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ChemComm
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Carbon nanohorns grown from ruthenium nanoparticles

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Received (in Cambridge, UK) 31st January 2002, Accepted 9th April 2002
First published as an Advance Article on the web 19th April 2002

A nanoscale ruthenium/gold bimetallic cluster of clusters has been used as a molecular precursor to produce pure ruthenium nanoparticles (seeds) as catalysts for the growth of carbon nanohorns (CNHs).

Carbon nanotubes (CNTs) have been one of the most intensely studied materials since their discovery in 1991.[1] Currently, the most widely adopted method for their synthesis is by chemical vapour deposition (CVD) of hydrocarbons using Ni, Fe, Co, Mo, *etc*., as catalysts.[2–4] Single-walled carbon nanohorns were first observed by Iijima *et al.* in 1999,[5] and recently a synthesis of nanoscale carbon structures with conical and cylinder-on-cone shapes was reported.[6] Field emission characteristics of CNTs have been widely studied, often for field emission displays.[7] It has been argued that the CNTs with the highest length/diameter ratio, hence the largest electrical field enhancement factor, are the best candidates in the carbon nanotube family for future emission devices. However, a recent publication indicates that the 'short and stubby' nanotubes with intermediate diameters show the best field emission characteristics.[8] In this communication, we report the use of a Ru/Au bimetallic cluster, $[\text{DAB-dendr-}[N(CH_2PPh_2)_2]_{16}(\mu{:}\eta^1{:}\eta^1\text{-}Au_2Ru_6C(CO)_{16})_{16}]$ (DAB-Ru96-Au32) to produce metallic nanoparticles *in situ* as catalysts for growth of short, stubby and horn-like carbon nanotubes. Characterisation by high resolution transmission electron microscopy (HRTEM) reveals that the carbon structure possesses semi-ordered graphitic features, which is novel and which should be of considerable potential in the development of nanoscale electron field emission devices.

The DAB-Ru96-Au32 precursor was prepared by binding the 16[P-N-P] tridentate terminal functionalities of the organic third generation dendritic core to the di-gold hexa-ruthenium $[Au_2Ru_6C(CO)_{16}]$ cluster unit.[9] For the growth of CNHs, a TEM grid coated with a thin carbon film was used as a substrate. It was first treated with isopropyl alcohol to produce plenty of –OH groups on the surface, followed by the deposition of the precursor cluster onto the substrate from a dichloromethane solution. Growth of the CNHs was performed by CVD. The catalyst was first annealed at 700 °C under ammonia (3 Torr). Subsequently acetylene was added ($C_2H_2 : NH_3 = 75 : 200$ sccm) as the precursor of carbon for the vapour deposition.

Fig. 1(a) shows a TEM image of the CNHs grown in this way. The CNHs are short and hollow with a ruthenium particle sitting at the top. The cavity diameter is dependent on the size of the encapsulated metal particle. This type of structure suggests a 'tip growth mechanism' under our experimental conditions. Fig. 1(b) shows that the CNHs are not uniform along their central axis. The lower part of the tube body has larger diameter, suggesting that a possible growth mechanism may first involve the core formation of the CNHs, which then acts as a substrate for subsequent thickening by deposition of secondary carbon atoms. Fig. 2 shows a HRTEM image for several other CNHs. It can be seen that the body of the CNHs does not correspond to a well-ordered graphitic structure such as normal multi-wall carbon nanotubes, nor of amorphous carbon. Instead they appear to possess an intermediate structure falling something between these two. Some well-layered graphitic regions are observed around the metal particles at the top, giving us an insight into the activity of the catalytic metal particle in the growing process.

