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Direct synthesis of uniform hollow carbon spheres by a self-assembly template approach†

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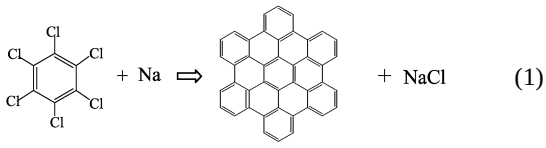
Hollow carbon spheres (50–100 nm) have been synthesized by a self-assembly approach using hexachlorobenzene and Na. NaCl which generated during the reaction has been successfully exploited as a template for the direct synthesis of porous carbon materials, which can be subsequently removed from carbon product by annealing above 1400 °C.

The discovery of fullerenes, carbon nanotubes and closed spherical carbon shells such as carbon onions and graphitic nanocones proved the existence of a new class of carbon materials with a characteristic highly curved graphitic network structure or the bucky-structure. These materials are produced usually by laser vaporization, resistive heating and arc discharge methods, which are sometimes inefficient and of low yield.[1]

Recently, different routes, such as a CCVD (catalytic chemical vapour deposition),[2] rational chemical method,[3] and carbon ion-implantation technique,[4] have been introduced into the synthesis of these novel carbon materials. However, most these methods are a multiple-step process and a catalyst was always required for the synthesis. Direct chemical routes have also been attempted but successful ones can only be achieved by use of suitable precursors and critical control of the reaction process.

Self-assembly provides a promising method for chemical synthesis of carbon materials with bucky-structure. Considering the structural characteristics, polygons, especially pentagons and hexagons with sp^2-hybridized carbon, can be regarded as the basic construction units for bucky-carbon materials. Recently, Qian *et al*. successfully assembled the laminated honeycomb-like structure of carbon nanotubes from hexachlorobenzene (HCB) and potassium by a solvothermal route (reaction temperature: about 350 °C) and with Co or Ni as catalyst and thus confirmed the self-assembly approach with polygons.[5] According to their report, the benzene solvent and the catalyst employed in the reaction were crucial for the assembling of hexagonal units into hollow tubes. But, until now, no study resulting in a high product yield has been described on the reaction of two solid reactants without the use of any solvent or catalyst.

In our study, HCB (2.9 g) and sodium (1.4 g) were mixed in a 80 ml stainless autoclave with glass liner. The autoclave was sealed and then heated at 160 °C for 10 h to get the as-synthesized samples. It was further washed with alcohol and treated with boiling water (1000 ml water per 1 g of sample) three times and then dried at 80 °C in air. The reaction follows the formula:



(1)

† Electronic supplementary information (ESI) available: SEM pictures of the products from simple mixing. See http://www.rsc.org/suppdata/cc/b2/b205723a/

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Initially, large sodium pellets and HCB powder were simply put together into the autoclave. Most of the reactants remained intact after autoclave reaction at 160 °C for 10 h: products could only be found within a limited depth of the outer shell of the sodium pellets. The as-synthesized products were black shells with unconsumed sodium encapsulated at the core. A sample treated by the above mentioned method was studied by SEM and XRD experiments.[6] SEM pictures show that there is a distribution in formed carbon materials: different morphologies are observed in this sample (see ESI†). The XRD pattern (not shown) reveals the predominantly amorphous structure of the carbon materials with only a broad hump at about $2\theta = 24°$. The formation of pores in the spongy-like structure as shown in the ESI may be attributed to the removal of NaCl by-product through water washing. The formation of tubular structure is a very interesting phenomenon since all mechanisms proposed for the growth of such kind of structure have been based on the performance of an active catalytic center.[5,7–9] The NaCl formed during the reaction might count for this since no other third solid component had ever been added in the reaction. The diversified morphologies in the sample might be caused by the non-homogeneous contact of the two reactants.

By thoroughly grinding the HCB powder with sodium pellets before loading into the autoclave,[10] a dramatic change in the products is observed under SEM (Fig. 1A): while the stoichiometrically mixed reactants in this case were completely consumed, a small amount of large spheres with a diameter of

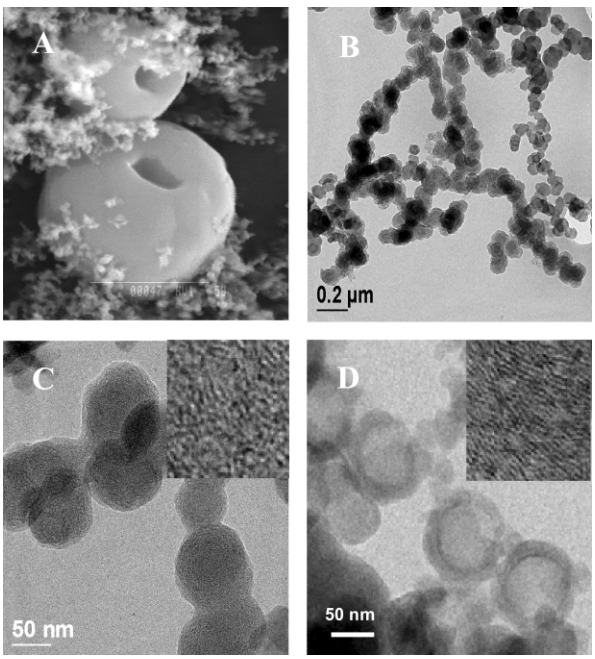

Fig. 1 SEM and TEM pictures of the products. A) is the SEM picture of the sample before washing. B) and C) are TEM pictures of the sample after washing. D) is the TEM of sample after washing and annealing at over 1400 °C. Insets of C) and D) show the detailed carbon structure by HRTEM.

