Exploring dynamics of resonance energy transfer in hybrid Quantum Dot Sensitized Solar Cells (QDSSC)

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Abstract
Graphene based nanomaterials are known to provide new avenues to improve semiconductor based light harvesting devices. This work makes use of graphene quantum dots (GQD) to improve the efficiency of a CdSe Quantum Dot Sensitized Solar Cell (QDSSC) by Förster Resonance Energy Transfer (FRET) mechanism. FRET describes non-radiative energy transfer between two adjacent molecules typically in range from 1 to 10 nm with one molecule as donor and other molecule as acceptor. If the acceptor is in close proximity of the excited donor, then their dipoles align resulting in transfer of excitation energy from donor to acceptor. Here graphene quantum dot acts as the energy donor to enhance light harvesting of CdSe quantum dot which acts as an acceptor in the hybrid solar cell. The introduction of GQD increases the efficiency of CdSe sensitized QDSSC from 0.18 to 0.28% showing an efficiency enhancement of 55%. The improved efficiency is mainly attributed to the 46% increase in current density of the GQD-CdSe solar cell compared to the CdSe QDSSC. The increased performance of the QDSSC owes to the existence of non-radiative energy transfer (FRET) between GQD and CdSe evident from photoluminescence (PL) quenching and lifetime measurements. This FRET system of GQD (donor)-CdSe (acceptor) shows an energy transfer of 48.7% providing new insights for selective light harvesting of the solar spectrum which can be utilised for various potential applications in future.

1. Introduction

Solar energy conversion and photovoltaics have assumed unprecedented importance in the recent times due to the emerging power crisis and environmental concerns. The third generation photovoltaics like Dye Sensitized Solar Cell (DSSC) have been extensively studied due to their low cost easy fabrication and good photoresponse in visible region. Nanocrystal based cells, are also known as Quantum dot (QD) cells, use semiconductor materials from transition metal groups in the size of few nanometers. When a photon strikes the semiconductor QD, electron-hole pairs are generated and electrons reach the conduction band (CB) of the QD. These conduction electrons from QD travel to the CB of wide band gap semiconductor TiO2 in a Quantum Dot Sensitized Solar Cell (QDSSC). Here the QD performs the same role as that of a sensitizing dye in DSSC. These semiconductor quantum dot as sensitizers have additional advantages of band gap tunability, high absorption coefficient, inorganic nature and multiple exciton generation [1].

Quantum dot sensitized solar cells developed along with DSSC have also shown great promise in the recent years with their exciting physical and chemical properties due to quantum confinement effects [2]. The QD based solar cells are predicted to show good efficiencies due to their unique property of multiple exciton generation involving formation of more than one electron - hole pair upon absorption of a single photon. The size/morphology, QD synthesis methods, device architecture etc play a vital role in the efficiency of QD sensitized solar cells [3].

Though QDSSC follows the same operational principle like DSSC the anchoring of QD to TiO2 is not as effective as a dye sensitizer. Hence in spite of major breakthroughs in efficiencies, QDSSC is yet to achieve the
level of performance of DSSC. In spite of these shortcomings, QDSSC research holds promise due to its interesting optical properties, stability and low cost compared to costly molecular dyes.

One of the successful methods in improving the photo-response of the solar cell is to design hybrid structures involving Förster Resonance Energy Transfer (FRET) mechanism. QDs with excellent photophysical properties like bright stable emission, large stokes shift and long fluorescent lifetimes satisfy the primary requisite for a FRET donor [4]. The advantages of QD as donor in QD-Dye nanohybrids leading to high efficiencies has been well documented in various reports [5]. But in contrast QD-QD hybrid systems suffer from shortcomings despite their photostability compared to organic dyes. Though QD-QD systems are feasible and have been successfully used in various biological applications the proper utilization of a QD-QD system with attractive efficiencies is yet to be realised in the QDSSC scenario [6]. The effective absorption of the sensitizer in the visible region is the key factor to any light harvesting assembly. Semiconductor quantum dots like CdSe absorb in the visible region have been used as sensitizers and energy donors in hybrid solar cells leading to considerable improvement in efficiencies [7–9]. The scope of CdSe QDs by utilizing their intrinsic properties can be further enhanced by combining them with appropriate systems. In this report we have used CdSe as acceptors and graphene quantum dots (GQD) as donors in the QD-QD FRET system. QDs by virtue of their unique configuration exhibit stable fluorescence which puts them in a better position over the conventionally used semiconductor QDs [10]. Apart from good optical behaviour, GQDs possess chemical stability, biocompatibility and low toxicity which makes them one of the most sought out new generation materials for a wide variety of applications [11].

