Understanding the growth modes of single-walled carbon nanotubes on catalysts

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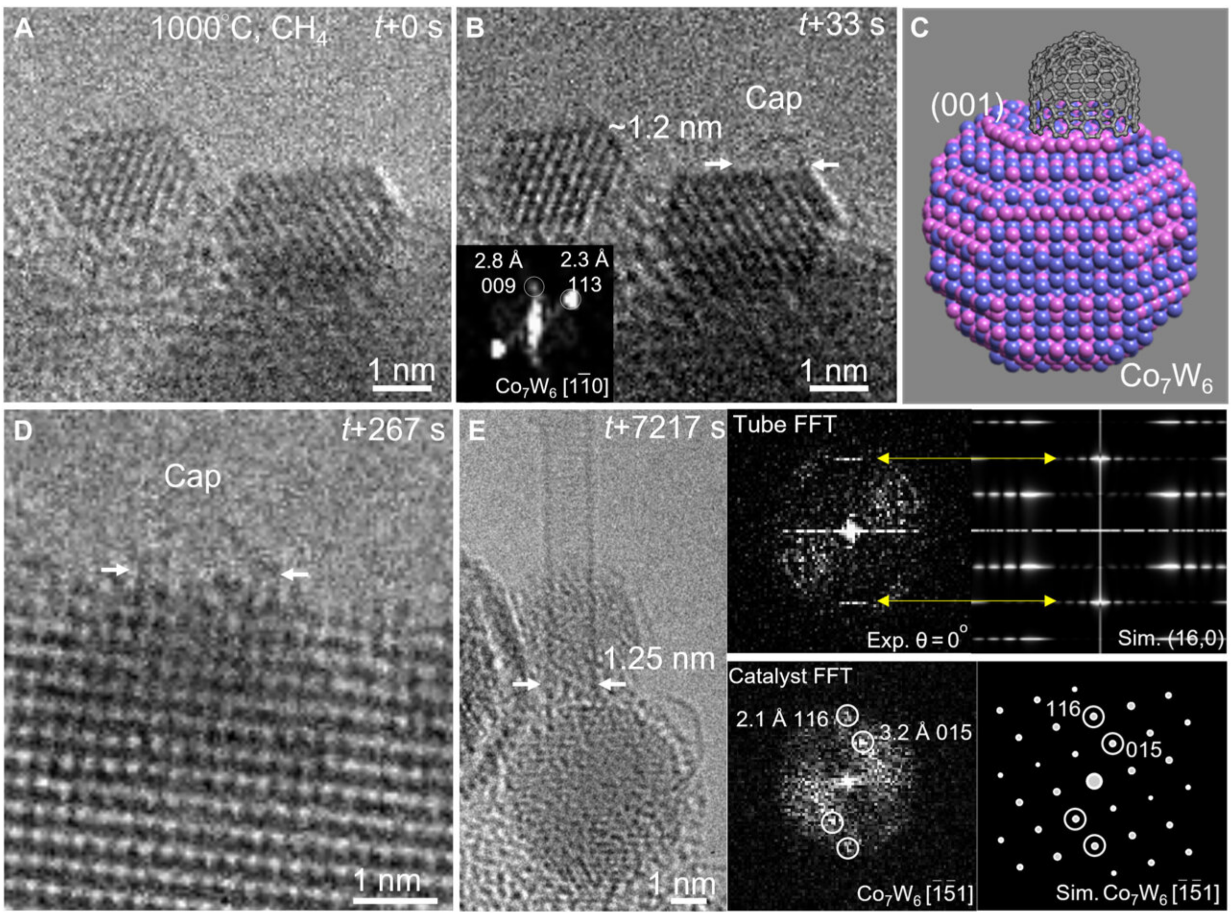


Aberration-corrected ETEM characterization of SWCNTs grown from an intermetallic Co_7W_6 catalyst. (A and B) Time-sequential ETEM images of SWCNT cap nucleated from solid intermetallic Co_7W_6 catalysts at 1000°C under CH_4 (50 Pa). Inset: The FFT of the seeded Co_7W_6 catalyst along the [1 1¯ 0] direction. (C) Scheme showing an SWCNT cap nucleating from the atomic edge of Co_7W_6 (001). The Co_7W_6 nanocrystal is along the [1 1¯ 0] direction. (D and

E) Other cap and SWCNT grown on the surface of Co_7W_6 catalysts captured by ETEM. FFT patterns of SWCNT and Co_7W_6 catalyst derived from TEM image (E). Simulated (16,0) SWCNT and Co_7W_6 [1ˉ5ˉ 1] were also shown (E). Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abq0794

Insights into the catalyst structure-function relationship of single-walled carbon nanotubes (SWCNTs) can provide an outlook to their growth mechanisms. In a new report now published in *Science Advances*, Feng Yang and a research team in molecular science, chemistry, materials genome engineering and physics in China used an in-situ aberration-corrected environmental transmission electron microscope (ETEM) to reveal the effects of the state and structure of catalysts.

