

Achievement of high-purity carbon nanofibres *via* peeling process

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The authors report a facile approach to high-purity carbon nanofibres (CNFs), by performing chemical vapour deposition on aluminium foils loaded with metal (nickel or cobalt) nitrates, and then peeling the as-grown CNFs off. The growth of CNFs was catalysed by metal nanoparticles and followed bottom-growth mechanism, and the high-purity CNFs were achieved due to detachment of CNFs from their underlying metal nanoparticles during the peeling process. This approach may pave a new way for the controlled and scalable synthesis of high-purity carbon materials.

1. Introduction: Carbon nanofibres (CNFs) have outstanding properties, such as high electrical conductivity, large surface areas, and high flexibility. Hence, they are widely used in a variety of areas, including electrocatalysts [1], lithium ion batteries [2], adsorbents for various oils [3], and filtration membranes for separation of oil/water mixtures [4]. So far, various synthetic approaches, including carbonisation [3], electrospinning [1], and electrolysis [5], have been investigated for the controlled synthesis of CNFs. Among them, chemical vapour deposition (CVD), where transition metals [such as nickel (Ni), cobalt (Co), copper (Cu), and their alloys] were usually utilised to catalyse growth of CNFs [4, 6–10], received considerable attentions, because of its advantages of easy operation and low cost. However, the transition metal catalysts were difficult to remove even after the multi-step work-up procedures as well as the use of toxic chemicals [11, 12], thereby hindering applications of the CNFs. Hence, it is of great significance for CVD approaches to fabricate high-purity CNFs.

Here, by loading metal (Ni or Co) nitrates on aluminium (Al) foils, and then performing CVD growth of CNFs and a following peeling process, we achieved controlled synthesis of CNFs with high purity. This was ascribed to bottom-growth mechanism of CNFs and detachment of CNFs from their underlying metal catalysts during the peeling process.

2. Experimental

2.1. Fabrication of high-purity CNFs: Fig. 1*a* shows schematics of fabrication process of high-purity CNFs. Firstly, metal nitrates were loaded on high-purity Al foils, by dipping Al foils in 0.1 M metal nitrate aqueous solution for seconds and drying. Then, CVD process was conducted at 440°C for 30 h with acetylene (80 sccm) as precursor and argon (8 sccm) as carrying gas. During this process, metal nitrates were firstly thermally decomposed to metal oxides, and then the resultant metal oxides were reduced to metal nanoparticles by carbon and hydrogen (Fig. 1*b*), both of which derived from pyrolysis of acetylene [13]. Subsequently, metal nanoparticles catalysed growth of CNFs, which followed bottom-growth mechanism [14, 15], and meanwhile carbon films were deposited on surfaces of Al foils to encapsulate the metal nanoparticles. Finally, CNFs were peeled off to achieve high-purity CNFs, while metal nanoparticles were left in the carbon films.

2.2. Characterisation: The CNFs were characterised by using scanning electron microscope (SEM, Hitachi SU8020),

transmission electron microscope (TEM, FEI Tecnai TF20), energy dispersive X-ray spectrometry (EDS), X-ray photoelectron spectrometer (XPS, Thermo Fisher K-alpha), and X-ray diffractometer (Philips X-Pert Pro).

3. Results and discussion: Firstly, we fabricated high-purity CNFs by loading nickel nitrates on Al foils before the CVD process. As shown in Fig. 2*a*, large quantity of high-purity CNFs can be obtained. As estimated, 30 mg of high-purity CNFs could be produced for Al foils with area of 1 cm². Enlarged SEM image (Fig. 2*b*) shows clearly that these CNFs are tortuous or twisted in morphology; similar morphology has been observed in other transition-metal-catalysed CNFs [9, 16]. TEM image (Fig. 2*c*) confirms solid nature of the high-purity CNFs, and also demonstrates that they contain no Ni nanoparticles. High-resolution TEM (HRTEM) image (inset in Fig. 2*c*) shows that high-purity CNFs have a low crystallinity, agreeing well with the previous report that low-temperature CVD usually resulted in low-crystalline carbon materials [9]. Both EDS (Fig. 2*d*) and XPS spectra (Fig. 3*a*) confirm that high-purity CNFs consist of only carbon elements, and this is further verified by their X-ray diffraction (XRD) pattern (Fig. 3*b*), which demonstrates only carbon [002] (at ~26.2°) and carbon [110] (at ~46.3°) peaks. Hence, in comparison with the previous CVD approaches, where high purity of the CNFs had to be achieved by post-treatments which consisted of use of toxic chemicals and tedious procedures [11], our approach can achieve the easy, low-cost, and eco-friendly fabrication of high-purity CNFs.

