

Thermodynamic and Electronic Properties of Fe, Ni, Co Atoms and Dimers in 4x4 Graphene

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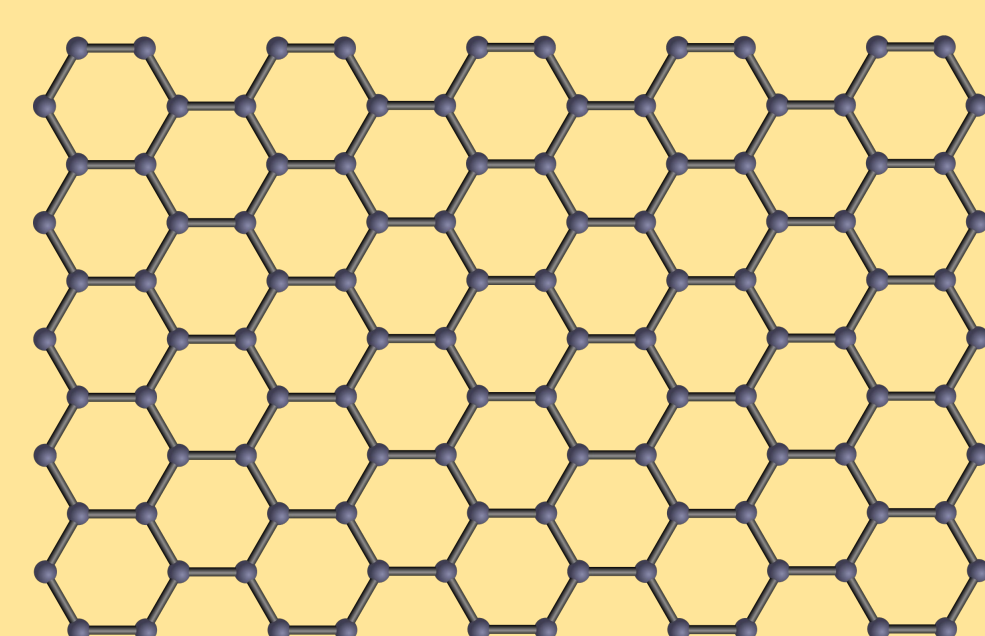
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INTRODUCTION

Two-dimensional materials have become increasingly prominent in technology due to the demands of the expanding field of materials science. Graphene is a single-layer 2D sheet of sp^2 hybridized carbon atoms, and graphene's electrons are delocalized--as with benzene. Due to this property, graphene is a zero-bandgap semiconductor with many other unique qualities. New innovative bulk manufacturing methods result in the feasibility of a widespread use of graphene in applications.

Computational chemistry is a growing field with applications in materials science, calculating for ex. electron density, magnetization, band structure. Spintronics is the study of solid-state electronic devices with ternary processing and information storage capabilities. Doping (embedding) ferromagnetic atoms in graphene alters its properties. Magnetic storage uses different patterns of magnetization in a magnetizable material, such as metal-doped graphene, to store data. Specific properties are ideal for applications in data storage and spintronics.



Top view of pristine graphene sheet

RESEARCH AIM

Investigate the thermodynamic and electronic properties of graphene-embedded Fe, Co, Ni atoms and dimers for data storage and spintronics applications.

