CrossMark

The Effect of U Atom Adsorption on the Structural, Electronic and Magnetic Properties of Single-Walled Carbon Nanotubes

YA NIE,[1,2] MU LAN,[1,2] XI ZHANG,[1,2] DINGYU YANG,[4]
and GANG XIANG ⓘ[1,2,3,5]

1.—College of Physical Science and Technology, Sichuan University, Chengdu 610064, China.
2.—Key Laboratory of High Energy Density Physics and Technology of Ministry of Education,
Sichuan University, Chengdu 610064, China. 3.—Key Laboratory of Radiation Physics and
Technology of Ministry of Education, Sichuan University, Chengdu 610064, China. 4.—College of
Optoelectronic Technology, Chengdu University of Information Technology, Chengdu 610225,
China. 5.—e-mail: gxiang@scu.edu.cn

We investigate the structural, electronic and magnetic properties of three
types of single-walled carbon nanotubes (SWNTs, zigzag, armchair and chiral)
with adsorption of a uranium (U) atom using density-functional theories.
Structural analysis shows that the site on the top of the hexagonal ring is the
most stable for the U atom adsorption on all the three types of SWNTs. Upon
adsorption, chemical bonds are formed between C atoms and the U adatom,
and the latter acts as a donor, resulting in a change of energy bands and
increases the Fermi level of SWNTs. Interestingly, upon absorption of non-
magnetic U element, all types of the SWNTs become magnetic, and the in-
duced magnetization is mainly contributed by the U adatom's $6d$ and $5f$
orbitals, which may be useful for carbon-based spintronic applications.

Key words: Magnetism, U atom, carbon nanotubes, adsorption, spintronics

INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have
been studied extensively both theoretically and
experimentally since they were discovered.[1]
Because of their excellent physical and chemical
properties,[2,3] SWNTs and SWNT-based materials
have been proposed for many applications including
SWNT-FETs (field effect transistors),[4] reinforce-
ment materials,[5] electrodes of Li-ion batteries[6] and
sensors.[7–13] Among all these applications, adsorp-
tion of molecules (or atoms) on SWNTs have drawn
a lot of attention due to the large surface-to-volume
ratio of SWNTs. The modifications of the physical
and chemical properties, such as electrical conduc-
tivity,[14] tensile strain[15] and solubility,[16] by adsorp-
tion of molecules have been studied. The correlation
between the structures and electronic properties in
nanoscale materials was also studied using
synchrotron x-ray microdiffraction technology.[17–22]
However, tuning of the magnetic properties of
SWNTs via adsorption of molecules or atoms is
rarely reported. On the other hand, the removal of
heavy metal ions by carbon nanotubes is also
scientifically and technologically important.[23] In
this paper, we investigate the U atom adsorption
of SWNTs (SWNTs:U) and study the adsorption
effect on the electronic and magnetic properties of
SWNTs. Although both pure SWNTs and U element
are nonmagnetic, surprisingly, we find that
SWNTs:U exhibits magnetism, which may be used
for SWNT-based spintronic applications.

