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Formation of CdSe nanocrystals onto oxidized, ozonized single-walled carbon nanotube surfaces†

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We present the *in situ* formation of crystalline CdSe quantum dots on the surfaces of oxidized, ozonized single-walled carbon nanotubes, which is a rational synthetic route to the synthesis of complex hierarchical assemblies.

Fundamental challenges in creating functional nanoscale devices involve the controlled synthesis, chemical manipulation, and assembly of nanoscale building blocks. Important objectives therein are to introduce complexity and to promote fundamental understanding of size-property correlations in this size regime. In this regard, the chemistry of single-walled carbon nanotubes (SWNTs), in particular, has been studied with a view towards facilitating their solubilization, purification, directed assembly, separation on the basis of length, diameter and chirality, and most relevantly, composite formation.[1–3]

Herein we illustrate the use of ozonized SWNTs as ligands for the controlled growth of CdSe quantum dots. These resulting nanotube–nanoparticle heterostructures have implications in catalysis, photovoltaic cells, and for the construction of nanoscale assemblies.[4,5] Previously, chalcogenide nanoparticles have been tethered to SWNTs by covalent chemistry utilizing functional groups, primarily localized at ends and defect sites.[1,6,7] However, these protocols require multiple steps with uncertain yield and necessitate the use of intermediary organic linkers. Recently, we reported the use of oxidized, functionalized multiwalled nanotubes (MWNTs) as ligands for the *in situ* growth of CdTe quantum dots.[8]

The key advance of the current work with functionalized SWNTs is that, in analogy to our studies with MWNTs, we have generalized the reactivity to incorporate nanocrystal functionalization at nanotube sidewalls as well.[1–3] That is, we take advantage of the presence of reactive oxygenated groups on the surfaces of ozonized SWNTs,[5,9] which serve as templates for the guided chemical growth of CdSe quantum dots. In effect, functionalized, ozonized SWNTs effectively nucleate coordinative formation of nanotube–nanocrystal heterostructures.

Covalent sidewall functionalization of SWNTs was achieved by an initial treatment with ozone, followed by primary ozonide cleavage with hydrogen peroxide, as has been reported previously (Fig. 1).[5,9] Carboxylic acids are expected as the predominant functional group on the heavily oxidized nanotube sidewalls.[5,9] These functional groups, collectively covering up to 30% of the external nanotube surface, now act as reactive sites to coordinate onto organometallic metal precursors to CdSe quantum dot formation. Briefly, CdO was dissolved in trioctylphosphine oxide (TOPO) at 320 °C, in the presence of ozone/H_2O_2 treated HiPco (high-pressure CO decomposition) SWNTs. A substoichiometric amount of tetradecylphosphonic acid (TDPA) was used to facilitate solubilization of CdO so that the Cd precursor could facilely complex with the oxygen-bearing SWNT sidewalls. This procedure is adapted from methods used to synthesize CdSe quantum dots.[10] A mixture of selenium and tributyl phosphine in trioctyl phosphine and toluene was then rapidly injected at 270 °C and quantum dots were allowed to grow at 250 °C under vigorous stirring for ~5 min. In subsequent workup and purification, toluene was added at 50 °C, followed by methanol, which then precipitated unattached CdSe nanocrystals. After filtration over a 0.2 μm PTFE membrane and extensive washing with toluene to remove all unattached nanocrystals, the remaining dark residue was dried and characterized.

In parallel experiments, we attempted to grow quantum dots by similar procedures on less functionalized tubes including (i) wet air-oxidized SWNTs (Fig. 1a), (ii) $KMnO_4/H_2SO_4$-treated MWNTs, and (iii) ozone-oxidized MWNTs. A compelling observation that confirms the existence of a chemical interaction of nanotubes with quantum dots is that the degree of immobilization of CdSe on the nanotube surface correlates with the degree of oxidation. Because of the relatively unreactive large diameter of the outer walls of MWNTs, these tubes were not extensively functionalized (<2% oxygenated sites). Indeed, sites for metal coordination to the nanotube were few and far between, after these comparatively mild oxidative treatments. Hence, we were unable to immobilize CdSe nanocrystals on MWNTs with this relatively low extent of oxidation. Similarly with air-oxidized and $KMnO_4/H_2SO_4$-treated MWNTs, which were mildly oxidized (<5% oxygenated sites) and hence bore a low density of functional groups, the number of quantum dots observed on the nanotube surface were correspondingly very low, barely forming at all.

