

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Controlling doping level of double-walled carbon nanotubes by using aromatic hydrocarbon complexes

Cite this: DOI: 10.1039/x0xx00000x

K.-Y. Chun^{a,*}

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The level of potassium doping in double-walled carbon nanotubes is controlled by using the potassium-aromatic hydrocarbon (AH) complexes. The concentration of doping increase when the large AH molecule complex is delivered. The crystalline perfection is also affected by the degree of K-doping.

Since carbon nanotubes (CNTs) have been investigated for many applications such as nanocomposite, supercapacitor, energy harvesting and solar cell, the adjustment of optic, electronic, and mechanical properties of CNTs have required the morphological and structural modification of CNTs.¹⁻⁴

For instance, doping into CNTs using potassium (K), nitrogen, boron, and cesium is a reliable method to modify the surface of CNTs and their electrical properties.⁵⁻¹⁰ Alkali metal doping such as K has particularly attracted much attention on the modification of the electronic properties of CNTs.¹¹⁻¹³ Some research groups reported the enhancement of electrical and thermal conductivity of CNTs, control of the K-doping level by reversibly intercalating and deintercalating, and short channel n-type CNT field-effect transistors with K-doped source and drain regions.¹⁴⁻¹⁶ K-doping into CNTs has been conventionally performed using the reaction of vaporized potassium in a complex procedure with high-energy consumption and a high cost process.¹⁵

Previously, we demonstrated the effective chemical K-doping in double-walled CNTs (DWNTs) at room temperature and its characterizations.¹⁷ Recently, Li *et al.* reported *in vitro* detection of superoxide anions released from cancer cells based on K-doped CNT-ionic liquid composite gels¹⁸ and the nitrite-selective sensing using K-modified graphene by using chemical K-doping at room temperature.¹⁹ However, the facile control of K-doping level has not been released yet.

In this communication, the effect of aromatic hydrocarbons (AHs) on the determination of K-doping level and crystalline

perfection of the DWNTs were demonstrated, which are chemically doped at room temperature.

High-quality DWNTs were synthesized by arc discharge (AD) method. The as-synthesized DWNTs have ~3.5 nm in diameter. The impurities of CNTs was removed by air oxidation at 450 °C for 1 h with conventional acid treatment.²⁰ Chemical complexes for K-doping were prepared by reacting K (200 wt % to DWNTs) with 0.2 mol/dm³ of three AHs (benzene, naphthalene, and anthracene) in 20 ml of 1,2-dimethoxyethane (1,2-DME, 99.5%). Purified DWNTs (20 mg) were reacted with chemical complexes using bath sonication and then stirred for 48 hrs using magnetic bar with 500 rpm at room temperature. The resulting product was thoroughly washed several times with ethanol. The morphologies and structures of K-doped DWNTs were characterized by scanning electron microscopy (SEM) (Hitachi, S-4700) and high-resolution transmission electron microscopy (TEM) (TECNAI, F20, 200kV). X-ray photoelectron spectroscopy (XPS) (VG-Scientific ESCALAB 250 spectrometer) was measured to confirm K-doping (X-ray: monochromatized Al K α line, step energy: 1486.6 eV with 0.1-eV resolution). Thermal analysis of the DWNTs was conducted by thermogravimetric analysis (TGA) (TA instruments, Q-50, 5 °C/min). Raman spectroscopy (Jobin-Yvon, LabRam HR) was operated using 514.5-nm Ar laser excitation to observe the defect degree of K-doped DWNTs.

To obtain the distribution of K atoms, XPS was measured using photon energy 1486.6 eV. The C at% against total components was relatively decreased forward to the long AHs (Fig. S1, ESI†). Interestingly, as shown in Fig. 1a, the concentration of doping increased from 5.8 to 7.7 at% with increase of the number of C₆-ring in the AHs. In the case of anthracene complex, doping concentration showed highest value as 7.7 at%. In our previous work, the K-doping concentration in the DWNTs grown by chemical vapor deposition (CVD) is 3.2 at % when phenanthrene complex used.¹⁷ In general, CNTs synthesized by AD method have high crystallinity compared to CNTs grown by CVD method. In this study, the degree

of K-doping of AD-DWNTs is larger than that of CVD-DWNTs even though the reason of different doping concentration has not been proved. The typical K 2p spectrum comprises two peak components at the binding energy of 293.3 and 296 eV.²¹ The difference of binding energy between these two peak components was about 2.7 eV and their intensity ratio was about 1.6:1. Two binding energies are ascribed to the spin-orbit-split doublet (K 2p_{3/2} and K 2p_{1/2}) of the K-oxides and K-cations, respectively.²² Here, no metallic K peak found corresponding to 294.6 eV.

