Letter to the Editor

Synthesis of millimeter-long vertically aligned carbon nanotube arrays on aluminum oxide buffer prepared by layer-by-layer assembly of boehmite nanoplates

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ARTICLE INFO

ABSTRACT

To synthesize vertically aligned carbon nanotube (VA-CNT) arrays longer than a millimeter using chemical vapor deposition (CVD), aluminum oxide buffer has to be deposited on supporting substrates to prevent diffusion and aggregation of catalyst nanoparticles. Currently, reliable deposition has to be made using expensive and time-consuming e-beam evaporation or thermal sputtering. Here, we report a simple, low-cost, and scalable method for buffer preparation using layer-by-layer assembly of boehmite nanoplates followed by thermal annealing. On top of buffer prepared using this method, we have grown VA-CNT arrays consisting of CNTs with a length of 1.3($\pm$0.1) mm, an inner diameter of 5.6($\pm$1.3) nm, and a wall number of 4($\pm$1) by using CVD with iron as catalyst and ethylene as carbon source.

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Vertically aligned carbon nanotube (VA-CNT) arrays have attracted increasing attention as new materials for making field emission displays, microfluidic devices, gas sensors, electrochemical double layer capacitors, catalyst supports, and dry adhesives [1]. In addition to these direct applications, VA-CNT arrays are precursors for weaving CNTs into continuous sheets and fibers [2]. To synthesize millimeter-long VA-CNT arrays using chemical vapor deposition (CVD), a buffer layer of aluminum oxide (Al_2O_3) is often required to separate the supporting substrate and catalyst nanoparticles [3,4]. The aluminum oxide buffer suppresses the diffusion and aggregation of catalyst nanoparticles [5,6] and promotes the aromatization of carbon atoms during CNT growth [7]. The buffer is usually deposited on the substrate before catalyst deposition using physical techniques such as e-beam evaporation and

thermal sputtering [4]. Buffer layers deposited using low-cost wet chemistry-based methods such as sol–gel, spin coating, dip coating, and layer-by-layer (LBL) assembly have only produced VA-CNT arrays with length up to several hundred micrometers [8,9]. To develop large-scale applications of VA-CNT arrays more than a millimeter in length, a wet chemistry-based method of buffer deposition is in need.

In this letter, we report the growth of millimeter-long VA-CNT arrays on silicon chips coated with alumina buffer layers deposited using layer-by-layer (LBL) assembly of boehmite (γ-AlOOH) nanoplates. This method involves four steps, including (1) immersion of a piece of silicon chip in polyethyleneimine (PEI) solution, (2) immersion of the chip in polyacrylic acid (PAA) solution, (3) immersion of the chip in boehmite suspension, and (4) annealing the chip at

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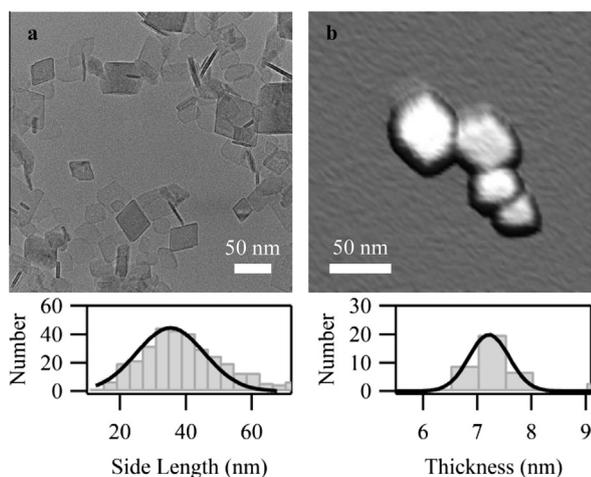 E-mail address: chongzheng.na@gmail.com (C. Na).

