence of sensitizer N719. Herein, we propose FRET from donor CdTe QDs to N719 acceptor [117], which is responsible for the observed suppression of the emission bands. The donor thus decays to the ground state while the acceptor is still excited. It results in the excitation of the acceptor from an indirect process, i.e., the acceptor effectively captures photons that are not directly absorbed by it. The faster excited state lifetime of the CdTe-N719 composite with respect to that of the free QDs is clearly noticeable in Fig. 10.18. Details of the spectroscopic parameters and the fitting parameters of the fluorescence decays are tabulated in Table 10.7.

The quantum yields ($Q_D$) of the donors in the absence of acceptor are measured with respect to a reference dye Rhodamine 123 ($Q_D = 0.9$) and presented in Table 10.8. From the average lifetime calculation for the CdTe-N719 adduct, we obtain the effective distance (using (10.3) and (10.4)) between the donor and the acceptor, $r_{DA}$ to be $3.72 \pm 0.03$, $4.14 \pm 0.06$, $4.38 \pm 0.08$ and $4.22 \pm 0.04$ nm for
Fig. 10.17 Steady-state emission quenching of different-sized CdTe QDs (a, QD1; b, QD2; c, QD3; d, QD4) in the presence of sensitizing dye N719 and ZnO NRs. Excitation was at 375 nm.

Fig. 10.18 The picosecond-resolved fluorescence transients of four different-sized CdTe QDs (a, QD1; b, QD2; c, QD3; d, QD4) in the absence and presence of sensitizing dye N719 (pink) and ZnO NRs (gray). The excitation wavelength was at 375 nm.

QD1 to QD4, respectively. It is to be noted that the insignificant variations in donor–acceptor distances compared to the radii of the QDs (measured from TEM image) can be rationalized from the fact that the origin of the PL arises essentially from surface states in the CdTe QDs [48]. Both the degree of overlap and distance between donor and acceptor have been accounted simultaneously for FRET.


