# Graphitic carbon nanostructures *via* a facile microwave-induced solid-state process†

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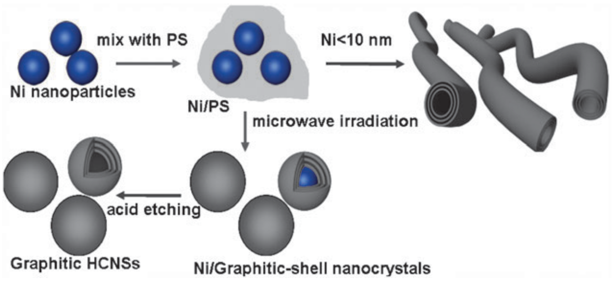
**A novel approach to fabricate highly graphitic carbon nanostructures such as carbon nanotubes (CNTs), metal/graphitic-shell nanocrystals and hollow carbon nanospheres (HCNSs) in a very short time is demonstrated.**

Graphitic nanostructured carbons,[1–3] especially those with highly curved graphitic structures, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), carbon nanohorns, and metal/graphitic-shell nanocrystals, hollow carbon nanospheres (or carbon nanocages) *etc*., are promising materials for electronic devices,[4] catalyst supports,[5] hydrogen storage,[6] magnetic-resonance-imaging agents,[7] delivery systems[8] *etc*. The rational construction of nanostructured carbon with a designated size, structure and morphology is motivated by the above mentioned potential applications due to their superior electrical,[9] mechanical,[10] and chemical properties,[11] biocompatibility[8] and well-defined structure. Carbon nanotubes and hollow carbon spheres or so-called carbon nanocages, especially those with a graphitic shell, are of particular interest. Normally these materials are fabricated by relatively complicated processes including CVD,[12] arc-discharge,[3] laser ablation,[13] a solvothermal method[14] or by just heating a carbon precursor in an oven,[15,16] where a high temperature and long reaction time are required.

Recently, Manohar *et al.* synthesized various types of nanocarbon using a simple microwave-assisted pseudomorphic self-templating transformation process.[17] The choice of a conducting polymer with pre-selected morphology is pivotal for the final carbon structures. Herring *et al.*[18] used a three-step process to make graphitic hollow carbon nanospheres (HCNSs) using laser pyrolysis to produce graphitization, and the product was a mixture of graphitic carbon spheres and amorphous carbon. It is desirable to seek a simple process. Here, a new microwave-assisted approach with an ordinary carbon precursor to prepare metal/graphitic-shell nanocrystals and CNTs in a very short time is reported. With proper chemical etching, highly graphitic HCNSs can be obtained.

Scheme 1 shows the schematic procedure for the fabrication of the graphitic nanostructured carbon. Monodispersed Ni nanoparticles with well-controlled particle size and size distribution were synthesized as reported previously.[19,20] The Ni nanoparticles and a carbon precursor such as polystyrene (PS) were blended in ethyl acetate and sonicated for half an hour. The solvent was evaporated in a rotary evaporator to give a homogeneous solid mixture of Ni nanoparticles and PS. The mixture was transferred into a quartz vial, and microwave-treated in a household microwave oven in an inert atmosphere. After less than one minute irradiation, Ni/graphitic-shell nanocrystals were obtained. The dissolution of the Ni cores using 1 M HCl in an ultrasonic bath for 2 h generated graphitic HCNSs. The experimental details are available in the ESI.†

