

Microwave synthesis of nanocarbons from conducting polymers†

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Bulk quantities of nanocarbons having pre-selected morphology can be synthesized in a simple and rapid microwave heating approach directly from conducting polymers.

We describe a simple and rapid microwave heating method to synthesize nanocarbons having pre-selected bulk morphology (spheres, fibers, tubes) directly from conducting polymers having similar morphology. When doped conducting polymers are heated in a conventional microwave oven in air, the temperature rises to red heat in a few seconds resulting in a rapid loss of heteroatoms, dopant ions, *etc.*, and in the conversion of conducting polymers to nanocarbons. The bulk morphology of the conducting polymer is retained after microwave heating, extending the potential use of our recently described seeding/templating methods to synthesize bulk quantities of nanofibers/nanotubes of all major classes of conducting polymers.^{1,2}

Defined as carbon materials in which there is control of either size or structure at length scales in the nanometer regime, nanocarbons are a rapidly growing class of soft electronic materials in which many of the properties of micron-sized carbon fibers are amplified.³ Current synthetic approaches to micron-sized carbon fibers from pitch-based precursors,⁴ or nano-sized fibers from carbon-containing gas, frequently require high temperatures for extended periods of time and the use (and subsequent removal) of inorganic templates.⁵ In a recent report, metal/carbon nanoarchitectures have been synthesized by hydrothermal metal-catalyzed carbonization when aqueous solutions of starch and AgNO₃ are heated to 160–200 °C.⁶ While metal-free micron-sized carbon fibers can be synthesized from polymer precursors, for example, from calcination of polyacrylonitrile fibers,⁷ bulk synthesis at the nanoscale regime (fibers) from polymers has remained a challenge. In this study, microwave absorbing, conducting polymers were used as precursors. When subjected to microwave radiation, nanostructured conducting polymer precursors are rapidly carbonized to nanocarbons in one step. Polypyrrole was chosen as a prototype polymer precursor system.

Polypyrrole nanospheres, nanofibers or nanotubes having average diameter in the 40–80 nm range (nanotubes having 5–8 nm inner tube diameter) were synthesized by seeding (or templating) a conventional chemical polymerization of pyrrole using V₂O₅ nanofibers as the structure-directing agent (Fig. 1a,b,c).² After all residual V₂O₅ nanofibers were removed, an accurately weighed amount (20–50 mg) of the nanostructured

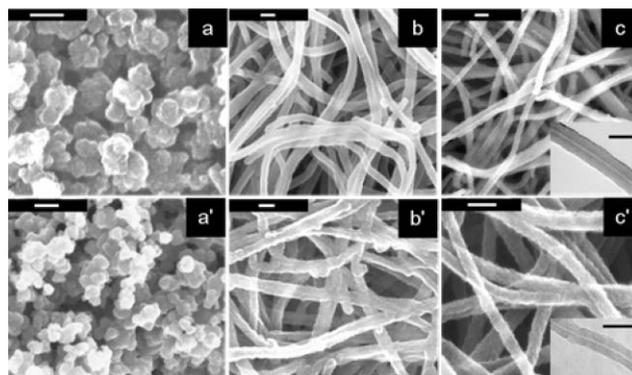


Fig. 1 Microwave synthesis of nanostructured carbon from doped polypyrrole. SEM images before (a,b,c) and after (a',b',c') microwave heating. Nanospheres (a/a'), nanofibers (b/b'), nanotubes (c/c'). Inset in c/c': TEM images showing nanotube with inner diameter. Scale: 100 nm.

polypyrrole was placed in a glass vial heated in a conventional microwave oven for 3–5 min. There is extensive sparking along the polymer surface accompanied by a rapid increase in temperature. If heating is continued beyond 3 min, the glass vial becomes red hot and melts, consistent with temperatures in excess of 800 °C. Microwave heating is accompanied by a 60–65% weight loss in the polypyrrole, consistent with loss of both backbone nitrogen atoms and dopant ions (Cl[−]). The elemental composition of carbon (by EDX and elemental analysis) increases dramatically upon microwave heating, for example, the carbon percentages for nanostructured spheres, fibers and tubes of polypyrrole·Cl (all around 56%) increases to 92, 93 and 94%, respectively, consistent with conversion to nanocarbons. The bulk morphology of the polypyrrole was retained in the nanocarbon product after microwave heating (Fig. 1a',b',c'), although there is an overall reduction in size dimensions. High resolution TEM images of the nanocarbon⁸ show a near-quantitative carbonization upon microwave heating with 0.34 nm separation between adjacent layers (Fig. 2B).

