SPATIALLY SEPARATED HOMO/LUMO AT INTERFACE OF POLYPYRROLE PHYSISORBED ON OXIDIZED NANODIAMOND FACETS

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Abstract

Nanodiamond particles (NDs) have recently risen in popularity owing to their unique and perspective properties. Merging NDs with organic molecules, such as polypyrrole (PPy), into hybrid organic-semiconductor functional systems gives rise to potential applications in photovoltaics, which is supported by prior experimentally observed charge transfer between bulk diamond and PPy. This work focuses on the most relevant (111) and (100) O-terminated ND facets with different coverage of surface terminating oxygens in ether, epoxide, ketone, and peroxide positions. We use density functional theory computations employing B3LYP functional and 6-31G(d) basis set. Energetically the most favorable oxidized ND facets were further optimized with PPy in physisorbed configurations. Analysis of geometry, binding energy, HOMO-LUMO gap, and charge transfer was done on the relaxed PPy-ND structures. Multiple hydrogen bonds are formed between PPy amino groups and O atoms on ND surface. PPy on 1 × 1 reconstructions is energetically favorable with exothermic binding energy (2.7 eV) and high charge transfer (up to 0.26 e⁻) in the dark. The HOMO-LUMO at the PPy-ND interface becomes spatially separated and significantly closer in energy (down to about 1 eV). These features may be beneficial for photovoltaic applications of nanodiamond.

Keywords: Diamond, nanoparticles, polypyrrole, density functional theory, charge transfer

1.   INTRODUCTION

Recent progress in nanotechnology and the increasing ability to characterize matter at the atomic-scale leads to the discovery of intriguing properties and obtaining novel materials with a vast potential for applications. Nanodiamond particles (NDs) have been a focus of nowadays research owing to their unique semiconducting, chemical, and optical properties, as well as tunable surface structure. The applications cover a large range of fields from biomedicine to optoelectronics including renewable energy. Combining NDs with organic molecules into joint organic-inorganic functional systems may result in novel functional devices. An example of a suitable organic material is polypyrrole (PPy), which is one of the most chemically stable conjugated polymers [1] with controllable conductivity. Its HOMO-LUMO gap is 1.3 - 3.2 eV, depending on the method of preparation [2]. Combining PPy with ND has potential use in photovoltaic (PV) applications based on an experimentally measured charge transfer between the bulk diamond and PPy [2]. We have recently reported a computational study of physisorption and chemisorption of PPy on ND facets passivated by hydrogen, which indicated energetic level alignment promising for PV applications [3]. Oxidized nanodiamonds represent an interesting complementary system as the surface dipole of the terminating C-O bonds of diamond is opposite with respect to the dipole of the C-H bonds and relatively stronger.

The most representative surface facets on NDs are (111) and (100) facets [4], [5]. Thermodynamic stability and surface reconstruction of O-terminated NDs under varying conditions and surface coverage of (111) and (100) facets were studied both theoretically [5]-[8] and experimentally [9]. On the 1 × 1 (111) ND surface facet, oxygen in the on-top (i.e. ketone) position with peroxide bridges is the most favorable [8]. On the 2 × 1 (111) facet, oxygen adsorption in on-top and bridge positions were pointed out as the only plausible positions [5]. The bridge configuration occurs preferably at 50% or lower oxygen coverage [4], [8]; 100% O coverage leads to dimerization [5]. On the 1 × 1 (100) facet, the bridge position is preferred at high surface coverage [4].

Alternatively, etherized 1 × 1 (100) structures with a bridging ether may be convenient [7]. For oxygen surface coverage up to 50% on (100), the 2 × 1 reconstruction is preferred over the 1 × 1 reconstruction [4] and epoxy structure is more favorable than the bridge structure [6]. The bridge position is stable at high surface coverage [6], [8].

In this study, we investigate a physisorption of PPy on the most stable, fully oxygen passivated 1 × 1 and 2 × 1 reconstructed (111) and (100) ND surface facets.