Fig. 1a, d and g show transmission electron microscope (TEM) images of the Ni nanoparticles. These obtained Ni nanoparticles have a relatively narrow size distribution, with sizes ranging from 600 nm to 8 nm (600, 350, 90, 40 and 8 nm, see also Fig. S1 and 2†). Ni nanoparticles dispersed in polymer have been found to be a very effective microwave absorber. Usually, Ni/polymer composites grow redhot in 10 s under microwave irradiation. After the microwave process a black magnetic powder is obtained, which is hydrophobic and can be easily dispersed in ethanol. The char yield is more than 45%. From the TEM images (Fig. 1e and f), it is clear that the Ni nanoparticles were well preserved after the microwave treatment, and a graphitic shell with quite homogenous shell thickness was formed around each Ni nanoparticle (see Fig. 1e, inset shows the graphitic structure of the carbon shell; Fig. S3† shows the SEM image of product from 90 nm Ni particles). For example, for the 40 nm Ni particles, a carbon shell about 3 nm thick was observed. The shells have a well-ordered onion-like graphitic structure that has layer spacing of 0.34 nm (Fig. S4†). After acid etching, most Ni cores were dissolved, leaving behind graphitic HCNSs with inner



**Scheme 1** Microwave-induced synthesis of Ni/graphitic-shell nanocrystals and graphitic HCNSs.

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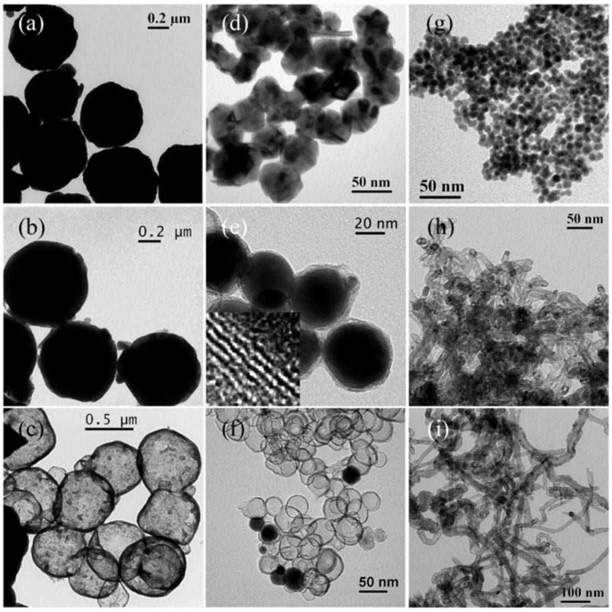

**Fig. 1** TEM images of Ni particles of different sizes (a, d, and g are 600, 40 and 8 nm, respectively); Ni/graphitic-shell nanocrystals (b and e) obtained from the microwave treatment of Ni/PS composites (the Ni core sizes are 600 and 40 nm); CNTs (h); and the products of b, e and h after acid etching (c, f, and i). (c) and (f) are graphitic HCNSs.

diameters the size of the original Ni particles (Fig. 1c and f). Around 5% of the Ni/graphitic-shell nanocrystals were preserved after acid digestion, indicating that some of the graphitic shells were perfect and could protect the Ni cores from acid etching. At the same time, if a shorter treatment time was used in the acid etching, partially dissolved Ni cores were obtained and spaces were observed between the Ni nanoparticles and graphitic shells (Fig. S6†). Those products may be used as the host for preparing hybrid materials. Fig. 2a shows typical XRD patterns of the Ni/PS composite, Ni/graphitic-shell nanocrystals and HCNSs. The peaks at 44.5° and 51.8° are the characteristic (111) and (200) diffraction of Ni. The broad peak at around 20°, assigned to PS, disappeared after microwave irradiation. Instead, a new peak at 26.5° was observed, which is due to the characteristic (002) diffraction of graphite. The graphitic structure of the Ni/graphitic-shell nanocrystals and HCNSs was confirmed by Raman spectroscopy (Fig. 2b). Only the peak at 1579 $cm^{-1}$ (G-band) was observed. This band corresponds to the $E_{2g}$ mode of hexagonal graphite and is related to the vibration of $sp^2$-hybridized carbon atoms in the graphite layer. Surprisingly, the D-band at 1358 $cm^{-1}$, associated with the vibration of amorphous carbon, was completely absent, indicating the complete graphitization of the products.