<table>
<thead>
<tr>
<th>t2</th>
<th>Sample</th>
<th>Observed wavelength (nm)</th>
<th>( \tau_1 ) (ns)</th>
<th>( \tau_2 ) (ns)</th>
<th>( \tau_3 ) (ns)</th>
<th>( \tau_{avg} ) (ns)</th>
<th>( k_{\text{PET}} \times 10^7 ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>QD1 (abs 445 nm)</td>
<td>520</td>
<td>0.93 ± 0.03 (30%)</td>
<td>6.80 ± 0.15 (38%)</td>
<td>35.80 ± 0.45 (32%)</td>
<td>14.30 ± 0.21</td>
<td>-</td>
</tr>
<tr>
<td>1.4</td>
<td>QD1 + N719</td>
<td>520</td>
<td>0.90 ± 0.03 (40%)</td>
<td>4.80 ± 0.12 (38%)</td>
<td>23.40 ± 0.38 (22%)</td>
<td>7.30 ± 0.14</td>
<td>( k_{\text{PET}} = 6.70 ± 0.16 )</td>
</tr>
<tr>
<td>1.5</td>
<td>QD1 + ZnO</td>
<td>520</td>
<td>0.21 ± 0.02 (61%)</td>
<td>4.20 ± 0.05 (25%)</td>
<td>21.30 ± 0.23 (14%)</td>
<td>4.20 ± 0.05</td>
<td>( k_{\text{PET}} = 17.00 ± 0.40 )</td>
</tr>
<tr>
<td>1.6</td>
<td>QD2 (abs 500 nm)</td>
<td>560</td>
<td>1.10 ± 0.15 (15%)</td>
<td>9.90 ± 0.78 (33%)</td>
<td>40.40 ± 0.95 (52%)</td>
<td>24.30 ± 0.77</td>
<td>-</td>
</tr>
<tr>
<td>1.7</td>
<td>QD2 + N719</td>
<td>560</td>
<td>1.20 ± 0.08 (25%)</td>
<td>7.50 ± 0.20 (43%)</td>
<td>34.90 ± 0.50 (32%)</td>
<td>14.70 ± 0.27</td>
<td>( k_{\text{PET}} = 2.60 ± 0.10 )</td>
</tr>
<tr>
<td>1.8</td>
<td>QD2 + ZnO</td>
<td>560</td>
<td>0.21 ± 0.02 (52%)</td>
<td>4.70 ± 0.07 (25%)</td>
<td>26.20 ± 0.16 (23%)</td>
<td>7.30 ± 0.06</td>
<td>( k_{\text{PET}} = 10.00 ± 0.40 )</td>
</tr>
<tr>
<td>1.9</td>
<td>QD3 (abs 550 nm)</td>
<td>610</td>
<td>0.84 ± 0.05 (3%)</td>
<td>16.20 ± 0.88 (45%)</td>
<td>43.60 ± 0.9 (52%)</td>
<td>29.90 ± 0.87</td>
<td>-</td>
</tr>
<tr>
<td>1.10</td>
<td>QD3 + N719</td>
<td>610</td>
<td>0.80 ± 0.08 (7%)</td>
<td>8.80 ± 0.27 (32%)</td>
<td>28.30 ± 0.68 (61%)</td>
<td>20.10 ± 0.51</td>
<td>( k_{\text{PET}} = 1.60 ± 0.03 )</td>
</tr>
<tr>
<td>1.11</td>
<td>QD3 + ZnO</td>
<td>610</td>
<td>0.22 ± 0.07 (61%)</td>
<td>4.30 ± 0.12 (13%)</td>
<td>27.40 ± 0.14 (26%)</td>
<td>7.80 ± 0.02</td>
<td>( k_{\text{PET}} = 9.50 ± 0.06 )</td>
</tr>
<tr>
<td>1.12</td>
<td>QD4 (abs 610 nm)</td>
<td>660</td>
<td>2.35 ± 0.17 (27%)</td>
<td>8.10 ± 0.94 (36%)</td>
<td>31.80 ± 1.40 (37%)</td>
<td>15.30 ± 0.90</td>
<td>-</td>
</tr>
<tr>
<td>1.13</td>
<td>QD4 + N719</td>
<td>660</td>
<td>2.18 ± 0.06 (36%)</td>
<td>7.10 ± 0.30 (36%)</td>
<td>27.30 ± 1.00 (28%)</td>
<td>10.90 ± 0.41</td>
<td>( k_{\text{PET}} = 2.60 ± 0.07 )</td>
</tr>
<tr>
<td>1.14</td>
<td>QD4 + ZnO</td>
<td>660</td>
<td>0.27 ± 0.02 (49%)</td>
<td>4.30 ± 0.50 (31%)</td>
<td>21.70 ± 0.13 (20%)</td>
<td>5.80 ± 0.19</td>
<td>( k_{\text{PET}} = 10.70 ± 0.20 )</td>
</tr>
</tbody>
</table>

The emission from CdTe QDs (emission at 520 nm, 560 nm, 610 nm, and 660 nm, respectively) was detected with 375 nm laser excitation. \( k_{\text{PET}} \) represents non-radiative (FRET/PET) rate constant. Numbers in the parentheses indicate relative weightages.
Table 10.8 Various FRET parameters* obtained for different sized CdTe QDs and N719 dye molecules

<table>
<thead>
<tr>
<th>FRET pairs</th>
<th>$J(\lambda) \times 10^{14}$ (M$^{-1}$ cm$^{-1}$ nm$^{-1}$)</th>
<th>$Q_D$</th>
<th>$R_0$ (nm)</th>
<th>$E_{TR}$ (%)</th>
<th>$r_{DA}$ (nm) from FRET</th>
<th>$r$ (nm) from TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD1 + N719</td>
<td>9.2 ± 0.2</td>
<td>0.18 ± 0.01</td>
<td>3.89 ± 0.05</td>
<td>0.490 ± 0.003</td>
<td>3.72 ± 0.03</td>
<td>2.00 ± 0.11</td>
</tr>
<tr>
<td>QD2 + N719</td>
<td>7.5 ± 0.3</td>
<td>0.29 ± 0.02</td>
<td>3.86 ± 0.07</td>
<td>0.400 ± 0.008</td>
<td>4.14 ± 0.06</td>
<td>2.50 ± 0.20</td>
</tr>
<tr>
<td>QD3 + N719</td>
<td>5.1 ± 0.2</td>
<td>0.45 ± 0.03</td>
<td>3.90 ± 0.07</td>
<td>0.330 ± 0.002</td>
<td>4.38 ± 0.08</td>
<td>3.50 ± 0.14</td>
</tr>
<tr>
<td>QD4 + N719</td>
<td>3.6 ± 0.1</td>
<td>0.40 ± 0.02</td>
<td>3.61 ± 0.04</td>
<td>0.290 ± 0.012</td>
<td>4.22 ± 0.04</td>
<td>4.50 ± 0.25</td>
</tr>
</tbody>
</table>

