AB INITIO CALCULATIONS OF CU$_N$@GRAPHENE (0001) NANOSTRUCTURES FOR ELECTROCATALYTIC APPLICATIONS

S. Piskunov, Y. F. Zhukovskii, M. N. Sokolov, J. Kleperis

Institute of Solid State Physics, University of Latvia,
8 Kengaraga Str., Riga, LV-1063, LATVIA
e-mail: piskunov@lu.lv

Substitution of fossil-based chemical processes by the combination of electrochemical reactions driven by sources of renewable energy and parallel use of H_2O and CO_2 to produce carbon and hydrogen, respectively, can serve as direct synthesis of bulk chemicals and fuels. We plan to design and develop a prototype of electrochemical reactor combining cathodic CO_2-reduction to ethylene and anodic H_2O oxidation to hydrogen peroxide. We perform *ab initio* calculations on the atomistic 2D graphene-based models with attached Cu atoms foreseen for dissociation of CO_2 and H_2O containing complexes, electronic properties of which are described taking into account elemental electrocatalytical reaction steps. The applicability of the model nanostructures for computer simulation on electrical conductivity of charged Cu$_n$/graphene (0001) surface is also reported.

Keywords: *Cu-decorated graphene, DFT, electronic properties, ESM*

1. INTRODUCTION

The electrocatalytic reduction of carbon dioxide is assumed to be reliable CO_2 converting process because it can be performed under low-pressure/temperature conditions, whereas relatively low cost of copper catalysts can facilitate the reduction pathway to hydrocarbons, e.g., ethylene [1]. However, the efficiency of these catalysts has still to be improved as large overpotentials are required for bulk Cu to reduce CO_2 to methane or ethylene while competing with the hydrogen evolution side reaction [2]. Within the last decade, a number of studies resulted in development of many interesting metal-containing catalysts. Nanostructures such as nanoparticles [3], and nanowires [4] have shown vastly improved activity or selectivity over bulk materials [5]. Recently, nanostructures derived from reduction of copper oxides have shown essentially improved efficiency of CO_2 reduction at lower overpotentials [6]. These materials were synthesized by using reduction of either thermally oxidized Cu or electrodeposited copper (I) oxide and showed improved current density, enhanced CO_2 reduction to carbon monoxide at low overpotentials and a partial suppression

of methane in favour of ethylene at higher overpotentials. Recently published data on plasma oxidized Cu-catalysts to produce oxides and a rough surface have shown Faradaic efficiency of 60 % for ethylene, which is the highest one achieved at the time of writing [7].

To provide a deeper insight into processes taking place during CO_2 reduction in the presence of nanostructured Cu catalyst, we plan to elaborate the method of electrochemical synthesis of Cu-decorated graphene. In this paper, we report the results of initial computer modelling steps of Cu_n@graphene nanostructure electronic properties. We are particularly interested in change of electronic properties with presence of applied voltage. This allows us to mimic current-voltage characteristics at the experimental electrochemical reactor for CO_2 reduction.

2. COMPUTATIONAL DETAILS

To investigate electronic properties of the slabs under study, we created corresponding models and performed first-principles calculations using a density-functional theory (DFT), as implemented in Quantum Espresso package [8]. Wave functions were represented in the plane wave basis set with energy cut-off achieving 40 Ry (544 eV). The Perdew-Becke-Ernzerhof (PBE) functional [9] was utilised for this aim. Core electron potentials were approximated within the projector augmented wave (PAW) method [10] that describes $2s^2 2p^2$ states for C (valence is four) and $4s^1 3d^{10}$ for Cu (valence is eleven). Simple monolayers were calculated using a corresponding supercell (SC) since Cu atop graphene required 5×5 SC underneath the single Cu atom or cluster. Monkhorst-Pack grid was used for Brillouin zone sampling [11], with different frequencies, depending on the system (for 5×5 graphene supercell, 6×6×1 grid was used).

Options required to investigate the charged systems properly are relatively limited. In this paper, to estimate the effect of applied voltage on the electronic structure, we used the effective screening medium (ESM) method [12]. In ESM, instead of having periodic boundary conditions in all three space directions, slab is considered to be sandwiched between semi-infinite media. Currently implemented options for media are vacuum-slab-vacuum, vacuum-slab-metal and metal-slab-metal.

In the current study, we cover ESM calculations (vacuum-slab-metal boundary conditions) of single graphene layer, graphene bilayer, Cu(111) monolayer as well as single Cu atom atop graphene. Calculations presented in this paper are building blocks and reference for future more complicated systems, as well as can serve for validation of the method. All properties of charged systems are presented with respect to the corresponding neutral system.