Not surprisingly, as seen in Fig. 2, we observe a reproducibly substantial quantity of quantum dots, dispersed along the heavily functionalized, ozonized nanotube sidewalls. The high-resolution

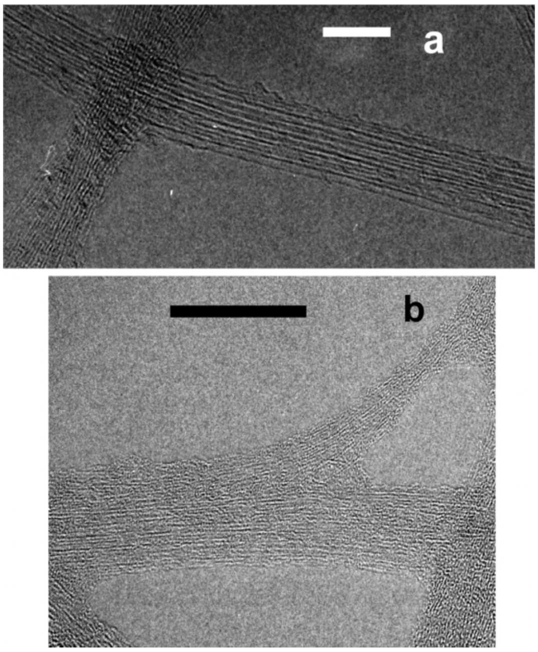

Fig. 1 High-resolution transmission electron micrographs of (a) air-oxidized, purified nanotubes and of (b) sidewall-ozonized SWNTs. Scale bars are 20 nm in each image. Please note aggregate bundle and kink defect formation as well as loss of crystallinity in highly oxygenated ozonized tubes.

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† Electronic supplementary information (ESI) available: additional HRTEM images; discussion of FT-IR and UV-visible-near IR data; XPS spectra. See http://www.rsc.org/suppdata/cc/b4/b404204b/

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lattice-resolved images confirm the presence of wurtzite and zinc-blende CdSe structures. Further corroboration comes from the energy dispersive X-ray spectroscopy (EDS) data in Fig. 2, indicating the presence of Cd and Se localized on the nanotubes in the form of quantum dots. Because outer tubes in a bundle are more extensively functionalized as compared with tubes in the inner core of the bundle, as well as more accessible to the monomer flux necessary for the growth of CdSe, we find a larger concentration of quantum dots on the exterior of the tubes. XPS measurements were also consistent with the expected formation of CdSe. Data showed peaks corresponding to Cd $3d_{5/2}$ fitted to 405.45 eV and to Se $3d_{5/2}$ fitted to 54.63 eV (S2, Supplementary Information†).

Raman spectroscopy is a sensitive probe of electronic structure and electron–phonon coupling in SWNTs.[11] As mentioned, ozonolysis of SWNTs is accompanied by an increase in the intensity of the Raman D band, due to disruption of the pseudo-1D lattice.[9] After quantum dot growth, we note that in the Raman spectra acquired at 632.8 nm laser excitation (Fig. 3), features associated with carbon nanotubes are largely preserved because of resonance enhancement.[12] At this wavelength, signals, *i.e.* LO modes, due to CdSe quantum dots grown on the tubes are not observed mainly because of the polydisperse nature of the generated nanocrystals, likely because the incident excitation is off-resonance.[13]

