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Hybrid Architectures of Metal Oxide Nanostructures Grown on Aligned Carbon Nanotubes

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The ability to fabricate heterogeneous assemblies of nanostructures enables a wide variety of new materials for energy conversion and storage applications, including electrodes for high-performance batteries, capacitors, catalysts, and photovoltaics [1]. Specifically, three-dimensional (3D) hybrid architectures comprising functional metal oxide nanostructures on electrically conductive supports can create structurally durable and electrically addressable devices and materials. Carbon nanotubes (CNTs) [2] are particularly attractive as scaffolds and templates for addressing other types of nanostructures due to their high electrical conductivity and superb mechanical robustness. Further, among many metal oxide nanostructures, ZnO nanowires (NWs) [3] have drawn considerable research interest since they exhibit UV-sensitive photoelectricity and piezoelectricity, originating from a wide band-gap (≈ 3.37 eV), large exciton binding energy (≈ 60 meV), and a non-central symmetric wurtzite crystal structure. We demonstrate the fabrication and characterization of 3D hybrid architectures of ZnO NWs (ZNWs) grown on organized CNTs.

ZNW/CNT hybrids are fabricated by a two-step chemical vapor deposition (CVD) process. First, vertically aligned CNT "forests" are synthesized on a Fe/Al2O3 thin film catalyst, in $C_2H_4/H_2/He$ gas flowing at atmospheric pressure at 775 ℃ [4]. Then, ZNWs are directly grown on the CNTs, at 6 Torr and 600 ℃, using a Zn metal foil as Zn vapor source and supplying O_2 to form ZnO [5]. Low temperature ZNW growth is essential to successful fabrication of ZNW/CNT hybrid structures without oxidative damage to CNTs [6]. Many CNT constructs including uniform forests, patterned microstructures, isolated bundles, and horizontally aligned sheets are used as ZNW growth supports, facilitating detailed structural characterization and device processing.

SEM images (Figs. 1b,c) show that ZNWs grow uniformly and radially from the CNTs within a forest, without disturbing the CNT alignment. EDS analysis (Fig. 1d) confirms that the structures grown on CNTs consist of Zn and O. Further, TEM imaging reveals that the ZnO nanocrystals directly contact the outer walls of CNTs (Figs. 2a,b). SAED patterns along with lattice-resolved imaging of an individual ZNW (Figs. 2c,d,e) indicates the ZNWs are highly crystalline and grow along the c-axis in the [0001] direction which is energetically favorable. EELS analysis under HAADF imaging (Fig. 3) discloses a sharp interface profile between ZnO and C, and the transition between O and C occurs completely within a distance of ≈2.5 nm. This intimate contact is necessary for transport across the ZNW/CNT interface, and is verified over large areas by electrical transport measurements. As expected from the classical vapor-solid growth model [7], many parameters including the furnace temperature influences the formation of ZnO nanostructures on CNTs (Fig. 4) [6]. Detailed aspects of the nucleation and growth of metal oxides on CNTs, as well as thin film devices demonstrating energy conversion and sensing behaviors, will be presented.

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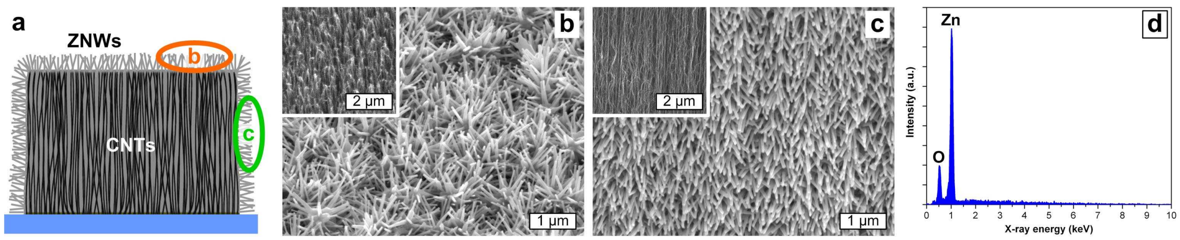

FIG. 1. ZNWs grown on vertically-aligned CNT forests. (a) schematic illustration; SEM images of (b) top surface and (c) sidewall. Insets to (b) and (c) on upper-left show as-grown CNT morphologies; (d) EDS spectra of the ZNW/CNT hybrid.

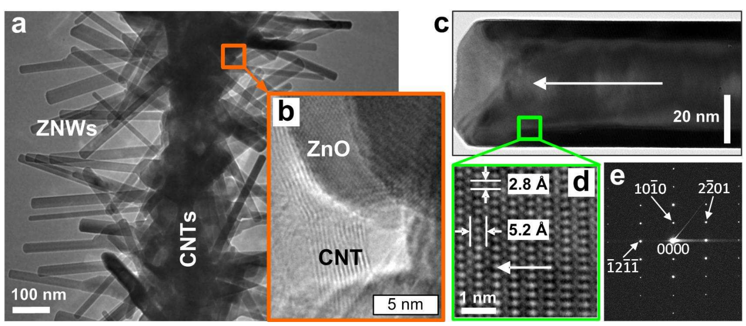

FIG. 2. (a) TEM image of a ZNW/CNT bundle with core diameter ≈ 100 nm and ZNW diameters ≈ 10-50 nm; (b) closer view of ZnO-CNT interface; (c) view of the tip of an individual ZNW. Lattice-resolved image (d) and electron diffraction pattern (e) of the ZNW verify typical wurtzite crystal structure and c-axis [0001] growth direction.

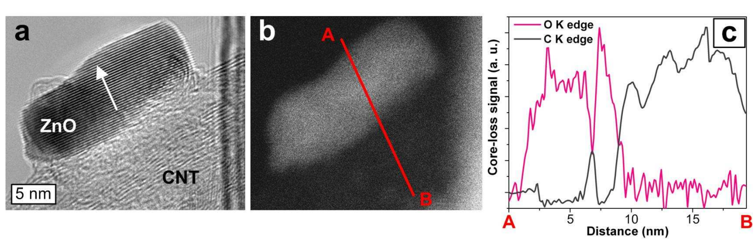

FIG. 3. (a) STEM and (b) HAADF imaging of ZnO-CNT interface. EELS line scan profiles (c) of C (using its K edge at 284 eV) and O (using its K edge at 532 eV) taken along the A-B line across the ZnO-CNT interface marked in (b) show a clear and chemically stable boundary.

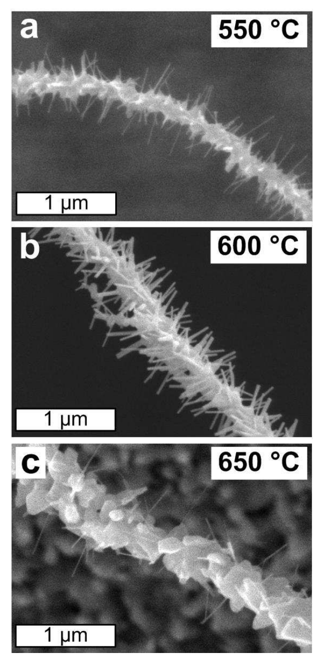

FIG. 4. Morphology of ZnO nanostructures grown on CNT bundles at different temperatures. The increased supersaturation of ZnO at higher temperature promotes a polycrystalline ZnO film deposition on the CNTs. ZNW formation is favored at lower temperatures.

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