Thermogravimetric analysis before and after microwave heating shows a significant increase in thermal stability consistent with the transformation of conducting polymer chains to carbon (Fig. 3).⁹ For example, there is continuous weight loss in the precursor polypyrrole·Cl nanofibers after 150 °C, which reaches ~80%, at 600 °C. In contrast, after microwave heating, there is only a ~5% weight loss at 600 °C in the corresponding nanocarbons. In addition, at 800 °C, there is still 25% residue in the nanocarbons compared to <2% for the precursor polypyrrole·Cl.

The aqueous electrochemistry is also significantly altered upon microwave heating. The characteristic Faradaic redox peaks of polypyrrole·Cl in the cyclic voltammogram² are replaced by a

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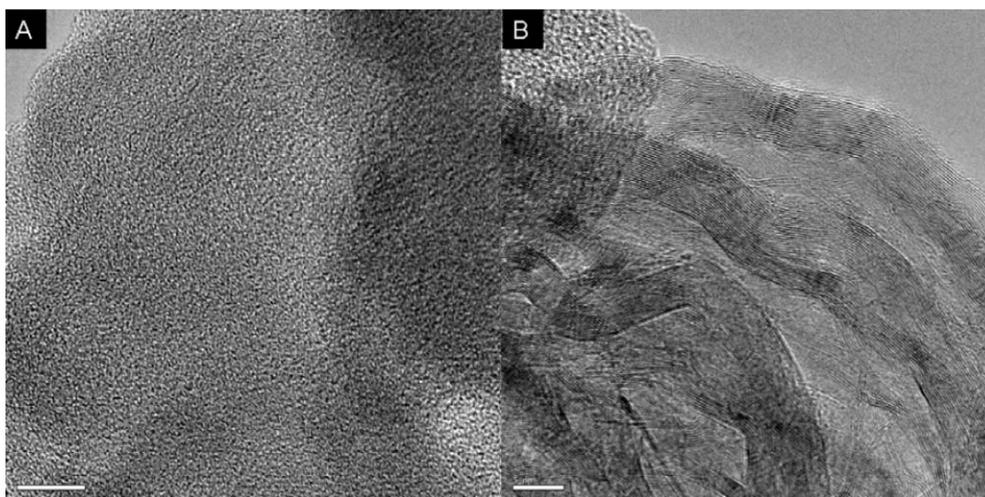


Fig. 2 Representative HRTEM images of polypyrrole-Cl nanospheres before (A) and after (B) microwave heating for 3 min. Scale: (A) 10 nm and (B) 5 nm.

capacitive rectangular “box structure” upon microwave heating, consistent with the conversion to nanocarbons. The Raman spectra (Fig. 4, inset) show that upon microwave heating, the characteristic sp^2 (G-band, 1580 cm^{-1}) and sp^3 (D-band, 1340 cm^{-1}) carbon peaks⁸ are significantly enhanced. The specific surface area also increases from $120\text{ m}^2\text{ g}^{-1}$ to $331\text{ m}^2\text{ g}^{-1}$ upon microwave heating, consistent with microporous carbonization.

Key to the microwave approach is the electronic conductivity of the polymer, for example, no nanocarbons are obtained when undoped conducting polymers, or electrically insulating polymers such as polyacrylonitrile are used. The conductivity of conducting polymers, 10^{-1} – 10^2 S cm^{-1} , is at an optimum range for microwave penetration into the bulk polymer, *i.e.*, it is sufficiently high to absorb microwave radiation, but not so high to limit absorption to the surface. As long as the polymer remains conducting, microwave absorption increases the temperature very rapidly resulting in loss of dopant ions and collapse of the polymer backbone to a carbon-rich structure. It is important for the polymer not to dedope too rapidly during the initial stages of

microwave heating while the temperature is still relatively low as is the case in HCl doped polyaniline (emeraldine-HCl) nanofibers.¹⁰ Even though emeraldine-HCl begins to spark vigorously as it is microwave heated, the sparks die down quickly, presumably as a result of protonic acid dedoping (loss of HCl) and conversion to electrically insulating emeraldine. Polypyrrole, polythiophene, PEDOT, *etc.*, cannot be dedoped by this process and are, therefore, more suited as precursor polymers. In microwave welding of plastics using polyaniline, this *in situ* dedoping could be an advantage by preventing runaway temperature increases.¹¹

