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High temperature selective growth of single-walled carbon nanotubes with a narrow chirality distribution from a CoPt bimetallic catalyst†

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Chirality-controlled synthesis of single-walled carbon nanotubes (SWCNTs) is a prerequisite for their practical applications in electronic and optoelectronic devices. We report here a novel bimetallic CoPt catalyst for the selective growth of high quality SWCNTs with a narrow chirality distribution at relatively high temperatures of 800 °C and 850 °C using atmospheric pressure alcohol chemical vapor deposition. The addition of Pt into a Co catalyst forms a CoPt alloy and significantly reduces the diameters of the as-grown SWCNTs and narrows their chirality distributions.

Single-walled carbon nanotubes (SWCNTs) are one-dimensional systems with unique properties and various potential and emerging applications.^{1,2} However, the heterogeneity of SWCNTs hinders their application in many fields, such as in electronic and optoelectronic devices, since the electronic and optical properties of SWCNTs depend sensitively on their geometric configurations, *i.e.*, chirality index (n , m).³ Recently, both theoretical and experimental studies have demonstrated that the property of catalysts is one of the key factors that formulate the structures of SWCNTs.^{4–17} Some specific catalyst systems, *e.g.*, CoMo,^{9,14} FeRu,¹² FeCu,¹¹ FeNi,^{15,17} CoMn,¹³ FeCo,^{8,10} have been shown to be able to grow narrow chirality distributed SWCNTs. It is worth noting that low growth temperature seems to be essential for the selective growth of SWCNTs with a small diameter and narrow chirality distribution on the catalysts loaded on commonly used porous supports, *e.g.*, silica or magnesium oxide, while high temperature typically leads to the growth of SWCNTs with relatively large diameters accompanied with broad chirality distributions.^{8–12,15,17–20} For example, small diameter (6, 5)-dominated SWCNTs usually grow at a low temperature of around 600 °C, while such selectivity disappears at higher synthesis temperatures of 750 °C and 800 °C.^{9,11,12} However, low growth temperature usually produces SWCNTs in small quantity and poor quality since it is adverse to SWCNT growth efficiency²¹ and might be not sufficient to heal the defects of SWCNTs during growth.^{22,23} As can be seen, SWCNT growth at low temperature typically

possesses a relatively high defect-induced D band in the Raman spectra.^{8,11,13,17,20,23,24}

Here, we developed a bimetallic CoPt catalyst for the selective growth of narrow chirality distributed SWCNTs at a high reaction temperature using atmospheric pressure alcohol chemical vapor deposition (CVD). The addition of Pt into a Co catalyst dramatically reduces the diameters and narrows the chirality distributions of the as-grown SWCNTs. Different from the previously developed catalysts, (6, 5)-dominated SWCNTs can be selectively grown at 800 °C by a CoPt catalyst and show very high quality. The formation of a CoPt alloy and its improved stability are believed to be responsible for the high temperature selective growth of SWCNTs with small diameters and narrow chiralities.

The SWCNT growth was performed using atmospheric pressure alcohol CVD on silica-supported Co and CoPt catalysts, as described in the ESI†. Scanning electron microscopy (SEM, Fig. S1, ESI†) and high-resolution transmission electron microscopy (HRTEM, Fig. 1a) characterizations confirm the growth of high quality SWCNTs. The diameter and chirality information of the SWCNTs were analyzed in detail using optical spectroscopic methods. Fig. 1b–d shows the Raman spectra of the SWCNTs grown at 800 °C from Co and CoPt catalysts, excited by three lasers. It can be clearly seen that the radial breathing modes (RBMs) of SWCNTs grown from Co show multi-peaks that locate at a wide range of 100–300 cm^{−1}. In sharp contrast, the RBMs of SWCNTs grown from the CoPt catalyst mainly locate at a much narrower region at around 250 cm^{−1}, indicating that CoPt grown SWCNTs possess much smaller diameter and a narrow diameter distribution as compared to those grown from the Co catalyst. More importantly, the high growth temperature ensures a high quality of the as-grown SWCNTs. Our narrow diameter distributed SWCNTs grown at 800 °C present a defect-induced D band to tangential G band intensity ratio of 0.05 (Fig. 1b), significantly lower than those grown at low temperatures of 600–700 °C reported in the literature recently.^{11,17,20,23,24} We also performed SWCNT growth on the CoPt catalyst at 750 °C and 700 °C, however, the yield and quality of SWCNTs are very poor at such low growth temperatures in atmospheric CVD (Fig. S2, ESI†).