Further GQDs have been explored as energy donors for N719 dyes with considerable efficiencies have been reported in the recent times [12]. A hybrid solar cell with GQD as energy donor to CdSe sensitized TiO2 solar cell has been designed in this experiment. The improved efficiency of the CdSe sensitized cell with the introduction of GQD has been justified by non radiative energy transfer mechanism using spectral matching, photoluminescence and lifetime measurements.

2. Experimental section

2.1. Materials

Cadmium chloride, selenium, 3-mercaptopropionic acid (MPA), L Ascorbic acid were purchased from Sigma Aldrich and used directly without further purification. TiO2 nanoparticles (P25), fluorine doped tin oxide (FTO-71)/Sq cm), hexachloroplatinatic acid (H2PtCl6), potassium iodide (KI) (99.5%) and N719 dye were obtained from Sigma-Aldrich and iodine (I2) from MERCK. Double distilled water (Millipore System), acetone, ethanol and methanol (≥99% Sigma Aldrich) were used as solvents.

2.2. Synthesis of CdSe QD and GQDs

CdSe quantum dots were prepared by previously reported method using a solution route at ambient temperature [13]. Briefly, aqueous solution of cadmium chloride was prepared with addition of a required amount of MPA (0.24 M) under constant stirring to get a clear solution at pH maintained between 9 and 10. Further selenium powder dissolved in hydrazine hydrate was slowly added to the solution to get a pale yellow colloid.

GQDs were prepared through a two-step process, that is formation of graphene oxide (GO) from graphite flakes and further reduction to graphene QDs as reported in literature with minor modifications. Firstly GO was obtained by oxidation of graphite treated with a mixture of H2SO4 and H2PO4 along with KMnO4 using Tour’s method [14] in an ice bath. Afterwards continuous stirring followed by addition of hydrogen peroxide resulted in the oxidised form of graphite. This solution on being subjected to ultrasonication leads to graphene oxide. The obtained graphene oxide (0.5 mg ml−1) is mixed with ascorbic acid solution (26.4 mg ml−1) kept under hydrothermal condition in a Teflon lined stainless steel autoclave at 200 °C for six hours. After cooling, the supernant liquid was taken out, centrifuged at 10,000 rpm and collected through a syringe filter to be used for further characterisations.

2.3. Fabrication of QDSSC device

The FTO glass plates were first cleaned using detergent solution followed by successive washing with distilled water, isopropanol and acetone using an ultrasonicator. These plates after drying were doctor bladed with 25 nm sized TiO2 paste prepared using TiO2 powder, ethanol and TritonX-100. These electrodes after air drying overnight were sintered at 450 °C for 30 min. On cooling, the area confinement of 0.25 cm2 was done and the TiO2 film was dipped in CdSe colloid for 2, 5 and 24 h. Further the GQDs were drop casted onto the photoanode kept at 40 °C in a hot air oven. The electrolyte was prepared by mixing 0.6 M 4-butyl methyl imidazolium iodide (BMII), 0.04 M Iodine (I2), 0.1 M lithium iodide (LiI), 0.1 M guanidiumthiocyanate (GuSCN) and 0.5 M tertiary...
butyl pyridine in acetonitrile. The hybrid photo-anode and electrodeposited platinum counter electrode were assembled to form a solar cell by sandwiching the redox electrolyte using binder clips.

2.4. Characterisation Techniques

The UV–vis spectrophotometer (T90, PG Instruments) was used to measure the nature of absorbance of the nanoparticles in the visible range of the solar spectrum. The size of the synthesized nanoparticles was determined by transmission electron microscopy (TEM) with Jeol/JEM 2100 using LaB6 source operated at 200 kV. Fourier transform infrared spectra (FTIR) of GQDs and CdSe were measured using PerkinElmer Spectrum Two FTIR spectrometer in the wavenumber range of 4000–450 cm$^{-1}$. The photoluminescent (PL) measurements were conducted using PerkinElmer LS 55 in the visible range. For measuring the performance of DSSC, current-voltage (I–V) characteristics were done using solar simulator (Scientech) under 1 sun illumination (100 mW cm$^{-2}$). The pulsed diode excitation of 370 nm from Flurocube-lifetime system (JOBIN-VYON) was used to measure lifetimes of the samples.

