

Modeling of Graphene Sensor Functionalized with Pt Nanoparticles by Molecular Dynamics and Grand Canonical Monte Carlo Simulations with Reactive Force Field

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Abstract

Graphene gas sensors have attracted much attention because of their high sensitivity. In reported numerical calculations, the size of simulated graphene sensors was limited because of a large calculation cost of density functional theory. In this work, we studied Pt nanoparticle (NP) functionalized graphene sensors by molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulation with reactive force field (ReaxFF). Thanks to a small calculation cost compared to DFT, sensor response of realistic scale Pt NP functionalized graphene sensor was successfully simulated. Our results indicated MD and GCMC simulations with ReaxFF would be a strong tool to understand sensing mechanism of realistic-scale sensors.

1. Introduction

Graphene has attracted much attention as a highly sensitive gas sensor because of their high surface to volume ratio. In order to enhance selectivity and sensitivity of the graphene sensors, surface functionalization with metal nanoparticles as well as organic compounds has been usually adopted [1]. To clarify the effects of functionalization on sensing, molecular adsorption to functionalized graphene have been studied by density functional theory (DFT) [2]. However, a large calculation cost of DFT has limit a size of functionalized graphene in the numerical simulations. Therefore, the mechanisms in realistic-scale of the functionalized graphene sensors have not been fully understood by the numerical calculations.

In this work, molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) simulation with reactive force field (ReaxFF) [3] was adopted to simulate the functionalized graphene. MD and GCMC simulations with ReaxFF can treat chemical reactions and charge transfer with a smaller calculation cost than DFT. In order to demonstrate the numerical simulation of realistic-scale functionalized graphene, hydrogen sensing by Pt functionalized graphene sensor was studied.

2. Calculation Methodology

MD and GCMC calculations were done by LAMMPS [4]. The parameters of ReaxFF was cited from Ref [5]. Schematic of the numerical simulations is shown as Fig. 1. Our simulation process consists of two parts. The first part performed by MD corresponded to functionalization of Pt NP on graphene. The second part performed by MD and GCMC corresponded to sensing by the Pt NP functionalized graphene. Simulated region was $2.950\text{ nm} \times 2.983\text{ nm} \times 3.100\text{ nm}$. In the horizontal directions, periodic boundary was set. The graphene and the Pt monolayer were positioned at the lower part of the simu-

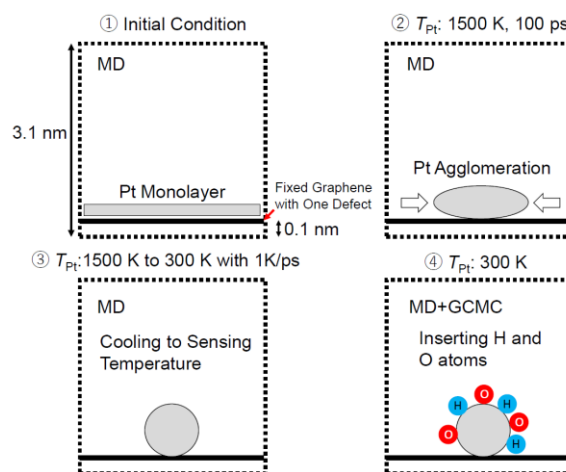


Fig. 1 Schematics of MD and GCMC simulations.

lated region. As a defect, one C atom was removed. The defect anchored the Pt NP to the graphene during the simulation. In experiments, defects are inevitably introduced in graphene during metal nanoparticle functionalization [6]. The graphene was fixed during the entire simulation. In the first 100 ps, temperature of the Pt layer (T_{Pt}) containing 99 atoms was set at 1500 K. Due to the low wettability, the Pt layer agglomerated, and the Pt NP was formed. Then, the Pt NP were cooled down to $T_{\text{Pt}} = 300\text{ K}$ with a cooling rate of 1 K/ps . After the cooling, the Pt functionalized graphene was simulated by MD at $T_{\text{Pt}} = 300\text{ K}$ with inserting and deleting H or O atoms by GCMC at every 10 fs. In order to confirm the validity of charge transfer in MD and GCMC, generalized gradient approximation DFT calculations were also performed for several atomic snapshots by SIESTA [7].

3. Results and Discussions

Fig. 2(a) shows a typical snapshot of the atomic position in MD simulation of the Pt NP formation on the graphene.

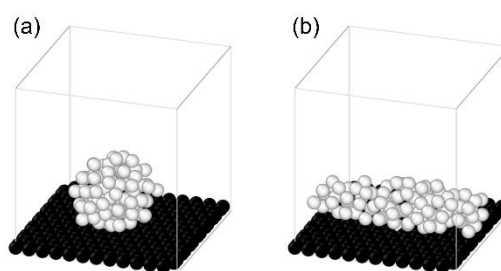


Fig. 2 (a) Snapshot of typical Pt NP functionalized graphene. (b) Snapshot of excluded simulation. The black and white balls represent C and Pt atoms, respectively.

