Graphitic carbon nitride quantum dots (g-C$_3$N$_4$) to improve photovoltaic performance of polymer solar cell by combining Förster resonance energy transfer (FRET) and morphological effects

Saurabh Pareek, Sobia Waheed, Aniket Rana, Punit Sharma and Supravat Karak

Organic & Hybrid Electronics Device Lab, Centre for Energy Studies, Indian Institute of Technology Delhi, New Delhi, India

Author to whom any correspondence should be addressed.

E-mail: saurabhporeek23@gmail.com, sobia.waheed@ces.iitd.ac.in, aniket.rana@gmail.com, punit.sharma@ces.iitd.ac.in and supravat@ces.iitd.ac.in

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Abstract

In this study, multifunctionality of graphitic carbon nitride quantum dots (g-C$_3$N$_4$ QDs) have been explored as a photovoltaic booster for polymer solar cell. Facile synthesis method of g-C$_3$N$_4$ QDs using organic solvent like o-dichlorobenzene which is commonly used for cell fabrication, has been demonstrated. Photovoltaic effect formation and various effects of QDs on energy transfer, carrier transport and nanoscale film morphology of the devices have been investigated thoroughly by incorporating g-C$_3$N$_4$ QDs as a third component into a well-established material combination of P3HT: PC$_{71}$BM blend films. While systematic variation of device performances was observed with varying concentration of QDs, at an optimal concentration of 2%, almost 40% performance improvement was achieved compared to the pristine devices. The g-C$_3$N$_4$ QDs were found to assist Förster resonance energy transfer (FRET) between the QDs and host polymer, improving overall energy harvesting capability of the devices. The emission spectra of g-C$_3$N$_4$ QDs (λ$_{Ems}$ = 400–550) and absorption spectra of P3HT (λ$_{Abs}$ = 400–600) were found to have overlapping features which enabled the QDs to transfer ultraviolet region photon energy to P3HT. The g-C$_3$N$_4$ QDs were also found to be favorable for maintaining nanoscale phase segregation of the active layer with improved crystallinity which is crucial for efficient exciton dissociation and faster charge extraction. The enhanced power conversion efficiency thus attributed to the combined consequences of improved morphology and FRET effect. This study opens new prospects for developing high-efficiency solution processable photovoltaic devices using g-C$_3$N$_4$ QDs as the third component of the active layer.

1. Introduction

In recent past, photovoltaic technology has shown rapid progress with promising outcome as alternative renewable sources to overcome the energy and environmental crisis of present era. At present, the technology is mainly centered to inorganic semiconductors such as crystalline/polycrystalline silicon, cadmium telluride or copper indium germanium selenide. However while maximum power conversion efficiency at cell level approaches to 15%–25%, high fabrication cost and material toxicity put doubts and limits for their widespread commercial deployment. As a viable solution, thin film based solar cells fabricated with π-conjugated organic semiconductors have emerged as an interesting alternative material choice with cost effective high-throughput roll-to-roll production compatibility [1–3]. Since Tang et al reported the first successful organic photovoltaic device with 1% power conversion efficiency (PCE) in 1986, great progress has been made in this field with currently power conversion efficiency approaching 16% for single junction cell, 17% in tandem cell and 26% for non-fullerene acceptor based devices under indoor light [4–6]. Major breakthroughs have resulted from innovative approaches, such as the development of bulk heterojunction architectures, synthesis of tailored push-
pull type low band gap materials, optimization of active layer morphology and electrode interfaces, and development of advanced device architectures such as inverted and tandem structures [7–14]. Recently ternary devices where two donor molecules are used instead of one, showed promising results as they can broaden the light harvesting properties of the devices by absorbing the complementary part of the solar spectrum. In addition, such devices are easy to fabricate as well as they do not involve the complex multi-layer deposition and sub cell balancing like tandem devices. So far several organic and inorganic material have been tested as the third component is solar cell for performance improvement [15–20]. Carbon based materials like carbon dots, graphene, graphene QDs etc have shown promising features particularly for OPV applications [20–22].