Both Figs. 1 and 2 indicate that the metal nanoparticles have a wide size distribution. The smallest metal particle shown in Fig. 1(a) is about 2 nm in diameter. As the size of a single precursor cluster is about 8 nm in diameter,[9] we consider that the 2 nm metal particle is possibly formed from the collapse of a single DAB-Ru96-Au32 molecule after burning off the organic dendritic core and the periphery CO ligands. The larger metal nanoparticles are obviously produced by the aggregation of smaller particles and their subsequent coalescence. Fig. 3

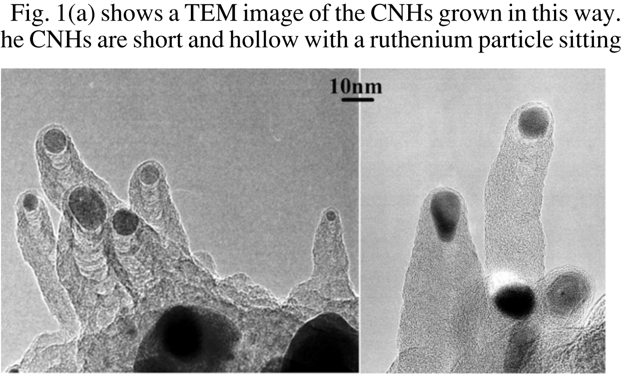

Fig. 1 TEM images showing that the CNHs have a hollow core and a partially ordered graphitic body. Catalytic particles (2–10 nm diameter) can be seen at the top of the nanohorns.

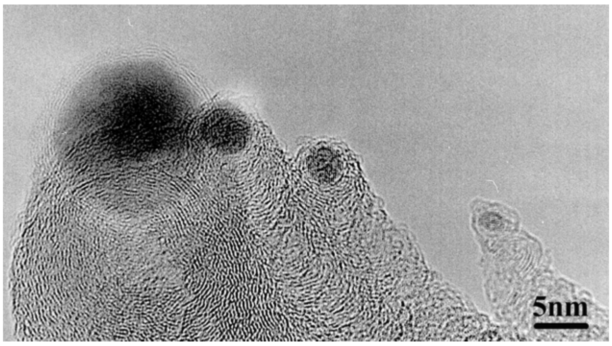

Fig. 2 TEM image showing a partially ordered graphitic structure of the CNHs. This image also shows a large dispersion in size for the Ru nanoparticles.

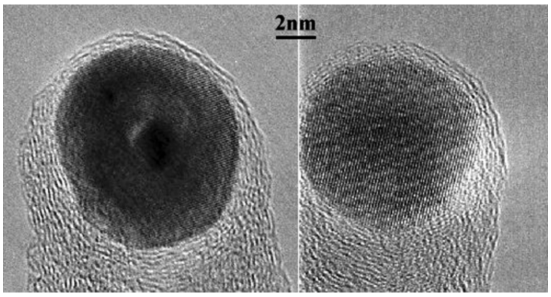

Fig. 3 High resolution TEM images of Ru particles (single crystals) at the tip of two CNHs. The left particle has a lattice spacing of 2.05 Å which corresponds to Ru(101) [2.051 Å], and the right particle has a measured spacing of 2.14 Å corresponding to Ru(002) [2.138 Å].

DOI: 10.1039/b201182b

shows an example of the crystal structure of the metal nanoparticles. Measurements of the crystal lattice spacing for several similar particles but with different crystal planes and fringes, confirm that they are pure ruthenium nanocrystals. This indicates that the thermal decomposition of the precursor results in the formation of Ru nanocrystals separating from the Au metal. This is consistent with the literature report that the Au and Ru do not alloy at elevated temperatures,[10] and the catalytic effect described above is arising from Ru rather than Au or an alloy of the two.

We have also carried out field emission measurements using the CNHs sample described above. The tests were carried out in a vacuum of 10^{-7} torr by applying a positive voltage to a tungsten current probe, with tip diameter of about 10 μm and measuring the current at the cathode. The separation between anode and cathode was set to 10 μm. Current–field characteristics, recorded at different areas of the sample, showed turn-on fields of the order of 5V $\mu m^{-1}$and saturation current densities as high as 1 mA cm^{-2}. The threshold field calculated for the nanohorns, *i.e.* the field that corresponds to an emitted current of 10^{-6} A, ranges between 6 and 10 V μm^{-1} in accordance with the values measured for multiwall carbon nanotube films.[8,11]

In conclusion, in this work we have demonstrated that well characterised DAB-Ru96-Au32 cluster can serve as a precursor of highly active ruthenium nanocrystals for the growth of stubby, horn-like carbon nanotubes.

J. G. thanks ICI and Schlumberger Cambridge Research for financial support.

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