Nanostructures

Well-Defined Carbon Nanoparticles Prepared from Water-Soluble Shell Cross-linked Micelles that Contain Polyacrylonitrile Cores**

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Carbon-based materials have traditionally played an important role in modern technologies, ranging from the manufacture of everyday-use products such as automobile tires (carbon fillers), through reinforcements in composites (carbon fibers), electrode materials for a variety of processes, to activated carbons widely used in separation techniques, to name just a few. In addition to those commodity materials, in recent decades there has been a dynamic growth in the area of advanced engineering carbon materials. Seminal events in this area include the development of synthetic diamond and highly oriented pyrolytic graphite in 1960.[1,2] In the last two decades, this field has been particularly reenergized by the discovery of fullerenes in 1985[3] and carbon nanotubes in 1991.[4] In addition to generating tremendous fundamental interest, these nanostructured forms of carbon have found, or are expected to find, numerous applications such as advanced fillers,[5,6] materials for energy and gas storage,[7,8] templates,[9] nanoprobes and sensors,[10] and elements for molecular electronics devices.[10,11] Two main groups of strategies for the preparation of engineering carbon materials include:[12,13] 1) pyrolysis of organic precursors (mostly polymeric) under inert atmosphere to yield large-scale engineering carbon materials and 2) physical/chemical vapor deposition techniques to produce well-defined nanostructured forms of carbon. Whereas techniques from the first group are applicable to large-scale production, they offer very limited control of the carbon (nano)structure. Techniques from the second group, while allowing for atomic-scale precision in nanostructure control, are relatively expensive, have limited yield, and require complex equipment.

Recently, we developed a novel, low-cost route to well-defined nanostructured carbon materials based on the pyrolysis of block copolymer precursors that contain polyacrylonitrile (PAN) and a sacrificial block (e.g., poly(*n*-butyl acrylate).[14,15] By this method, the carbon nanostructure is templated after the nanostructure of the PAN domains, which are formed through self-assembly and driven by phase separation between PAN and the sacrificial block. Upon pyrolysis, PAN domains are converted into increasingly graphitic carbon, whereas the sacrificial phase is volatilized. The prerequisite for this approach is the ability of the PAN domains to retain their nanostructure upon thermal treatment. The necessary stabilization is achieved through thermal treatment (heating in the presence of air to 230 °C), a process well-known in the field of carbon fibers,[16] which causes the PAN precursor to form cyclic, ladder, and eventually cross-linked species. Nanostructured carbon materials derived through this novel route hold considerable promise in many areas such as: field emitters, supercapacitors, and photovoltaic cells. One appealing advantage of this approach is the possibility of combining it with currently used device-fabrication techniques that rely on thin-film processing and lithography. One of the potential issues here, however, is the processability of the precursors: PAN and its block copolymers are soluble in a narrow range of solvents such as: *N*,*N*-dimethylformamide (DMF), ethylene carbonate (EC), dimethylsulfoxide and *N*-methylpyrrolidone (NMP).

As one of the possible ways of addressing this challenge, herein we present an alternative approach, which now relies on the use of covalently stabilized micellar precursors that are soluble in aqueous systems. These precursors belong to a class of shell cross-linked nanoparticles (shell cross-linked knedels, SCKs), formed by self-assembly and covalent stabilization of amphiphilic block copolymers.[17–22] PAN block constitutes the core of the SCKs and the sacrificial block (e.g., poly(acrylic acid), PAA) forms a water-soluble shell, and some of the carboxylic acid groups from the PAA block within the shell layer are covalently cross-linked following the micellization process, which occurs in a mixture of DMF and water.

The use of nanostructured amphiphilic block copolymers as a template to form inorganic nanostructures has numerous precedents.[23–26] The use of SCKs rather than simple micelles in this study is motivated by their colloidal stability and their ability to retain their nanostructure upon processing into thin and ultrathin films,[18,23] and, as demonstrated below, upon subsequent thermal treatment. Processability into thin films is of particular importance when nanostructures are to be patterned or organized into ordered arrays.

