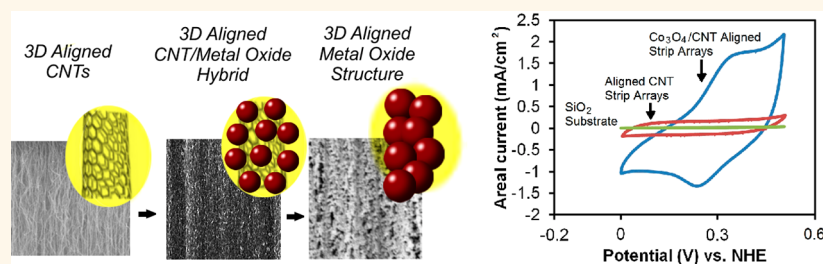


Fabrication of Three-Dimensional Carbon Nanotube and Metal Oxide Hybrid Mesoporous Architectures

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ABSTRACT



Three-dimensional (3D) vertically aligned carbon nanotube (CNT) patterns were utilized as templates for fabricating mesoporous hybrid architectures composed of CNTs and various crystalline metal oxide (MO; M = Co, Zn, Mn) nanoparticles by a microwave-assisted chemical approach. Post-synthesis thermal treatment of the CNT/MO patterns culminated in structural reorganization, depending on the treatment conditions. In air, CNTs were removed by oxidation. The remaining MO architectures preserved the shape and alignment of the original 3D CNT patterns, but with different porosity characteristics and improved MO crystallinity. Elastocapillary condensation and bending were demonstrated to be useful tools for further architecture alteration. The mesoporous nature of the CNT/MO hybrids and the MO materials were confirmed by N_2 -BET measurements. CNT/ Co_3O_4 aligned strips were used as an example to demonstrate the potential application of the CNT/MO architectures as electrode materials for supercapacitive storage. Galvanostatic measurements showed that the CNT/ Co_3O_4 strips were stable up to 1000 charge–discharge cycles at a current density of $377 \mu A/cm^2$ with a specific capacitance as high as 123.94 F/g.

KEYWORDS: carbon nanotubes · crystalline metal oxide nanoparticles · hybrids · mesoporous materials · 3D architectures · microwave-assisted synthesis · pseudocapacitor

Carbon nanotubes (CNTs) are considered to be a particularly interesting class of functional materials because modification to their surface or structure typically results in novel materials with improved physical (electric, thermal, and mechanical) and chemical properties for a diverse set of applications.^{1–13} One approach is to enhance CNT properties using inorganic materials. This is done through the decoration of the CNT with a thin layer of nanoparticles. Ajayan *et al.*¹ first reported fabrication of CNT/ V_2O_5 structures by grinding purified CNTs with vanadium oxide powder and sintering the material. This resulted in a thin layer of V_2O_5 on the surface and in the intertube space of the CNTs.¹ Later, several groups reported the decoration of CNTs with inorganic particles such as

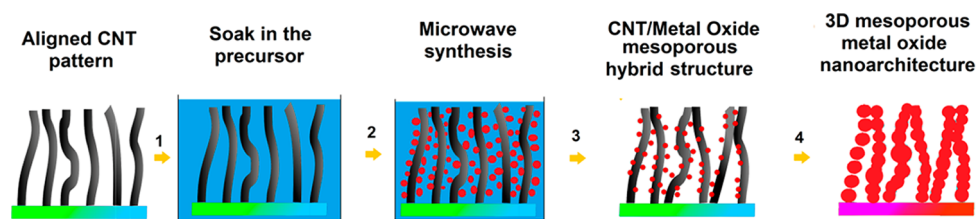
ZnS ,² ZnO ,^{3–5,13} Cu_2O ,⁶ Ce_2O_3 ,⁷ CoO , NiO ,¹¹ Fe_3O_4 ,¹² and Fe_2O_3 .¹⁴ One can divide these reported synthesis methods into two main categories: those that are based on (1) the dispersion of CNTs in a metallic precursor solution followed by a chemical synthesis step (*i.e.*, hydrothermal,^{14,15} microwave synthesis,² or ultrasonication³) or (2) the functionalization of CNT sidewalls with organic ligands followed by the physical or chemical attachment of nanoparticles.^{6,12} Both method types, however, use dispersed CNTs and lead to bulk composite materials that incorporate randomly oriented CNTs among an inorganic matrix. Such structures render a poor connection between the CNTs and the matrix which ultimately affects the hybrid properties. Furthermore, this approach is not suitable for fabricating

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Scheme 1. Schematic representation of the experimental steps showing the fabrication of 3D mesoporous hybrid CNT/oxide architectures and 3D mesoporous metal oxide structures.

