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Electronic properties and optical absorption of graphene-polyvinylidene fluoride nanocomposites: A theoretical study

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HIGHLIGHTS

- Various properties of graphene-PVDF nanocomposites were studied theoretically.
- Electronic gap of graphene shifts to conducting nature, on composite formation.
- Adsorption is spontaneous above ~870 K, and endothermic in nature.
- B3LYP and PBE0 functionals are suitable in describing absorption.
- Optical absorption gets enhanced on nanocomposite formation.

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ABSTRACT

Graphene/polyvinylidene fluoride (graphene/PVDF) nanocomposites were studied using Density functional theory (DFT)/Time dependent density functional theory (TDDFT) calculations. Five nanocomposite configurations were constructed. Electronic properties like binding energy, electronic gap and work function were calculated. The most stable structure was determined. The electronic gap of graphene shifts from semiconducting to conducting, on nanocomposite formation. Workfunction of the most stable nanocomposite was 4.34eV ± 0.05eV, close to that of the pristine graphene (4.33eV ± 0.05eV). Thermochemical analysis showed that the adsorption is spontaneous above ~870 K, and endothermic in nature. TDDFT calculations were performed for B3LYP, LSDA, BHHLYP and PBE0 functionals. B3LYP and PBE0 are suitable in describing optical absorption. Optical gap of graphene shrinks, and light absorption gets enhanced on nanocomposite formation.

1. Introduction

Polymer composites have been an active area of research due to the considerable enhancement in electronic, mechanical, conductive and thermal properties, and also in energy harvesting, energy conversion and storage devices [1–10]. Among the various nanomaterials, graphene, a novel two-dimensional (2D) carbon nanomaterial, owing to its excellent thermal, mechanical, electrical, thermoelectric and optoelectronic properties, has attracted a considerable attention as a promising building block for several novel multifunctional materials, e.g. biosensor, photovoltaic devices, supercapacitors etc. [11–15].

Most recent application of graphene is in polymer nanocomposites in which the polymer matrix composite incorporates nanoscale filler materials. Recently graphite oxide (GO) has been used to prepare graphene-based nanocomposites [16]. Graphene significantly improves the properties of polymer based composites and interestingly due to its very high surface conductivity; it forms several electrically conductive polymer composites. Several approaches like solution mixing have been used for incorporating GO derived fillers into a variety of polymers, including polyimides [17], polyacrylamide [18], polycarbonate [19] and poly(methyl methacrylate) (PMMA) [20,21]. Poly (vinylidene fluoride) (PVDF) nanocomposites based on functionalized graphene sheets were prepared from GO and expanded graphite by solution processing and compression molding [22]. Infact, the dispersion of GO in the polymer matrix has been improved by modification with polymers and surfactants and by mixing of functionalized graphene into polymer matrix has resulted in substantial improvement in thermal, mechanical and electrical properties [23–28].

A single atomic sheet of graphene can absorb 2.3% of incident

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white light [29]. Due to its universal wideband absorption, graphene is a suitable candidate for a saturable absorber [30–32]. In addition, its nonlinear optical behavior makes it highly useful in ultrafast photonics [33]. The use of graphene is motivated by the fact that single walled nanotubes (SWNTs) have been used as effective saturable absorbers for the mode locking of lasers to generate ultrashort pulses in the telecommunication bandwidth [34,35]. SWNT-polymer composite have proven to be effective saturable absorbers owing to its large modulation depth and ultrafast recovery time [36–39]. Later, Bao et al. showed that a small loading (0.07 wt%) of functionalized graphene enhances the total optical absorption of poly(vinyl acetate) (PVAc) by 10 times [40], indicating that electrospun graphene nanocomposites are promising candidates as efficient photonic materials for the generation of ultrashort pulses in fiber lasers. In another study by Tang et al., graphene-based PVDF nanocomposite membrane was used as a saturable absorber for a high-power fiber laser mode locker [41].

Here, we plan to study the ground state electronic properties and optical absorption in graphene-PVDF nanocomposites using Density functional theory (DFT) and Time dependent density functional theory (TDDFT). Electronic and optical HOMO-LUMO gaps, oscillator strengths, UV–visible absorption wavelengths, and state transitions was computed and analyzed.

2. Methodology

The graphene-poly (vinylidene fluoride) [graphene/PVDF] nanocomposite was studied using the Density functional theory (DFT)/Time dependent density functional theory (TDDFT) calculations. In this study, pure graphene nanoflake ($C_{24}H_{12}$) and pure PVDF (β phase) $(-CH_2-CF_2-)_8$ were used as the parent samples. Further, graphene/PVDF nanocomposties were constructed by attaching the pure graphene nanoflake to pure PVDF on various sites and orientations, as shown in Fig. 1. In total, seven samples were studied. The sample naming terminology is “gr” (for pure graphene ($C_{24}H_{12}$), “nc1-nc5” for graphene/PVDF nanocomposites and “PVDF” for pure β phase PVDF $[(-CH_2-CF_2-)_8]$. The nanocomposites vary from each other in the aspect of position and orientation of graphene. Only singlet states were considered for all calculations.