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[**] The National Science Foundation (T.K. DMR-0304508, K.M. DMR-0090409 and K.W. DMR- 9974457 and 0210247) and the ATRP/CRP Consortia at Carnegie Mellon University are acknowledged for funding. Justin Legleiter is acknowledged for the help with height histogram analysis. Jeffrey L. Turner is acknowledged for schematic drawings of SCK nanoparticles.

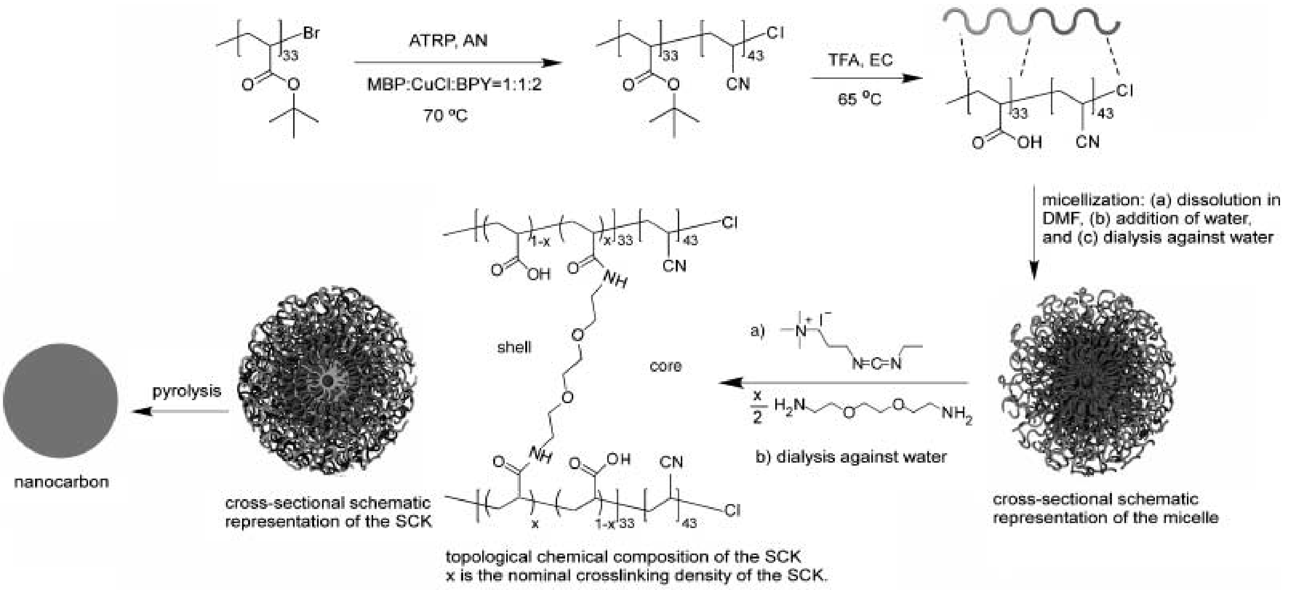
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200353401

