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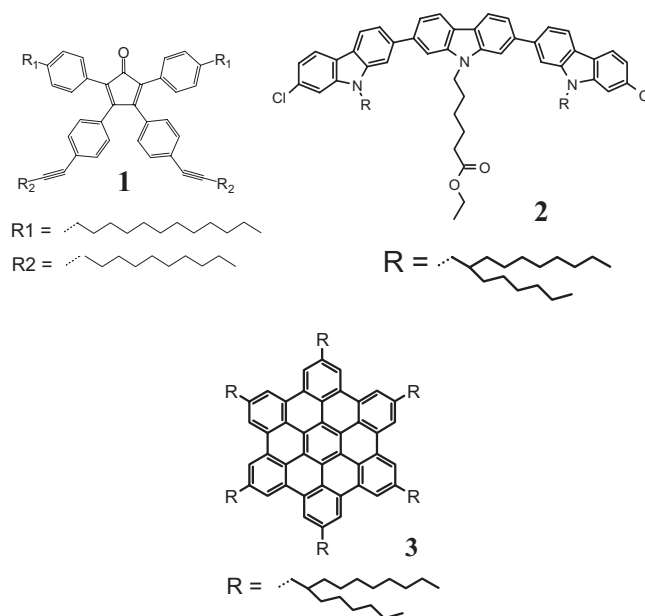
# From Well-Defined Carbon-Rich Precursors to Monodisperse Carbon Particles with Hierarchic Structures\*\*

By Linjie Zhi,\* Jianjun Wang, Guanglei Cui, Marcel Kastler, Bruno Schmaltz, Ute Kolb, Ulrich Jonas, and Klaus Müllen\*

The creation of nanoscale particles with well-defined structures has long been considered as a promising approach to generate materials with novel properties. Carbonaceous nanoparticles (CNPs) with defined architectures, such as carbon nanotubes (CNTs), C<sub>60</sub>, carbon onions, carbon spheres, and carbon rods are particularly attractive owing to their unique electronic properties and many potential applications.<sup>[1]</sup> At the same time, when these CNPs are regularly organized, additional functions appear.<sup>[2]</sup> Such materials are believed to have hierarchic structures,<sup>[3]</sup> in which the organization of the CNPs forms the first-order structure (FOS) and the configuration of the single CNP forms the second- or higher-order structure (SOS or HOS). Because both the FOS and HOS are responsible for the properties of the bulk material, simple methods to prepare multidimensional carbon materials with hierarchic structures are needed. Template methods are commonly used to produce 3D order in which the silica opal or inverse opal crystals are the most frequently selected templates.<sup>[3b,4]</sup> Carbonaceous materials have been prepared in these templates by using sucrose or phenolic reactants as precursors,<sup>[5]</sup> but only amorphous CNPs were obtained. Alternatively, chemical vapor deposition (CVD) over inverse opals was reported to produce crystalline carbons.<sup>[4a]</sup> Unfortunately, such CVD procedures resulted in inverse carbon opals, not CNPs, and the control over the carbon structures was limited. The preparation of well-defined CNPs with 3D organization is still a challenge owing to the difficulties of controlling molecular interactions at high temperatures.

Recent studies on solid-state pyrolysis (SSP) have implied that the structures of CNPs could be controlled by choosing well-defined organometallic precursors.<sup>[6–9]</sup> Thus, CNTs were

obtained in high yield from SSP of diphenylethyne-metal complexes,<sup>[6]</sup> while dicobalthexacarbonyl-functionalized poly(*p*-phenyleneethynylene) afforded carbon-cobalt spheres.<sup>[7]</sup> Our previous SSP of dendritic polyphenylene-cobalt complexes resulted in uniformly shaped carbon-cobalt nanorods with rectangular cross sections,<sup>[8]</sup> whereas disclike structures with extended  $\pi$ -systems furnished bamboolike CNTs and carbon shell/metal core cablelike structures.<sup>[9]</sup> However, in all these experiments, the metal catalysts play a more important role for product formation than the chemical structure of the precursors; and these processes incorporate metals into the pyrolysis products. To prepare metal-free CNPs with defined structures, the design of the precursors requires more attention. Our recent attempts at precursor-defined pyrolyses (PDP) produced graphitic nanotubes with brick-walled structures<sup>[10]</sup> and CNTs with 3D porous-walled structures.<sup>[11]</sup>



