Chemical Bath Deposition of Aluminum Oxide Buffer on Curved Surfaces for Growing Aligned Carbon Nanotube Arrays

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ABSTRACT: Direct growth of vertically aligned carbon nanotube (CNT) arrays on substrates requires the deposition of an aluminum oxide buffer (AOB) layer to prevent the diffusion and coalescence of catalyst nanoparticles. Although AOB layers can be readily created on flat substrates using a variety of physical and chemical methods, the preparation of AOB layers on substrates with highly curved surfaces remains challenging. Here, we report a new solution-based method for preparing uniform layers of AOB on highly curved surfaces by the chemical bath deposition of basic aluminum sulfate and annealing. We show that the thickness of AOB layer can be increased by extending the immersion time of a substrate in the chemical bath, following the classical Johnson–Mehl–Arram–Kolmogorov crystallization kinetics. The increase of AOB thickness in turn leads to the increase of CNT length and the reduction of CNT curviness. Using this method, we have successfully synthesized dense aligned CNT arrays of micrometers in length on substrates with highly curved surfaces including glass fibers, stainless steel mesh, and porous ceramic foam.

1. INTRODUCTION

Multiwalled carbon nanotubes (CNTs) made of concentric rolls of graphene sheets often have diameters in the order of nanometers but can grow up to centimeters in length. The quasi-one-dimensional structure gives CNTs remarkable electrical conductivity,2–4 heat conductivity,5,6 and tensile strength,7,8 as well as a high surface-to-volume ratio,9,10 making them excellent anisotropic materials for manufacturing microelectronics, reinforcing polymers, and supporting nanocatalysts.11–13 In these applications and devices, a large number of CNTs are often used together to create complex macroscopic structures. To preserve anisotropy during scale-up, individual CNTs can be aligned along their longitudinal directions, forming CNT arrays. Previously, aligned CNT arrays have been synthesized on relatively flat substrates using thermal chemical vapor deposition (CVD).14,15 One of the standard methods for large-scale CNT production15,16

Compared to flat substrates, synthesizing CNT arrays on fibers, meshes, and foams that have highly curved surfaces is still challenging. A main technical hurdle is how to create an even layer of aluminum oxide buffer (AOB, γ-Al2O3) before growing CNT arrays using CVD. A buffer layer is a required component of the CVD operation, in which CNTs grow from metallic catalyst nanoparticles at high temperatures (usually 600–800 °C) at the expense of a hydrocarbon compound.17 Without the buffer layer, catalyst nanoparticles would coalesce with one another or diffuse into the substrate at the high temperatures in CVD, leading to rapid deactivation of the catalyst and cessation of CNT growth.17–20 A variety of materials have been investigated as buffer, including aluminum oxide (Al2O3), titanium nitride (TiN), titanium dioxide (TiO2), calcite (CaCO3), and silicon dioxide (SiO2);21–23 among which, γ-Al2O3 is often considered as the most effective buffer material for growing CNT arrays.24

For flat substrates with fully open and accessible surfaces, AOB can be prepared by both physical and chemical methods, including atomic layer deposition (ALD), electron beam physical vapor deposition (a.k.a. e-beam evaporation), thermal evaporation, spin coating, dip coating, the sol–gel process, and the layer-by-layer (LBL) assembly.25–39 When the substrates have spatially complex structures such as highly curved surfaces, particularly those hidden in torturous pores, the creation of a uniform AOB layer to support the growth of CNT arrays is no longer feasible by using most of the existing methods. To our knowledge, aligned CNT arrays have only been synthesized on highly curved surfaces either treated using the expensive ALD method40,41 or with preexisting oxide coatings that can act as buffer, for example, ceramic fibers made of aluminum oxide42,43 and stainless steel with chromium oxide.44,45

