Uniform Carbon and Carbon/Cobalt Nanostructures by Solid-State Thermolysis of Polyphenylene Dendrimer/Cobalt Complexes

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Uniform Carbon and Carbon/Cobalt Nanostructures by Solid-State Thermolysis of Polyphenylene Dendrimer/Cobalt Complexes**

By *Bassem El Hamaoui, Linjie Zhi, Jishan Wu,** Ute Kolb*, and *Klaus Müllen**

In the pursuit of novel high-performance materials, great interest has been devoted to both tubular and spherical carbon nanoclusters.[1] Encapsulation of foreign metal nanoparticles,

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especially magnetic Fe, Co, and Ni, inside carbon spheres prevents their environmental degradation and allows the use of magnetic carbon/metal nanoparticles in information-storage media and as catalysts in medicinal chemistry.[2] Laser ablation, arc discharging, and chemical vapor deposition have been employed to prepare carbon nanotubes (CNTs), however, in all cases, the products contained unwanted amorphous carbon and catalyst particles, which resulted in a tedious purification process. While carbon-coated metal nanostructures have been prepared by arc discharge processes[2a–c] and solid pyrolysis of surfactant-wrapped metal particles,[2e] a general high-yielding synthetic method towards uniform carbon/metal nanostructures is still a challenge. The solid-state pyrolysis of organometallic complexes has recently emerged as an alternative method towards novel carbon and carbon/metal nanostructures. However, mixtures of metal particles with CNTs, carbon onions, and amorphous carbon structures were usually obtained.[3–5] Ethynyl-functionalized polyphenylene dendrimers can serve as precursors because of their carbon-rich character and facile complexation with cobalt carbonyl at the peripheries.[6] Herein, we demonstrate that the solid-state thermolysis of polyphenylene dendrimer/cobalt complexes affords i) uniform carbon/cobalt nanorods with special cross-sections never before reported, ii) carbon/cobalt nanospheres, and iii) CNTs, depending on the molecular structures of the precursors and heating procedures.
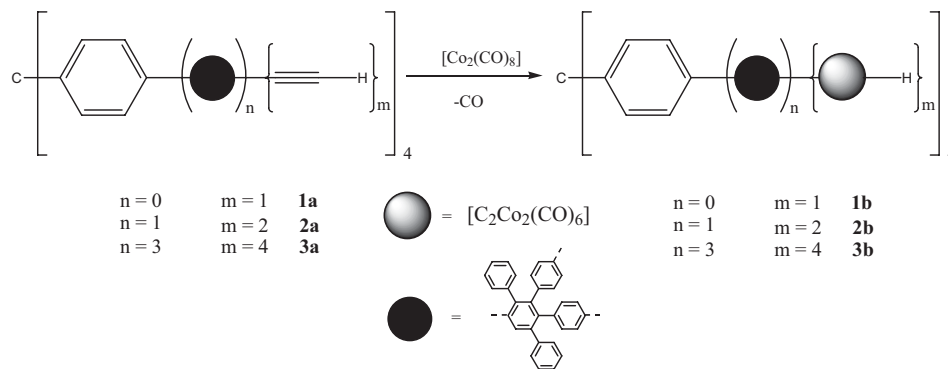
The ethynyl moieties surrounding the polyphenylene dendrimers **1a**, **2a**, and **3a**[7] can be readily complexed by reaction with excess $[Co_2(CO)_8]$ to result in dendrimers **1b**, **2b**, and **3b**, which contain multiple $[C_2Co_2(CO)_6]$ cluster sites in 45, 35, and 37 % yields, respectively (Scheme 1).[8] The incorporation of the metal carbonyl units is confirmed by three strong absorption bands in the Fourier-transform infrared (FTIR) spectra in the region of 2019–2094 cm^{-1} (ν_{Co-CO}), which is typical for $[Co_2(CO)_6RCCR]$ clusters. The ^1H and ^{13}C NMR spectra disclose obvious signal shifts for the protons and carbons of the ethynyl groups, which indicates a complete complexation (S-Fig. 1 in Supporting Information (SI)).