3D architectures and hierarchical nanostructures with specified CNT orientations.

A few studies were reported recently on the decoration of randomly oriented or aligned CNTs with metal oxides (MO) using the atomic layer deposition (ALD) technique.^{8–10} Hu *et al.*⁸ coated CNT forests with ZnO using ALD and measured their piezoelectric characteristics after transferring the material onto a flexible polyurethane substrate. They showed that CNTs act as current carrier and improve the device conductivity. Lin and co-workers¹³ fabricated a hybrid film of CNT/ZnO by coating ZnO onto a solution-dispersed CNT film *via* ALD and utilized this as a UV photodetector. Li *et al.*¹⁰ also used ALD to coat plasma-enhanced chemical vapor deposition (PECVD)-grown vertically aligned CNTs with ZnO nanoparticles and measured their optical properties. In another approach, Reddy *et al.*¹⁶ used porous alumina templates to first make MnO₂ tubular shells and then filled the inside core with CNTs using a CVD method. Although these methods represent significant progress toward the fabrication of 3D hybrid CNT/MO structures, they lack generality in terms of structural geometries, nature of the oxide, and the morphologies that can be obtained. In addition, ALD methods are relatively time-consuming, expensive, and they have limited coating depth. It is desirable to develop synthesis methods that are both more cost-effective and versatile. However, only a few studies have been attempted so far and with limited success.¹⁷ In this paper, a rapid and convenient microwave-assisted approach for fabricating 3D CNT/MO hybrid architectures is reported. It yields a wide variety of complex geometries (through patterning or capillary forces) and is suitable for making various metal oxide structures including cobalt, zinc, and manganese oxides which are demonstrated here. To our knowledge, there is no report on the synthesis of 3D aligned hybrid CNT/metal oxide structures with such diversity in shape and composition.

Another significant feature of our approach is that CNTs can act as sacrificial templates that can be easily extracted from the hybrid CNT/MO structures to create their architectural mesoporous MO “negatives”. Previous attempts at fabricating mesoporous materials used either organic templates, such as surfactants, or inorganic frameworks, such as silica (*e.g.*, MCM-41, SBA-15, and KIT-16).^{20–22} The new CNT-based synthesis

approach presented here can be a unique alternative for the fabrication of 3D mesoporous structures either in the form of CNT/MO hybrids or MO nanostructures, which could have significant applications in optoelectronics and/or energy generation/storage including photovoltaics, batteries, and supercapacitors.

RESULTS AND DISCUSSION

Scheme 1 shows the experimental steps involved in this chemical approach for the synthesis of 3D CNT/MO mesoporous architectures using CNT patterns as templates. A substrate with arrays of vertically aligned CNT patterns is first immersed into a metallic precursor solution (Scheme 1, step 1) under mild vacuum conditions (27 inHg vac) so that the precursor molecules infiltrate the intertube space. The solution is then microwave irradiated for 30–60 s (Scheme 1, step 2). Microwaves are known to accelerate the nucleation and formation of MO nanoparticles *via* rapid local heating.²³ This induces the growth of a monolayer of crystalline metal oxide nanoparticles (10–30 nm in diameter) directly onto the surface of individual CNTs, while preserving the overall configuration and shape of the original CNT patterns. Next, the nanoparticle-decorated 3D CNT arrays are removed from solution and dried at 80 °C in air (Scheme 1, step 3). Fabrication of a wide range of 3D architectures is attainable. The initial CNT patterns can be defined by standard photolithography. By varying the precursor species, concentration, pH, as well as the microwave irradiation conditions, the nature, size, and density of the metal oxide can be determined. During drying, the CNTs (coated with MO nanoparticles) undergo elastocapillary-induced densification which offers flexibility in tuning the density and morphology of the final structure. The final annealing step in Scheme 1 offers another advantage, by allowing further tweaking of the hybrid structures *via* the gaseous environment and temperature. This annealing step can be used, for example, to increase the crystallinity and size of MO nanoparticles with CNTs preserved (in an inert gas, such as argon) or CNT removed (in O₂ or air), to reduce MO to a metallic phase (*e.g.*, in H₂ atmosphere) or to dope them with desired dopants (*e.g.*, in N₂ gas). To demonstrate the versatility of our microwave-assisted chemical approach, two different architectures of three different MOs (*i.e.*, ZnO, Co₃O₄, and MnO₂) were fabricated

