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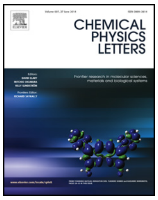

Nonlinear optical response and transparency of hexagonal boron nitride hybrid graphene nanoribbons

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ABSTRACT

The second-order nonlinear optical (NLO) properties of a set of hexagonal boron nitride (BN) hybrid graphene nanoribbons (*h*-BN-GNRs) are studied using density functional theory (DFT) methods. It is found that the β_0 values of all *h*-BN-GNRs in our studied systems are much larger than those of the corresponding hexagonal boron nitride (BN) hybrid carbon nanotubes (*h*-BN-CNTs) [*J. Phys. Chem. C* 117 (2013) 10039]. Importantly, we find that the tradeoff of nonlinearity and transparency could be well modulated by controlling the shape, size, and hybrid position of the *h*-BN ribbons in GNRs.

1. Introduction

The hexagonal boron nitride (BN) hybrid graphene nanoribbons (*h*-BN-GNRs) as novel nanomaterials have attracted great attention [1–11] from theoretical and experimental chemists and physicists due to their novel structural, optical, and electronic properties. The *h*-BN-GNRs have complementary electronic properties of pure graphene and *h*-BN and it is most likely that new properties would be created from the hybridized graphene and *h*-BN because of the tunable electronic energy gap [12–14]. Especially, recent successful syntheses of monolayers of BN-hybridized GNRs by chemical vapor deposition and other methods encourage one to investigate *h*-BN-GNRs [15–18].

On the other hand, the researches and designs of materials with large nonlinear optical (NLO) response [19–23] are of current interest because of the possibility of their use in photonic device applications such as optical data storage [24], optical communication, and optical limiting [25]. The emergence of *h*-BN-GNRs materials brings an opportunity for us to develop new high-performance NLO nanomaterials. It is well-known that the pure graphene and *h*-BN nanoribbons have no or very small first hyperpolarizabilities due to their centrosymmetric structures or large band gaps. For *h*-BN-GNRs, they have obvious and unique advantages as NLO materials compared to graphene and *h*-BN. First, the *h*-BN-GNRs could yield a rich variety of non-centrosymmetric conjugated structures because of the charge redistribution as *h*-BN is inserted into GNRs, which is a prerequisite for designing second-order NLO materials. Second, the *h*-BN-GNRs have tunable gaps [26] by controlling the shape, size, hybrid position, and covering area of the *h*-BN ribbons, which is another important factor to modulate the nonlinearity and transparency tradeoff. Therefore, more and more attention is paid to investigate nonlinear optical responses of *h*-BN-GNRs. More recently, Karamanis et al. [10] have studied the second-order NLO responses of a series of hexagonal boron nitride coronene ($B_{12}N_{12}$) hybrid hexagonal graphene nanoribbons, in which the β_0 value of *h*-$B_{12}N_{12}$—C_{84} is 7.3×10^3 au at the CAM-B3LYP level. However, the β_0 value of hexagonal boron–nitride hybrid carbon nanotube (*h*-$B_{10}N_{10}$—C_{30}) is 1.05×10^4 au at the same level of theory reported by Su et al. [27]. In previous investigations, the NLO of modified GNRs is better than that of corresponding modified CNTs [28]. A question is therefore produced: why the NLO response of the larger size *h*-BN-GNR is not as good as small size h-BN-CNTs? In addition, in practical applications, the transparency of materials at the used laser wavelength is of great importance. Unfortunately, the above studies did not report this information. Thus, in this work, a comparison of second-order NLO responses between *h*-BN-GNRs and *h*-BN-CNTs are done, including size, shape, and position. Moreover, we investigate the tunable relationship between nonlinearity and transparency of *h*-BN-GNRs. It is our expectation that this work could provide important information for designing high-performance NLO carbon-based materials.

2. Computational methods

Based on the structures of four BN-hybrid finite (5, 0)CNTs (BN-1, BN-2, BN-3, and BN-4) reported by Su [27], we construct four corresponding BN-hybrid finite GNRs (*h*-BN-(5,5)GNR-1,

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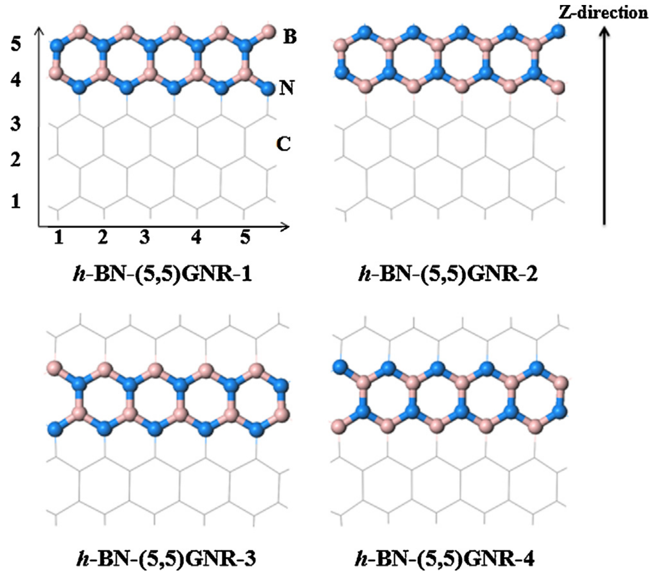