RESEARCH METHODOLOGIES

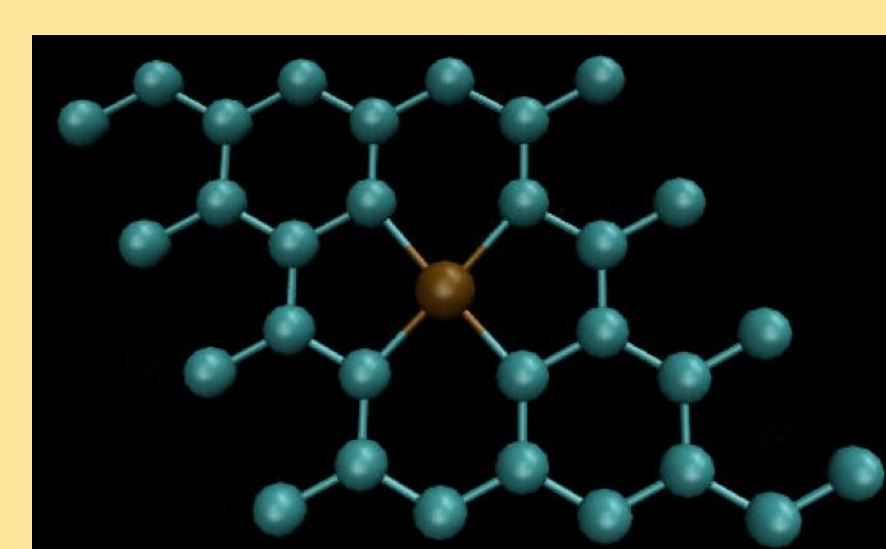
Plane-wave density functional theory calculations are used to optimize geometries of all configurations and systems through Quantum Espresso (PWSCF v5.0.1).

Parameters for metal-graphene systems:

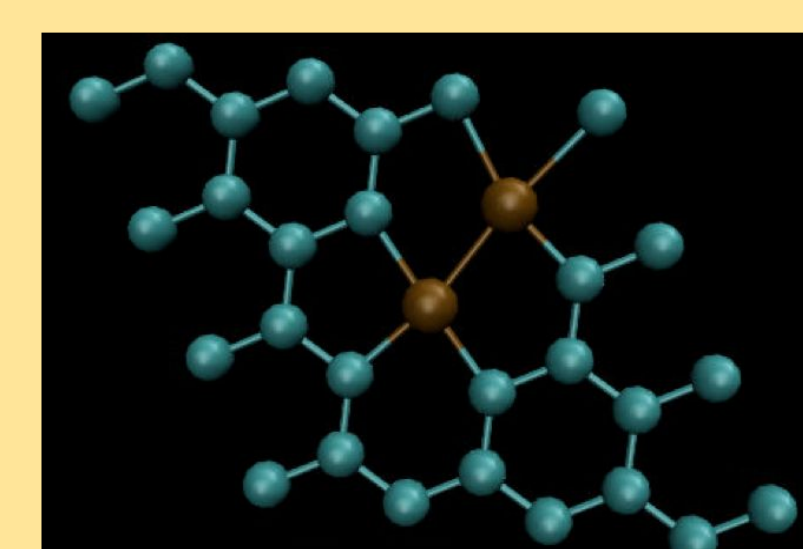
- Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) ultrasoft pseudopotential
- Perdew Burke Ernzerhof (PBE) generalized gradient approximation
- Supercell Dimensions: $9.84 \text{ \AA} \times 9.84 \text{ \AA} \times 9.84 \text{ \AA}$
- Monkhorst-Pack K-Point grid of $4 \times 1 \times 1$