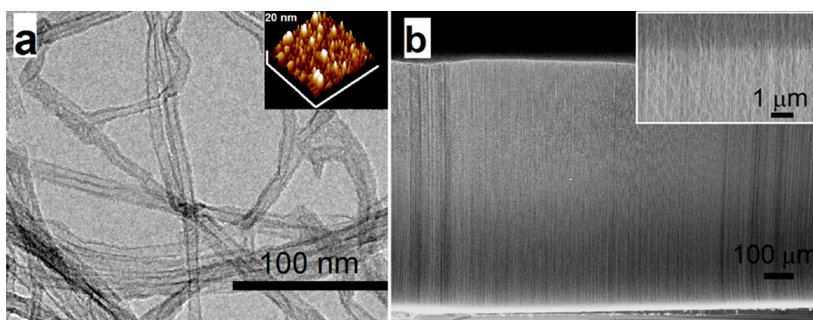


Figure 1. Vertically aligned CNTs synthesized by CVD. (a) TEM image of CNTs. Inset: AFM image of Fe catalyst particles (which were annealed at 725 °C). (b) SEM images of CNT forest. Inset: Zoomed-in image of the aligned CNTs.

(Figure 2), starting from CNT walls and hollow pillars. The corresponding zinc, cobalt, and manganese precursor solutions used are described in the Methods section.

The porous nature of the initial CNT patterns and alignment of the large aspect ratio CNTs are the key enabling factors in this approach. The CNTs grown by chemical vapor deposition (CVD) have an average outer diameter of 7 nm (Figure 1a) and an intertube distance of 50 nm (Figure 1b, inset), which are closely correlated to the density and size of the Fe catalyst particles (Figure 1a; inset shows AFM of the catalyst particles). With a simple thermal atmospheric CVD system, growth of CNTs up to a length of 1 mm was achieved at a high yield of 3 mg/cm² (Figure 1b). Depending on the photolithographically defined Fe catalyst patterns (typical dimensions of 10–500 μm), various geometries of vertically aligned nanotube structures can be fabricated. Example of CNT walls and hollow pillar architectures are shown in Figure 2a,f. The possibility of altering the spatial feature of the 3D CNT structures with liquids, termed elastocapillary condensation, was also explored.^{18,19} CNT walls were bent using DI water to form aligned strips on the surface, which preserved the CNT alignment after deformation (Figure 2b,c). Similar structure modification could be achieved with precursor solutions, as confirmed experimentally. Figure 2d shows the aligned CNT strips laid down on the substrate and coated with cobalt oxide (Co₃O₄) nanoparticles as synthesized. When using patterns of aligned CNTs in the hollow pillar format (Figure 2f), densification during the drying step transforms them to a more condensed and needle-like structure (Figure 2g). By manipulating the original size of the CNT hollow pillars, it is possible to obtain various shapes, ranging from needle-like structures (smaller objects) to volcano-like morphologies (larger objects). Recent reports suggest that a wide range of interesting 3D architectures can be fabricated through liquid condensation processes such as these and are potentially applicable in making 3D CNT/MO hybrids.^{18,19}

Evident from the energy-dispersive X-ray spectroscopy (EDX) analysis and SEM images (Figure 2d,e) is

that annealing of the CNT/Co₃O₄ strips in air at 650 °C removed the CNTs and increased the size of the Co₃O₄ nanoparticles and pores, while preserving the original alignment. Figure 2h shows that a highly porous, hollow needle-like ZnO architecture can be achieved after annealing of the CNT/ZnO hollow pillars (Figure 2g) in air. These results demonstrate that thermal annealing is effective in removing CNT templates to achieve high-porosity 3D architectures of nanoparticulated MOs that are applicable to various metal oxides and morphologies. The high fidelity of the remaining MO architectures is only possible when a complete and yet uniform layer of MO nanoparticles decorate the individual CNTs, as shown in Figure 2j. The inset of Figure 2j shows a TEM image of Co₃O₄ nanoparticles estimated to have an average diameter of 30 nm, produced after annealing in air and dispersion in solution. A single fibrous structure composed of 15–20 nm ZnO particles created after annealing and removal of its single CNT template is displayed in Figure 2k. Neighboring ZnO nanoparticles are fused during annealing to become a self-supporting structure. These results indicate that our method could also be a novel approach for the one-dimensional assembly of nanoparticles, a subject of intensive research.²⁴