Although the microwave heating is carried out in air, we do not see evidence for backbone oxidation (or oxygen containing species) after carbonization. The reasons for this are unclear, although we believe the rate at which the temperature increases upon microwave heating is playing an important role. For example, unlike thermal heating in a furnace (in air) where there is sufficient time for oxygen to react with the polymer backbone, microwave heating results in extremely high temperatures in a very short

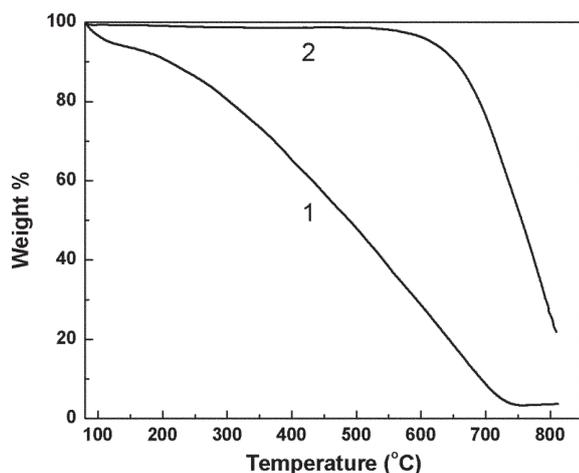


Fig. 3 Thermogravimetric analysis plots for polypyrrole-Cl before (1) and after (2) microwave heating (N_2 flow 20 ml min^{-1} , $10\text{ }^\circ\text{C min}^{-1}$).

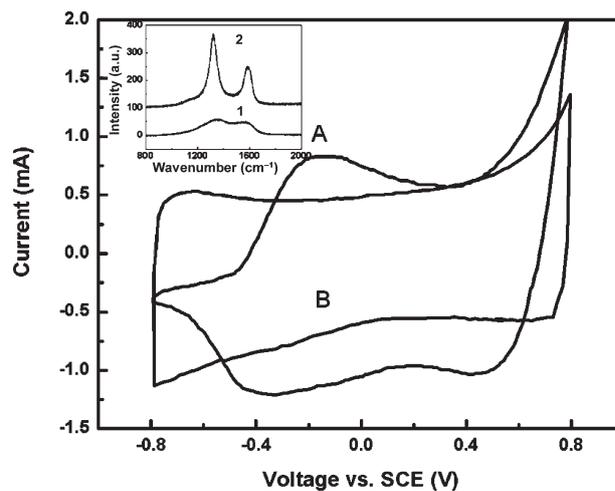


Fig. 4 Cyclic voltammograms of polypyrrole before (A) and after (B) microwave heating. Inset: Raman spectra of polypyrrole before (1) and after (2) microwave heating.

period of time (in seconds). We believe that at these temperatures, carbonization is near instantaneous and occurs well before oxygen can react with the polymer backbone.

In addition to gaining direct synthetic access to nanocarbons from conducting polymers, metal/carbon nanocomposites can be readily synthesized by exposing the conducting polymer precursors to aqueous solutions of noble metal ions prior to microwave heating. We have shown, for example, that when polypyrrole-Cl nanofibers or nanotubes are immersed in aqueous AgNO₃, silver metal clusters (10–20 nm) deposit directly on the fiber surface (and in pores of tubes).^{1,2} Subsequent microwave heating yields composites of Ag nanoparticles embedded in carbon nanofibers and tubes. It is to be noted that synthetic access to these technologically important metal/nanocarbon systems is possible primarily *via* the intermediacy of conducting polymer precursor, *i.e.*, no metal deposition occurs when nanocarbons themselves are exposed to aqueous noble metal ions. Our microwave method to nanocarbons could be viewed as “carbonization-in-an-hour” which complements and supplements the recently reported “carbonization-in-a-day” approach.⁶ This approach could open new opportunities in the design and development of new fuel-cell catalyst and energy storage systems and next-generation gas and analyte sensors based on nanocarbons.

In summary, we describe a new method to synthesize nanocarbons having pre-selected bulk morphology. Described for the first time are: (i) the direct conversion of doped conducting polymers to nanocarbons by microwave heating; (ii) retention of bulk nanostructured morphology upon microwave heating; (iii) a new method to synthesize metal/carbon nanocomposites by leveraging the redox active properties of conducting polymer precursors. The method is general and can be used in the major

classes of conducting polymers, and their direct conversion to nanocarbons by microwave heating could herald the first large scale commercial use for conducting polymers.

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