Molecular geometry results viewed through Visual Molecular Dynamics

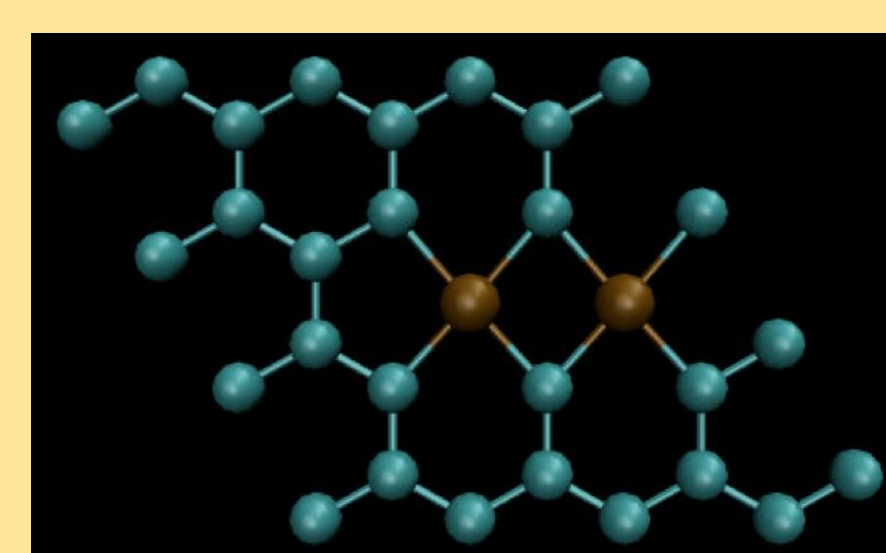
CONFIGURATIONS



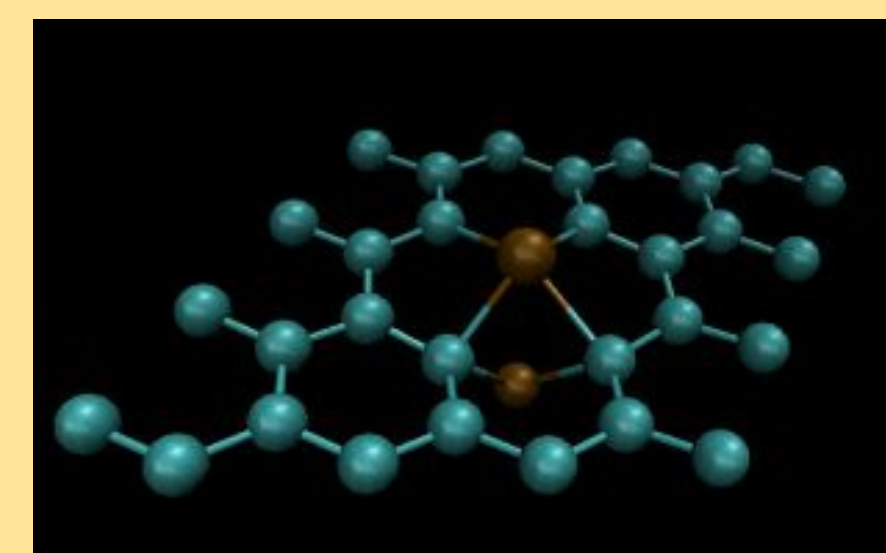
Single Atom



Double Atom - Diagonal*



Double Atom - Side



Double Atom - Stacked*

*Note: these diagrams represent the possible metal atom configurations. Single atom and double atom (side) are analyzed in this study.

DATA AND FINDINGS

Data collected through Quantum Espresso

Single Atom Embedded Metal Configuration

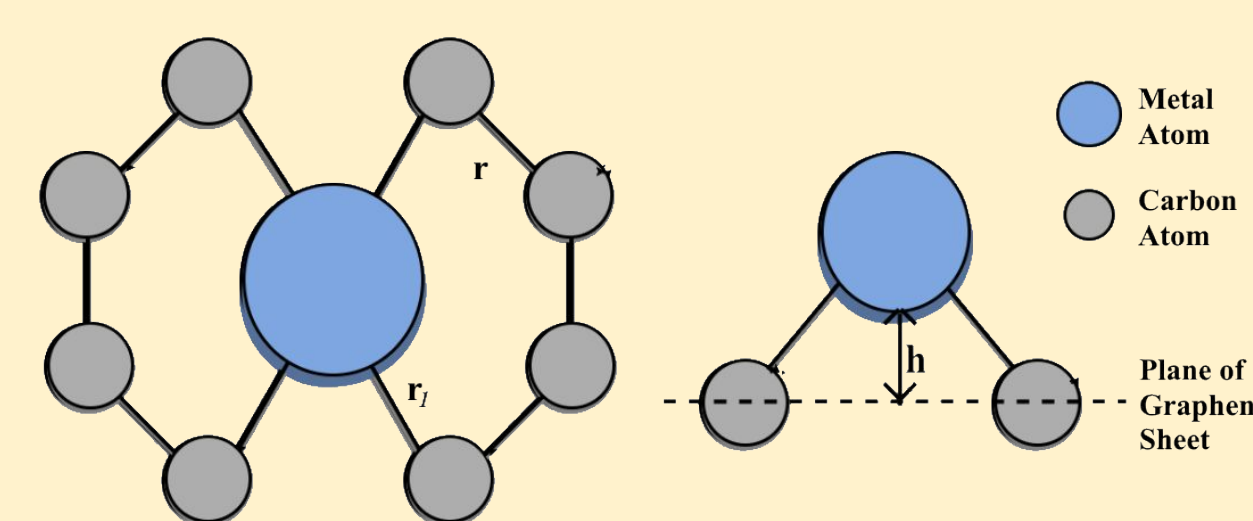
Configuration	Buckling Height (Å)	Enthalpy (ev)	Net Magnetization (Bohr mag/cell)	Absolute Magnetization (Bohr mag/cell)
Iron (Fe)	0.519	-6.398	3.90	3.93
Cobalt (Co)	0	-6.088	1.13	2.42
Nickel (Ni)	0	-6.538	0.11	0.16

