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Theoretical studies on the possible sensitizers of DSSC: Nanocomposites of graphene quantum dot hybrid phthalocyanine/tetrabenzoporphyrin/tetrabenzotriazaporphyrins/*cis*-tetrabenzodiazaporphyrins/tetrabenzomonoazaporphyrins and their Cu-metallated macrocycles

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ABSTRACT

The feasibility of nanocomposites of cir-coronene graphene quantum dot (GQD) with phthalocyanine, tetrabenzoporphyrin, tetrabenzotriazaporphyrins, *cis*-tetrabenzodiazaporphyrins, tetrabenzomonoazaporphyrins and their Cu-metallated macrocycles as a sensitizer of dye-sensitized solar cells (DSSC) are investigated. Based on the first principles density functional theory (DFT), the geometrical structures of the separate GQD and 10 macrocycles, 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 time-dependent DFT. The feasibility of the nanocomposites as the sensitizer of DSSC is examined by the charge spatial separation, the electron transfer, the molecular orbital energy levels of the nanocomposites and the electrolyte, and the conduction band minimum of TiO_2 electrode. The results demonstrate that all the nanocomposites have enhanced absorptions in the visible light range, and their molecular orbital energies satisfy the requirement of sensitizers. However, only two of the ten considered nanocomposites demonstrate significantly charge spatial separation. The GQD-Cu-TBP is identified as the most favorable candidate sensitizer of DSSC by the most enhanced in optical absorption, obvious charge spatial separation, suitable LUMO energy levels and driving force for electron transfer, and low recombination rate of electron and hole.

1. Introduction

In recent years, searching for renewable and environmentally friendly energy sources has become a current topic of interest due to the continuous depletion of fossil fuels and serious environmental issues. 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 photoelectronic absorption efficiencies and lower production cost. DSSC has been regarded as one of the most promising alternatives for traditional silicon-based solar cells because of their facile fabrication process, and the possibility of large-scale manufacture [1]. However, an efficient sensitizer is needed to harvest the solar energy and to transfer electrons in DSSC effectively. In recent years, many groups are devoted to the development of the novel sensitizer to improve the efficiency of DSSC. Among the various sensitizers of organic dyes, phthalocyanine (Pc) is a very robust one with its extraordinary high extinction coefficients in the 600 to 700 nm light region [2–4]. Moreover, Pc is thermally and chemically stable and has appropriate redox properties for sensitization of TiO_2 films. Hence, it is regarded as a perfect light-harvesting material for light-to-energy conversion devices, and remarkable progress has been made in the use of Pc as a sensitizer of DSSC [5–10].

Additionally, the semiconductor tetrabenzoporphyrin (TBP) also is a potential sensitizer of DSSC because of the intense and tunable absorption in the red or near-infrared region, transparency over the high energy portion of the visible range [3]. TBP has a strong peak linear attenuation coefficient and can absorb a significant fraction of light [11]. In 2009, Matsuo et al. [12] reported TBP was used to make solution-processed organic solar cells with a relatively high efficiency of 5.2%. Noguchi and co-workers [13] reported TBP organic thin film showing that the carrier mobility is three times higher for the film prepared at a lower temperature than that prepared at higher temperatures. In 2015, Dao et al. [14] investigated the enhancement efficiency of organic solar cells by utilizing various phthalocyanine–TBP hybrid macrocycles.

Although the Pc and TBP can be used as sensitizers, they lack strong absorption in the most part of the visible light region, which limits them

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as the highly efficient sensitizers of DSSC because the satisfactory efficient sensitizer should be strong absorption in the range from UV to infrared wavelength, especially the visible light range. Therefore, to make Pc and TBP become more effective sensitizer, one should modify Pc and TBP with some functional light absorbing materials or construct nanocomposites with other molecules to enhance the optical absorption in the visible light range.

The nanocomposites of dyes and quantum dots (QD) proves to be efficient to harvest solar energy, because the nanocomposites are superior light absorption properties as compared to the individual components from which it is made [15,16]. Among the various nanocomposites of QDs, the ones made of the graphene quantum dot (GQD) are received great attention, which makes them as a potential candidate for the fabrication of nanocomposites with favorable properties. In 2010, Li et al. [17] through their pioneering work have shown that periodic graphene can also be realized in the form of QDs. GQD has also many particular properties, which makes it become a promising candidate material for next-generation ultra-thin optoelectronic devices and building blocks of the future electronics devices [18–20]. Unlike the bulk graphene, GQD has a band energy gap because of quantum confinement [21,22] and exhibit strong photoluminescence [23–25]. GQD applications in renewable energy resources like photovoltaics [26], in electronics and optoelectronics such as photodetector [27] and phototransistor [28] have already been demonstrated by many types of research.

In fact, GQD can possibly be used as a sensitizer or co-sensitizer of DSSC. Very recently, Tsai et al. [29] report that a high efficiency of 16.55% in *n*-type Si heterojunction solar cells can be achieved by employing GQD as a sensitizer. In 2015, Mihalache et al. [30] reported an efficiency enhancement of DSSC using N3 dye co-sensitized with GQDs. They achieved an overall cells efficiency of 2.15% compared to that of the reference efficiency 1.92%. By combined GQDs and N719 dye, Fang et al. [31] obtained a better DSSC efficiency of 6.1% with a net PCE improvement of ~19% compared with the reference DSSC efficiency of 5.1%.

