Applied Surface Science 421 (2017) 252–259

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Density functional theory calculations on transition metal atoms adsorbed on graphene monolayers

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ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form 17 October 2016
Accepted 22 October 2016
Available online 24 October 2016

Keywords:
Density functional theory
Graphene
Transition metal adsorption
Overlap population

ABSTRACT

Transition metal atom adsorption on graphene monolayers has been elucidated using periodic density functional theory under hybrid and generalized gradient approximation functionals. More specifically, we examined the adsorption of Cu, Fe, Zn, Ru, and Os on graphene monolayers by calculating, among others, the electronic density-of-states spectra of the adatom-graphene system and the overlap populations of the adatom with the nearest adsorbing graphene carbon atoms. These calculations reveal that Cu form primarily covalent bonds with graphene atoms via strong hybridization between the adatom orbitals and the sp band of the graphene substrate, whereas the interaction of the Ru and Os with graphene also contain ionic parts. Although the interaction of Fe with graphene atoms is mostly covalent, some charge transfer to graphene is also observed. The interaction of Zn with graphene is weak. Mulliken population analysis and charge contour maps are used to elucidate charge transfers between the adatom and the substrate. The adsorption strength is correlated with the metal adsorption energy and the height of the metal adatom from the graphene plane for the geometrically optimized adatom-graphene system. Our analysis shows that show that metal adsorption strength follows the adatom trend Ru ≈ Os > Fe > Cu > Zn, as verified by corresponding changes in the adsorption energies. The increased metal-carbon orbital overlap for the Ru relative to Os adatom is attributed to hybridization defects.

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1. Introduction

Graphene is the basic structure for forming carbon nanotubes (CNTs), fullerene, and graphite. One dimensional CNTs can be metallic or semi-conducting [1], while two dimensional graphene has unique sub-lattice symmetry and is a zero-gap semi-conductor [2]. Graphene and CNTs have been extensively studied due to their potential applications in the fields of microelectronics, hydrogen storage, and chemical sensors [3–5]. Graphene's extreme mechanical strength of 130 Pa and it's high thermal and electrical conductivity [6–8] made it a strong candidate for serving as flexible cell phone panel displays and televisions. The carbon allotrope graphene, which was accidentally discovered by Novoselov et al. [9] is an excellent candidate for theoretical study. For example, although, the Mermin-Wagner theorem [10] states that perfect 2D crystals are not thermodynamically stable and thus, should not exist, graphene existence as stacked 2D layers is possibly due to the presence of microscopic buckling [11] and intrinsic ripples [12] in the monolayer structure. Graphene hexagonal lattice with sp^2 hybridization gives rise to interesting new physics, such as anomalous quantum Hall effect and presence of massless Dirac fermions, thus providing evidence of the new important discoveries due to its lower dimensionality [13,14].

Fabrication of electronic devices for applications and electronic transport measurements require graphene contract with metal electrodes [15]. For example, graphene transistors operating at gigahertz frequencies require layers of Ti and Pd as source and drain electrodes [16]. Therefore, the atomistic study of metal-graphene interface is essential to controllably alter graphene and CNT properties. Adatom alkali, transition, and noble metal adsorption on graphene monolayers has been studied by Chan et al. using periodic spin-polarized density functional theory (DFT) [17]. Migration energies (i.e., energy for adatom to move to a different adsorption site) have been reported by Nakada and Ishi [18], using periodic DFT under the local density approximation (LDA). The high migration energies of some transition metals adsorbed on graphene (e.g., Fe, Co, Mn, etc.) lead to stable adatom-graphene systems under room temperature conditions. Ishii et al. reported similar calculations using local and generalized gradient approximation (GGA) DFT for adatom adsorption on graphene as a precursor for CNTs

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http://dx.doi.org/10.1016/j.apsusc.2016.10.144
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[19]. It was found that Mo and Ru adatoms strongly bind on the graphene surface. Amft et al. studied adsorption of Cu, Ag, and Au on graphene and examined the effect of van der Waals interactions during adsorption [20]. The adsorption of Fe, Mn, and Co on graphene has been studied by Mao et al. [21] using spin-polarized DFT. The hcp site was found to be the preferred adsorption site for these atoms, with Mn and Co adatoms to be metallic, whereas Fe is semi-half metallic. The adsorption of 15 different transition metal and noble metal atoms has been studied by Hu et al. using DFT under GGA [22]. Small metal adsorption energies (E_{ads}) were found for half-filled d-orbital transition metals and Au, Ag, and Zn adsorbed on graphene.

In this work, we are using periodic DFT to study the adsorption of the transition metals Cu, Fe, Zn, Ru, and Os on graphene monolayers, thus covering a wide variety of metals with different adsorption behaviors on graphene. For example, Ru and Os strongly bind on graphene surface, whereas the interaction of Zn with graphene is minimal (vide infra). Here, we examine the effect of the adatom basis set and the functional used in the DFT calculated electronic and structural properties of adatom-graphene systems. Elucidation of the adsorption of these transition metals on graphene explain how the presence of these atoms affect the electronic and structural properties of graphene monolayers, which may lead to nanomaterials of improved electron transport properties relative to clean graphene. Adatom-graphene interaction is analyzed using changes in the E_{ads}, the distances between adatoms and the graphene monolayer, changes in density-of-states (DOS) spectra, charge transfers between the adatom and graphene monolayer, and overlap populations between the adatom and the nearest graphene carbon atom.