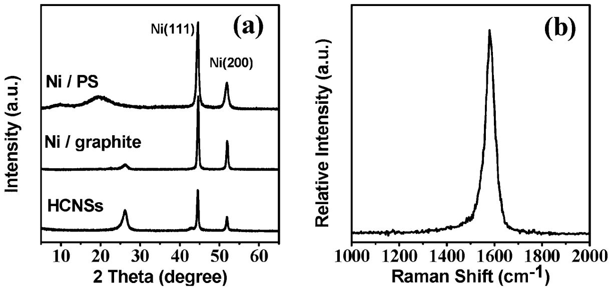

**Fig. 2** (a) XRD patterns of 40 nm Ni/PS composite, Ni/graphitic-shell nanocrystals and graphitic HCNSs; (b) Raman spectrum of 40 nm Ni/graphitic-shell nanocrystals.

It is interesting to note that, when the Ni nanoparticles were 8 nm, graphitic MWCNTs in a considerable proportion (at least 40%) were produced by the microwave synthesis method. Most of the CNTs were bamboo-like with an outer diameter between 8 and 13 nm and a length between 200 and 600 nm (Fig. 1h and i and Fig. S7b and c†).

The BET surface areas of acid-treated samples (40 and 8 nm) were 105.2 and 159.5 $m^2\ g^{-1}$, respectively. Since there is an absence of amorphous carbon, a relatively low surface area is reasonable. The $N_2$ adsorption isotherms of HCNSs showed a typical H3-type hysteresis loop (ESI†), which implied a 3D caged pore structure with a small entrance size ($<4$ nm).[21] It is probable that the ultrasonic bath produced irregular little clefts in the graphite shells through which the acid entered and dissolved the Ni cores.

It has been reported that for microwave reactions where metal particles are involved, the metal particles can be very effectively coupled to the microwave field, leading to the fast and highly effective synthesis of inorganic materials.[22] The control experiment using conventional furnace heating produced aggregated Ni/carbon structures with irregular sizes and shapes, which confirmed the advantage of the microwave-assisted approach over the conventional one (Fig. S9†).

The formation mechanism of these microwave-induced nanostructured carbons is discussed below. When the metal (in this case Ni) nanoparticles are placed in a microwave field, due to the high dielectric coefficient of the metal, the microwave is absorbed and thus decays rapidly as it penetrates into the Ni particles. When the surface of a large Ni particle (*e.g.* 350 nm Ni particles, Fig. S1†) is heated violently by the microwave irradiation, the interior temperature may rise only slowly in the weaker field. Therefore, while the bulk temperature is still below the melting point, the surface temperature may get high enough to cause the pyrolysis of PS and produce a graphitic shell that has the original shape of the catalyst particle (see Fig. S1†). On the other hand, the temperature of small particles (such as 40 nm particles) will be more homogeneous compared to the large ones. Taking into consideration a lower melting point caused by the finite size effect, small catalyst particles (40 nm, Fig. 1d) will tend to completely melt very rapidly. Upon their reaction with the carbon source, spherical Ni/graphitic-shell nanocrystals are produced. When the size of the Ni nanoparticles is even smaller (8 nm, Fig. 1g), the products tend to be the CNTs, which matches the need to minimize the energy associated with the nucleation of the graphene layer.[23] We believe the synthesis case here is similar to the CVD methods, but also different because there is a substantial amount of Ni/graphitic-shell nanocrystals. This may be due to the very short reaction time for the microwave-induced graphene growth, that is, although CNTs should be the stable product from thermodynamic considerations, some Ni particles were quenched as Ni/graphitic-shell nanocrystals due to the very short reaction time.

In summary, a novel, mild and convenient approach to synthesize highly graphitic nanostructured carbon by microwave irradiation was demonstrated. With simple precursors, narrowly distributed metal/graphitic-shell nanocrystals, graphitic HCNSs with well-controlled sizes, and CNTs can be obtained. Although the potential of this method is not yet fully explored, it can already be seen to provide a simple, fast, and easily scaled-up approach to produce nanostructures for applications such as magnetic-resonance-imaging agents,[7] catalyst supports,[24] electrochemical capacitors,[25] *etc*.

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