

Bimetallic nanoparticles aligned at the tips of carbon nanotubes†

Sophie Hermans,^a Jeremy Sloan,^b Douglas S. Shephard,^a Brian F. G. Johnson*^a and Malcolm L. H. Green*^b^a University Chemical Laboratories, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW.
E-mail: bfgjl@cam.ac.uk^b Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR.
E-mail: malcolm.green@chem.ox.ac.uk

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Cluster-derived bimetallic nanoparticles have been deposited onto multi-wall carbon nanotubes and shown to be generally homogeneously dispersed, of uniform small sizes, of the same composition as the starting mixed-metal clusters, and to have a tendency to align at the tips of the tubules.

Carbon nanotubes, due to their small dimensions, large aspect ratio and low density, are very promising for a variety of applications. These include nanoscale fibres,¹ nanoelectronic devices,² probes for AFM and STM microscopy,³ as field emitters arrays,⁴ and as electrode materials.⁵ In this paper, we report the use of multi-wall carbon nanotubes as supports for bimetallic nanoparticles and, additionally, the observation that some of these nanoparticles tend to align at the tips of open nanotubes. The bimetallic nanoparticles, once activated, have already been shown to display excellent catalytic activity.⁶ The new composite materials described here could therefore function as efficient heterogeneous catalysts in a variety of processes where a carbonaceous or conducting support is crucial.

Mixed-metal clusters of ruthenium in association with either tin or platinum have been deposited onto multi-wall carbon nanotubes (MWNTs) that had been opened in refluxing concentrated HNO₃ according to an established procedure.⁷ In a typical experiment, MWNTs were mixed with the molecular cluster compounds in dichloromethane–isopropanol (1:1 v/v). The resulting suspension was stirred at room temperature for 30 min and the solvents were then left to evaporate slowly in air. The clusters deposited onto MWNTs included [Ru₆C-

(CO)₁₆SnCl₂],⁸ [PPN][Ru₆C(CO)₁₆SnCl₃],⁸ [Ru₅C(CO)₁₄Pt(COD)]⁹ and [Ru₆C(CO)₁₆Pt(COD)].⁹ The specimens were examined in a 300 kV JEOL 3000F field emission gun high resolution transmission electron microscope (HRTEM; C_s = 0.57 nm; point resolution = 0.16 nm). Images were acquired with a Gatan model 794 (1 k × 1 k) CCD camera. Energy dispersive X-ray spectra (XEDS; LINK 'ISIS' system) were obtained using a 0.5 nm diameter electron probe.

The results obtained with each cluster type were found to be very similar, and typical examples are presented in Fig. 1. Nanoparticles can clearly be seen to be decorating the MWNTs and it can be seen from the low magnification image in Fig. 1(a) that they are evenly distributed over the MWNTs walls. The clusters were found primarily on the external surface although some migrated into the internal cavities, presumably through the open ends of the MWNTs. The external nanoparticles were crystalline with the various {hkl} fringes orientated randomly with respect to the MWNT axis. The size distribution was narrow, with an average particle size of 1.8 ± 0.5 nm. The bimetallic nature of the nanoparticles was verified by XEDS and the elemental ratio of the two metals was the same as that of the starting cluster (see ESI†).

Only a few cases of metallic particles decorating the exterior of carbon nanotubes have been reported in the literature, and these were obtained by a variety of routes (see ESI†).^{10–17} The particle sizes described ranged from 1 to 30 nm, most of which are larger than the sizes reported here. Only one report on *bimetallic* particles was found in the literature, *i.e.* Ru–Pt bimetallic particles formed inside nanotubes *via* a template method.¹⁸ Our approach is thus a unique way to produce well-dispersed homogeneous bimetallic nanoparticles with controlled composition on the MWNTs surface.

One question that arises is the mode of attachment of the clusters on the carbon surface (see ESI†). MWNTs are made of folded sheets of graphene that may also be visualised as concentric sets of elongated fullerenes. The interaction of

† Electronic supplementary information available: XEDS spectrum of the sample prepared from [Ru₅C(CO)₁₄Pt(COD)]; Table listing reports on nanotubes decorated with nanoparticles from the literature; Suggested binding modes of clusters to MWNTs. See <http://www.rsc.org/suppdata/cc/b1/b109923j/>

