# Fabrication of Rare-Earth Biphthalocyanine Encapsulated by Carbon Nanotubes Using a Capillary Filling Method

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Carbon nanotubes (CNTs) have inspired considerable research interest in the past decade because of their unique optical, electronic, magnetic, and mechanical properties and have been regarded as a promising candidate for versatile applications.[1−6] However, CNTs often exist in the form of highly tangled ropes, and the inert nanotubes cannot be dissolved in any organic solvent, which prevent their application in various devices. On the other hand, various chemical approaches are available for tailoring the structure of the open, long, and cylindrical tubes to fabricate nanotube-based devices, which would be of major interest. The functionalization of the open ends, enrobing of the exterior walls, and filling of the interior cavities will stimulate the synthesis of novel one-dimensional (1-D) hybrid materials.[7−11]

Because of their excellent and unique physical properties, CNTs have been applied to the preparation of composites with metallic and organic materials. Our previous work demonstrated that the photoconductivity of an oxotitanium phthalocyanine/multiwalled carbon nanotube (MWCNT) composite was improved due to the photoinduced charge transfer from the excited oxotitanium phthalocyanine to MWCNT.[12] It is well-known that high efficiency of photoinduced charge transfer can be achieved in the donor−acceptor heterojunction with an interpenetrating bicontinuous network.[13] However, fabricating CNTs-based composites with the desired interpenetrating bicontinuous network morphology remains a great challenge to improve the photosensitivity.

So far, most studies in the field relate to the contact between the guest materials and the shell of CNTs. It has been reported that CNTs can act as a nanosize reactor to synthesize robust metal clusters and nanowires.[14] Research has shown that organic solution and fusible metal oxide with low surface tension can wet the graphite shell; as a result, the cavities of CNTs can be filled by foreign materials with the aid of a spontaneous capillary driving force.[15−19] However, only a few studies had been reported trying to fill optically and electronically active organic materials into the cavities of CNTs. Moreover, it is generally believed that by encapsulating guest materials into CNTs, one could synthesize nanorods with confined crystalline structure and high interfacial area with CNTs. These hybrid composites, consisting of 1-D nanostructured dots and wires, should spawn new applications in nanoscience and advanced nano-optoelectronic devices.

This work focuses on the fabrication of novel 1-D MWCNT/rare earth biphthalocyanine hybrid materials. The erbium biphthalocyanine ($HErPc_2$) nanorods and nanowires were encapsulated by the hollow MWCNTs via the capillary filling method. The objective is to prepare the organic/inorganic hybrid materials by combining the complementary properties of MWCNTs and rare-earth biphthalocyanine compound.

The chaotic tangled MWCNT ropes were first cut into short pipes by chemical etching in acid,[20] and the opened pipes were then filled with $HErPc_2$ from $CHCl_3$ solutions containing $HErPc_2$. Ebbesen and co-workers[21] revealed that the upper threshold for the surface tension of the liquid wetting MWCNTs is 180 mN/m. $HErPc_2$ has considerable solubility in chloroform with a surface tension as small as 27 mN/m. The threshold is wide enough for capillary filling and the surface tension of the solution can be easily manipulated by the concentration of $HErPc_2$. Figure 1 presents the transmission electron microscopy (TEM; JEM 200CX, JEOL) photographs of the morphology of $HErPc_2$ encapsulated by MWCNTs and the electron diffraction patterns taken from the selected area of the $HErPc_2$ nanorod. Chainlike $HErPc_2$ crystals are formed in the cylindrical cavities after capillary filling for 2 days (Figure 1a), indicating that the $HErPc_2$ solution can indeed wet the outer layer