Here we explore graphitic carbon nitride, an emerging 2D material analogous to graphite composed of 2-dimensional sheets of heptazine interconnected by tertiary amines [23], as a photovoltaic performance booster for polymer solar cell. Although it has been widely used as photocatalysts for water splitting, electrocatalysts for oxygen reduction, for solar fuels etc [24–27] but we are unaware of many studies for its photovoltaic application [28, 29]. It possess promising material properties such as n type semiconducting nature, strong absorption in UV-visible region, high chemical stability and tunable optoelectronic properties which could be useful for OPV application [30–32]. Interestingly, g-C3N4 QDs found to absorb in the ultraviolet region while emitting visible photons which can be reabsorbed by polymer molecules. Here we want to explore this unique feature of g-C3N4 QDs to broaden the energy harvesting spectra of polymer solar cells by incorporating them as the third component into the active layer.

In this study, g-C3N4 QDs were synthesized in organic solvent by chemical oxidation of bulk g-C3N4 followed by hydrothermal treatment and used as third component with varying concentration into the active layer of poly(3-hexylthiophene-2,5-diyl): [6,6]-phenyl-C71-butryc acid methyl ester (P3HT:PC71BM) blend films. Here for the first time we demonstrate non radiative Förster resonance energy transfer (FRET) between g-C3N4 QDs and host polymer P3HT, leading to a significantly improved cell efficiency. The QDs were also found to play crucial role as crystallinity improver of the active layer. Various effects of g-C3N4 QDs on morphology and optoelectronics properties of the device were investigated thoroughly to understand the energy transfer mechanism and performance improvement in details.

2. Experimental

2.1. Materials

Melamine (C3H6N6, 99%), Poly (3,4-ethylenedioxy thiophene)-poly(styrenesulfonate) (PEDOT: PSS, 1.3 wt% dispersion in H2O, conductive grade), Lithium Fluoride (LiF) and P3HT, PC71BM were purchased from Sigma Aldrich and 1-Material respectively. All the chemicals were used as received without purification.

2.2. Synthesis of graphitic carbon nitride quantum dots (g-C3N4 QDs)

The bulk g-C3N4 was prepared using thermal polymerization of melamine [33, 34]. 100 mg of bulk material was acidified by nitric acid (10 M) under ultra-sonication for 4 h. After acidification material was refluxed at 100 °C for 18 h allowed to cool to room temperature followed by removal of acid. The remaining product washed with deionized (DI) water until neutral and redispersed in DI by ultra-sonication for 2 h. The suspension so formed was heated in PTFE lined autoclave at 200 °C (12 h), filtered and dried under vacuum overnight. The product so obtained was dispersed in o-dichlorobenzene (DCB) by ultra-sonication for 4 h, finally filtered through 0.22 μm membrane to obtain highly dispersed g-C3N4 QDs [35–37]. The scheme for bulk and g-C3N4 QDs are shown in figures S1 and S2 is available online at stacks.iop.org/NANOX/1/010057/mmmedia respectively in supporting information.

2.3. Device fabrication

For active layer preparation P3HT and PC71BM were mixed in 1:0.8 weight ratio in chlorobenzene by overnight stirring at 40°C, filtered by 0.45 μm PTFE filter. The g-C3N4 QDs were added to filtered P3HT:PC71BM with different volume concentration (1%, 2%, 3%, 4%, 6%, 8%) and again stirred overnight. The device fabrication basically involves five steps viz. (1) cleaning the ITO substrates by ultra-sonication in soap solution, deionized water, acetone and isopropanol with each step for 15 min subsequently dried with N2 gun and placed in oven at 120 °C overnight. (2) Ozone treatment for dried ITO substrates for 20 min (3) Ozone treated ITO was coated with PEDOT: PSS layer at 3500 rpm (60 s), annealed at 150 °C for 30 min (4) Active layer of P3HT: PC71BM (1:0.8) with and without g-C3N4 QDs were deposited on the PEDOT: PSS later at 1000 rpm (60 s), annealed at 120 °C for 20 min under N2 atmosphere. (5) Finally device was transferred to vacuum chamber for sequential deposition of LiF (0.6 nm) and Al (100 nm) top electrode at 5 × 10−6 mbar vacuum. For SCLC measurement the electron only and hole only device were prepared. For the former one active layer of P3HT: PC71BM with and without g-C3N4 QDs were directly coated on cleaned ITO substrate (without UV-Ozone treatment) at 1000 rpm.
(60 s), annealed at 120 °C for 20 min, finally transferred to vacuum chamber for sequential deposition of LiF (0.6 nm) and Al (100 nm) at 5 × 10⁻⁶ mbar vacuum. For the later one (hole only) ozone treated ITO was coated with PEDOT: PSS layer at 3500 rpm (60 s), annealed at 150 °C for 30 min. The active layer of P3HT: PC71BM with and without g-C₃N₄ QDs were then coated at 1000 rpm (60 s), annealed at 120 °C for 20 min, finally transferred to vacuum chamber for sequential deposition of Au (100 nm) at 5 × 10⁻⁶ mbar vacuum. The active area of all devices was 2 × 2 mm².