The spherical SCKs used throughout this study were formed from poly(acrylic acid)-*b*-polyacrylonitrile (PAA-*b*-PAN) copolymers, which in turn, were obtained by hydrolysis of poly(*tert*-butyl acrylate)-*b*-polyacrylonitrile (P*t*BA-*b*-PAN) (Scheme 1). Well-defined block copolymers with polydispersity indexes (PDI) <1.2 were prepared by atom-transfer radical polymerization (ATRP),[27,28] which is one of the most robust controlled/living radical polymerizations, thus providing polymers with narrow molecular-weight distributions, controlled molar masses, complex architectures and functionalities.[28–33] A bromine-terminated poly(*tert*-butyl acrylate) (P*t*BA–Br) macroinitiator was synthesized and then chain extended with acrylonitrile by halogen exchange[34,35] to increase the relative rate of initiation versus propagation (for experimental conditions see Supporting Information). With the same starting P*t*BA–Br, different block lengths of PAN or the relative ratios of PAN and P*t*BA were achieved by controlling the conversion of acrylonitrile (AN) during the reactions. In this study, we focused on one well-defined block copolymer: $\mathrm{P}(t\mathrm{BA})_{33}$-*b*-$\mathrm{P(AN)}_{43}$. The hydrolysis of P*t*BA-*b*-PAN was performed at 65 °C in ethylene carbonate by reactions with anhydrous trifluoroacetic acid (TFA), which was confirmed by ^{1}H NMR spectroscopy to give high conversion of *t*BA into acrylic acid. Micellization of PAA-*b*-PAN was carried out by dissolving the block copolymer in DMF and then adding water at a controlled rate ($15\,\mathrm{mL\,h^{-1}}$) to induce micelle formation. Low final concentrations, about $0.25\,\mathrm{mg\,mL^{-1}}$, were used, to prevent intermicellar crosslinking at the later step. Following the removal of DMF by dialysis (cellulose membrane dialysis tubing, MWCO 3500 Da) against water and activation with a water-soluble carbodiimide (1-[3′-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide), the acrylic acid groups present within the shell layer of the micelles were then cross-linked with a diamine, 2,2′-(ethylenedioxy)-bis(ethylamine), to yield covalently stabilized SCK nanoparticles. Results of our previous work with SCKs that contain PAA shells indicate that partial shell crosslinking renders charged nanoparticles with ionizable acrylic acid groups still present in the shell.[19] Electrostatic repulsion between such SCKs has been shown to favor formation of sparse ordered arrays, it may also aid in preventing the aggregation of colloidal suspensions. Thus, this study has focused on SCKs with 50 % shell-crosslinking density, based on the stoichiometry of the amine functional groups of the diamino crosslinker to the carboxylic acids from PAA-*b*-PAN block copolymers present in the shell.

Thin and ultrathin films of the SCK carbon precursors were prepared by drop casting aqueous SCK solutions onto freshly cleaved mica then the samples were allowed to dry in air. The dried samples were then subjected to 2 h annealing at 230 °C in contact with air to stabilize the PAN domains, and subsequently pyrolyzed by heating at $20\,^\circ\mathrm{C\,min^{-1}}$ from room temperature to 600 °C under flowing nitrogen gas. Because of the limited thermal stability of mica, samples to be subjected to pyrolysis at 900 °C were deposited on clean silicon wafers.

The morphology and size distributions of the SCK precursors and carbon nanoparticles obtained after pyrolysis were characterized with the aid of tapping-mode AFM (see Supporting Information). The use of solutions with concentrations ranging from 0.1 to $0.025\,\mathrm{mg\,mL^{-1}}$ led to the deposition of isolated SCKs on the surface (Figure 1 a–d), thus facilitating size analysis of individual objects. Height distributions of the particles obtained with the aid of custom-developed AFM image analysis software are shown in Figure 1 e–h. The widths of the distributions were characterized through the ratio of weight-average and number-average heights $\bar{H}_\mathrm{w}/\bar{H}_\mathrm{n}$. As deposited, the SCKs samples exhibited a very narrow distribution of heights ($\bar{H}_\mathrm{w}/\bar{H}_\mathrm{n}=1.01$) with a



Scheme 1. Illustration of the five-step synthesis of carbon nanoparticles: 1) formation of a diblock copolymer P*t*BA-*b*-PAN by ATRP; 2) formation of an amphiphilic block copolymer PAA-*b*-PAN; 3) formation of polymer micelles through self-assembly; 4) formation of SCKs after cross-linking of the shell layer of polymer micelles; 5) formation of nanostructured carbon particles through pyrolysis. MBP = methyl 2-bromopropionate, BPY = 2, 2′-bipyridine, TFA = trifluoroacetic acid, AN = acrylonitrile.

