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Graphene and graphene nanomesh supported nickel clusters: Electronic, magnetic, and hydrogen storage properties

Mohamed M. Fadlallah,^{*,†,‡} Ali G. Abdelrahman,[¶] Udo Schwingenschlögl,[§]
and Ahmed A. Maarouf^{*,||}

[†]Department of Physics, Faculty of Science, Benha University, Benha, Egypt

[‡]Center for Nanotechnology, Zewail City of Science and Technology, Giza 12588, Egypt

[¶]Department of Basic Science, Faculty of Computer and Information Science, Ain Shams University, Cairo, Egypt

[§]King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division (PSE), Thuwal 23955-6900, Saudi Arabia

^{||}Department of Physics, Institute for Research and Medical Consultations, Imam Abdulrahman Bin Faisal University, Dammam 31441, Saudi Arabia

E-mail: mohamed.fadlallah@fsc.bu.edu.eg; amaarouf@iau.edu.sa

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Abstract

Small-sized nanoparticles are widely used in applications such as catalysis, nano-electronics, and hydrogen storage. However, the small size causes a common problem: agglomeration on the support template. One solution is to use templates that limit the mobility of the nanoparticles. Graphene nanomeshes (GNMs) are two dimensional

porous structures with controllably passivated pores. In this work, we employ first principles calculations to investigate the potential for using GNMs as support templates for Ni clusters and, at the same time, study their magnetic and hydrogen storage properties. We consider two Ni clusters (Ni_6 and Ni_{13}) and two GNMs (O-terminated and N-terminated), comparing our results to those of isolated Ni clusters and those of Ni clusters on graphene. High stability of the Ni clusters is found on the N-GNM in contrast to the O-GNM. We quantify the hydrogen storage capacity by calculating the adsorption energy for multiple H_2 molecules. The values on $\text{Ni}_x/\text{N-GNM}$ are significantly reduced as compared to the corresponding isolated Ni_x clusters, but a high hydrogen storage capacity is maintained. The fact that $\text{Ni}_x/\text{N-GNM}$ hosts spin polarization is interesting for spintronic applications.

Keywords

Density functional theory, hydrogen storage, Ni cluster, graphene, nanomesh

1 Introduction

Carbon dioxide emissions from ordinary fuels and the consequent global warming are driving the quest for clean, renewable, and cheap energy sources.¹ Hydrogen is one potential candidate, as it is environmentally friendly and has the highest energy per mass of any fuel.² Therefore, high-capacity hydrogen storage is a desirable technological goal and many experimental^{3,4} and theoretical^{3,5} efforts have aimed to improve the process. In addition to the gas/liquid storage of hydrogen in high-pressure vessels, a focus is developing on materials-based storage.^{6,7} Due to their large surface area and moderate cost, C-based nanomaterials are considered for hydrogen storage.⁸ For example, carbon nanotubes doped with Ca, Co, Fe, Ni, and Pd have high storage capacities at standard temperature and pressure.⁹ Li trapped in a graphene double vacancy¹⁰ and Ni-decorated graphene¹¹ store up to 5 H_2 molecules per

Li/Ni atom. High hydrogen storage capacities also are predicted for Ca-decorated zigzag graphene nanoribbons,¹² porous graphene oxide,¹³ and porous graphene doped with various elements.^{14,15}

A graphene nanomesh (GNM, also called porous graphene) is a two dimensional material formed by creating a lattice of pores in graphene. The sizes and geometries of the pores control the electronic properties of the GNM, which can be semiconducting or semimetallic.^{16–19} Pore passivation by species such as H, O, and N can be used to dope GNMs^{18,20,21} and control their magnetic properties.²² The pores also offer a possible route to boost the chemical reactivity, allowing GNMs to be utilized as templates in various applications, for example, as electrostatic and chemical traps.²³ GNMs have been fabricated with pore sizes between 5 nm and 200 nm,^{24,25} making them suitable templates for catalytic nanoparticles,^{11,23} molecular sensors,^{26,27} and nanoparticles for hydrogen storage.¹⁵

In this work, we consider Ni_6 and Ni_{13} clusters, isolated, on graphene, and on O- and N-passivated GNMs (O-GNM and N-GNM, respectively). We study their magnetic and hydrogen storage properties both with and without templates.