3. Results and discussion

3.1. TEM and SEM analysis

TEM studies were conducted to understand the shape and morphology of the GQD and CdSe colloids. Figure 1 represents the TEM images of GQD (figure 1(a)) and CdSe (figure 1(b)) showing homogenous distribution of particles. The sizes are observed to be below 10 nm as seen from the TEM images. The synthesized CdSe and GQD are well dispersed and uniformly distributed making them suitable for solar cell fabrication. The presence of fringes along with the bright spots in SAED pattern (inset a and b) shows the crystalline nature of the samples.

From figure 1(a) (inset) the inter-planer distance d is calculated to be 0.34 nm corresponding to 002 plane of graphitic carbon [15]. Similar calculation from SAED pattern of figure 1(b) (inset) gives value of 0.22 nm corresponding to 220 plane of CdSe QD [16].

The SEM and EDAX spectrum of the hybrid photo-anode are presented in figures 2(a) and (b) respectively. The peaks corresponding to C, Cd, Se indicate the presence of these elements in TiO$_2$ photo-anode.

3.2. Optical properties

Fourier transform infrared (FTIR) analysis of the GQD and CdSe are shown in figures 3(a) and (b) respectively. The GQD synthesized in this work is hydrophilic as evident from the presence of carboxylic and hydroxyl groups as seen in the graph. The GQD shows a broadband centred at 3487 cm$^{-1}$ representing free O–H bonding. The bands at 1647 cm$^{-1}$ and 1647 cm$^{-1}$ reveal the presence of COOH bonding and aromatic ring respectively [17].

The 3455 cm$^{-1}$ peak in the CdSe correspond to the O–H vibration and the small peaks at 2923 cm$^{-1}$, 2855 cm$^{-1}$ correspond to the CH stretching vibrations due to MPA molecules respectively. The peaks at 1644 cm$^{-1}$, 1399 cm$^{-1}$ correspond to the vibration of free carboxylic acid and symmetric stretching vibration of C–O groups as reported elsewhere [18].

GQDs are known to absorb at shorter wavelength region due to the pi-pi* transition of the aromatic network in its basal structure. It is seen that GQD shows strong absorption at UV region with a peak at 268 nm and a tail extending in the visible region in accordance with the previous reports (Figure 4 a). The peak around 268 nm also...
indicates the small size of the samples due to quantum confinement effect [19] which has been well supported by TEM results. The Raman spectrum (Figure 4 b) shows two distinct bands D and G at 1349 and 1593 cm⁻¹ respectively. The peak at 1337 cm⁻¹ can be assigned to D band, which is mainly attributed to the vibrations of carbon atoms due to the presence of structural defects. And the peak at 1583 cm⁻¹, which corresponds to G band, is due to in-plane vibrations of sp² bonded carbon atoms. An intensity of the disordered D band to the crystalline G band ID/IG is found to be around 0.84 [20].
Figure 5(a) shows the prepared GQD and CdSe solutions for solar cell applications. Figure 5(b) shows the increase in absorption of the CdSe solution with increasing amount of GQD in 200–400 nm region. The increase in absorbance in CdSe upon addition of GQD may be responsible for the increase in light absorption by the CdSe photo-anode. However it is seen that major absorption in the region of 300–400 nm corresponding to the absorption of the two quantum dots. This narrow spectral window may be the reason for the lower efficiencies of the solar cells used in this study.

3.3. PL quenching and FRET parameters

Figure 6(a) shows the absorption spectra of CdSe in 200–300 range with a tail extending to the visible region, whereas a broad emission peak starting from 357 nm up to 600 nm is seen in the case of GQDs. There is a reasonable overlap between the CdSe QD acceptor absorption spectrum and GQD donor emission spectrum abiding by the primary conditions of FRET study that the fluorescence emission spectrum of the donor and the UV–vis absorbance spectrum of the acceptor must overlap with each other. Similarly the quenching of fluorescence spectra of GQD with successive addition of CdSe is studied as shown in figure 6(b) provides evidence of resonance energy transfer from donor(GQD) to acceptor (CdSe). The overlap integral and quenching data is used to quantify the FRET parameters in this system.

The FRET radius $R_0$ (in nm) corresponding to the distance between the donor and acceptor at which probability of energy transfer is 50% is given by

$$R_0 = 0.0211(k^2 \times n^{-4} \times Q_D \times J_o)^{1/6}$$

where $k^2$ is taken to be 2/3, $n$ is the refractive index of water taken to be 1.33, $Q_D$ is the quantum yield and $J_o$ is the spectral overlap integral between the donor emission and acceptor absorption.
The spectral overlap integral is expressed as

\[ J = \int_0^\infty I_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \]