Next, the pore characteristics of the initial CNT patterns, CNT/MO hybrids, and the MO architectures were examined. Brunauer–Emmett–Teller (BET) measurements showed that the CNT patterns have a specific surface area of 548 m²/g, which closely matches the theoretical specific area of MWNTs with an average 5 nm inner diameter and 7 nm outer diameter, which is between 400 and 800 m²/g for MWCNTs with 2 to 5 interwalls. This indicates the accessibility of these individual CNTs, devoid of bundles commonly encountered in solution-dispersed methods reported previously. It is suspected that the highly aligned structure of CNTs, which allows N₂ gas molecules to penetrate deeper into the structure, is another factor leading to the higher BET surface area achieved in this study compared to randomly ordered CNTs, which is between 20 and 300 m²/g.²⁵ The adsorption–desorption curves (inset of Figure 3) of both the vertically aligned CNTs and aligned

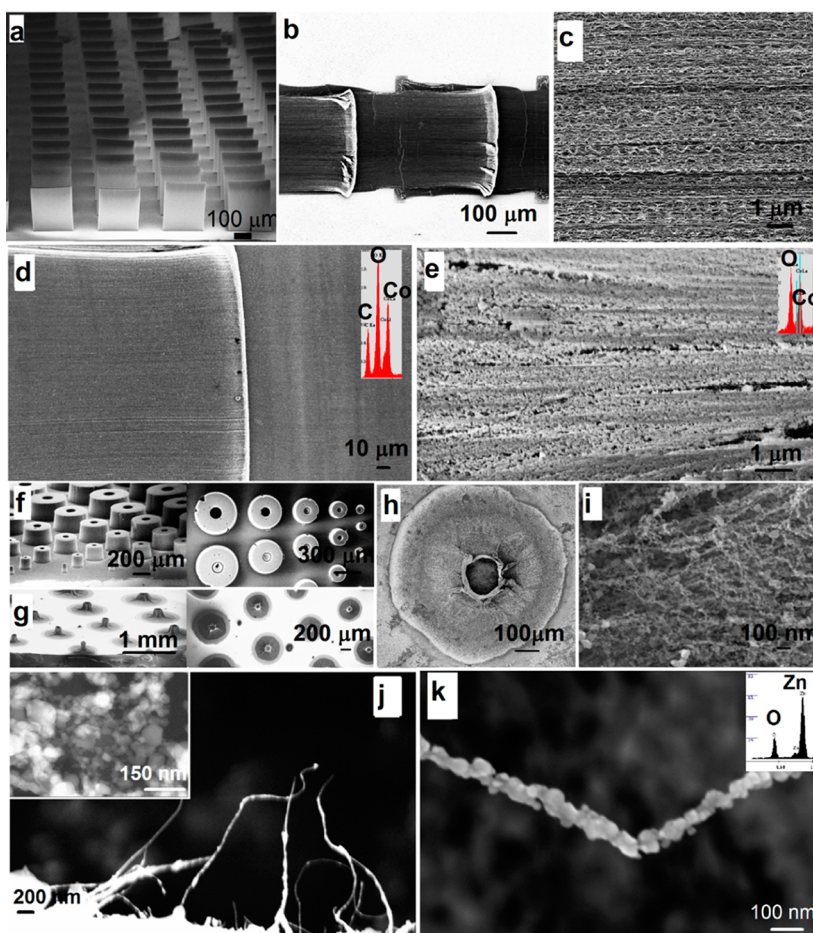


Figure 2. SEM images of the aligned CNTs, 3D hybrid CNT/MO architectures, and 3D MO architectures. (a) CVD-grown vertically aligned CNT walls. (b) CNT walls laid down to form strips on a SiO_2 substrate using an aqueous medium. (c) Expanded image of the corresponding CNT strips. (d) CNT strip/ Co_3O_4 hybrid (inset shows EDX). (e) Co_3O_4 strips after annealing of the corresponding CNT/ Co_3O_4 hybrid in air at 650°C (inset shows EDX). (f) Hollow pillars of vertically aligned CNTs. (g) Liquid condensed hollow needles. (h) ZnO hollow needles. (i) Expanded images of ZnO hollow needles. (j) CNTs decorated with Co_3O_4 nanoparticles (inset is the TEM image of Co_3O_4 nanoparticles). (k) SEM image of a typical fibrous structure constructed of ZnO nanoparticles after annealing and removal of the CNT template.