Herein, we combine PDP and template methods to develop a general approach towards CNPs with hierarchic structures. Three carbon-rich molecules with totally different functionalities and thermal behaviors were chosen as precursors. The principle of choosing precursors is that the starting compound should contain at least two parts; one part must lead to the carbon material in high yield after pyrolysis, while the other

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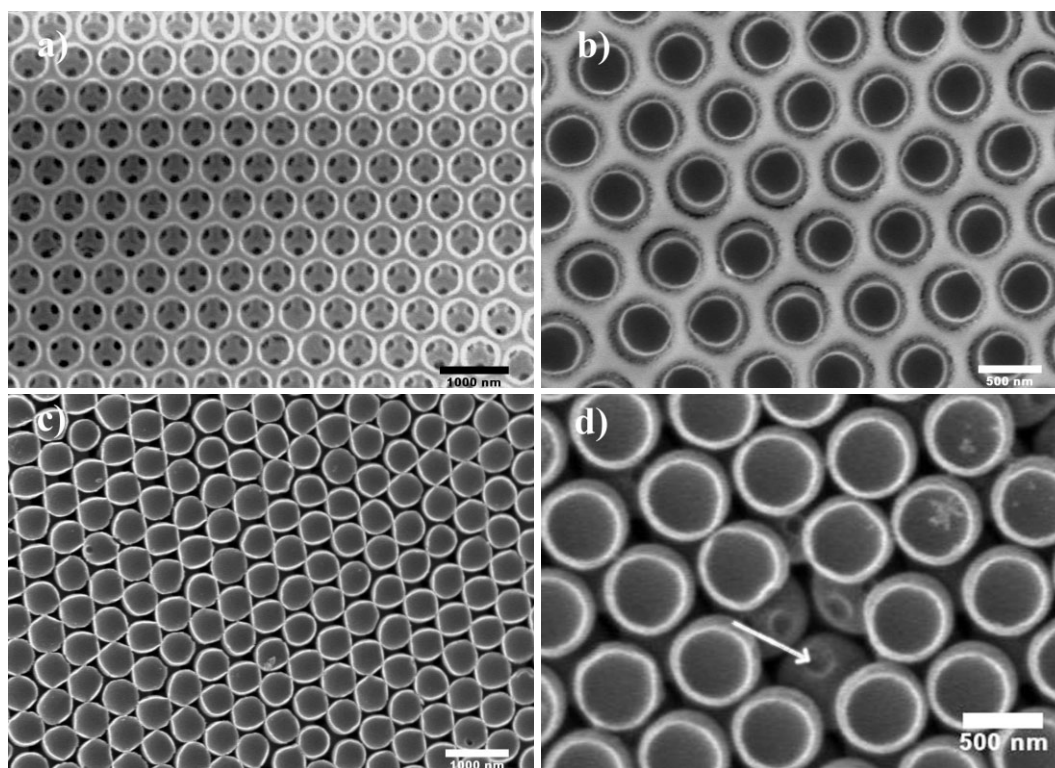
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part must supply flexibilities for processing and for multifunctionalization of the CNPs. In this work, compounds with a rigid  $\pi$  part and a soft alkyl part were designed as precursors. Well-organized monodisperse CNPs, such as spherical particles with 3D porous structures, hollow carbon orbs containing small Pt particles, and graphitic microbeads with or without slits were obtained. CNPs with totally different FOS and HOS were thus controllably prepared by using structurally different precursors.

