Chem. Mater. **2007,** *19,* 6376–6378

Synthesis and Characterization of Platinum Nanowire–Carbon Nanotube Heterostructures

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Received August 14, 2007
Revised Manuscript Received September 24, 2007

Composite nanostructures are important to both an understanding of scientific fundamentals in nanoscience and potential applications in nanoscale systems, because of their many desirable properties, which can be tailored by fine-tuning the composition, morphology, size, and organization patterns of the primary nanobuilding blocks.[1] Accordingly, considerable effort has been made, in recently years, to fabricate nanocomposites with core–shell,[2] coaxial nanocable,[3] and one- and two-dimensional (1D and 2D) heterojunction structures.[4] In particular, the assembly of 1D nanostructures containing different materials is important for many electronic, optoelectronic, and sensing applications.[5–11] Various 1D heterostructures have been reported; examples include the synthesis of hierarchical ZnO−In_2O_3 nanostructures using an evaporation method,[5] aligned ZnO heterojunction arrays on GaN, $Al_{0.5}Ga_{0.5}N$, and AlN substrates by a vapor–liquid–solid (VLS) process,[6] Si−SiO_2 hierarchical heterostructures by using self-assembly and VLS methods,[7] hierarchical W nanothorn arrays on WO_3 nanowhiskers by a two-step evaporation process,[8] mulitwalled carbon nanotube (MWCNT)−ZnS heterojunctions by a combination of ultrasonic and heat treatment,[9] carbon nanotube (CNT)−Si nanowire heterojunctions by a VLS process,[4a] a-CNT-Ag nanowire heterojunctions by a combination of electrochemical deposition and chemical vapor deposition (CVD),[10] and single-walled carbon nanotube (SWCNT)−Au nanorod 1D heterojunctions through the selective solution growth of Au nanorods on SWCNT.[11] Among them, CNT-based heterostructures are of particular interest because of their unique geometric morphologies (high aspect ratios and surface areas), as well as the remarkable electronic, thermal, and the mechanical properties intrinsically associated with CNTs.[12] Pt nanostructures are shown to possess novel physical and chemical properties useful in chemical sensors[13] and biosensors,[14] catalytic applications[15] and, particularly, electrocatalysts in polymer electrolyte membrane (PEM) fuel cells.[16] The large-scale formation of heterojunctions of Pt with other nanomaterials (particularly CNTs) is anticipated to extend the possibilities of Pt nanostructures for potential applications. Although a variety of Pt nanostructures, including particles,[17] tubes,[18] wires,[19] dendritic structures,[20] and multipods,[21] have been studied extensively, the formation of single-crystal Pt nanowires (Pt NWs) has been the subject of fewer studies.[19a,c] In particular, the direct growth of single-crystalline Pt NW−CNT heterojunctions remains a big challenge.

In this communication, we describe a cost-effective and efficient approach for the large-scale synthesis of heterojunctions between single-crystalline Pt NWs and MWCNTs, through their contact in the absence of prior CNT functionalization. Our work represents a new type of heterostructure with many benefits. First, the procedure is very simple and can be performed at room temperature, using commercially available reagents, without the need for templates or potentiostats. Second, no CNT functionalization process, in which

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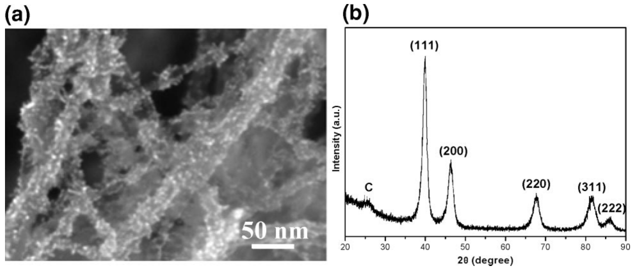

Figure 1. (a) SEM image of Pt NW-MWCNT heteronanostructures. (b) XRD pattern of the Pt NW grown on CNTs. The C peak is from the MWCNTs.

harsh oxidizing acids are used to produce carboxylic acid sites on the surface, is required, thus preserving the electronic structure of the CNTs. Third, Pt NWs are grown directly onto the surfaces of the CNTs, without using any ligands or protecting groups; this both simplifies the synthesis and permits good mixing, with better interfacing between the two nanophases. Fourth, the process is carried out in an environmentally benign aqueous solution. Fifth, the surface density of Pt NWs on the MWCNTs can be effectively controlled through the proper choice of the concentration ratio of MWCNTs, serving as cores, and the Pt precursor. Sixth, there are many potential applications for these structures; for example, Pt NWs will serve as tiny, reproducible, electrical contacts for integrating MWCNTs in electronic, photonic, and sensing nanodevices, while metal nanostructures of various shapes, supported on MWCNTs, will be useful in both electrocatalysis and electrochemical sensing applications.

