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# Detonation chemistry of a CHNO explosive: catalytic assembling of carbon nanotubes at low pressure and temperature state

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**The detonation of a CHNO explosive was used for the first time to synthesize carbon nanotubes effectively at low pressure and temperature by introducing a cobalt catalyst and/or paraffin into the detonation system.**

Using detonation chemistry for peaceful purposes is an interesting and challenging issue, especially for nanostructure constructions due to simple processing and low production cost.[1] Typical detonation of nitro-hydrocarbons (CHNO) can produce nano-sized pure carbon particles with both $sp^3$ and $sp^2$ bonded structures.[1a] Detonation synthesis of $sp^3$ diamond nanoparticles has been intensively studied and successfully industrialized.[1a,2] A diamond content as high as 80 wt% is available following this procedure.[2c] The synthesis generally employs high-energy explosives and operates at very high loading densities (2–3 g $cm^{-3}$) to reach a detonation Chapman–Jouguet (CJ) state with extremely high pressures and temperatures, typically a few tens GPa and thousands degrees.[1a,2] The reasons are that the diamond-to-graphite phase transformation often occurs in the normal range of pressure and that the size reduction and the large difference between surface energies of diamond and graphite forms lead to great changes in phase diagrams of nano-sized carbon particles compared to that of bulk carbon and significantly raise the pressure level of graphite–diamond kinetic boundary line.[3] Nano-sized diamond nanoparticles are formed at a CJ point that is above the raised graphite–diamond kinetic line, at which $sp^3$ diamond structure is thermodynamically stable.

On the other hand, the raised graphite–diamond kinetic boundary line of the size-reduced carbon widens the graphite phase zone, that is, $sp^2$ graphite structures can be well formed under mild detonation conditions. If proper conditions are selected, it is possible for the detonation-resulting small carbon species to assemble into carbon nanotubes (CNTs), which are constructed by $sp^2$ bonded pure carbon walls (multi-walled or single-walled) and have drawn great attention in the scientific community due to their unique properties and wide potential applications.[4] Here we report an efficient synthesis of $sp^2$ carbon nanotubes by catalysis-assisted detonation of picric acid (PA) at very low CJ pressure and temperature.

The detonation of PA (2 g) were performed in a sealed stainless steal pressure vessel (10.8 ml), connected with a pressure gauge, and induced by rapid heating (20 °C $min^{-1}$) to 310 °C. When the detonation occurs, about 40 MPa pressure (shock wave) and 900 °C temperature are produced inside the vessel. After the detonation, the vessel was cooled in air and emptied of gaseous products, and then the solid products were collected.

Initially, we attempted to synthesize CNTs by a detonation of PA alone, but this failed. Very little solid carbon (about 5 wt% of carbon in fed PA) was collected due to the high O : C atomic ratio (7 : 6) and low hydrogen content (H : C = 1 : 2) in PA, most of the produced small carbon species being oxidized to gaseous CO. In the situation of diamond synthesis, in which detonation occurs at high CJ pressure and temperature, and equilibrium favours the reaction $2CO \rightarrow CO_2 + C$ (solid).[1a] Under our experimental conditions, however, CO is kinetically stable and the O/C atomic ratio is still high (0.92) after complete oxidation of all H atoms to $H_2O$, thus a large amount of CO is produced. In addition, the obtained solid product consists of $sp^2$ graphite-like amorphous nanoparticles, with sizes of 10–70 nm. No tubular structure is formed likely due to too low temperature, corresponding to the employed low loading density (0.2 g $cm^{-3}$) of PA, to allow the development of $sp^2$ networks.