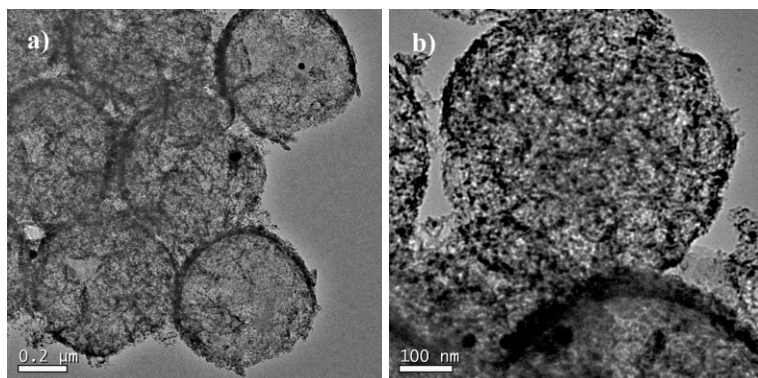
The cyclopentadienondiene and alkyne dienophile units of **1** can react in an intermolecular Diels–Alder cycloaddition to form thermally stable hyperbranched polyphenylenes. The long alkyl chains ( $R_1$  and  $R_2$ ) makes **1** solution processible and susceptible to yield porous structures at high temperatures.<sup>[11]</sup> A 3D macroporous silica inverse opal was chosen as a template (Fig. 1a) and **1** was introduced into the pores of the template by drop-casting a tetrahydrofuran (THF) solution of **1** on the inverse opal. Stepwise heating of the **1**-loaded template at 250 °C for 2 h and then 350 °C for 2 h under argon produced crosslinked hyperbranched polyphenylene,<sup>[11]</sup> which was further pyrolyzed at 600 °C for 5 h to result in carbonaceous particles inside the pores of the silica inverse opal (Fig. 1b). After removing the template by using a dilute HF solution, well-aligned, monodisperse CNP films were obtained (Fig. 1c). These films were constructed layer by layer; and every layer was composed of orderly organized CNPs. Interestingly, two kinds of CNPs were formed in this case. The

CNPs in the top layer of the film were semispheres with a bowl-shaped wall structure (Supporting Information S-Fig. 1). Obviously, these semispheres originate because of the particular morphology of the top layer inverse opal shown in Figure 1a. The openings of the opal were formed, during the template preparation, from partial coverage of the top-layer polystyrene (PS) microparticles with silica nanoparticles before pyrolysis (Supporting Information, S-Fig. 2, see also the Experimental for details).<sup>[12]</sup> The formation of the bowl shape was probably due to the surface tension of the melt composed of **1** and the small contact angle between the melt and the silica surface at high temperatures. Inside the film, spherical carbon particles were found (Fig. 1d and S-Fig. 1). The diameter of the spheres was smaller than that of the original PS spheres used for inverse-opal preparation, possibly due to the shrinking of the precursors during thermal treatment. The overall thickness of the CNP film could be varied by tuning the number of layers in the templating colloid crystals.

As expected, these CNPs were highly porous (Fig. 2). Transmission electron microscopy (TEM) characterization showed that the channels were connected with each other to form a 3D porous SOS (Fig. 2b). The pores have different sizes, and most of them are smaller than 10 nm, leading to a huge surface area within the spheres. In contrast, the minimal heat treatment of the template loaded with **1** to 350 °C resulted in solid spheres without porous structures. This was due to the thermal behavior of **1**. According to differential scan-



**Figure 1.** SEM images of a) a silica inverse opal template, b) carbonaceous materials formed within the template, and c) well-organized CNPs obtained after removing the template. d) Carbon spheres (as indicated by the arrow) were aligned underneath the bowl-shaped semispheres.



**Figure 2.** TEM images of a) well-organized porous carbon spheres and b) magnified spheres with 3D highly porous structures treated at 600 °C.