*Overlap integral ($J(\lambda)$), quantum yield ($Q_D$) in the absence of acceptor, Förster distance ($R_0$), FRET efficiency calculated from time-resolved study ($E_{TR}$), and donor–acceptor distance ($r_{DA}$) between the FRET pairs and radius ($r$) of QDs measured from TEM images.
efficiency estimation. The energy transfer efficiency from QD to N719 is observed
to decrease with a subsequent decrease in overlap integral, which is consistent with
previous studies [118, 119]. The calculated FRET parameters are also presented in
Table 10.8.

Although FRET is an interesting phenomenon that requires neither physical
contact nor charge exchange, however, direct attachment of the CdTe QDs with
the ZnO NRs leads to photo-induced electron transfer (PET) from QDs to the
conduction band of ZnO. Similar PET studies have been reported in the literature,
which is a fundamental process of QDSSC that ultimately pilots a direct sensitiza-
tion of the solar cell performance [48, 120, 121]. The rate of charge recombination,
energy transfer, and charge injection processes (reactions i, ii, and iii, respectively)
dictate the emission decay of CdTe QDs.

\[
\text{CdTe} + h\nu \rightarrow \text{CdTe}(e + h) \rightarrow \text{CdTe} + h\nu' \quad \text{(recombination)} \quad (10.1) \\
\text{dye} + h\nu' \rightarrow \text{dye}^* \quad \text{(energy harvesting)} \quad (10.2) \\
\text{CdTe}(e + h) + \text{ZnO} \rightarrow \text{CdTe}(h) + \text{ZnO}(e) \quad \text{(electron harvesting)} \quad (10.3)
\]

Figure 10.18 shows the emission decay of CdTe QDs anchored to ZnO NR films
on a quartz plate, recorded with 375 nm diode laser excitation. As observed in the
previous studies, both heterogeneity of samples and varying degree of surface
defects introduce multi-exponential decay behavior to the charge recombination
process [47, 48]. A significant decrease in QD lifetime, however, was observed in
the presence of ZnO NRs. In particular, the fast component, which contributes
nearly 61% of the decay, shows a major decrease in lifetime from 0.93 ± 0.03 to
0.21 ± 0.02 ns in the smallest QD-ZnO composite. The apparent rate constants, \(k_{int}\),
were determined for the non-radiative processes by comparing the lifetimes of
CdTe in absence (\(\tau_0\)) and in presence (\(\tau\)) of N719 and ZnO NRs, using (10.10).

\[
k_{int} = \frac{1}{\tau} - \frac{1}{\tau_0} \quad (10.10)
\]

For the smallest QD (i.e., QD1), the apparent rate constant for charge injection
into ZnO NRs was estimated to be \(1.7 \times 10^8 \text{ s}^{-1}\), whereas the rate of energy
transfer from QD1 to N719 is \(6.7 \times 10^7 \text{ s}^{-1}\). Therefore, it is evident that the charge
injection from the excited CdTe to the ZnO NRs occurs with a rate constant that is
an order of magnitude higher than that of energy transfer between CdTe to N719. It
should be noted that the above estimation of average lifetimes takes into account
both short and long-lived components. A major population of the charge injection
process occurs with a greater rate constant (as high as \(10^9 \text{ s}^{-1}\)) if we compare only
the fast component of the emission transients. For example, ~61% of the emission
decay of CdTe QDs on ZnO surface occurs with a lifetime of 0.21 ± 0.02 ns,
indicating the major fraction of the charge injection event occurs on an ultrafast
time scale.
Fig. 10.19 Two different architectures of CdTe QD decorated dye-sensitized ZnO NR substrates, namely, (a) ZnO-QD-N719 and (b) ZnO-N719-QD. (c) The picosecond-resolved fluorescence transients of CdTe QD2 showing PET and FRET in two different architectures. The excitation wavelength was 375 nm and the emission was monitored at 560 nm.

