Mixed Gaseous detonation fabrication of CNTs and CNTsdoping with Fe based composites

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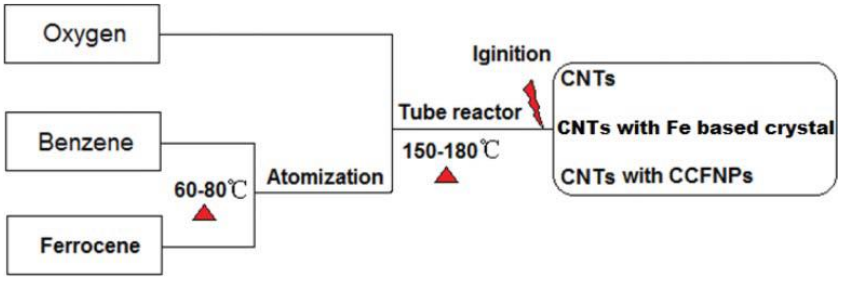
1 Background

A Since their discovery and large-scale synthesis, CNTs has attracted enormous interest due to their various unique physical and chemical properties which exhibit excellent structural flexibility and fluidity. One of the main challenges in the chemical industry has been the development of low-cost, recyclable and effective substrates (catalysts) upon which well-structured CNTs can grow. However, it is still challenge to develop a novel methodology for the large-scale fabrication of functional CNTs. It is widely known that there is a high nucleation barrier for growing carbon based materials and that certain pretreatments are necessary to provide the initial nucleation sites. For example, nanoparticles of transition metals, such as Ni, Fe and Co are used as catalysts for growing CNTs. In this work we firstly report the simple, inexpensive, low-temperature, gaseous and solution gasification new technology for the rapid production of CNTs and the related nanomaterials. Therefore, we designed a series of novel experiments to investigate the condensation and formation of carbon structural nanomaterials in gaseous mixed precursor rapid chemistry reaction, which the gaseous mixture precursor detonation technology roadmap illustrated in Scheme1. The detonation technique facilitates the shock wave transient expansion (at ms-molecule reaction level) and nanomaterial growth under extreme chemistry reaction conditions (high temperature, low pressure and rapid chemical reaction) which can help overcome the activation barrier for the chemical bond energy. The experimental results demonstrate that CNTs and CNTs doping with Fe-based nanomaterials can be obtained by detonation of gaseous mixture precursors.



Scheme 1. Reaction scheme for the preparation of CNTs/CNTs doping with Fe

based nanocrystal of technology roadmap

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2 Fabrication of CNTs and CNTs with Fe based composites

During the rapid gaseous or gaseous detonation reaction process, this is very fast and complex one. The gaseous detonation was performed in a sealed Titanium alloy casting tube reactor connected with a heating and cooling cycle apparatus, which can effectively regulate the temperature of the tubular reactor. When the rapid gaseous mixture detonation reaction occurs, temperature, pressure and velocity peaks of more than one thousand degree, 3–10 MPa and more than two Mach were generated in the tube reactor. After the rapid reaction, the vessel was rapid recovery of initial reaction conditions throughout the chemistry reaction experienced about 2–5 ms. And then the toxic gaseous products were purified and removed by the copper heating pipes and calcium hydroxide solution, the black solid products on the inner wall were collected for further characterizations (Scheme 1). So these 0.6 g/0.9 g/1.25 g of Ferrocene was added into 27–35 ml of Benzene at 60–80℃, the yellow mixed solution was obtained and then atomized in the tube reactor. Meanwhile, the sample was heated up to 150–180℃ at a heating rate of 10℃/min, held for 10 min and ignited the gaseous mixture and then cooled to room temperature. It is worth mentioning that on how to put ferrocene fully dissolved into benzene solution at a certain temperature, which is one of the important conditions to achieve an effective synthesis of the target products (Table 1).

Table 1. The reactants of the experimental gas-liquid mixture and the product characteristics.

Samples	Pressure O_2/Pa	Solution Mixtures[a] C_6H_6/ml:$C_{10}H_{10}Fe$/g	Mole Ratio[b] C:Fe	Product
1	0.8–1.0	27–35: –		Amorphous carbon
2	0.8–1.0	27–35 : 0.60	≥55.4:1	CNTs
3	0.8–1.0	27–35: 0.90	≥40.7:1	CNTs with Fe based crystal
4	0.8–1.0	27–35: 1.25	≥18.6:1	CNTs with CCFNPs

[a]The same density of C_6H_6 and $C_{10}H_{10}Fe$ is for these experiments.
[b]The values are calculated from the reactants of carbon and Fe ions involved in the mixture precursors. During the gaseous detonation process, they do not represent the real ratios of carbon and Fe ions that actually participate in the formation of solid materials since the carbon atoms from the Benzene (C_6H_6) and Ferrocene ($C_{10}H_{10}Fe$).

3 Results and Discussion

So the experimental conditions used in this work, due to deficient oxygen atoms, these gaseous atoms tend to combine as H2O, CO, CO2 and a large amount of free carbon, which were provided for carbon nanostructural materials or composites:

$$C_6H_6(g) + O_2(g) \rightarrow CO(g) + H_2(g) + C(s) \quad (1)$$

$$Fe(C_5H_5)_2(g) + O_2(g) \rightarrow CO(g) + H_2(g) + C(s) + Fe(s) \quad (2)$$

After gaseous mixture detonation reaction, some black deposits can be found at the inner wall and the very end of the tube reactor, which account for 18–26% of theweight loss of the mixed reactants. The black deposit contains 50 wt% of carbon nanotubes.