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Here, we report a general and facile method for preparing AOB on substrates with highly curved surfaces for growing CNT arrays using CVD. We show that after a substrate is immersed in a chemical bath containing aluminum sulfate (Al₂(SO₄)₃) and sodium bicarbonate (NaHCO₃), a thin layer of AOB can be formed after annealing. The thickness of the AOB layer can be controlled by adjusting the immersion time, thereby allowing the process to be optimized for efficiency. Using silicon chip, glass fiber, stainless steel mesh, and ceramic foam as model substrates, we further show that aligned CNT arrays up to hundreds of micrometers in length can be readily synthesized using conventional CVD after the substrates are treated by this chemical bath deposition (CBD) method. The key feature of CBD is the controlled crystallization of basic aluminum sulfate (BAS; Al₃(H₂O)(SO₄)₂(OH)₆), which has previously been used to synthesize aluminum oxide and oxyhydroxide particles.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods

All chemicals were of analytical grade and purchased from Sigma-Aldrich. Deionized (DI) water was generated on site using a Millipore system. Glass fibers (diameter: 4 μm), stainless steel mesh (AISI 304; 400 × 400 openings per square inch), and porous cordierite (Mg,Fe)₂Al₃(Si₅AlO₁₈) monolith arrays (14 openings per square inch) were purchased from Technical Glass (Painesville Twp., OH), Grainger (Lake Forest, IL), and Gaoke Ceramic Co. LTD (Jiangxi, China), respectively.

The chemical bath solution was prepared by dissolving sodium bicarbonate powder in a saturated aqueous solution of aluminum sulfate. Once all NaHCO₃ is dissolved, DI water was immediately added to increase the solution pH to 3.8. The solution was filtered through a 0.22 μm filter to remove any residual powder. The filtered solution was transparent with a pH of 3.8, which has previously been used to synthesize aluminum oxide and oxyhydroxide particles.

2.2. Synthesis of Aligned Carbon Nanotube Arrays

To grow CNTs, the magnetite-coated substrate was placed in a quartz boat at the center of a 2-in. quartz tubing, which was housed in a tube furnace. The furnace was ramped to 750 °C in the flow of 500 scm argon. Once the temperature reached 750 °C, 100 sccm hydrogen was introduced to transform iron oxide nanoparticles to metallic iron catalysts. The growth of CNTs was initiated by introducing 100 sccm ethylene. A trace amount of water vapor was added to the reactor by bubbling a small amount of argon through a water tank. After 5 min of growth, the furnace was cooled to the ambient temperature under argon protection.

The morphology and quality of AOB layer and CNT arrays were examined using scanning electron microscopy (SEM; FEI Magellan 400), transmission electron microscopy (TEM; FEI 80–300 at 300 kV), atomic force microscopy (AFM; Park System XE-70), powder X-ray diffraction (XRD; Advance 8 at 40.0 kV and 120 mA with Cu Kα radiation), Raman spectroscopy (Renishaw RM2000 with He–Ne laser excitation line 532 nm), and ellipsometry (Gaertner Scientific). Sample preparation and data interpretation were performed following standard protocols.

3. RESULTS

We synthesize aligned carbon nanotube arrays on highly curved surfaces using a method involving three main steps as illustrated in Figure 1. The first step is the chemical bath deposition of basic aluminum sulfate. This step is carried out by immersing a substrate in an acidic solution of aluminum sulfate and sodium bicarbonate for at least 15 min. In this process, BAS crystallizes into a thin film on the surface of the substrate:

$$3\text{Al}_2\text{SO}_4\text{H}_2\text{O} + 10\text{NaHCO}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O}\text{Al}_3\text{Si}_2\text{O}_5\text{(OH)}_4 + \text{Na}_2\text{SO}_4 + 10\text{CO}_2$$

Second, BAS is converted to γ-Al₂O₃ by annealing at 750 °C for 1 h, releasing sulfur trioxide gas and water vapor:

$$2\text{Al}_2\text{(H}_2\text{O})\text{SO}_4\text{H}_2\text{O} \rightarrow 3\text{Al}_2\text{O}_3 + 4\text{SO}_3 + 9\text{H}_2\text{O}$$

Last, the substrate is further decorated with magnetite nanoparticles, which are reduced to iron nanoparticles by hydrogen in CVD and catalyze CNT growth in the presence of ethylene. The first two steps together produce the aluminum oxide buffer layer, which is the focus of this study. The catalyzed growth of CNTs using magnetite nanoparticles and CVD is a well-established technique; therefore, the third step is performed under preset standard conditions. In the remainder of this article, we describe our investigation on the mechanism and control of γ-Al₂O₃ formation and the quality of the subsequently grown CNT arrays.