Powders of **1b**, **2b**, or **3b** were placed in a quartz tube and sealed under vacuum. Each compound was first heated to the decomposition temperature (determined by thermogravimetric analysis) and maintained at this temperature for about two hours. They were then heated to a higher temperature at different heating rates and held at these temperatures for different periods of time. After cooling to room temperature, the obtained solid samples were submitted to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis.

Compound **1b** burns in the solid-state upon slight scratching. Surprisingly, heating **1b** at 130 °C for two hours in a quartz tube resulted in a high yield of regular rod-like structures with diameters ranging from 200 to 500 nm (Fig. 1a and S-Fig. 2a in SI). TEM images show that the rod-like structures are composed of uniformly dispersed amorphous carbon and Co nanoparticles with diameters around 1–2 nm (Fig. 1b). The monodisperse Co nanoparticles arise from the decompo-

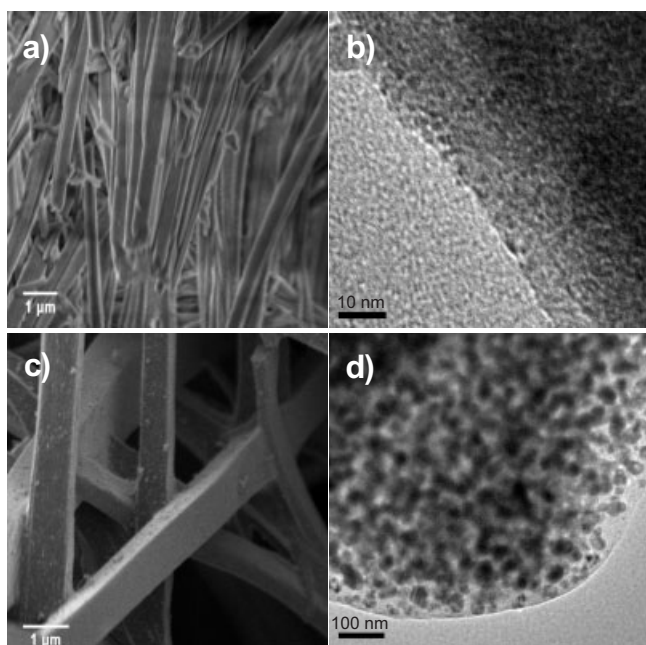**Scheme 1.** Synthesis of polyphenylene dendrimer/cobalt complexes.

Figure 1. SEM (a,c) and TEM (b,d) images of the obtained carbon/Co materials from **1b**: a,b) heating at 130 °C for two hours (2.2 °C min⁻¹ from room temperature); c,d) further heating at 800 °C for 8 h (5.6 °C min⁻¹ from 130 °C).

sition of $[C_2Co_2(CO)_6]$ clusters as previously reported by Vollhardt et al.[3] After rapid heating (> 5 °C min⁻¹) and further pyrolysis at 600 °C for 8 h, nanorods with both rectangular and cylindrical cross-sections were formed with diameters of 200–300 nm and lengths of up to tens of micrometers (S-Figs 2b,c in SI). Upon heating **1b** at 800 °C for 8 h, SEM images revealed that uniform nanorods with a unique rectangular cross-section and a cross-section width of 0.8–2 μm were obtained in high yield (Fig. 1c and S-Fig. 2d in SI). TEM analysis disclosed that the rods formed at both 600 and 800 °C were still composed of well-dispersed carbon and Co nanoparticles, however, the diameters of the particles are larger for the latter (20–40 nm) (Fig. 1d). The formation of unique nanorods with a rectangular cross-section is surprising and

should be related to the original morphology during the 'exothermic' decomposition of **1b** at 130 °C. The sizes of the Co nanoparticles increase with prolonged heating time and increased temperature, probably due to the coalescence of small nanoparticles.

