H$_2$ ADSORPTION AND STORAGE ON Ni4 CLUSTER EMBEDDED IN MULTIVACANCY DEFECTED GRAPHENE. A DFT AND THERMODYNAMIC STUDY

R.E. Ambrusi[a], A.G. Morelli, V. Orazi[a], J.M. Marchetti[b], A. Juan[a], M.E. Pronsato[a]

a- IFISUR - Universidad Nacional del Sur - 8000 Bahía Blanca - Argentina. E-mail: ruben.ambrusi@uns.edu.ar

b-Faculty of Science and Technology - Norwegian University of Life Sciences - Døbakveien 31 - 1430 Ås - Norway

IfiSur
Instituto de Física del Sur

Introduction

Carbon materials such as graphene can efficiently storage hydrogen only at cryogenic temperatures since hydrogen molecules weakly physisorb on the surface [1]. Decorating graphene with transition metals trapped by defects increases considerably the storage capacity reinforcing the bonding and also by the spillover process [2,3].
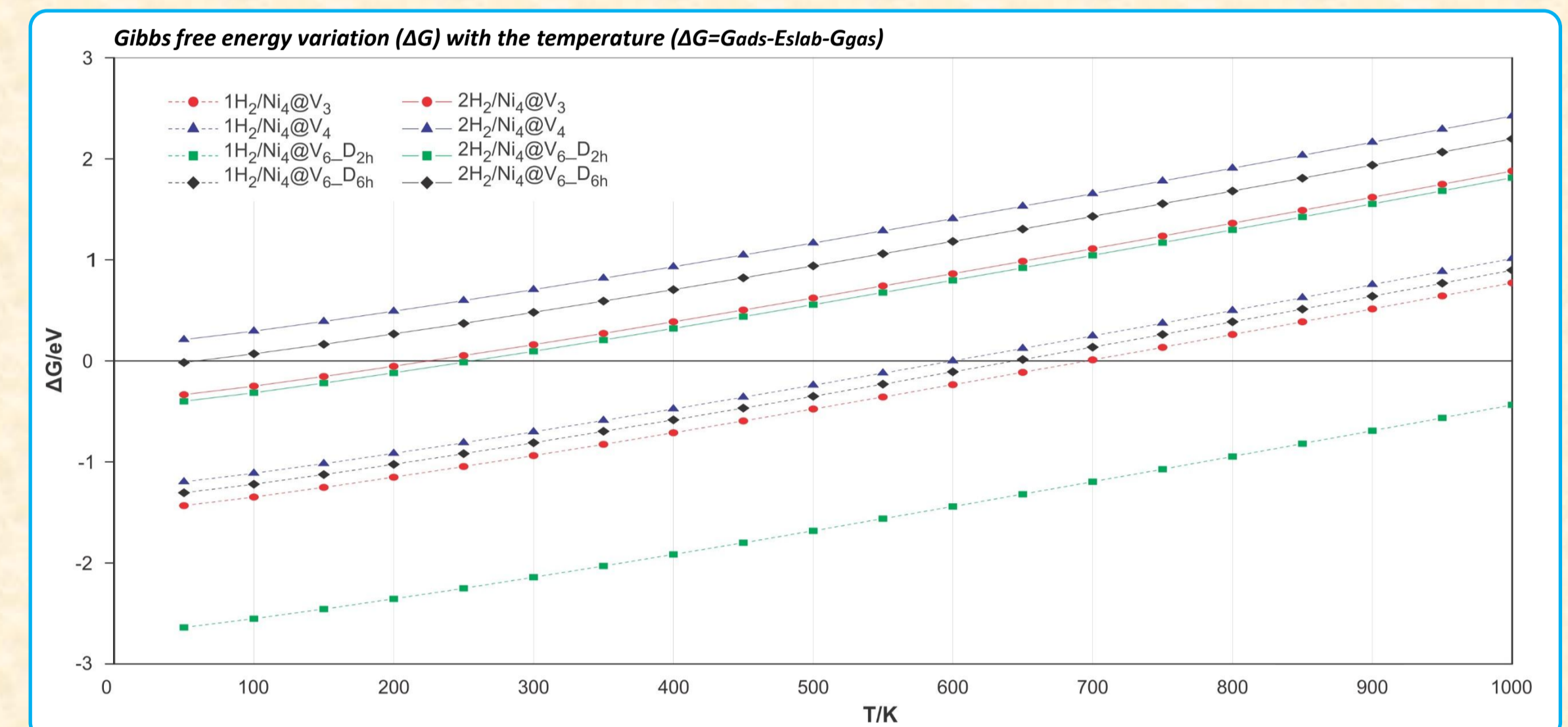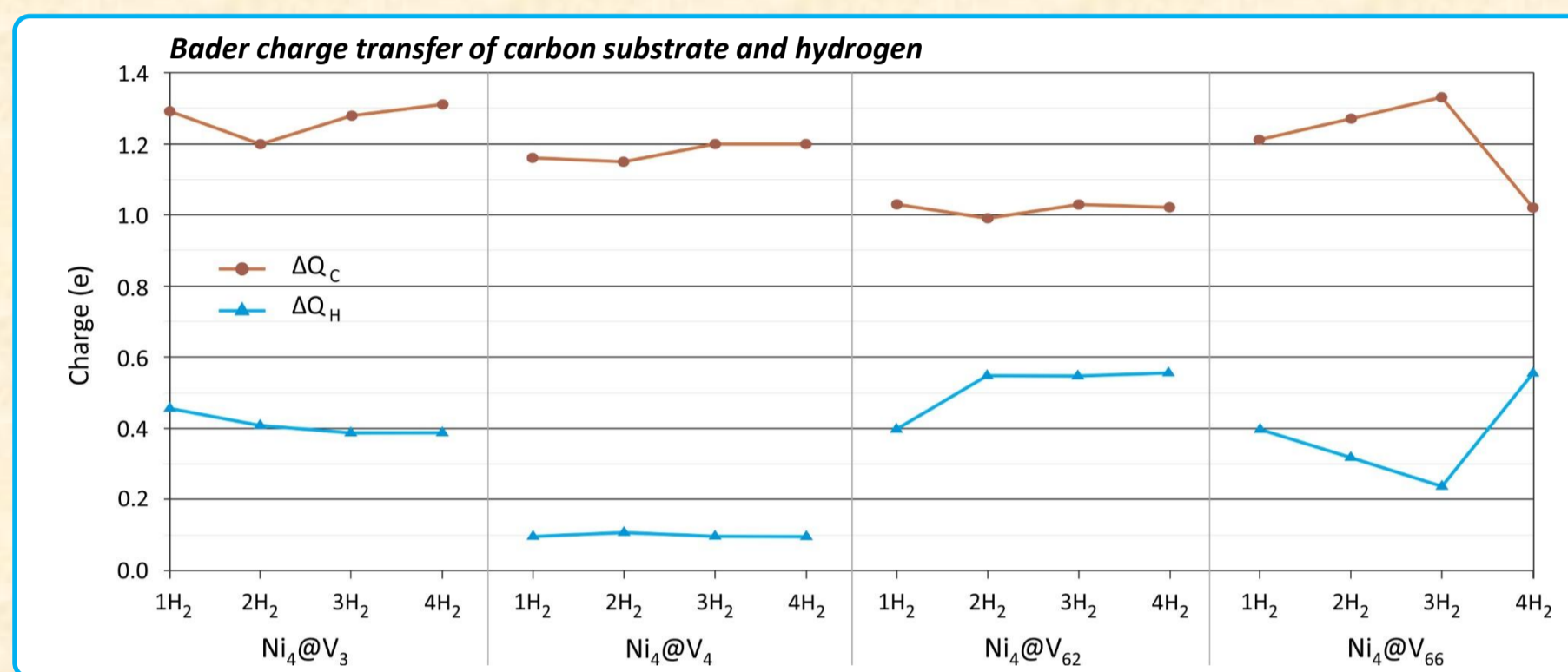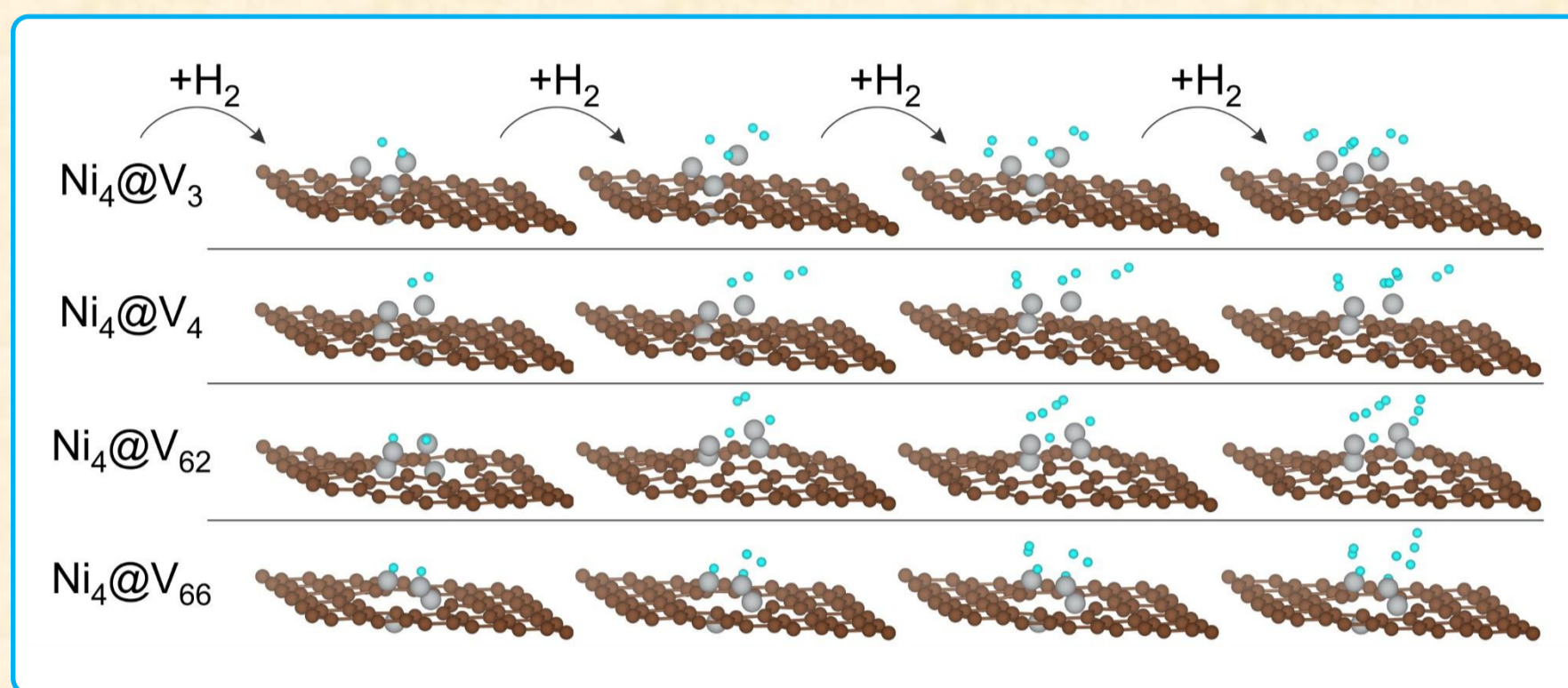
In the present work, Hydrogen adsorption stability, geometry, electronic structure and mechanism has been investigated on Ni4 cluster embedded in graphene with three, four and six vacancies by density functional theory (DFT) calculations. An energetic analysis of hydrogen adsorption by addition of one to four H$_2$ molecules was performed for each system in order to determine their hydrogen storage capacity. Dispersion force contribution to the adsorption energy is quantitative evaluated to know whether H$_2$ molecules adsorption behavior is dominated by chemical or van der Waals interactions. A further analysis of this type of interactions is also addressed by total and partial density of states. Bonding and charge transfer characteristics for the different steps involved in the adsorption mechanism are also included. Special attention is given to the effects caused by this new Ni/graphene interface to the hydrogen adsorption behavior. Besides, the Gibbs free energy change with temperature was obtained according to statistical mechanics through a canonical ensemble approach.