2.4. Measurement and characterization
X-ray diffraction pattern were recorded on Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.54 Å), at scan speed of 0.33 °s⁻¹. HRTEM images were recorded by FEI Tecnai TF20 high resolution transmission electron microscope at an accelerating voltage of 200 KV. Atomic force microscope measurement were performed on Bruker Dimension Icon with Scan Assyst atomic force microscope in tapping mode. FTIR spectra were recorded by Thermo scientific NICOLET iS50 FT-IR spectrometer in ATR mode for identification of functional groups and bonding in the range of 4000–600 cm⁻¹. The UV-Visible absorption were recorded by Perkin Elmer Lambda 1050 UV-Vis NIR spectrophotometer in the range of 300 to 800 nm. The Photoluminescence spectra were measured by SCHIMADZU RF-6000 PC fluorescence spectrophotometer at an excitation wavelength of 350 nm and 490 nm. The current density versus voltage (J-V) characteristic were measured by using keithley 2401 source meter under stimulated AM1.5G irradiation of 76 mW cm⁻² using AAA LED solar simulator.

3. Results and discussion
3.1. Synthesis and characterization of g-C₃N₄ QDs
In this study, we have synthesized the g-C₃N₄ QDs in o-dichlorobenzene purposefully to maintain its compatibility with the device fabrication process. The structural change and chemical composition of prepared material were investigated by XRD, TEM and FTIR spectroscopy. Figure 1 shows the X-ray diffraction pattern of bulk g-C₃N₄ and g-C₃N₄ QDs. The bulk g-C₃N₄ shows two diffraction peaks around 13.1° (100) and 27.5° (002) as reported in literatures [38]. For g-C₃N₄ QDs the highly intense peak corresponding to (002) plane slightly shifts towards higher angle compared to the bulk material, indicating the decrease in the interplanar stacking of aromatic units from 0.322 nm for bulk to 0.318 nm for QDs. Reduction in peak intensity for (100) plane might be associated to reduction in size of layer [38].

Figure 2(a) shows the transmission electron microscopy image of bulk g-C₃N₄ representing large number of stacked layers of C–N aromatic motif and the corresponding SAED pattern in the inset of figure 2(a) reveals random orientation of layers. Figure 2(b) shows the TEM image of the QDs, formed by chemical oxidation of flakes, figure 2(d) shows particle size distribution in the range of 1–10 nm with average size around 4 nm. The figure 2(c) shows the HRTEM fringes with 0.318 nm inter-planar spacing which matches well with the d-spacing measured from x-ray diffraction.

The FTIR spectrum of bulk g-C₃N₄ and g-C₃N₄ QDs are shown in figure 3. For the bulk material, broad band features were observed around 3400–3000 cm⁻¹ corresponds to stretching vibration of primary and secondary
amines and H bonding [39]. The bands between 1600–1200 cm$^{-1}$ arises from stretching vibration associated with aromatic C–N heterocycle [40, 41] whereas the sharp bands around 880–800 cm$^{-1}$ corresponds to out of plane breathing mode of heptazine motif [33, 42]. No significant change in the structure of QDs were observed as all characteristic vibrational bands similar to the bulk g-C$_3$N$_4$ were identified, confirming that the heptazine structure is retained for the QDs. However, several new bands were observed for QDs around 1000 and 1700

Figure 2. TEM images (a) Bulk g-C$_3$N$_4$, (b) g-C$_3$N$_4$ QDs, (c) HRTEM Fringes of g-C$_3$N$_4$ QDs, and (d) Particle size distribution of g-C$_3$N$_4$ QDs with Gaussian fit.

