Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 206 (2019) 216–223

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Theoretical studies on the feasibility of the hybrid nanocomposites of graphene quantum dot and phenoxazine-based dyes as an efficient sensitizer for dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 11 June 2018
Received in revised form 2 August 2018
Accepted 5 August 2018
Available online 06 August 2018

Keywords:
Charge spatial separation
Optical absorption
Graphene quantum dot
Phenoxazine-based byes
Nanocomposites

ABSTRACT

The feasibility of the hybrid nanocomposites of the graphene quantum dot (GQD) and the phenoxazine-based dyes as the efficient sensitizer of the dye-sensitized solar cell (DSSC) is investigated. Based on the first principles density functional theory (DFT), the geometrical structures of the separate GQDs, the phenoxazine-based dyes, and their hybridized nanocomposites are fully optimized. The energy stabilities of the obtained structures are confirmed by harmonic frequency analysis. The optical absorptions of the optimized structures are calculated with the time-dependent DFT (TDDFT). The feasibility of the nanocomposites as the sensitizer of DSSC is examined by the charge spatial separation, the molecular orbital energy levels of the nanocomposites and the I^-/I_3^- electrolyte, and the conduction band minimum of TiO_2 electrode. The results demonstrate that three of the eight considered nanocomposites satisfy the requirement of DSSC. Among them, GQD4-POXB with large LHE, high V_{oc}, and enhancement absorption becomes the most promising candidate as a feasible sensitizer. These findings are helpful for the design of the sensitizer of DSSC or the solar energy harvesting materials with the nanocomposites.

1. Introduction

Recently, searching for renewable and environmentally friendly energy sources has become a global interest motif due to the long-term shortage issues of fossil fuels and serious environmental issues. The abundance of energy coming from the sun makes solar cells a very attractive alternative for the major sources used today. With the potential of becoming a clean and renewable energy source, dye-sensitized solar cells (DSSC) have drawn much attention because of their relatively high photoelectric absorption efficiencies and lower production cost. A typical DSSC consists of a wide band gap semiconductor photoanode, an anchored molecular sensitizer, a redox electrolyte and a counter electrode [1–3]. In these components, the sensitizer dye plays a vital role in the light-harvesting efficiency and an efficient sensitizer is needed to harvest the solar energy and to inject electrons in DSSC. The development of new sensitizer for DSSC is very important to improve the overall efficiency of the cell through a better understanding about the function of the cell and its limitations. In recent years, many theoretical and experimental studies have focused on designing novel sensitizer for improving DSSC performance [4]. Among the wide range of organic dyes being investigated for application in DSSC, phenoxazine-based sensitizer could be a hopeful sensitizer in DSSC due to the satisfactory electrochemical characteristics [5,6]. Phenoxazine dyes have been used in other applications, such as laser dyes [7], hole-transporting materials [8], and host-guest systems [9]. Despite phenoxazine-based sensitizer potential for application to DSSC, some structures of them do not have very strong absorption in the visible light region, thus they have not led the high-efficient DSSC. Recently, Chermahini et al. [10] have reported a series of phenoxazine-based dyes. The results show that the dye with a furan spacer (POXF) is the most efficient sensitizer for DSSC due to the largest light-harvesting efficiency, high open-circuit photovoltage and red-shifted absorption. However, the optical absorption of some phenoxazine-based dyes is not obvious in the visible light range. Such as the phenoxazine as the electron donor and cyanoacrylic acid as the electron acceptor groups, and benzene (POXB) and pyrrole (POXP) act as the π-spacers. Although the POXB and POXP satisfy the requirement of the energy level as a sensitizer, they are not the efficient sensitizer of DSSC because they lack strong absorption in the most part of the visible light region. The satisfactory efficient solar cell sensitizer to harvest solar energy should have strong absorption in the range from UV to infrared wavelength of the sun. Therefore, to make POXB and POXP become more effective sensitizer, one should enhance the optical absorption of these structures in the

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https://doi.org/10.1016/j.saa.2018.08.012
1386-1425/

visible light range by modifying the structures with some functional ligands or hybridizing quantum dots (QDs). In fact, the dye sensitizer consisting of many nanocomposites prove to be efficient to harvest solar energy, because the nanocomposites can have superior properties as compared to the individual components from which it is made [11,12]. Among the various QDs, graphene quantum dot (GQD) demonstrated most of the excellent features and optical properties, which make them a potential candidate for the fabrication of nanocomposites with favorable properties. Unlike the bulk graphene, GQD has a band gap because of quantum confinement [13–15] and exhibit strong photoluminescence (PL) [16–18]. Nowadays, GQD has become a multifaceted candidate material for next-generation ultrathin optoelectronic devices, and building blocks of the future electronics devices [19–21]. The applications of GQD in renewable energy resources like photovoltaics [22], in electronics and optoelectronics such as photodetector [23] and phototransistor [24], have already been demonstrated by an enormous amount of investigations. By varying the size of GQD, one can tune the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of GQD over a wide range of wavelengths from the ultraviolet through the visible to the infrared light range, which has been confirmed by Mahasin et al. [25] from the experiment which the PL of GQD can be sensitively tuned by controlling its size, shape, edge configuration, chemical functionalization and doping heteroatoms.