2. Computational methods

Graphene is modeled as two-dimensional 4 × 4 and 6 × 6 hexagonal lattices with 32 and 72 carbon atoms, respectively. Adsorption of a single metal atom on the 4 × 4 and 6 × 6 graphene lattices corresponds to about 3% and 1.4% adatom surface coverage. The transition metals of Cu, Fe, Zn, Ru, and Os are placed as adatoms to the graphene substrate. The optimal geometries of the adatom-graphene systems are obtained using periodic restricted DFT [23–25]. Fig. 1 shows the 4 × 4 and 6 × 6 graphene substrates and the metal adsorption sites. The CRYSTAL09 [26] program is used to calculate the electronic properties and optimal geometries of the adatom-graphene systems under the B3LYP hybrid semiempirical functional [27] and the PBE0 non-empirical parameter-free functional [28,29]. Here, the B3LYP functional has the same exact and exchange functionals as the original B3LYP functional, whereas the VWN correlation functional is replaced by VWN5 [30]. For comparison purposes, some calculations are repeated with the GGA PBE functional [31]. The graphene lattice parameter obtained by using B3LYP and PBE0 functionals is 2.45 Å and 2.44 Å, respectively. These values are very close to the experimentally obtained graphite lattice parameter of 2.46 Å [32]. CRYSTAL09 employs Gaussian type function basis sets centered at the atoms. Similar to our past work for Fe adsorbed on graphene [33], the graphene carbon atoms are described by the contracted triple-ζ [4s3p1d] basis set [34], which is optimized for crystalline calculations. The adatoms of this work are described by all-electron atomic basis sets of various sizes, with the exception of Os and Ru that effective core pseudopotentials (ECP) are used [35,36].

Brillouin zone integrations (Monkhorst-Pack grid) [37], the Fermi energy, and the density matrix calculations (Gilat grid) [38,39] were performed on a 24 × 24 grid. For the systems of this work, a smaller grid of 12 × 12 did not affect the obtained electronic and structural properties. The Fermi surface was smeared with a Gaussian of 0.005 Hartrees for convergence purposes. Moreover, the SCF energy convergence was achieved by using Anderson quadratic mixing [40], coupled with additional mixing of the occupied with the virtual orbitals. The SCF energy threshold value for our calculations was set at 10^{-12} Hartrees and 10^{-9} Hartrees for the clean graphene substrates and the adatom-graphene systems, respectively (default value is 10^{-7} Hartrees). A large integration grid was used (XLGRID keyword): This is a pruned grid with 75 radial and 974 angular points. Densities-of states (DOS) spectra and crystal orbital overlap populations (COOP) for selected pair of atoms [41] were calculated directly by CRYSTAL09. The XcrySDen graphical package was used for the charge density plots of this work [42]. Charge transfers were calculated using Mulliken population analysis [43] and by direct integration of the DOS spectrum. The stability of the final geometry conformations was secured via post-geometry optimizations of the final structure (FINALRUN keyword set to 4).

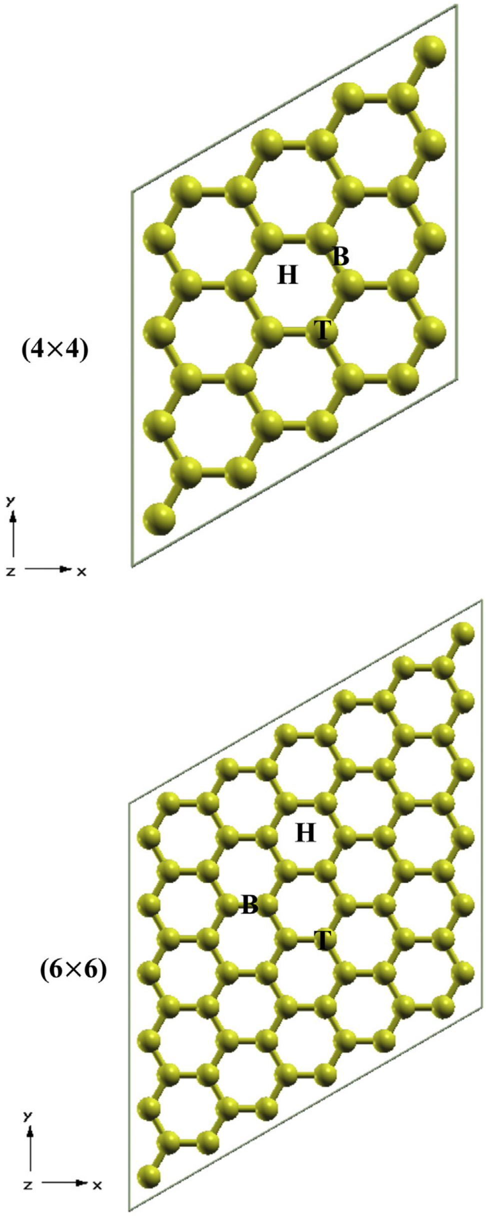

Fig. 1. Graphene substrates used. Top. (4 × 4). Bottom. (6 × 6). T, B, and H stand for adsorption at the atop, bridge, and hcp sites, respectively.

The E_{ads} is defined as $E_{ads} = E_{X/graphene} - E_X - E_{graphene}$, where X is the adatom and is a measure of the adatom interaction with the

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