In order to investigate the mechanism of co-sensitization of CdTe QDs in the layered architectures (Fig. 10.19a, b) related to DSSC fabrication, picosecond-resolved fluorescence study was performed (Fig. 10.19c). The fluorescence transient of the bare QDs not in the vicinity of N719 and/or ZnO is shown in the figure as a reference. In the ZnO-QD-N719 architecture (Fig. 10.19a), QDs are sandwiched between ZnO NRs and N719. In these conditions, QDs can either directly transfer electrons to the conduction band (CB) of ZnO NRs or can non-radiatively transfer energy to sensitizer N719. The fluorescence decay parameters, as shown in Table 10.9, are comparable to the distinct lifetimes of an electron transfer process (Table 10.7). Therefore, the picosecond-resolved fluorescence transient of CdTe QDs in the ZnO-QD-N719 architecture reveals a "direct injection" of charge carriers from QDs to ZnO NRs via PET. It is to note that the role of the capping ligands of the colloidal QDs has been demonstrated to have paramount importance on the efficient charge separation at the QD-polymer interface [122]. In this respect, the electron transfer pathway is found to prevail over the FRET process with short chain 3-MPA ligands associated to CdTe QDs. In the other architecture, ZnO–N719–QD (Fig. 10.19b), the QDs are separated by a layer of N719 molecules from the ZnO NRs whereby light harvesting could only occur through FRET from QDs to N719. It is being conventional that the N719 dye binds the ZnO by using its carboxylic groups [123], as a result the residual chains of N719
Table 10.9  Dynamics of picosecond-resolved luminescence transients of CdTe QDs (QD1–QD4) in the presence and absence of sensitizer N719 and ZnO NRs*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Observed wavelength (nm)</th>
<th>$r_1$ (ns)</th>
<th>$r_2$ (ns)</th>
<th>$r_3$ (ns)</th>
<th>$r_{avg}$ (ns)</th>
<th>$k_{trap} \times 10^7$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QD2 (abs 500 nm)</td>
<td>560</td>
<td>1.10 ± 0.15 (15%)</td>
<td>9.90 ± 0.78 (33%)</td>
<td>40.20 ± 0.95 (52%)</td>
<td>24.30 ± 0.77</td>
<td>–</td>
</tr>
<tr>
<td>ZnO–N719–QD2</td>
<td>560</td>
<td>1.20 ± 0.18 (33%)</td>
<td>7.00 ± 0.65 (45%)</td>
<td>32.00 ± 0.86 (22%)</td>
<td>10.60 ± 0.54</td>
<td>5.30 ± 0.31</td>
</tr>
<tr>
<td>ZnO–QD2–N719</td>
<td>560</td>
<td>0.72 ± 0.09 (59%)</td>
<td>4.50 ± 0.45 (33%)</td>
<td>22.80 ± 0.82 (8%)</td>
<td>7.30 ± 0.27</td>
<td>9.60 ± 0.38</td>
</tr>
</tbody>
</table>

*The emission from CdTe QD (emission at 560 nm) was detected with 375 nm laser excitation. Numbers in the parentheses indicate relative weightages.
are free and away from the ZnO, which allows them to interlace with the 3-MPA ligands of the QDs via efficient hydrophilic interactions. This sort of an association results in an average distance between the donor and the acceptor, which lies within the Förster radius and allows an efficient energy transfer. The assorted lifetimes (Table 10.9) of the QDs in this particular configuration are comparable to the decay parameters of the energy transfer route (as shown in Table 10.7), which reveals that an additional “indirect-excitation” of N719 can be introduced by using the sensitivity of FRET and this type of engineered solar cells should contribute to higher photocurrents. The non-radiative rate constants ($k_{nr}$) in these two architectures, as presented in Table 10.9, are almost analogous to the $k_{nr}$ values of the individual systems that lead to either energy or electron transfer pathways (Table 10.7).