The nanorods produced at 600 °C show high resistance to acid, for example, treatment of the sample with 53 % HNO_3 over several days did not destroy the regular structures, which suggests that these well-dispersed carbon/Co materials are candidates for magnetic applications such as ferrofluids,[9] catalysts,[10,12] and ultrahigh-density storage media.[11] The magnetic separability of the carbon/Co materials obtained after pyrolysis at 600 and 800 °C was tested by placing a magnet near the glass vial. The black powder was attracted by the magnet, which confirms that these materials are magnetic.[2]

The nanorods are composed of both a carbon source and catalytically active Co nanoparticles, which suggests the fabrication of novel carbon or carbon/Co nanostructures under slow heating procedures (1.5 °C min⁻¹). This leads to the 'growth' of CNTs from the surface of the nanorods where the cobalt particles (catalyst) are located on the tip of the formed nanotubes (Figs 2a,b). The interior of the rods is still composed of carbon and cobalt nanoparticles. The growth of the CNTs suggests that the nanorods serve as a feedstock for both carbon and catalyst and act as a support for the growth.

Thermolysis of **1b** in the presence of tetraphenylmethane (**1c**) as an additional carbon source (at ratios of **1b**/**1c** between 1:1 and 1:2) increased the amount of CNTs on the surface of the nanorods, which still possess a rectangular cross-section (S-Figs 3a–c in SI). A **1b**/**1c** ratio of 1:4 led to irregular tree-like nanostructures, in which small carbon/Co nanorods were grown from the main 'trunk' (Fig. 2c), while a 1:8 ratio gave large amounts of uniform CNTs accompanied by amorphous material (Fig. 2d and S-Fig. 3d in SI). Hence, the carbon/Co nanorods formed from **1b** can be used as catalytic centers as well as for templates for further CNT formation from the rods.[12]

SEM images of the pyrolysis products from the higher generation dendrimers **2b** and **3b** under a fast heating rate (> 4 °C min⁻¹) reveal uniform spherical structures that contain both cobalt nanoparticles and carbon (Fig. 3c, and S-Fig. 4d
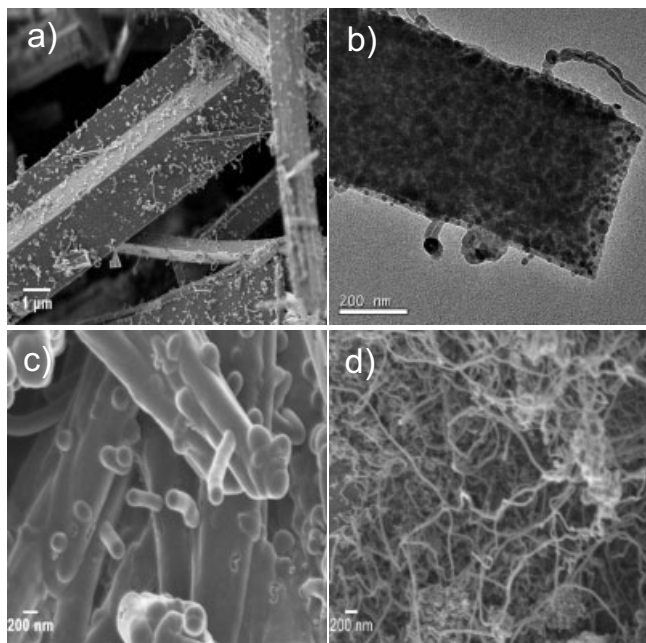
Figure 2. a) SEM and b) TEM images of the carbon/Co materials obtained from **1b** after slow heating (1.5 °C min^{-1} from 130 °C) to 800 °C and holding for 8 h; and SEM pictures of materials after thermolysis of a mixture of **1b/1c** at different ratios: c) 1:4, and d) 1:8 (heating from room temperature to 130 °C at 2.2 °C min^{-1} for 2 h, and then to 800 °C at 1.1 °C min^{-1} for 8 h).

in SI). TEM images reveal that the spheres consist of cobalt nanoparticles covered with semicrystalline carbon shells and metal-free graphitic onions (S-Fig. 4c in SI). At a lower heating rate, multiwalled CNTs grow at the surface of the nanospheres (Figs 3a,b, and S-Fig. 4a,b in SI). Again, a slow heating rate and longer holding time results in CNT formation, probably due to the improved diffusion of the carbon over the Co nanoparticles.