To evaluate the (n , m) selectivity of the as-grown SWCNTs from different catalysts, we dispersed the SWCNTs in a D₂O containing 2% (wt/v) sodium cholate hydrate (SC) for UV-vis-NIR

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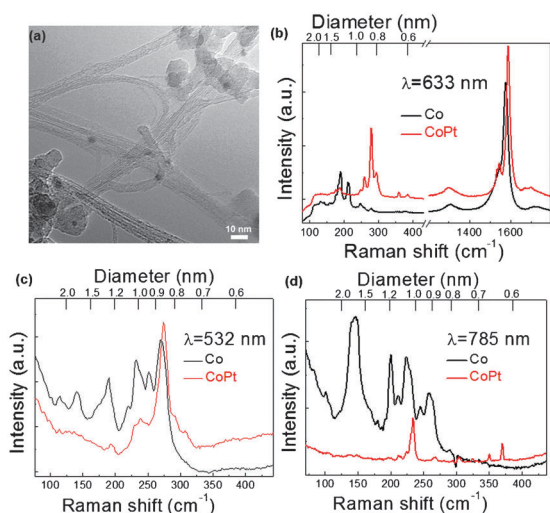


Fig. 1 (a) A HRTEM image of SWCNTs grown from a CoPt catalyst at 800 °C. (b) Raman spectra of the SWCNTs grown from Co and CoPt catalysts, excited by a 633 nm laser. (c) and (d) RBM regions in the Raman spectra of the SWCNTs grown from Co and CoPt catalysts excited by 532 nm and 785 nm lasers. The SWCNT diameters were calculated using the formula $d_t = 223.5/(\omega_{\text{RBM}} - 12.5)$, where d_t is the SWCNT diameter in nm, ω_{RBM} is the Raman shift of RBMs of SWCNTs in cm⁻¹.^{10,13,25,26}

absorption spectroscopy and photoluminescence excitation/emission (PLE) measurements. The absorption peaks at around 850–1500 nm, 480–800 nm, and 350–480 nm can be assigned to electron transitions between the first and second van Hove singularities for semiconducting SWCNTs (denoted as S_{11} and S_{22}) and the first van Hove singularities for metallic SWCNTs (denoted as M_{11}), respectively. As can be clearly discerned in Fig. 2a, for an 800 °C grown sample, the Co catalyzed SWCNTs have S_{11} peaks in the range of 1000–1350 nm. In contrast, the major S_{11} absorption peaks for the CoPt catalyzed SWCNTs blue shift to the low wavelength side, indicating the narrowing of SWCNT diameters since the energy gaps between van Hove singularities are roughly inversely proportional to the SWCNT diameters.^{27,28} The narrowing of SWCNT diameters for the CoPt catalyzed SWCNTs is in good agreement with the multi-laser Raman measurement results discussed above. More significantly, the CoPt catalyzed SWCNTs have only a few dominant peaks in

the S_{11} region, indicating a narrower chirality distribution. The strongest peak located at 981 nm is assigned to (6, 5) SWCNTs with a small diameter of 0.742 nm. In contrast, the optical absorption spectra of the SWCNTs grown from the Co catalyst and other catalysts at 800 °C^{10,14,18,23,24} typically present rather smooth features and no peaks are dominant, indicating that no specific (n, m) SWCNTs are selectively grown. It is also worth to note that the SWCNTs grown from the CoPt catalyst possess a much lower background at a high photon energy side in the optical absorption spectrum as compared to the Co catalyzed sample, suggesting few carbonaceous impurities and a higher purity of SWCNTs grown from the CoPt catalyst.²⁹

The PLE mapping results also indicate that (6, 5) SWCNTs are highly enriched in the sample grown from the CoPt catalyst (Fig. 2b), showing sharp contrast with the SWCNTs grown on Co (Fig. S3, ESI†) and other catalysts at 800 °C^{11,12,14,19} which typically possess large diameter and a relatively broad chirality distribution. It is difficult to calculate the absolute abundance of each (n, m) SWCNT due to the unknown (n, m)-dependent optical absorption cross section and quantum yields.^{9–12} Nevertheless, one can still compare the selectivity of SWCNTs grown using different methods in a relative sense by comparing the intensity ratio of PLE.^{9–12} Based on the PLE intensity ratio, we deduce that (6, 5) SWCNTs occupy 30% in all semiconducting SWCNTs in our CoPt catalyzed sample grown at 800 °C.

We have found that SWCNTs with small diameters and a narrow chirality distribution can also be grown at even higher temperature of 850 °C from the CoPt catalyst, as shown in Fig. 2c and d, and Fig. S4 (ESI†). The optical absorption and PLE spectra confirm the enrichment of only a few (n, m) SWCNTs, where (7, 6) SWCNTs with a diameter of 0.876 nm present the highest absorbance and PLE intensity. Compared with the CoPt catalyzed SWCNTs grown at 800 °C, the diameter of the SWCNTs grown at 850 °C slightly shifts to the larger side. Nevertheless, the small diameter (7, 6), (7, 5) and (6, 5) SWCNTs still dominate the absorption and PLE spectra of the 850 °C grown sample. From the PLE spectrum shown in Fig. 2d, we deduce that the above three SWCNTs occupy 60% abundance in all semiconducting SWCNTs.