Scanning electron microscopy (SEM) was employed to characterize the morphologies of the products. A typical photomicrograph of the nanostructures is shown in Figure 1a; it reveals that many nanowires, shaped like thorns, have grown on the CNT stems. The powder X-ray diffraction (XRD) pattern, shown in Figure 1b, reveals that the Pt NWs crystallized in a face-centered cubic (fcc) structure similar to bulk Pt.

Transmission electron microscopy (TEM) was used to determine further details of the heteronanostructures. Numerous Pt NWs, with lengths in the 10–30 nm range, were found to have grown over the entire CNT surface, forming well-ordered heterostructures (Figure 2a). Some Pt NWs have assembled into three-dimensional flower-like superstructures on CNTs. An enlarged section of the image, shown in Figure 2b, indicates that the nanowires grew radially, on the surface of MWCNTs, with diameters of 3–4 nm. Selected-area electron diffraction (SAED) patterns reveal several bright concentric rings (inset to Figure 2b), attributable to the {111}, {200}, {220}, and {311} crystal planes of a fcc Pt crystal. This confirms that the Pt NWs, synthesized by this method, crystallize in a phase similar to bulk Pt.[19a] The crystallographic orientation of the Pt NWs was investigated by high-resolution (HR) TEM, as shown in Figure 2c,d. The closely packed nanowire arrays contain single-crystal atomic structures (Figure 2c), growing along the ⟨111⟩ direction, with a lattice spacing, between the {111} planes, of 0.23 nm, in agreement with the value in a bulk Pt crystal. Figure 2d displays the interfacial region between a Pt NW and the CNT on which it lies. The intact MWCNT structure and the crystalline Pt NW fringes are clearly observed. From the figure, the spacing between adjacent MWCNT walls has been determined to be 0.34 nm, similar to that in graphite. The nanowire lying on the nanotube has grown along the ⟨111⟩ direction, with a lattice spacing of 0.23 nm. The fast Fourier transform (FFT) of the atomic lattice fringing, in the inset to Figure 2d, corresponding to the zone in the square, further demonstrates the crystallinity of the nanowire.

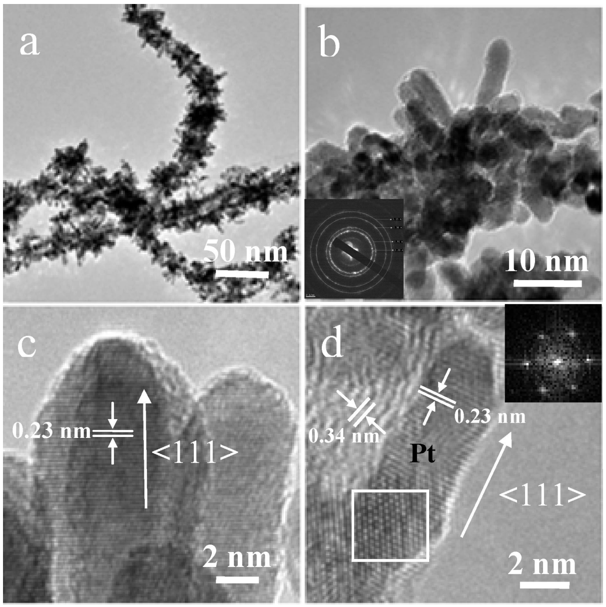

Figure 2. Typical TEM imagess of Pt NW−MWCNT heteronanostructures: (a) a low-magnification TEM image; (b) a medium-magnification TEM image, with the inset showing the SEAD pattern obtained from the heteronanostructures; (c) an HRTEM image of the Pt NW array; (d) an HRTEM image of the interface of the Pt NW and the MWCNT stem, with the FFT in the inset, corresponding to the square area of the photomicrograph.

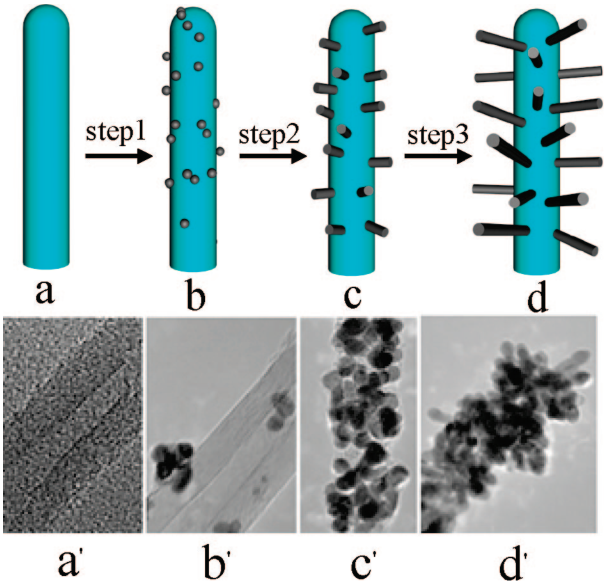

Figure 3. Schematic illustrations of the formation and shape evolution of Pt NW−MWCNT heteronanostructures. (a−d) Schematic illustrations of the growth steps of the heteronanostructures; (a′−d′) TEM photomicrographs corresponding to a−d, respectively.