When cobalt acetate, $Co(Ac)_2$, is introduced with PA, with $Co(Ac)_2$ : PA molar ratios of 1 : 20–1 : 30, the solid carbon yield is significantly enhanced after detonation and carbon nanotubes are well grown. In the obtained product, tubular structural carbon is the dominant component, with a content of 80–90%. The main impurities are cobalt-encapsulated onion-like nanoparticles and a minority of graphite-like amorphous carbon particles. Additionally, the gaseous detonation products mainly contain $CO_2$, $N_2$ and $H_2O$, with little CO. These results indicate that cobalt nanoparticles, formed by a quick decomposition of $Co(Ac)_2$ during the detonation, play an excellent catalytic role in the disproportion reaction of CO and in the nucleation and growth of CNTs. Both the direct explosive decomposition of PA and the subsequent CO disproportion reaction on the surface of cobalt particles provide the small carbon building blocks for CNT assembling. The former process is similar to the catalysis-assisted arc-discharge and laser-evaporation of graphite carbon for CNT syntheses,[4,5] and the latter process is similar to the catalytic CO disproportionation approach.[6]

Considering part of carbon atoms involved in PA being consumed by $CO_2$ formation, liquid paraffin† is introduced into the PA-$Co(Ac)_2$ system, with a paraffin–PA weight ratio of 1 : 4. The heat produced from the detonation quickly decomposes the paraffin (this may be also catalyzed by the formed cobalt particles[7]) into small carbon species and hydrogen radicals. The former directly participates in CNT assembling and the latter captures oxygen from PA and forms $H_2O$, which effectively enhances the solid carbon formation and depresses the carbon consumption from $CO_2$ formation as indicated by the analyses of gaseous product.

Elemental analyses using energy dispersive X-ray spectrometry shows that the detonation product of PA–$Co(Ac)_2$–paraffin consists mainly of carbon and cobalt; very little oxygen and nitrogen are also evident, possibly resulting from adsorbed $N_2$ and $H_2O$. X-Ray diffraction results reveal that carbon exhibits an $sp^2$ graphite structure, with a diffraction line at a $d$ value of 3.342 Å (002), and that cobalt has a metallic cubic structure, with diffraction lines at $d$ values of 2.052 (111), 1.776 (200) and 1.258 Å (220). $HNO_3$ and $HClO_4$ treatment[8] of the detonation product was performed to remove cobalt and $sp^2$ bonded carbon, and showed no residue, suggesting there is no $sp^3$ diamond carbon in the detonation product.

The introduction of paraffin enhances the synthesis efficiency due to its high carbon content and generating additional carbon building blocks for CNT assembling. A content of CNTs as high as 80–90% in the detonation product of PA–$Co(Ac)_2$–paraffin can be obtained reproducibly, as observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 1).‡ The produced CNTs are multi-walled, having outer diameters of 12–50 nm and lengths of 0.5–40 μm. All tubes are separated from each other and show tangled morphologies. Most of the tube walls are well crystallized and

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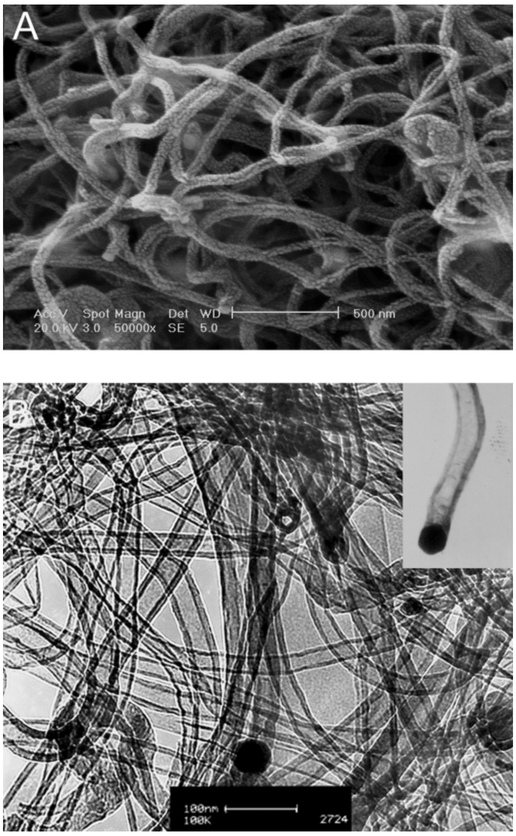