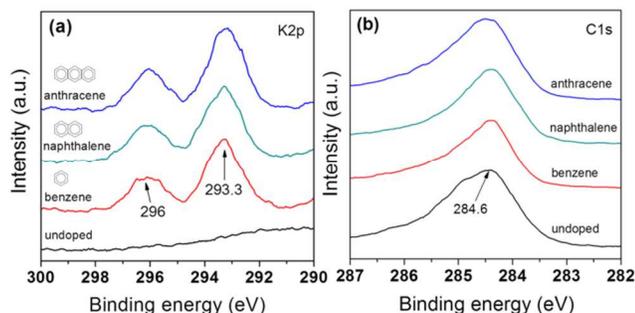


Fig. 1 XPS scan spectra using 1486.6 eV: (a) K 2p core-level spectra. K at %; Undoped DWNTs: 0, benzene: 5.8, naphthalene: 6.5, anthracene: 7.7 (b) C 1s core-level spectra. C at %; Undoped DWNTs: 72.6, benzene: 65.5, naphthalene: 58.4, anthracene: 54.1.

In Fig. 1b, the C 1s peak for the K-doped DWNTs was observed at 284.6 eV and was very consistent with sp² graphite carbon. The peak at 284.6 eV is assigned to the C–C and C–H bonding. As a number of C₆-ring of AHs increased, the area of C 1s was degraded from 65.5 to 54.1 at %. Undoped DWNTs was 72.6 at%. It indicates that the C₆-rings in the AH complexes affects the consistent reduction of C-atoms binding and the generation of disorder or defects in the DWNTs.

Usually, the K-doping using chemical reaction method is achieved by large expansion stress inside of DWCNT bundles entangled by strong van der Waals force. Actually, due to the swallow potential along the direction of K⁺ ion transfer in the isomer of K⁺-AHs, K⁺ cation easily moves over the AHs plane.²³ In our system, the various AHs-K complexes give different intensity of stress to the CNTs and may intercalate the inside both of CNT bundles and graphite sheets, providing an each doping degree in the CNTs.

Fig. 2a shows the SEM image of as-synthesized CNTs including carbonaceous particles and many metal catalyst particles. After purification, the large amounts of entangled carbon filaments were observed (Fig. 2b). The K-doping was additionally confirmed by using energy dispersive spectrometer (EDS) in the case of benzene-K complexes (Fig. S2, ESI†). The distribution of K in the CNTs looks very broadly in the acceptable active area as 5.1 at% which is consistent with XPS analysis. The amorphous carbon and metallic catalyst were almost removed as shown in the TEM image of Fig. 2c. A highly ordered crystalline structure was also observed in the inset of Fig. 2c. After K-doping, the morphologies of DWNTs was changed to defective and disordered aspect as shown in Figs. 2d, e, and f. Interestingly, the degree of defects tends to rise according to the increase of C₆-ring in the AHs. In the case of anthracene with three C₆-rings, more defects and cuttings in the CNTs were observed than those in other cases of AHs. Here, it is found that the types of K-AHs complexes afford not only the difference of K-doping concentration, but also the degree of defects in the DWNTs.

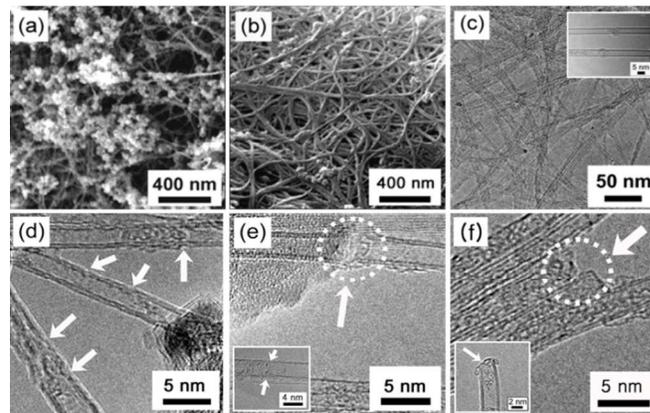


Fig. 2 SEM and TEM images of DWNTs: SEM images (a) as-synthesized DWNTs, (b) purified DWNTs. TEM images (c) low-magnified image of purified DWNTs (inset: purified DWNTs with high crystalline graphite layers.) Highly magnified typical TEM images of K-doped DWNTs according to the various types of aromatic hydrocarbons (d) benzene, (e) naphthalene, and (f) anthracene complex.

