



Nanocomposites of few-layer graphene oxide and alumina by density functional theory calculations



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ARTICLE INFO

Article history:

Received 1 July 2015

Received in revised form 5 November 2015

Accepted 8 November 2015

Available online 21 November 2015

Keywords:

Graphene oxide

Al₂O₃

Nanocomposite

Interface

DFT

ABSTRACT

The atomistic and electronic structure and oxygen stoichiometry of nanocomposites between alumina and graphene oxide were investigated by density functional theory calculations. The nanocomposite was described as interfaces between α -Al₂O₃ (0001) surfaces and graphene oxide; the latter was defined with oxygen bound as epoxy groups and a C:O atomic ratio of 4:1. The optimized composite structure with 1–3 layers of graphene oxide in between Al₂O₃ contains bridging Al–O–C bonds at the interface. Reduction of the composite was investigated by removal of oxygen from the interface Al–O–C bonds, within the graphene oxide layers and in Al₂O₃. It was found that removal of oxygen within the graphene oxide layers is essentially independent of the Al₂O₃ interface, i.e., the same as in pure graphene oxide. Oxygen was, however, more strongly bound in the interface Al–O–C bonds by 0.80 eV, and reduction of graphene oxide to graphene is accordingly preferred within the graphene oxide layers rather than at the oxide interface.

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1. Introduction

Composites between graphitic materials and metal oxides have the potential to exhibit complementary functional properties of the constituents: graphitic materials exhibit exceptional electrical, thermal, optical and mechanical properties, whereas metal oxides can act as a mechanically and chemically robust matrix with synergistic dielectric or semiconducting properties [1,2]. Such composites can for instance be used as conductive material for high-temperature applications and thermoelectric devices [3], photocatalyst for water splitting [4] and electrode material in lithium ion batteries [5] and electrochemical capacitors [6].

Graphene oxide (GO) has emerged as an important graphitic material in particular as it can be produced from graphite by cost-effective chemical methods and is easily dispersed in water; GO can therefore be processed via a range of techniques of commercial viability [7,8]. Thermal or chemical reduction of GO is necessary to regain the desirable properties of pristine graphene, at least to some extent. While GO with saturated sp³ carbon is an insulator, reduced GO can reach electrical conductivities similar to graphite, i.e., two orders of magnitude lower than graphene. GO is nonetheless an interesting material in itself, e.g., as a catalyst [9], water membrane

[10], or for sensing applications [7]. Furthermore, for interfaces between graphene and metal oxides, bonds may form between oxide ions in the metal oxide and graphene, and GO structures should accordingly be considered in determining the properties of such interfaces [11].

Fan et al. [12] recently prepared nanocomposites between Al₂O₃ and graphene with GO as precursor and simultaneous reduction and densification via spark plasma sintering. The nanocomposite contained α -Al₂O₃ grains encompassed by a few graphene layers which were well dispersed in the ceramic matrix, and exhibited an electrical conductivity of 10³ S m⁻¹ for an estimated 2.35 vol.% graphene. Furthermore, it was reported that the charge carrier type changed from p-type to n-type as the graphene content increased. The mechanical and microstructural properties of such nanocomposites have also been reported [13,14].

The interface between α -Al₂O₃ (0001) and pristine graphene has been investigated computationally to elucidate its atomistic and electronic structure [11,15,16]. Several other interfaces between graphene and metal oxides or semiconductors have been studied by computational approaches including ZnO, MgO, SiO₂ and SiC [17–21]. On the other hand, computational studies involving GO tend to focus on structural aspects of the isolated material due to the significant non-stoichiometry and disorder present—(reduced) graphene oxide can refer to a plenitude of compositions and structures depending on its synthesis procedure and treatment [22]. It is

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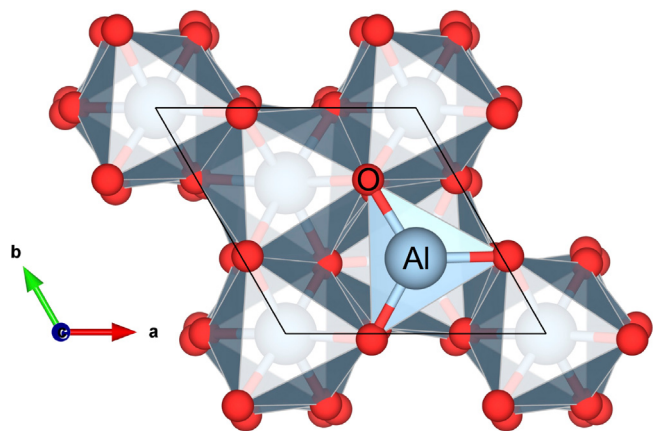


Fig. 1. Relaxed structure of the α - Al_2O_3 (0001) unit cell showing a trigonal planar AlO_3 unit at the surface.

therefore important to study interfaces with GO due to its increased use as graphitic material.

The major functional groups in GO are epoxy, hydroxyl and carbonyl on the basal plane of the graphene sheet, and carboxyl at the edges [22]. The functional groups are randomly distributed and their concentration is highly variable. Upon thermal reduction of GO, significant mass loss occurs as CO, CO_2 and H_2O is released, e.g., 60 and 85 % under Ar flow at 300 and 1300 °C, respectively [12]. Bagri et al. [23] found epoxy groups to be prevalent among the remaining oxygen groups for most initial configurations after annealing at 1000–1500 K by molecular dynamics simulations.