3. RESULTS AND DISCUSSION

In the beginning, we analyse the total charge per atom at different voltages as calculated with constant bias potential shown in Fig. 1. One could observe a linear dependence of total charge from voltage for all the investigated systems, with copper slab having a steeper line, meaning copper accumulates charge easier with voltage, which corresponds well with a known fact of copper superior conductivity.
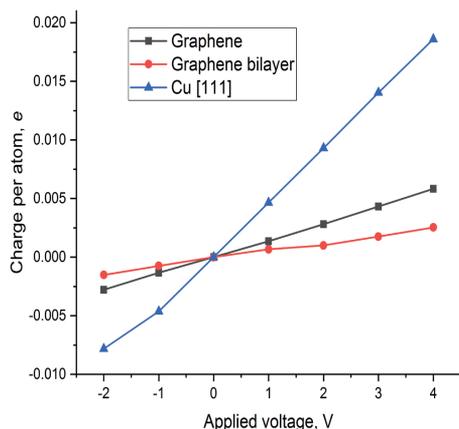
31

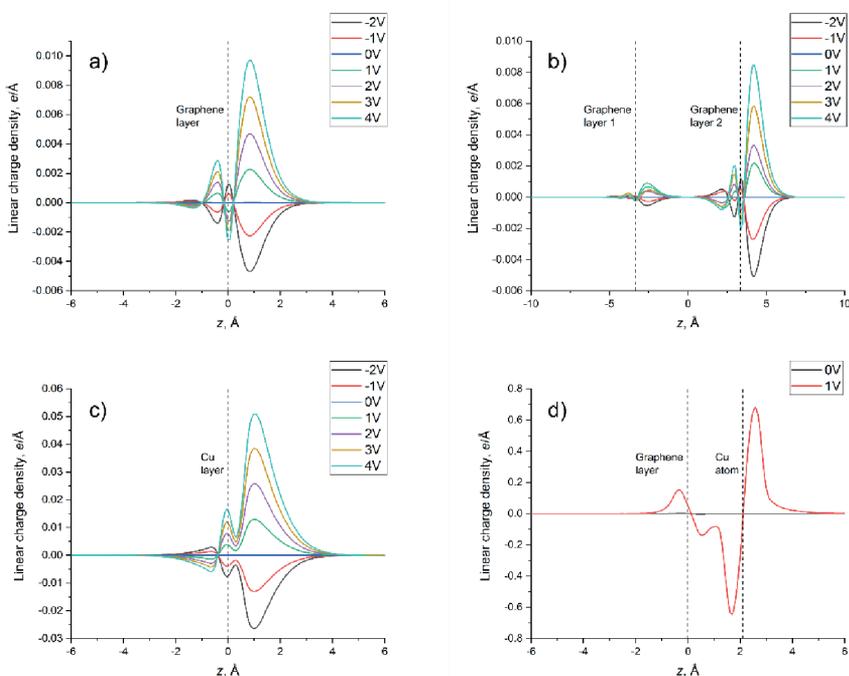*Fig. 1.* Charge *per* atom versus applied voltage in different systems.

Fig. 2. Linear charge density versus vertical axis *z* for different systems: a) graphene monolayer; b) graphene bilayer; c) Cu [111] monolayer, d) single Cu atom atop graphene. Dashed lines denote *z* position of elements of a system. Vacuum and metal boundary conditions are not shown but are implied on the left and on the right, respectively (outside plotting range). Charge density is displayed with respect to the corresponding uncharged system.

Another thing that could be noticed is that the charge per atom of graphene bilayer is lower than on a monolayer. By comparing Figs. 2a and 2b, it can be concluded that the second graphene layer has a negligible effect on the charge density of the layer, closest to metal. To include interaction between layers, one has to use more sophisticated methods to estimate van der Waals forces, which are out of scope of this paper.

It is well seen that the charge dissipates from graphene and Cu surfaces similarly (Figs. 2a and 2c), reaching zero at about 3 Å outside the surface. Peaks for Cu densities have been found to be higher, although a care has to be taken when comparing these absolute numbers because a number of atoms in the system is different, 2 for graphene and 4 for Cu in this case.

When putting single Cu atom atop graphene, three sites were considered: directly above atom, above centre of a side of a hexagon or above centre of a hexagon. However, calculations yielded similar results with no site being favourable over another, so we put it above the centre of hexagon.

