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Enhancing the Efficiency of DSSCs by the Modification of TiO_2 Photoanodes using N, F and S, co-doped Graphene Quantum Dots

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ABSTRACT

We report an enhanced power conversion efficiency (PCE) of 11.7% ± 0.2 and a fill factor (FF) of 71% for dye-sensitized solar cells (DSSC) with an active area of 0.16 cm^2 after modifying the TiO_2photoanode with size-selective (ca. 2 nm) N,F,S-codoped graphene quantum dots (NFS-GQDs) that exhibit a photo-luminescence quantum yield (PLQY) of 70%. An upward shift in the Fermi level has been observed, perhaps responsible for the improved performance along with the possibility of preventing the back electron transfer from TiO_2. Mott Schottky analysis indicates a shift (52 mV)in the flat band potential, which is directly related to the V_{oc} of the system. Detailed characterization (IPCE, TCSPC etc) indicates the important role of hetero atoms in facilitating the enhanced performance. Thus, our results suggest that the incorporation of size controlled, hetero atom doped GQDs can enhance the efficiency of DSSCs enabling more opto-electronic applications.

1. Introduction

The ever growing appetite for energy demand with respect to the expanding world population and modernization has brought several daunting challenges to mankind due to the relentless usage of conventional energy sources [1]. Some of these could be solved by utilizing more renewable resources like solar and wind and the availability of many new materials has helped to increase the pace of deployment. Among the various solar energy systems investigated over the years, conventional silicon solar cells have received much attention due their high efficiency. However, high manufacturing cost and its inadequate performance under diffused sunlight hinder their widespread utilization. Third generation solar cells potentially replace the conventional silicon cells with their low processing cost, ease of fabrication, moderate efficiency and better performance during cloudy days. Of late, Dye-sensitized solar cells (DSSCs) have grabbed more attention in this category. DSSC works under diffused sunlight mainly because the semiconductor acts as charge carrier and dye as photon collector, whereas in silicon solar cells, silicon acts as both the charge transport carrier as well as the source for photo-electrons. Dye molecules are sensitive enough to collect the photons under diffused sunlight thus paving the way for this crucial difference [2].

There are several ways of modifying DSSC in order to improve the power conversion efficiency (PCE). Photoanode modification is one of the important methods in addition to designing new redox couple with lower potential, molecular engineering of the dye and the alteration in the counter electrode composition especially using inexpensive and efficient materials as substitutes for Pt [3]. Since the photoanode in DSSC acts as light harvesting part as well as charge carrier its modification could, in principle, play a crucial role in enhancing the PCE contribution. Commonly used

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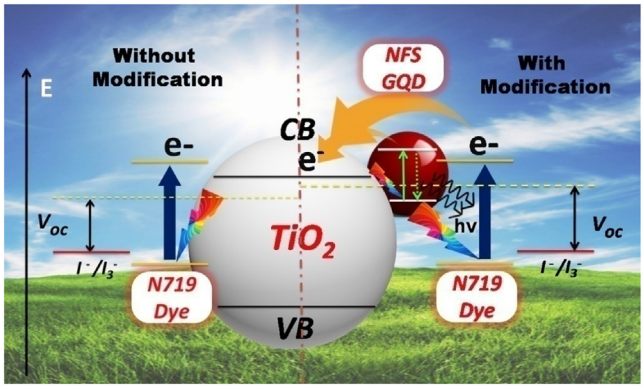
photoanode is TiO_2 due to its relatively high energy conversion efficiency, high specific surface area, non-toxicity and low cost. However, one of the major limitations of this material is its random electron transport resulting in the recombination of electron-hole pair which leads to poor performance [4]. Continuous efforts are going on to improve the performance of the cell from the beginning [2]. Gao et al. has reported an efficiency of 11.1% after modifying the dye while Yella *et al.* [5] has obtained 12.3% using a modified electrolyte having a more facile cobalt(II/III) redox system [6]. However, the cobalt based electrolyte is environmentally not benign and also quite expensive. Many groups are trying to improve the stability of the electrolyte using gel based electrolytes and ionic liquids which are beneficial for bright sunny days [7]. In comparison, modification strategies on the anode [8–11] have not been greatly successful and the efficiency continues to remain moderate despite its prevalence and wide popularity. Hence, there is an urgent requirement for improving the anode configuration to make DSSCs more efficient and reliable for wider utilization.

