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Stable colloidal Co–Pd nanocatalysts for carbon nanotube growth

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The standard preparation method for catalysts for surface-bound growth of carbon nanotubes (CNT) is to sputter or evaporate the metal catalyst (Fe, Co, and Ni) onto the surface. A lower cost method for large areas is to use liquid delivery. Colloids have the advantage of containing the catalyst in nanocluster form. Our previously developed colloidal catalysts were successful for growth but had limited shelf-life due to oxidation and coagulation. Here, we develop an air-stable colloidal catalyst with long shelf-life of many months to years.

1 Introduction Catalytic chemical vapour deposition (CVD) is the most useful method to grow carbon nanotubes (CNT) and nanofibres (CNF) on surfaces because it allows a high degree of structural control. The catalyst is often deposited on the surface as a thin film and then transformed into catalytically active nanoparticles by heating. On the other hand, liquids [1, 2] or colloidal nanoparticles are valuable catalyst precursors [3, 4], as they can be applied to many surfaces with uneven geometries such as meshes and 3D matrices [5]. They also allow patterning at low cost over large areas on flat surfaces by methods such as nano-imprinting [6]. We have previously developed a pure Co colloid that has proved to be a highly efficient catalyst for CNF growth using plasma enhanced CVD (PECVD). However, transition metal colloids tend to be unstable in air [7], and these applications require a more stable system. Here, we report the development of stable bimetallic Co/Pd colloids for nanotube growth. We also give a systematic description of the variation of catalytic activity and nanofibre structure on the colloid composition.

Mixed metal nanoparticles often outperform mono-metal analogues in classical catalysis due to a synergetic effect [8]. Bi-metallic catalysts have been previously used to catalyse nanotube growth in the laser, arc and CVD methods, for better yield, diameter control, higher selectivity or to lower growth temperatures [9–15]. Often, the metals were simply alloyed together. However, colloids and poly-nuclear clusters have the advantage over thin films of having a pre-formed metal core. We can tailor the size, composition and ordering of this core for the particular catalytic reaction [16]. Colloidal precursors can be prepared with a narrow size distribution, which is an advantage in controlling the type of nanotube formed.

2 Method The Co/Pd nanoparticles were prepared using the procedure described by Dominguez-Dominguez et al. [17]. The complete solubility of Co, Fe and Ni with Pd [18] allows the preparation of a range of mixed metal colloids with different Co/Pd contents. The suspensions are stable for several months and may be stored and handled in air.

In detail, 0.8 g of poly-*n*-vinyl pyrrolidone was added to 120 ml of anhydrous ethylene glycol. Different amounts of Co acetate was added to the mixture and was stirred for 3 h at 80 °C (solution 1). Different amounts of Pd(II) acetate was dissolved in 50 ml of 1-4 dioxane with stirring for 2 h (solution 2). Solution 1 was cooled to 0 °C, and solution 2 was poured in. The pH of this mixture was adjusted to 9–10 by adding 1 M NaOH solution. The bright yellow transparent solution was capped and heated to 100 V with vigorous stirring. The solution turns brown indicating a colloid has formed, and the suspension was cooled to room temperature.

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Phys. Status Solidi B **246**, No. 11–12 (2009)

2437

Original

Paper

The nanoparticles were purified as follows. An aliquot containing the desired amount of colloid was treated with a large excess of acetone. This extracted the protecting polymer to the acetone phase, causing flocculation of the colloid. This is purified by either decanting or centrifuge. After removing the acetone phase, the purified colloids were re-dispersed in MeOH by gentle stirring. The stability of this bimetallic colloid is seen by the glycol dispersions were stable for 8 months after preparation, with no aggregation of the colloid.

High resolution transmission electron microscopy (HRTEM) analysis confirms the presence of Co/Pd nanoparticles with diameters of 2–3 nm. Their composition was confirmed by elemental analysis and energy dispersive X-ray analysis (EDX), see Fig. 1.

N-doped Si wafers covered with a 200 nm-thick SiO_2 film (Si-Mat) were diced into ~1×1 cm^2 substrates, surface cleaned (30 min sonication in isopropanol and acetone) and then coated with the colloidal suspension. As previously [6], uniform CNF growth is obtained when a ~50 mL droplet of the colloidal suspension is deposited on the surface and the solvent is allowed to evaporate at room temperature and ambient pressure. Unlike our previous experiments with transition metal colloids [5, 6] this procedure can be now performed on an open bench with no oxidative decomposition of the colloid taking place, and the colloids are stable in air for several months. This is a significant practical advantage.