METHODS

We have performed the spin polarized first-prin-
ciples calculation based on density-functional the-
ory (DFT). The *Vienna ab initio simulation package*
(VASP) code[24] is used. The projector augmented
wave (PAW) potential[25] is employed to describe the
core electrons, and the generalized gradient approx-
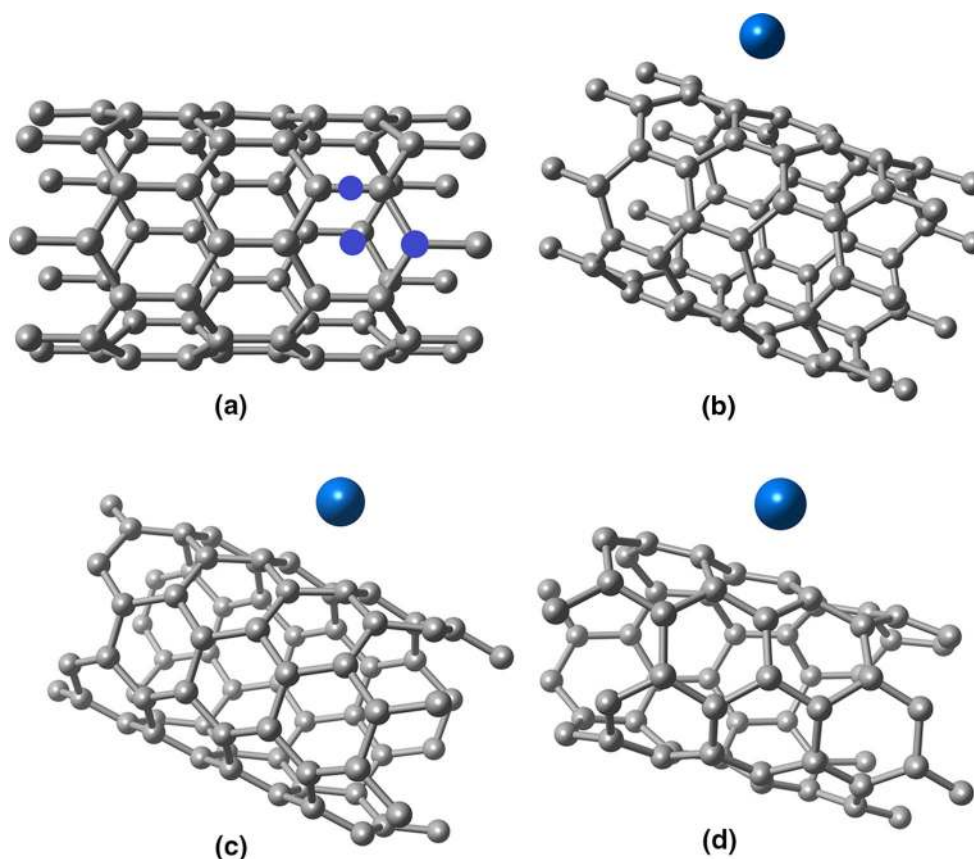imation (GGA) of Perdew–Burke–Ernzerhof

Fig. 1. Illustration of SWNTs with a U adatom. The grey balls represent C atoms and blue ones represent U. (a) The three possible sites for U atom adsorption. The most stable site is the top of the hexagonal ring; (b) in Z-SWNT; (c) in A-SWNT; (d) in C-SWNT.

(PBE)[26] is adopted for exchange and correlation. The GGA + U approximation[27] is taken into account to describe the localization of the f electrons of U element. With the Dudarev's approach,[28] the single parameter U_{eff} is chosen as 4 eV, which is very close to the value used by Durarev et al.[29] and to some experimental findings.[30,31] The kinetic energy cutoff of 520 eV is used and the tolerance for electron convergence is set as 0.000001 eV while the force is converged within 0.01 eV/Å. Entire calculations, including relaxation calculations, static calculation and density of state (DOS) calculations, have been employed with a $(1 \times 1 \times 7)$ k-mesh scheme. All atomic positions are optimized by minimization of the total energy and atomic forces, and collinear magnetic calculation is used to calculate magnetic moments.

Three types of SWNTs have been studied, including zigzag (7,0; Z-SWNT), armchair (4,4; A-SWNT) and chiral (5,2; C-SWNT). For Z-SWNTs, we investigate three possible sites for the U atom adsorption, including the hollow site (on the top of the hexagonal ring), bridge site (on the C–C bond) and the top site (on top of one C atom), respectively, as shown in Fig. 1a. The structure of Z-SWNTs including 56 C

Table I. Average bond lengths l and corresponding binding energies E_b of the U–C bond in Z-SWNT:U, A-SWNT:U and C-SWNT:U

U–C bond	l (Å)	E_b (eV)
Z-SWNT:U	2.630	5.78
A-SWNT:U	2.586	5.74
C-SWNT:U	2.640	6.09

atoms in each unit supercell was initially constructed maintaining a C–C distance at 1.42 Å, and then optimized. After the optimization, one U atom was attached to the tube wall in each unit cell and the stability was investigated.