Figures 1A,B display the diameter of CNTs were 40±15 nm and their length were 8±2 mm. The nanotubesexhibit very wide channels and show continuously hollow shaped morphologies. HRTEM images C,D also reveal the hollow structures of nanotubes are with the diameters ~45 nm and the wall thickness ~15±5 nm. Besides the round end shown in Figure 1C, some CNTs with even open ends and some with spheroidal caps were also observed, which are multishell nanotubes with diameter of 40±5 nm and 30–40 walls, the spacing of the lattice fringes is about 0.335 nm (Figure 1D). Figure 2 show TEM images, which

reveal the structural of CNTs, Fe based nanocrystal and carbon coated Fe nanoparticles(CCFNPs). The transmission electron microscopy (TEM) shows the presence of CNTs bundles clutter stacked together, nearly all CNTs are grown with very a little nanoparticles in the bundles.

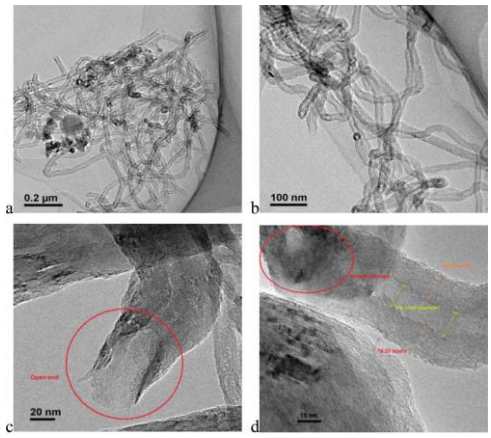

Figure 2. The carbon soot purified by absolute ethanol and acetone, (A,B) the obtained CNTs are multiply walled with diameters about 40 nm and lengths about 8 mm.The yield of CNTs/nanoparticles about 20–30 wt%, barely any trace of amorphous carbons found in the purified samples, (C,D) the hollow CNTs with a spheroidal caps and the CNTs with even open ends

And then, with the molar ratio of iron ions to increase, the preparation of CNTs with core-shell structural nanoparticles is about ~28 wt% of the as produced carbon soot, the diameter of CNTs is decreasing while its length is also shorten to 300±50 nm. Of these obtained products, many CCFNPs with coreshell structure were observed from the Figure 3A,B which grain size is distributed in a large range about 10-60nm. The multishell hollow nanotubes with the inner diameters are 10±5 nm and 10-30layers of carbon walls. It is noteworthy that the spheroidal nanoparticles are wrapped in the ends of carbon nanotube, which show similar to inner diameter distribution. The nanocrystals are the main iron according to inset EDS and EDX patterns (Inset in Figure 3C,D), HRTEM image (Figure 3C) indicates that a big black ellipsoidal core were wrapped in the end of tube, the length of the ellipsoid are two times than the width of that and the carbon wall is about 10 nm. Figure 3D shows that a big black core ware wrapped in graphitic carbon coating shell, the diameter of core is about 50±5 nm with the thickness of the coating layer is about 15±2nm.

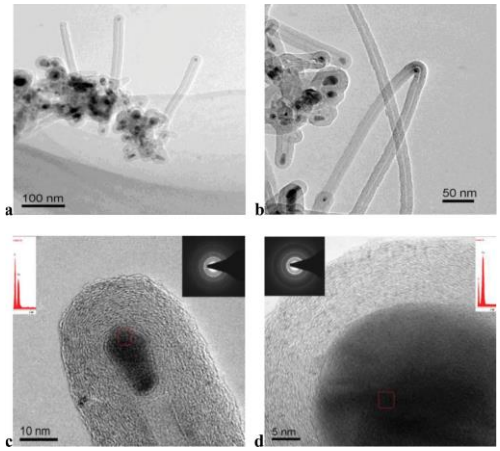

Figure 3. TEM and HRTEM with EDX images of the hollow CNTs, CNTs with Fe nanocrystal, (A,B) TEM of the purified carbon soot, the Fe nanocrystal in the end of CNTs with 300±50 nm, some carbon coated Fe based nanoparticles between the CNTs, (C,D) HRTEM image manifests the core/shell coated structure of the carbon coated Fe based nanoparticles and graphitic structure of the carbon shell, the inset EDS and EDX pattern of the coated bcc-Fe nanocrystal core (red box).

4 Conclusions

In summary, The results showed a new high yield pathway to produce CNTs and CNTs with Fe based composite materials directly from gaseous mixture detonation technique. This method offers a novel approach to modulate the relative ratio of sp^2-bonded carbon to form self-assembled carbon nanostructures. We observed that the Benzene/oxygen system detonation only generated a profusion of amorphous carbon nanomaterials. And then a high yield of CNTs can be successfully generated by Benzene/oxygen system combined with Fe ions mixture detonation,through adjusting their mole ratio of carbon and Fe ions.The objective products in tuned by controlling the rapid reaction conditions, such as the gaseous mixture components and initial reaction conditions etc.

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