The varying sizes and shapes of CdSe nanocrystals observed indicate that the functionalized nanotubes influence the size, shape, and growth of the nanocrystals. To explain this mechanistically, several possibilities are likely. Our previous studies indicate that nanotubes act as sterically bulky ligands in the growth of the quantum dots and hence, are likely able to spatially hinder monomer access to one side of the growing crystallite, thereby causing dispersion in the aspect ratio.[8,14]

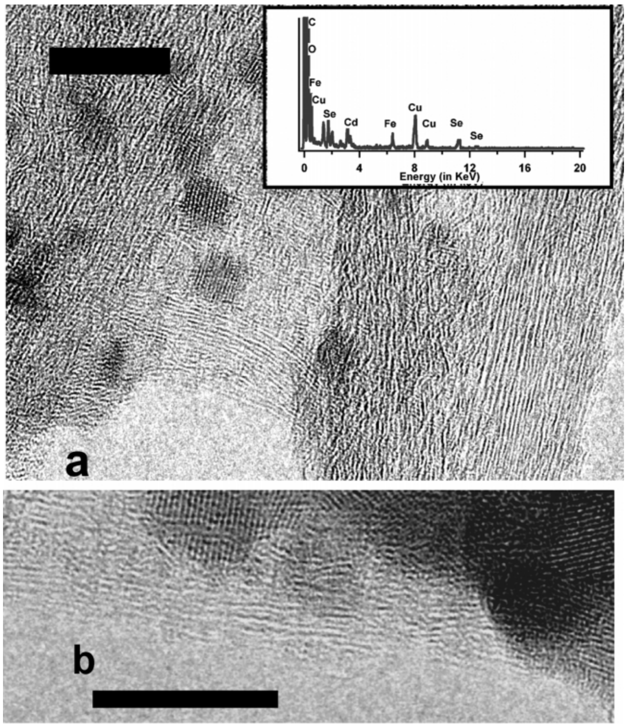

Fig. 2 High-resolution TEM images of CdSe-SWNT heterostructures. Substantial nanocrystal coverage at nanotube junctions and between bundles (a) as well as along sidewalls (b) are shown. Overall coverage of nanocrystals was limited to ~10–15% of total surface area of ozonized tubes. EDS spectra (inset to a) indicate expected elemental signals. Cu and Fe signals arise from TEM grid and catalyst impurities from the HiPco process, respectively. Scale bars are 10 nm in each case.

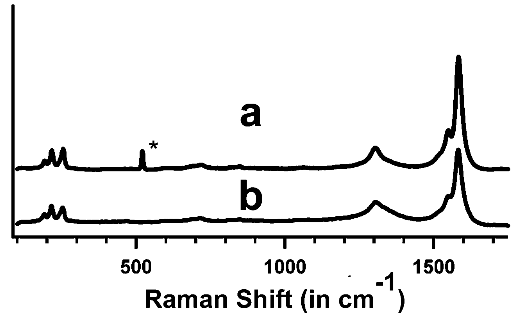

Fig. 3 Raman spectrum of (a) ozonized SWNTs and (b) CdSe-ozonized SWNT heterostructures at 632.8 nm excitation. Starred peak arises from the silicon substrate.

Another factor influencing quantum dot formation is the competitive, preferential attachment of the growing crystal facet to the nanotube ligand, as opposed to the molecular, acid-capping ligand, as has been observed with crystal growth in systems, containing mixed ligands.[14,15] The degree of the influence of SWNTs in determining the resultant dimension range of quantum dots formed likely depends on parameters such as the site of attachment, the density of functional groups, as well as the extent of nanotube aggregation, *i.e.* size of the ligand.

Chemical attachment of quantum dots onto nanotube surfaces can thus be confirmed by (a) dispersion in quantum dot sizes and shapes; and (b) control experiments with mildly oxidized tubes.

In conclusion, we report a highly successful synthetic strategy for the fabrication of CdSe-SWNT heterostructures based on the *in situ* growth of quantum dots onto functionalized nanotube surfaces. The degree of quantum dot immobilization scales with the extent of SWNT oxidation. Future studies will focus on developing ordered assemblies of these heterostructures and studying their charge transfer properties.

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