2 Computational methods

All calculations are performed using the QUANTUM ESPRESSO plane wave density functional theory package.²⁸ Spin-polarized calculations are employed to determine the electronic and magnetic properties. For the exchange correlation functional we use the generalized gradient approximation in the scheme of Perdew-Burke-Ernzerhof. A $9 \times 9 \times 1$ Monkhorst-Pack²⁹ k -mesh and a 40 Ry energy cut-off are used. A 6×6 graphene supercell is built, with a 15 Å thick vacuum separation to prevent interaction along the c-direction. GNMs with hexagonal pores are obtained by removing 12 C atoms and saturating the pore edge with 6 O or 6 N atoms. All systems are structurally relaxed to reduce the atomic forces below 0.002 Ry/Bohr. At the start of the structural relaxation the bottom of the Ni clusters is located

about 3 Å above the graphene/GNM plane.

3 Results and discussion

3.1 Ni₆ and Ni₁₃ clusters

We begin by studying the magnetic and hydrogen storage properties of Ni₆ and Ni₁₃ clusters, which are found experimentally³⁰ and theoretically³¹ to be the most stable Ni clusters. Their optimized structures (Fig. 1a,b) show average Ni-Ni bond lengths of 2.31 Å and 2.37 Å, respectively, and magnetic moments per Ni atom of 1.4 μ_B and 0.9 μ_B , in agreement with previous calculations.^{31,32} The density of states (DOS) (Fig. 1c,d) demonstrates that the Fermi energy is located in the spin-down Ni 3d states for Ni₆ with a spin-up gap of about 2 eV, while for Ni₁₃ both spin channels are metallic. We note that all atoms of Ni₆, but only 12 atoms of Ni₁₃, constitute the surface of the cluster.

Figure 1: Optimized structures of (a) Ni₆ and (b) Ni₁₃, and (c,d) corresponding DOS. Optimized structures of (e) Ni₆ and (f) Ni₁₃ with H₂ molecules adsorbed, and corresponding (g) E_{ad} and (h) μ per Ni atom as functions of n .

We calculate the storage capacities of the Ni_{*x*} clusters ($x = 6, 13$) by adding H₂ molecules, one at a time, allowing the system to structurally relax after each addition. The adsorption energy of the n^{th} molecule is

$$E_{ad}(H_2^{(n)}) = E(Ni_x + (n - 1) H_2) + E(H_2) - E(Ni_x + n H_2), \quad (1)$$

where $E(Ni_x + n H_2)$ is the total energy of the cluster with n adsorbed H₂ molecules and E_{H_2} is the total energy of an isolated H₂ molecule. The isolated Ni₆ and Ni₁₃ clusters are capable of adsorbing up to 13 H₂ molecules with E_{ad} larger than 0.1 eV (Fig. 1e,f). For both

clusters we find that the average Ni-Ni bond length does not change after H₂ adsorption, while the average Ni-H bond length is 1.61 Å. The average E_{ad} is 0.36 eV for Ni₆ and 0.41 eV for Ni₁₃.

The magnetic moments of both clusters tend to decrease with increasing number of adsorbed H₂ molecules (Fig. 1g,h). To explain this observation, we analyze the Löwdin charges and find for Ni₆ that adsorption of an H₂ molecule shifts Ni₆ 4s spin-up states above the Fermi energy and Ni 3d spin-down states below the Fermi energy, thereby decreasing the magnetic moment of the cluster. Moreover, a partial charge of 0.04 electrons is transferred to the H₂ molecule, which is therefore elongated from 0.75 Å to 0.89 Å. This dissociative H₂ adsorption has been reported for Ni and other metal particles.^{33–36} Additional H₂ molecules lead to similar effects. Löwdin charge analysis certifies that the magnetic moments of the Ni atoms with H₂ molecules adsorbed are reduced (typically by 15 %) as compared to the other Ni atoms. H₂ adsorption on Ni₁₃ also shifts spin-up and spin-down states across the Fermi energy in opposite directions and the magnetic moment of the cluster decreases. The fact that this decrease is smaller than for Ni₆ can be attributed to the fact that only the surface atoms participate in the Ni-H bonding.