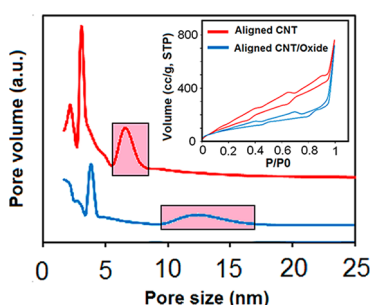


Figure 3. Pore size distribution of the aligned CNT structure (red) and aligned CNT decorated with Co_3O_4 nanoparticles (blue). Inset shows the corresponding adsorption–desorption isotherms.

CNT/ Co_3O_4 hybrid structures show a typical hysteresis attributed to a mesoporous structure, while exhibiting different pore sizes and BET surface areas. The first two peaks in Figure 3 are attributed to the intratubular pores, which were preserved before and after Co_3O_4 synthesis. However, the peaks were weakened after the Co_3O_4 synthesis, which could be attributed to the

blockage or partial filling of the intratubular pores with nanoparticles. The size of the mesopores attributed to intertubular spaces increased after Co_3O_4 formation (refer to the shaded boxes in Figure 3). The BET specific surface area of the nanoparticle-decorated aligned CNTs is approximately $357\text{ m}^2/\text{g}$, and the pore sizes are between 9 and 18 nm. The ability of the CNTs to absorb high levels of microwave energy and trigger localized heating enabled the rapid decoration of Co_3O_4 nanoparticles on the CNT outer surfaces.^{26–28}

The nanoparticles that decorate the CNT surfaces can also fill the mesopore spaces in aligned CNT arrays and create new connections between adjacent CNTs and form pores of various sizes that result in the formation of new surface configurations.

The crystallinity of the MO nanoparticles was examined by X-ray diffraction (XRD). Figure 4a,b shows the XRD patterns of the CNT/ZnO and CNT/ Co_3O_4 hybrid structures after microwave irradiation (before annealing) as well as after annealing in air. It is evident from the differences between the breadth of the XRD

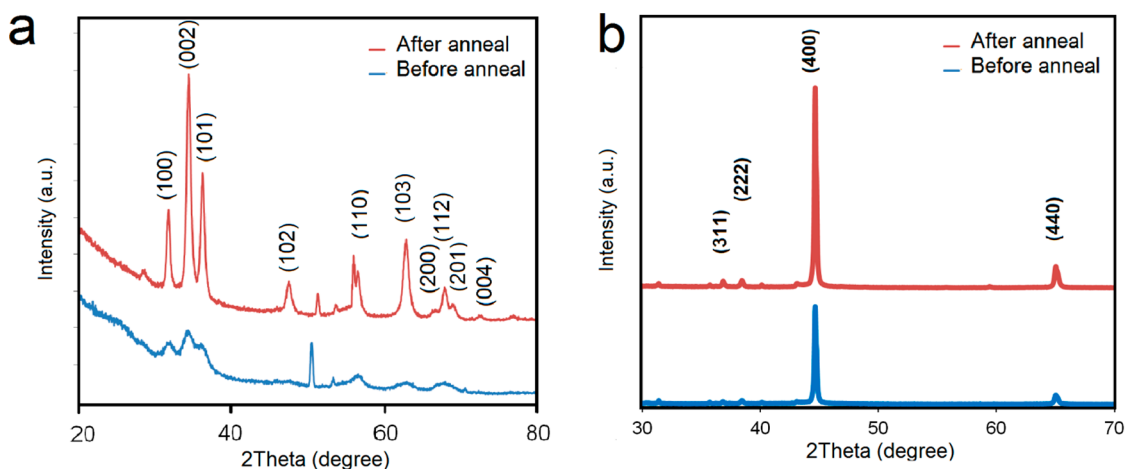
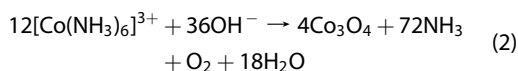
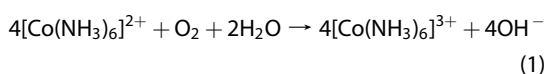


Figure 4. (a) XRD patterns of CNT/ZnO hybrid architecture after microwave synthesis (blue) and annealing at 650 °C in air (red). (b) XRD patterns of CNT/Co₃O₄ hybrid architecture after microwave synthesis (blue) and annealing at 650 °C in air (red).