The effectiveness of QD decoration in solar cell performance was evaluated by employing them in a photoelectrochemical cell with the two different architectures (Fig. 10.19a, b) as discussed before. The use of CdTe QDs as a sensitizer in photoelectrochemical cells have been investigated by several research groups [19, 48, 124, 125]. DSSC devices fabricated with N719 dye as sensitizer in the presence and the absence of CdTe QDs (QD1 and QD2) were characterized by wavelength-dependent photocurrent spectroscopy (Fig. 10.20a, b) and photocurrent–voltage ($I$–$V$) measurements (Fig. 10.20c); the resulting photovoltaic parameters are summarized in Table 10.10. The wavelength-dependent photocurrent is the number of electrons collected under known photon intensity that was evaluated from the short-circuit photocurrent ($I_{sc}$) measured for different incident wavelengths ($\lambda$). The inset of Fig. 10.20a shows the wavelength-dependent incident power of the monochromator. The photocurrent vs. wavelength plot of the ZnO–QD–N719 architecture is presented in Fig. 10.20a, which shows a spectral response in the range of 350–750 nm. In devices without any modification of the dye sensitizer with QDs, the broad photocurrent spectrum is attributed to the photo-generated charge carrier in sensitizer N719 [20]. As shown in the figure, the presence of QD1 ($\lambda_{abs} = 440$ nm) and QD2 ($\lambda_{abs} = 500$ nm) into the sensitization process lead to a dramatic increase in the photocurrent in the spectral region of blue photons indicating the occurrence of a direct injection of electrons from QDs to ZnO NRs, similar to the observations made by the picosecond-resolved fluorescence studies (Fig. 10.19c). In this case, it is to be noted that dye (N719) loading was lower in ZnO–QD–N719 architecture compared to that of ZnO–N719 assembly due to prior attachment of QD to the ZnO NRs. Therefore, at 530 nm (maximum optical absorption in N719) the photocurrent was found to be lower in ZnO–QD–N719 compared to ZnO–N719 system. Hence, a fair comparison of wavelength-dependent photocurrent and overall device performance of these architectures is not likely when the amounts of dye present in different architectures are not similar. For a better assessment, we engineered devices with similar dye loading in ZnO–N719–QD and ZnO–N719 solar cells. The ZnO–N719–QD architecture shows increased photocurrent (Fig. 10.20b) compared to ZnO–N719 system throughout the spectral region as additional photo-generated charge carriers from N719 dye (via FRET) add up to the net photocurrent. Figure 10.20c shows the $I$–$V$ characteristics of solar cells with ZnO–N719–QD architecture as compared to solar.
Fig. 10.20 Photocurrent vs. wavelength spectra for DSSCs comprising (a) ZnO–QD–N719 and (b) ZnO–N719–QD architectures, respectively. The inset shows incident power vs. wavelength plot. (c) Photocurrent–voltage (J–V) characteristics for ZnO–N719–QD architecture.

cells sensitized with dye only. As shown in Table 10.10, the calculated values of FF and the overall power conversion efficiencies of ZnO–N719-based DSSCs are found to improve in the presence of QD assembly. Overall, the analysis of photo-device data in the measured ZnO–N719–QD configuration reflects similarly the co-sensitization of CdTe QDs tagged with the sensitivity of FRET as observed by the picosecond-resolved fluorescence study (Fig. 10.19c).
Table 10.10 Device performance* of the DSSCs made of two different architecture of QD loading

<table>
<thead>
<tr>
<th>Device with N719</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (μA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO–N719–QD1</td>
<td>0.63 ± 0.04</td>
<td>720 ± 36</td>
<td>35.27 ± 2.70</td>
<td>0.16 ± 0.01</td>
</tr>
<tr>
<td>ZnO–N719–QD2</td>
<td>0.71 ± 0.03</td>
<td>720 ± 29</td>
<td>30.99 ± 1.31</td>
<td>0.16 ± 0.01</td>
</tr>
<tr>
<td>ZnO–N719</td>
<td>0.69 ± 0.05</td>
<td>620 ± 33</td>
<td>29.92 ± 0.50</td>
<td>0.13 ± 0.01</td>
</tr>
</tbody>
</table>

*Short circuit photocurrent densities ($J_{SC}$/cm$^2$), open-circuit voltage ($V_{OC}$), fill factor (FF), and efficiency (η).