3.2 Ni clusters on pristine graphene

We next discuss results for the Ni clusters adsorbed on graphene (Ni_x/G), with a binding energy of

$$E_b = \frac{1}{x}(E(Y) + E(\text{Ni}_x) - E(\text{Ni}_x + Y)), \quad (2)$$

where Y is the graphene or GNM template. Ni₆ shows slight deformations (Fig. 2a) with an average Ni-Ni distance of 2.35 Å. The average Ni-C distance is 2.09 Å, the binding energy per Ni atom is 0.16 eV, and the magnetic moment per Ni atom is 1.0 μ_B . For Ni₁₃ (Fig. 2b) we obtain an average Ni-Ni bond length of 2.41 Å, an average Ni-C distance of 2.07 Å, a binding energy per Ni atom of 0.20 eV, and a magnetic moment per Ni atom of 0.9 μ_B .

The deformation of the Ni_{13} cluster is not significantly affected by how it faces graphene; it ends up having triangular faces only. Löwdin charge analysis indicates that the average charge transfer from a Ni atom to graphene is 0.4 electrons for Ni_6 and 0.6 electrons for Ni_{13} , which explains the difference in the binding energy per Ni atom between the two clusters. The (partial, P) DOS (Fig. 2c,d) shows mainly Ni 3d spin-down states at the Fermi energy and spin-up gaps of 0.25 eV for Ni_6/G and 0.70 eV for Ni_{13}/G .

The relaxed structures after H_2 adsorption (Fig. 2e,f) demonstrate that the maximum number of adsorbed H_2 molecules is lower than in the case of the isolated clusters, which is due to the binding between some Ni atoms and graphene. The adsorption has no significant effect on the average Ni-C distance. Both systems can adsorb 8 H_2 molecules (Fig. 2g,h) with an average H-H distance of 0.91 Å and 0.84 Å and an average E_{ad} of 0.38 eV and 0.50 eV for Ni_6/G and Ni_{13}/G , respectively. Because of the interaction with graphene, the magnetic moments are lower than those of the isolated clusters, with Ni_6/G being completely depolarized at maximum H_2 load. When more H_2 molecules are adsorbed, again Ni spin-up/down states are shifted above/below the Fermi energy, which decreases the magnetic moment.

3.3 Ni clusters on GNMs

We find that the Ni clusters bind weakly (binding energy per Ni atom: 0.08 eV for Ni_6 and 0.07 eV for Ni_{13}) to the O-GNM, which is reflected by average Ni-O distances of 2.10 Å for Ni_6 and 2.13 Å for Ni_{13} (Fig. 3a,b). The average Ni-Ni distance is 2.31 Å for Ni_6 and 2.40 Å for Ni_{13} . We find at the Fermi energy mainly Ni 3d spin-down states (Fig. 3c,d). Moreover, 6 H_2 molecules can be adsorbed on $\text{Ni}_6/\text{O-GNM}$ and 8 H_2 molecules on $\text{Ni}_{13}/\text{O-GNM}$ (Fig. 3e,f), with an average H-H distance of 0.90 Å and 0.85 Å and an average E_{ad} of 0.52 eV and 0.49 eV, respectively. Again, the adsorption of H_2 molecules reduces the magnetic moment (Fig. 3g,h).

Figure 2: Optimized structures of (a) Ni₆/G and (b) Ni₁₃/G, and (c,d) corresponding DOS/PDOS. Optimized structures of (e) Ni₆/G and (f) Ni₁₃/G with H₂ molecules adsorbed, and corresponding (g) E_{ad} and (h) μ per Ni atom as functions of n .

Figure 3: Optimized structures of (a) Ni₆/O-GNM and (b) Ni₁₃/O-GNM, and (c,d) corresponding DOS/PPDOS. Optimized structures of (e) Ni₆/O-GNM and (f) Ni₁₃/O-GNM with H₂ molecules adsorbed, and corresponding (g) E_{ad} and (h) μ per Ni atom as functions of n .

