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# Capillarity and silver nanowire formation observed in single walled carbon nanotubes

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**Single walled carbon nanotubes (SWNTs) exhibit similar capillarity properties to those exhibited by multiple walled carbon nanotubes (MWNTs); SWNTs, previously filled in low yield (*ca.* 2%) by solution chemistry techniques, can be filled in high yield (up to *ca.* 50%) by the liquid phase method; compositions from the KCl–$UCl_4$ and AgCl–AgBr systems were used to fill SWNTs without causing them significant chemical or thermal damage; in the case of the latter, exposure to light or an electron beam resulted in the partial photolytic reduction of SWNT incorporated silver halides to continuous metallic silver 'nanowires' within the capillaries.**

It has been demonstrated that molten media such as $PbO_x$, $V_2O_5$ and $MoO_3$ can fill MWNTs by capillary action.[1–3] This ability of such materials to be so incorporated depends on three characteristics of the filling materials: (i) they must 'wet' the capillaries and have surface tensions below a threshold value in the range 100–200 mN $m^{-1}$;[4] (ii) their overall melting temperature must be low enough to preclude thermal damage to the MWNT capillaries; and (iii) they must not attack MWNTs chemically. A modification to the capillary method has extended both the range and complexity of materials available for filling of MWNTs by capillarity.[5] This technique is based on the deposition of either eutectic or non-eutectic components from a mixed metal salt system. Here, we show how the melting properties of the KCl–$UCl_4$[6] eutectic melting system [Fig. 1(a)] and also those of the AgCl–AgBr[7] solid solution [Fig. 1(b)] system can be used to introduce continuous fillings of solid phase materials into SWNTs. The filling yield obtained from these liquid phases and mixtures greatly exceeds that obtained previously by the solution-deposition filling technique.[8]

The conditions for preparing SWNTs filled with compositions from the KCl-$UCl_4$ and AgCl–AgBr systems were established from surface tension/composition data (Tables 1 and 2)[9] and the phase relations depicted in Fig. 1(a) and (b). The SWNTs used in this study were prepared according to the high yield catalytic arc synthesis method reported by Journet *et al.*[10] A structural representation and HRTEM lattice image of an empty 'kinked' unfilled SWNT obtained by the catalytic method are shown in Fig. 2(a) and (b), respectively. All of the halide mixtures were ground and weighed under dry box conditions, and in the case of the silver halide mixtures, exposure to light was minimised. The halide samples were ground together with SWNTs and sealed under vacuum in silica quartz ampoules. The ampoules were passed at 3 cm $min^{-1}$ through a 30 cm three-zone tube furnace with a temperature gradient spanning 300 °C and held for 30 min. at a maximum temperature of *ca.* 100 °C higher than the liquidus or melting temperature of the filling material [see Fig. 1(a) and (b)]. The resultant mixture was then furnace cooled for 3 h to room temperature. The filled specimens were characterised by high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDX).

In the case of the KCl–$UCl_4$ system, the pure end component $UCl_4$ apparently attacked the SWNTs and no filling was observed. In addition, the KCl end member was found to be too

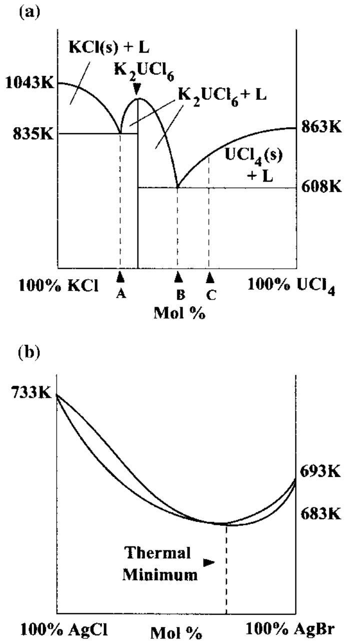

**Fig. 1** (a) KCl–$UCl_4$ pseudobinary eutectic melting system. Compositions A, B and C were used to fill SWNTs. (b) Diagram showing the melting properties of the AgCl–AgBr solid solution system. AgCl, AgBr and the thermal minimum ($AgCl_{0.2}Br_{0.8}$) were used to fill SWNTs.

**Table 1** Melting temperatures and surface tensions of compositions used to fill SWNTs in the KCl-$UCl_4$ system [see also Fig. 1(a)]

| Composition [see Fig. (1b)] | KCl–$UCl_4$ (mol %) | Filling temperature/K | Surface tension/mN $m^{-1}$ |
|---|---|---|---|
| KCl | 100 | 1143 | 93.13 |
| A | 73.2 : 26.8 | 935 | 64.98 |
| B | 50 : 50 | 700 | 54.00 |
| C | 39.33 : 60.67 | 842 | 50.54 |
| $UCl_4$ | 0 : 100 | 963 | 26.8 |

**Table 2** Melting temperatures and surface tensions of compositions used to fill SWNTs in the AgCl–AgBr system [see also Fig. 1(b)]

| Composition | Filling temperature/K | Surface tension/mN $m^{-1}$ |
|---|---|---|
| AgCl | 833 | 173.08 |
| AgBr | 800 | 151.3 |
| $AgBr_{0.2}Cl_{0.8}$ | 783 | 154.4 |