Theoretical Model

DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP), which employs a plane wave basis set and a periodic supercell method. The generalized gradient corrected approximation Perdew, Burke, and Ernzerhof functional was used. The Kohn-Sham equations were solved variationally using the projector augmented wave method. Spin polarization was considered in all the calculations. The Grimme's DFT-D2 method was employed to account for the van der Waals (vdW) dispersion interactions. The graphene unit cell consists of two carbon atoms with a lattice parameter a = 2.46 Å, which matches well with the theoretical and experimental values. Subsequently, a relaxed 6x6 graphene supercell with a 14.76 Å in-plane lattice constant and a 20 Å vacuum layer was used to model the systems. The four-vacancy system was constructed by elimination of carbon atoms with D3h symmetry and for the six vacancy case two symmetry configurations were considered, D2h and D6h. Adsorption energies of the nth H$_2$ molecule adsorbed on Ni4 embedded cluster in graphene with vacancy defects, up to the maximum capacity, were calculated employing: E$_{ads(total)}$=E(Ni4+G+V+nH$_2$)-E(Ni4+G+V+(n-1)H$_2$)-E(H$_2$), E$_{ads(total)}$ is the total adsorption energy of the nth H$_2$ molecule, E(Ni4+G+V+nH$_2$) and E(Ni4+G+V+(n-1)H$_2$) are the total energies of n H$_2$ and (n-1) H$_2$ molecules adsorbed on Ni4 embedded cluster in defected graphene. E(H$_2$) is the energy of the isolated H$_2$ molecule. According to this definition, a negative adsorption energy corresponds to stable adsorption on Ni embedded in defected graphene. DFT-D2 method considers the total energy (E$_{total}$) as the sum of two terms E$_{KS}$ and E$_{vdW}$ are Kohn-Sham and van der Waals energies. Additionally, a canonical ensemble in the harmonic limit was applied in order to calculate the Gibbs free energy. For this model, the normal mode frequencies were calculated in VASP.

Results

Bader charge transfer of carbon substrate and hydrogen

*Gibbs free energy variation (ΔG) with the temperature (ΔG=G$_{ads}$-E$_{slab}$-G$_{gas}$)*

For all systems, as four hydrogen molecules were added, positive values for the averaged charges relative to the valence charge of C and H atoms were obtained and negative values for Ni atoms. In addition ΔQ$_C$ and ΔQ$_H$ are positive in all the cases.

This is consistent with a charge transfer from Ni atoms in the cluster to the graphene and to the H$_2$ molecules adsorbed. Based on the ΔQ$_H$ values, the hydrogen molecules on Ni4@V3 and H$_2$/Ni4@V62 systems are in general more negatively charged, on the contrary H$_2$/Ni4@V4 has a lower charge transfer from Ni to H atoms. This charge transfer is lower in the second and fourth molecule for this system because there is a physical interaction between these molecules and the Ni cluster. However, the first and third molecules, based on adsorption energies and H-H bond distance calculated values, are adsorbed molecularly through a physical chemical interaction. In these cases, the small charge transfer is due to a Kubas type interaction where a donation and a backdonation occurs. The physical (van der Waals) and Kubas type interactions explain the absence of an increment in ΔQ$_H$ with the addition of H$_2$ after the second adsorbed molecule in H$_2$/Ni4@V3 and H$_2$/Ni4@V62 systems. The large charge transfer to the first H$_2$ molecule for the systems H$_2$/Ni4@V3, H$_2$/Ni4@V62 and H$_2$/Ni4@V66 is due to dissociation during the adsorption. The increment ΔQ$_H$ after the last molecule adsorption in H$_2$/Ni4@V66 can be explained based on the fact than the last adsorbed molecule affects the interaction of other molecules with the Ni cluster. For the same reason an increase or decrease of the charge transfer to hydrogen occurs in the hydrogen addition process for the other systems.

Based on the adsorption energies and bond distances, the first H$_2$ molecule dissociates in all the systems except H$_2$/Ni4@V4. Energy absorption of a second and a third H$_2$ molecule ranges between -0.3 and -0.7 eV with a 0.8-0.9 Å H-H bond distance, corresponding to a physico-chemical mechanism. The 4th molecule adsorbed has a purely physical interaction with the surface (0.1 eV). The stability analysis with the temperature suggests that the second molecule for H$_2$/Ni4@V3 and H$_2$/Ni4@V6_D2h systems can be desorbed at temperatures close to 298 K, suitable for hydrogen reversible adsorption-desorption at ambient conditions. A stable dissociative adsorption up to more than 600 K promises a hydrogen storage efficiency improvement by spillover, which occurs at lower temperatures.