Before applying the CBD-annealing method to fibers, meshes, and foams, we first use a flat silicon chip to validate...
the deposition mechanism. Figure 2a−c compares the silicon chip before BAS deposition, after BAS deposition for 1.5 h, and after annealing, respectively, using atomic force microscopy. The AFM images show that a film of nanoparticles is formed on the top of the chip’s surface after the chip has been immersed in the chemical bath, consistent with the polycrystalline nature of BAS deposition.47 According to the height of the nanoparticles, the deposition of nanoparticles increases the root-mean-square (RMS) roughness of the surface from 0.5 to 2 nm. After annealing, the nanoparticles shrink with a reduction of RMS roughness from 2 to 1.4 nm, suggesting the formation of γ-Al2O3 by dehydration. The structural identities of BAS and γ-Al2O3 are provided by powder X-ray diffraction, as shown in Figure 2d along with the spectrum of the silicon chip. BAS and γ-Al2O3 show distinctly different diffraction patterns from their unique rhombohedral48 and cubic49 phases, as illustrated in Figure 2f and g, respectively.

Figure 3 shows an aligned CNT array grown on the AOB-coated silicon chip after being immersed in the chemical bath for 1.5 h. Scanning electron microscopy reveals that the CNT array grows vertically and uniformly, forming a dense forest (Figure 3a). Microscopically, individual CNTs are curled into a repeating wave with an array length of 1 on the order of 100 nm (Figure 3b). A curviness index is defined to characterize this morphology: ϕ = l_S / l, where l_S is the true length of the CNT. For perfectly straight nanotubes, we would expect ϕ = 1. For the sample shown in Figure 3b, we estimate ϕ = 1.17(±0.05), suggesting that CNTs are relatively straight. Although aligned CNT arrays grown on substrates have excellent mechanical strength, a few CNTs can be removed by extended sonication for an hour, permitting the examination of the quality of individual CNTs using transmission electron microscopy.45 Little amorphous carbon deposit is visible under TEM (Figure 3c), suggesting that the conversion of ethylene to CNT is highly efficient. High-resolution TEM reveals that CNTs have uniform diameters with a relatively narrow size distribution around 9.4(±1.9) nm and an average wall number of 4.6(±1.7) (insets of Figure 3c). Raman spectroscopy shows that CNTs have a high degree of graphitization with an in-plane graphene crystallite size Lg of 10.7 nm, as estimated using the empirical equation Lg = 8.28(Ic/I_D) with Ic/I_D = 1.3 (Figure 3d).50

The critical parameter controlling the outcome of AOB preparation and thus the quality of CNT array is the time for a substrate to be immersed in the chemical bath. To maximize the length of aligned CNT arrays, we vary the immersion time t from 15 min to 3 h and examine AOB thickness τ.
of CNT arrays, and curviness index $\varphi$. The correlations of these parameters are shown in Figure 4. As $t$ is extended, $\tau$ increases exponentially (Figure 4a). The two parameters show a relationship conforming to the classical Johnson–Mehl–Avrami–Kolmogorov rate law:51–53

$$\tau = \tau_0[1 - \exp(-kt^n)]$$ (3)

where $\tau_0$ is the maximal thickness of AOB that the chemical bath can create, $k$ is the rate constant of BAS deposition, $n$ is a dimensional parameter. Least-squares regression gives $\tau_0 = 211(\pm13)$ nm, $k = 0.063(\pm0.031)$ h$^{-1}$, and $n = 1.9(\pm0.6)$ ($R^2 = 0.96$). The estimate of $k$ is consistent with the crystallization process sufficiently slow to produce an even layer of BAS. The estimate of $n \approx 2$ is consistent with the fact that the crystallization of BAS on a surface is a two-dimensional nucleation process.