Figure 3. FTIR spectra of Bulk g-C$_3$N$_4$ and g-C$_3$N$_4$ QDs.
which are assigned to stretching vibrations of C–O and C=O due to chemical oxidation [43]. Due to the size effect and partial breakage of tri-s-triazine ring, several vibrational bands between 1000 and 1800 cm\(^{-1}\) were found missing or with reduced intensity for the QDs as well [43, 44]. The g-C\(_3\)N\(_4\) QDs were found well dispersed in DCB due to the presence of additional functional groups, layered structure and small size [28] which is essential for device application.

3.2. Effect of QDs on morphology of P3HT: PC\(_{71}\)BM blend active layer

The effect of incorporation of g-C\(_3\)N\(_4\) QDs on crystallization and nanoscale phase segregation of P3HT: PC\(_{71}\)BM active layer were investigated by grazing incidence X- Ray diffraction and AFM studies. Figure 4 shows the XRD pattern for P3HT: PC\(_{71}\)BM films with and w/o QDs at different concentration and its magnified image is shown in figure S3 (supporting information). Two characteristic peaks attributed to edge on orientation of P3HT lamella structure were observed around 5.32\(^\circ\) (100) and 10.69\(^\circ\) (200) with d-spacing of 1.6–1.7 nm, suggesting high degree of crystallinity with in plane \(\pi\)–\(\pi\) stacking of conjugated polymer ring and out of plane stacking of alkyl group perpendicular to substrate [45, 46]. No significant change in the XRD pattern was observed on addition of small amount of QDs except slight change in FWHM of the (100) peak which indicates change of crystallite size of the active layer. Among all the samples 2% doped sample showed maximum intense peak at 5.32\(^\circ\), possibly representing highest degree of crystallinity. The crystallite size, measured using Scherer method, of P3HT in 2% doped sample was found to be around 18.5 nm which is slightly higher compared to pristine film by 0.6 nm and further decreased with increasing concentration of QDs (18.07 nm for 4%, 17.9 nm for 6% and 8%) which could be linked to stacking defects in P3HT: PC\(_{71}\)BM thin film. The increased crystallite size of P3HT is expected to show better charge transport properties due to improved phase separation [16, 47–49].

Figure 5 shows the AFM images for the corresponding films. The effect of g-C\(_3\)N\(_4\) QDs incorporation on molecular aggregation was monitored by analysing the surface topology and estimating the film roughness. Smooth features with surface roughness of about 0.78 nm were observed for the pristine P3HT:PC\(_{71}\)BM film while after incorporation of QDs, the surface roughness increased to 1.7 nm for 2% sample. However surface roughness decreased further with increasing concentration of QDs (1.06 nm, 0.88 nm, 0.82 nm for 4%, 6% and 8% samples respectively) but still higher than that of pristine film. It has been previously reported that such moderate changes of surface roughness in nm range arises due to reorientation and better crystallization of polymer chains. Therefore it can be safely assumed that our AFM results are consistent with XRD which indicates 2% samples are having improved crystallinity of P3HT. Such effect of g-C\(_3\)N\(_4\) QDs on film morphology could be useful for photovoltaic application as it will lead to increased effective donor-acceptor interface area which is extremely crucial for exciton dissociation in OPVs [45].