2.   COMPUTATIONAL METHODS

The first-principles density functional theory (DFT) method implemented in Gaussian 09 electronic structure software [10] was used for the optimization of all of the structures employing B3LYP functional with the 6-31G(d) basis set. We used (111) and (100) ND surface slabs consisting of 3 C layers of 6 × 6 pattern and surface terminating layer of O atoms. The slabs represented a corner of ND, hence always three "outer" surfaces of ND were functionalized with oxygens and the remaining three "inner" surfaces representing inner cut planes were saturated with hydrogen atoms, which were fixed during the optimizations. More details on the computational setup are provided in our prior work [3].

Based on the literature and our preliminary calculations, we choose the most probable 1 × 1 and 2 × 1 surface reconstructions of both (111) and (100) surface with fully passivated oxygens in ether, epoxide, ketone, and peroxide positions. For both reconstructions of both surface slabs, the oxygen structure with the lowest relative total energy after optimization was chosen for further simulations with absorbed PPy. For the 1 × 1 (111) surface slab was chosen 100% termination with peroxides, for the 2 × 1 (111) 50% of epoxides, for the 1 × 1 (100) 50% with ethers and for the 2 × 1 (100) 50% with epoxides. Note that in the case of ethers and epoxides, the 50% surface coverage generates fully passivated forms.

To study the contact formation, different non-equivalent positions of physisorbed PPy (represented by six Py units) on the relaxed slabs were optimized. Chemisorbed PPy was not calculated due to the high activation barrier for oxygen to be replaced with PPy. The top C layer with the terminating O atoms and PPy were allowed to relax during these further optimizations. For each of the four ND slabs, several initial PPy-ND configurations were tried. The structure with the lowest relative energy with respect to the optimized 1 × 1 (111) or 2 × 1 (100) O-terminated ND slabs was then taken for analysis of geometry, binding energy (E_b), HOMO-LUMO gap, and charge transfer (Δq).

3.   RESULTS AND DISCUSSION

Figures 1 and **2** show the relaxed structures of PPy on ND slabs. The geometry of ND remained almost unchanged. The originally planar character of PPy modifies into an out-of-plane structure as a result of electrostatic interactions between PPy and ND. Multiple H-bonds are created between amino groups of PPy and surface O atoms of ND.

The binding energies E_b, related to the energetic preferences of the interactions are summarized in **Table 1**. The binding energies were calculated as the difference of total energies of the relaxed structures before and after the contact formation according to the formula:

$$(1)$$

$$E_b = (E_{slab} + E_{PPy}) - E_{con},$$

where E corresponds to total energies of C:H slab (E_{slab}), PPy molecule (E_{PPy}), and PPy-C:H structure (E_{con}). Positive E_B corresponds to an exothermic process, i.e. thermodynamically favorable, whereas negative value corresponds to an endothermic process.
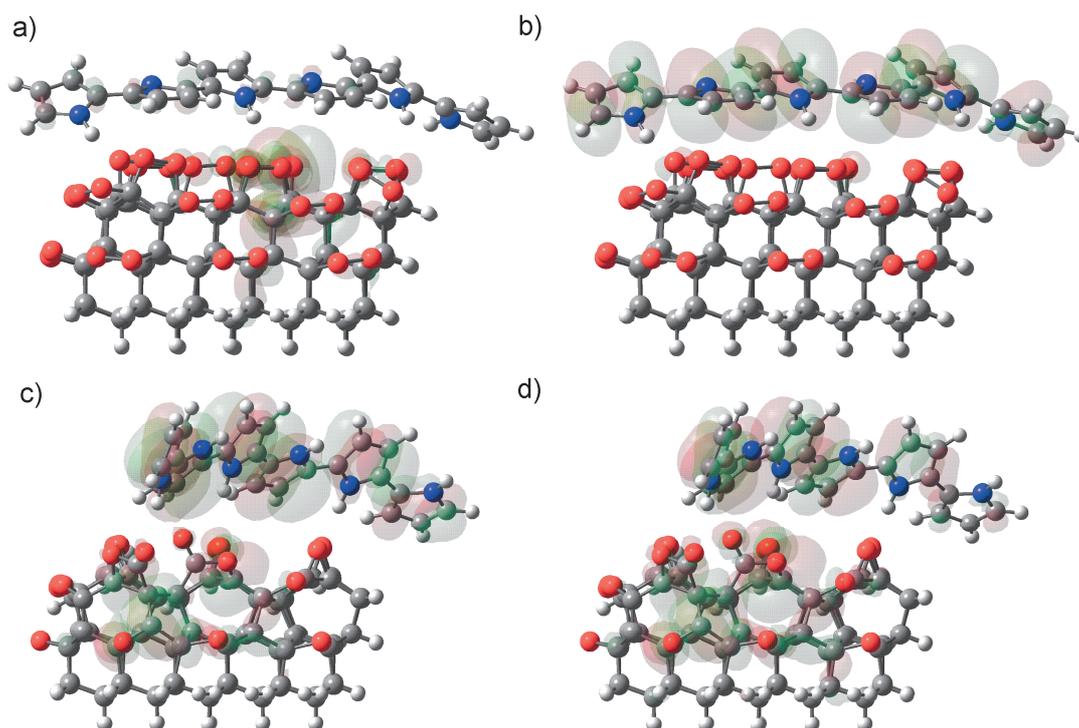
Figure 1 PPy physisorbed on peroxide-terminated 1 × 1 (111) ND slab, side view of HOMO (a) and LUMO (b). PPy physisorbed on epoxide-terminated 2 × 1 (111) ND slab, side view of HOMO (c) and LUMO (d). C atoms are in gray, H atoms are in white, O atoms are in red, and N atoms are in blue
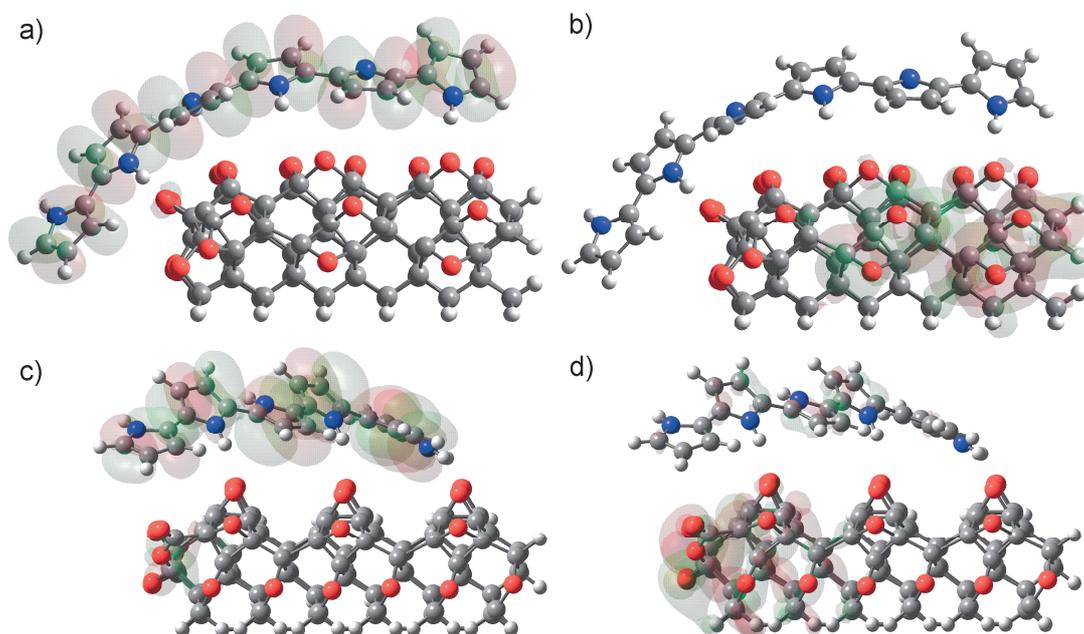
Figure 2 PPy physisorbed on ether-terminated 1 × 1 (100) ND slab, side view of HOMO (a) and LUMO (b). PPy physisorbed on epoxide-terminated 2 × 1 (100) ND slab, side view of HOMO (c) and LUMO (d). C atoms are in gray, H atoms are in white, O atoms are in red, and N atoms are in blue

Formation of all of the calculated structures is exothermic, the highest binding energy of around 2.7 eV is obtained for the case of PPy on 1 × 1 reconstructed facets. The values for the 1 × 1 reconstructed facets are 1.68 - 1.84 eV higher than the values obtained for the 2 × 1 reconstructed facets.