Theoretically, the binding energy between AHs and K⁺ ions is slightly decreased according to the increase of C₆-ring in the AHs.^{23,24} In other words, the highly mobile K⁺ ions is more easily transported under large C₆-ring complex and effectively doped in the DWNTs. In particular, anthracene, linear AHs with large size, can introduce a more consecutive binding energy than that of other AHs and is able to afford mapping on the large surface area of CNTs to form π -stacking interaction. Consequently, the difference of binding energies between AHs and K⁺ ions, which provide intercalation compounds, can be an important factor to achieve the difference of K-doping level. Moreover, the attack of K-AHs complexes to the surface of CNTs can give a large enlargement of bundles and layer spacing in the CNTs, resulting in the degradation of crystalline perfection. Regarding the AHs with DWNTs in the absence of potassium, the degradation of DWNTs can be occurred because the AH molecules easily slide and move on a C–C bond of the DWNT surface.²⁵ In other words, complex solution mixtures without potassium are able to make the degradation of DWNT surfaces because the role of the AHs ion radicals is to guide and attack the doping reaction in the solution. However, the optimized-complex mixtures including potassium, AHs and solvent with different binding energy mainly contribute to give stress accompanied by the vacancies of CNT bundle networks and the enlargement of interlayer spacing of CNTs.¹⁷

TGA curves for each DWNTs were demonstrated (Fig. S3, ESI†). The decomposition was carried out in ambient air at a low heating rate of 5 °C/min. The initial purity of the purified DWNTs is about 89%. It indicates that the residual impurities including iron and iron oxide catalyst are mostly eliminated. Interestingly, the gasification temperature shows a shift to the low temperature after K-doping, but purity is almost the same with pristine DWNTs. It is known that the defect or disorder of DWCNTs is increased and residual impurities are a little removed due to the K-doping.

Raman spectroscopy was also studied to confirm the change of crystalline perfection owing to the K-doping. The variations of the radial breathing mode (RBM) frequencies of the K-doped DWNTs are shown in Fig. 3a. As increasing C₆-ring of AHs, the intensity of high frequencies in the RBM mode decreases. Also, the peaks indicating the DWNTs with small diameter disappear due to the structural deformation of the DWNTs after K-doping. The G band at 1592.6 cm⁻¹ and the D band at 1344.4 cm⁻¹ were detected in tangential mode (Fig. 3b). The G band

correspond to stretching and bending E_{2g} mode due to the in-plane vibrational movement of carbon atoms.²⁶ The D band indicate A_{1g} (vibrational mode) caused by disorder and defect of C–C bond, which is a highly dispersive spectral feature.²⁷ The tangential mode shows no significant line shifts or broadening according to the K-doping concentration. The G band splits into two components G+ at 1592.6 and a G- at 1570.9 cm^{-1} due to the different force constants for C–C bonds along the tube length and circumferential directions.²⁸ The significant changes of intensity and shift in the G+ and G- frequencies were not observed, suggesting that the force constant for the C–C bonds along the tube length and circumferential direction in bundled DWNTs is not largely affected by the intercalation of K-AHs complexes.

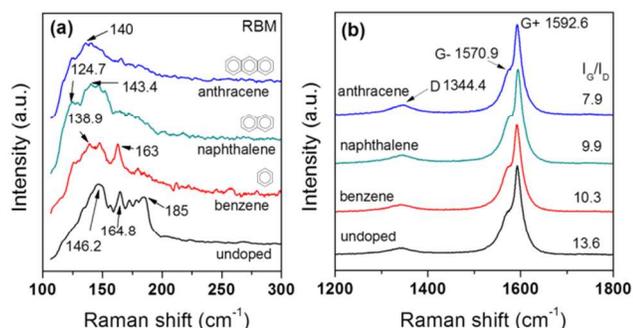


Fig. 3 Raman spectra using 514.5-nm Ar laser: (A) Radial breathing modes (low frequency). (B) Tangential modes (high frequency). (a) Undoped DWNTs, K-doped DWNTs (b) 5.81 (benzene), (c) 6.47 (naphthalene), and (d) 7.7 K at% (anthracene complex).

However, the disorder-induced D band of tangential mode shows a consistent increase in intensity, which the slow incorporation of K atoms might result in the change of defect degree in the hexagonal lattice of DWNTs. Also, the reduction of the intensity value of crystallization (I_G/I_D), in the range from 10.3 to 7.9, implies that the graphitization of DWNTs is clearly degraded according to more active reaction with longer C_6 -ring in the AH complexes and CNTs. Therefore, the behavior of crystalline perfection of DWNTs is strongly attributed to the types of AHs complexes during the K-doping.

Conclusions

In conclusions, the control of potassium doping level of the DWNTs is possible by using the types of aromatic hydrocarbons-potassium complexes in appropriate polar solvent. The combination of aromatic hydrocarbons and potassium is very important factor to make different doping level in the DWNTs. Like aromatic hydrocarbons, the guidance of metal alkali can play an important role to tailor the mechanical and electrical properties of carbon nanotubes even though the precise control of chemical doping is further required.

