Band Gap Opening and Optical Absorption Enhancement in Graphene using ZnO Nanoclusters

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Abstract—Electronic, optical and transport properties of the graphene/ZnO heterostructure have been explored using first-principles density functional theory. The results show that Zn$_{12}$O$_{12}$ can open a band gap of 14.5 meV in graphene, increase its optical absorption by 1.67 times covering the visible spectrum which extends to the infra-red (IR) range, and exhibits a slight non-linear I-V characteristic depending on the applied bias. These findings envisage that a graphene/Zn$_{12}$O$_{12}$ heterostructure can be appropriate for energy harvesting, photodetection, and photochemical devices.

Index Terms—graphene, nanocluster, band gap, absorption spectrum.

I. INTRODUCTION

Graphene as a 2D carbon allotrope has drawn tremendous attention worldwide because of its unique properties for electronics, spintronics, and surface sciences [1-2]. It is a promising material for high-performance nanoelectronics due to its high carrier concentration, mobility, and stability [3-4]. However, widespread adoption of graphene for electronic devices in particular still faces challenges because it lacks an energy band gap as a result of band degeneracy at the Dirac point. Breaking translational symmetry or sublattice symmetry could be an option to introduce a band gap in graphene. From density functional studies, it is apparent that a band gap can be opened in graphene in a variety of ways including chemical edge-functionalization [5, 6] and quantum confinement with graphene nanoribbons [5-9], nanomesh [10], periodic nanoholes [7,11], silicon doping [12], oxygen doping, strain, vacancy induced, [13] etc. Experimentally it has been proven that a band gap ranging from 2.5 meV to 450 meV can be opened in graphene with the application of strain or electric-field [14], decoration with Si-rich two-dimensional islands [15] and the introduction of defects [11], formation of perforated graphene using black copolymer (BCP) lithography [16], and adsorption of patterned hydrogen [17] and water molecules [18]. Most of these methods require precision tools or complex lithographic process to achieve band gaps that in some instances are negligible. Pala et al. investigated a novel process to open band gap by decorating graphene using different nanoparticles where special attention was given to ZnO nanoseeds [19].

ZnO has a wide band gap of 3.37 eV and large exciton binding energy of ~60 meV (2.4 times of the room-temperature thermal energy) [20]. Hence, the incorporation of ZnO with graphene could be a promising heterostructure for electronic and optoelectronic devices such as solar cells, field emission, displays, sensors, light emitting, and detection devices in UV-visible spectral range. It could also be used in the photocatalytic degradation of organic pollutants under UV or visible light irradiation [21, 22]. ZnO nanoparticles also possess thermal and mechanical stability and require a rapid and inexpensive synthesis technique using available cost-effective standard semiconductor device fabrication technologies [20].

The experimental absorption energies of small ZnO nanoparticles are found to be very close to the optical excitation energy of Zn$_{12}$O$_{12}$ cluster calculated in the framework of time-dependent density functional theory (DFT) [23]. This observation leads the authors of Ref. [23] to conjecture that the surface structure of small ZnO nanoparticles is very similar to that of a Zn$_{12}$O$_{12}$ nanocluster because the excitation energies of former (~3.83 eV) are in good agreement with that of later (3.83 eV). Therefore, we have study the Zn$_{12}$O$_{12}$ nanocluster on graphene.

In the present work, first-principles calculations are employed to investigate the effects of Zn$_{12}$O$_{12}$ on the electronic, transport, and optical properties of graphene. We found that the current-voltage response of the graphene/Zn$_{12}$O$_{12}$ heterostructure is slightly non-linear due to the occurrence of a small band gap in graphene. In addition, the optical absorption co-efficient of the heterostructure reflects enhanced optical properties.