Figure 1. Geometric structures of four isomers of *h*-BN-(5,5)GNR-*n* (*n* = 1–4).

h-BN-(5,5)GNR-2, *h*-BN-(5,5)GNR-3, and *h*-BN-(5,5)GNR-4) by cutting BN-hybrid CNTs along the axis of tubes (see Figure 1). M and N in (M, N)BN-GNRs were used to represent the dimension of BN-hybrid GNRs: M denotes the zigzag edge, and N denotes the armchair edge. In addition, we also construct different sized BN-hybrid GNRs (see Figure 2). The geometrical structures are optimized using the popular exchange-correlation density functional theoretical method-the B3LYP method (Becke's nonlocal three-parameter exchange and correlation functional with the Lee–Yang–Parr correlation functional) at the 6-31G(d) basis set. All optimized structures are minimum points on the potential energy surface as confirmed by sequential harmonic frequency calculations.

In this study, we employed the finite field (FF) approach to calculate static polarizability (α_0) and first hyperpolarizability (β_0) for all the systems.

When a system is in a weak and stable applied electric field, its energy can be written as [29]:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma \cdots \quad (1)$$

where E^0 is the molecular energy without the electric field, and F_α is an electric field component along α direction; μ, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the dipole moment, polarizability, and first hyperpolarizability, respectively.

The polarizability (α_0) is defined as follows:

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

The static first hyperpolarizability (β_0) is defined as follows:

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_y^2)^{1/2} \quad (3)$$

where

$$\beta_x = \frac{3}{5}(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$$

$$\beta_y = \frac{3}{5}(\beta_{yyy} + \beta_{yxx} + \beta_{yzz})$$

$$\beta_z = \frac{3}{5}(\beta_{zzz} + \beta_{zxx} + \beta_{zyy})$$

Recently, many studies [10,27] have demonstrated that for the evaluation of the NLO properties of BCN-related species, a long-range corrected DFT method, for example CAM-B3LYP, can provide more reasonable and accurate predictions. Su et al. used the CAM-B3LYP method to calculate NLO properties of *h*-BN-CNTs. For a comparison of NLO between *h*-BN-GNRs and *h*-BN-CNTs, thus we also choose the same method (CAM-B3LYP/6-31+G*) for all the *h*-BN-GNRs [27]. Besides, the time-dependent DFT (TD-DFT) procedure was employed to calculate the crucial electronic transitions of the related systems, in which the CAM-B3LYP/6-31+G(d) method was adopted.

All of these calculations were performed with the GAUSSIAN 09 program packages [30].

3. Results and discussions

3.1. Geometrical structures, energy, and NBO charges

The optimized structures of four isomers for *h*-BN-(5,5)GNRs ($B_{10}N_{10}C_{30}$) are shown in Figure 1, and main geometrical parameters are listed in Table 1. Generally, an isomer with lower total energy has higher thermodynamic stability. At the

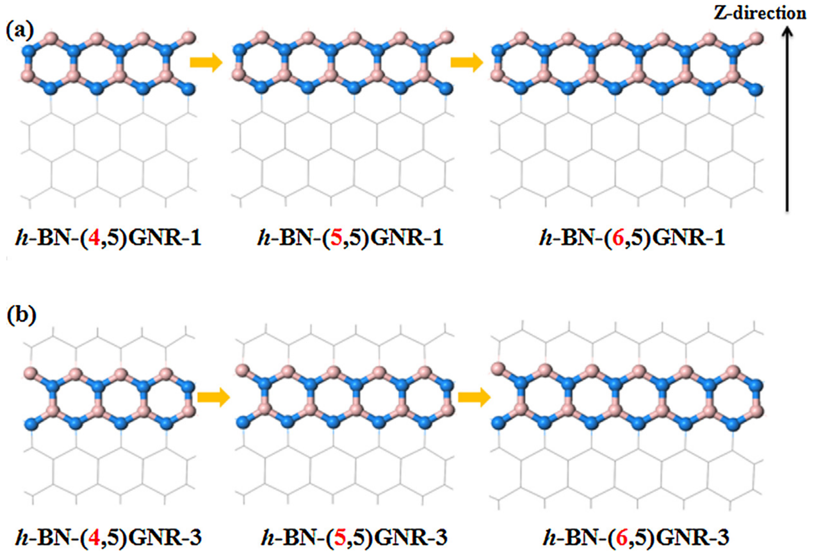

Figure 2. Geometric structures of different sizes of *h*-BN-(M,N)GNR-1 and *h*-BN-(M,N)GNR-3 (*M* = 4, 5, and 6; *N* = 5).