Figure 3 shows the schematic diagrams (a−d) and corresponding TEM images (3a′−d′) that illustrate the growth process we propose for our heterostructure formation. The entire process is composed of three steps. First, the pristine MWCNTs (15–30 nm in diameter) are used as supports in the synthesis of the heteronanostructures (step 1, Figure 3a,a′). At room temperature, the chemical reduction of H_2PtCl_6 by HCOOH produces Pt nuclei. The as-formed nuclei deposit on selected CNT sites and act as sites for further nucleation, through the absorption of Pt^{4+} ions, leading to the formation of clustered particles. With the reduction of H_2PtCl_6, a high density of nuclei forms on the surfaces of MWCNTs. Pt, continuously supplied from solution, is deposited on the Pt nuclei, resulting in short Pt "nanosprouts" (step 2). The length of the sprouts increases, producing Pt nanothorns (step 3). The resulting high density of Pt NWs on MWCNT is shown in Figure 3d,d′. The seed-mediated growth mechanism is not fully understood, but it is believed that anisotropic growth, preferentially in the $\langle 111\rangle$ direction, is promoted by the very slow reduction rate and the lowest energy principle.[22]

Interestingly, the Pt NW growth density on MWCNTs can be effectively modulated by controlling the weight ratio of CNTs to Pt precursor, while keeping other parameters constant to ensure nanowire growth. Figure 4 shows SEM photomicrographs, at three magnifications, of the product when a large amount of H_2PtCl_6 precursor (Pt/C = 4:1) was used at room temperature. We can see that entire surfaces of CNTs are covered with a high density of Pt NWs. From Figure 4b, the enlarged SEM image of zone I in Figure 4a, we see that increasing the Pt precursor concentration has increased the Pt nanowire surface density. A more detailed image of the nanostructure (Figure 4c, an enlarged image of zone II in Figure 4a) reveals many Pt NWs, self-assembled at an angle to the MWCNT core, forming nanowire arrays with multiple junctions to the CNT. The Pt NWs were confirmed to have diameters of approximately 4 nm and lengths of several tens of nanometers.

In summary, Pt NW arrays were self-assembled onto the surfaces of MWCNTs by a facile solution method at room temperature, forming Pt NW−MWCNT heterojunction nanostructures. The Pt NW surface density on CNTs could be easily controlled by manipulating the Pt precursor/MWCNT weight ratio. These new nanostructures are scientifically interesting and have great potential in sensors and nanoelectronics and as electrocatalysts in fuel cells and other electrochemical applications.

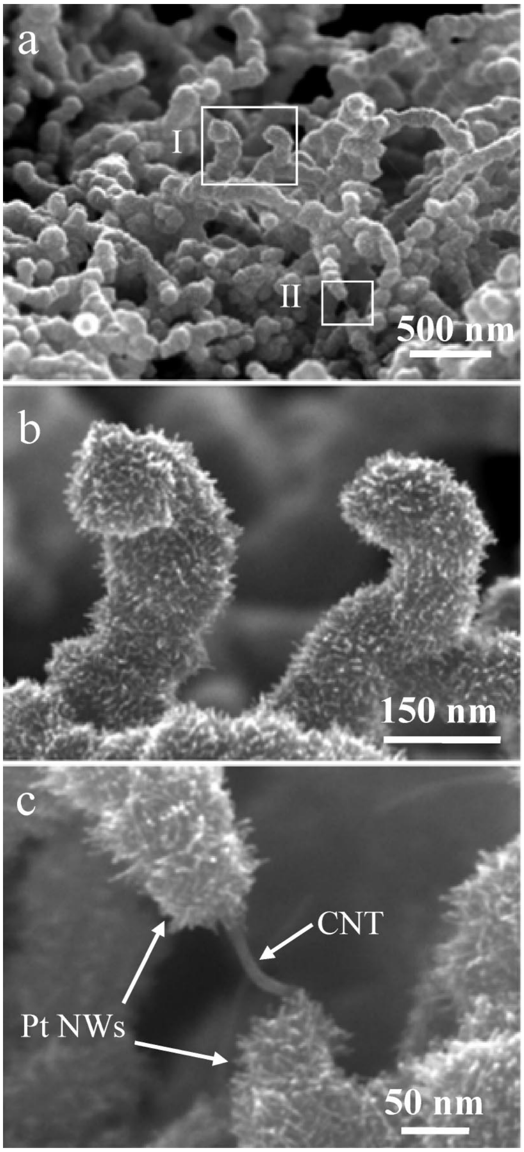

Figure 4. SEM images, at three magnifications, of the product when a large amount of H_2PtCl_6 precursor (Pt/C = 4:1) was used.

Acknowledgment. This work is supported by the Natural Sciences and Engineering Research Council of Canada and by General Motors of Canada. S.S. thanks Mr. Jean-Philippe Masse for help with TEM characterization and Mr. Ryan Porter for useful discussions regarding the heterojunction growth process.

Supporting Information Available: Details of experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM7022949

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