Calculations were performed using the FIREFLY code version 8.1.0 [41]. Self-consistent-field (SCF) electronic structure calculations were performed. The Pople's N-31G split valence basis set 6-31 + G (d) was used for ground state geometry optimizations, which were carried out using the internal coordinates and with a convergence limit of 10^{-6} hartree on the total energy. The structures were firstly relaxed using the steepest descent algorithm in Avogadro package [42]. It was then followed by a more accurate calculation using Becke's three parameter functional with the Lee-Yang-Parr correlation functional (B3LYP) level of theory [43,44]. The geometry optimizations were confirmed as minima on the potential energy surface (PES) by evaluating the Hessian and ensuring the absence of any imaginary frequency. Single point energy calculations were performed on the ground state (S_0) geometries with the help of TDDFT calculations. No symmetry constraints were considered for ground state geometry optimizations. Electronic properties like binding energy, electronic gap and work function are calculated. Furthermore, the ground state DFT calculations are used to analyze the stabilities of all the nanocomposite samples (nc1-nc5), followed by the thermochemistry data analysis.

Later, the electronic transitions between occupied and unoccupied states were calculated at Restricted Hartree Fock (RHF) and

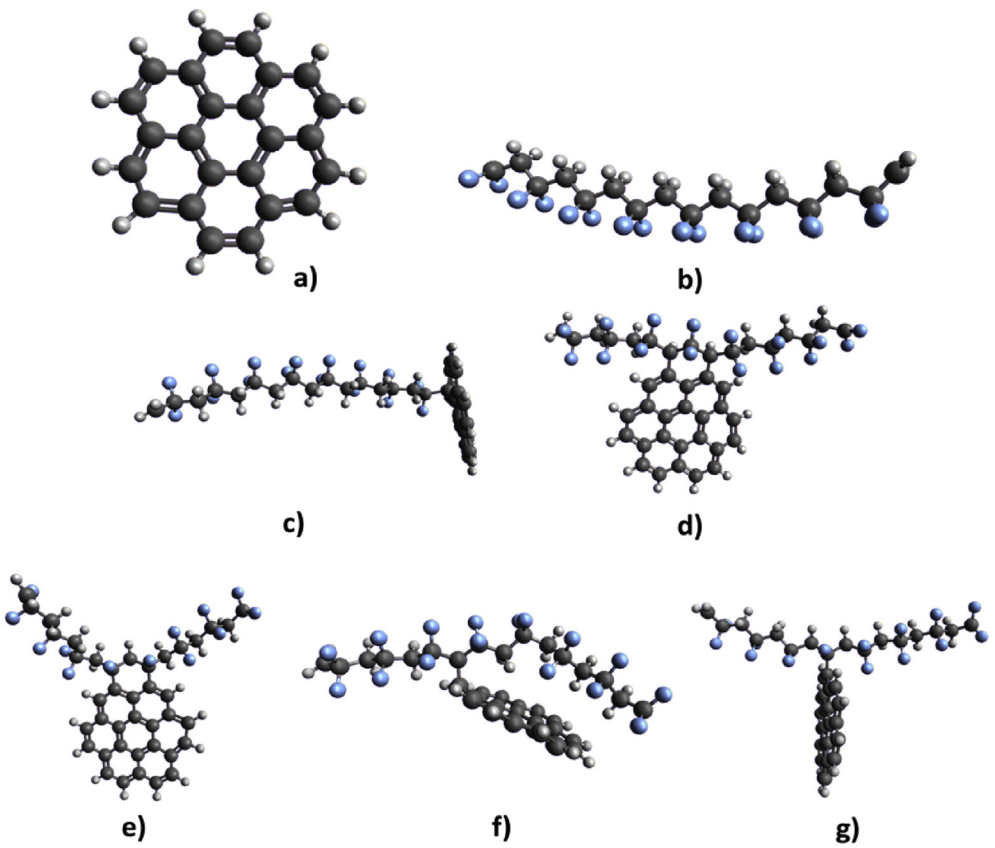

Fig. 1. The ground state optimized geometries of the samples considered. a) gr, b) PVDF, c) nc1, d) nc2, e) nc3, f) nc4 and g) nc5. Samples nc1-nc5 are the graphene PVDF nanocomposites with different positional configurations. Samples “gr” and “PVDF” are pure graphene ($C_{24}H_{12}$) and pure PVDF ($(-CH_2-CF_2-)_8$).

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