Preparation and properties of buckypaper–gold nanoparticle composites†

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Received 11th January 2010, Accepted 2nd March 2010
First published as an Advance Article on the web 10th March 2010
DOI: 10.1039/c000522c

Highly conductive buckypaper-gold nanoparticles composites have been prepared by the *in situ* electroless deposition of gold nanoparticles during the filtration that resulted in increases in conductivities of up to 684% at very low gold content.

Carbon nanotube (CNT)–metal nanoparticle composites have been the subject of intensive research in recent years.[1–4] Gold–nanotube composites are of particular interest, due to a range of their potential applications including glucose biosensors and the voltammetric detection of mercury.[5,6] It has been demonstrated that Au nanoclusters can be effectively anchored *via* hydrophobic interactions between the thiol functional group of the nanoparticles and the acetone-activated nanotube surface.[7] Gold nanoparticles (Au NPs) can be electrochemically deposited onto carbon nanotubes.[8,9] Also it was found that acid treated nanotubes which were heated under reflux with $HAuCl_4$ can form Au NPs of size 1–7 nm.[10] However, most of these processes involve the harsh treatment of nanotubes with concentrated mixtures of strong oxidising agents, such as sulfuric and nitric acid which can damage the nanotubes.[11] Single-walled nanotubes (SWNTs) possess a redox potential of +0.5 V *versus* the standard hydrogen electrode;[12] (Au^{3+}) and (Ag^{+}) have standard redox potentials of +1.43 and +0.8 V respectively and therefore can be spontaneously reduced onto the nanotubes. Choi *et al.* observed a highly selective electroless deposition of metal nanoparticles onto SWNTs as a result of a direct redox reaction between ions and nanotubes.[13] Upon immersion of SWNTs in $HAuCl_4$ (Au^{3+}) and Na_2PtCl_4 (Pt^{2+}) solutions, Au and Pt metal nanoparticles spontaneously formed on the sidewalls of the SWNTs. Qu *et al.* developed substrate-enhanced electroless deposition, which enabled control of the shape and size of the nanoparticles. This has been used for an effective site-selective deposition of metal nanoparticles onto specific areas of carbon nanotubes.[14,15]

Buckypaper is a thin sheet made from aggregates of carbon nanotubes which might have many potential applications including flexible electrodes for displays, thermally conductive materials for integrated circuits, antistatic coatings, sensors, armor plating and substrates to grow nerve cells and biological tissues.[16–18] Its conductivity can be up to $\sim 10^6$ S/m.[19,20] The mechanical properties of buckypaper are dominated by the nature of the junctions between individual tubes,[21] although tube entanglement is also important.[22]

Electroless deposition of copper metal onto buckypaper has been shown to give large increases in both conductivity and tensile properties.[23]

Here we describe the formation of new buckypaper–gold nanocomposites by spontaneous *in situ* deposition of Au NPs from gold salt solution onto the surface of nanotubes in a nanotube mat during the buckypaper preparation. Briefly, SWNT and multiwalled nanotube (MWNT) based buckypaper–gold composites were prepared adding 0.035 g of each type of CNTs to 0.01 M $HAuCl_4 \cdot 3H_2O$ solution in N-methyl pyrrolidone (NMP). The suspensions were sonicated in a sonic bath for 3 h to ensure that the CNTs were evenly dispersed through the gold–NMP solution. To produce a flat homogeneous sheet of buckypaper the nanotubes were vacuum filtrated through a porous alumina membrane (Anodisc 47 mm in diameter) and washed with deionised water and ethanol. The free standing buckypapers were peeled from the membrane and left to dry at 40 °C. After the films were dried they were cut into strips of width ~3 mm and lengths of up to 3.5 cm. Film thickness was between 100 μm and 120 μm. Control samples without the gold salt were prepared similarly.

The products have been characterised by FT-IR spectroscopy (ESI†), electron microscopy, thermogravimetric analysis (TGA), electrical and mechanical measurements. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analysis of SWNT/Au NP buckypaper clearly demonstrated the presence of spherical Au NPs (Fig. 1). The diameter of the particles was 3.2 ± 0.9 nm. Fig. 2 shows TEM and SEM images of MWNT/Au NP buckypaper. The Au NPs here had a diameter of 7.2 ± 0.9 nm. Energy dispersive X-ray spectroscopic (EDX) analysis confirmed the presence of gold particles (Fig. 1 and 2).

TGA has shown that there was 5.67 mass % of gold metal in the SWNT buckypaper composite and 3.25 mass % gold in the MWNT composite (see ESI†). The higher quantity of metal for the SWNT–Au-composite sample would suggest a larger surface energy of the SWCNT and therefore a higher redox potential.

The buckypaper was then cut into strips of equal dimensions for conductivity and mechanical tests. The conductivity was measured

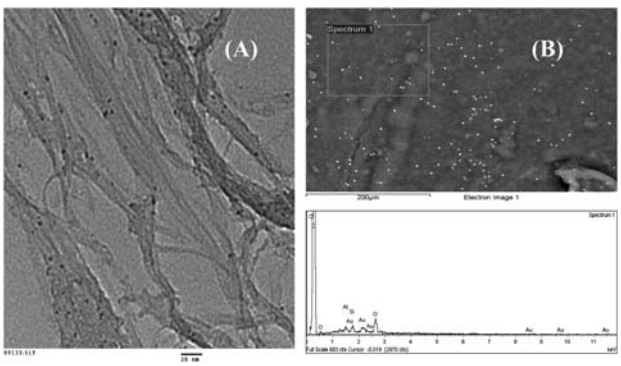

Fig. 1 (A) TEM image; (B top) SEM of the SWNT/Au NP buckypaper surface, (B bottom) EDX of the selected area.