II. COMPUTATIONAL METHODOLOGY

Calculations are performed using first-principle methods based on DFT implemented in Atomistix ToolKit (ATK) package [24]. The exchange-correlation functional is approximated by the Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (GGA-PBE) with a double-$\zeta$ polarized basis set [25-27]. First, the graphene/Zn$_{12}$O$_{12}$ heterostructure, consisting of 5x5 supercell of graphene and a Zn$_{12}$O$_{12}$ nanocluster (as shown in Fig. 1(a) and (b)), has been

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fully relaxed (lattice constant and atomic positions) until the maximum atomic force and stress on each atom are less than 0.01 eV/Å, 0.05 eV/Å, respectively. A grid mesh cut-off energy of 75 Ha and 1×3×3 k-points for the integration of the first Brillouin zone are chosen. A vacuum separation of 15 Å perpendicular to the structure is considered to form a free-standing ultrathin film to suppress adjacent image interactions. To describe long-range van der Waals (vdW) interactions, the Grimme vdW correction (DFT-D2) is considered [28]. The k-points are increased to 1×101×101 for calculations of electronic, transport, optical properties.

The electron transport calculations are performed using GGA/PBE combined with non-equilibrium green’s function (NEGF). A fast Fourier transform (FFT) solver is used to solve Poisson equation.

The schematic of the two electrode system for the graphene/Zn12O12 heterostructure is presented in Fig. 1(c). The optical absorption spectrum is calculated using the Kubo-Greenwood formula [30]. The susceptibility tensor in this method given as follows [29]

\[ I(V_{bias}) = \frac{2e}{h} \int T(\epsilon, V_{bias}) \left[ f(\epsilon - \mu_L) - f(\epsilon - \mu_R) \right] d\epsilon \]  (1)

Where \( f \) is the Fermi-Dirac distribution function, \( \mu_L, \mu_R = \pm eV_{bias}/2 \) represents the chemical potentials of the left and right electrodes, and \( T(\epsilon, V_{bias}) \) is the energy and voltage dependent transmission function. The transport setup consists of two graphene electrodes of 2 Å with the graphene/Zn12O12 structure as central region. The supercell was oriented in such a way that the transport direction connecting L and R was aligned parallel to the armchair direction within the structure, as shown in Fig. 1(c) The optical absorption spectrum is calculated using the Kubo-Greenwood formula [30]. The susceptibility tensor in this method given as follows

\[ \chi_{\omega}(\omega) = -\frac{e^2 \hbar^4}{m^2 \epsilon_i V \omega^2} \sum_{nm} \frac{f(E_m) - f(E_n)}{E_m - h\omega - i\hbar\Gamma} \pi_n^* \pi_m \]  (2)

Where, \( \pi_n \) means \( i \)-component of the dipole matrix element between \( n \) and \( m \) states, \( \Gamma \) is the broadening, \( V \) is the volume, \( f \) is the Fermi function and \( E_m, E_n \) corresponds to eigenvalues of \( m(n) \) state. The dielectric constant \( \varepsilon_\omega \) can be written in terms of the susceptibility tensor \( \chi(\omega) \), using linear response theory as follows

\[ \varepsilon_\omega(\omega) = 1 + \chi(\omega) \]  (3)

The refractive index, \( n \), is related to the complex dielectric constant through

\[ n + ik = \sqrt{\varepsilon_\omega} \]  (4)

Here, \( \kappa \) is the extinction coefficient. Finally, the optical absorption coefficient is related to the extinction coefficient through [31]

\[ \alpha_c = \frac{2\omega}{c} \kappa \]  (5)

For optical properties calculation, Hartwigsen, Goedecker, Hutter (HGH) pseudopotential is used for exchange-correlation functional with a good description of virtual states far above the Fermi level.

III. RESULTS AND DISCUSSION

The shortest separation distance between an atom of the adsorbed Zn12O12 nanocluster and the closest C atom of the graphene monolayer in the graphene/Zn12O12 complex is 2.86 Å which is in agreement with the previous result [32]. The bond length between Zn and O is found to be in the range of 1.86 Å-1.97 Å which concurs with reported data [33]. From the relaxed geometries of the nano-complexes, it is found that there is no significant structural change of Zn12O12 nanocluster with respect to their free counterparts whereas graphene undergoes a small local structural distortion.