**Fig. 1** SEM (A) and TEM (B) images of a typical product from the detonation of a PA–Co(Ac)$_2$–paraffin mixture, showing that tubular structures are dominant. Inset of B shows one tubule capped by a cobalt particle.

constructed by several to tens graphite layers parallel to the tube axis, with an interlayer spacing of 0.34 nm as revealed by high-resolution TEM (Fig. 2), but some of them have obvious defects in the graphite networks. Cobalt nanoparticles are frequently located at the ends of the CNTs, with sizes close to the diameters of the tubes (inset of Fig. 1B), suggesting that the CNT growth mechanism in the present process is similar to that in the catalytic decomposition of hydrocarbons,[9] in which the tubules grow by the extrusion of carbon, dissolved in a metallic catalyst particle that is over-saturated in carbon at one part of the surface.

However, there are large differences between the present detonation process and the traditional catalytic decomposition of hydrocarbons or CO. In our process, the system temperature is generated by the exothermic decomposition of explosive following a self-heating process and drops quickly after the detonation.[§] Additionally, all carbon species for CNT assembling are supplied in an extremely short period (on a microsecond time-scale), and a high gas pressure (tens of MPa) is produced. Under such conditions, the instant density of carbon species inside the reactor is very high, about 0.009 mol cm$^{-3}$ carbon atoms, while the tube growth is very effective so that 80–90% tube content is available. This means that the CNT growth rate is extremely high, in accord with the theoretical estimation: a multi-wall CNT with 5 nm diameter and 1000 μm length grows in $10^{-3}$–$10^{-4}$s.[10] On the other hand, the fluctuating system temperature and the high density of carbon species are perhaps responsible for the formation of the structural defects. The introduction of paraffin increases the number of defects, especially for high paraffin–PA ratios.

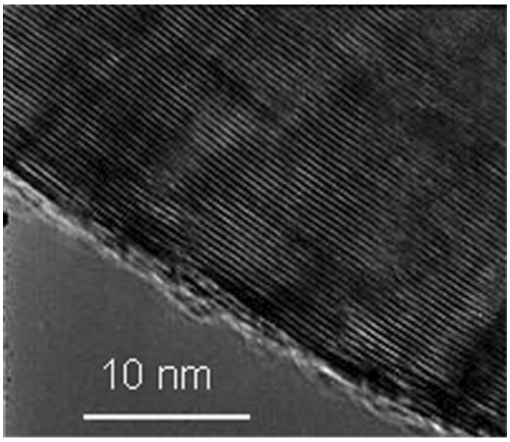

**Fig. 2** High-resolution TEM image showing that the tube walls are well crystallized.

Our synthesis of CNTs by a detonation process is certainly not the first. Kroke *et al.*[11] recently observed CNTs being formed after a detonation of 2,4,6-triazido-*s*-triazine ($C_3N_{12}$), although they employed a specially prepared explosive with very low carbon content and operated at a high CJ pressure (1.63 GPa), which resulted in a very low content of CNTs of only 2%.

In our approach, a very common CHNO explosive, PA, is employed, a catalyst and additional hydrocarbon are introduced into the detonation system, and the detonation occurs at very low CJ density and pressure. Such a detonation process is chemically much different from that for pure C/N explosives and undoubtedly facilitates practical operation. On the other hand, compared to the other processes for CNT syntheses, our process is characterized by high-density and high-pressure conditions, which experimentally shows that CNTs can grow in such an environment and provides an alternative process for CNT synthesis and a new route for theoretical studies on tubule growth, especially in high density environments and in the presence of metal catalysts.

## Notes and references

[†] The employed paraffin has a boiling point of 300 °C and carbon and hydrogen content of 82 wt% and 18 wt%, respectively.

[‡] SEM and TEM analyses were carried out at a scanning electron microscope (Philips XL30-FEG) and transmission electron microscope (Philips CM200-FEG), respectively.

[§] During experiments, we stop heating while the detonation occurs and place the reactor in air for cooling.

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