Carbon nanofibres were grown by DC PECVD [19]. As-prepared samples are heated up to 650 °C for 10 min in NH_3 (200 sccm, 0.6 mbar). A DC discharge is then ignited (600 V, <20 W power), and C_2H_2 is introduced at 200:50 sccm NH_3:C_2H_2 (0.7 mbar). We typically choose a 30 min
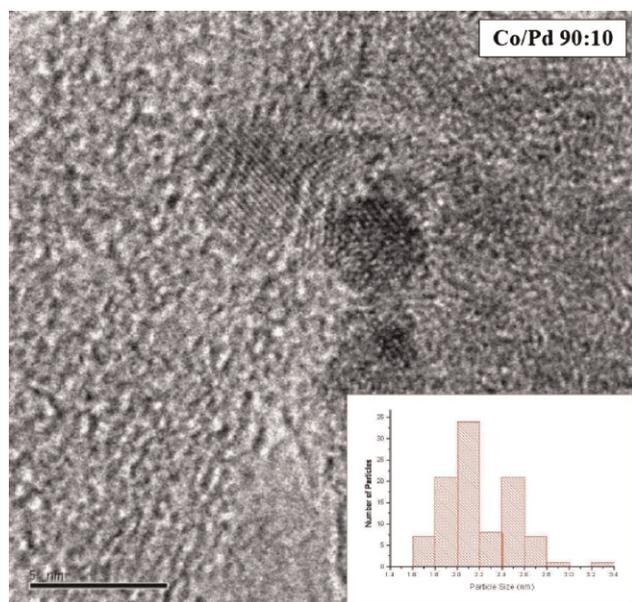
deposition time. As-grown samples were characterised by scanning electron microscopy (SEM, LEO VP1540 FEGSEM) and HRTEM (JEOL JEM-3011, 300 kV). CNFs were scratched from the samples and dispersed onto Cu/lacey C grids for HRTEM.

3 Results and discussion Figure 2 shows the vertically aligned forests of nanotubes grown from Co/Pd colloids with 90:10 and 10:90 molar ratios, respectively. The CNFs are isolated not bundled, the typical microstructure found in PECVD. The vertical alignment is due to the plasma's electric field. The CNF yield is similar for both catalyst systems. To our knowledge, this work is the first successful report of CNF grown by CVD from pure colloidal Pd nanoparticles, rather than Pd thin films [20].

Figure 3 shows HRTEM images of individual CNFs grown using Co/Pd colloids with different molar ratios. HRTEM and Rutherford backscattering (RBS) shows a tip growth mechanism for all colloid compositions probed. The CNF diameter is controlled by the size of the catalyst nanoparticle.

In both cases, we see that the average CNF diameter is ~10 times larger than in the as-prepared colloid, indicating that a significant nanoparticle sintering has occurred at the CVD stage. It is possible that the plasma encourages this
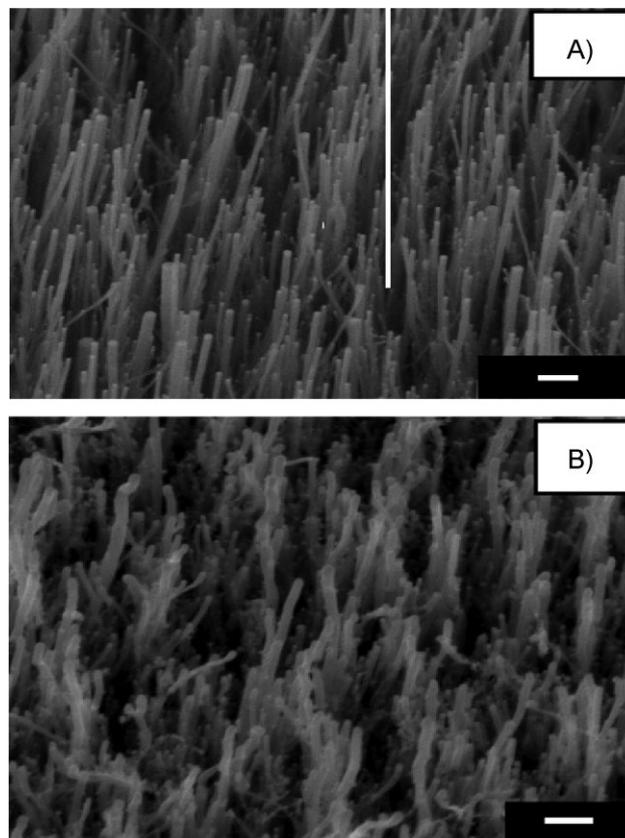

Figure 1 (online colour at: www.pss-b.com) Micrograph of the colloid and a particle size distribution.

