Surface & Coatings Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Density functional theory of graphene/Cu phthalocyanine composite material

A. Jomphoak [a,b], R. Maezono [b], T. Onjun [a,*]

[a] *Sirindhorn International Institute of Technology (SIIT), Thammasat University, Pathum Thani 12121, Thailand*
[b] *Japan Advanced Institute of Science and Technology (JAIST), Nomi, Ishikawa 923-1292, Japan*

ARTICLE INFO

Article history:
Received 24 December 2015
Revised 30 May 2016
Accepted in revised form 7 June 2016
Available online xxxx

Keywords:
Graphene
Copper phthalocyanine
Density functional theory

ABSTRACT

The molecular structure of graphene–copper phthalocyanine was predicted using the density functional theory with three different optimization methods, including local density approximation (LDA), generalized gradient approximation (GGA), and a conventional hybrid, B3LYP, functionals. Based on the molecular structure of graphene–copper phthalocyanine, some properties can be obtained. It was found that the distance between graphene sheet and the copper phthalocyanine molecule was about 3.155–3.734 Å. The adsorption of copper phthalocyanine molecule on the graphene layer was found to be a spontaneous process with the shortest distance between the two layers. In addition, the presence of the copper phthalocyanine molecule on the graphene layer resulted in a decrease of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap, and therefore, increased reactivity compared to isolated copper phthalocyanine and graphene. Thus, the presence of copper phthalocyanine can enhance charge transport in graphene, which leads to a high-quality transparent conductive material.

1. Introduction

Copper phthalocyanine (CuPc) in a solid form is a highly stable organic material with numerous applications in industry, such as switches, solar cells, gas sensor, and molecular electronics [1,2]. CuPc has shown special physical and chemical properties as a class of macro-cyclic planar compounds. In the case of electronics, the properties of the CuPc interface with other organic or inorganic materials normally dominate the performance of CuPc-based devices. Numerous experiments on its optical, magnetic, and electric properties have been conducted to understand the interfaces of CuPc with other materials [3–8].

Because CuPc is a complex of a macro-cyclic compound with an extended system of π density, it adsorbs on graphite and other molecules of carbon [9], for the development of electrodes where the CuPc behaves as a mediator in electrochemical processes of charge transfer. It is useful for the detection of a diversity of organic molecules [9]. Recently, it was discovered that CuPc can enhance the electrical properties of graphene for use as a high-quality transparent conductive film [10]. Thus, it is of great interest to investigate the molecular structure of graphene/CuPc to gain knowledge of the properties of this composite material.

For the monomer of CuPc, the experimental structure in the crystalline state has been determined by three-dimensional X-ray diffraction data [11] for its bond length and bond angle (see Table 1 for comparison with our DFT calculations). Based on density functional theory (DFT), the previous computational studies for the electronic structure of CuPc composite materials are reported in Refs [12–18]. The geometries from previous experimental measurements and our theoretical calculations are further discussed in the third section. The calculated energy gap of CuPc between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) from another author [10] is 1.42 eV by applying the DFT method based on the Vosko–Wilk–Nusair (VWN) local spin-density potential with Becke's gradient correction for exchange and Perdew's gradient correction for correlation [19].

The first principle calculations of graphene/CuPc molecular structure can deliver a well-founded basis for the interpretation of experimental data and underline the physics of such systems. The relation between calculated properties and theirs experimental phenomena will be explored. The computational results are useful information to elucidate the formation of graphene/CuPc complex for both experimental conditions and industrialized synthesis. In this work, CuPc on a monolayer graphene was selected as a model system for simulation. Bond lengths and angles obtained with the different functionals used in this work are provided as electronic supplementary material.

The present work aims to simulate the molecular structure, formation, stability, and adsorption energies of graphene/CuPc using the Materials Studio software package either with local density approximation (LDA), or generalized gradient approximation (GGA), or a conventional hybrid, B3LYP, functionals. The details of these methods are shown in

---

* Corresponding author.
E-mail address: thawatchai@siit.tu.ac.th (T. Onjun).

http://dx.doi.org/10.1016/j.surfcoat.2016.06.015
0257-8972/© 2016 Elsevier B.V. All rights reserved.

Please cite this article as: A. Jomphoak, et al., Surf. Coat. Technol. (2016), http://dx.doi.org/10.1016/j.surfcoat.2016.06.015

Table 1
Structural parameters (bond length in Å and bond angle in degrees) of CuPc calculated with different exchange-correlation functionals; atom labels from Fig. 1, and experimental data [11] reported for comparison.

Properties		Experimental data [11]	Simulation results					
			LDA	% error	PBE	% error	B3LYP	% error
Bond length (Å)	Cu–N1	1.935	1.990	2.842	2.024	4.599	2.006	3.669
	N1–C2	1.366	1.409	3.148	1.421	4.026	1.411	3.294
	C2–N2	1.328	1.335	0.527	1.353	1.883	1.345	1.280
	C2–C3	1.453	1.435	− 1.239	1.450	− 0.206	1.443	− 0.688
	C3–C4	1.400	1.431	2.214	1.446	3.286	1.436	2.571
	C3–C5	1.388	1.406	1.297	1.421	2.378	1.411	1.657
	C5–C6	1.377	1.413	2.614	1.423	3.341	1.413	2.614
	C6–C7	1.400	1.416	1.143	1.428	2.000	1.418	1.286
Angle (°)	C2–N1–C1	107.3	107.478	0.166	107.853	0.515	107.886	0.546
	N1–C2–N2	127.6	125.179	− 1.897	125.413	− 1.714	125.801	− 1.410
	N1–C2–C3	110.4	109.214	− 1.074	108.940	− 1.322	108.962	− 1.303
	C2–N2–C8	NA	126.711	–	126.832	–	126.093	–
	C2–C3–C4	NA	107.008	–	107.049	–	107.088	–
	C4–C3–C5	NA	120.937	–	120.769	–	120.859	–
	C3–C5–C6	NA	117.908	–	117.916	–	117.675	–
	C5–C6–C7	NA	121.135	–	121.308	–	121.494	–

