One-step solid-state thermolysis of a metal–organic framework: a simple and facile route to large-scale of multiwalled carbon nanotubes†

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We report a simple and facile solid-state approach to large-scale synthesis of multiwalled carbon nanotubes (MCNTs), for the first time, by one-step direct thermolysis of a metal–organic framework [$Ni_3(btc)_2 \cdot 12H_2O$] (btc = benzene-1,3,5-tricarboxylato) in a one-end closed conventional horizontal tube furnace under relatively low temperature without using any additional carrier gas or catalyst.

Carbon nanotubes (CNTs) have received research attention worldwide in recent years not only due to their unique structures and properties,[1] but also their favorable and potential applications in the fields of energy sources, electronics, information, catalysis, and mechanism,[2] and current efforts are mostly focused on CNT fabrication techniques and the exploration of their relative properties.[3] Methods reported so far have been developed mainly including arc-discharge, laser ablation, and metal-catalyzed chemical vapor deposition (CVD). Different methods and reaction conditions result in CNT products with different structures and properties as well as different yields. For its simple synthetic process, solid-state pyrolysis has emerged as an alternative route to CNTs. Chen and co-workers[4] reported the smallest carbon nanotubes by the pyrolysis of tripropylamine molecules in the channels of porous zeolite $AlPO_4$ single crystals. Pyrolysis of organometallic precursors *in vacuum or closed system* has been used for preparing many kinds of carbon nanostructures such as CNTs and carbon onions.[5] To date, the control of CNTs in terms of type, diameter, length, morphology, orientation, and especially large-scale synthesis of CNTs from a simple, controllable and low-cost method remains a key challenge.[6]

Meanwhile, recent years have witnessed the rapid development of metal–organic frameworks (MOFs) due to their intriguing structures and interesting properties.[7] Herein, we present, for the first time, a simple and facile synthetic route to multi-walled CNTs (MCNTs) by one-step solid-state thermolysis of the MOF [$Ni_3(btc)_2 \cdot 12H_2O$] (btc = benzene-1,3,5-

tricarboxylato) (Ni-MOF) in a one-end closed conventional horizontal tube furnace under relatively low temperature (see experimental details in ESI†), in which the Ni-MOF can provide both ideal carbon sources and metal catalysts for the formation of MCNTs during the thermolysis process. Thermogravimetry (TGA) curves (see Fig. S2, ESI†) show that the Ni-MOF is very thermostable and has a high decomposition temperature of > 500 °C, which makes it a good precursor for thermolysis. Large-scale and uniform MCNTs were synthesized by thermolysis of the MOF just at its complete decomposition temperature of 500 °C.

The shape and microstructure of the resulting products were investigated by field emission scanning electron microscopy (FE-SEM). Fig. 1(a) shows low-magnification FE-SEM images of the products. Typical FE-SEM images at higher magnification (Fig. 1(b) and (c)) further reveal tube-like products with remarkably uniform shape and size that are normally only obtained using more complex techniques. Little of other forms or amorphous carbon has been found. The synthesized CNTs have diameters ranging from 30 to 60 nm and lengths of up to several micrometers. More fascinatingly, the CNTs yield is rather high, up to 65% based on the percentage of carbon in the precursor Ni-MOF.

The crystalline structures and phase purity of the synthesized products were examined by Raman spectra and powder X-ray diffraction (XRD). Fig. 2(a) illustrates the typical Raman spectra of the as-synthesized MCNTs, in which the first-order modes of the Raman spectra of the CNTs show a strong sharp peak at 1590 cm^{-1} (G line), being assigned to the high-frequency E_{2g} first-order mode, and a strong sharp peak at 1350 cm^{-1} to the D line.[8] From XRD analysis (Fig. 2(b)), the as-synthesized product is confirmed to be carbon (JCPDS file no. 75-0444) and the four diffraction peaks are well-matched to the (002), (100), (004) and (110) crystal faces of pure solid carbon. The strong diffraction peak of (002) shown in XRD patterns indicated that high crystallinity of CNTs were obtained by our route.

More information on the tubular microstructure of the as-prepared MCNTs was revealed by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Fig. 3(a) shows low-magnification TEM images of the as-synthesized CNTs, indicating that the nanotubes have an outer diameter in the range of 10–30 nm and a length of up to 0.3–0.5 μm and the inner diameters are 10–20 nm. The spacing between the rolling layers in the perpendicular direction to the tube axis is 0.34 nm, which is almost the same as the d_{001}