Anodes could be modified using a variety of size selective quantum dots (QDs) like CdSe and CdTe in order to get beneficial size quantization effects by tuning the bandgap [12]. The primary advantage of using quantum dots in the photoanode is to harness the photons in the UV region so that they might act as co-sensitizer. However, the main drawback of using Cd based quantum dots are toxicity and the lack of long term stability. Incorporation of carbon nanostructures in TiO_2 photoanode minimizes the back electron transfer to electrolyte as well as enhancement of electron transport in TiO_2 which improves the overall photovoltaic parameters [13]. In recent times, carbon (1D or 2D) nanostructure modified photoanodes for DSSC applications show an increased dye adsorption, rapid electron transport and low recombination rate, hence these factors conclude the photovoltaic performance by synergistic effect between the carbon/semiconductor network [14–16]. Graphene Quantum Dots (GQDs) could be the preferred materials due to not only its low cytotoxicity, but because of the ease of functionalization and processability. Consequently, many attempts have been made in the past for the incorporation of graphene quantum dots (GQDs) in the photoanode in order to enhance the efficiency along with simultaneous improvements in the dye so that the performance of quantum dot sensitized/co-sensitized solar cell with and without dye could be compared [12,17–22]. Unfortunately, the low photoluminescence quantum yield (below 20%) of the pristine GQDs obviates its effective utilization. Yan and co-workers [23] have used large, stable, colloidal GQDs for modifying the anode, the power conversion efficiency was not very high with a short-circuit current density (J_{sc}) of 200 $\mu A\,cm^{-2}$, due to the suboptimal interaction of large GQDs and TiO_2 surface. In comparison, N-doped carbon quantum dots (NCQDs) have shown relatively better performance with rutile TiO_2 where both improved open-circuit voltage (V_{oc} of 0.46 V), and J_{SC} (of 0.69 mA cm^{-2}) could be measured with an overall conversion efficiency of 0.13% [24]. In addition to this, direct doping of TiO_2 using N and S exhibited a narrow bandgap which could shift significantly towards the visible region thus enhancing the performance further [4,25,26]. Apart from this, few groups also used GQDs for modifying the counter electrodes coupled with graphene foam to display enhanced efficiency. For example, Chang et al. [27] in this way has observed an efficiency of 9.59% ascribed mainly to the electro-catalytic effect of the GQDs on graphene foam. The combination of TiO_2-GQD-Dye helped in tuning the electronic levels of GQDs and also in such a cascaded configuration of energy levels that enhanced charge collection and separation were possible. Another important aspect in this case was the energy transfer from GQDs to dyes promoting the application of GQDs in solar cells due to the overlap between the luminescence of GQDs and the absorption of dye molecules. Further, Mihalache et al. has investigated that the charge and energy transfer process occurs simultaneously between GQDs and TiO_2 due to the change in energy level alignment and also acts as co sensitizers [28]. The fluorescent carbon quantum dots modified TiO_2 can enhance the incident photon to current efficiency (IPCE) from 70% to 96% after modification. However, the photo voltage is decreased for this modified electrode due to increase in recombination resistance resulting back electron transfer to redox species [29]. Although the electron recombination to the redox electrolyte couple was expected to be diminished because of the inhibition of the back electron transfer to the electrolyte by the GQDs, there were many unanswered questions about the role of GQDs, especially its size dependence, stability and interactions on TiO_2 surface, in improving the performance of DSSCs [11,12,28]. Recently, doped GQDs exhibit unique behavior especially in tuning the optical properties and electronic band structure that utilized for optoelectronic device applications. Fluorinated GQDs have been synthesized by hydrothermal route which exhibit higher blue luminescence compared to the fluorinated 2D graphene sheets and hence it could be a potential candidate for opto electronic devices [30]. Likewise, nitrogen doped GQDs show in the form of pyrrolic and pyridinic structure which tune up the optical properties and hence it introduces new energy level for electronic device applications [31]. These improved PL enhancement in the visible region potentially applied as a co-sensitizers for DSSC applications.

Here we report an interesting strategy to modify the photo anode of DSSC using NFS-GQDs in the TiO_2 meso-porous network in order to overcome the above problems and also to enhance the light harvesting efficiency with an alluring PCE value of 11.7%. More specifically, the co-doping of these selected heteroatoms has been a critical parameter to reveal astounding performance as the N doping has helped to reduce the bandgap of TiO_2 while S could facilitate the electron transfer process and F in the effective binding with the TiO_2 surface [4]. Thus, the performance improvement could be reflected in the standard configuration of NFS-GQDs modified anodes by a prominent shift of the visible region of the N719 dye towards the red region, indicating that more number of photons would be absorbed in the covered region. This obviously acted as a charge carrier to facilitate the accelerated electron transport and also to suppress the electron recombination rate. Interestingly, the dangling "F" from the NFS-GQDs could also possibly make hydrogen bonding with the −OH groups of the TiO_2 nano-particles contributing to enhanced stability. Thus, our results illustrate the possibility of improving the next-generation DSSC anodes which could probably be coupled with more proficient counter electrodes and modified dye or altered electrolytes to



Scheme 1. A schematic representation of the NFS-GQD modified anode showing the Fermi level change (an upward 52 mV shift in the flat band potential compared to bare TiO_2) due to modification where CB indicates conduction band and VB indicates valence band.