As the AOB thickness increases, the length and curviness of CNT arrays vary systematically, as shown in Figure 4b,c. $l$ increases exponentially with $\tau$, giving a maximum length of $l_{\text{max}} = 333(\pm15)$ nm. In comparison, $\varphi$ decreases exponentially with $\tau$, giving a minimal value of $\varphi_{\text{min}} = 1.14(\pm0.01)$. The correlations of $l$ and $\varphi$ with $\tau$ indicate that increasing the thickness of AOB layer promotes the growth of longer and straighter CNTs. At this length, CNTs are split into two arrays, with one on each side of the supporting substrate, CNTs grow perpendicular to the conventional CVD. When glass fibers are used as the supporting substrate, CNTs grow perpendicular to the fiber length and in the radial direction (Figure 5a). After 1.5 h of CVD growth, the length of CNTs can reach 100 $\mu$m, approximately 25 times the diameter of the glass fiber support. At this length, CNTs are split into two arrays, with one on each side of the fiber and consisting of approximately half of the total amount of CNTs. Similar to CNTs grown on the silicon chip, the arrays on glass fibers are formed by a high density of well-aligned CNTs (Figure 5b). CNTs grown on an AOB-coated stainless steel mesh are split in 4 arrays, each pointing to an orthogonal direction around a stainless steel wire (Figure 5c,d). The mesh-supported CNTs are only ca. 30 $\mu$m, which is

Figure 4. Optimization of chemical bath deposition (CBD) immersion time for growing aligned carbon nanotube (CNT) arrays. (a) Increase of aluminum oxide buffer (AOB) thickness $\tau$ with increasing of immersion time $t$. (b) Asymptotic increase of CNT array length $l$ with $\tau$. (c) Asymptotic decrease of CNTs’ curviness index $\varphi$ with $\tau$. (d) Invariance of CNT diameter $\phi$ with $\tau$. Fit functions: a, eq 1; b and c, exponential ($l = 333[1 - 2.6 \exp(-0.13t)]$, $\varphi = 1.2[1 + \exp(-0.15t)]$, $R^2 = 0.98$); d, average ($\tau = 9.2(\pm0.2)$ nm).

Figure 5. Scanning electron micrographs of vertically aligned carbon nanotube (CNT) arrays grown on (a, b) glass fibers (GFs), (c, d) stainless steel mesh (SSM), and (e, f) porous corderite monolith (PCM), all of which are coated with aluminum oxide films using the chemical bath deposition method. Insets in a, c, and e are GFs, SSM, and PCM before the CNT growth. Scale bars: a, 200 $\mu$m; b, 20 $\mu$m; c, 200 $\mu$m; d, 20 $\mu$m; e, 500 $\mu$m; inset of e, 500 nm; f, 5 $\mu$m. Time for chemical bath deposition: 1.5 h (resulting buffer thickness, ca. 35 nm).
approximately half the size of the mesh openings. Compared to glass fiber and stainless steel mesh, CNT arrays grown on a ceramic foam have much reduced long-range organization. The arrays form localized patches of ca. 50 μm in size (Figure 5e). Accompanied with the lack of organization is the reduced length of CNTs, which are only 5 μm long (Figure 5f). The differences in CNT length and morphology suggests that the underlying substrate, in addition to the coated AOB layer, exerts significant controls over CNT growth, which requires investigation in future studies. In spite of the differences, however, the new CBD-annealing method is successful to facilitate the growth of micrometer-long CNT arrays on these substrates with highly curved surfaces, particularly permitting the growth of CNT arrays on porous substrates for the first time without using expensive atomic layer deposition.