In order to discuss the stability, we calculate the binding energy E_b with the relation given by

$$E_b(U) = E(U) + E(SWNT) - E(SWNT:U) \qquad (1)$$

where $E(U)$ is the energy of an isolated U atom, $E(SWNT)$ is the total energy of the pristine SWNT super-cell and $E(SWNT:U)$ is the energy of the SWNT:U system.
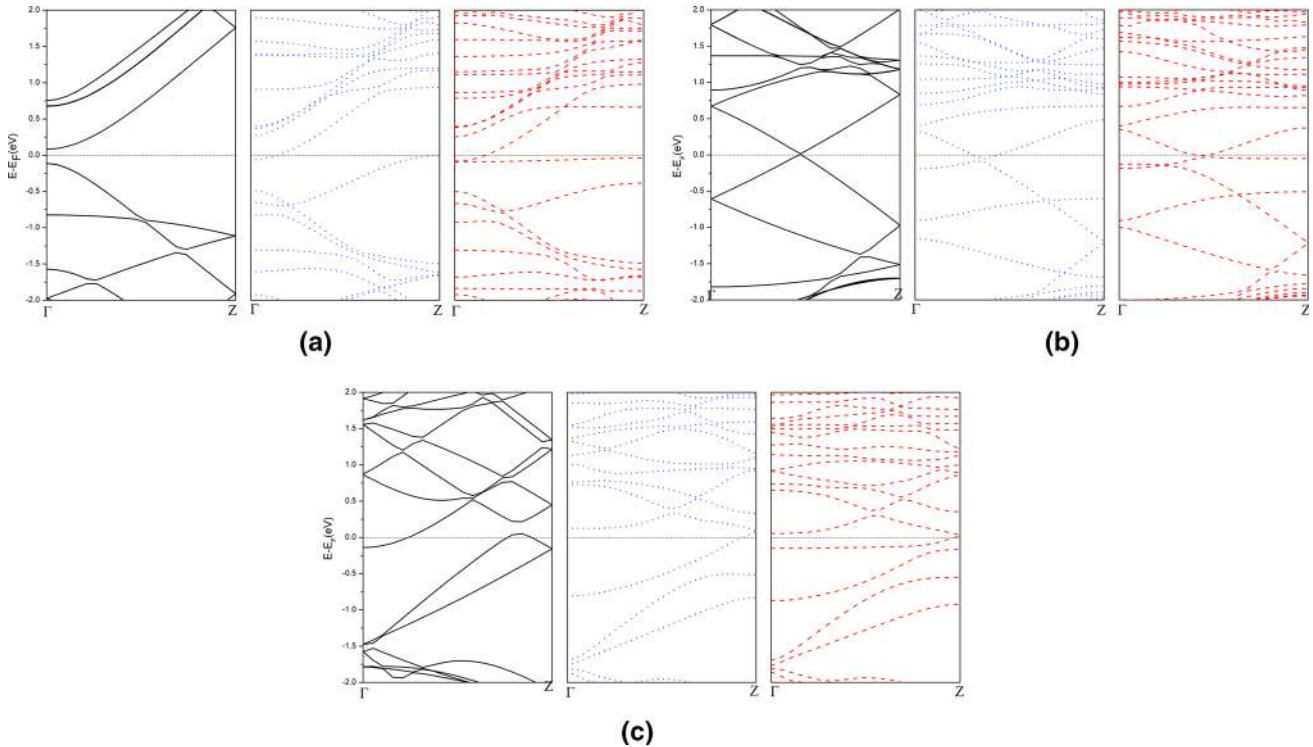
Fig. 2. Electronic band structures of (a) Z-SWNT (black line) and Z-SWNT:U (the blue line represents spin-up bands and the red line spin-down bands); (b) A-SWNT and A-SWNT:U; and (c) C-SWNT and C-SWNT:U (Color figure online).

Our calculation results show that the most stable site for U atom adsorption on Z-SWNTs is the hollow site, as shown in Fig. 1b. Similarly, for A-SWNTs and C-SWNTs, the structures including 64 C atoms and 52 C atoms in each unit cell are constructed and optimized, and the most stable sites for the adsorptions of U atom are the hollow sites, too, as shown in Fig. 1c and d, respectively.

RESULTS AND DISCUSSION

Adsorbed on top of the hexagonal ring, the U adatom is about 2.4–2.8 Å away from its six nearest C atoms of the three types of SWNTs. The average bond lengths (l) between U and its six nearest C atoms, and the corresponding binding energies are displayed in Table I. From Table I, one can see that C-SWNT:U has the largest binding energy with the largest average bond length, while A-SWNT:U has the smallest binding energy with the smallest average bond length. Z-SWNT:U lies in between.