Constant bias potential calculations for this system are much more demanding and at the time of writing convergence of system at 1 V only was achieved (results are demonstrated in Fig. 2d). It could be clearly seen that the main charge of the system is around Cu atom, which might explain its catalytic properties.

4. CONCLUSIONS

In this study, we present results of large-scale first-principles calculations on the charged single graphene (0001) monolayer and bilayer, Cu(111) monolayer as well as single Cu atom atop graphene (0001) monolayer performed within the effective screening medium (ESM) method. The results demonstrate that the suggested model with ESM method is valid and can be used for modelling of Cu-decorated graphene. The acquired results will be used as building blocks for later modelling of larger systems that will include CO_2 and H_2O.

REFERENCES

1. Kuhl, K. P., Cave, E. R., Abram, D. N., & Jaramillo, T. F. (2012). New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.*, *5*, 7050–7059.

2. Zhang, Y.-J., Sethuraman, V., Michalsky, R., & Pereson, A. A. (2014). Competition between CO reduction and H evolution on transition-metal electrocatalysts. *ACS Catal.*, *4*, 3742–3748.

3. Reske, R., Mistry, H., Behafarid, F., Cuenya, B. R., Strasser, P. (2014). Particle size effects in the catalytic electroreduction of CO on Cu nanoparticles. *J. Am. Chem. Soc.*, *136*, 6978–6986.

4. Zhu, W. Zhang, Y.-J., Zhang, H., Lv, H., Li, Q., Michalsky, R., Peterson, A. A., & Sun, S. (2014). Active and selective conversion of CO_2 to CO on ultrathin Au nanowires. *J. Am. Chem. Soc.*, *136*, 16132–16135.

5. Mistry, H., Varela, A. S., Kuehl, S., Strasser, P., & Cuenya, B. R. (2016). Nanostructured electrocatalysts with tunable activity and selectivity. *Nat. Rev. Mater.*, *1*, 16009.

6. Ren, D., Deng, Y., Handoko, A. D., Chen, C. S., Malkhandi, S., & Yeo, B. S. (2015). Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper (I) oxide catalysts. *ACS Catal.*, *5*, 2814–2821.

7. Mistry, H., Varela A. S., Bonifacio C. S., Zegkinoglou,I., Sinev, I., Choi, Y.-W., … Cuenya, B. R. (2016). Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. *Nat. Commun.*, *7*, 12123.

8. Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car., R., Cavazzoni, C., … Wentzcovitch, M. (2017). QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matt.*, *29*, 465901.

9. Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. *Phys. Rev. Lett.*, *77*, 3865–3868.

10. Kresse, G. J., & Jouber, D. (1999). From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, *59*, 1758–1775.

11. Monkhorst, H. J., & Pack, J. D. (1976). Special points for Brillouin-zone integrations. *Phys. Rev. B*, *13*, 5188–5192.

12. Otani, M., & Sugino, O. (2006). First-principles calculations of charged surfaces and interfaces: A plane-wave nonrepeated slab approach. *Phys. Rev. B*, *73*, 115407.

CU_N/GRAFĒNA (0001) NANOSTRUKTŪRU *AB INITIO* APRĒĶINI ELEKTROKATALĪTISKAJIEM PIELIETOJUMIEM

S. Piskunovs, J. F. Žukovskis, M. N. Sokolovs, J. Kleperis

K o p s a v i l k u m s

Fosilo ķīmisko procesu aizstāšana, kombinējot atjaunojamās enerģijas avotu vadītās elektroķīmiskās reakcijas, un paralēli H_2O un CO_2 izmantošana oglekļa un ūdeņraža iegūšanai, attiecīgi, var kalpot kā neorganisko ķīmisko vielu un degvielu tieša sintēze. Mēs plānojam izstrādāt elektroķīmiskā reaktora prototipu, kas apvieno katodisko CO_2 reducēšanu līdz etilēnam un anodisko H_2O oksidēšanu līdz ūdeņraža peroksīdam. Mēs veicam ab initio aprēķinus ar atomu formāta 2D grafēna modeļiem ar pievienotiem Cu atomiem, kas paredzēti CO_2 un H_2O saturošu kompleksu disociācijai, kuru elektroniskās īpašības ir aprakstītas, ņemot vērā elementārās elektrokatalītiskās reakcijas pakāpes. Tika ziņots arī par modelēto nanostruktūru piemērotību uzlādētās Cu_N/grafēna (0001) virsmas elektriskās vadītspējas datormodelēšanai.

06.12.2018.