750 °C. Thickness of the buffer layer can be controlled by repeating LBL assembly (steps 2 and 3) before performing annealing (step 4). Conditions used in buffer preparation are described in detail in Supplementary Materials.
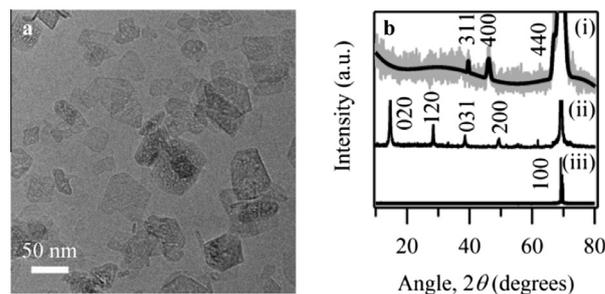
The key material of the new deposition method was the boehmite nanoplate. We synthesized boehmite nanoplates by hydrothermal transformation of aluminum isopropoxide (see Supplementary Materials) [10]. The nanoplates were deposited on a silicon chip by drop casting for microscopic examination before being used for LBL assembly. As shown in Fig. 1a, boehmite nanoplates were revealed as rhomboids by transmission electron microscopy (TEM). Based on measurements of 350 nanoplates, we estimated the average side length of the nanoplates to be 33.4 (±10.3) nm, as shown by the Gaussian fit of the length histogram underneath Fig. 1a. As shown in Fig. 1b, the thickness of nanoplates was measured using atomic force microscopy and estimated to be 7.0(±0.4) nm.

We annealed the nanoplates drop-cased on the silicon chip at 750 °C for 30 min to mimic the annealing step in the actual buffer preparation. As shown in Fig. 2a, the nanoplates became porous after annealing with mostly conserved shapes. Using powder X-ray diffraction (XRD), the porous nanoplates were identified as face-centered cubic γ-Al$_2$O$_3$, which had a XRD pattern different from both orthorhombic boehmite and the silicon chip, as shown in Fig. 2b.

For growing VA-CNT arrays, we deposited boehmite nanoplates on a silicon chip using LBL assembly and then transformed boehmite to γ-Al$_2$O$_3$ by annealing. A typical γ-Al$_2$O$_3$ coated silicon chip was visualized using scanning electron microscopy (SEM), as shown in Fig. 3a from top and side views (figure and inset, respectively). The entire chip surface was covered by γ-Al$_2$O$_3$ nanoplates. From the side view, we measured the thickness of the γ-Al$_2$O$_3$ buffer layer, which was correlated to the number of assembly cycles, as illustrated in Fig. 3b. A linear regression gave an estimate of the thickness per assembly cycle to be 19(±3) nm or approximately 3 times the thickness of boehmite nanoplates.
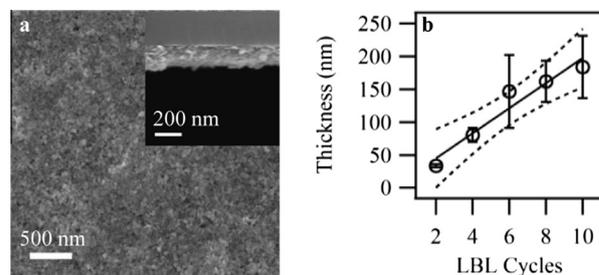

Fig. 2 – Morphology and crystalline structure of annealed boehmite nanoplates. (a) Transmission electron micrograph of annealed nanoplates obtained after removing them by sonication from the supporting silicon chip and depositing them on a copper grid. (b) Powder X-ray diffraction pattern of (i) annealed nanoplates as γ-Al$_2$O$_3$, (ii) original boehmite nanoplates as γ-AlOOH, and (iii) the bare silicon chip.

To grow millimeter-long VA-CNT arrays, we further deposited magnetite (Fe$_3$O$_4$) nanoparticles [11] on the γ-Al$_2$O$_3$ buffer layer (see Supplementary Materials for details). After the chip was annealed again at 750 °C to remove any remaining organic molecules from LBL assembly, VA-CNT arrays were grown in a quartz tubing using ethylene as carbon source and the mixture of hydrogen and argon (1:1) as carrier gases. Hydrogen reduced magnetite nanoparticles to iron nanoparticles, which were excellent catalysts for CNT growth by CVD.

A dense VA-CNT array grown on the γ-Al$_2$O$_3$ buffer is shown with an overall view in Fig. 4a with a close view in Fig. 4b. Interestingly, we found that the length of the VA-CNT array did not vary significantly with the thickness of the γ-Al$_2$O$_3$ buffer layer, as shown in Fig. 4c. Using buffer layers of less than 200 nm thick, we were able to grow VA-CNTs with a length of 1.3(±0.1) mm long. In comparison to buffer-separated magnetite nanoparticles that catalyzed the growth of VA-CNT arrays, magnetite nanoparticles deposited directly on a silicon chip without buffer produced sparse growth of carbon nanotubes, as shown in Fig. 4d.