4. DISCUSSION

The successful growth of CNT arrays on glass fiber, stainless steel mesh, and ceramic foam relies on the chemical bath deposition of basic aluminum sulfate, which is converted to aluminum oxide buffer upon annealing. Compared to existing AOB preparation methods, CBD succeeds in preparing AOB on these structurally challenging substrates because it uses the in situ crystallization of BAS as the mechanism for delivering the AOB precursor. In this section, we discuss the rationale for the design of the CBD-annealing method as well as the possible mechanisms responsible for the formation and morphology of the CNT arrays grown on substrates that have been treated using this method.

4.1. Chemical Bath Deposition. To understand the importance of the in situ crystallization of BAS in the design of the CBD-annealing method, we first summarize the mechanisms for delivering AOB and its precursors used by existing methods. In e-beam evaporation, metallic aluminum or aluminum oxide is evaporated under the bombardment of a beam of high-energy electrons under vacuum. The metal and oxide vapors are then delivered to the surface of a substrate by electrostatic attraction, which requires a straight and clear pathway between the source and the surface and thus is not suitable for substrates with highly curved surfaces and particularly those with surfaces hidden in tortuous pores. In thermal evaporation, the vapor is generated by heating a solid source while the substrate is placed underneath the source to receive the vapor through diffusion. The amount of material deposited at a specific location on the surface is proportional to its distance to the source, which is variable for a substrate with highly curved surfaces.

Compared to physical methods such as e-beam and thermal evaporation, solution-based chemical methods operated under the ambient pressure always involve two steps, including the formation of a layer of AOB precursor and the conversion of the precursor to AOB by annealing. Spin coating and dip coating use the aqueous solution of aluminum hydroxide (Al(OH)₃) as precursor. The solution is delivered by either casting or immersion, which do not require a clear pathway to the substrate. However, because the substrate must be separated from the solution before annealing can be performed, a delicate balance between gravity and capillarity is required to maintain an even distribution of the adsorbed solution once the substrate is removed from the solution in order to form an even AOB layer. When the surface is curved, gravity acts on the solution differently at different parts of the surface, leading to the redistribution of precursor solution and thus an uneven AOB layer after annealing.

Different from spinning and dip coating methods that coat substrates with aluminum hydroxide solution before annealing, sol–gel and layer-by-layer assembly use solid precursors. The sol–gel process uses γ-AlOOH (boehmite) nanoparticles as the AOB precursor. Typically, the oxyhydroxide gel is first created by the hydrolysis of aluminum alkoxides and then delivered by immersing a substrate into the gel. Similar to dip coating using solution, the imbalance between gravity and capillarity on highly curved surfaces can cause an uneven distribution of the precursor gel before annealing is complete. To prevent the potential interference of gravity, the layer-by-layer assembly method attaches premade γ-AlOOH nanodisks on substrates using organic linkers. However, the use of premed nanodisks of tens of nanometers in diameter can lead to cracks in the AOB layer deposited on highly curved surfaces upon annealing. In addition, both gels and suspensions containing γ-AlOOH nanoparticles and nanodisks are difficult to pass through tortuous pores.

The only chemical method that is sufficiently versatile to deposit oxide coatings on fibers and foams is atomic layer deposition. In this method, the substrate is placed in a vacuum chamber and alternately exposed to trimethylaluminum (Al₃(CH₃)₃) and water vapor. The alternating process allows trimethylaluminum first absorbs on the substrate surface and then transforms to aluminum oxide in situ by reacting with water. In spite of the success of ALD, the requirement of vacuum limits its potential for scale-up and the use of pyrophoric trimethylaluminum poses safety concerns.

The analyses of the existing AOB preparation methods suggest that a solution-based chemical method is economically and operationally attractive if an AOB precursor can be deposited on curved surfaces by an in situ reaction similar to that in ALD, through which the precursor is firmly attached to the surface while the substrate is still immersed in the precursor solution. Previous studies of AOB precursors have been mostly focused on aluminum (oxy)hydroxide compounds; however, the chemistry of aluminum (oxy)hydroxide is complicated by the formation of stable Keggin cations. Attempts to precipitate aluminum (oxy)hydroxide from an hydroxide solution often end up either in failure or without kinetic control.

