Applied Surface Science 392 (2017) 277–285

Contents lists available at ScienceDirect

Applied Surface Science

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

Magnetic properties of the 2D Fe_n core X_m (X = C, N, O, Cl, S and F) shell clusters embedded in graphene

Ming-Yu Zhao [a], Ru-Meng Zhao [a], Wei Li [a], Ya-Qiang Ma [a], Tian-Xing Wang [a], Xian-Qi Dai [a,b,*]

[a] College of Physics and Material Science, Henan Normal University, Xinxiang, Henan 453007, China
[b] School of Physics and Electronic Engineering, Zhengzhou Normal University, Zhengzhou, Henan 450044, China

ARTICLE INFO

Article history:
Received 23 July 2016
Received in revised form 2 September 2016
Accepted 12 September 2016
Available online 14 September 2016

Keywords:
Magnetic property
Graphene
Core/shell

ABSTRACT

Utilizing first-principle calculations, the structural, electronic and magnetic properties of monolayer graphene embedded with Fe_n/X_m (X = C, N, O, Cl, S and F) core/shell clusters are investigated, where n = 1, 2, 3 and m = 4, 6, respectively. We find that the graphene embedding with the Fe_n/X_m core/shell clusters are magnetic except the Fe/S_4, Fe_2/C_4 and Fe_3/Cl_6 core/shell clusters. The graphene embedding with the Fe_3/F_6 core/shell cluster has the largest magnetic moment in these systems. Magnetism for Fe_n/X_m core/shell clusters embedded in monolayer graphene can be ascribed to the ferromagnetic coupling between the Fe atoms. Our calculations demonstrate that Fe atoms are successfully isolated at various C, N, O, Cl, S and F shells in graphene to preserve the high-spin state. On the other hand, the high-spin state is also effectively controlled by the amount of Fe atoms. The electron spin can be stored in magnetic thin film, lithographically prepared quantum dots, and electromagnetic traps. The Fe_n/X_m core/shell clusters embedded in graphene can be considered to have potential applications in nanoelectronics, spintronics and magnetic storage devices.

1. Introduction

Two-dimensional (2D) nano-material such as graphene [1], which was successfully isolated via mechanical exfoliation, is currently the subject of intense theoretical and experimental research especially for the spintronic applications [2,3]. As is known, substitutional doping and adsorptive doping are the efficient approaches to tune the properties of the materials and have been widely used to induce the magnetic ground state of the nonmagnetic semiconducting materials. Introducing transition metal (TM) in a 2D system is an effective route to modulate its magnetic and electronic properties. Previous works have revealed that TM doping not only profoundly influences the electronic structures of 2D materials, but also promote magnetic properties of the system. Yang et al. reported that TM atom can profoundly modulate the magnetism of monolayer ZrS_2 [4]. Substitution of two C atoms by one of these species is preferred (the ideal choice is phosphorus), as it helps optimize graphene-based devices and provide analogous doping schemes in other graphenelike materials [5].

A supercapacity memory device [6–8] requires the high-spin state of an isolated individual atom. The Fe element is a redox active element with a wide range of spin states. The spin state of the Fe atoms is the key to governing the magnetism of materials. Jaiswal et al. reported that ribbons with a single Fe impurity per unit cell exhibit magnetic ground state independent of the site of the impurity atom [9]. Caliskan and Hazar studied the influence of a substitutionally doped Fe atom on the electronic structure [10]. Lin et al. showed that the spin state of single Fe atoms systematically varies with the coordination of neighboring nitrogen or oxygen atoms [11].

To our knowledge, Magnetic properties of Fe_n/X_m core/shell clusters embedded in graphene sheet are not clear now. To fully understand and modulate the magnetic property of the Fe_n/X_m system, a systematic study is required. The rest of the paper is organized as follows. In Section 2, we summarize calculational methods and models. The results and discussions will be presented in Section 3. Finally, the conclusions are given in Section 4.

* Corresponding author at: College of Physics and Material Science, Henan Normal University, Xinxiang, Henan 453007, China.
E-mail address: xqdai@htu.cn (X.-Q. Dai).

http://dx.doi.org/10.1016/j.apsusc.2016.09.056
0169-4332/

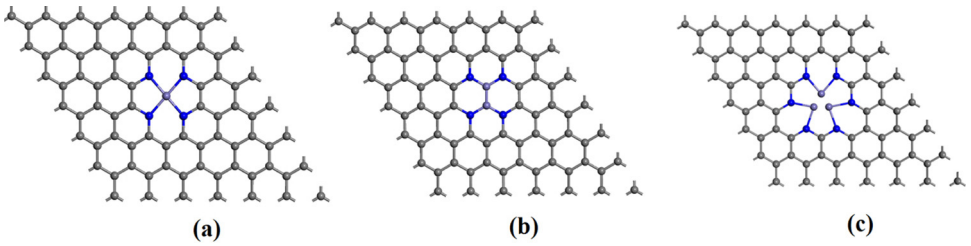

Fig. 1. Structure of the supercell used for the calculations: (a) Fe/X_4 (b) Fe_2/X_4 (c) Fe_3/X_6 core/shell clusters embedded in monolayer graphene. The purple, grey and blue spheres represent Fe and X atoms, respectively.