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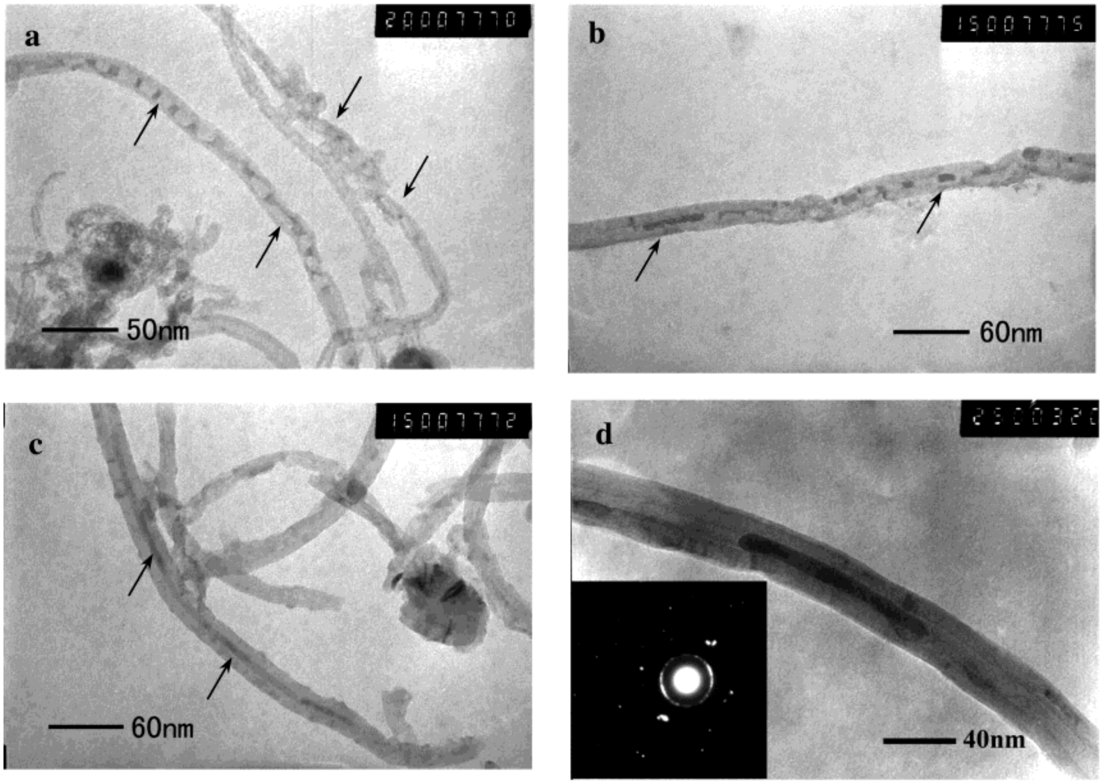

**Figure 1.** TEM imaging of chainlike $HErPc_2$ crystals, nanorods, and nanowires encapsulated by MWCNT after capillary filling times of 2 days (a), 3 days (b), and 5 days (c). The electron diffraction pattern of the selected area from an $HErPc_2$ nanorod (d) is given in the inset of (d).

of MWCNTs. Therefore, the liquid is adsorbed into the cavities by the capillary force. By prolongation of the capillary filling time to 3 days, some $HErPc_2$ nanorods form at tens of nanometers in length and 10 nm in diameter (Figure 1b). After 5 days, the $HErPc_2$ nanowires of several micrometers are formed in the MWCNTs' cavities with the same diameter (Figure 1 c), and about 15% of the capillary filling efficiency is calculated from the TEM measurement.[11] The electron diffraction pattern of the selected area from the nanorod shown in Figure 1d suggests the formation of polycrystalline $HErPc_2$ in the cavity of MWCNT.

In addition to the capillary filling time, the $HErPc_2$ crystal morphology that is constructed in the channel of MWCNTs template can also be tailored by means of varying the concentration of $HErPc_2$ and the opened MWCNTs mold. Saturated $HErPc_2$ solution in chloroform lead to a lower filling efficiency (<5%) due to the increase of the surface tension of the solution. The filled tubes are usually those with large diameter, and the narrow tubes (<5 nm in diameter) are less favorable to be filled due to the low wetting threshold. Figure 2 shows the $HErPc_2$ nanowires encapsulated by MWCNTs with different inner diameters. Since the electronic properties of CNTs depend heavily on their diameters and chiralities, versatile hybrid composites with very interesting features are expected to be prepared by this method.

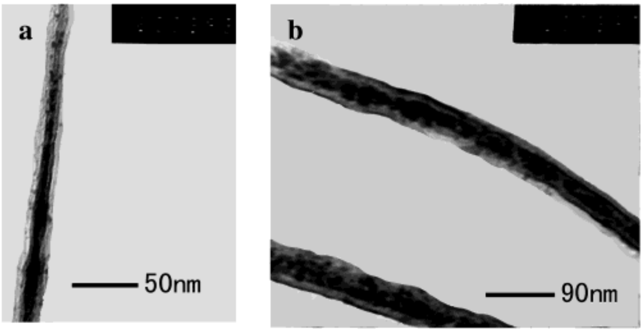

**Figure 2.** TEM image of $HErPc_2$ nanowires encapsulated by MWCNTs templates with inner diameters of 10 nm (a) and 25 nm (b).

It is also interesting to find that all the $HErPc_2$ crystals in the cavities appears to be very stable, even after long exposure time to the 120-keV electron beam. This may be due to the carbon shell isolating the $HErPc_2$ crystals from the outside environment. This protection prevents the decomposition of $HErPc_2$ upon exposure to the high-energy electronic beam, implying that the cavities of MWCNTs can provide a protective barrier against irradiation, especially for the biomolecules.