A successful deposition of a new AOB precursor can be rationally designed by reconsidering the balancing anion used to initiate precursor crystallization. Because polyaluminum cations are positively charged, a balancing anion is required to facilitate its crystallization from a stable aqueous solution. Recent studies have established that sulfate is an effective balancing anion for crystallizing polyaluminum cations, possibly due to both its divalence according to the Schultz-Hardy rule and the unique size of the anion. Sulfate has been extensively used in both scientific experiments such as the crystallization of Keggin structures as well as engineering applications such as the promotion of coagulation in water treatment. BAS is also well recognized as an important intermediate for preparing aluminum oxide particles with controllable sizes and morphologies. The chemistry of BAS crystallization has not been utilized to create AOB surface coatings until now.

4.2. Length and Curviness of CNTs. In the process of creating AOB by CBD and annealing, we have identified the time that a substrate is immersed in the chemical bath as an important parameter for controlling AOB thickness and thus
the length and curviness of CNT arrays. The positive correlation of AOB thickness and immersion time can be readily understood since the amount of BAS deposition increases with time. The mechanisms through which AOB thickness regulates the length and curviness of CNTs are less obvious. Here, we discuss them in detail with the aid of two physical models.

The growth of CNTs by chemical vapor deposition is a catalyzed process. As illustrated in Figure 6a, ethylene reacts at the surface of iron nanoparticles to provide carbon precursor(s), which dissolves into the melted nanoparticles. The continuous supply of precursor(s) creates supersaturation in the liquid nanoparticles, resulting in the continuous growth of crystalline carbon in the form of multiwalled CNTs. The rate of CNT growth is regulated by the rate of precursor formation at the nanoparticle surface, which is proportional to the area of exposed nanoparticle surface. The surface area of catalyst nanoparticles can be reduced by the diffusion of iron through AOB into the substrate and the coalescence of nanoparticles. As shown in Figure 6b, increasing AOB thickness can greatly reduce the loss of iron by diffusion. As shown in Figure 6c, increasing AOB thickness can also increase its surface roughness (error bars in Figure 4a; cf. Figure S1 in the Supporting Information) and thus the barrier for coalescence.61

Eventually, an AOB layer sufficiently thick and rough can prevent diffusion and coalescence nearly completely, leaving most of the catalyst surface exposed. As a result, the growth rate of CNT reaches a maximum value. Both the increase of CNT growth rate with increasing AOB thickness and its eventual stabilization are observed in our experiments, as shown in Figure 4b. The minimum immersion time required to reach stabilization of 1.5 h is selected in our experiments to prepare glass fibers, stainless steel mesh, and ceramic foam.

The formation of curviness in CNT arrays is believed to be a result of the attraction exerted by neighboring nanotubes although the detailed mechanism remains to be clarified.42,43 Here, we propose a four-step mechanism based on this idea. As illustrated in Figure 7, the initial growth of a nanotube from a catalyst nanoparticle can be considered to be straight until the top of the nanotube touches a neighboring nanotube due to inter-CNT attraction or the tilt of underlying surface (Figure 7a). The attraction exerted by van der Waals force and π–π interaction42,43 from the neighboring nanotube creates frictional resistance in the vertical direction. As a result, the top of the nanotube is pinned in place. Further growth of CNTs produces a new stretch of nanotube, which has to be accommodated by bending (Figure 7b). The bending of CNT generates an elastic force, pushing upward against frictional resistance, which eventually allows the newly grown CNTs slide through the pinning point (Figure 7c). Once passing through the pinning point, the extension of CNTs follows an angle heading toward another neighboring nanotube on the opposite side (Figure 7d). Repeating these steps will create wave-like curviness, as shown in Figure 3b.