where \( \varepsilon \) is the molar absorption coefficient in M\(^{-1}\) cm\(^{-1}\), \( \lambda \) is the wavelength of the light in nm and \( I_D \) is the emission intensity of the donor normalized on the wavelength scale [21]. The quantum yield (Qs) of GQD was calculated using quinine sulphate in 0.1 M H\(_2\)SO\(_4\) as reference \((Q_R = 0.54)\) using the following equation

\[ Q_S = \frac{F_S \times A_R \times n_r^2 \times Q_R}{F_R \times A_S \times n_r^2} \]

where \( F_s \) and \( F_R \) are integrated fluorescence emission of sample and reference respectively. \( A_R \) and \( A_S \) are the absorbance at the exciting wavelength of the reference and sample and \( n \) is the refractive index of the medium (1.33 for water), which is same for both sample and reference that is water in this case (see table 1).

From the calculation \( R_0 \) was found to be 2.8 nm pointing towards FRET mechanism which occurs in the range of 1–10 nm [22]. The energy transfer \( E_T \) in terms of \( R_0 \) is given by the following equation

\[ E_T = \frac{R_0^6}{r^6 + R_0^6} \]

where ‘\( r \)’ is the distance between the donor-acceptor pair of GQD-CdSe FRET system.

### 3.4. Solar cell characterizations and lifetime measurements

To utilise FRET to improve energy harvesting in real energy conversion application QD-QD hybrid architecture in DSSC was constructed and tested for improved cell performance as shown in figure 7. The device fabrication was done through different methods (a) CdSe dip coated into TiO\(_2\) and GQD drop casted on it (sample is coded as GQD-CD) (b) GQD alone (GQ1), GQD dip coated first and then CdSe drop casted (GQ2), and both CdSe and GQD dip coated (GQ3).

The TiO\(_2\) photoanodes were dip coated in CdSe solution for various dipping times 0.5, 2, 5, 12 h for QDSSC configuration and two hours dipping was seen to give the best efficiency. The CdSe cell with 2 h dipping was chosen to be used as the hybrid cell because of its optimum performance. It is observed that the efficiency of the CdSe cells does not improve with increasing the dipping time.

The poor performance of CdSe cells with higher dipping time could be due to the aggregation of QDs on the surface leading to higher resistance to electron transfer [23]. The results for CdSe cells with various dipping times and different combinations of hybrid cells of GQD and CdSe have been tabulated in table 2.
From the values presented in table 2, it is observed that photoanode with dip coating of CdSe and drop casting of GQD (GQD-CD-TiO₂-2 h) shows the maximum efficiency compared to hybrid cells GQ2 and GQ3. The dip coating of both quantum dots in GQ3 gives lesser efficiency of 0.016% which may be due to the incomplete attachment of the sensitizers to the photo-electrode surface due to the leakage of water based sensitizers. The GQ2 system first sensitizes with GQD and then sensitizes with CdSe shows an efficiency of 0.088%. Highest efficiency of 0.28% is observed for the cell with CdSe dip coating (2 h) followed by GQD drop casting over TiO₂ photo-electrode.

The reason for the lowered efficiency in GQ2 is that GQD having lesser sensitizing ability compared to CdSe is not suitable for being the first sensitizing layer to TiO₂ photo-anode as shown in table 1. This also confirms that the FRET donor (GQD) helps the acceptor in facilitating electron transfer to photo-anode and does not act as a co-sensitizer. The most favoured device design is the acceptor being the first sensitizing layer followed by donor as represented in GQD-CD system. The GQD-CD hybrid cell shows an efficiency enhancement of 55% from 0.18% to 0.28%. The GQD-CD photo-anode had an improved Jsc of 0.62 mA cm⁻² compared to 0.424 mA cm⁻² of bare CdSe photo-anode showing 46% enhancement. Similarly Voc also showed improvement from 0.688 V to 0.735 V in a hybrid QD cell showing an increase of 6.7%. It is seen that the increase in Voc contributes majorly to the efficiency enhancement compared to the slight increase of Voc of the hybrid cell. This also supports energy transfer between GQD and CdSe leading to more excited states in CdSe driving more electrons to the conduction band of TiO₂ resulting in increased photocurrent generation [24]. From table 1 it is seen that the light harvesting, which was ineffective due to low quantum yield of GQD (5.26%) is made effective by transferring photons to CdSe (QY-34%) in the hybrid sample.

To confirm the energy transfer from GQD to CdSe QD, decay measurements were taken using Time Correlated Single Photon Counting (TCSPC) studies using a laser excitation of 370 nm and fitted using a three exponential function. The average decay times obtained are 0.41 and 0.21 ns for GQD and GQD-CD combination (b) CdSe Lifetime.