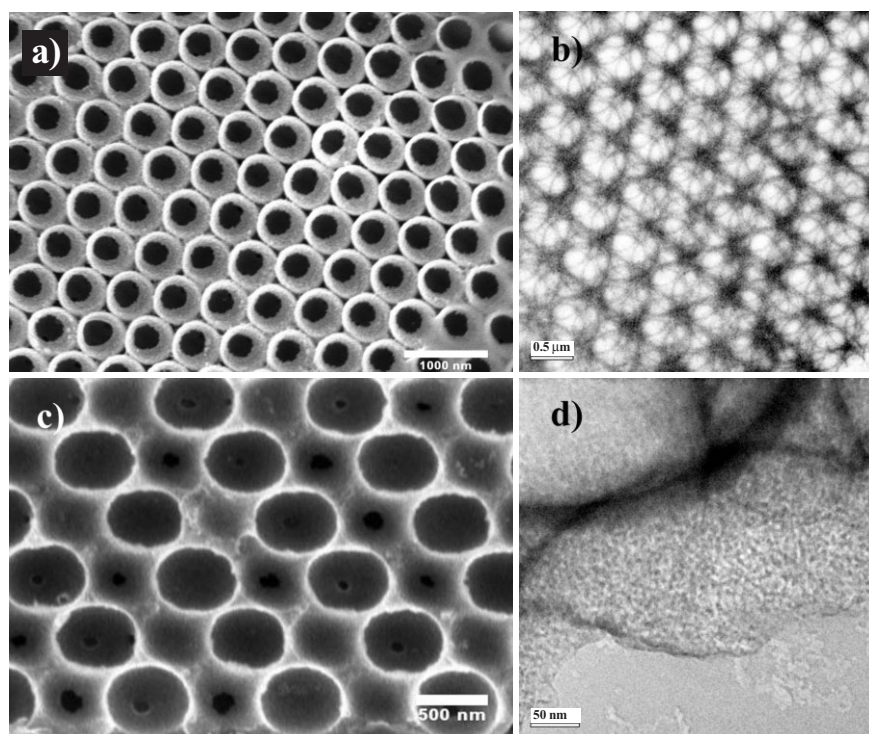
ning calorimetry (DSC) and thermogravimetric analysis (TGA) only crosslinking reactions between the precursor molecules occurred below 380 °C. Only at temperatures higher than 400 °C did the alkyl chains of **1** begin to cleave. One can speculate that an increase of the temperature to 600 °C resulted in a complete decomposition of the alkyl chains, which then evaporated through the cavities and left a porous structure.

Stepwise pyrolysis was necessary to ensure complete crosslinking of **1** at intermediate temperature to obtain thermally stable polyphenylene materials, which then formed the carbonaceous frameworks of the porous spheres after carbonization at 600 °C. This is the first example of the preparation of highly porous carbon spheres by controlled decomposition of alkyl chains of the crosslinked precursor. These interesting CNPs hold promise as absorbents for hydrogen storage, gas sensors, and catalyst supports.

Besides the concept of producing porous structures through the pyrolyses of alkylated hyperbranched polyphenylenes, other strategies for forming multifunctional CNPs are possible by PDP. Precursor **2**, i) is again a combination of a rigid  $\pi$ -part and a soft alkyl part, ii) is an electron-rich species with heteroatoms that offer the potential for complexing metals, and iii) contains chloro substituents that could facilitate crosslinking upon thermal treatment. CNPs obtained by PDP from **2** (Fig. 3) are hollow carbonaceous spheres. These CNPs were aligned in an ordered fashion and most of them stuck together, thereby forming a porous FOS, that is, a CNP membrane (Fig. 3a). This is obviously the replica of the silica inverse opal template. At the same time, the

hollow macropores (> 50 nm) of every CNP produced the SOS of the membrane. The highly porous shell of every hollow sphere, containing mesopores (from 2 to 50 nm) with an average pore size below 10 nm, gave rise to the unique HOS of the membrane. In a subsequent step, metal particles could be introduced into the CNPs by an in situ reduction method.<sup>[13]</sup> When a mixture of **2** and hexachloroplatinic acid was loaded into the silica template, stepwise heat treatment of the mixture at 300 °C for 2 h, at 400 °C for 2 h, and then at 450 °C for 2 h allowed very small Pt particles (5 nm) to disperse homogeneously in the shell of the carbon hollow spheres (Fig. 3d). These porous carbon-supported Pt particles are expected to have applications as high-performance catalysts.

The formation of hollow CNPs from **2** suggested that homogeneous films were produced on the surface of the silica. These films probably resulted from the strong interactions between **2** and the silica surface and the subsequent crosslinking reactions among **2** at high temperatures. According to TGA (Supporting Information), the weight loss of precursor **2** at 500 °C is about 53 %, which is close to the weight percent of alkyl chains in **2**, suggesting the complete loss of alkyl chains and the formation of thermally stable crosslinked carbon-rich frameworks, where the carbazole units were mostly main-



**Figure 3.** Scanning electron microscopy and TEM images of well organized carbonaceous hollow spheres obtained by the PDP method using compound **2** as a precursor. a,b) Top view of the aligned hollow spheres showing the face centered cubic (fcc) (111) plane of the film. c) Side view of the membrane revealing the fcc (110) plane. d) High-resolution TEM image showing homogeneously dispersed small Pt particles in the wall structure of the hollow spheres.

