Carbon 118 (2017) 184–191

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

# Adsorption of graphene to nickel (111) using the exchange-hole dipole moment model

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ARTICLE INFO

*Article history:*
Received 10 January 2017
Received in revised form
16 February 2017
Accepted 9 March 2017
Available online 14 March 2017

## ABSTRACT

Graphene is a promising material for a number of technological applications due to its unique electronic properties. It can be mass produced by depositing carbon atoms on metal scaffolds, such as nickel. This work presents a detailed study of graphene adsorption on the nickel (111) surface using the exchange-hole dipole moment (XDM) dispersion correction. XDM is shown to accurately model graphene-nickel interactions, providing adsorption energies in excellent agreement with available experimental data and with RPA calculations. All six graphene-nickel orientations studied present a physisorption energy minimum, but only three exhibit chemisorption. The physisorption and chemisorption minima are close in energy, and are separated by a barrier of ~1 kJ/mol per carbon. The relative strength of the chemisorption and physisorption interactions is found to depend heavily on the nickel lattice constant. Thermal expansion stabilizes chemisorption relative to physisorption. The pairwise dispersion coefficients depend strongly on the graphene-nickel distance, and their variation is determined by the exchange-hole dipole moments. If this dependence of the dispersion coefficients with the environment is properly captured, a pairwise dispersion correction (like XDM) is suitable to model surface adsorption.

## 1. Introduction

Graphene and its potential applications have received much attention over the past decade. Interest in this material grew as a result of the seminal investigation by Novoselov et al., in which the authors presented an experimental procedure, the “scotch-tape” method, to isolate high-quality stable graphene layers from graphite [1]. In the past few years, numerous papers have detailed graphene's unique electronic structure and properties [1–14]. Though the scotch-tape method is well suited to creating laboratory samples of graphene, the process is not applicable in the industrial scale. A promising scalable method for commercial graphene manufacturing involves depositing carbon atoms on metallic scaffolds [15–18], via processes such as chemical vapor deposition (CVD).

In the CVD method, small molecules, such as methane and ethanol, are vaporized at high temperature (~1000 K). The resulting carbon soot is deposited on a metal surface, producing a single monolayer of adsorbed graphene. Once the monolayer is synthesized, a polymer resin is applied to the graphene surface and the metal is typically removed with an acid bath. The graphene layer can then be transferred to the desired substrate and the polymer resin dissolved [16,19–21]. Nickel is an excellent substrate for graphene synthesis because it is both inexpensive and its (111) surface has cell dimensions commensurate with graphene [22–26]. It has been shown that multi-layer graphene can be manufactured similarly, although the exact mechanism as to how multi-layers form is still under debate [6,14,16,20].

Multiple studies of the graphene-nickel system using density-functional theory (DFT) have been published [26–33]. These articles show that generalized gradient approximation (GGA) functionals alone grossly fail to predict experimental adsorption energies and geometries of the graphene-nickel system because GGAs do not adequately describe London dispersion interactions. Even when dispersion interactions are taken into account (e.g. by using one of the multiple available dispersion corrections [34–39]), reproducing the experimental graphene-nickel adsorption energies and interlayer distances is a challenge [27–30]. The difficulties arise from the competing factors that determine the nature of the metal-graphene interaction in this system. Experimentally, graphene is known to chemisorb on the nickel (111) surface [22,40]; its

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http://dx.doi.org/10.1016/j.carbon.2017.03.024
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adsorption energy and distance depend critically on a fine balance between Pauli repulsion, dispersion, and the strength of the incipient chemical bond between graphene and the metal surface [41].

The random-phase approximation (RPA) method [26,42] is a significant improvement over both the local density approximation (LDA) and GGA functionals regarding the calculation of intermolecular interactions. Unlike dispersion-corrected GGAs, RPA incorporates dispersion interactions in a non-empirical ,seamless fashion, albeit at a much higher computational cost. Mittendorfer et al. [26] and Olsen et al. [42] used RPA calculations to show that graphene not only chemisorbs on nickel, but also physisorbs at larger interlayer distances, giving the adsorption potential energy surface (PES) a characteristic double-minimum profile, with the chemisorption and physisorption minima being very close in energy. Since RPA is too expensive for large surface models, GGA-based functionals have been proposed that include dispersion either via an explicit non-local correlation contribution [43–45] or by adding a dispersion energy correction [37–39,46–49]. Janthon et al. [27] recently examined the ability of several of these density functionals to predict the graphene-nickel adsorption energy. Good adsorption energies and interlayer distances were obtained with optB86b-vdW [44,50] and DFT-D [48]. The latter is somewhat surprising given that both vdw-TS and DFT-D overestimate the strength of molecular physisorption on noble metal surfaces [51–53]. More recent developments of the same functionals (DFT-D3 and MBD) offer better performance [54].