Table 1 Binding energy (E_b), charge transfer (Δq), HOMO-LUMO gap, HOMO and LUMO values

Structure	E_b [eV]	Δq [e⁻]	HOMO-LUMO gap [eV]	HOMO [eV]	LUMO [eV]
1 × 1 (111)	-	-	3.32	-6.35	-3.03
2 × 1 (111)	-	-	3.09	-4.41	-1.32
1 × 1 (100)	-	-	3.29	-5.22	-1.93
2 × 1 (100)	-	-	2.50	-5.42	-2.92
PPy - 1 × 1 (111)	2.76	0.26	1.09	-4.39	-3.30
PPy - 2 × 1 (111)	1.08	0.12	0.40	-3.52	-3.12
PPy - 1 × 1 (100)	2.71	0.19	1.71	-3.53	-1.83
PPy - 2 × 1 (100)	0.87	0.08	0.35	-3.22	-2.87

The calculated HOMO-LUMO gap of PPy is 3.36 eV, agreeing well with theoretical [11] and experimental [2] values. Band gap of bulk diamond is 5.48 eV. The calculated HOMO-LUMO gaps of the O-terminated NDs are in the range of 3.09 - 3.32 eV except for the HOMO-LUMO gap of 2.50 eV for the 2 × 1 (100) slab. Similar results of HOMO-LUMO gaps, equal to 2.76 and 3.72 eV, were obtained for fully passivated O-terminated diamond nanocrystals (with small enough size below 2 nm) by DFT [12]. Band gap in the range of 2.0 and 2.6 eV was also obtained for the O-terminated (100) bulk diamond surface by DFT [13]. After the physisorption of PPy, the HOMO-LUMO gaps significantly decreased by 1.6 - 2.7 eV. Upon the PPy adsorption, the HOMO energy of the ND is increased in the PPy-ND complex in all cases. The LUMO energy decreases in the case of PPy on (111) but increases in the case of PPy on (100) facets.

There is also a considerable spatial separation of HOMO and LUMO at the PPy-ND interface in all cases except the 2 × 1 (111) ND where it is only moderate. HOMO is located mostly on PPy and LUMO is located mostly on ND for all the cases except for PPy on the 1 × 1 (111) ND slab, for which the separation is opposite. Generally, the HOMO and LUMO are found in areas with a significant interaction between PPy and ND, where the most pronounced modification with respect to the separate components happens. This is mostly in the ND corner enclosed by oxygens. Thus the nanoparticle form of diamond may be important for such strong interaction.

The spatial separation of HOMO and LUMO is convenient for photovoltaic applications. It was calculated by DFT for the case of H-terminated NDs interacting with PPy [3] or diamond with adsorbed buckminsterfullerene (C60) [14], for which it was also observed experimentally [15]. Under illumination, the HOMO-LUMO spatial separation can promote dissociation of excitons and thereby lead to a generation of free charge carriers. Moreover, it increases the efficiency of a photovoltaic cell by decreasing the probability of recombination processes.

Charge transfer was calculated as the difference between the number of donated electrons from ND to PPy, and the number of electrons back donated from PPy to ND based on summing up molecular orbitals redistributed to both of the fragments [16]. The positive values of charge transfer, shown in **Table 1**, thus correspond to the net transfer of electrons from ND to PPy. After the absorption, the formerly electrically neutral PPy and the intrinsic O-terminated ND thus become oppositely charged. This may again facilitate the exciton dissociation under illumination. The highest charge transfer of 0.26 e⁻ is observed for PPy on the 1 × 1 (111) structure. The values of the charge transfer are consistent with the binding energy. The higher the binding energy, the greater is the charge transfer. Generally, the values of charge transfer were relatively high comparing with the values obtained for physisorption of PPy on the H-terminated NDs without any H-bonds [3]. The calculated charge transfer mirrors the changes in the frontier molecular orbitals.

4. CONCLUSION

We showed in our calculations that even without chemisorption there is a considerably strong interaction between PPy and O-NDs in terms of PPy structural changes, high exothermic binding energy, high charge transfer and pronounced changes of HOMO-LUMO energy levels at the PPy-ND interface. Formation of hydrogen bonds plays probably an important role in these phenomena. The results also showed that the complex of PPy with O-terminated ND might be suitable for photovoltaic applications since spatially separated HOMO-LUMO orbitals may promote separation of photogenerated charge carriers.

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