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New nanotube synthesis strategy – application of sodium nanotubes formed inside anodic aluminium oxide as a reactive template

Lung-Shen Wang,[a] Chi-Young Lee*[b] and Hsin-Tien Chiu*[a]
[a] *Department of Applied Chemistry, National Chiao Tung University Hsinchu, Taiwan, 30050 (R. O. C.). E-mail: htchiu@cc.nctu.edu.tw; Fax: 886-3-5723764; Tel: 886-3-5731514*
[b] *Materials Science Center, National Tsing Hua University Hsinchu, Taiwan, 30043 (R. O. C.)*

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Formation of Na nanotubes inside the channels of anodic aluminium oxide (AAO) membranes has been achieved by decomposing NaH thermally on AAO. The as-produced material, Na@AAO, is applied as a reactive template to prepare other tubular materials. Reacting Na@AAO with gaseous C_6Cl_6 generates carbon nanotubes (*ca.* 250 nm, wall thickness of 20 nm, tube length of 60 μm) inside the AAO channels. Highly aligned bundles of nearly amorphous carbon nanotubes are isolated after AAO is removed.

Template assisted synthesis of materials with one dimensional (1D) structure has attracted much attention.[1] Anodic aluminium oxide (AAO) membranes are used frequently to aid the formation of such structures inside their straight, cylindrical and uniformly sized high density channels. Many substances have been fabricated into 1D nanomaterials in the form of wires, rods and tubes employing this strategy.[1,2] In these cases, the templates usually play a passive role. While they assist the formation of nanoshapes, they are not consumed in the reactions. On the other hand, we may inquire whether it is possible to influence the physical shape of a solid product by a material functioning both as template and reactant. After searching the literature, we could only find limited examples supporting this concept.[3] This encouraged us to explore a common reagent which can serve as a "reactive template", which not only performs as a reagent but also assists shaping the product into a designed nanostructure. Here, we wish to demonstrate a simple new method to prepare Na nanotubes inside AAO (Na@AAO) and to employ it as a reactive template to produce carbon nanotubes.

NaH was placed on a piece of AAO and decomposed at 623 K to generate an air-sensitive silvery plate.† The plate turned white when it was left in air for 1 h. A scanning electron microscopic (SEM) image of the as-synthesized product, after brief exposure to air during handling, is shown in Fig. 1.‡ The averaged channel pore diameter, 250 nm, is close to the supplier's specification, 200 nm. Although energy dispersive spectroscopy (EDS) cannot resolve elemental distribution within the displayed structure precisely,[4] it shows that Na spreads uniformly inside the straight AAO channels. The Na content on the channel walls, estimated from the EDS data, is higher than that within the AAO skeleton. Based on the above information, we conclude that Na covers the AAO channels as straight tubes with a uniform size, 60 μm in length (the thickness of AAO) and 250 nm in diameter. Using NaH as the source of Na was the key step to produce Na@AAO. We attempted to form Na@AAO by melting a piece of bulk Na metal on top of an AAO but without success. This might be due to the strong cohesive force within the liquid Na, which prevented it from flowing into the nanosized AAO channels. On the other hand, decomposing NaH thermally, tiny Na particles probably formed and flowed into the AAO channels to produce Na@AAO, as summarized in Scheme 1.

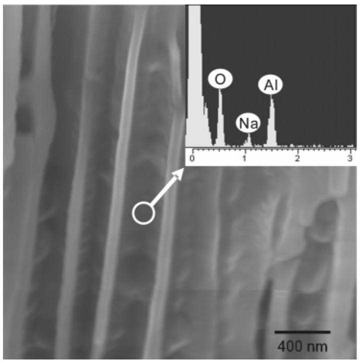
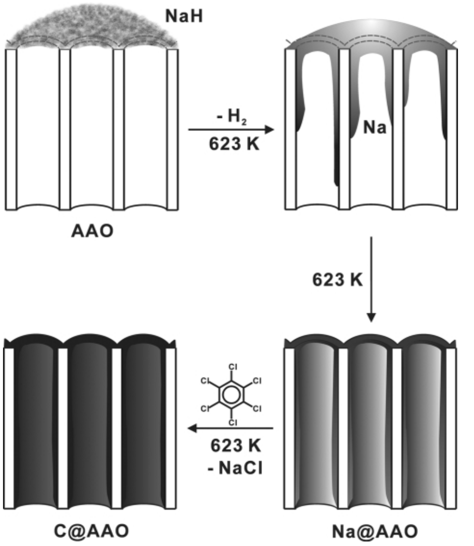


Fig. 1 Cross-sectional SEM image of Na@AAO after brief exposure to air. The inset shows EDS of elemental distribution inside a channel.



Scheme 1 Reaction steps to form Na@AAO and C@AAO.