The team linked the different growth modes to the distinct chiral selectivity of single-walled carbon nanotubes grown on non-metallic and intermetallic catalysts. The outcomes can provide insight to design catalysts for chirality-regulated growth of single-walled carbon nanotubes.

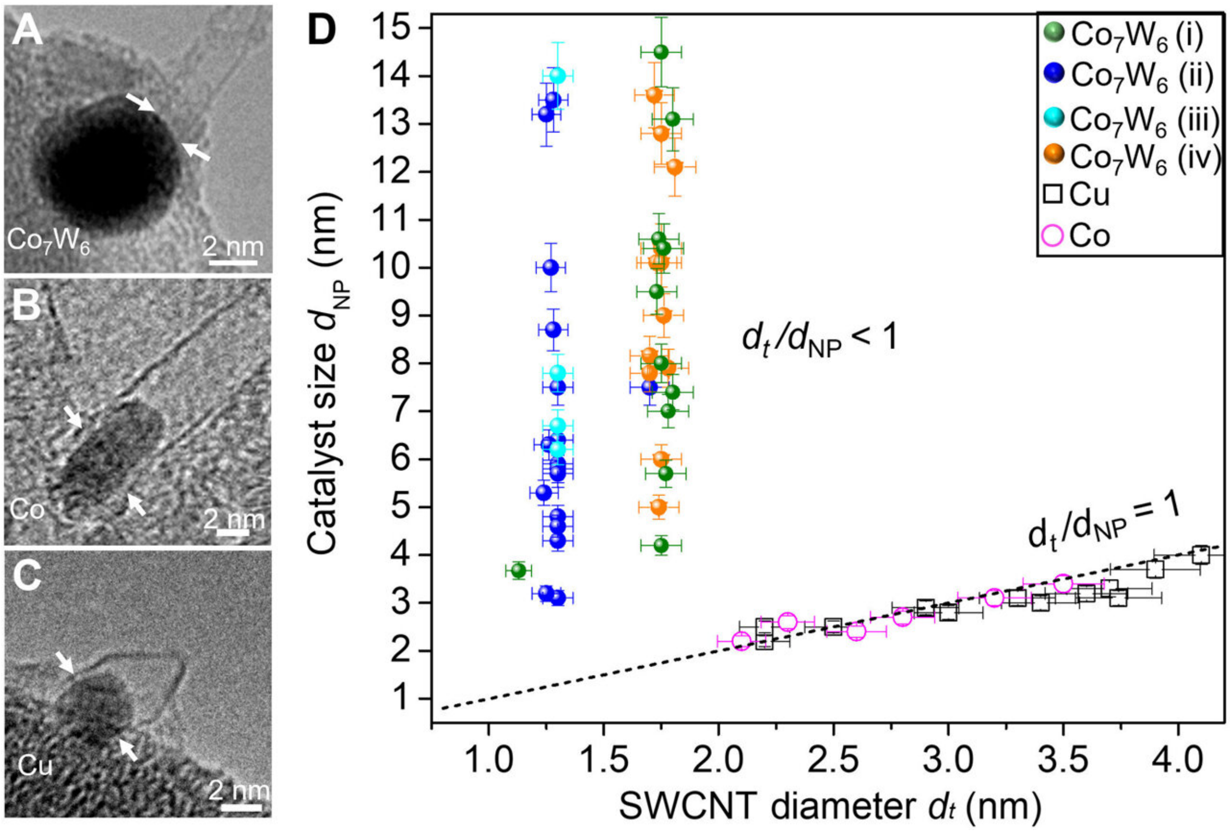
Heterogenous catalysis

The role of catalyst structure and performance is vital for heterogeneous catalysis. For instance, the active sites of nanocatalysts are thought to be precursors leading to the high selectivity of small molecules. The chiral structure of larger single-walled carbon nanotube molecules is more complex and require two chiral indices for their identification.