Electron diffraction analysis of the Co particles formed in this work reveal the formation of a new cobalt crystal other than cubic close-packed (ccp) and hexagonal close-packed (hcp). A regular hexagonal lattice structure with parameters of 2.5 and 16 Å is observed. Co crystals of this new structure

were recently reported by Zhi et al.[13] and were obtained from the solid-state pyrolysis of Co/phthalocyanine.

In conclusion, when subjected to solid-state thermolysis under vacuum, polyphenylene dendrimer/cobalt complexes yielded i) carbon/Co nanorods with unprecedented cross-sections, ii) carbon/Co nanospheres (under fast heating rates), and iii) CNTs (under slow heating rates). Nanorods of the shape and composition observed here have never before been reported. These carbon/metal materials could be regarded as carbon and catalyst sources and as templates for CNT formation from the surface of the rod or sphere under controlled heating procedures. The unique carbon nanorods are candidates for nanoelectrodes as well as templates for the catalytic growth of novel carbon nanostructures. The core/shell carbon/cobalt nanostructures also have potential applications in catalytic electron-transfer reactions and as magnetic materials.[2]

Experimental

The synthesis of **1b** is given as an example for the clustering reactions of dicobalt octacarbonyl on the dendrimers with peripheral ethynyl functionalities: [$Co_2(CO)_8$] (1642 mg, 4.8015 mmol) was added to **1a** (100 mg, 0.24 mmol) dissolved in CH_2Cl_2 (8 mL) under an argon atmosphere; the mixture was stirred for 3 days, and the solvent was then removed under vacuum. After chromatographic work-up with petroleum ether/dichloromethane as eluent, the title product was obtained as a red powder in 45 % yield. FTIR (KBr pellet): 2019 (s), 2054 (s), 2094 cm^{-1} (vs, CO); ^{1}H NMR (250 MHz, CD_2Cl_2, room temperature (rt)): $\delta = 7.47$ (d, $J^3 = 8.5$ Hz, 8H, CH$_{arom}$.), 7.25 (d, $J^3 = 8.2$ Hz, 8H, CH$_{arom}$.), 6.44 (s, 4H, CH); ^{13}C NMR (75 MHz, CD_2Cl_2, rt): $\delta = 199.7$, 146.4, 135.9, 131.6, 129.9, 90.0 (C$_{Cluster}$), 73.7 (C$_{Cluster}$), 65.3 (C$_{quat}$).

Compound **2b** was prepared as described above for compound **1b** to give a red powder, yield 35 %: FTIR (KBr pellet): 2023 (s), 2054 (s), 2093 cm^{-1} (vs, CO). ^{1}H NMR (250 MHz, CD_2Cl_2, rt): $\delta = 7.61$ (s, 4H, CH$_{arom}$.), 7.16–6.67 (m, 88H, CH$_{arom}$.), 6.28, 6.26 (2 × s, 8H, CH). ^{13}C NMR (75 MHz, CD_2Cl_2, rt) $\delta = 199.9$, 144.9, 141.8, 141.4, 141.3, 141.1, 140.9, 140.6, 140.1, 139.9, 139.8, 139, 135.2, 134.8, 132.4, 132.3, 132, 131.4, 130.7, 130.3, 129.4, 129.1, 128, 127.2, 126.7, 125.9, 90.5 (C$_{Cluster}$), 90.4 (C$_{Cluster}$), 63.9 (C$_{quat}$).

Compound **3b** was prepared as described above for compound **1b** and obtained as a red powder, yield 37 %: FTIR (KBr pellet): 2021 (s), 2052 (s), 2092 cm^{-1} (vs, CO). ^{1}H NMR (250 MHz, CD_2Cl_2, rt): $\delta = 7.51$ (s, 4H, CH$_{arom}$.), 7.47 (s, 4H, CH$_{arom}$.), 7.42 (s, 4H, CH$_{arom}$.), 7.40–6.40 (m, 232H, CH$_{arom}$.), 6.26, 6.25 (2 × s, 16H, CH$_{arom}$.). ^{13}C