In this paper, we investigate the adsorption of graphene on nickel (111) using GGA functionals combined with the exchange-hole dipole moment (XDM) dispersion correction [39,46,55–57]. XDM has been previously shown to accurately model a wide variety of systems where dispersion interactions play an important role: small noble gas clusters [58,59], molecular dimers [60–62], supramolecular systems [63], and molecular crystal absolute [64] and relative lattice energies [65,66]. More relevant to this paper, we have demonstrated previously that XDM successfully predicts physisorption of molecules to surfaces [67,68]. An important point to note in these studies is that XDM shows good performance in widely different systems without any change to the formalism, implementation, or damping parameters, hence making it an ideal candidate for studying chemistry on surfaces and the interaction between inorganic materials and organic molecules.

In the remainder of this paper, we show that XDM describes the graphene-nickel system accurately. Our results reproduce reported RPA potential energy surfaces [26,42] and agree with available experimental adsorption energies [69]. We also show that the predicted mode of adsorption (chemisorption or physisorption) is highly sensitive to the nickel lattice constant, and that accounting for thermal effects favors the chemisorption state. The results are discussed in the context of the mechanism of bilayer graphene formation on nickel substrates.

## 2. Computational methods

Periodic-boundary DFT calculations were performed using the pseudopotential/plane-wave approach and the Projector Augmented Wave (PAW) formalism [70]. Calculations were carried out using the XDM implementation in Quantum ESPRESSO [46,71] with the B86bPBE functional [72,73], known to perform well in conjunction with XDM [61,64]. Calculations using the LDA [74] and PBE [73] exchange-correlation functionals were also conducted for comparison. An $8 \times 8 \times 1$ $\Gamma$-centered **k**-point grid was used, with a plane-wave cutoff of 60 Ry, a density expansion cutoff of 800 Ry, and cold smearing [75] with a smearing parameter of 0.01 Ry.

The XDM dispersion functional is a correction to the base DFT energy:

$$E = E_{\text{base}} + E_{\text{XDM}} \tag{1}$$

$$E_{\text{XDM}} = -\frac{1}{2} \sum_{n=6,8,10} \sum_{i \neq j} \frac{C_{n,ij} f_n(R_{ij})}{R_{ij}^n} \tag{2}$$

In this equation, $i$ and $j$ run over atoms in the system and $R_{ij}$ is the interatomic distance. $f_n$ is a damping function that attenuates the dispersion correction at short range, and the $C_{n,ij}$ are pairwise dispersion coefficients. Each $C_{n,ij}$ is approximated non-empirically via second-order perturbation theory using the multipole moments of the electron plus exchange-hole distribution and atom-in-molecule polarizabilities for the interacting atoms [39].

The nickel (111) surface was modeled as an infinite slab consisting of six atomic layers. All calculations used a $(1 \times 1)$ surface unit cell, with a vacuum of 25 Å inserted in the $z$-direction to separate each slab from its periodic image. Six orientations of graphene on nickel were considered for this study (see Fig. 1). The adsorption energies were calculated as the difference between the graphene-nickel system and the energies of the bare surface and isolated graphene sheet, whose geometries were optimized independently:

$$E_{\text{adsorption}} = -\left(E_{\text{adsorbate}} - E_{\text{surf}} - E_{\text{graph}}\right) \tag{3}$$

Throughout the article, adsorption energies are reported per carbon atom.

Potential energy surfaces (PES) for adsorption were generated by systematically varying the $z$ distance between graphene and the nickel surface and performing a series of single-point energy calculations. The experimental lattice constants of graphene and nickel at room temperature are similar, but not exactly equal, and lattice vibrations cause a small, but not negligible, thermal expansion. As such, the dependence of the adsorption energy on the bulk lattice constant of the nickel slab was analysed. Note that this lattice constant defines the length of the two symmetry-equivalent $x, y$-axes for the nickel slab, and the nickel-nickel interlayer distances as well. Calculations were performed with the lattice constant ranging between 2.45 Å and 2.50 Å in 0.01 Å increments. This range encompasses the minimum-energy interatomic distances in bulk nickel (2.450 Å with B86bPBE-XDM and 2.451 Å with PBE-XDM) and in graphene (2.462 Å with both functionals), as well as the minimum-energy lattice constant of a pure nickel (111) surface (2.465 Å with B86bPBE-XDM and 2.464 Å with PBE-XDM). It also encompasses the experimental interatomic distances in graphite (2.46 Å [76]), in bulk nickel (2.49 Å [76]), and in the nickel (111) surface (2.49 Å [77]). The final PES, minimum-energy structures, and adsorption energies for all orientations were obtained by quadratic interpolation between the results for each discrete value of the nickel lattice constant. This was done due to the strong dependence of the XDM dispersion coefficients on both the lattice constant and graphene-nickel separation (see the Supplementary Material).

Finally, the nature of the graphene-nickel interaction was investigated using Bader's Quantum Theory of Atoms in Molecules (QTAIM) [78,79]. QTAIM atomic charges were calculated using the Yu-Trinkle algorithm [80] implemented in the CRITIC2 program [81]. The differences between the QTAIM charges for the isolated nickel and graphene sheet and the adsorbate determines the degree of charge transfer.