After the peeling process, we further dissolved the Al foils to liberate the carbon films deposited on surfaces of Al foils during CVD. From TEM images (Figs. 4*a* and *b*), we can see that there are many Ni nanoparticles embedded in these carbon films, confirming that high-purity CNFs were achieved by detaching CNFs from Ni nanoparticles during the peeling process. In addition, this result also reveals that Ni nanoparticles were always located at bottoms of CNFs during their growth, verifying that Ni-catalysed growth of CNFs was through bottom-growth mechanism [14, 15], though the detailed process (vapour–liquid–solid [17], or vapour–solid–solid [18]) is not clear. Furthermore, the easy detachment of CNFs from Ni nanoparticles during the peeling process reveals that adhesion of CNFs to the Ni nanoparticles was weak, due probably to the lattice mismatch between CNFs and Ni nanoparticles [19]. Also, this result indicates that adhesion of Ni nanoparticles to Al foils was tightly enough during the peeling process. We think this may be attributed to two factors: (i) carbon films encapsulating Ni nanoparticles increased adhesion of Ni nanoparticles to

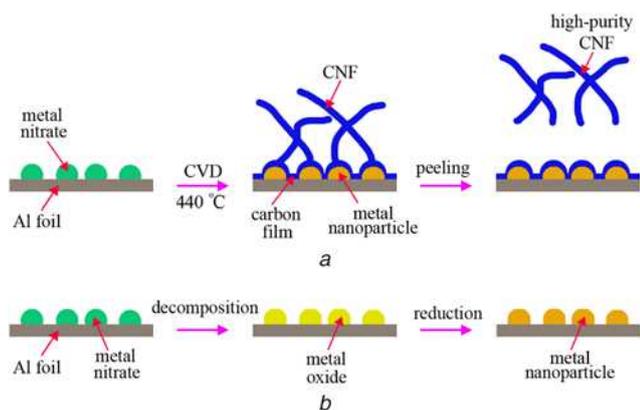


Fig. 1 Schematics showing fabrication of high-purity CNFs
a The corresponding evolution of metal nitrates during CVD (*b*)
b Schematics of evolution of metal nitrates during CVD

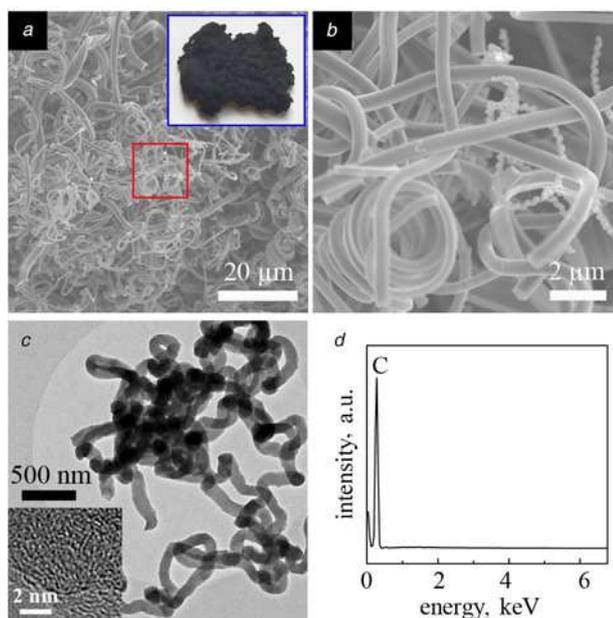


Fig. 2 Characterisation results of high-purity CNFs fabricated by using nickel nitrates
a SEM image. Inset: Photograph
b Enlarged SEM image of red square area in (*a*)
c TEM image. Inset: HRTEM image
d EDS spectrum

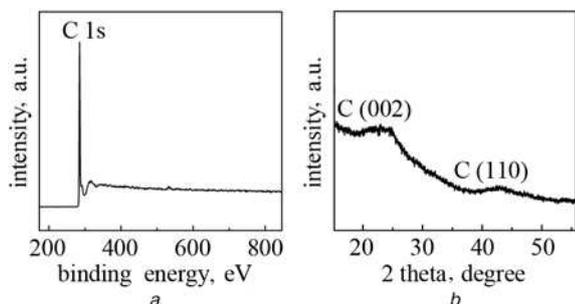


Fig. 3 XPS spectrum
a XRD pattern
b of high-purity CNFs fabricated by using nickel nitrates

Al foils; and (ii) annealing during the CVD process resulted in inter-diffusion of Ni nanoparticles and Al foils [20], leading to enhanced adhesion of Ni nanoparticles to Al foils.