The electronic structures of pure SWNT and SWNT:U systems are then investigated, as shown in Fig. 2. One can see that the adsorption of the U atom drives the band structures of SWNTs to redistribute, and makes contribution to the bands near the Fermi level. For instance, while Z-SWNT is a semiconductor, Z-SWNT:U becomes metallic, as shown in Fig. 2a. Interestingly, spin polarized bands appear and magnetism occurs after the U adsorption in all three types of the SWNTs,

although all the pure SWNTs are nonmagnetic, as plotted in Fig. 2b and c.

In order to analyze the electronic and magnetic contributions, we plot the total density of states (TDOS) for the Z-SWNT:U systems in Fig. 3a. The partial DOSs (PDOS) of the U adatom and the six nearest C atoms near the Fermi level for all the three types of SWNTs are also presented in Fig. 3b, c and d. For Z-SWNT:U, one can see that the bands, which cross the Fermi level with both spin-up and spin-down parts, are evidently contributed by the U adatom's 7s and 6d electrons. The nonsymmetrical distribution of the 5f orbitals is obvious, while nearly four electrons located in spin-down channel and spin-up channel stay almost empty. Then we can conclude that the magnetic moment stems from the charges of the U adatom. Besides, in this metallic system, a charge transferring from the U adatom to the SWNT occurs and thus the Fermi level of Z-SWNT moves up due to the reception of charge. Consequently, the U adatom acts as a donor element. In fact, a very narrow band appears near the Fermi level in the spin-down part, which corresponds to the doping state of the U adatom. This U-doped system may be useful for spintronic applications. Similar outcomes are obtained for A-SWNT:U and C-SWNT:U, as plotted in Figs. 2 and 3.