Figure 2 SEM images of CNFs grown using (A) Co/Pd 10:90 colloid and (B) Co/Pd 90:10 colloid. Scale bars: 200 nm.
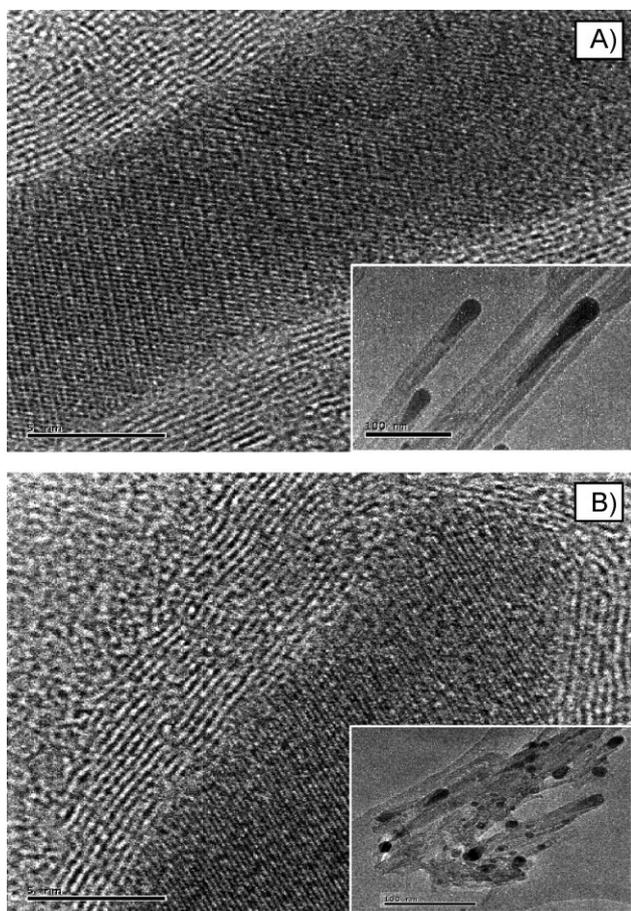
Figure 3 HRTEM images of CNFs grown using (A) Co/Pd 10:90 colloid and (B) Co/Pd 90:10 colloid. Scale bars: 5 nm. Insets: TEM images of individual CNFs. Scale bars: 100 nm.

Figure 4 Variation of catalyst aspect ratio and CNF average diameter with colloid composition. Dashed lines are a guide for the eye only.

sintering [21, 22]. We are looking at ways to reduce this effect, such as changing the support layer [23].

There are noticeable differences between the CNFs. The Co-rich system produces nanofibres with a 32 ± 8 nm diameter, while the Pd-rich system produced nanofibres with 21 ± 7 nm diameter. The Pd-rich colloids result in CNFs with a more hollow structure, with thicker graphitic walls forming a low angle with the CNF axis, and occasional bamboo intersects (Fig. 2a). CNFs grown from Co-rich colloids have a more pronounced herring-bone structure, with thicker walls and graphitic layers stacking densely on the bottom of the catalyst particle (Fig. 2b). Graphitisation increases with Co content of the catalyst. Ichi-Oka et al. [24] observed that Co is more active than Pd in the formation of graphitic carbon.

The different CNF morphologies arise from the different behaviour of the catalyst during growth. We find that the aspect ratio of the catalyst nanoparticle depends strongly on the catalyst composition. The catalyst has a more round shape for Co-rich catalysts but is quite elongated for Pd. The aspect ratio increases with Pd content, rising from 1.4 for Co/Pd 90:10 to 4.3 for a pure Pd colloid (Fig. 4). As the
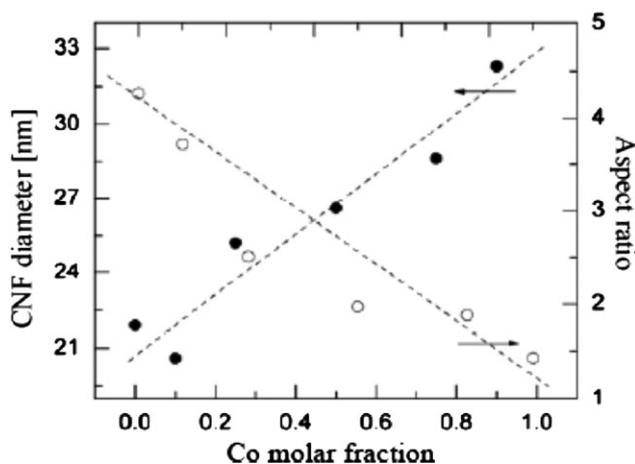
catalyst particle is elongated along the CNF axis for high Pd content, the particles have a thinner cross-section, and this leads to smaller CNF diameters (Fig. 4).

The catalyst nanoparticles have been observed in *in situ* TEM to undergo continuous re-shaping during nanotube growth [25]. This occurs while the catalyst is still solid. The melting points of the Co/Pd alloys do not vary much with temperature [26] so that the different shapes in Fig. 2 indicate either a variation of the creep rate of the metal, or that the carbon walls interact more strongly with the metal in one case. The ends of graphitic layers are anchored to surface steps on the catalyst crystal, and this is stronger for the case of Co. The continuous elongation and contraction of catalyst particles with a wedge-shaped tail leads to herringbone-like CNFs, as in Fig. 3b. On the other hand, C solubility and diffusion rates are lower in Pd and this may lead to the more bamboo-like structure.

Importantly, the CNF diameter is affected by the variation in the molar composition of the colloids. We observed an increasing tendency for the catalyst nanoparticles located at the CNF tips to elongate as the Pd molar content increased. These results represent a step forward in achieving controlled growth of CNFs by using wet catalyst systems such as colloid suspensions. Improvement of the delivery method of the colloid on the substrates will be pursued to obtain a more disperse catalytic system which will render valuable information on the growth.

In conclusion, we have shown that colloidal suspensions of binary Co/Pd colloids, not suffering from oxidative decomposition in air and a long shelf-life of many months, are efficient catalysts for CNF growth.

Original

Paper

Phys. Status Solidi B **246**, No. 11–12 (2009)

2439

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