Double Atom (Side) Embedded Dimer Configuration

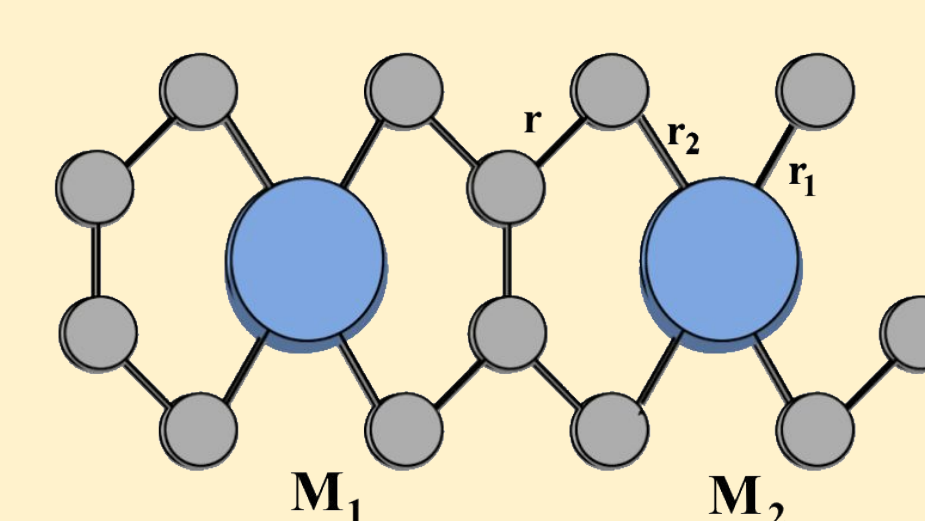
Configuration	Buckling Height (Å)	Enthalpy (ev)	Net Magnetization (Bohr mag/cell)	Absolute Magnetization (bohr mag/cell)
Iron-Iron (fe-2)	1E-5	-4340.37	4.38	5.50
Cobalt-Cobalt (Co-2)	6E-4	-4341.22	2.38	2.78
Nickel-Nickel (Ni-2)	5E-4	-4341.72	0.00	0.00

Reference Diagrams

Note: the bond length of C-C in pristine graphene is 1.40 \AA



Single Embedded Metal Atom: h represents the buckling height, the perpendicular distance from the metal atom to the plane of graphene. Buckling is caused when the electron cloud of an embedded metal atom repels the surrounding electron clouds of nearby carbon atoms



Double Embedded Metal Atoms: $M1$ and $M2$ represent the doped metal atoms. Pairs are exclusively homonuclear couples of Fe, Co, and Ni. Heteronuclear pairings are not analyzed in this study. Note: buckling height of a double atom complex is recorded as the average of the h of $M1$ and $M2$.