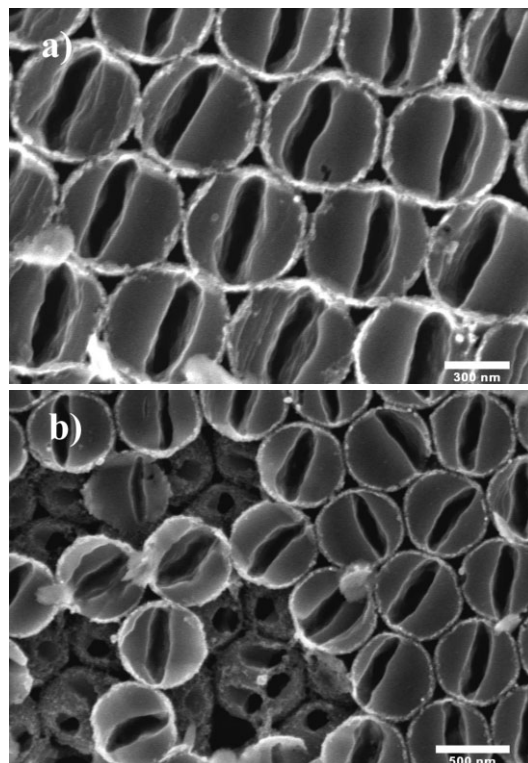


tained. After removing the template, the film that had previously covered the silica surface was released from the silica to form a replica of the inverse opal. In addition, the small Pt particles dispersed in the carbon matrix can tentatively be ascribed to the existence of nitrogen-rich species in the precursor.<sup>[14]</sup> Due to the optical<sup>[15]</sup> and electronic<sup>[16]</sup> properties of poly(2,7-carbazole), interesting photovoltaic behaviors of these hierarchic-structured, carbon-rich membranes can be expected.

Precursor **3** is a typical discotic mesogen,<sup>[17]</sup> and tends to form columnar aggregates owing to the pronounced aromatic  $\pi$ -stacking between the discs. Compared with hexa(4-dodecyl-phenyl)-*peri*-hexabenzocoronene (HBC-PhC12), compound **3** has very good solubility in organic solvents because of the branched long alkyl chains and because the melting point (96 °C) is low, allowing processing from solution or from the melt. Compound **3** thus appears to be an ideal precursor for the pyrolytic formation of graphitic species.

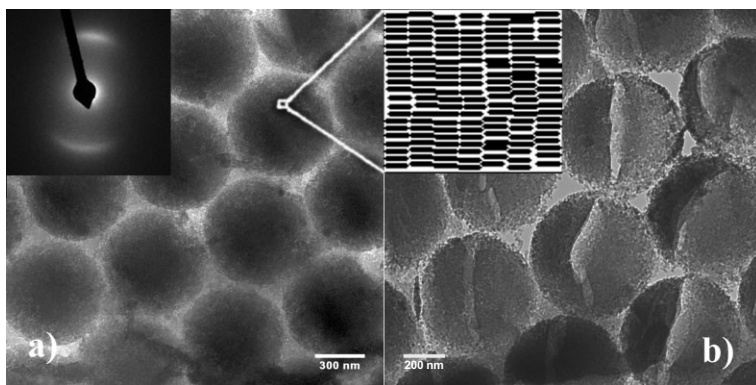
After stepwise thermal treatment of the **3**-loaded inverse opal at 400 °C for 2 h, 500 °C for 2 h, and then at 600 °C for 5 h, CNPs were formed in the pores of the template. After removal of the template, carbonaceous spheres were obtained, as shown in Figure 4. These monodisperse CNPs were organized layer by layer into an ordered lattice. Interestingly, the spheres of the top layer have a special shape compared to the bowl-shaped semispheres formed from **1**. These top-layer spheres were also bowl-shaped semispheres (SI, S-Figure 3), but with a slit on the bottom of the bowl (Fig. 4a). One of the possible reasons for this outcome is the crystallization of the molecular discs during heat treatment, leading to a density change of the sphere by shrinking and splitting of the solid surface. Underneath these slit-containing bowls, carbon spheres with several pits on the surface were formed (Fig. 4b). Generally, these pits came from the sinter necks of the inverse-opal template, which were produced during the preparation of the template.<sup>[18]</sup> However, these sinter necks are more obvious than those formed from **1** (Fig. 1d arrow), suggesting stronger surface tension and crystalline behavior of precursor **3** during heat treatment.