about 10 μm and a larger amount of smaller ball-like particles are produced. Upon boiling water wash, the large spheres totally disappeared, whereas the small ball-like particles with diameter of 50–100 nm remained unchanged (Fig. 1B), suggesting that these large spheres are NaCl particles formed according to eqn. (1) that are removed by the water wash. It is interesting that although after three times washing in boiling water (1000 ml water per 1 g sample), XRD still shows that there are strong diffraction peaks at 2θ = 27.8, 32, 45.5 (compared to these, the peaks of carbon here are very broad and weak), which indicates the existence of NaCl occluded in these ball-like particles. Most likely it is just the template effect of this reaction-generated NaCl that leads to the effective transformation of nearly all the consumed HCB into these uniformed ball-like carbon particles (the yield of these ball-like particles is 80–90% according to SEM and TEM observations).

Annealing of the water washed sample was carried out in N_2 flow for 4–6 h at a temperature above 1400 °C. TEM pictures depict a very detailed description of the significant change in these ball-like carbon materials. Fig. 1C shows the solid carbon spheres before annealing. In Fig. 1D for the sample after high temperature annealing, it is obvious that the spheres became hollow. A very remarkable difference also appears between the XRD patterns (Fig. 2) of the two samples that the very strong NaCl diffraction peaks of the sample before annealing almost disappear in the annealed sample which implies that most of the occluded NaCl was driven away from the carbon spheres by heating (b.p.$_{NaCl}$ = 1413 °C) and the carbon capsules marvellously became hollow spherical shells with a cavitiy within them. This and the TEM pictures (Fig. 1C, D) further confirm the template effect of NaCl particles. This result differs from the report by Chi-Young Lee *et al*. in which nanosized graphite with laminated structure dominated 70% of the final products by ^{13}C-NMR and HRTEM.[11]

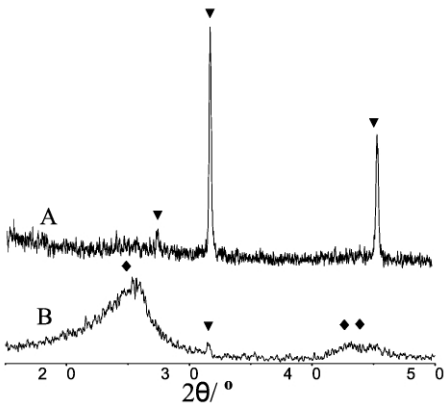

Fig. 2 XRD patterns of the products (A) before and (B, enlarged) after annealing. Strong NaCl peaks (marked with ▼) exist in (A) and almost disappear in (B). Diffraction peaks of carbon (marked with ◆) appear in (B).

HRTEM pictures show that the structure of carbon materials also changed by annealing. There are no very regular laminated layers but only small graphitic fragments existing within the carbon spheres before annealing (Fig. 1C, inset). When this sample was annealed at 1400 °C for 4 h, the HRTEM presents a quite different pattern. The fingerprint-like structure shows a much more uniformed arrangement of shells (Fig. 1D, inset). It's obvious that a graphitization process occurred during annealing and the small graphitic fragments further assembled into larger ordered layers. The inter-space between two adjacent layers is around 0.35 nm corresponding to the (002) diffraction peak at about 2θ = 25.4°, as can be discriminated from the narrowed hump. In addition, the weak hump at about 2θ = 44.2° splits into 2 peaks at 43.2° and 45.1° which can be attributed to (100) and (101) diffraction peaks of graphite respectively (Fig. 2B). The discrepancy between the observed and the theoretical peak positions is most probably caused by the defects and curvature of the laminated structure.

In conclusion, the reactions between HCB and Na (without catalyst and solvent) were conducted in a moderate temperature autoclave reactor. Through a homogenenous contact of the reactant, uniformed ball-like carbon particles (50–100 nm) were synthesized by a self-assembly approach. The NaCl generated during the reaction is suggested to be working as a template for the formation of these carbon spheres. Upon annealing the sample at boiling point of NaCl, the creation of large pores in the ball-like carbon materials is observed, which has the potential of serving as micro-reactor for catalytic reactions.

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10 Great care should be taken in handling the two possible dangerous chemicals.

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