Electronic structure: TDOS and PDOS projected on C, Ni and H atoms
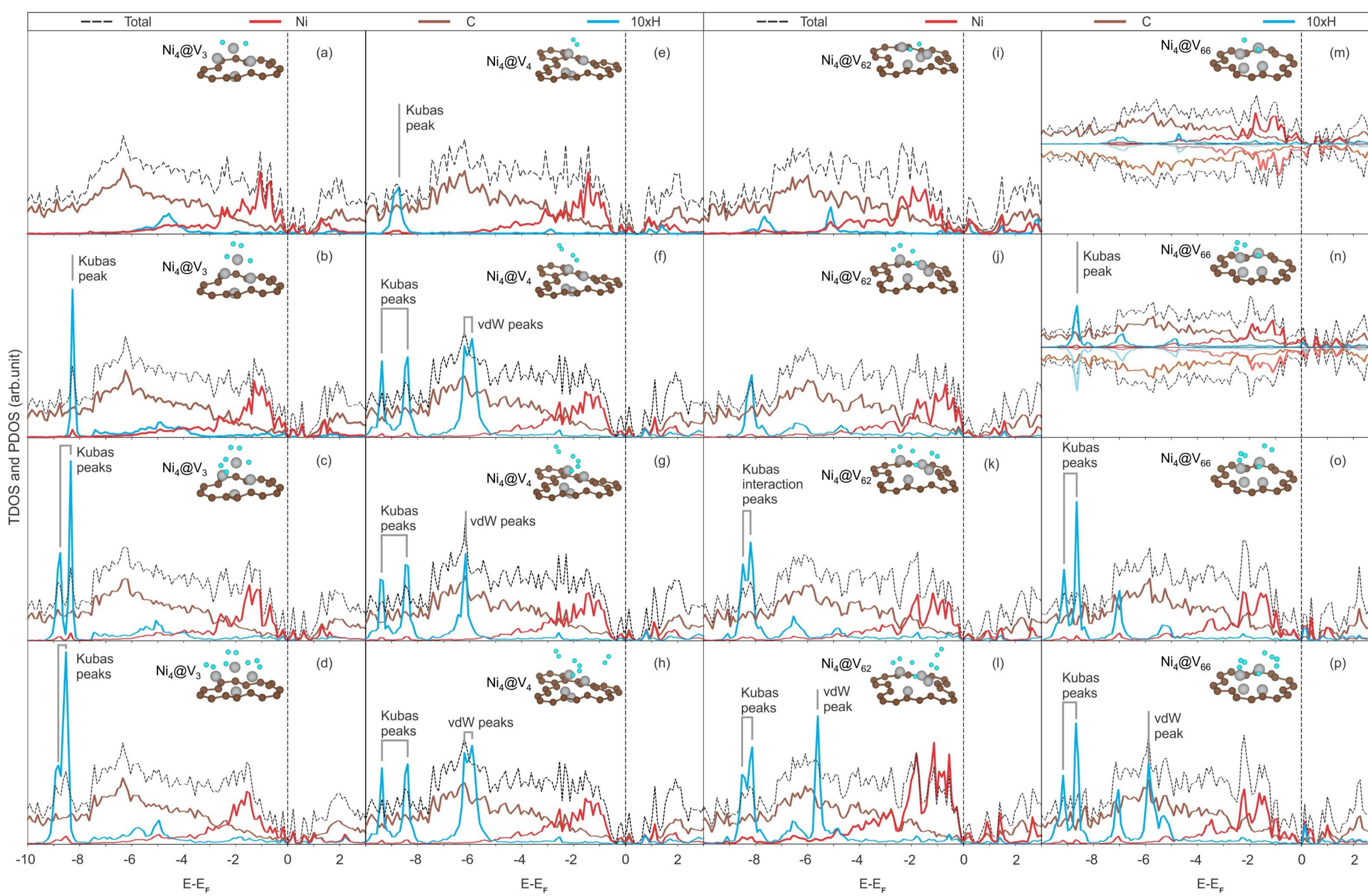
The Ni and H atoms PDOS explain almost all the TDOS behavior around the Fermi level, meaning that a highly hybridization of these states occurs due to the interaction between hydrogen molecules and embedded Ni cluster.