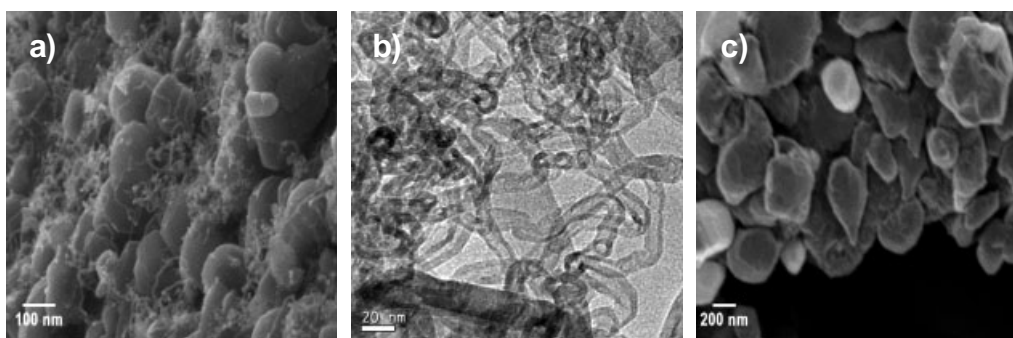**Figure 3.** a) SEM and b) TEM images of the obtained thermolysis product from **3b** under slow heating from 200 to 900 °C at 2 °C min^{-1} and holding for 24 h; c) SEM of the nanospheres formed under fast heating from 200 to 800 °C at 5 °C min^{-1} and holding for 8 h.

NMR (125 MHz, CD$_2$Cl$_2$, rt): $\delta = 200.0$, 144.9, 142.3, 141.9, 141.7, 141.5, 141.2, 140.7, 140.6, 140.2, 140.0, 139.8, 139.7, 139.2, 138.9, 138.6, 135.2, 134.8, 132.5, 132.4, 132.0, 131.6, 130.7, 130.4, 129.4, 129.1, 128.8, 128.0, 127.3, 126.8, 126.1, 90.7 (C$_{Cluster}$), 90.6 (C$_{Cluster}$), 73.1 (C$_{Cluster}$), 73.0 (C$_{Cluster}$).

^{1}H and ^{13}C NMR spectra were recorded in deuterated solvents, such as CD$_2$Cl$_2$, on a Bruker DPX 250 and a Bruker DRX 500 spectrometer, using the proton or carbon signal of the solvent as an internal standard. The thermolysis reactions were carried out in sealed quartz tubes in a temperature controlled electromagnetic oven. SEM measurements were performed on a LEO 1530 field-emission scanning electron microscope. High-resolution TEM studies were conducted on a Philips Tecnai F30 analytical TEM at an operating voltage of 300 kV and on a TEM EM420 electron microscope at an operating voltage of 120 kV. The samples were dispersed in ethanol under ultrasonic irradiation and the suspension was dropped onto a TEM copper grid with a carbon film. TGA measurements were performed on a Mettler Toledo TS0801R0 device at a heating rate of 10 °C min^{-1} between 0 and 900 °C under an inert atmosphere.

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Using Resonance Energy Transfer to Improve Exciton Harvesting in Organic–Inorganic Hybrid Photovoltaic Cells**

By *Yuxiang Liu*, *Melissa A. Summers*, *Carine Edder*, *Jean M. J. Fréchet*, and *Michael D. McGehee**

Polymer-based solar cells[1,2] share many common features with other types of organic solar cells,[3] which are collectively called "excitonic solar cells".[4] The operation of excitonic solar cells is fundamentally different from that of conventional solar cells in that the absorption of photons creates Frenkel-type excitons with a binding energy around 0.4–1 eV.[5] Because of the large binding energy, excitons can only efficiently dissociate at a heterojunction interface with favorably offset energy levels. The exciton diffusion length of most conjugated polymers is less than 10 nm,[6,7] which is much smaller than the optical absorption path length, even at the maximum absorption wavelength. To use materials with small exciton diffusion lengths and make reasonably efficient cells, electron donor and acceptor materials have been blended into bicontinuous structures known as bulk heterojunctions.[8–21] In these cells, the size of each phase should be comparable to or less than the exciton diffusion length so that excitons can reach the interface before geminate recombination. However, for organic semiconductors that are highly immiscible, controlling

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