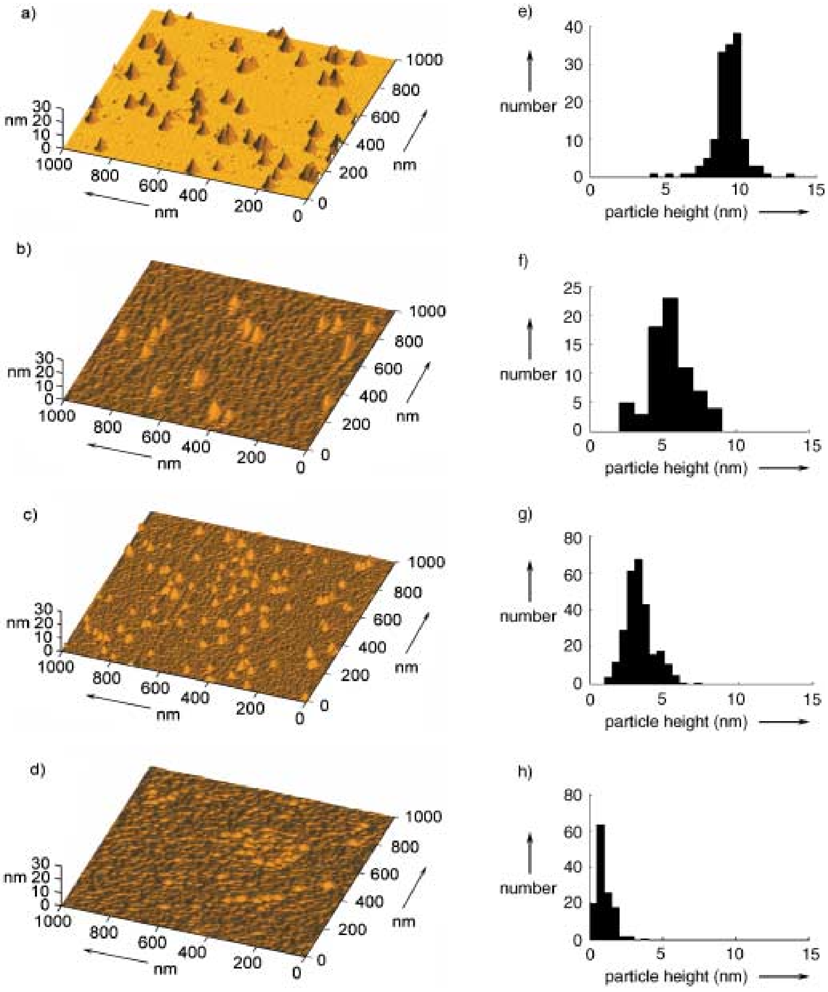


Figure 1. a)–d) Tapping mode AFM images of nanoparticles: a) SCKs on mica; b) nanoparticles stabilized on mica in air at 230 °C for 2 h and c) after heating under nitrogen at 20 deg min^{-1} from room temperature to 600 °C; d) after pyrolysis of thermally stabilized SCKs on a silicon wafer, obtained by heating under nitrogen at 20 °C min^{-1} from 230 °C to 900 °C. e)–h) Height distributions of SCKs and carbon nanoparticles determined from AFM images: e) SCKs; f) carbon nanoparticles stabilized at 230 °C; g) carbon nanoparticles pyrolyzed at 600 °C and h) carbon nanoparticles pyrolyzed at 900 °C

number-average height $\bar{H}_n = 9.0 \pm 0.5$ nm. In comparison, the diameter of these SCKs in solution determined by dynamic light scattering (DLS) was equal to 34 ± 2 nm. This difference indicated that upon deposition on mica, the SCK nanoparticles became flatter, as described earlier for partially cross-linked SCKs.[36,37] Upon thermal stabilization and pyrolysis, the average heights of the nanoparticles decreased with an increase of processing temperature, as expected for mass loss due to volatilization of the sacrificial shell block and carbonization of PAN.

The progress of PAN carbonization was monitored with the aid of FTIR spectroscopy (Figure 2) and Raman scattering spectroscopy (Figure 3). To facilitate sufficient IR-absorption and Raman scattering intensity, multilayer SCK films deposited on silicon wafers, rather than sub(monolayers), were used in this part of the study (for surface morphology of such films after pyrolysis at 900 °C see Supporting Information). The FTIR spectra taken prior to thermal treatment showed a characteristic strong absorption band at approximately 2240 cm^{-1}, which corresponds to CN groups of PAN. The spectra of samples pyrolyzed at 600 °C and 900 °C show broad and strong absorption bands between 1600 and 1300 cm^{-1}, indicating the formation of C=C and C=N bonds derived from the cyclization and cross-linking reactions involving CN groups. At the same time, the intensity of the absorption bands due to CN groups diminished with the increase in pyrolysis temperature and finally disappeared after treatment at 900 °C. These observations are consistent with reported data on PAN pyrolysis, according to which, heating in air at 230 °C (thermal stabilization stage) leads predominantly to cyclization, whereas subsequent pyrolysis under an inert atmosphere is dominated by progressive dehydrogenation and denitrogenation of PAN.[16] The observed red shift of C=C and C=N absorptions upon increase of pyrolysis temperature is consistent with an increase in conjugation.