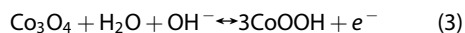
reflections that annealing increases the crystallinity of the ZnO and Co₃O₄ structures. Rapid synthesis of ZnO nanostructures using a microwave-assisted approach has been previously reported in detail by this group, where rapid local heating was also observed to accelerate nucleation and growth.²³ XRD results show that crystalline cobalt oxide (Figure 4b) and manganese oxide (Supporting Information Figure S1) nanostructures were also successfully synthesized with the microwave irradiation process.

The synthesis of Co₃O₄ nanoparticles involves the initial formation of hexamine complexes [Co(NH₃)₆]²⁺ and [Co(NH₃)₆]³⁺ in aqueous ammonia. These complexes are absorbed onto the CNT surfaces where they decompose to Co₃O₄ under microwave irradiation in air in a basic medium (see Supporting Information for reactions describing analogous MnO₂ nanostructure formation).²⁹



This general method is potentially relevant in developing new hybrid structures of CNT/MO patterns to use in novel electronic and optoelectronic applications such as photovoltaic devices and supercapacitors. For the latter, galvanostatic and cyclic voltammetric (CV) tests were performed to illustrate the capacitive characteristics of the aligned CNT/Co₃O₄ strips (shown in Figure S2; see Methods for details). The high aspect ratio strips (500 μm wide, 1 cm long) were supported on an insulating SiO₂ substrate and electrically contacted at one end. CV tests were conducted at scan rates of 10, 30, 50, and 100 mV/s between 0 and 0.5 V versus normal hydrogen electrode (NHE) in a 2 M KOH aqueous electrolyte. The CV curves (Figure 5a) reveal two peaks: an oxidation peak around 0.3 V and the

corresponding reduction peak at 0.25 V. Pure Co₃O₄ electrodes exhibit quasi-reversible redox reaction at the same potentials where redox is described as^{30,31}



In our CNT/Co₃O₄ hybrid mesoporous architectures, the aligned CNTs act as current collectors for electron transfer, enabling efficient redox at rapid scan rates up to 100 mV/s. This highly mesoporous nature of the CNT/Co₃O₄ electrode also is an enabling feature: the polarization is essentially independent of scan rate over the range of 10–100 mV/s (see Figure 5a), indicating that there is no limitation to ion or electron transport in this regime. Another important feature of such hybrid electrodes is their pseudocapacitive capacity for both electric double layer capacitance and bulk redox behavior. Figure 5b shows the dramatic change that occurs on coating CNTs with Co₃O₄ nanoparticles. The shape of the CV curve when the electrode is composed of aligned CNTs alone is typical of electrical double layer capacitors, whereas the CNT/Co₃O₄ shows significant pseudocapacitive behavior. We note that the contribution from the supporting SiO₂ substrate is negligible.

The aligned CNT/Co₃O₄ strips showed excellent stability under galvanostatic cycling with a fixed charge and discharge current of 200 μA (377 μA/cm²). The Coulombic efficiency was about 87 to 92%, and the capacitance did not change significantly (within 5%) in 1000 cycles (Figure 5c), with representative charge–discharge cycles shown in Figure 5d. Over the 1000 cycles, the CNT/Co₃O₄ strips exhibited a consistent areal capacitance of 30.84 mF/cm², and specific capacitance of 168.22 F/g (based on weight of Co₃O₄) or 123.94 F/g (based on weight of CNT/Co₃O₄). The measured thickness of the CNT/Co₃O₄ strips was about 10 μm, which correlates to a volumetric capacitance of 30.84 F/cm³.