Fig. 10.21 (a) Schematic representation of photoconductivity measurement setup by using FTO as one of the electrodes and a small (4 mm diameter) drop of mercury (Hg) on top of the film as a counter electrode. (b) Photoconductivity responses of ZnO NRs (inset), ZnO–N719, and ZnO–N719–QD2 arrays under bias voltage of 2.5 V. The photocurrent was measured across the thickness of the films with 25 mW cm$^{-2}$ incident power from a halogen light source.

The photoconductivity measurement [25] of the ZnO NR, ZnO–N719 and ZnO–N719–QD thin films were carried out in order to better understand the contribution of QDs via FRET to the net photocurrent in the devices. Figure 10.21b shows the photocurrent response for the ZnO NR (inset), ZnO–N719, and...
ZnO–N719–QD2 thin films. An improved photocurrent was observed for the ZnO–N719–QD2 thin film (~260 µA) under illuminated conditions compared to the ZnO–N719 thin film (~190 µA). This shows that an additional “indirect excitation” of N719 can be obtained by decorating the dye molecules with CdTe QDs. For the model DSSCs prepared with the same arrangement of ZnO–N719–QD, we observed a similar enhancement of photocurrent (Fig. 10.20c) in the presence of CdTe QDs, which further confirms the contribution of FRET towards the improvement of efficient energy harvesting in dual-sensitized solar cells.

4 Conclusion

In summary, we have characterized the defect centers, in particular, the oxygen vacancy centers in ZnO NPs and also explored the dynamics of light harvesting in near-infrared region by using OX1 chromophore. By studying picosecond-resolved fluorescence transients at 550 nm, we have shown that efficient FRET (~93 %) occurs from doubly-charged oxygen vacancy centers (V\textsubscript{O}\textsuperscript{2+}) to the acceptor OX1 in the ZnO–OX1 adduct. Comparatively, a less efficient (63 %) light harvesting dynamics was found by monitoring the emission peak at 495 nm, which arises from singly charged oxygen vacancy centers (V\textsubscript{O})\textsuperscript{+}. The overall picture that evolved from our studies is summarized in Scheme 10.1. It is to be noted that the FRET distance (r\textsubscript{DA}) is dependent on the emission wavelength of ZnO NPs whether it arises from surface or near bulk states. Therefore, r\textsubscript{DA} can be interpreted as a parameter that signifies the distance between the probe (OX1) and the different vacancy states of ZnO NPs. Our experimental observations may find relevance in the light harvesting devices using ZnO NPs.

Subsequently, time-correlated single photon counting spectroscopy was carried out to understand the resonance energy transfer phenomenon in a ZnO–N719 system, which is extensively used in DSSCs, as illustrated in Scheme 10.2. The semiconductor ZnO NPs were found to transfer their excited state energy to N719 sensitizers at the surface of the NPs. The observed energy transfer process in the presence of high-energy photons leads to a significant increase in J\textsubscript{SC} (~78 %) in ZnO-based DSSCs leading to more than ~118 % increased energy conversion efficiency (η), whereas TiO\textsubscript{2}-based solar cells showed marginal increase in J\textsubscript{SC} and a slight efficiency improvement (~9 %). It has been found that the energy transfer process does not involve any physical migration of electron from photoex- cited ZnO to the sensitizing dyes. Our study may find relevance in the enhancement of high-energy photon harvesting, which utilizes semiconductor defect centers without any further accumulation of external co-sensitizers. The observed FRET processes in the light harvesting dynamics open a novel way toward the utilization of new materials containing appreciable amount of defect states. These findings provide the importance of the various semiconductors containing inherent optical defect centers and how the defect centers can be beneficially utilized for light harvesting/sensitization.
Scheme 10.5 Dual-sensitization in QD-decorated DSSCs: The system consists of a fluorinated tin oxide (FTO) on which semiconductor ZnO NR (gray cylinder) is fabricated. The sensitizer dye N719 (small red circle) and 3-MPA-capped CdTe QDs (big green circle) are bound to ZnO NR by surface adsorption. The directly attached QDs lead to sensitization via efficient charge injection from excited semiconductor nanocrystal, CdTe into ZnO NR. Moreover, the QDs that are within the close proximity of sensitizing dye N719 introduce an additional indirect excitation of N719 by using the sensitivity of FRET. The upshot of the above dual-sensitization mode is found to be reflected in the overall solar cell performance.