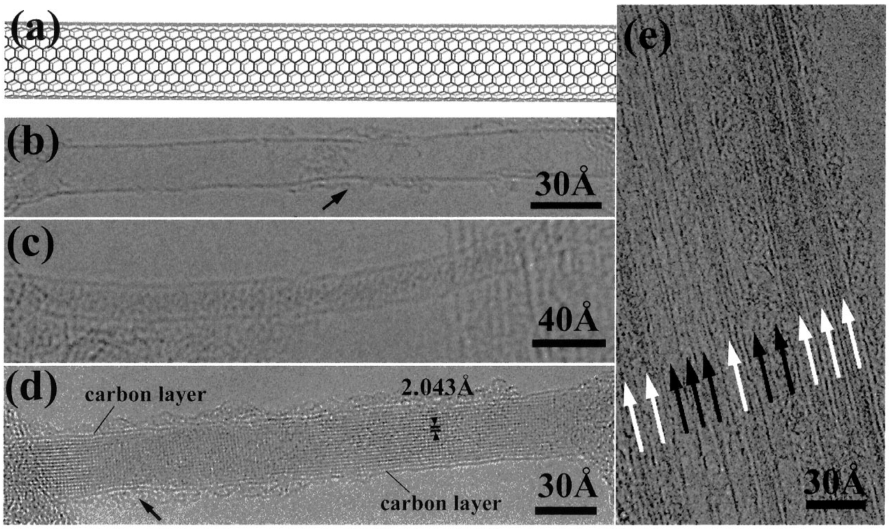

**Fig. 2** (a) Schematic structural representation of a SWNT. (b) HRTEM image showing an empty SWNT. The defect region near the centre (arrowed) is possibly caused by the incorporation of non-six-membered rings into the graphene wall. (c) SWNT continuously filled with a KCl–UCl$_4$ eutectic mixture [composition A, Fig. 1(a)]. (d) Wide capillary SWNT continuously filled with Ag metal formed by capillary insertion of AgCl followed by photolytic decomposition. The indicated *d*-spacings correspond to the (020) lattice planes of Ag metal. Note 'kink' causing distortion in the Ag microstructure [*cf.* Fig. (b)]. (e) Showing high yield incorporation of AgBr into an SWNT bundle. Filled SWNTs are indicated by light arrows; unfilled SWNTs by dark arrows.

beam sensitive to be directly observed at room temperature *via* HRTEM. However, the three lower melting compositions A, B and C [Fig. 1(a)] were able to wet and fill the SWNTs without causing them significant damage. For composition A, corresponding to one of two eutectics in the KCl-UCl$_4$ system [see Fig. 1(a)], an amorphous homogenous product of composition $(KCl)_x(UCl_4)_y$ (with $x/y \approx 3:1$) was obtained inside SWNTs. Fig. 2(c), shows a HRTEM micrograph of a discrete (10,10) SWNT continuously filled with the $(KCl)_x(UCl_4)_y$ eutectic mixture. Fillings obtained with compositions B and C (not shown) were found to be either crystalline or polycrystalline.

For the AgCl–AgBr system, the melting range was both lower and narrower than for the KCl–UCl$_4$ system [see Fig. 1(b)]. An important difference was that both end components were able to fill SWNTs without damaging them. The filling yields for the various compositions were found to be $AgCl_{0.2}Br_{0.8} \geqslant AgBr > AgCl$ with approaching 50% filling for the highest yield specimen and *ca.* 20% for the lowest. A difficulty with directly observing the SWNT incorporated products in these kinds of experiments by HRTEM was that the silver halides are both light and electron beam sensitive. However, in the case of SWNTs with lower diameters, phototolytic reduction was apparently retarded and EDX showed that SWNT bundles incorporated with either of the two silver halides still contained both the metal and the respective halogen. For wide bore SWNTs, this was not the case and several were observed with pure Ag filling. Figure 2(d) shows a HRTEM image of a large diameter [≈ 38 Å; *ca.* (28,28) nanotube] SWNT completely filled with 17 layers of silver metal. The initial filling medium in this case was AgCl. A noticeable 'kink' in the SWNT (arrowed), possibly originating from defects present in the original SWNT [*cf.* Fig. 2(b)], causes a corresponding distortion in the incorporated crystal. The *d*-spacing of the material, measured relative to nearby 3.4 Å (0002) graphene fringes (not shown) was measured to be 2.04 ± 0.05 Å, which corresponds to the (200) *d*-spacing of Ag metal and not to the corresponding (020) *d*-spacing in AgCl (2.775 Å), which has a similar $Fm\bar{3}m$ cubic unit cell.[11] Fast Fourier transforms (FFTs) calculated from the lattice image of the incorporated crystal (not shown) also indicated that the Ag wire was veiwed close to a [100] projection and that the (020) lattice fringes belonged to this projection. Fig. 2(e) shows a HRTEM micrograph of the product of a high yield SWNT filling with AgBr within a bundle of (10,10) SWNTs. The paths of empty and filled SWNTs are indicated by dark and light arrows, respectively, and the difference in contrast between the empty and filled SWNTs is clearly visible. Several bundles similar to those illustrated in Fig. 2(e). were observed in this specimen with up to 50% of similarly filled SWNTs.

An important aspect of this work concerns the mechanism of opening of the SWNTs. Previously, we stated that SWNTs could be opened by gently refluxing in HCl.[8] However, none of the filling experiments described in this communication required a separate opening step which indicates that either one is unnecessary (*i.e.* the SWNTs are already open at at least one end) or that the fullerenic end caps of SWNTs are selectively attacked by the molten media during the filling process.

In conclusion, we have demonstrated a simple and reproducible method for the continuous filling of the capillaries of SWNTs in high yield with a variety of materials, thereby showing that these types of nanotubes exhibit similar wetting and capillarity properties to MWNTs. The advantages of using SWNTs over MWNTs in these types of filling experiments is that the former are relatively much more uniform and defect free structures in comparison to the latter and their composite properties will be correspondingly more uniform. The physical properties of the composite materials formed by the methods decribed here are expected to be considerably modified with respect to those of unfilled SWNTs.

## Notes and references

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