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The energy transfer efficiency (ϕ) and rate of energy transfer kT is expressed through the following formula in terms of lifetime

| Sample          | Jsc (mA cm⁻²) | Voc (V) | FF (%) | Efficiency η (%) |
|-----------------|---------------|---------|--------|------------------|
| CdSe-TiO₂-0.5 hr| 0.196         | 0.454   | 50.4   | 0.045            |
| CdSe-TiO₂-2 hr  | 0.424         | 0.688   | 62.0   | 0.180            |
| CdSe-TiO₂-5 hr  | 0.308         | 0.661   | 57.7   | 0.117            |
| CdSe-TiO₂-12 hr | 0.240         | 0.537   | 50.4   | 0.065            |
| GQD-CD-TiO₂-2 h | 0.620         | 0.735   | 61.4   | 0.280            |
| GQ 1 (GQD—TiO₂) | 0.054         | 0.316   | 63.7   | 0.010            |
| GQ2 (CD-GQD- TiO₂) | 0.365     | 0.523   | 47.7   | 0.088            |
| GQ3 (GQD-CD—TiO₂) | 0.080      | 0.474   | 43.8   | 0.016            |

Figure 8. (a) Lifetime measurement of GQD and GQD-CdSe (GQD-CD) combination (b) CdSe Lifetime.
where $\tau_{DA}$ and $\tau_D$ are the lifetimes of donor in presence and absence of acceptor respectively [25]. From the average lifetime values the energy transfer is calculated to be 48.7% as shown in table 3.

From the lifetime measurements it is seen that the hybrid sample of GQD-CdSe (GQD-CD) has an improved lifetime of 0.21 ns compared to the acceptor (CdSe) lifetime (i.e. 0.14 ns) which is in accordance with the principles of FRET. The signature of FRET is seen from the loss of fluorescence of the donor or an increase of fluorescence of an acceptor molecule. In other words FRET decreases the lifetime of donor’s (GQD) $\tau_D$ excited state (0.41 ns to 0.21 ns) on addition of acceptor GQD-CdSe ($\tau_{DA}$) [26].

The Hybrid system in this investigation effectively uses low quantum yield (QY) long lifetime of GQD to pair with high QY and lower lifetime of CdSe to demonstrate excellent possibility of FRET in solar cells. The donor to acceptor distance is within the range of 0.5R₀ to 1.5R₀ indicating the efficient energy transfer from GQD to CdSe. FRET mechanism using Jablonski diagram describes the nature of energy transfer from the Donor to the Acceptor during the FRET process and has been illustrated in figure 9. The calculated quantum yield is 0.056 and 0.35 respectively for GQD and CdSe quantum dots.

### 4. Conclusion

The FRET between GQD as donor and CdSe as acceptor has been explored for the first time in a QDSSC. The QDs synthesized through a known protocol were investigated for energy transfer efficiencies in a QD-QD hybrid system. The PL quenching experiments and lifetime measurements confirmed the energy transfer from GQD to CdSe QD. The solar cell studies were conducted to exploit this energy transfer to improve the efficiency of the solar cells. The dip coating time optimisation was done from 0.5 h to 12 h and 2 h dipping gave the best result. Further various solar cell combinations were used and the best efficiency was showed by solar cell having dip coated CdSe QD as the first sensitizing layer and GQD drop casted on top of it. The energy efficiency improved from 0.18% to 0.28% showing 55.5% enhancement in the efficiency. The major contribution to efficiency

### Table 3. FRET parameters of the GQD-CdSe hybrid sample.

|      | GQD ($\tau_D$) | CdSe ($\tau_A$) | GQD-CdSe ($\tau_{DA}$) | $kT$ (transfer rate) | $\phi_{ET}$ |
|------|----------------|-----------------|------------------------|---------------------|-------------|
| 0.41 ns | 0.14 ns         | 0.21 ns         | 2.29 x 10⁸ s⁻¹           | 48.7%               |

Figure 9. Schematic showing the FRET mechanism between GQD and CdSe quantum dots.
comes from $J_{sc}$ which increases to 0.62 mA cm$^{-2}$ compared to 0.424 mA cm$^{-2}$ of bare CdSe photo-anode showing 46% enhancement. The $V_{oc}$ increases slightly from 0.688 V to 0.735 V in a hybrid solar cell showing an enhancement of 6.8%. The FRET mechanism is elucidated through PL quenching and lifetime measurements showing energy transfer of about 48.7%. Though the efficiency presented in this FRET system is low this combination is likely to be helpful in harnessing selective regions particularly near UV regions of the electromagnetic spectrum for major breakthroughs in future applications.

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