DISCUSSION, ANALYSIS, AND EVALUATION

Analysis of Energies

Analysis on energy must be made relative to systems with similar graphene vacancies because carbon structures differ between different complexes. Hence single atom-systems cannot be compared to dimer-systems with regard to enthalpy.

With embedded single atom enthalpy, there were no outstanding values (enthalpy trend: $Co > Fe > Ni$). Regardless of spontaneity, smaller enthalpy values are more thermodynamically favorable--thus in terms of thermodynamic stability Ni is the most favorable and Co is the least.

With embedded dimer enthalpy, the trend in enthalpies was $Fe-2 > Co-2 > Ni-2$. Following the same path of logic, Ni-2 is the most favorable and Fe-2 in the group of dimers.

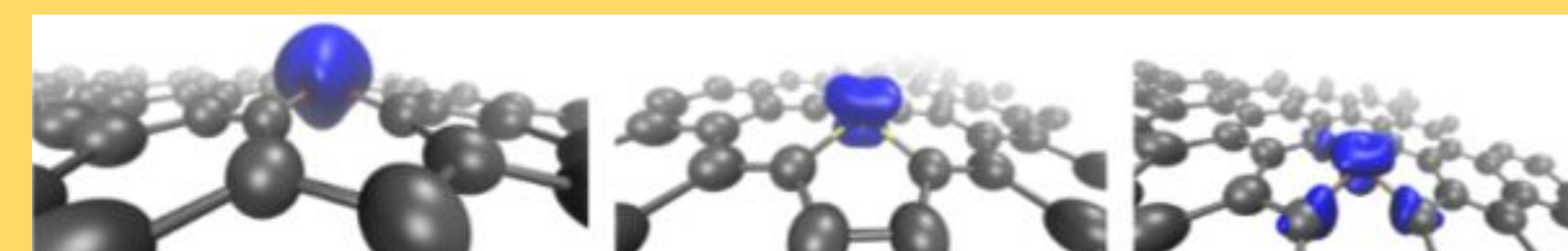
Analysis of Geometries

As referred under Reference Diagrams, buckling height represents a measure of interference between the metal atom's electron cloud and the surrounding cloud of delocalized electrons above the plane of carbon atoms. Thus, the greater the buckling height, the higher the level of interference, and the less stable the complex is.

Of the single atom configurations, Co and Ni both had negligible buckling height and Fe had a substantially larger buckling height of 0.519 \AA ; of the double atom configurations, buckling height was miniscule in comparison, with an apparent trend ($Co-2 > Ni-2 > Fe-2$).

In terms of buckling height, we found that Co, Ni, and the dimer complexes are stable options (refer to C-C bond length of 1.4 \AA), and Fe is the most unstable option.

Analysis of Magnetization



Fe single-atom system

Co single-atom system

Ni single-atom system



Fe dimer system

Co dimer system

A visual for the Ni dimer system is not shown because the system is magnetically neutral.

- In the Fe single atom system, all magnetization is localized, spread over the s and d orbitals of the Fe atom.
- In the Co single atom system, all magnetization is localized, spread over Co's d orbitals.
- In the Ni single atom system, magnetization is delocalized, spreading to the four nearby carbon atoms.

We found that the Fe and Co single atom systems have the potential to store data because they preserve magnetic moment throughout the plane. Ni, however, has delocalized magnetization, resulting in a material that cannot store data bits as effectively.

- In both the Fe and Co dimer systems, magnetization is largely localized around each metal atom and split evenly between the two atoms.
- The shape of the magnetic field of each atom within each dimer system is similar to its respective single atom system magnetic field. Thus, magnetization is spread over the same respective orbitals.

The Fe dimer system is promising for applications in data storage and spintronics because the region of space between the magnetization of the metal atom and the negative magnetization of the carbon atoms (shown in red) is significant. On the other hand, the Co dimer system has small magnetizations on adjacent carbon atoms that potentially make it ineffective for electronic applications.