3.3. Effect of QDs on optical properties of the film

The absorption spectra of g-C\(_3\)N\(_4\) QDs, P3HT and photoluminescence spectra of g-C\(_3\)N\(_4\) QDs are shown in figure 6(a). It is clearly evident that fluorescence spectra of g-C\(_3\)N\(_4\) QDs significantly overlaps with absorption spectra of P3HT in the wavelength range between 400–500 nm. Hence, Förster resonance energy transfer (FRET) is expected to occur between g-C\(_3\)N\(_4\) QDs to P3HT. However the strength of such interaction will strongly depend on the overlap integral of g-C\(_3\)N\(_4\) QDs and P3HT and the
Figure 5. AFM images (a) P3HT: PC71BM, (b)–(e) 2%, 4%, 6% and 8% of g-C₃N₄ QDs concentration and (f) roughness estimation.

Figure 6. (a) Optical characteristics of g-C₃N₄ QDs and P3HT, (b) PL spectra of P3HT and their mixture with different concentration of g-C₃N₄ QDs.
Förster radius (Ro) which is basically the separation distance between donor and acceptor component. In our case the Ro is found to be 3.01 nm which further confirms the feasibility of efficient FRET effect formation between g-C$_3$N$_4$ QDs and P3HT, as in general more than 50% FRET efficiency is observed for Ro less than 10 nm [15, 18, 50]. To further quantify the effect formation, we investigated the photoluminescence spectra of pure g-C$_3$N$_4$ QDs, P3HT and mixture of P3HT: g-C$_3$N$_4$ QDs with varying concentration as shown in figure 6(b).

The pure g-C$_3$N$_4$ QDs showed peak emission intensity at around $\lambda = 440$ nm, while pristine P3HT film showed PL peak around $\lambda = 680$ nm. However when QDs were introduced in P3HT, the emission intensity of QD decreased and that of P3HT increased with increasing concentration of g-C$_3$N$_4$ QDs. The emission intensity of P3HT in the mixture was found higher than that of pristine P3HT which is mainly due to energy transfer via FRET from QDs to P3HT generating more number of exciton [51]. Quenching and sensitized emission from QDs and P3HT was found to get clearly escalated, indicating photon energy over this range causing efficient excitonic energy transfer from g-C$_3$N$_4$ QDs to P3HT [17, 52].

The effect of g-C$_3$N$_4$ QDs on optical properties of P3HT: PC$_{71}$BM blend films were further studied by UV-Vis absorption spectroscopy as shown in figure 7(a). The band observed around 380 nm, corresponds to absorption of PC$_{71}$BM molecule whereas other three bands around 490 nm, 556 nm and 600 nm are originated from P3HT molecule. The main absorption peak around 490 nm was attributed to $\pi$-$\pi^*$ transition of P3HT conjugated backbone whereas two vibronic shoulders around 556 and 600 nm were believed to be due to absorption from extended conjugation and inter chain stacking of P3HT, indicating well-ordered crystalline structure [45, 46, 53]. Absorption features of the QDs are not visible due to it’s low concentration and superimposing feature with PC$_{71}$BM. The absorption peaks corresponding to 0-0 ($\lambda = 600$ nm) and 0-1
(λ = 556 nm) transition are related to solid state H-type aggregate coupling. According to Spano’s model the intensity ratio between 0-0 and 0-1 transition peak (i.e. \( A_{0-0}/A_{0-1} \)) estimates the Frenkel type exciton bandwidth (W) which in turn relates to degree of crystallinity by the following expression [16, 54].

\[
\frac{A_{0-0}}{A_{0-1}} = \left[ \frac{1 - 0.24W/Ep}{1 + 0.073W/Ep} \right]^2
\]

Where Ep is vibrational energy due to symmetrical stretching of C–C bond (∼180 meV) [55].

Figure 7(b) shows the variation in Frenkel exciton bandwidth for P3HT as a function of g-C\(_3\)N\(_4\) QDs concentration. W decreases from 89.6 meV for the pristine film to 84 meV for 2% doped sample and further increases with increasing concentration. The exciton bandwidth W is fundamentally related to dispersive or amorphous nature of H type aggregate. Smallest bandwidth corresponds to more ordered structure and thus expected to show higher conductivity [56–58]. Here, the addition of small amount of g-C\(_3\)N\(_4\) QDs (2%) to the blend film found to have similar effect on the π–π* transition efficiency of P3HT, leading to better ordered morphology of the active layer [49]. These results are consistent with our previous morphological analysis too (XRD and AFM), as discussed above.