Graphitization of carbon upon pyrolysis of organic precursors can be conveniently studied with the aid of Raman scattering, by monitoring the characteristic set of bands between 1200 and 1700 cm^{-1}. The peak around 1600 cm^{-1} indicates the presence of graphitic species that corresponds to the Raman-allowed E_{2g} mode, called the graphite mode (G-band).[38,39] The presence of disordered species is indicated by the presence of a defect-induced Raman band called the defect A_{1g} mode (D-band), centered on 1350 cm^{-1}.[40] Typically, the progress of graphitization upon pyrolysis is followed by comparing the growth and sharpening of the G-band and diminution of the D-band. A similar trend has been observed in this study, although the G-band was not

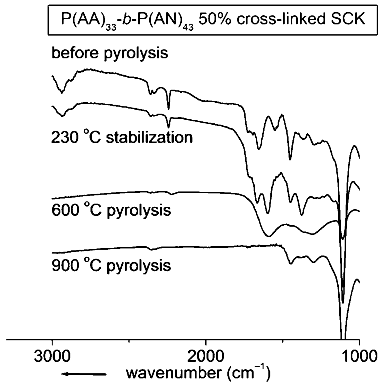


Figure 2. FTIR spectra of multilayer films of nanoparticles on a silicon wafer (transmittance in arbitrary units).

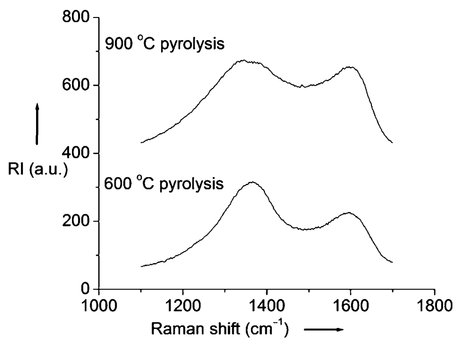


Figure 3. Raman spectra of carbon nanoparticles pyrolyzed at 600 °C and 900 °C on a silicon wafer (RI = Raman Intensity).

nearly as sharp and distinct as those typically reported for PAN-derived carbon fibers[41,42] or even as in nanostructured carbons derived from "bulk" block copolymers that contain PAN, as described in our earlier work.[14] The less-ordered nature of the graphitic species formed upon pyrolysis of SCKs can be explained by very high surface-to-volume ratio of this system, which leads inevitably to a more frequent occurrence of structural defects.

In conclusion, well-defined carbon nanoparticles were developed through pyrolysis of shell cross-linked PAA-*b*-PAN nanoparticles prepared by micellization and cross-linking of amphiphilic block copolymers in aqueous systems. These low-dimensional nanostructures were characterized by AFM and DLS. FTIR and Raman spectroscopy confirmed their partially graphitic nature. Nanostructured carbon materials prepared according to this route are expected to find many applications, such as antistatic coatings, materials for field emitters, specialized electrodes, and sensors. One of the particularly important advantages of this route is the use of covalently stabilized water-soluble precursors, thus facilitating environmentally friendly processing conditions. In addition, manipulation of solvent systems and copolymer composition may open the way to extend this approach to other low-dimensional nanostructures similar to those observed in other block copolymer systems.[43,44] Some of these extensions envisioned include: the preparation of carbon nanorods from shell-crosslinked cylindrical micelles; hollow carbon nanospheres made from shell cross-linked polyacrylonitrile-*b*-poly(acrylic acid) grafted from silica nanoparticles; hollow carbon nanotubules derived from shell-crosslinked densely-grafted single polymer brushes with polyacrylonitrile inner layer and poly(acrylic acid) outer layer.

Received: November 25, 2003
Revised: March 15, 2004 [Z53401]

Keywords: block copolymers · carbon · nanostructures · pyrolysis

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