Furthermore, analysis shows that there are several pairs of equal-energy U 6d and 5f peaks and C 2p peaks located below the Fermi level. This
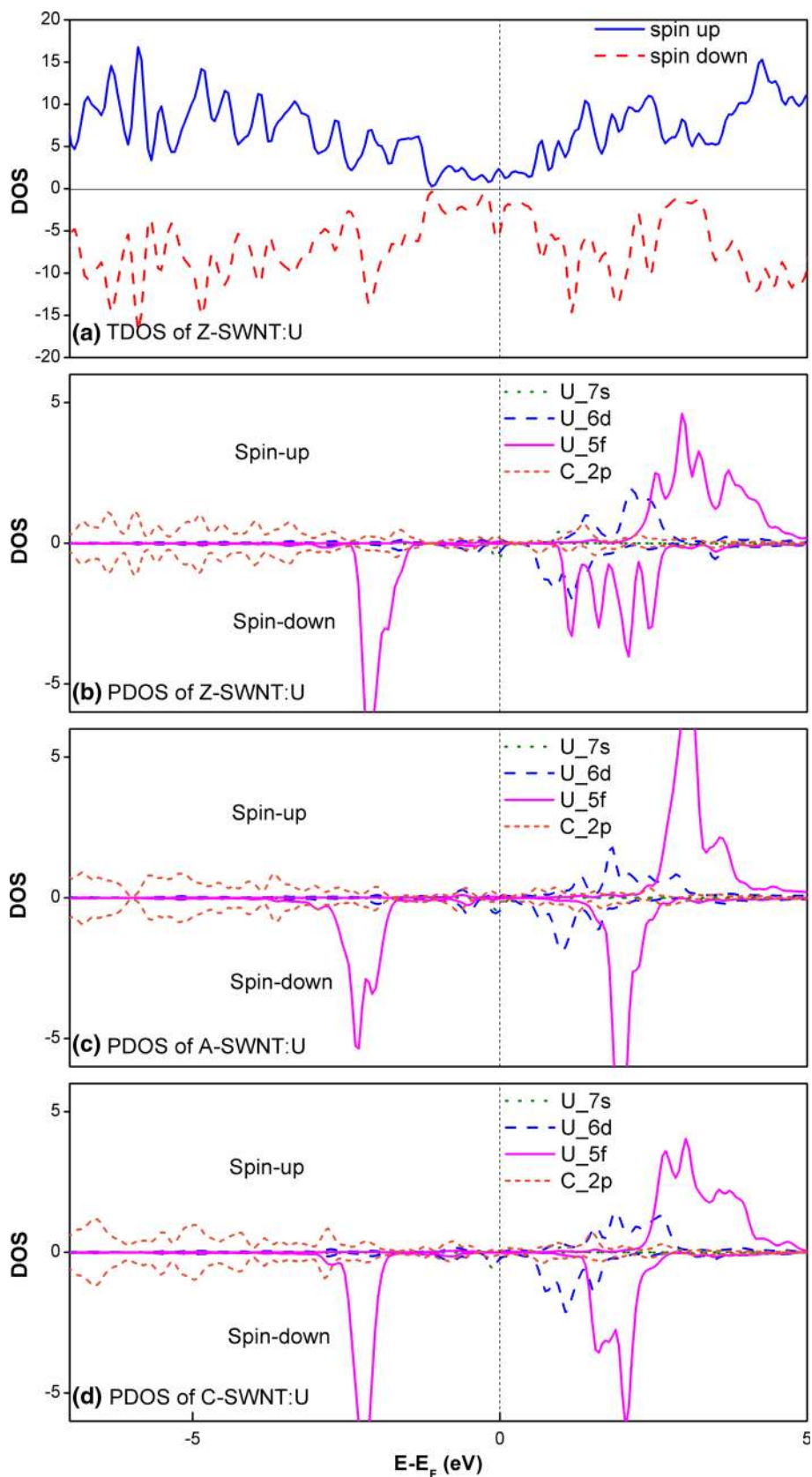
Fig. 3. (a) TDOS of Z-SWNT:U. The black dash line represents the Fermi level. The blue solid line stands for the spin-up charge and the red dashed line for spin-down. (b) PDOS of Z-SWNT:U; (c) PDOS of A-SWNT:U; (d) PDOS of C-SWNT:U. The green, blue and pink lines represent 7s, 6d, 5f electrons of the U atom, respectively. The orange lines represent 2p electrons of the six C atoms near U (Color figure online).
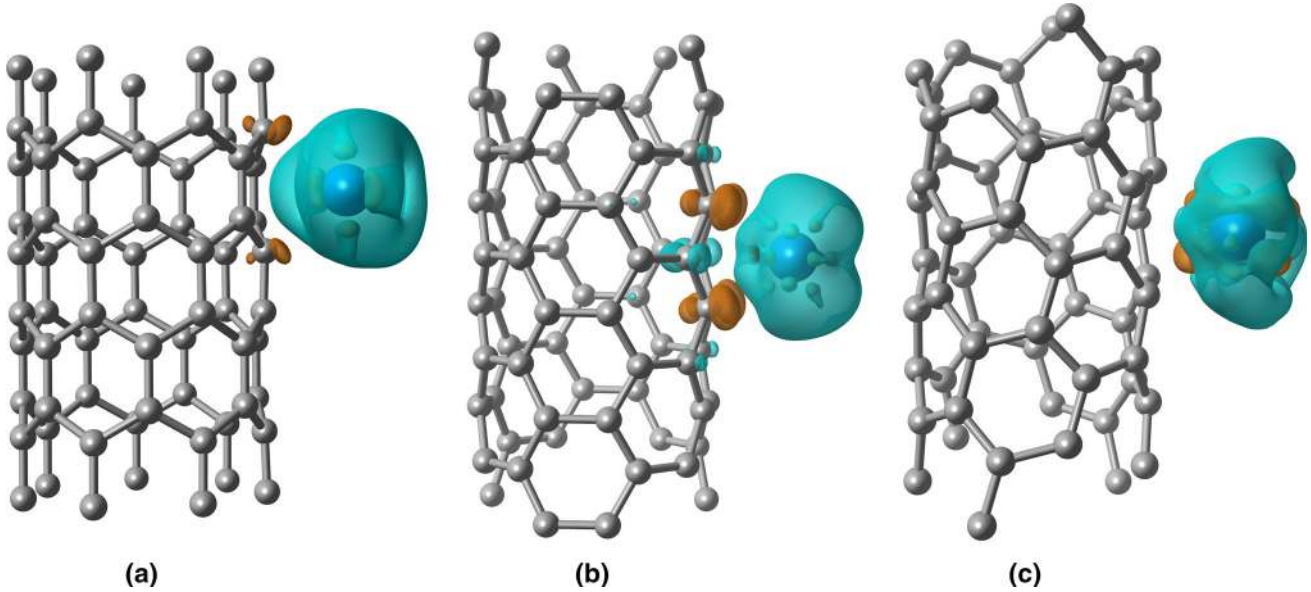
Fig. 4. Magnetization density of (a) Z-SWNT:U, (b) A-SWNT:U, and (c) C-SWNT:U. The orange (light blue) isosurface represents the spin-up (down) charges of 0.002 eV/Å^3 (Color figure online).