The selective growth of (6, 5)-dominated small diameter SWCNTs at a high temperature of 800 °C is the most important feature of the CoPt catalyst. For the previously developed catalyst systems, mostly large diameter SWCNTs, such as (9, 8) or (13, 12) SWCNTs, can be selectively enriched at such high reaction temperatures.^{21,30} (6, 5) SWCNT seems to be the most easily selectively grown SWCNT, but it tends to grow at a relatively low reaction temperature of around 600 °C. In contrast, small (6, 5) SWCNTs are dominant in the CoPt catalyzed samples grown at 800 °C, and still have a high abundance in the samples grown at 850 °C (18%, see Fig. 2d). We ascribe the selective growth of small diameter SWCNTs at high temperature to the improved stability of the CoPt catalyst against sintering. XRD characterization shows the formation of a CoPt alloy (Fig. S5, ESI†), agreeing with the CoPt binary phase diagram where the two metals can form alloys within a wide composition range.³¹ The CoPt alloy possesses a higher melting point than Co, which mitigates the high temperature sintering and aggregation of the catalyst nanoparticles.^{31,32} In addition, the intimate alloying of CoPt and strong Co–Pt interaction also weaken the CoPt alloy

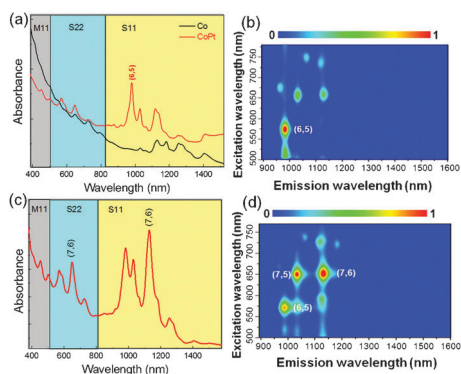


Fig. 2 UV-vis-NIR absorption and PLE spectra of the SWCNTs grown from CoPt catalysts at 800 °C (a and b) and 850 °C (c and d). The absorption spectrum of the SWCNTs grown from a Co catalyst at 800 °C is presented as black curve in (a) for comparison.

nanoparticles from aggregation and growing up.¹² The above two features ensure the CoPt alloy catalyst with good high temperature stability, facilitating the selective growth of small SWCNTs at high temperature. This suggests that the CoPt bimetallic catalyst has a different selective growth mechanism than that of CoMo, FeCu, and CoMn bimetallic catalyst systems, where the second metal (Mo, Cu, and Mn) is in oxide or carbide states that function to disperse Co and Fe catalysts and prevent them from aggregation, while no alloy is formed in these catalyst systems.^{9,11,13} We also noted that there are still weak Co diffraction peaks for the CoPt bimetallic catalyst (Fig. S5, ESI†), which may also take part in the SWCNT growth in the bimetallic CoPt catalysts. However, taking the facts that its intensity is rather weak compared with the CoPt alloy phase and the monometallic Co catalyst, and the yield of SWCNTs grown from CoPt is similar to that from the Co catalyst, we believe that most SWCNTs are grown from the CoPt alloy rather than from a small amount of co-existing Co in the bimetallic system. Since high growth temperature renders a high quality of the SWCNTs, as demonstrated by Raman and optical absorption spectra shown above, we believe that such high quality and narrow chirality SWCNTs are attractive for electronics and optoelectronics.

Usually, large chiral angle SWCNTs are easy to grow selectively.^{9–12,14,15,17,19,20,24} It is interesting to note that CoPt catalysts further shift this trend to the higher angle side. For example, (8, 4) SWCNTs have a high relative abundance of 14%, the third highest PLE intensity, in CoMoCAT SWCNTs prepared using CO as a carbon source,⁹ and have the highest intensity in FeRu-CH₄ CVD SWCNTs.¹² In contrast, (8, 4) SWCNTs only occupy 6% and 10% abundance in the CoPt catalyzed SWCNTs grown at 800 °C and 850 °C, respectively, much less than the abundance of larger chiral angle (6, 5)/(7, 5)/(7, 6) SWCNTs, despite their similar diameters (Fig. 3). A chiral angle dependent growth rate has been proposed recently to explain such phenomena,³³ which is shown to be independent of the growth conditions. However, the results presented here indicate that this process should also be related to the properties of catalysts and the SWCNT growth conditions.

In conclusion, we have developed a bimetallic CoPt catalyst for the selective growth of high quality SWCNTs with small diameter and a narrow chirality distribution using atmospheric pressure alcohol CVD. Different from the commonly used catalysts, narrow chirality distributed SWCNTs can be selectively grown at high growth temperatures of 800 °C and 850 °C, which renders the high quality of the as-grown SWCNTs. The formation of a CoPt alloy in the bimetallic catalysts is believed to increase the catalyst stability and might be responsible for the selective growth of SWCNTs with a narrow chirality distribution at high temperature.

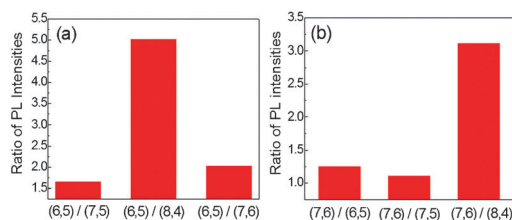


Fig. 3 PLE intensity ratios of various (*n*, *m*) SWCNTs grown at 800 °C (a) and 850 °C (b).

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