![Graphene/Zn12O12 heterostructure](image)

The interaction between the nanocluster and the graphene layer is expected to be small. However, it was discovered that there is an effective charge transfer between the adsorbed metal/metal oxide nanoparticles and graphene [30]. Our Mulliken population analysis suggests that a net negative charge of 0.104 e is transferred from the graphene layer to the nanocluster due to the differences between the electron affinities of the nanocluster and that of graphene.

Bandstructure, as well as the density of states (DOS) of the Zn12O12 decorated graphene complex, is considered to visualize the impact on electronic property. In neutral graphene, a zero band gap semiconductor, the lowest conduction band and the upper valence band are degenerate at Fermi level (EF). The graphene band structure and corresponding DOS are significantly affected by the presence...
of Zn_{12}O_{12} nanoclusters. As can be seen in Fig. 2, the upper valence band and lower conduction shift apart at $E_F$ due to the charge transfer. From the fully relaxed complex structure, it is clear that the graphene-nanocluster interaction region is slightly deformed which could be the reason for A-B sublattice symmetry breaking at least locally and consequently opening the band gap through a charge transfer process near the Dirac point. Thus, 14.5 meV band gap is found near the K-point as can be seen in the Fig. 2 insets. This band gap is comparable to the experimental finding in the Ref. [19] (7.36 meV) where ZnO nanoparticles are randomly distributed to tune the band gap by varying the particles size and densities. Moreover, the band gap is close to the previous theoretical finding (25 meV) [32] but did not match exactly. The reason might be vdW interaction which was not included in the previous calculations.

![Fig. 2. (a) Bandstructure and (b) density of states of graphene/ Zn_{12}O_{12}](image)

Optical absorption coefficient study results in Fig. 3(a) show that the absorbance increased by 1.67 times while maintaining the same characteristics as pure graphene covering the visible and infra-red (IR) spectrum. This excellent photo responsiveness of the graphene/Zn_{12}O_{12} heterostructure could make it a promising candidate for solar energy and photo detecting devices. Because the Zn_{12}O_{12} nanocluster opens a band gap in graphene, it is logical to claim that the structural complex could generate significant current once the device is fabricated and the bias is applied in a simple two electrode device. The I-V characteristics of the graphene/Zn_{12}O_{12} shows ambipolar behavior where forward and reverse bias produces similar current in the device as seen in Fig. 3(b). Instead of linear behavior like pristine graphene [2], a slight nonlinear I-V characteristic is apparent for the energy gap because of Zn_{12}O_{12} nanocluster induced symmetry breaking in graphene [34].

![Fig. 3. (a) Optical absorption coefficient and (b) I-V characteristics of graphene/ Zn_{12}O_{12} two electrode system.](image)

First-principles calculation envisaged the influence on electronic, transport and optical properties induced by a Zn_{12}O_{12} nanocluster on graphene. The results show that this nanocluster opens a sizable band gap as a result of charge transfer. The optical absorption coefficient increases within the visible range and beyond while maintaining the similarity in graphene’s characteristics making the heterostructure useful for potential solar energy and photo detecting devices. The I-V characteristics of the graphene/Zn_{12}O_{12} heterostructure exhibit a slight nonlinear behavior because of symmetry breaking. Increasing nanocluster density on graphene could provide a practical way to open sizable band gap and tune it for graphene.