The capacitance of cobalt oxide structures in the forms of mesoporous composites or thin films ranges

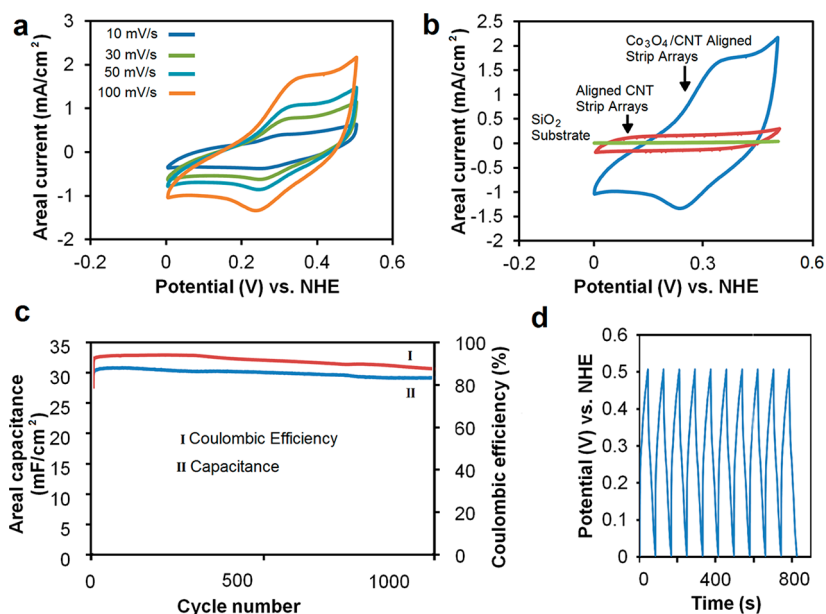


Figure 5. Electrochemical measurements of aligned strips of hybrid CNT/Co₃O₄ in a 2 M KOH electrolyte. (a) Cyclic voltammograms at scan rates of 10, 30, 50, and 100 mV/s. (b) CVs of the SiO₂ substrate, pristine aligned CNT, and aligned CNT/Co₃O₄ hybrid strips at a scan rate of 100 mV/s. (c) Areal capacitance and Coulombic efficiency over 1000 charge–discharge cycles. (d) Galvanostatic charge–discharge vs time at 200 μ A.

from 70 to 400 F/g.³¹ These values are much less than the theoretical specific capacitance of Co₃O₄ (3560 F/g) that comes from redox reaction.³² Researchers worldwide are striving to improve the achievable capacitance value. Proposed recently is an approach that calls for the use of binder-free hybrid materials to enable direct contact between the metal oxide and the current collector without blocking the electrical conductivity of the electrode. In this regard, Yuan and co-workers³² recently made a free-standing Co₃O₄/reduced graphene oxide/CNT paper electrode, which exhibited an electrochemical capacitance of 378 F/g at 2 A/g and 297 F/g at 8 A/g. The method presented here is another approach to achieve such binder-free hybrid materials with comparable or superior capacitance, and it is applicable to a variety of oxides in addition to Co₃O₄. We anticipate that an order of magnitude improvement may be achieved through optimization of the architectural geometry.

CONCLUSION

The role of aligned 3D CNT patterns in templating and fabricating mesoporous CNT/MO hybrid structures and 3D mesoporous MO architectures using a

microwave-assisted chemical technique has been demonstrated. The porous nature of the aligned CNT patterns along with their high specific surface area (548 m²/g) allowed the decoration of single nanotubes with MO nanoparticles in this microwave-chemical process. The fabricated CNT/MO hybrid structures preserved the alignment, 3D morphology, and porous nature of the original CNT patterns while still presenting a high surface area (350 m²/g for CNT/Co₃O₄) and a slightly larger pore size of 9–18 nm than the pristine aligned CNTs. An electrode composed of CNT/Co₃O₄ aligned strips exhibited an areal capacitance of 30.84 mF/cm², a specific capacitance of 123.94 F/g, and a Coulombic efficiency of about 87–92% over 1000 charge–discharge cycles. We believe this microwave-chemical approach is very versatile in terms of the nature of the oxide and the architecture that can be achieved. It can also be applied to the synthesis of other mesoporous CNT and inorganic hybrids, such as CNT/metal hydroxide and CNT/metal, with nanoparticulated metal hydroxides/metals strongly coupled to long (0.1–1 mm) and highly conductive CNTs, which could find advanced applications in energy storage and catalysis.