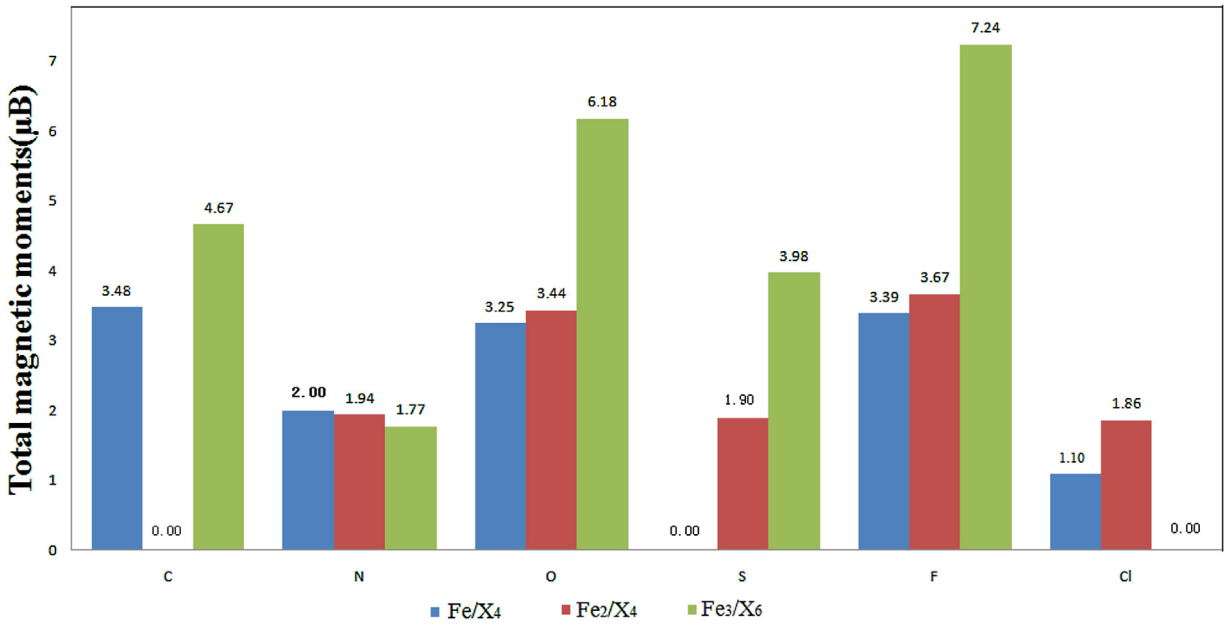

Fig. 2. Total magnetic moments of the supercell for monolayer graphene embedded with Fe/X_4, Fe_2/X_4, Fe_3/X_6 core/shell clusters.

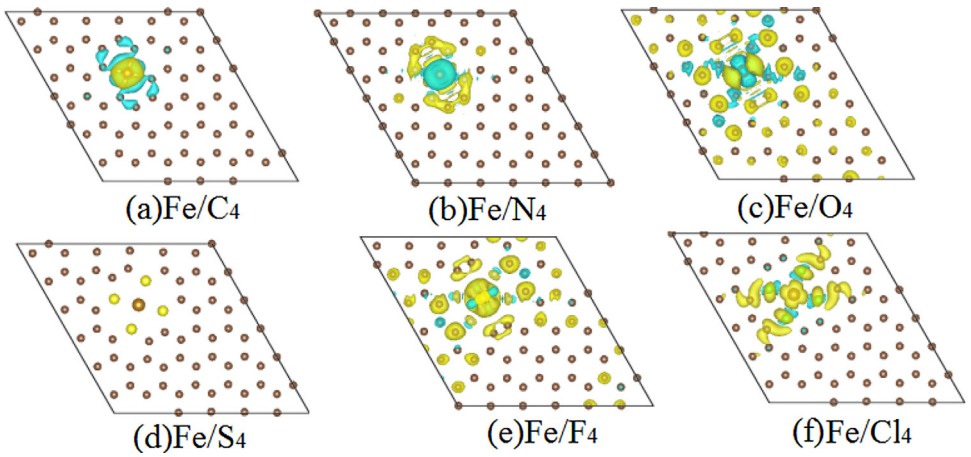

Fig. 3. Spin density for Fe/X_4 core/shell clusters embedded in a 6×6 monolayer graphene supercell. Yellow and cyan isosurfaces represent positive and negative spin densities, respectively. The isosurface value is 0.009 e/Å^3. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Calculation methods and models

We have performed spin-polarized density functional theory (DFT) calculation using projector augmented wave (PAW) potentials [12] and Perdew-Burke-Ernzerhof (PBE) of function [13] as implemented in the Vienna Ab initio simmlation Package (VASP) [14–17] to describe exchange and correlation interactions. PAW-PBE method has been shown to be very effective for cluster [18] and surface calculations [19,20]. The wave functions are expanded in plane waves with a kinetic energy cutoff of 500 eV. A 6×6 graphene supercell is used, where a minimum of 15 Å vacuum spacing is maintained between the adjacent graphene layers. The Brillouin zone (BZ) is sampled using a $5 \times 5 \times 1$ k-point grid [21]. Gaussian smearing method is conducted for partial occupancies.