Consequently, many attempts have been made for the different size GQDs sensitized composite materials in order to enhance the efficiency along with simultaneous improvements in the performance of DSSC. In a very recent article, Mandal et al. [26] performed a theoretical investigation on the electronic structure of porphyrin functionalized GQDs. The possibility of forming type-II nanohybrids is explored by varying either the size of the GQD or by attaching different functional groups to the porphyrin moiety. Considering that POXB and POXP satisfy the energy level requirement as a sensitizer for DSSC but their light absorptions are very poor in the light visible region, we construct the hybrid nanocomposites of GQD with POXB or POXP to enhance the optical absorption in the light visible region. In order to fully evaluate the possibility of these nanocomposites as a sensitizer of DSSC, we optimize their geometrical structures with the hybrid density functional theory (DFT) methods and confirm the energy stability with frequency analysis. The optical absorption properties are calculated with the time-dependent DFT (TDDFT) method [27]. The results demonstrated that the optical absorption of the nanocomposites is significantly enhanced in comparison to those of the separate GQD, POXB or POXP. After analyzing the energy level and electronic density of LUMO and HOMO, the charge spatial separation and the optical absorption in the visible light range, we identify that seven of the twelve hybrid nanocomposites satisfy the requirement of sensitizer for DSSC. These findings can provide a helpful guide for developing efficient DSSC with the nanocomposites of GQD with POXB, or POXP.

2. Models and Computational Methods

The considered GQDs, POXB and POXP are modeled in Fig. 1. The GQDs with different sizes are cut from a large graphene sheet. We build up symmetry GQD1($C_{54}H_{18}$), GQD2($C_{66}H_{20}$), GQD3($C_{80}H_{22}$) and GQD4($C_{96}H_{24}$). The nanocomposites of the GQDs with POXB or POXP are represented by GQD*n*-(POXB or POXP) ($n = 1, 2, 3, 4$). The geometrical structures of the nanocomposites are constructed by attaching the POXB and POXP molecule with the GQDs through an amide linkage. As a result, the POXB or POXP moiety is attached to the GQD through a single C—C linkage. The optimized geometries of all the nanocomposites presented in Fig. 2. The geometrical configurations of the separate GQDs, POXB, POXP and their hybridized nanocomposites are optimized using the hybrid DFT method as implemented in the Gaussian 09 program [28]. The B3LYP [29,30] method with the 6–31 + G (d) basis set [31] is used because the reliability of the theoretical level is confirmed by Chermahini et al. [10]. B3LYP is a gradient-corrected hybrid DFT with exchange-correlation functional in Becke's three-parameter form, which includes a mixture of Hartree-Fock (HF) exchange with the Vosko, Wilk and Nusair (VWN) functional III for local correlation and the correlation functional of Lee, Yang, and Parr (LYP) for non-local correlation. The structure optimizations are performed with a solvent of tetrahydrofuran (THF). The default convergent criteria of Gaussian 09 are used

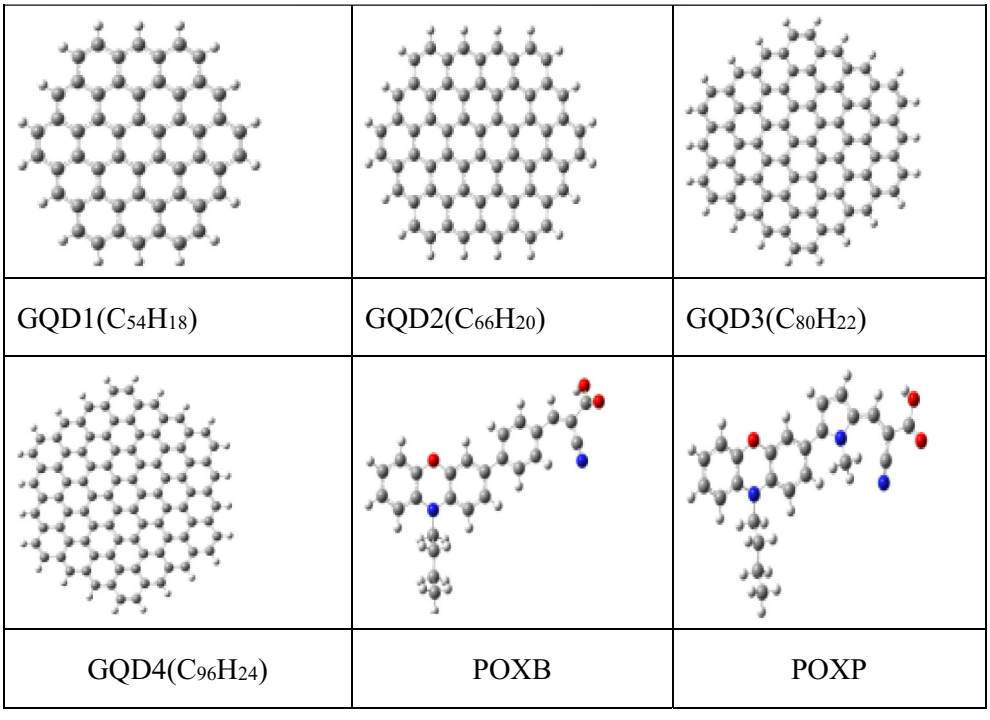

Fig. 1. The optimized structures for GQD1($C_{54}H_{18}$), GQD2($C_{66}H_{20}$), GQD3($C_{80}H_{22}$), GQD4($C_{96}H_{24}$), POXB, and POXP.