Considering GQD, Pc and TBP can be used as a sensitizer or co-sensitizer for DSSC, one can construct nanocomposites of Pc and TBP with QD to strengthen the solar energy absorption. At the same time, tetrabenzotriazaporphyrins (TBTAP), *cis*-tetrabenzodiazaporphyrins (TBDAP), tetrabenzomonoazaporphyrins (TBMAP) can be regarded as hybrid structures of Pc and TBP. Moreover, the optical properties of the Cu-metallated macrocycles mentioned above, representing by Cu-TBP, Cu-TBMAP, Cu-TBDAP, Cu-TBTAP, and Cu-Pc have also been investigated [32,33]. However, the feasibility of nanocomposites of GQD and the above macrocycles as sensitizers of DSSC has not been explored. To 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 (TD-DFT) method [34]. The results demonstrated that the optical absorption of the nanocomposites is significantly enhanced in comparison to those of the GQD or the macrocycles. After analyzing the energy level and electronic density of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), the charge spatial separation and the optical absorption in the visible light range, we identify that the nanocomposites of GQD with Pc or Cu-TBP are the most potential candidate sensitizers of DSSC. These findings can provide a helpful guide for developing efficient DSSC with nanocomposites of GQD and macrocycles.

2. Computational Methods

The cir-coronene $C_{54}H_{18}$ structure is used to stand for the present GQD. The present specific size is chosen according to the detail discussion about the structural parameters and optical properties by Li et al. [35]. The larger GQD including more C atoms (for examples 96 atoms which are often used to investigate one GQD in the literature) will make the demand on computing resources for the large nanocomposites. Five macrocycles including Pc, TBP, TBTAP, TBDAP, TBMAP, and GQD are considered as shown in Fig. 1(a). Pc and TBP are organic compounds with the formula $(C_8H_4N_2)_4H_2$ and $C_{36}H_{22}N_4$, respectively. Moreover, the Cu-metallated macrocycles mentioned above, representing by Cu-TBP, Cu-TBMAP, Cu-TBDAP, Cu-TBTAP, and Cu-Pc are also shown in Fig. 1(a). The nanocomposites consisting of GQD and 10 macrocycles are constructed by grafting one phenyl ring of the macrocycles on the GQD through an amide linkage. The geometrical configurations of nanocomposites are optimized using hybrid DFT method implemented in the Gaussian 09 program [36]. The B3LYP [37,38] method with LANL2DZ basis set [39,40] is used for all atoms in the nanocomposites. 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 default convergent criteria of Gaussian 09 are used for the energy and force constants. The optimized geometries of all nanocomposites are presented in Fig. 1(b). To confirm the energy stability of the structures, we also calculated the harmonic frequencies for all structures at the same theoretical level.

Based on the optimized geometries of nanocomposites, the optical absorption properties are calculated by employing the TD-DFT method. The optical spectra are obtained through the explicit solution of the time-dependent Kohn-Sham equations with a time-propagation [41,42]. This algorithm is particularly effective to treat the large nanocomposites [43,44] as the present ones. The TDDFT calculations are performed with Octopus software package [45]. The local-density approximation (LDA) [46] and Hartwigsen-Goedecker-Hutter (HGH) pseudopotential [47] are used to make the TD-DFT calculations feasible for nanocomposites. The time step is 0.002 hbar/eV and the maximum steps are 5000.

3. Results and Discussion

3.1. Geometrical Structures and Vibrational Spectra of QDs and Nanocomposites

The optimized geometrical structures of all the nanocomposites of the 10 macrocycles hybrid GQD are shown in Fig. 1(b). To evaluate the energy and chemical stabilities of the considered structures, the range of the harmonic frequencies are calculated and collected in Tables 1 and 2. To visually demonstrate the vibrational spectra of the nanocomposites, we have plotted all the vibrational spectra in Fig. 2. Both the tables and the figures demonstrate that the vibrational spectra of all the nanocomposites are positive, and no negative value occurs, which confirms that all the considered structures are stable in energy. The energy gap (E_g) between HOMO and LUMO are calculated and presented in the two tables. The present E_g of GQD is 2.824 eV at the B3LYP/LANL2DZ theoretical level, which is larger than the 1.96 eV with standard DFT but smaller than the 4.68 eV with GW method [35]. The present E_g of GQD including 54 carbon atoms (plus 18 hydrogen atoms) is larger than the 1.10 eV of the hexagonal GQD atoms and 1.25 eV of the triangular GQD with 200 carbon atoms [16]. The E_g of the macrocycles from 2.077 eV to 2.408 eV, which is slightly larger than the theoretical with B3LYP/6-311G(d,p) in the literature [33]. On the whole, as the number of meso nitrogen atoms increases from zero to four, the E_g of the metal-free macrocycles decreases gradually, which means that the chemical stability slightly decreases. However, the Cu-metallated macrocycles have not shown the same trend.

From Table 2, one can find that the E_gs of the nanocomposites of GQD and the macrocycles are smaller as compared to that of the separate GQD itself. The values of E_gs of the nanocomposites are from 2.040 eV to 2.366 eV, which means that the nanocomposites are moderate chemical stability as the separate macrocycles. Meanwhile, the absorption