According to the model depicted in Figure 7d, the curviness index, defined as the ratio of the length of individual CNTs to the length of CNT array, can be computed using parameters within half of a wave cycle. Here, \( \varphi = 2l_s/l_a \) where \( l_s \) is the amplitude and \( l_a \) is half of the wavelength. The scaling factor 2 is obtained by approximating the length of curvy CNTs using the sinusoidal function. In this equation, \( l_s \) is approximately the distance between catalyst nanoparticles, which is controlled by their surface density; therefore, \( l_s \) is constant in our experiments. \( l_a \) is a function of CNT growth rate, which increases with the increase of AOB thickness. As a result, \( \varphi \) decreases as \( l_a \) increases, as observed in Figure 4c.

4.3. Splitting of CNT Arrays. The splitting of CNT arrays into six groups has been reported previously for spherical substrates, each pointing to one of the six orthogonal directions in three-dimensional Cartesian coordinate system.64,65 This is consistent with the splitting of CNT arrays into 4 orthogonal groups on the wires of stainless steel mesh, as shown in Figure 5c,d, which may be considered as two-dimensional cylindrical substrates. The splitting of CNT arrays is likely a result of balancing inter-CNT attraction and the resistance originated from CNT’s rigidity.66 In the absence of inter-CNT attraction, the growth of CNTs should follow the radial directions around a cylindrical substrate, as shown in Figure 8a. For relatively short CNTs, we have neglected the influence of gravity by considering CNTs are rigid nanotubes. When inter-CNT attraction is considered, CNTs will group with close neighbors. The splitting into 4 groups produces the least stress for CNTs at the outer boundaries of each group, as shown in Figure 8b. The increase of CNT length permits longer deflection under the same rigidity, leading to bundling of CNTs from different
groups. As shown in Figure 5a and 8c, only two groups exist for the long CNT arrays grown on glass fibers. The relationship between CNT length and the number of array groups on fibers has been investigated previously by other researchers.\textsuperscript{43}

5. CONCLUSIONS

We have successfully created AOB layers on structurally challenging substrates using chemical bath deposition of basic aluminum sulfate and annealing. The CBD-annealing method can provide new opportunities for growing aligned CNT arrays on substrates with curved surfaces such as fibers, meshes, and foams. These substrates are important materials used to strengthen structures, build electronic devices, and support catalyst nanoparticles.\textsuperscript{67−69} Although these materials have relatively large geometric surface areas, even greater surface areas are preferred to improve physical contact, facilitate electron collection, and increase catalyst loading.\textsuperscript{70,71} Conductive CNTs with high specific surface areas are ideal materials for adding surface areas to engineering materials without adding much weight. CNTs can also provide the engineering materials with new functionalities with their excellent electronic, absorptive, and mechanical properties.\textsuperscript{72−74} CNT arrays grown on stainless steel mesh and ceramic foam have already been investigated as advanced electrodes, filters, and catalyst supports.\textsuperscript{44,45,70,75} Further understanding of the formation, property, and morphology of CNT arrays grown on these substrates may lead to new insights for better incorporating CNTs into hierarchical and composite structures used in future applications.

In addition to preparing substrates for CNT growth, the aluminum oxide layer created by CBD and annealing can be directly used as the corrosion resistance barrier for alloys,\textsuperscript{76,77} the electrical insulator in microelectronics,\textsuperscript{78,79} and the passivation layer for organic electronic devices and solar cells.\textsuperscript{80,81} Traditionally, aluminum oxide layers for corrosion protection are created by dip coating where the control of thickness is not stringent.\textsuperscript{76} Similar to the case of CNT growth, the use of BAS-CBD may greatly simplify the coating process for substrates with curved surfaces. The creation of pinhole-free aluminum oxide layers with a thickness of a few nanometers requires the use of the expensive atomic layer deposition. The new BAS-CBD method may provide a cost-effective alternative for electronic applications.

- **ASSOCIATED CONTENT**

  - **Supporting Information**

    Figure S1: Increase of surface roughness with the increase of the thickness of aluminum oxide buffer layer. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b01002.

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