Pure single-walled carbon nanotubes have unique properties and tremendous application potential across next-generation electronics and biosensing applications. In order to rationally design synthetic processes of chirality-specific single wall carbon nanotubes, it is vital to understand how such structures grew from a catalyst nanoparticle.

Depending on the properties of catalysts and the conditions of chemical vapor deposition involved, single walled carbon nanotubes can either undergo a vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) process. The VLS process can catalyze the decomposition of carbon precursors, leading to the dissolution of molten catalysts, nucleation and further growth of single-walled carbon nanotubes. The VSS process is similar, although the catalyst remains solid, while carbon diffusion is likely to be different.

The role of catalysts can be evaluated to determine the structure of single-walled carbon nanotubes, and this is a significant topic in research. Researchers had previously used environmental transmission electron microscopy (ETEM) as an effective tool to directly visualize catalysts and nanotube growth.

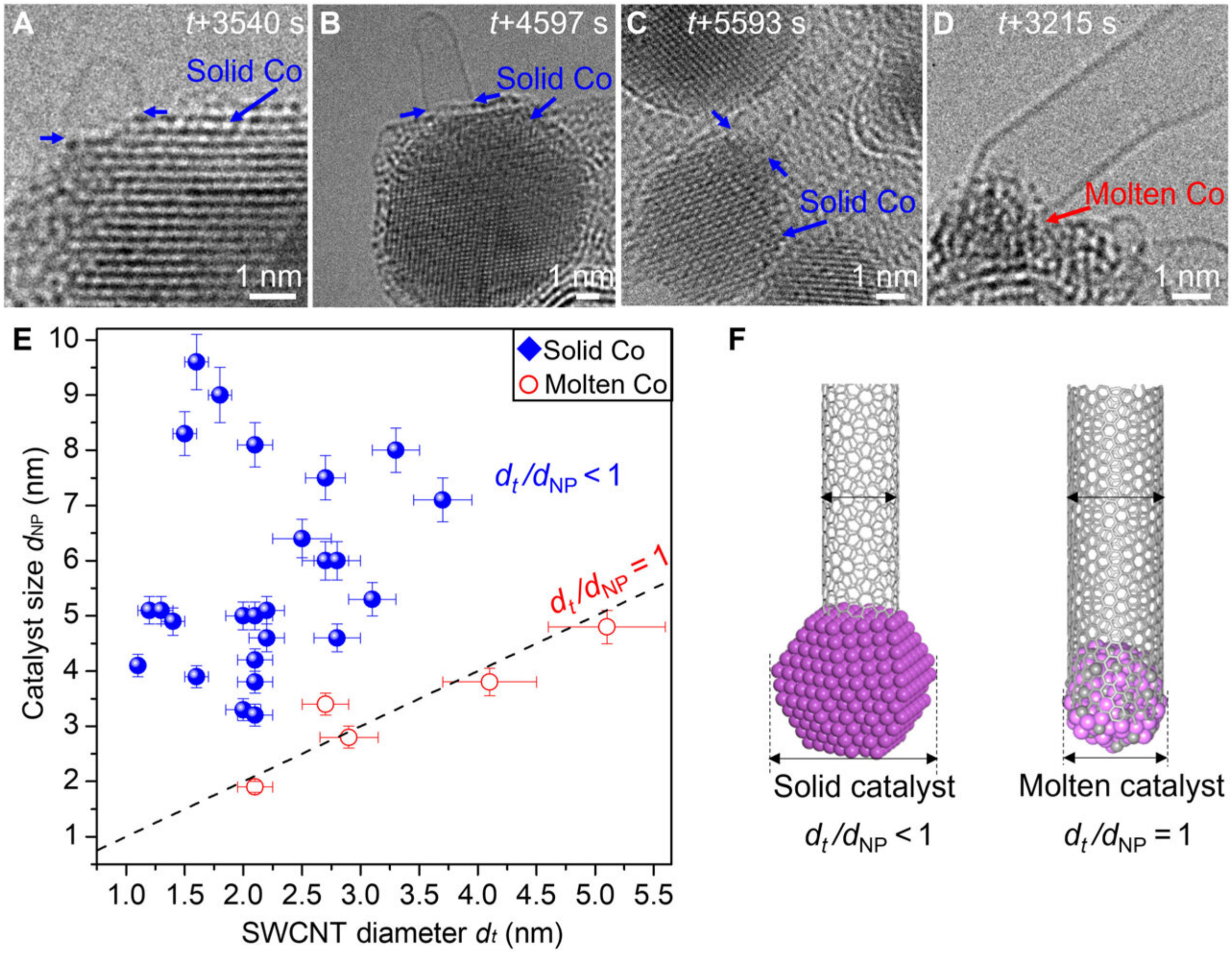