Table II. The magnetic moments of U atoms and total magnetic moments of corresponding supercells in Z-, A- and C-SWNT:U systems

	Magnetic moment of U (μB)	Magnetic moment of supercell (μB)
Z-SWNT:U	− 3.85	− 3.92
A-SWNT:U	− 3.70	− 3.81
C-SWNT:U	− 3.90	− 4.03

indicates that the hybridization of U 6d and 5f orbital and C 2p orbital results in the adsorption of the U atom on Z-SWNTs by chemical bonds, not only by physical interaction. However, the contributions to the magnetic moment from 7s orbitals are too little to be important because the 7s shells are filled. Similar results are found for A-SWNT:U and C-SWNT:U.

The magnetization density of the Z-SWNT:U system's ground state is shown in Fig. 4a, where the U adatom shows a magnetic moment of -3.85 μB (μB for a Bohr magneton. As a result, the U adatom has a spin-down magnetic moment, and induces small spin-up magnetic moments on the nearest two C atoms. It shows that although both pure SWNTs and the U element are nonmagnetic, the adsorption causes the magnetism in the SWNT:U system. Since magnetic materials can be easily and remotely collected by electromagnetic ways, the SWNT:U systems may find potential application in dealing with nuclear waste in nuclear power stations. The magnetization densities of A-SWNT:U and C-SWNT:U are also plotted in Fig. 4b and c. The A-SWNT:U has the characteristics

similar to Z-SWNT:U, but the inductive magnetic moments of C atoms are larger than those of Z-SWNT:U. In Fig. 4b, we can see that the U atom has a spin-down magnetic moment and the nearest four C atoms possess spin-up magnetic moments; in addition, the farther C atoms possess spin-down magnetic moments. However, for the same minimum value of isosurface, C-SWNT:U induces negligible magnetic moments on C atoms near it.

For convenient comparisons, we plot the magnetic moments of U adatoms in these three types SWNTs and total magnetic moments of corresponding supercells in Table II. As shown in Table II, the total magnetic moment for each type SWNT is mainly contributed by the U adatom's electrons.

CONCLUSIONS

In this work, the first-principles calculations are implemented to explore the structural, electronic and magnetic properties of U-adsorbed SWNTs. The stability of the adsorption is investigated and the top of the hexagonal ring is found to be the most stable site for SWNTs. The absorbed U atom acts as

a donor and the adsorption of U atoms can effectively change the electronic structures of SWNTs. The magnetism occurs upon U atom adsorption for all the three types of SWNTs, which is resulted from the charge redistribution due to the adsorption and mainly contributed by U $6d$ and $5f$ orbitals. The SWNT:U systems maybe useful for applications in carbon-based spintronics.