Turning to the N-GNM, we first notice that both clusters form short bonds (1.94 Å for Ni₆ and 1.97 Å for Ni₁₃) to the N atoms at the pore edge (Fig. 4a,b), because N has one valence electron more available than O. The average Ni-Ni distance is 2.31 Å for Ni₆ and 2.39 Å for Ni₁₃. We find at the Fermi energy that the C p_z states dominate in the spin-up channel and the Ni $3d$ states in the spin-down channel (Fig. 4c,d). The Ni-N bonds at the pore edge are much stronger than the Ni-O bonds in the case of the O-GNM (binding energy per Ni atom: 1.42 eV for Ni₆ and 0.7 eV for Ni₁₃). Both starting configurations of the Ni₁₃ cluster in the GNM pore give the same equilibrium structure. The cluster becomes slightly deformed having only triangular faces, different from the severe deformations occurring at

unpassivated graphene vacancies.³⁷ We obtain for Ni₆ a hydrogen storage capacity of 6 H₂ molecules (Fig. 4e), with an average H-H distance of 0.87 Å and an average E_{ad} of 0.36 eV. As for Ni₁₃ a smaller fraction of the cluster atoms is involved in the Ni-N binding at the pore edge, a higher hydrogen storage capacity of 8 H₂ molecules is achieved (Fig. 4f), with an average H-H distance of 0.85 Å and an average E_{ad} of 0.45 eV. Similar to the other studied cases, the adsorption of 6 H₂ molecules reduces the magnetic moment (Fig. 4g,h). It turns out that the N-GNM offers the lowest mobility for the anchored Ni clusters (Fig. 5). However, the H₂ storage capacity is low due to the fact that charge is consumed by the covalent bonds with the pore edge. This can be remedied by using large pore N-GNMs to host bigger Ni clusters and achieve H₂ storage properties close to those of the isolated clusters.

Figure 4: Optimized structures of (a) $\text{Ni}_6/\text{N-GNM}$ and (b) $\text{Ni}_{13}/\text{N-GNM}$, and (c,d) corresponding DOS/PPDOS. Optimized structures of (e) $\text{Ni}_6/\text{N-GNM}$ and (f) $\text{Ni}_{13}/\text{N-GNM}$ with H_2 molecules adsorbed, and corresponding (g) E_{ad} and (h) μ per Ni atom as functions of n .

Figure 5: Binding energy per Ni atom of the Ni clusters on the different templates.

For Ni_x/G the spin-up DOS is always gapped and the spin-down DOS always finite at the

Fermi energy, which indicates that this system can be used as spin filter (because transport is permitted only for one spin component). As an analysis of the wavefunction demonstrates for the $\text{Ni}_{13}/\text{N-GNM}$ that the Ni $3d$ states (dominate at the Fermi energy the spin-down channel) are localized on the cluster while the C p_z states (dominate at the Fermi energy the spin-up channel) are delocalized, also this system can act as spin filter. When the pore density is decreased the spin-down states will slowly recover their graphene character and the spin filtering properties will be lost.

4 Conclusion

GNMs are porous graphene structures that are currently considered for applications in nanoelectronics, chemical separation, and molecular sensing. During or post fabrication, their pore edges can be selectively passivated to match the target application. Here, we use density functional theory to explore possible utilization for hydrogen storage as templates for anchoring Ni clusters on that H_2 molecules can be adsorbed. We also study the magnetic properties. We find that the N-GNM is capable of firmly anchoring the Ni clusters through strong binding to the pore N atoms, while the O-GNM binds clusters only weakly. On the N-GNM the Ni_6 and Ni_{13} clusters can host up to 6 and 8 H_2 molecules, respectively. The H_2 storage properties of larger clusters are expected to approach those of Ni clusters on graphene, as the fraction of Ni atoms involved in the binding to the GNM decreases. We also find that for small numbers of adsorbed H_2 molecules ($n = 2$ to 4 or 5) there is some variation in the adsorption energy per molecule (~ 0.1 eV) due to the low density of H_2 molecules. This variation decreases as more H_2 molecules are added to the Ni clusters. For larger clusters less variation in the adsorption energies is expected, as the molecules are more homogeneously distributed over the cluster.

We observe half-metallic properties for Ni_x/G , opening potential for spin filtering applications. On the other hand, $\text{Ni}_{13}/\text{N-GNM}$ shows at the Fermi energy a finite DOS for both

spin channels. However, spin filtering is also possible in this case, as one spin channel is due to delocalized graphene-like states, and the other due to localized Ni states.

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