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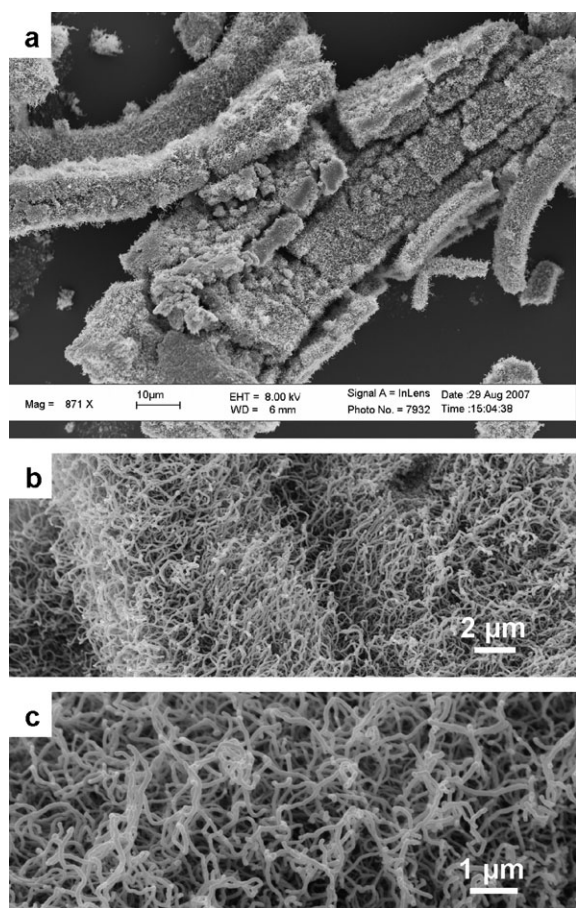[c] Institut für Anorganische Chemie der Universät Regensburg, Regensburg, Germany

Fig. 1 (a) Low-magnification FE-SEM image of the as-synthesized typical MCNTs obtained by thermolysis of the Ni-MOF in a one-end closed horizontal tube furnace at 500 °C for 20 h; (b) and (c) medium-magnification FE-SEM images from (a).
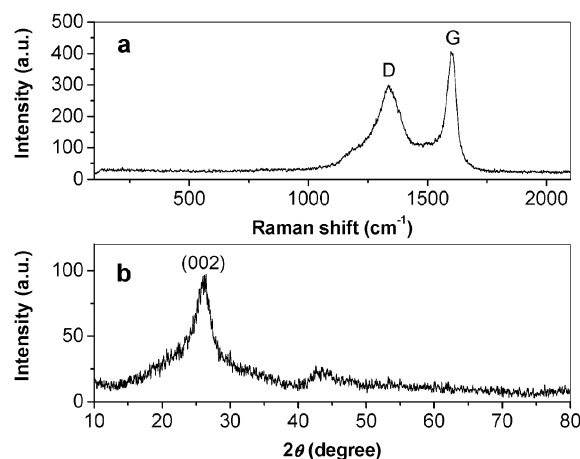

Fig. 2 (a) Raman spectrum and (b) XRD pattern of the as-synthesized typical MCNTs by thermolysis of the Ni-MOF in a one-end closed horizontal tube furnace at 500 °C for 20 h.

spacing of graphite. This is in excellent agreement with the XRD result presented above. Moreover, the HRTEM images in Fig. 3(b) shows clearly that these nanotubes have bamboo-like structures with hollow inert structures and the tube walls can be clearly seen, which shows that the synthesized carbon tubes are in the range of the nanometer scale. These CNTs have closed but amorphous tips and the thickness of the tube walls is about 3–5 nm.

The thermolysis temperature and reaction time play important roles in the formation of MCNTs. Thermolysis of the Ni-MOF at 400 °C for 20 h resulted in complex products with color changing from pale to grey and black from left to right in the ceramic boat where the precursor Ni-MOF was placed before thermolysis. XRD results of the three products (see Fig. S4, ESI†) show that lower temperature is not suitable for the growth of CNTs. To investigate the effect of reaction time on the final products, different samples were prepared at 500 °C for reaction times from 5 to 10 and 15 h. XRD of these products (see Fig. S5, ESI†) indicates that with the increase of the reaction time, the peaks of the carbon become much clearer and the nickel content decreases. A long heating process may thus be essential for the formation of pure CNTs. The FE-SEM images of the samples prepared at different reaction times at 500 °C are depicted in Fig. 4, indicating that

large-scale CNTs can be obtained using our method and the length of the formed CNTs increases with the increase of reaction time.