CONCLUSIONS, IMPLICATIONS, NEXT STEPS

- With regard to geometries, single atom Fe is the most structurally unstable system, whereas the other systems tested are stable.
- Analyzing energy, single atom Ni and dimer Ni were the most thermodynamically favorable of each group. Co and Fe in both groups weren't as thermodynamically favorable.
- In terms of magnetization, Ni cannot be used for data storage because of its delocalized magnetization in the single atom system and its lack of magnetization in its dimer system.
- Single atom Co, single atom Fe, and Fe dimer show potential for spintronics and data storage because magnetization is localized on the metal.
- Overall, according to the data obtained, the Co single-atom system or the Fe dimer system seem to be the most promising solutions to the research aim.

As a fairly new material, graphene has immense potential. Already, projected uses range from biosensors and sterilization to camera lenses and lubricant. Its special properties result in things like its electrons moving close to the speed of light and imitating relativistic laws of physics, as well as incredible strength. However, graphene has many characteristics that have yet to be discovered. Future steps that can be taken for our project include examining different atom configurations, different elements, or further analysis of data that we were unable to collect, such as band structure.

REFERENCES

- Avdoshenko, Stan M., et al. "Society Organometallic Complexes of Graphene: Toward Atomic Spintronic Using a Graphene Web." ACS Nano, vol. 5, 2011, www.researchgate.net/publication/51757648_Organometallic_Complexes_of_Graphene_Toward_Atomic_Spintronic_Using_a_Graphene_Web_Accessed 11 Sept. 2017.
- de La Fuente, Juan. "Graphene Applications and Uses." Graphene, www.graphene.com/pages/graphene-applications/WjH7N7Kvcs.
- "Global Demand for Graphene after Commercial Production to be Enormous, says Report." Armatoo, 28 Feb. 2014, www.armatoo.com/news.aspx?newsID=29510. Accessed 30 Oct. 2017.
- "Graphene Market value to cross \$200 million by 2024." Global Market Insights, Inc. "GlobeNewswire, 25 July 2017, globe.newswire.com/news-release/2017/07/25/105753903/en/Graphene-Market-value-to-cross-200-million-by-2024-Global-Market-Insights-Inc.html. Accessed 30 Oct. 2017.
- Huang, Xiaomeng, et al. "Highly Flexible and Conductive Printed Graphene for Wireless Wearable Communications Applications." Nature News, Nature Publishing Group, 17 Dec. 2015, www.nature.com/articles/nnano.2015.267. Accessed 30 Oct. 2017.
- Johll, Harman, et al. "Density functional theory study of Fe, Co, and Ni adatoms and dimers adsorbed on graphene." Physical Review, PDF, 2009.
- Lin, Xiaojin, et al. "Metals on Graphene: Interactions, Growth Morphology, and Thermal Stability." Open Access Journals, 31 Jan. 2013, www.oajournals.com/journal/crystals.
- Roberts, Glenn. "Graphene-Wrapped Nanocrystals Power New Fuel Cell Design." News Center, Lawrence Berkeley Lab, 17 Mar. 2016, wwwnewscenter.lbl.gov/2016/03/17/new-fuel-cell-graphene-wrapped-nanocrystals/.
- Smiths, Belinda. "Five New Uses for Miracle Material Graphene." Cosmos, 2 Mar. 2016, cosmosmagazine.com/technology/five-new-uses-miracle-material-graphene.
- "This Month in Physics History October 22, 2004: Discovery of Graphene." APS News, 2nd ser., vol. 18, no. 9, Oct. 2009, www.aps.org/publications/apsnews/2009/10/physicshistory.cfm. Accessed 30 Oct. 2017.
- Yang, Yong, et al. "Graphene Based Materials for Biomedical Applications." Materials Today, Elsevier, 13 Nov. 2013, www.sciencedirect.com/science/article/pii/S1369702113000815.