TEM characterization demonstrated that most of the bulk CNPs were completely filled particles (Fig. 5a) and, in the top layer, bowl-shaped semispheres were formed (Fig. 5b). In this case, well-organized CNPs formed the FOS. The SOS was represented by the fully filled particles and slit-containing spheres, which were formed mainly due to the structure inducement of the precursor, **3**. Interestingly, besides FOS and SOS, HOS could also be tuned by choosing different precursor structures. Selected area electron diffraction characterization (inset of Fig. 5a) disclosed that the CNPs shown in Figure 5 were constructed from aligned discotic structures with a distance of 0.35 nm between discs, suggesting a graphitic structure (inset of Fig. 5b). This is obviously due to the  $\pi$ -aromatic stacking and prearrangement of the discotic pre-



**Figure 4.** SEM images of CNPs obtained by thermal treatment of compound **3** in the template; a) top-layer sphere with bowl-shaped morphology and slit structures, b) underneath the top layer, ball-shaped spheres were formed.

cursor molecules. Conductivity measurements of the CNPs showed that the product, obtained after thermal treatment of **3**, was semiconducting (the surface resistance of the film measured by a 4-probe method is about 100 M $\Omega$ ) and thus attractive for fabrication of microelectronic devices. At the same time, a large number of graphenes was anchored on the surface of the carbon spheres with their edges exposed to the



**Figure 5.** TEM images of the obtained carbon spheres by thermal treatment of compound **3**; the inset of a) shows the electron diffraction pattern of the carbon spheres; the inset of b) illustrates the graphitic structures of the spheres formed by stacking of the discotic precursors.

outside of the spheres, providing highly active<sup>[10]</sup> CNPs for further chemical functionalizations.

In summary, a general method for preparing CNPs with controllable hierarchic structures FOS, SOS, and HOS was developed by combining the PDP and the template method. The structures of the organic precursors determine the SOS and HOS of the obtained CNPs. CNPs with 3D mesoporous SOS were achieved by thermal decomposition of alkyl chains, while graphitic spheres were obtained when a discotic molecule was chosen as the precursor. Multifunctional CNPs with unique SOS with hollow macropores and interesting HOS-containing mesopores incorporating small metal particles were formed by PDP. At the same time, other templates with different architectures could also be used in this method to produce CNPs with novel FOS. This method is expected to provide versatile access to CNPs with unique hierarchical structures for potential applications as functional materials in energy storage, electron transport, catalytic reactions, and biochemical interactions.

## Experimental

The porous silica opals were prepared by depositing a bimodal colloidal mixture of 626 nm PS particles and 6 nm silica nanoparticles in suspension by vertical lifting on quartz substrates. Pyrolysis of this binary colloidal structure resulted in an inverse opal with interconnected macropores [12]. Compounds **1** [11], **2** [19], and **3** [17] were synthesized according to procedures described elsewhere. The compounds were dissolved in THF (for **1** and **3**) or acetone (for **2**) (5–30 mg mL<sup>-1</sup>), and the solution was introduced into the template by drop-casting. The amount of substance loaded into the template can be controlled by the concentration of solution and by the volume of solution applied to the silica template. All the heat treatments of the samples were carried out on quartz slides in an electric furnace under an argon atmosphere. The templates were dissolved in a 5 % aqueous HF solution. The template-free samples were washed with water and ethanol, dried under vacuum, and subjected to further characterization. Scanning electron microscopy measurements were performed on a LEO 1530 field emission scanning electron microscope. TEM studies were conducted on a Philips EM420 electron microscope operating at 120 kV. DSC measurements were performed on a Netsch DSC 200 instrument (Germany) at a scanning rate of 10 K min<sup>-1</sup>. TGA measurements were recorded on a Mettler TG50 thermobalance.

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