Notes and references

^a Center for Bio-Artificial Muscle and Department of Biomedical Engineering, Hanyang University, Seoul, 133-791, South Korea. Fax: 82 2 2291 2320; Tel: 82 2 22204540; E-mail: kychun@gmail.com

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

- 1 K. -Y. Chun, Y. Oh, J. Rho, J. -H. Ahn, Y. -J. Kim, H. R. Choi and S. Baik, *Nature Nanotech.*, 2010, **5**, 853.
- 2 Z. Tang, C. Tang and H. Gong, *Adv. Func. Mater.*, 2012, **22**, 1272.
- 3 J. Lohrman, C. X. Zhang, W. Zhang and S. Q. Ren, *Chem. Commun.*, 2012, **48**, 8377.
- 4 Y. Jo, J. Y. Cheon, J. Yu, H. Y. Jeong, C. -H. Han, Y. Jun and S. H. Joo, *Chem. Commun.*, 2012, **48**, 8057.
- 5 R. S. Lee, H. J. Kim, J. E. Fischer, A. Thess and R. E. Smalley, *Nature*, 1997, **388**, 255.
- 6 M. Terrones, *Small* 2005, **1**, 1032.
- 7 J. C. Carrero-Sánchez, A. L. Elias, R. Mancilla, G. Arrellin, H. Terrones, J. P. Laclette and M. Terrones, *Nano Lett.*, 2006, **6**, 1609.
- 8 R. Sen, B. C. Satishkumar, A. Govindaraj, K. R. Harikumar, M. K. Renganathanb and C. N. R. Rao, *J. Mater. Chem.*, 1997, **7**, 2335.
- 9 M. Nath, B. C. Satishkumar, A. Govindaraj, C. P. Vinod and C. N. R. Rao, *Chem. Phys. Lett.*, 2000, **322**, 333.
- 10 C. -L. Sun, H. -W. Wang, M. Hayashi, L. -C. Chen and K. -H. Chen, *J. Am. Chem. Soc.*, 2006, **128**, 8368.
- 11 L. Grigorian, G. U. Sumanasekera, A. L. Lpoer, S. Fang, J. L. Allen and P. C. Eklund, *Phys. Rev. B*, 1998, **58**, R4195.
- 12 G. Gao, T. Cagin and W. A. Goddard III, *Phys. Rev. Lett.*, 1998, **80**, 5556.
- 13 T. Miyake and S. Saito, *Phys. Rev. B*, 2002, **65**, 165419
- 14 A. M. Rao, P. C. Eklund, S. Bandow, A. Thess and R. E. Smalley, *Nature*, 1997, **388**, 257.
- 15 M. Bockrath, J. Hone, A. Zettle, P. L. McEuen, A. G. Rinzler and R. E. Smalley, *Phys. Rev. B*, 2000, **61**, R10606.
- 16 A. Javey, R. Tu, D. B. Farmer, J. Guo, R. G. Gordon and H. Dai, *Nano Lett.*, 2005, **5**, 345.
- 17 K. -Y. Chun and C. J. Lee, *J. Phys. Chem. C*, 2008, **112**, 4492.
- 18 X. -R. Li, B. Wang, J. -J. Xu and H. -Y. Chen, *Nanoscale* 2011, **3**, 5026.
- 19 X. -R. Li, F. -Y. Kong, J. Liu, T. -M. Liang, J. -Y. Xu and H. -Y. Chen, *Adv. Func. Mater.* 2012, **22**, 1981.
- 20 B. Ha and C. J. Lee, *Appl. Phys. Lett.* 2007, **90**, 023108.
- 21 H. H. Huang, X. Jiang, Z. Zou, W. S. Chin, G. Q. Xu, W. L. Dai, K. N. Fan and J. F. Deng, *Surf. Sci.*, 1998, **412**, 555.
- 22 S. Li, E. T. Kang, K. G. Neoh, Z. H. Ma, K. L. Tan and W. Huang, *Appl. Surf. Sci.*, 2001, **181**, 201.
- 23 S. Ikuta, *J. Mol. Struct. (Theochem)*, 2000, **530**, 201.
- 24 S. Hashimoto and S. Ikuta, *J. Mol. Struct. (Theo. Chem.)*, 1999, **468**, 85.
- 25 F. Tournus and J. C. Charlier, *Phys. Rev. B*, 2005, **71**, 165421–8.
- 26 C. Thomsen and S. Reich, *Phys. Rev. Lett.*, 2000, **85**, 5214.
- 27 N. R. Raravikar, P. Keblinski, A. M. Rao, M. S. Dresselhaus, L. S. Schadler and P. M. Ajayan, *Phys. Rev. B*, 2002, **66**, 235424–1.
- 28 M. S. Dresselhaus and P. C. Eklund, *Adv. Phys.* 2000, **49**, 705.