The 1-D hybrid materials were studied by X-ray diffraction (XRD; Rigaku D/max). The results obtained from the purified MWCNTs, $HErPc_2$, and the MWCNTs/$HErPc_2$ composites are shown in the Supporting Information. The diffraction pattern of MWCNTs shows two peaks at $2\theta = 25.6$ and 44.28°, corresponding to (002) and (101) reflections, respectively.[22] $HErPc_2$ exhibits an intense peak at $2\theta = 8.52°$, corresponding to an interplanar distance of 10.37 Å. The relatively high intensity of their peak confirms the crystal structure consisting of oriented parallel planes. $HErPc_2$ encapsulated by MWCNTs exhibits the characteristic peak of $HErPc_2$ at $2\theta = 8.32°$, corresponding to the interplanar distance

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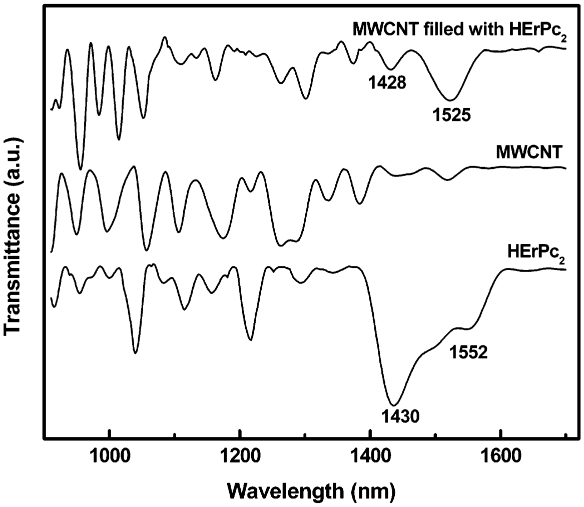

**Figure 3.** NIR transmittance spectra of HErPc$_2$, MWCNTs, and HErPc$_2$ nanowires encapsulated by MWCNTs, which were prepared by capillary filling for 5 days.

of 10.62 Å, though the peak is much weaker and broader than that of pure HErPc$_2$. The (002) and (101) reflections of MWCNTs are also observed in the hybrid. The interplanar distance shifts from 10.37 Å for bulky HErPc$_2$ to 10.62 Å for the HErPc$_2$ encapsulated nanowires. The planar HErPc$_2$ prefer to stack into cylindrical crystals with their axes parallel to each other with the aid of intermolecular interaction facilitated by the $\pi$-conjugated electron orbit.[23] The interplanar distance corresponds to the space between the stacking axes of HErPc$_2$ molecules (please see the Supporting Information). The confined geometry provides the preferential growth direction for HErPc$_2$ crystallites, allowing HErPc$_2$ crystallites to orient unidirectionally along the channel. The increased interplanar distance of HErPc$_2$ molecules suggests a loose molecular stacking in HErPc$_2$ nanowires, which might result from the confined geometry within the MWCNTs template.

The near-infrared (NIR) photoresponse property of the 1-D MWCNT/HErPc$_2$ hybrid material was investigated by the NIR transmittance spectra (FTIR; MIR 8000, oriel), and the results obtained from the HErPc$_2$, MWCNT, and MWCNT/HErPc$_2$ hybrid material are depicted in Figure 3. There is a main peak at 1430 nm with a shoulder at around 1552 nm for HErPc$_2$ powders, which may originate from the intramolecular ring-to-ring charge transfer in the biphthalocyanine complex.[24] The broad and featureless absorption bands of MWCNTs that range from 900 to 1300 nm are induced by the wide distribution of nanotube diameter. Upon filling HErPc$_2$ into the cavities of MWCNTs, the 1-D hybrid material exhibits two new peaks at 1428 and 1525 nm, which are the typical absorptions of HErPc$_2$. The blue-shifted absorption bands of the 1-D hybrid compared to those of pristine HErPc$_2$ are caused from the loosely packed HErPc$_2$ crystals in the confined circumstance of MWCNT cavities, as has been demonstrated by the XRD results above. With the combination of the good photoconductivity in both the visible and the NIR region, the stability against thermal and chemical decomposition of rare earth biphthalocyanines, and the high conductivity of MWCNTs, fabrication of the 1-D MWCNT/HErPc$_2$ hybrids may provide us the possibility of fabricating NIR photodetector devices.[25]

In conclusion, the organic/inorganic hybrid material of HErPc$_2$ encapsulated by MWCNTs was obtained by using a simple capillary filling method. A range of distinct nanowires could be designed with different MWCNTs templates. HErPc$_2$ nanorods or nanowires constructed in the channel of MWCNT templates may be up to 10 $\mu$m in length. The 1-D MWCNT/HErPc$_2$ hybrids show a characteristic absorption in the near-infrared region. The hybrid composites are expected to combine the electrochromic, liquid crystal, molecular conductive and magnetic properties of rare-earth biphthalocyanines, and unique features of MWCNTs. This work may spawn new interest in both fundamental nanoscience research and the development of nanodevices.

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**Supporting Information Available:** Figures of X-ray diffraction patterns and possible molecular stacking patterns (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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