Section 2. The effects of three different exchange-correlation functionals on the computed electronic structure of CuPc and the comparison of the computed results and the experimental data are systematically discussed in Section 3. The qualitative differences between these functionals have been observed, and the pros and cons of using these functionals are critically studied for describing interfaces of CuPc with graphene, summarized in the last section.

2. Computational details

In this work, the reported DFT calculations were carried out by using the Materials Studio® v7.0.200 by Accelrys Software Inc. The choices of the exchange-correlation functionals were selected according to previous calculations. The local density approximation (LDA) was used in other former calculations at each point in space, and it was approximated per particle exchange-correlation energy by a homogenous electron gas plus the unchanged local density [15,18]. Others [12–14,18] used different aspects of the generalized gradient approximations (GGA) by introducing density gradient corrections to the exchange-correlation energy.

The electronic structure of graphene, CuPc, and graphene/CuPc in our work were studied using the LDA, GGA, and B3LYP functionals to optimize geometries of graphene/CuPc. The Perdew–Burke–Ernzerhof (PBE) [20] exchange-correlation functional was adopted within the generalized gradient approximation (GGA) with a fraction of the exact Hartree–Fock exchange, as well as the combined fractions of exchange and correlation gradient corrections. The double numerical (DN) basis set was used, along with the 3.5-basis file for all the simulations. The convergence tolerance for the maximum force and maximum displacement for normal geometry optimization were set to 0.02 Ha Å^{-1} and 0.05 Å, respectively.

The treatments of spin polarization in many calculations have been different. Most calculations have used an unrestricted spin configuration, but some have taken a spin-restricted approach. In the case of CuPc, copper is not generally associated with magnetic properties because the single occupied 4 s orbital of the Cu atom significantly leads to spin splitting [9]. Consequently, CuPc must be treated in a spin-

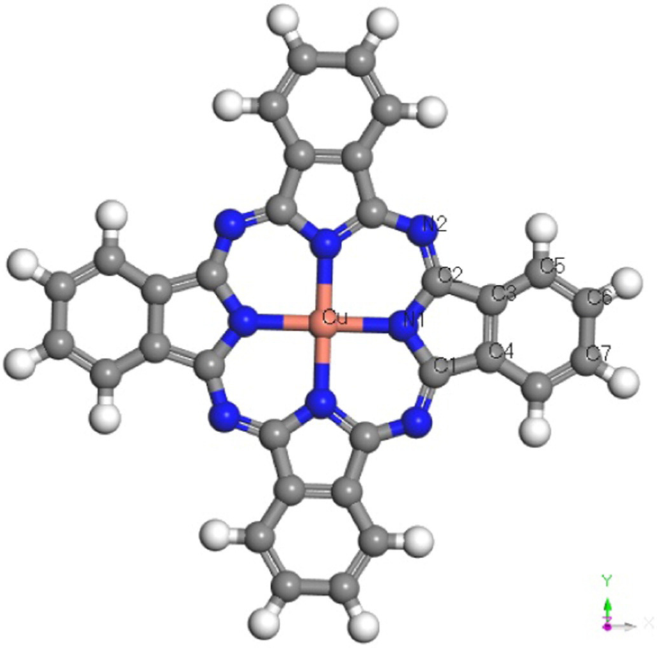

Fig. 1. Schematic view of the CuPc molecule.

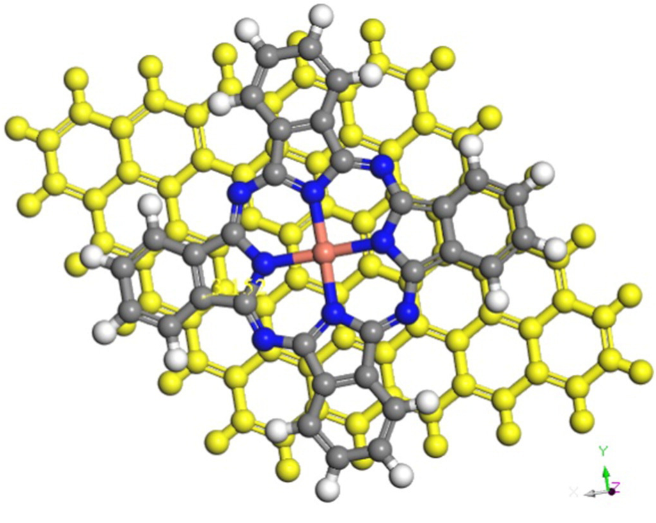

Fig. 2. The molecular structure of graphene/CuPc: the highlighted structure in yellow represents the graphene layer.

Please cite this article as: A. Jomphoak, et al., Surf. Coat. Technol. (2016), http://dx.doi.org/10.1016/j.surfcoat.2016.06.015