Ex situ TEM characterization of SWCNTs grown from catalysts. (A to C) Ex situ TEM images of SWCNTs grown with Co_7W_6 (A), Co (B), and Cu (C) catalysts. (D) The statistic ex situ TEM measurements of SWCNT diameter as a function of catalyst size. A total of 48 and 18 SWCNTs were observed from Co_7W_6 and monometallic (Cu and Co) catalysts, respectively. The carbon feeding conditions for Co_7W_6 catalysts marked with (i) to (iv) are Ar–ethanol/H_2 50:30 (i), 200:50 (ii), 200:150 (iii), and CH_4/H_2 200:20 (iv) cm^3 min^{-1}. Error bars arise from the uncertainty (5%) of the TEM measurements. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abq0794

In this work, Yang et al presented a comprehensive analysis of the growth of single walled carbon nanotubes on intermetallic and monometallic catalysts to investigate the tube-catalyst size correlation. They used an ETEM to detect nucleation and studied the growth of nanotubes on catalyst nanoparticles to understand the state and structure of catalysts and the growth mode of single-walled carbon nanotubes in intermetallic structures.

ETEM investigations of SWCNTs grown from intermetallic catalysts

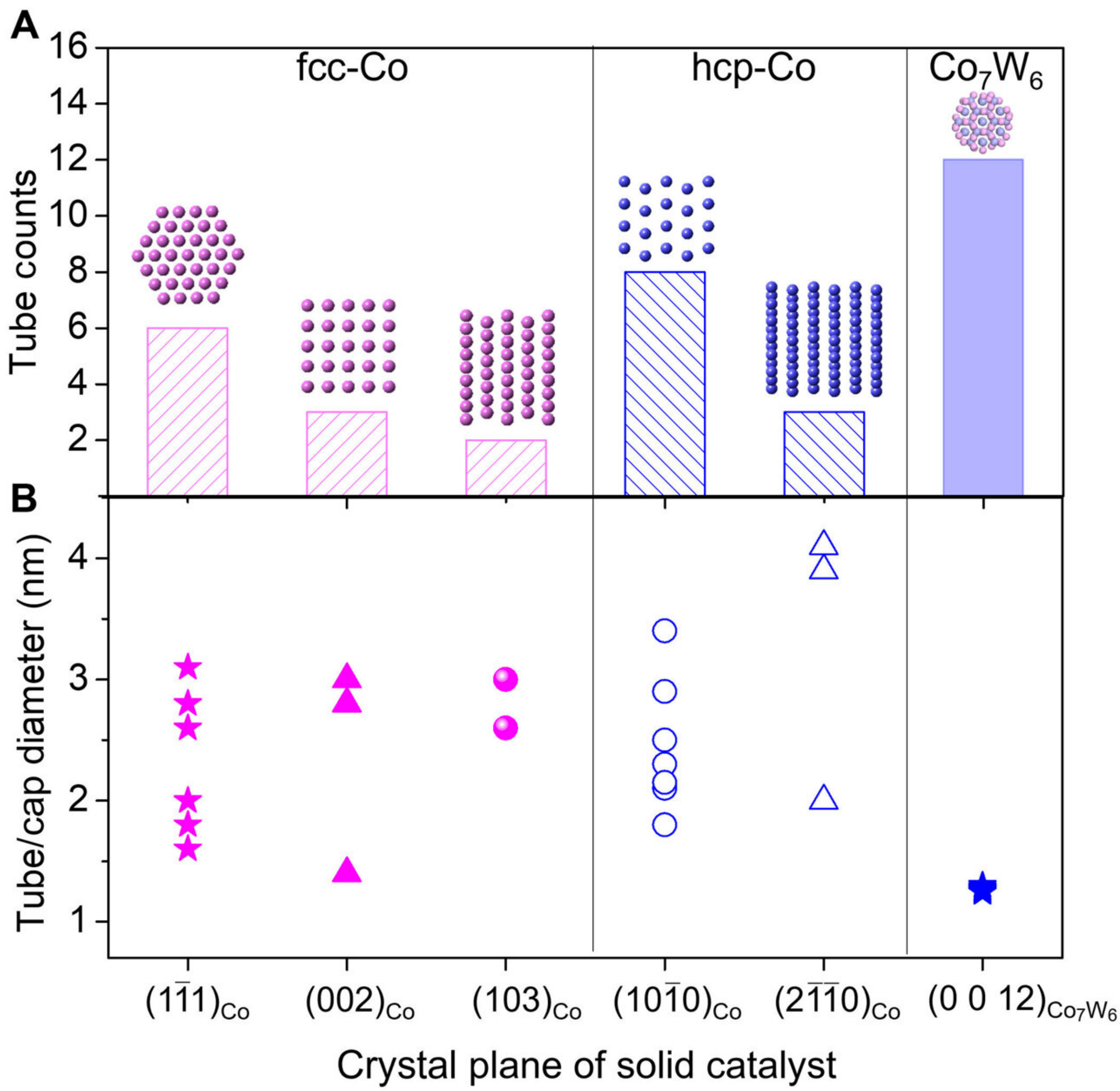
To prepare the intermetallic tungsten cobalt (W-Co) catalyst, Yang et al used W-Co polyacid cluster precursors. The team studied the growth of single-walled carbon nanotubes on the intermetallic catalysts at 1,000 degrees C with an image resolution at the angstrom level. The metallic nanocrystals maintained a stable structure during the nucleation of the single-walled carbon nanotube cap.