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† Electronic supplementary information (ESI) available: Experimental details, FT-IR, and TGA curves. See DOI: 10.1039/c000522c

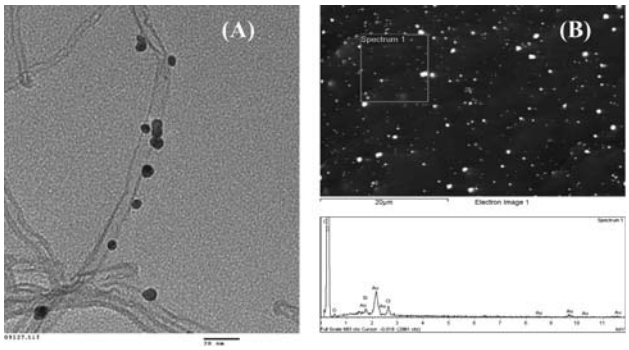

Fig. 2 (A) TEM image; (B top) SEM of the MWNT/Au NP buckypaper surface, (B bottom) EDX spectrum of the selected area.

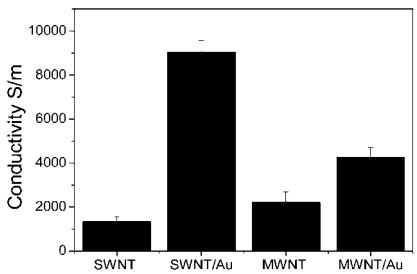

Fig. 3 Conductivity values for strips of SWNT and MWNT buckypaper and their corresponding gold composites.

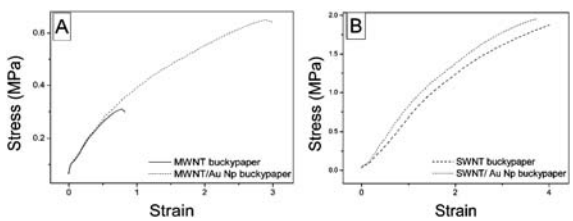

Fig. 4 Sample stress-strain curves for (A) MWNT–buckypaper and (B) SWNT buckypaper.

across 4 strips using 4 point probe technique and the results were averaged. It was found that the Au NP-buckypaper composites had a greatly increased conductivity over that of pristine buckypaper (Fig. 3) The MWNT buckypaper composite doubles its electrical conductivity over that of the MWNT buckypaper sample going from 2224 S/m to 4261 S/m. A much larger increase from 1322 S/m to 9039 S/m was observed for SWNT buckypaper composites. Thus the SWNT/Au NP buckypaper demonstrated a 684% increase in conductivity. This larger increase in conductivity can be explained by several factors. Firstly the SWNTs reduced more gold by weight than the MWNTs due to a higher redox potential. Secondly the particle size relative to the nanotube diameter was larger which would cause the Au NPs to have more of a chance of bridging across two nanotubes.

Stress–strain curves were recorded for the pristine buckpapers and buckypaper composites (Fig. 4). An average for each of the Young's modulus (Y), ultimate tensile strength (UTS) and toughness values was taken for SWNT and MWNT buckypaper and composites (Table 1). The Au NP–buckypaper composites demonstrated a lower

Table 1 Mechanical properties of SWNT and MWNT buckypaper

Sample name	Y (MPa)	UTS (MPa)	Toughness
SWNT buckypaper	6.48 ± 1.02	18.80 ± 0.32	$4.60 \times 10^7 \pm 0.91 \times 10^7$
SWNT/Au NP buckypaper	5.33 ± 0.92	19.55 ± 0.15	$6.14 \times 10^7 \pm 1.60 \times 10^7$
MWNT buckypaper	3.75 ± 0.12	3.09 ± 0.24	$1.83 \times 10^6 \pm 0.34 \times 10^6$
MWNT/Au NP buckypaper	2.12 ± 0.24	6.64 ± 0.14	$9.31 \times 10^6 \pm 2.59 \times 10^6$

Young's modulus. This is more pronounced for the MWNT buckypaper than for the SWNT buckypaper. There was an increase in both the UTS and the toughness for the Au NP–buckypaper composites, in fact, a maximum increase in toughness of 505% for the SWNT/Au NP was measured (Fig. 4). Bulk gold has Y = 79 GPa and UTS of 100 MPa which are much lower than that of carbon nanotubes and would theoretically lower the overall mechanical properties. Nanoindentation investigations demonstrate that the mechanical properties are dependent on the size of the nanoscale object being studied.[24] When comparatively ductile metals such as aluminium and gold have their grain size refined into the nanoscale, the otherwise soft material can be springy and hard.[25] The addition of the gold decreases the stiffness of the buckypaper composites but increases the breaking point and the area under the curve.

In summary, we have demonstrated that gold nanopartycles have been spontaneously deposited onto the nanotubes during filtration giving buckypaper composites with significantly increased conductivity at very low gold content (3.25 and 5.67 mass %). Some improvements in mechanical properties were also observed. Thus this relatively facile approach allows us to substantially improve the conductivity of buckypaper based materials, which could be potentially utilised in catalysis, flexible electrodes, conductive substrates and coatings. In our future research we plan to further develop this technique for the highly aligned buckypaper, which has much higher original conductivity. We also believe that metals such as silver, platinum and palladium can be deposited into a nanotube matrix in a similar way enabling to prepare a series of new buckypaper–metal nanoparticle composites with broad range of important potential applications.

The authors gratefully acknowledge the financial support of Science Foundation Ireland and CRANN.

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