ACKNOWLEDGEMENTS

REFERENCES

1. S. Iijima, *Nature* 354, 56 (1991).
2. M. Ouyang, J.L. Huang, and C.M. Lieber, *Acc. Chem. Res.* 35, 1018 (2002).
3. M.F.L. De Volder, S.H. Tawfick, R.H. Baughman, and A.J. Hart, *Science* 339, 535 (2013).
4. H.R. Byon and H.C. Choi, *J. Am. Chem. Soc.* 128, 2188 (2006).
5. S. Kumar, T.D. Dang, F.E. Arnold, A.R. Bhattacharyya, B.G. Min, X. Zhang, R.A. Vaia, C. Park, W.W. Adams, R.H. Hauge, R.E. Smalley, S. Ramesh, and P.A. Willis, *Macromolecules* 35, 9039 (2002).
6. Ch Ban, Zh Wu, D.T. Gillaspie, L. Chen, Y. Yan, J.L. Blackburn, and A.C. Dillon, *Adv. Mater.* 22, E145 (2010).
7. J. Kong, N.R. Franklin, C. Chou, M.G. Chapline, S. Peng, K. Cho, and H. Dai, *Science* 287, 622 (2000).
8. H. Chang, J.D. Lee, S.M. Lee, and Y.H. Lee, *Appl. Phys. Lett.* 79, 3863 (2001).
9. J. Kong, M.G. Chapline, and H. Dai, *Adv. Mater.* 13, 1384 (2001).
10. J.J. Davis, K.S. Coleman, B.R. Azamian, C.B. Bagshaw, and M.L.H. Green, *Chem. Eur. J.* 9, 3732 (2003).
11. A. Qureshi, W.P. Kang, J.L. Davidson, and Y. Gurbuz, *Diam. Relat. Mater.* 18, 1401 (2009).
12. S.J. Pearton, F. Ren, Y.L. Wang, B.H. Chu, K.H. Chen, C.Y. Chang, W. Lim, J. Lin, and D.P. Norton, *Prog. Mater Sci.* 55, 1 (2010).
13. B.H. Son, J.Y. Park, S. Lee, and Y.H. Ahn, *Nanoscale* 7, 15421 (2015).
14. U. Dettlaff-Weglikowska, V. Skakalova, R. Graupner, L. Ley, and S. Roth, *Mater. Res. Soc. Symp. Proc.* 772, 179 (2003).
15. L.G. Zhou and S.Q. Shi, *Comput. Mater. Sci.* 23, 166 (2002).
16. Q.W. Li, J. Zhang, H. Yan, M.S. He, and Z.F. Liu, *Carbon* 42, 287 (2004).
17. N. Tamura, A.A. MacDowell, R. Spolenak, B.C. Valek, J.C. Bravman, W.L. Brown, R.S. Celestre, H.A. Padmore, B.W. Batterman, and J.R. Patel, *J. Synchrotron Radiat.* 10, 137 (2003).
18. A.S. Budiman, G. Lee, M.J. Burek, D. Jang, S.M. Han, N. Tamura, M. Kunz, J.R. Greer, and T.Y. Tsui, *Mater. Sci. Eng. A* 538, 89 (2012).
19. C.Y. Khoo, H. Liu, W. Sasangka, R.I. Made, N. Tamura, M. Kunz, A.S. Budiman, C.V. Thompson, and C.L. Gan, *J. Mater. Sci.* 51, 1864 (2016).
20. I. Radchenko, S.K. Tippabhotla, N. Tamura et al., *J. Electr. Mater.* 45, 6222 (2016).
21. H.P.A. Ali, I. Radchenko, J. Zhao, L. Qing, and A.S. Budiman, *J. Mater. Des. Appl.* 1, 1 (2017). https://doi.org/10.1177/1464420717695354.
22. H.-A.-S. Shin, B.-J. Kim, J.-H. Kim, S.-H. Hwang, A.S. Budiman, H.-Y. Son, K.-Y. Byun, N. Tamura, M. Kunz, D.-I. Kim, and Y.-C. Joo, *J. Electron. Mater.* 41, 712 (2012).
23. V.K. Gupta, O. Moradi, I. Tyagi, S. Agarwal, H. Sadegh, R. Shahryari-Ghoshekandi, A.S.H. Makhlouf, M. Goodarzi, and A. Garshasbi, *Crit. Rev. Environ. Sci. Technol.* 46, 93 (2016).
24. G. Kresse and J. Furthmuller, *Phys. Rev. B* 54, 11169 (1996).
25. P.E. Blöchl, *Phys. Rev. B* 50, 17953 (1994).
26. J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865 (1996).
27. V.I. Anisimov, J. Zaanen, and O.K. Andersen, *Phys. Rev. B* 44, 943 (1991).
28. S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, and A.P. Sutton, *Phys. Rev. B* 57, 1505 (1998).
29. S.L. Dudarev, D. NguyenManh, and A.P. Sutton, *Philos. Mag. B* 75, 613 (1997).
30. J. Schoenes, *J. Chem. Soc. Faraday Trans. II* 83, 1205 (1987).
31. A. Kotani and T. Yamazaki, *Prog. Theor. Phys. Suppl.* 108, 117 (1992).