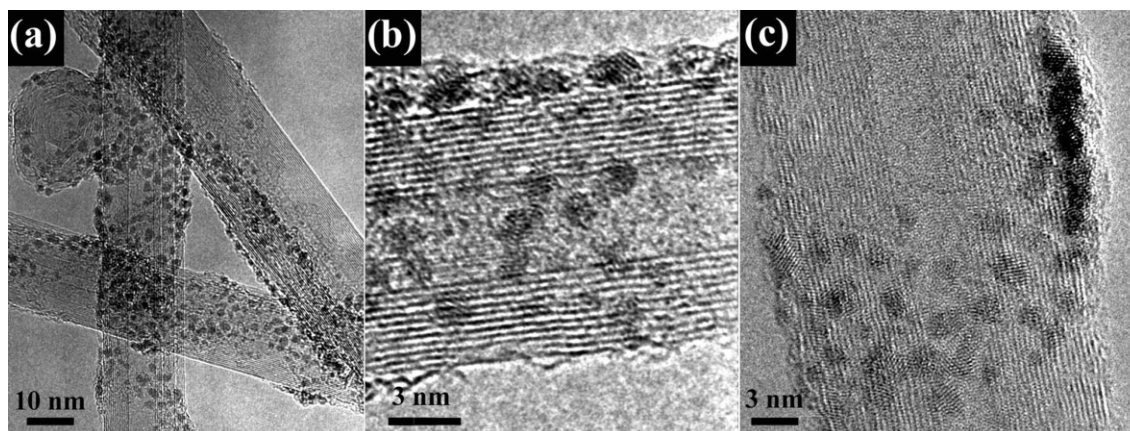


Fig. 1 HRTEM micrographs of nanoparticles derived from [Ru₆C(CO)₁₆Pt(COD)] decorating carbon nanotubes: (a) lower magnification and (b) high magnification HRTEM images; (c) HRTEM micrograph of nanoparticles derived from [Ru₅C(CO)₁₄Pt(COD)] on carbon nanotubes. The spacing between the carbon layers equals 3.4 Å.

fullerenes with Ru clusters has been investigated and was shown to involve π -bonds between a C_6 ring and a triangular face of the cluster.¹⁹ We believe that a similar interaction occurs between the clusters and MWNTs. C=C bonds within the carbon nanotube could also play a role akin to that of a η^2 ligand for the Pt atom by displacement of the COD ligand, or for the Sn atom by displacement of two Cl^- , by analogy with a trisium cluster derivative of C_{60} .²⁰ Another possibility is the interaction of point defects and dislocations, which are zones of higher reactivity, on the carbon surface with the clusters. Interactions between ruthenium carbonyl and the edges and corners of the graphitic layers of the carbon support, demonstrably free of surface functional groups, has been observed during the preparation of a Ru catalyst supported on graphite.²¹ Additionally, C_{70} has been shown to react selectively with metallic entities on sites presenting a greater degree of curvature, where the carbon atoms display higher reactivity.²² A third option arises from the presence of oxygen functionalities on the surface of MWNTs, which are produced during their purification/opening by oxidation. These groups could act as anchors for the clusters *via* ligand exchange. This would parallel results obtained with $[PPN][Ru_6C(CO)_{16}SnCl_3]$ deposited onto MCM-41,⁶ where EXAFS studies demonstrated the role of the Sn atom in the anchoring process by ligand exchange of Cl^- for surface O atoms.

Of particular relevance in this respect was the observation that nanoparticles smaller than those found on the external MWNT surfaces (diameter *ca.* 0.8 nm) tended to align themselves evenly in a straight line within the tips zone of the MWNTs (Fig. 2). These particles may consist of only single molecular clusters anchored at the terminus of the graphene sheets. This result raises the question of the nanotube–cluster interaction further. It is known that the tips of MWNTs present a higher concentration of oxygenated groups, due to the

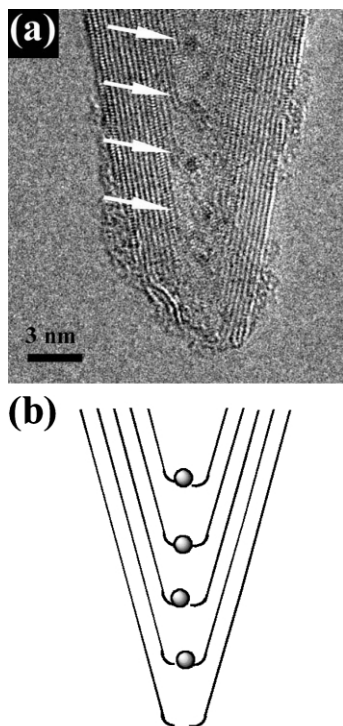


Fig. 2 (a) HRTEM micrograph of nanoparticles derived from $[Ru_5C(CO)_{14}Pt(COD)]$ on carbon nanotubes, showing the nanoparticles at the tips. (b) Schematic representation.

presence of more pentagonal defects at the tips, which are more sensitive to oxidation. However, the tips of purified nanotubes are also opened by the oxidative treatment, leaving a high proportion of ‘dangling’ bonds at the termini, which might bind to metals more strongly than oxygenated functions. By analogy, a Pt complex has been shown to react at the edge of semibuckminsterfullerene ($C_{30}H_{12}$), rather than on the benzene ring at the pole.²³ From the observed arrangement of the tip clusters, it could also be deduced that mechanical ‘blocking’ occurs with two sides of an open cap acting as ‘pincers’ for the particles, as shown schematically in Fig. 2(b).

The materials described here could act as heterogeneous catalysts in applications where a carbonaceous support is important. For example, a Ru/nanotubes catalyst displayed enhanced selectivity compared to ruthenium on active carbon.¹⁴ Electrochemical applications may also be considered and our Ru–Pt/C composite materials could, for example, be used as electrocatalysts for direct methanol fuel cell applications.

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