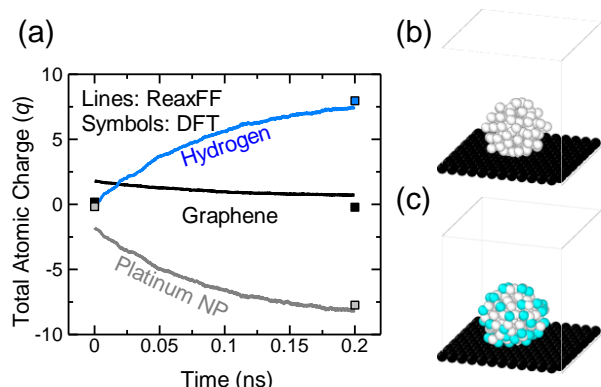


Fig. 3 (a) Time-dependent excess charges in graphene, Pt NP and H atoms calculated by ReaxFF (lines) and DFT (symbols) normalized by the elementary charge. At the time $t = 0$ ns, the number of H atoms was 0. Snapshots of atomic position used for DFT calculation at (b) $t = 0$ ns and (c) $t = 0.2$ ns. The black, white and sky-blue balls represent C, Pt and H atoms, respectively.

We can confirm the agglomeration of the Pt layers and the functionalization of the Pt NP to the graphene. With a low probability, Pt atoms were agglomerated and connected via the periodic boundary as shown in Fig. 2(b). In charge transfer analysis, the cases shown in Fig. 2(b) were excluded and the Pt NP with the diameter over 1 nm was studied.

Fig. 3(a) shows time-dependent excess charges in the graphene, the Pt NP, and the H atoms after the Pt NP functionalization. Clean Pt surface adsorbs H and O atoms. Therefore, atomic insertion rather than deletion was mainly occurred in GCMC. The results of ReaxFF were extracted from the average of 5 different MD and GCMC simulations with inserting H atoms. In order to validate the amount of the charge transfer, charges derived from DFT calculations for atomic snapshots shown as Figs. 3(b) and (c) were also shown in Fig. 3(a). Before inserting H atoms, the graphene was positively charged. This tendency agrees with the work function difference between graphene and Pt [8]. By the H atom insertion, the graphene was negatively charged both in ReaxFF and DFT. The charge transfer derived from ReaxFF and DFT corresponded electron doping of $1.21 \times 10^{13} \text{ cm}^{-2}$ and $0.44 \times 10^{13} \text{ cm}^{-2}$, respectively. Calculated charges from MD and GCMC simulations with ReaxFF reasonably reproduced DFT results.

Typical sheet carrier concentration of graphene ranges from 10^{12} cm^{-2} to 10^{13} cm^{-2} . Experimentally observed sensor response, that is a change in sheet carrier concentration, of the Pt NP functionalized graphene was around 3-5% at high hydrogen concentration [6]. The calculated change in sheet carrier concentrations of $1.21 \times 10^{13} \text{ cm}^{-2}$ from ReaxFF and $0.44 \times 10^{13} \text{ cm}^{-2}$ from DFT were larger than those expected from experiments.

In actual sensing condition, the atmosphere contains oxygen, and the surface of the Pt NP are expected to be oxidized. In order to evaluate the effect of oxygen on hydrogen sensing, O atoms were inserted during 0.2 ns before the H atom insertion. Fig. 4(a) shows time-dependent excess charges in the graphene, the Pt NP, the O atoms and the H atoms. Even after the O atom insertion, slight negative doping to the graphene by the H atoms was observed. The negative doping success-

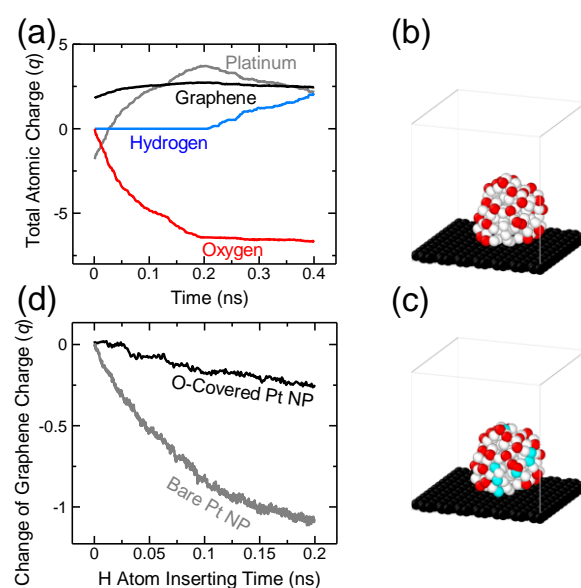


Fig. 4 (a) Time-dependent excess charges in graphene, Pt NP, H atoms and O atoms calculated by ReaxFF. At the time $t = 0$ ns, the insertion of O atoms started. At the time $t = 0.2$ ns, the insertion of H atoms started. Snapshots of typical atomic position at (b) $t = 0.2$ ns and (c) $t = 0.4$ ns. The black, white, red and sky-blue balls represent C, Pt, O and H atoms, respectively. (d) Change in graphene charge during the H atom insertion.

fully explains the observation of the experimental sensor response in the atmosphere. After the O atom insertion, the surface of the Pt NP was covered by the O atoms as shown in Fig. 4(b). Such O atoms did not desorb from the surface at 300 K, and the adsorption of the H atoms was prevented as shown in Fig. 4(c). Therefore, the O-covered Pt NP functionalized graphene showed less than 1/4 charge transfer than that of the bare Pt NP functionalized graphene as shown in Fig. 4(d). The suppression of the charge transfer agrees with the experimentally observed small sensor response in the atmosphere.

4. Conclusions

By MD and GCMC with ReaxFF, the sensor response of the Pt NP functionalized graphene was studied. Due to the small calculation cost compared to DFT calculation, large Pt NP with the diameter over 1 nm was successfully treated. Obtained charge transfer was semi-quantitatively agrees with that derived by DFT calculations. Therefore, MD and GCMC with ReaxFF can be a helpful tool for atomistic analysis of realistic-scale sensors.

Acknowledgements

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