After the adsorption of the first molecule which dissociates on the surface, the Ni4@V3 system presents wide dispersion in energy due to the overlap between H atoms and Ni states. The second molecule is adsorbed molecularly generating a new peak (8.5 eV), related with the interaction between the H$_2$ molecular state (σ state) and the Ni cluster band. The addition of the third and fourth molecule generates another peak (9 eV) and a noticeable increase in the peak corresponding to vdW interactions respectively.

For the Ni4@V4 system the first hydrogen molecule adsorbed does not dissociate on the surface. Consequently, a H$_2$ sigma and Ni states hybridization peak (-8 eV) is observed. With the addition of a second H$_2$ molecule, a peak of H$_2$ states not interacting with Ni band (-6 eV, vdW interaction), which causes the splitting of the peak of the first molecule. The third H$_2$ molecule adsorption modifies the latter peaks, contributing to the states corresponding to s electrons interacting with Ni bands, but also presenting states associated with dispersion interactions. A fourth H$_2$ molecule increases the peak at -6 eV (vdW peak) in width and height. In all the cases, the small peaks between -3 and 0 eV correspond to H2σ* antibonding states occupied during the Kubas type interaction.

The PDOS for H$_2$/Ni4@V62 is again, a consequence of a dissociative adsorption, with widely dispersed hydrogen and Ni hybridized states for the first H$_2$ molecule. The second H$_2$ molecule presents molecular adsorption and can be identified by the characteristic peak (-8 eV). Also an increase in states around the Fermi level is observed, which can be attributed to the occupation of σ* antibonding states resulting from a Kubas type interaction. The main characteristics of PDOS most important peaks remain practically unchanged after the adsorption of a third molecule, because it follows the same mechanism as the second. Additionally a peak between -5 and -6 eV appears since dispersion interactions dominate the adsorption of the fourth molecule. An explanation of the PDOS of the H$_2$/Ni4@V66 system can be reached performing almost the same analysis.

Conclusions

The adsorption of hydrogen on Ni4 cluster embedded in multivacancy graphene was investigated. Three main interactions were identified; pure chemical, Kubas type interaction and van der Waals interactions. Different characteristic adsorption peaks in the PDOS were associated with these adsorption mechanisms. Dissociated adsorption, presents wide dispersion in energy due to the overlap between H$_2$ dissociated atoms and Ni states. A peak at approximately 8.5 eV was identified with a Kubas type interaction, with also contributions of small peaks between 3 and 0 eV corresponding to occupied H2σ* antibonding states. Additionally a peak between 5 and 6 eV appears when dispersion interactions dominate the adsorption. Furthermore, Bader charge, OP and BO calculations confirm the mechanisms and interactions proposed considering energetic and PDOS analysis. The first H$_2$ molecule dissociates on H$_2$/Ni4@V3, H$_2$/Ni4@V62 and H$_2$/Ni4@V66 but the subsequently added molecules adsorb molecularly. H$_2$/Ni4@V3 can adsorb up to four hydrogen molecules with the last molecule adsorbed by a physico-chemical Kubas type interaction. This observation leads to propose the latter system as a promising material with outstanding properties for application in hydrogen storage. For the other systems, the fourth molecule adsorb physically. Additionally, the stability analysis with the temperature for this system, suggests that the second molecule can be desorbed at temperatures close to 298 K, which is suitable for hydrogen reversible adsorption-desorption at room temperature.

In summary, based on the overall study performed in this work, Ni4 cluster embedded in multivacancy defected graphene can have an outstanding behavior capable to adsorb up to four hydrogen molecules under appropriate conditions for hydrogen storage. Additionally, the overall structure after hydrogen adsorption conserves the stability and geometric structure with only slight changes on the metal cluster and substrate. Furthermore, the dissociation of the first molecule adsorbed opens the possibility to improve the hydrogen adsorption capacity by spillover phenomena that can also inspire other theoretical and experimental works to achieve deeper under-standing in this aspect.

References

[1] Y. Yürüm, A. Taralp, and T. N. Veziroglu, Int. J. Hydrogen Energy, 34 (2009) 3784.

[2] J. W. Lee, H. S. Kim, J. Y. Lee, and J. K. Kang, Appl. Phys. Lett. 88 (2006) 6.

[3] L. Chen, A. C. Cooper, G. P. Pez, and H. Cheng, J. Phys. Chem. C 111 (2007) 18995.