REFERENCES

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, “Two-dimensional gas of massless Dirac fermions in graphene,” Nature Letters, vol. 438, pp. 197-200, 2005. doi:10.1038/nature04233
[2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, “Electric field effect in atomically thin carbon films,” Science Reports, vol. 306(5696), pp. 666-669, 2004. doi: 10.1126/science.1102896
[3] Y.M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H. Y. Chiu, A. Grill, and P. Avouris, “100-GHz transistors from wafer-scale epitaxial Graphene,” Science, vol. 327(5966), pp. 662, 2010. doi:10.1126/science.1184289
[4] H. Xu, Z. Zhang, H. Xu, Z. Wang, S. Wang and L. Peng, “Top-gated graphene field-effect transistors with high normalized transconductance and designable Dirac point voltage,” ACS nano, vol. 5(6), pp. 5031–5037, 2011. doi:10.1021/nn200459e
[5] V. Surya, K. Iyakutti, H. Mizuseki, and Y. Kawazoe, “Tuning electronic and magnetic properties of silicon nanoborons,” RSC Adv., vol. 6, pp. 17046-17058, 2016. doi: 10.1039/C5RA26107D
[6] M. M. Monshi, M. S. Aghaei, and I. Calizo, “Edge functionalized germanene nanoborons: impact on electronic and magnetic properties,” RSC Adv., vol. 7, pp. 18900-18908, 2017. doi: 10.1039/C6RA25083A
[7] S. M. Aghaei, Band gap tuning of armchair silicon nanoborons using periodic hexagonal holes,” J Appl. Phys., vol. 118, pp. 103404, 2015. doi: 10.1063/1.4930139
[8] Y. Son, M. L. Cohen, and S. G. Louie, “Energy gaps in graphene nanoborons" Physical Review Letter, vol. 97(21), pp. 216803, 2006. doi: 10.1103/PhysRevLett.97.216803
[9] M. Y. Han, B. Ozyilmaz, Y. Zhang, and P. Kim, “Energy band-gap engineering of graphene nanoborons” Physical Review Letter, vol. 98(20), pp. 206805, 2007. doi: 10.1103/PhysRevLett.98.206805
[10] X. Liang, Y.-S. Jung, S. Wu, A. Imsch, D. L. Olynick, S. Cabrini, and J. Bokor, “Formation of bandgap and subbands in graphene nanomeshes with sub-10 nm ribbon width fabricated via nononprint lithography,” Nano letters, vol. 10, no. 7, pp. 2454-2460, 2010. doi: 10.1021/nl100750v
[11] S. M. Aghaei and I. Calizo, “Density functional theory study on energy band gap of armchair silicon nanoborons with periodic nanoholes” MRS Advances, vol. 1(22), pp. 1613-1618, 2016. doi:https://doi.org/10.1557/adv.2016.123
[12] M. S. Azadbeh, A. Kokabi, M. Hosseini, and M. Faridmanesh, “Tunable bandgap opening in the proposed structure of silicon-doped graphene,” Micro & Nano Letters, vol. 6, no. 8, pp. 582-585, 2011. doi:10.1049/mnl.2011.0195
[13] V. Surya, K. Iyakutti, H. Mizuseki, and Y. Kawazoe, “Tuning electronic structure of graphene: a first-principles study,” IEEE Transactions on Nanotechnology, vol. 11, no. 3, pp. 534-541, 2012. doi: 10.1109/TNANO.2011.2182358
[14] Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, and Z. X. Shen, "Uniaxial strain on graphene: Raman spectroscopy study and band-gap opening," ACS nano, vol. 2, no. 11, pp. 2301-2305, 2008. doi: 10.1021/nn00459e
D.H. Lee, J. Yi, J.M. Lee, S.J. Lee, Y. Doh, H.Y. Jeong, Z. Lee, U. Paik, J.A. Rogers and W.I. Park, "Engineering electronic properties of graphene by coupling with Si-rich, two-dimensional islands." ACS Nano, vol. 7(1), pp. 301-307, 2012. doi: 10.1021/nn304007x

M. Kim, N.S. Safron, E. Han, M.S. Arnold, P. Gopalan, "Fabrication and characterization of large-area, semiconducting nanoperforated graphene materials." Nano Lett., vol. 10(4), pp. 1125-1131, 2010. doi: 10.1021/nl9032318

R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit. "Band gap opening in graphene induced by patterned hydrogen adsorption." Nat. Mater., vol. 9(4), pp. 315-319, 2010. doi:10.1038/nmat2710