Aberration-corrected ETEM characterization of SWCNTs grown from solid and molten Co catalysts. (A to D) Aberration-corrected ETEM images of SWCNT and cap nucleated from solid (A to C) and molten (D) Co catalysts at 600°C. (E) Statistic ETEM measurements of tube diameter as a function of catalyst size. A total of 30 interfaces were observed at 600°C. Error bars arise from the uncertainty (5%) of the TEM measurements. (F) Schemes showing two growth modes of SWCNTs from solid and molten catalysts. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abq0794

The outcomes showed how the vapor-solid-solid (VSS) process led to carbon atom migration to the surface of the solid nanocrystal catalyst to nucleate, leading to the growth of a nanotube. This process is different from the vapor-liquid-solid (VLS) process, which facilitates carbon dissolution into the catalyst. The nanoparticles exhibited diverse catalyst morphology.

The team credited the outcomes to the less efficient carbon feeding mechanisms via the VSS process than through the VLS process, which led to larger catalyst particles to facilitate the growth of single-walled carbon nanotubes.

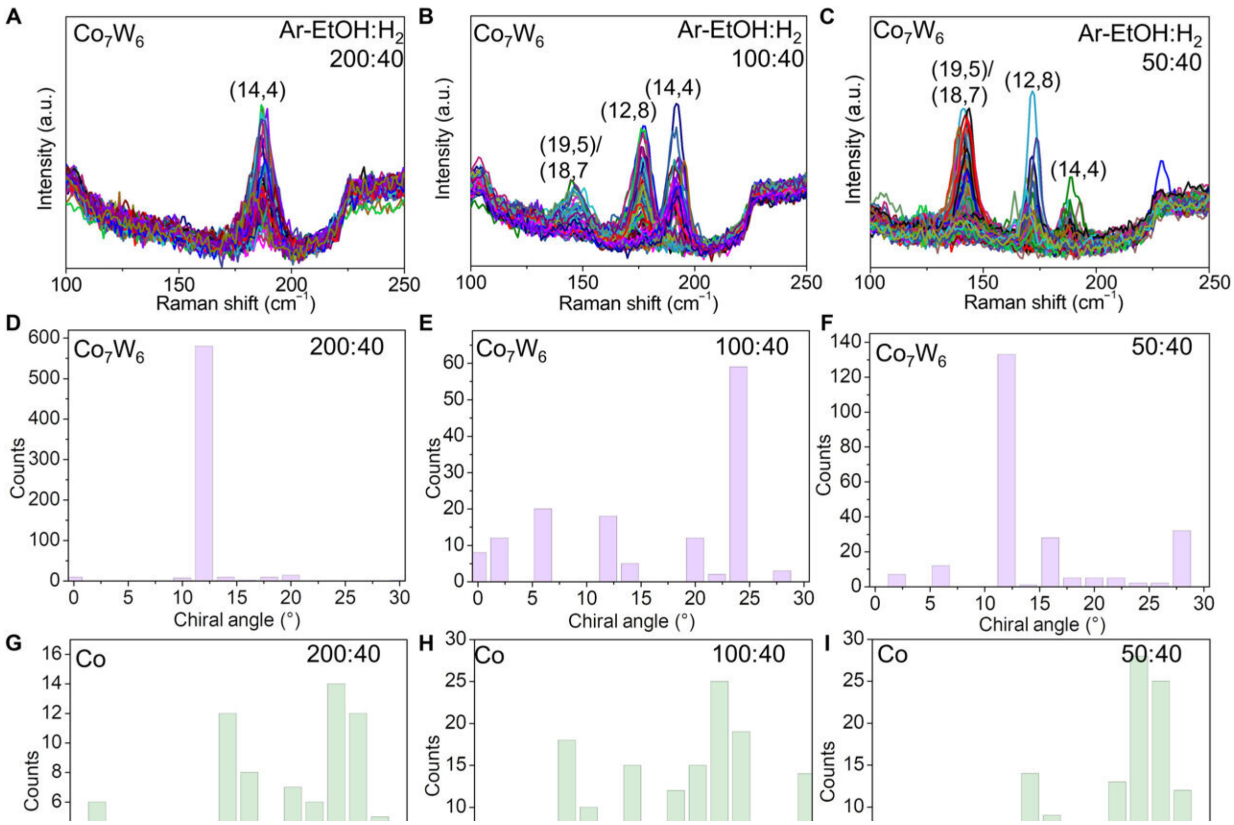


Statistical analysis of SWCNTs and caps nucleating from different planes of Co and Co_7W_6 catalysts from TEM. (A) Distribution of 21 SWCNTs/caps nucleating from different Co crystal planes and 12 (12,6) SWCNTs nucleating from the (0 0 12) plane of Co_7W_6. The corresponding atomic crystal planes of fcc and hcp Co are also shown. (B) Correlation between active Co facets and diameter of SWCNTs/caps. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abq0794

Additional characterizations of the SWCNTs

The scientists conducted chemical vapor deposition-based growth of single-walled carbon nanotubes in transmission electron microscopy (TEM) grids of thin films to perform TEM analysis. They measured the diameters of the carbon nanotubes and the size of the catalyst nanoparticles attached on the tubes. They further analyzed the nucleation of single-walled carbon nanotubes from cobalt catalysts in environmental transmission electron microscopy at 600 degrees Celsius. The cobalt nanoparticles maintained a crystallized-solid state.