To examine the reactive template strategy, we performed the following experiment. A piece of Na@AAO was reacted with the vapor of hexachlorobenzene (C_6Cl_6) at 623 K for 20 h in a tube furnace.§ A black solid disk with the original shape of the AAO plate was obtained. NaCl was formed as a by-product and vaporized during a high temperature treatment (1073 K) under vacuum. The salt could be washed away by an aqueous solution also. In Fig. 2a, the isolated product, open-ended nanotubes

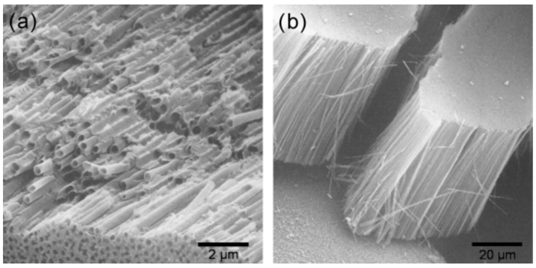


Fig. 2 (a) Cross-sectional view of carbon nanotube arrays inside AAO channels. (b) Bundles of carbon nanotubes after removal of AAO by 48% HF.

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grown inside the AAO channels, is shown. The diameter of the tubes is *ca*. 250 nm, the same as the channel diameter of Na@AAO shown in Fig. 1. After the AAO was removed by a HF solution, bundles of highly aligned nanotubes (*ca*. 60 µm in length) were isolated (Fig. 2b). EDS study identified that the tubes were composed nearly quantitatively of carbon. From transmission electron microscopic (TEM) studies, the diameter of the tubes is confirmed, as shown in Fig. 3a, to be *ca*. 250 nm.¶ By varying the channel pore diameter of the AAO employed, the diameter of the carbon nanotubes (CNT) can be altered accordingly. The wall thickness is found to be *ca*. 20 nm as shown in Fig. 3b. The image shows that the wall is yet to be fully graphitized, a significant difference from the structure of Iijima-type CNT.[5] Reacting Na with C_6Cl_6 is known to form related carbon materials.[6] Employing the reactive template Na@AAO shapes the carbon product further into arrays of CNT, shown as C@AAO in the last step of Scheme 1. This low temperature stoichiometric reaction stands out against other CNT growth processes, such as vapor–liquid–solid (VLS) methods, in which high temperature and catalysts are frequently required.[7]

In conclusion, we have demonstrated a novel synthesis methodology for nanostructured materials. The reactive template strategy is exemplified by the preparation of Na@AAO and the use of it to generate high-density ordered arrays of CNT. In theory, varying the template structure and the halide source would generate a wide variety of nanomaterials. Extending this new strategy is in progress.

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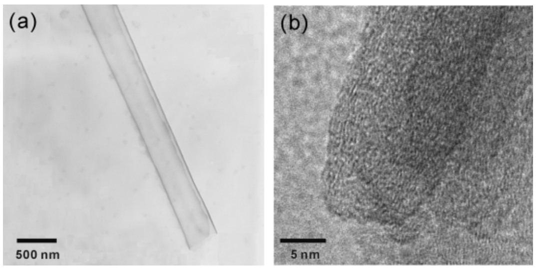

Fig. 3 (a) TEM image of a carbon nanotube prepared at 623 K and annealed at 1073 K. (b) HRTEM image of the wall of the open end.

Notes and references

† **Caution**: Both NaH and Na are highly reactive toward water. Na@AAO membranes were prepared by thermolyzing NaH on AAO under an argon atmosphere. Typically, NaH (Aldrich, 0.40g, 0.017 mmol) was placed above a piece of AAO, (Whatman Anodisc 13, pore diameter: 200 nm, thickness: 60 µm) and heated inside a tube furnace at 623 K under 1 atm of Ar (flow rate: 30 sccm) for 1 h. The product maintained the original shape and turned silvery. Upon exposed to air, it turned white.

‡ The solid products on carbon tapes were coated with a thin layer of gold (~5 nm) and characterized by SEM (JEOL JSM-6330F at 15 kV), (HITACHI S-4000 at 25kV) and (JEOL JSM-6500F at 15 kV).

§ Reacting Na@AAO with C_6Cl_6 (*Toxicity*: LD_{50} oral, mouse = 4 g kg^{-1}; Aldrich, vaporized at 393 K) inside a tube furnace at 623 K under 1 atm of Ar atmosphere (flow rate: 30 sccm) for 20 h generated a black product, which stayed in the original physical shape of AAO. The as-synthesized black plate was heated to 1073 K under vacuum for 1 h. After the thermal treatment, the product was immersed in 48% HF at room temperature for 9 h to remove AAO. It was further washed with boiling water and dried at 373 K in air to offer the carbon nanotubes.

¶ The samples on carbon film coated copper grid were investigated by TEM (JEOL JEM-2000 FXII at 200 kV) and HRTEM (Philips TECNAI 20 at 200 kV).

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