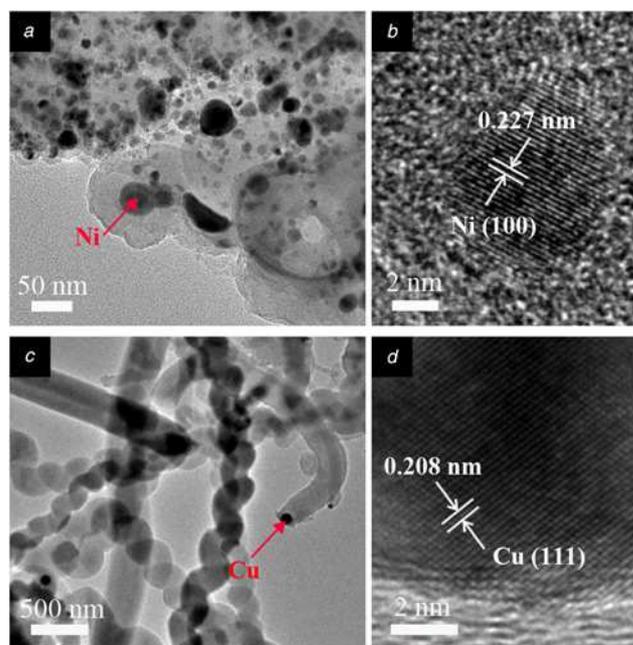


Fig. 4 Characterisation results of carbon films after peeling process and CNFs fabricated by using copper nitrates
a TEM image of carbon films
b HRTEM image of Ni nanoparticles embedded in carbon films
c TEM image of CNFs
d HRTEM image of Cu nanoparticles on tips of CNFs

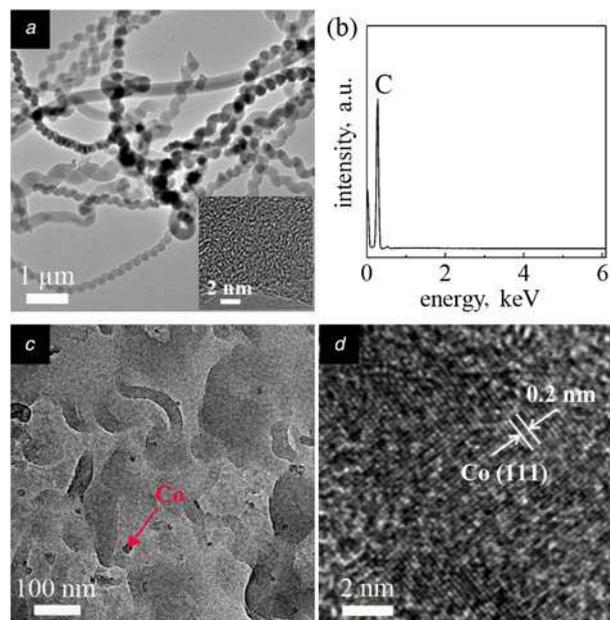


Fig. 5 Characterisation results of high-purity CNFs fabricated by using cobalt nitrates and carbon films after peeling process
a TEM image of high-purity CNFs. Inset: HRTEM image
b EDS spectrum of high-purity CNFs
c TEM image of carbon films
d HRTEM image of Co nanoparticles embedded in carbon films

It has been reported that growth of CNFs, which was catalysed by Cu nanoparticles, could follow tip-growth mechanism [4]. Hence, in order to highlight the important role of bottom-growth mechanism in the fabrication of high-purity CNFs, we replaced nickel nitrates by copper nitrates, and then performed the same CVD and peeling processes. As expected, the resultant CNFs

contained many Cu nanoparticles, and Cu nanoparticles were located on tips of the CNFs (Figs. 4c and d). This result evidences that Cu-catalysed growth of these CNFs was through tip-growth mechanism, and bottom-growth mechanism is crucial for the achievement of high-purity CNFs by using our approach.

In addition to nickel nitrates, we also obtained the high-purity CNFs via loading cobalt nitrates on Al foils, performing the similar CVD, and finally peeling the CNFs off. TEM image (Fig. 5a) shows that these CNFs have the similar morphology to those achieved by using nickel nitrates, and they also have a low crystallinity. EDS spectrum (Fig. 5b) verifies that these CNFs contain no Co elements, indicating high purity of these CNFs. Furthermore, TEM images (Figs. 5c and d) of carbon films deposited on Al surfaces reveal that Co nanoparticles are embedded in these carbon films. This indicates that Co-catalysed growth of CNFs was through bottom-growth mechanism [10], and high-purity CNFs were achieved by detaching CNFs from Co nanoparticles during the peeling process. In addition, this result also verifies the weak adhesion of CNFs to Co nanoparticles as well as the tight adhesion of Co nanoparticles to Al foils.

4. Conclusion: In summary, by utilising bottom-growth mechanism of CNFs and easy detachment of CNFs from underlying Ni or Co catalysts during the peeling process, we achieved facile and controlled fabrication of CNFs with high purity. To our knowledge, this is the first report on the synthesis of high-purity CNFs by using this approach, and this work may offer new opportunities for the low-cost, large-scale, and eco-friendly fabrication of high-purity carbon materials.

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6 References

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