In the present work, we have investigated interfaces between GO and Al_2O_3 (0001) surfaces in order to understand the structural properties and chemical bonds in the nanocomposites. Structural models were constructed and optimized with respect to the distribution of oxygen groups in GO and lateral position of GO relative to Al_2O_3 (0001). Furthermore, the electronic structure and energetics of oxygen removal was considered in the Al_2O_3 and GO parts of the composite material to determine whether reduction of the nanocomposites behave differently from that of GO. The C:O ratio was fixed to 4:1 in the reference state, which represents GO or weakly reduced GO depending on the preparation method [7,8]. Further oxygen removal therefore corresponds to a mild or initial reduction, and is not associated with mass loss as CO_2 .

2. Computational procedures

DFT calculations were performed using the projector-augmented wave (PAW) method [24,25] as implemented in VASP [26–28]. The generalized gradient approximation due to Perdew, Burke and Ernzerhof [29] (GGA-PBE) was employed for obtaining a suitable structural model of the Al_2O_3 –GO interface. Final calculations of atomistic and electronic structure and energetics were performed with the hybrid functional due to Heyd et al. [30] with a screening factor of 0.2 (HSE). Hybrid functionals – intermixing 25% exact Hartree-Fock exchange – provide significantly improved band gaps, band edge positions and defect levels for semiconductors and insulators including metal oxides [31,32]. The van der Waals forces that are of significant importance for graphene structures were taken into account through the semi empirical correction scheme due to Grimme [33] (DFT+D2). This approach has been successfully applied for describing geometries of graphene-related structures [34,35], and interfaces between graphene and metal oxides [11,16,18–20].

Calculations were performed with a 500 eV plane-wave energy cut-off and a $4 \times 4 \times 1$ k-point sampling for the rhombohedral α - Al_2O_3 unit cell. Atomic positions and cell parameters were opti-

mized until the residual forces for the relaxed atoms were within $0.02 \text{ eV } \text{\AA}^{-1}$ with a self-consistency energy convergence of 10^{-6} eV . The Al_2O_3 (0001) surface was constructed as an Al-terminated slab of 12 Al-layers and 6 O_3 -layers, i.e., the same size as the $R\bar{3}c$ unit cell, and with a 25 Å vacuum layer between the periodic images of the slab. Structural and electronic properties have been shown to be converged for the same 18-layer surface slab [36].

GO models were constructed from 2×2 graphene cells with a C:O ratio of 4:1 and oxygen bound as epoxy groups on each side of the graphene sheets in various configurations. Epoxy is among the prevalent oxygen groups (in addition to hydroxyl and edge groups) characterized experimentally and reported to be among the most stable in computational studies [9,23,37–39].

Composite cells were constructed with 1 and 3 identical parallel layers of GO in between Al_2O_3 (0001) surfaces. The a and b cell parameters were fixed to those of the relaxed Al_2O_3 cell—an approach corresponding to the GO material adapting to a fixed Al_2O_3 matrix by compressive strain in the GO layers. Interfaces with (tensile) strained graphene have been shown to offer an essentially equivalent description of electronic properties that do not depend significantly on the exact geometry of the graphene layer [40]. The lateral positions of the GO layers were optimized by translation along the a and b lattice vectors. For the model with 3 GO layers, the GO layers adjoining the Al_2O_3 (0001) surfaces were kept geometrically equivalent while the lateral position of the middle GO layer was optimized separately.

Reduction of the composite was investigated by considering the energetics of oxygen removal from various sites in $2 \times 2 \times 1$ supercells (240 atoms). As such, the stability of oxygen vacancies was considered in the composite model with a C:O ratio of 4:1 in the GO layers as the reference state. Oxygen vacancies associated with the GO part of the composite cell are accompanied by a change in hybridization from sp^3 to sp^2 in GO and are therefore not effectively charged as in typical ceramic materials. In the Al_2O_3 part of the composite, oxygen takes an oxidation state of -2 and a vacancy therefore yielded two excess electrons in the GO states close to the valence band maximum (VBM) of Al_2O_3 . Due to the considerable difference in the chemical environment of oxygen in the Al_2O_3 and GO parts of the composite, initial GGA-PBE calculation were performed to evaluate the most stable sites and final calculations were performed with HSE and a convergence criteria of $0.05 \text{ eV } \text{\AA}^{-1}$.

The charge of oxide ions in the Al_2O_3 , GO and interface part of the composite cell was evaluated by Bader analysis of the charge density [41]. The enthalpy of oxidation of graphene to GO, i.e., energy of dissociative chemisorption of O_2 on graphene, was calculated according to

$$\Delta E^{\text{ox}} = E_{\text{GO}}^{\text{tot}} - E_{\text{Graphene}}^{\text{tot}} - nE_{\text{O}_2}^{\text{tot}} \quad (1)$$

where $E_{\text{GO}}^{\text{tot}}$ and $E_{\text{Graphene}}^{\text{tot}}$ are the total energies of the GO and the graphene cells, respectively, $E_{\text{O}_2}^{\text{tot}}$ is the total energy of the spin-polarized O_2 molecule, and n is half the number of oxygen in GO.

3. Results and discussion

3.1. Structure of bulk, surface and composite models

The calculated lattice parameters of bulk α - Al_2O_3 , $a = 4.755 \text{ \AA}$, $c = 12.985 \text{ \AA}$, were within 0.2% of experimental values at room temperature [42], and the relaxed structure of the α - Al_2O_3 (0001) surface was in excellent agreement with other computational studies; the outer Al ion relaxed inward by 0.74 \AA forming an approximate trigonal planar AlO_3 coordination (Fig. 1) and the surface energy is 1.52 J m^{-2} [36,43,44]. The calculated band gap of α - Al_2O_3 was 8.15 eV (direct) which compares well with the experimental (optical) band gap, 8.8 eV [45]. For the (0001) surface, the

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