METHODS

Synthesis of Aligned CNTs. Vertically aligned CNTs were grown using a chemical vapor deposition (CVD) method with high purity ethylene, hydrogen, and argon as the synthesis gases (70:70:70 sccm) in a 1 in. tube furnace (Lindberg). The growth temperature was 725 °C, and the catalyst used was a 4 nm Fe film e-beam evaporated on Si(100)/SiO₂ wafers. The growth

time was between 30 and 60 min with no preannealing step. The typical ramping up time (from 25 to 725 °C) is 12 min. After growth, the chamber was first cooled slowly to 350 °C in approximately 30 min and then rapidly to room temperature in 10 min. The Fe film was patterned by standard photolithography using AZ3330 photoresist and LOR15A as the lift-off resist.

Synthesis of Metal Oxides and Decoration of CNTs. To demonstrate the CNT-templated synthesis of ZnO, Co₃O₄, and MnO₂

crystalline nanoparticles, three different metallic precursor solutions were used.

Cobalt Oxide/CNT. In 30 mL of DI water, 10 mL of ammonium hydroxide solution (NH₄OH, 30%, ACS GR, Alfa Aesar) was added while the mixture was stirred. Cobalt acetate powder (0.11 g of C₄H₆CoO₄, ACS GR, Sigma-Aldrich) was added to the mixture. This solution was then used as the precursor for the synthesis of cobalt oxide/CNT hybrid structures.

Zinc Oxide/CNT. Ammonium hydroxide solution (10 mL of 30% mNH₄OH, Alfa Aesar) was stirred with 30 mL of deionized (DI) water. Zinc acetate dihydrate (0.2 g of Zn(OOCCH₃)₂·2H₂O, ACS GR, Alfa Aesar) was added slowly to the solution. The homogeneous clear solution was used as the precursor for the fabrication of ZnO/CNT hybrid structures.

Manganese Oxide/CNT. Potassium permanganate (0.158 g of KMnO₄, ACS GR, EMD chemicals) was dissolved in 40 mL of deionized water, and 1 mL of hydrochloric acid (HCl, 37%, EMD chemicals) was added dropwise to the stirred mixture. The blue solution was used as the precursor for the synthesis of the manganese oxide/CNT hybrid nanostructures.

Microwave Synthesis of Metal Oxides (MO). Three-dimensional CNT patterns were plasma cleaned in an oxygen atmosphere to render them hydrophilic. The CNT forests were impregnated by a metallic precursor solution using suction filtration with a slight vacuum and allowed to stand for 30 min to permit the solution to diffuse into the porous structure of the tubes. The materials were placed in a microwave oven (2.45 GHz, 900 W) and irradiated for 30 to 60 s. The CNT patterns, decorated with MO nanoparticles, were dried at 80 °C and annealed at 650 °C.

Characterization. The shape and morphology of the obtained CNT/MO patterns were characterized by scanning electron microscopy (SEM, Zeiss LEO 1550). Elemental analysis of the MOs was performed using electron diffraction analysis (EDX). Phase identification of the oxides was established with X-ray diffraction analysis using a PANALYTICAL X'Pert Pro MRD X-ray diffractometer. The surface area and pore size distribution measurements were performed by Brunauer–Emmett–Teller (BET) analysis using a Quantachrome autosorb automated gas sorption system. The nanostructure identification was performed by transmission electron microscopy (TEM, JEOL JEM-2010, 200 kV high-resolution TEM).

Electrochemical Measurements. Electrochemical measurements (Biologic-VMP3) were conducted on as-fabricated aligned strips of CNT/Co₃O₄ structures deposited on a Si/SiO₂ substrate. The sample was partially coated with gold to ensure low impedance connections. An image of the sample is shown in Figure S2. A three-electrode cell, using 2 M KOH as the electrolyte, was employed for measurements where the substrate was used as the working electrode, a platinum wire served as the counter electrode, and a double junction Ag/AgCl electrode filled with 3.5 M potassium chloride (KCl) half-cell served as the reference electrode. Galvanostatic cycling and cyclic voltammetry with a potential limitation (−0.2 V to +0.3 V vs Ag/AgCl) were used to measure the capacitance and charging/discharging current density of the CNT/Co₃O₄ strips.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Figures S1, S2, and a description of the synthesis of MnO₂ nanostructures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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