We also provided a mechanistic explanation for the excitation-dependent recombination processes and the catalytic activity of Au NPs in the ZnO–Au NCs, as schematically shown in Scheme 10.4. A better understanding of the charge-transfer processes at the semiconductor–metal interface is crucial for optimizing the performance of such materials in photocatalysis and DSSCs. Our results demonstrate that the excited ZnO NPs resonantly transfer visible optical radiation to the Au NPs upon below band-gap excitation of the semiconductor. A singly charged vacancy center of the ZnO semiconductor is demonstrated to be responsible for the visible optical radiation transfer from ZnO NPs to Au NPs, whereas a combination of the energy transfer between surface defects and surface plasmon of Au NPs, as well as thermalization of photogenerated electron–hole pair and their recombination in the ZnO NPs is believed to take place simultaneously upon above band-edge excitation. We observe that the prepared ZnO–Au NCs are stable and efficient enough for the environmental purification of organic pollutants. As a low-cost photovoltaic cell, the incident photon-to-current conversion efficiency and short-circuit current is significantly improved in presence of Au NPs, which is attributed to the better electron mobility of the ZnO–Au NCs. This approach may give rise to a new class of multifunctional materials with possible applications in energy-conversion devices.

Finally, we have demonstrated the utilization of dual-sensitization in DSSCs as schematically represented in Scheme 10.5. The steady-state and the time-resolved luminescence measurements on 3-MPA-capped CdTe QDs reveal the size-dependent charge injection characteristics of ZnO photoelectrodes. The QDs that are not in a direct contact with the semiconductor can harvest visible light, which is
resonantly transferred to sensitizer N719 dyes, thereby offering an indirect excitation of the dye molecules. To investigate the improvement of light-harvesting because of QD decoration in a DSSC, wavelength-dependent photocurrent, photocurrent–voltage (J–V) characteristics, and photoconductivity measurements were performed for both the QD-assembled and reference (only sensitizing dye) devices. The co-sensitization in the presence of CdTe QDs leads to a significant increment in photocurrent throughout the visible spectral region and also enhances the short-circuit current density as additional photogenerated charge carriers from N719 dye (via FRET) adds up to the net photocurrent. As we continue to modify, study, and improve such FRET pair sensitizers, the realization of truly inexpensive, stable, and efficient DSSCs grows nearer.

**Acknowledgements** S.S. thanks UGC (India) and A.M. thanks CSIR (India) for fellowships. We thank DST (India) for financial grants DST/TM/SERI/2k111/103. We thank Tanujal Bora (Asian Institute of Technology, Bangkok), Sunandan Baruah (Assam Don Bosco University, Guwahati), Kartik Lakshman, Htet H. Kyaw (Sultan Qaboos University, Sultanate of Oman), and Prof. A.K. Raychaudhuri (S. N. Bose National Centre) for the collaboration work.

**References**

1092 59. Yang, P., Yan, H., Mao, S., Russo, R., Johnson, J., Saykally, R., Morris, N., Pham, J., He, R.,
1096 (2007)
1099 64. Ajuria, J., Etxebarría, I., Cambarau, W., Munecas, U., Tenza-Zaera, R., Jimeno, J.C., Pacios,
1102 Science 334, 1530–1533 (2011)
1108 2402–2406 (2008)
1111 72. Yoshida, T., Zhang, J.B., Komatsu, D., Sawatani, S., Minoura, H., Puapote, T., Lincof, D.,
1114 Environ. Sci. 4, 3448–3455 (2011)
1117 (2010)
1125 105, 074308 (2009)
10 Engineering FRET-Based Solar Cells: Manipulation of Energy and Electron...