Effect of SWCNT charge on a carbon adatom diffusion

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Synopsis Negative charges on an armchair single-walled carbon nanotube (SWCNT) can enhance the migration of a carbon adatom on its external surface, along the direction of the tube axis. Stronger binding of the adatom to SWCNT caused by CNT charging causes longer lifetimes of adatom before desorption and consequent increases of its migration distance by several orders of magnitude. This contra-intuitive result supports the hypothesis of diffusion enhanced SWCNT growth in the volume of arc plasma.

High-pressure, arc-discharge plasma, utilizing carbon electrodes can be used for producing high quality, defect-free SWCNT. However, despite the successful development of this method, detailed understanding of all physical and chemical processes taking place during the SWCNT synthesis in the arc is challenging. In addition, in the arc-discharge method, the nanotube surface is subject to the flux of plasma ions and electrons, which are capable of charging the SWCNT.

We explored the adsorption and migration behavior of a carbon adatom on negatively charged, armchair (5,5) SWCNT of finite length (Fig. 1a), finding significant increase in the migration distance when |q| > 4e. The transition rates were determined using first-principles DFT calculations. Simulations of carbon adatom migration (Fig. 1b) were conducted using the Kinetic Monte-Carlo method. We found that while the CNT charging only slightly affects the barriers to adatom diffusion along nanotubes (Fig. 1c), it significantly increases their adsorption energies. This seemingly counterintuitive observation is the result of increased electron density in the region between the carbon adatoms and the carbon atoms of the SWCNT. The consequence of this added density is an increase in the covalent coupling between adatoms and SWCNTs. In concert with relatively lower diffusion energy barriers, this enhanced coupling increases the lifetime of adatoms on the surface of the SWCNTs, allowing for longer migration distances before desorption back to plasma (Fig. 2).

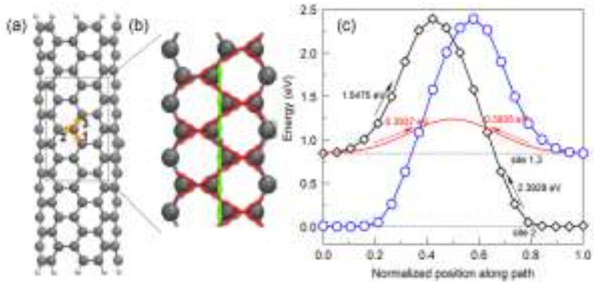

Figure 1. (a) Equilibrium adsorption sites marked by yellow stars, (b) possible migration paths, the green arrows are paths with lower energy barriers (between sites 1 and 3), and (c) energy profiles of migration barriers between the equilibrium sites for an adatom on a (5,5) SWCNT.

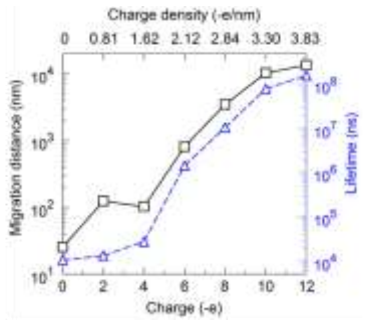

Figure 2. Migration distance, (the black line with squares), and lifetime, (the blue dashed line with triangles), of a carbon adatom as a function of the charge on a (5,5) SWCNT of 2 nm long. Charge density in the middle of the tube for each case is shown on the upper axis.

These findings indicate an enhanced carbon adatoms flux on the external surface of SWCNTs toward the metal catalyst, which could lead to a profound increase in the growth rate of SWCNTs in the arc plasma volume.

References

[1] L. Han and P. Krstic, ", Carbon **116**, 174 (2017).

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