

First-principles calculations on the curvature evolution and cross-linkage in carbon nitride

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Abstract

First-principles calculations were utilized to study the formation mechanisms and structural features of fullerene-like carbon nitride (FL CN_x). Cohesive energy comparisons reveal the energy cost for different defects arising from substitution of C for N as a function of the nitrogen concentration. In FL CN_x, combinations of pentagons and heptagons compete in causing graphene sheet curvature during the addition of CN-precursors and single species. Also, cross-linkage between graphene layers in FL CN_x can be explained by the bond rotation due to incorporated N atoms. The computational results agree with recent experimental observations from the growth of FL CN_x thin films.

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1. Introduction

Fullerene-like carbon nitride (FL CN_x) compounds can be synthesized in the form of thin solid films by physical vapor deposition methods at a relatively low substrate temperature [1]. In FL CN_x the substitutional nitrogen at carbon sites in graphene layers promotes their bending and cross-linkage [1], enabling the material to extend the strength of a planar sp²-coordinated carbon network in three dimensions [2].

Like for fullerenes, the pentagon incorporation in FL CN_x is considered the key to the formation of curved graphene sheets [3]. Density functional theory (DFT) calculations [4] and quantum chemistry results [5,6] indicate that nitrogen incorporation promotes formation of pentagons and suggest increased reactivity of the carbon

sites next to nitrogen which can result in cross-linking between the as-formed corrugated graphene layers. The energy costs for incorporation of other defects such as Stone-Wales (SW) defects and four-membered rings, which also can contribute to the sheet curvature, have not been evaluated yet.

In a previous Letter, the role of the preformed CN species in the deposition flux was found important for the pentagon formation as to the evolution of curvature of the graphene sheets [7]. By performing geometry optimizations and cohesive energy calculations within the framework of DFT in its generalized gradient approximation (GGA), this Letter reports on two additional key issues of the FL CN_x structure evolution:

- (i) the energy cost as a function of the nitrogen concentration for a variety of curvature promoting defects. The input parameters are relevant to experimental findings, such as a nitrogen concentration between 10 and ~30 at.% observed in FL CN_x [8,9];
- (ii) the implication of the bond rotation on the cross-linkage.

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2. Computational details

The energy cost for substitutional N at C sites was investigated by geometry optimization of model systems containing different types of defects. To study the cross-linkage, in a recursion model for the FL CN_x structure evolution we added C and CN precursors to optimized planar CN_x clusters. The details of the optimization strategies are presented elsewhere [7].

The calculations were carried out using the GAUSSIAN 03 program [10]. For the DFT–GGA the Perdew Wang exchange–correlation functional (PW91) [11] and the B3LYP hybrid functional [12] have been used. Both are known to provide an accurate description of the structural and electronic properties of CN_x [7] and similar systems, e.g., the aza-fullerene ($C_{48}N_{12}$) [13–15].

3. Results and discussion

3.1. Energy cost for substitutional N at C sites

By optimizing sequences of structurally identical model systems with different (0–50 at.%) nitrogen concentrations, the energy cost for substitutional nitrogen at carbon sites as a function of the nitrogen concentration was obtained for purely hexagonal (graphene) structure of CN_x , systems containing: a singular pentagon, a double pentagon defect, a SW defect, and a four-membered ring.

Optimized model systems are shown in Fig. 1, whereas the dependences of $|\Delta E_{\text{coh}}|/n$ (where n is the total number of both carbon and nitrogen atoms) on the nitrogen concentration for these structures are displayed in Fig. 2. As expected from previous calculations [4,16], the energy cost to form a pentagon (or pentagons) in carbon network is significantly reduced if nitrogen is incorporated

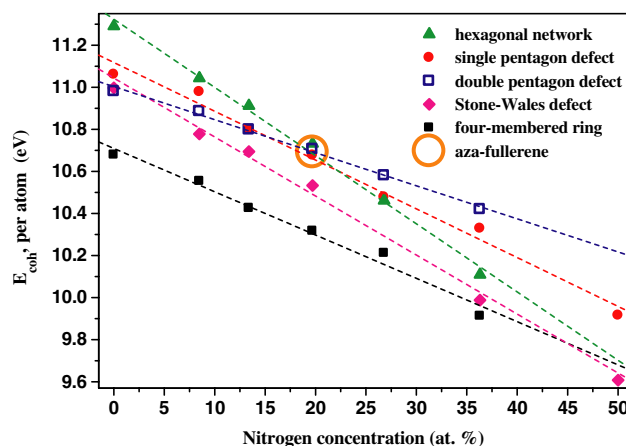


Fig. 2. PW91 cohesive energies per atom as a function of the nitrogen concentration. Nitrogen atoms were added at given sites of the model systems shown in Fig. 1 in order to achieve the corresponding nitrogen concentrations. The triangles correspond to purely hexagonal network, the circles to systems with a singular pentagon, the open squares to systems with a double pentagon defect, the diamonds to configurations with a SW defect, and the solid squares to systems with a four-membered ring. The aza-fullerene $C_{48}N_{12}$ [13] is included for comparison. The dashed lines connecting the points are depicted by linear fit in order to guide the eye. For the highest nitrogen concentration well-optimized structures were obtained only for some of the systems.

in the sheet. Consequently, the purely hexagonal system is energetically most favorable only for nitrogen concentrations below ~ 20 at.%. For higher nitrogen concentrations, the systems containing pentagons become more stable than the graphene layer. It is suggestive that the confirmed as stable aza-fullerene molecule contains exactly 20 at.% nitrogen, i.e., the approximate concentration for which pentagon defects become as stable as the graphene structure. In contrast to previous studies, in which only singular pentagons (Fig. 1b) have been considered, the present Letter also includes a study of double pentagon defects (patches of two pentagons and

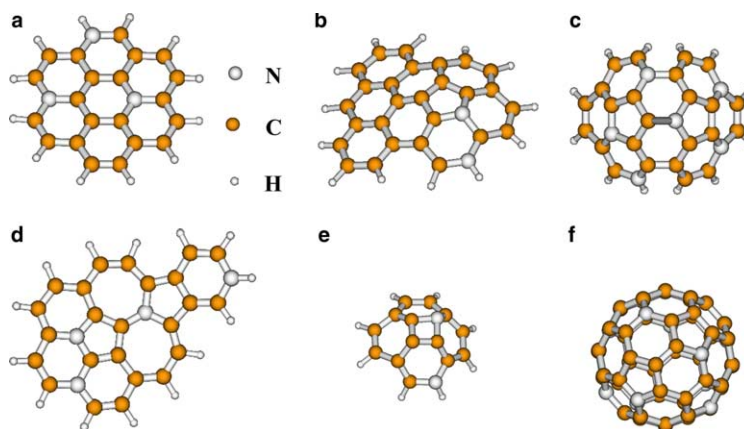


Fig. 1. Typical CN model systems optimized in order to evaluate the cost for substitutional N at C sites at different nitrogen concentrations in: (a) hexagonal network, and structures containing (b) a pentagon, (c) a double pentagon defect, (d) a SW defect, and (e) a four-membered ring. The aza-fullerene $C_{48}N_{12}$ [13] (f) is considered as a benchmark.

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