The formation mechanism that accounts for the possible growth of the MCNTs is essentially composed of decomposition, reduction, nucleation and growth. With the increase of temperature, the precursor Ni-MOF lost its lattice water and this was evicted from the quartz tube. With a further temperature increase, the precursor began to show decomposition of its organic ligands which decomposed into carbon, and different gases including hydrogen, carbon monoxide and benzene, together with other fragments from the incomplete decomposed ligands. This can be proved by the results of TGA-MS and the reported literature[9] which also established the decomposed gases. Reduction by the formed carbon and decomposed gases converted Ni^{2+} into Ni. The formed CNTs did not appear on the surface of the remaining nickel particles (see Fig. S3, ESI†) after reaction, but appeared on the wall of the ceramic boats mainly to the right of where the precursor Ni-MOF was placed before thermolysis. The Ni particles act
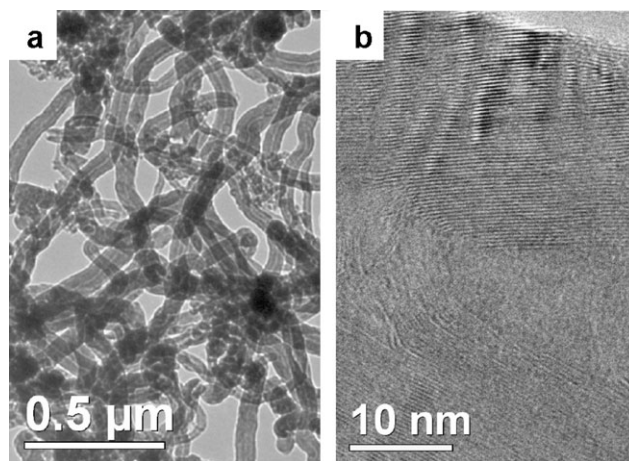

Fig. 3 (a) TEM and (b) HRTEM images of the as-synthesized MCNTs by thermolysis of the Ni-MOF in a one-end closed horizontal tube furnace at 500 °C for 20 h.
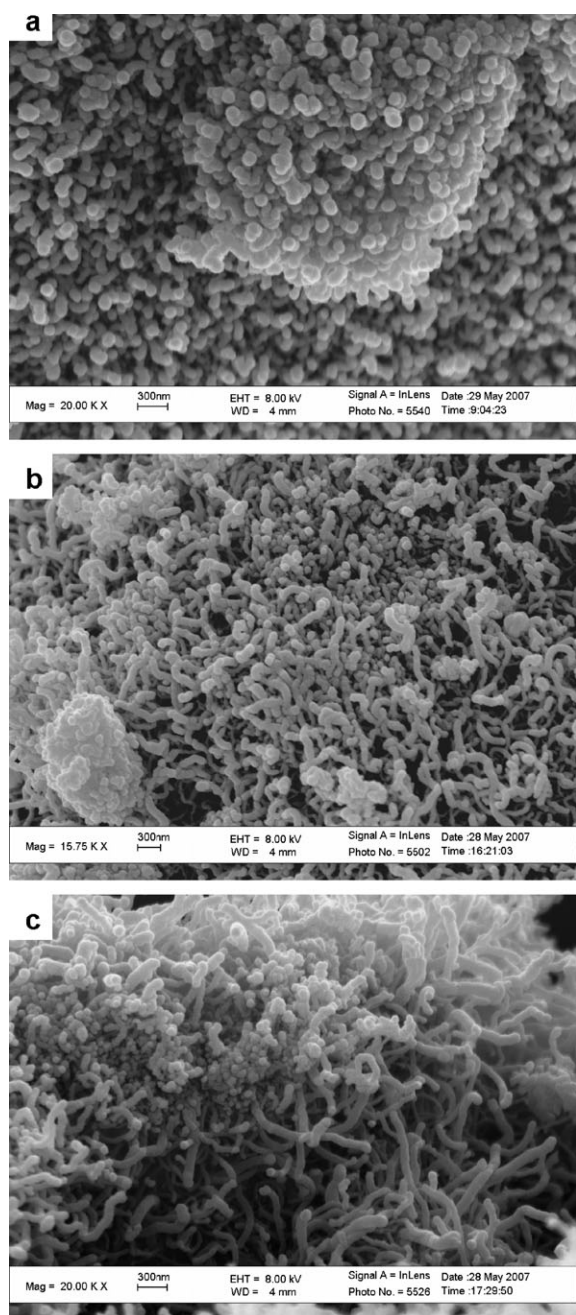
Fig. 4 High-magnification FE-SEM images of the as-synthesized MCNTs by thermolysis of the Ni-MOF at 500 °C in a one-end closed horizontal tube furnace for different reaction times: (a) 5 h, (b) 10 h, and (c) 15 h.

as catalyst for the formation of CNTs. With the (111) and (311) graphene planes of nickel providing strong epitaxial fits with graphite,[10] CNTs were perfectly formed. Further studies on the mechanistic details are in progress.

In conclusion, by a one-step solid-state thermolysis of the Ni-MOF in one-port sealed quartz tube furnace, we have successfully controlled the growth of large-scale MCNTs with high yield and achieved the transformation of an MOF to CNTs. This is an unprecedented approach for the fabrication of CNTs and also opens another gateway for applications of MOFs. Compared with the reported methods for the synthesis of CNTs, the advantage of this synthetic route lies in its simplicity including easy synthesis, environmental friendliness with use of a benign precursor, relatively low temperature, and providing carbon sources and catalysts during thermolysis process at the same time, as well as high yield of CNTs product. This process also builds a linkage between MOFs and CNTs.

Notes and references

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