We further examined the morphology of individual CNTs using TEM after removing them from VA-CNT arrays by sonication. As shown in Fig. 5a and inset, individual CNTs were

Fig. 1 – Morphology and size of boehmite nanoplates. (a) Transmission electron micrograph of boehmite nanoplates deposited on a copper grid with a side-length histogram. (b) 3-D atomic force micrograph of boehmite nanoplates drop-casted on a silicon chip and a thickness histogram. Solid curves are Gaussian fits.
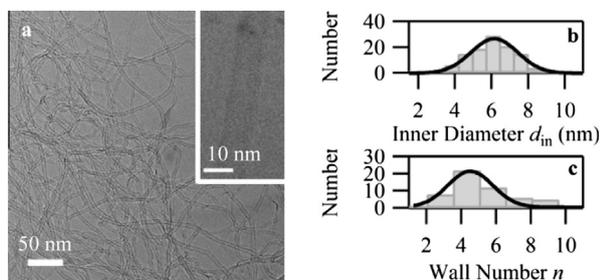

Fig. 3 – Aluminum oxide buffer layer formed on a silicon chip by layer-by-layer (LBL) assembly of boehmite and annealing. (a, b) Top and side views of γ-Al$_2$O$_3$ coated chip under scanning electron microscope. (c) Linear correlation between buffer thickness and number of LBL cycles. The dotted curves bracket 95% confidence intervals of the linear regression shown as the solid line.
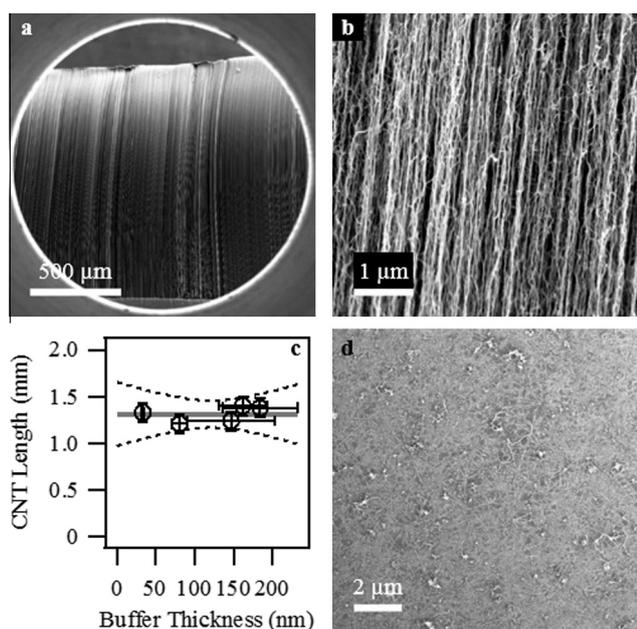
Fig. 4 – Vertically aligned carbon nanotube arrays grown on aluminum oxide buffer prepared using boehmite nanoplates. (a, b) Side views of an array under scanning electron microscope at different scales. (c) Invariance of nanotube length with buffer thickness. (d) Carbon nanotubes grown without buffer.

observed as uniform nanotubes. Base on measurements made on individual CNTs, we estimated that they had an average inner diameter of $d_{in} = 5.6(\pm1.3)$ nm and an average wall number of $n = 3.8(\pm1.3)$. Considering each graphene layer in CNTs has a thickness of approximately $\delta = 0.334$ nm, we further estimated the outer diameter of CNTs to be $d_{out} = d_{in} + 2\delta n = 8.1(\pm1.6)$ nm.

In summary, the synthesis of millimeter-long VA-CNT arrays was made possible by creating γ-Al_2O_3 buffer on silicon chips using LBL assembly of boehmite nanoplates and annealing. The length of VA-CNT arrays was shown to be insensitive to buffer thickness, which could greatly simplify the quality control of buffer deposition. In comparison, buffer thickness often needs to be painstakingly controlled when physical methods such as e-beam evaporation and thermal

sputtering are used (see Supplementary Materials). Furthermore, the LBL assembly of premade boehmite nanoplates is a wet chemistry-based method that is relatively easy to be scaled up.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.09.034.

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Fig. 5 – Individual carbon nanotubes removed from vertically aligned carbon nanotube arrays. (a) Transmission electron micrograph of removed nanotubes (inset: image at high resolution). (b, c) Statistical analyses of nanotube inner diameter and wall number. Solid curves are Gaussian fits.