F. Yavari, C. Kritzinger, C. Gaire, L. Song, H. Gulapalli, T. Borca-Tasciuc, P.M. Ajayan, N. Koratkar. "Tunable band gap in graphene by the controlled adsorption of water molecules." Small, vol. 6(22), pp. 2535-2538, 2010. doi:10.1002/smll.201001384

C. Al-Amin, P. K. Vabbina, M. Karabiyik, R. Sinha, C. Wang and N. Pala, "Band gap engineering of single layer graphene by randomly distributed nanoparticles," Journal of Materials Science: Materials in Electronics, vol. 27(7), pp. 1-6, 2016. doi: 10.1007/s10854-016-4722-z

P. K. Vabbina, A. P. Nayak, A. M. Katzenmeyer, P. Nayyar, N. Pala and M. S. Islam, "Synthesis of crystalline ZnO nanostructures on arbitrary substrates at ambient conditions." In SPIE NanoScience+ Engineering, pp. 81060H-81060H, International Society for Optics and Photonics, 2011. doi:10.1117/12.899418

K.R. Lee, S. Park, K.W. Lee, J.H. Lee. "Rapid Ag recovery using photocatalytic ZnO nanopowders prepared by solution-combustion method." J Mater Sci Lett, vol. 22(1), pp. 65–67, 2003. doi:10.1023/A:1021738526590

T. Xu, L. Zhang, H. Cheng, and Y. Zhu. "Significantly enhanced photocatalytic performance of ZnO via graphene hybridization and the mechanism study." Applied Catalyst B: Environmental, vol. 101(3), pp. 382-387, 2011. doi:10.1016/j.apcatb.2010.10.007

J. M. Matxain, J. M. Mercero, J. E. Fowler, and J. M. Ugalde, "Electronic excitation energies of ZnO clusters." J. Am. Chem. Soc., vol. 125 (31), pp. 9494-9499, 2003. doi:10.1021/ja0265404

Atomistix ToolKit version 2014.1, QuantumWise A/S (www.quantumwise.com).

M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, "Density-functional method for nonequilibrium electron transport." Phys. Rev. B, vol. 65(16), pp. 165401, 2002. doi: 10.1103/PhysRevB.65.165401

J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, "The SIESTA method for ab initio order-N materials simulation." J. Phys. Condens. Matter, vol. 14(11), pp. 2745, 2002. doi: stacks.iop.org/JPhysCM/14/2745

J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett., vol. 77(18), pp. 3865, 1996. doi: https://doi.org/10.1103/PhysRevLett.77.3865

J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett., vol. 77(18), pp. 3865, 1996. doi: https://doi.org/10.1103/PhysRevLett.77.3865

Grimme S, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction." J. Comput. Chem., vol. 27(15), pp. 1787-1799, 2006. doi: 10.1002/jcc.20495

M. Yigal, and N. S. Wingreen. "Landauer formula for the current through an interacting electron region." Phys. Rev. Lett., vol. 68(16), pp. 2512-2515, 1992. doi: https://doi.org/10.1103/PhysRevLett.68.2512

W. A. Harrison, Solid State Theory, Dover Publications Inc., NY, USA, 1980

D. J. Griffiths, Introduction to Electrodynamics, Prentice Hall, 1999

B. Das, B. Choudhury, A. Gomathi, A. K. Manna, S. K. Pati, and C. N. R. Rao, "Interaction of inorganic nanoparticles with graphene." Chem. Phys. Chem., vol. 12(5), pp. 937–943, 2011. doi: 10.1002/cphc.201001090

S. S. Carara, R. J. C. Baistaa, and H. Chacham, "Modifications in graphene electron states due to a deposited lattice of Au nanoparticles: Density functional calculations." Physical Review B, 80(11), pp. 115435 2009. doi: 10.1103/PhysRevB.80.115435

C. Stampfer, J. Güttinger, S. Hellmuller, F. Molitor, K. Ensslin, T. Ihn, "Energy gaps in etched graphene nanoribbons", Physical review letters, vol. 5, pp. 056403, 2009. doi: 10.1103/PhysRevLett.102.056403