The figure 8 shows the PL emission spectra for P3HT and the blend film with and w/o g-C\(_3\)N\(_4\) QDs under the excitation of 490 nm. The PL signature for P3HT around 680 nm corresponds to π–π* electronic transition whereas the shoulder around 760 nm corresponds to excitons decaying radiatively between intermediate states [59, 60]. As expected, for the P3HT: PC\(_{71}\)BM blend film, the emission intensity quenches significantly compared to pristine P3HT due to photo-induced charge transfer between the donor acceptor molecules. Interestingly, the emission drops further with the introduction of g-C\(_3\)N\(_4\) QDs in the blend film (shown in the inset of figure 8). This indicates that introduction of g-C\(_3\)N\(_4\) QDs as the third component into the active layer improves the morphology as discussed above and leads to enhanced photo induced charge transfer across the donor/acceptor interfaces [20].

### 3.4. Photovoltaic performance of devices

Finally the photovoltaic performances of the devices were tested under simulated solar radiation condition of AM 1.5G with 76.2 mW cm\(^{-2}\) intensity by measuring their Current density (J) versus voltage (V) characteristics as shown in figure 9(a). Detailed photovoltaic parameters like open circuit voltage (V\(_{oc}\)), short circuit current density (J\(_{sc}\)), fill factor (FF) and power conversion efficiency (PCE) are summarized in table 1 and figure 9(b). The energy band diagram of material used is shown in figure S7.

The pristine P3HT:PC\(_{71}\)BM based devices exhibit a short circuit current density (J\(_{sc}\)) of 7 mA cm\(^{-2}\), an open circuit voltage (V\(_{oc}\)) of 0.6 V and FF of 41%, resulting in PCE of 2.26%. With incorporation of g-C\(_3\)N\(_4\) QDs, a gradual increase was observed both in J\(_{sc}\) and FF, leading to enhanced PCE. The best device with 2% g-C\(_3\)N\(_4\) QDs showed J\(_{sc}\) of 10.39 mA cm\(^{-2}\), FF of 44%, V\(_{oc}\) of 0.62 V with PCE of 3.72% which is almost ~40% higher than reference device. Such improved device performances can be primarily attributed to the increased in FF and J\(_{sc}\) due the g-C\(_3\)N\(_4\) QDs induced FRET and morphological effects formation [16, 46]. The PCE began to decrease with increasing concentration of g-C\(_3\)N\(_4\) QDs beyond 2% as shown in figure 9(b), however 1%–4% devices were
still showing better device performance than pristine one. The PCE dropped significantly on increasing the concentration beyond 4% mainly due to decrease in FF and Jsc.

To understand the effect of QDs on device operation further, the dark J-V characteristic of the devices were investigated as shown in figure 10. Devices with lower concentration of g-C3N4 QDs (<4%) showed smaller leakage current in Reverse bias region, even compared to the pristine devices. The highest rectification ratio of \( \sim 10^4 \) at \( \pm 1 \) V was observed for the 2% mixed devices while devices with higher concentration of g-C3N4 QDs (>4%) showed significantly large leakage current. This could be due to the fact that g-C3N4 QDs gets agglomerated at higher concentration and acts as recombination sites, providing parasitic leakage path for the charge carriers \([19, 22, 61]\).

To quantify the direct impact of g-C3N4 QDs on the charge transport properties of the devices, we have fabricated electron only and hole only devices with the following architectures of ITO.
Figure 10. Dark J-V characteristic of P3HT: PC_{71}BM with different concentration of g-C_{3}N_{4} QDs.

Figure 11. J-V curve of (a) electron only device, (b) hole only device of P3HT: PC_{71}BM with different concentration of g-C_{3}N_{4} QDs.
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ORCID iDs

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ORCID iDs

Saurabh Pareek https://orcid.org/0000-0002-0461-9930
Supravat Karak https://orcid.org/0000-0002-0650-8353

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ORCID iDs

Saurabh Pareek https://orcid.org/0000-0002-0461-9930
Supravat Karak https://orcid.org/0000-0002-0650-8353

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