The in-situ observations of cobalt catalysts were consistent with the TEM results, the outcomes demonstrated the diverse growth modes of VLS and VSS mechanisms. Yang et al further analyzed the chiral selectivity of single-walled carbon nanotubes and the effect of carbon feeding conditions on chiral selectivity under these two growth modes.



Chiral angle distribution of SWCNTs grown on different catalysts. (A to C) Raman spectra of SWCNTs grown from Co_7W_6 catalysts at 1050°C. Excitation wavelength: 532 nm. (D to L) Chiral angle distributions of SWCNTs grown from Co_7W_6 (D to F), Co (G to I), Fe (J), Ni (K), and Cu (L) catalysts at 1050°C. The carbon feeding conditions are indicated in each panel: Ar through the ethanol bubbler is 200, 100, and 50 cm^3 min^{-1}; the H_2 feeding rate is fixed at 40 cm^3 min^{-1}. Credit: *Science Advances* (2022). DOI: 10.1126/sciadv.abq0794

Outlook

In this way, based on a series of experimental characterizations, Feng Yang and colleagues showed how single-walled carbon nanotubes grew from molten catalysts. During the study outcomes, the diameters of the resulting nanotubes depended on the size of the corresponding catalyst nanoparticles.

The work highlights a collaborative effect of catalysts and kinetics to give rise to the selective growth of single-walled carbon nanotubes (SWCNTs). The team envision structure-regulated growth of SWCNTs in the future, by carefully assessing the interfacial structure between the catalyst nanocrystal and the nucleated nanotube for improved kinetic growth.

More information: Feng Yang et al, Growth modes of single-walled carbon nanotubes on catalysts, *Science Advances* (2022). DOI: 10.1126/sciadv.abq0794

Feng Yang et al, Chirality-specific growth of single-walled carbon nanotubes on solid alloy catalysts, *Nature* (2014). DOI: 10.1038/nature13434