Supplementary Information for:

Structure and Activity Relationship for Single-Walled Carbon Nanotube Growth Confirmed by In-Situ observations and Modeling

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This Document includes:

EELS Identification Structure Identification Catalyst Nanoparticle Data Computational Details Movie Descriptions

Other Supplementary Materials for this manuscript includes the following: Movie S1, S2, S3, S4, S5

1. EELS Identification

Electron energy loss spectroscopy (EELS) was used to determine the presence of Co nanoparticles and the MgO support. An EELS map (Fig. S1) was acquired at room temperature with no gases inside the specimen chamber after cleaning the sample by heating in 300 Pa of oxygen at 900 C for 30 minutes. Isolated nanoparticles containing Co are shown in red (Fig. S1b)), while the Mg and O regions, forming MgO support, are in blue and green, respectively. Zero loss peak, acquired concurrently with core-loss data, was used to calibrate the spectra¹. Deconvoluted and background subtracted EELS spectrum confirm the existence of Co with characteristic L₃ and L₂ peaks at 784.44 \pm 0.54 eV and 800.06 \pm 0.11 eV, respectively (Fig. S1c)). The chemical state of Co-based nanoparticles was then determined by comparing the onset edge and characteristic peak positions to known structures as described by Egerton². Our measured values closely match peak positions of the CoO phase³ (Table S1).



Fig. S1 EELS performed inside the TEM surveying catalyst and support. Image in a) is at 160 kx magnification and 80 kV and in STEM mode. Green box labelled Spectrum Image is where the energy spectrum is measured. The beam location and area to account for spatial drift are also designated. The EELS spectrum is shown in b), where Co is highlighted in red, and the Mg and O peaks are blue and green, respectively. EELS Spectrum in c) is extracted from Co-rich region marked by an arrow in b) and shows the Co-L₃ and Co-L₂ peaks.

Table S1 Energy loss peak positions of Co-L₃ (E_{L3}) and Co-L₂ (E_{L2}) for Co nanoparticles compared to the reported values.³

	$E_{L3} (eV)$	$E_{L2} (eV)$	Ref.
Metallic Co	781	796.5	
CoO	785.5	801.5	[3]
Co ₃ O ₄	787	802.5	
Nanoparticles measured	784.44 ± 0.54	800.06 ± 0.11	This work
% Diff. from CoO	0.14%	0.18%	

2. Structure Identification

The algorithm, CrystalBall⁴, was used to determine the phases and associated planes from the Fast Fourier Transform (FFT) data. Experimentally obtained d-spacings and angles were matched with reference phases in literature^{5–7} containing Co, O, Mg, and C. Initially, CrystalBall matches the measured phase with the reference phases and outputs close matches within a certain specified error. Subsequently, the algorithm takes these close matches and matches them with the reference angles to find a close match within that, determining the possible Miller planes within the phase. Finally, the program outputs the closest matching zone axis that best corresponds with the previous parameters.

The d-spacings and angles are each matched using the smallest possible error, which are then gradually increased if no fit is found within the error range. If there are multiple possible fits with a certain error, the data is reviewed and the smallest overall percentage error of both d-spacings and angles is determined to be the correct phase and associated Miller planes. In some cases, both Co₂C and Co₃C match a particular nanoparticle, but the correct phase is the one phase with uniformly less error. Table S2 is one example of this. All the nanoparticle information measured and processed this are tabulated in the Table S3, S4, and S5.

Table S2 An example of one nanoparticle's measured d-spacing and angle that matches both
Co ₂ C and Co ₃ C structures. The Co ₂ C structure has an overall lower error value and is therefore
determined to be the correct phase.

Matching	Measured	Reference	Error	Miller	Angle	Reference	Error	Zone Axis
Structure	d-Spacing	d-Spacing	(%)	Plane	Between	Angle	(%)	
	(nm)	(nm)			Planes (°)	(°)		
Co ₂ C	0.2264	0.2213	2.305	(0 2 0)	58.40	56.676	3.042	[100]

	0.2554	0.2432	5.038	(0 1 1)	69.43	66.648	4.009	
	0.2395	0.2432	1.501	(0 -1 1)	127.72	123.324	3.565	
Co ₃ C	0.2264	0.2379	4.822	(1 2 1)	58.40	55.96	4.36	[0 -1 2]
	0.2554	0.2379	7.370	(-1 2 1)	69.32	62.02	11.77	
	0.2395	0.2535	5.523	(-2 0 0)	127.72	117.98	8.256	

3. Catalyst Nanoparticle Data

Presented are measured and reference structures of the nanoparticles measured and included in the analysis. The corresponding matching structure and Miller planes of each nanoparticle are reported along with the percentage error of each structure's measured d-spacing and angle. Table S3 reports active catalysts, Table S4 reports deactivated catalysts, and Table S5 reports inactive catalysts.

Table S3 Obtained structure and data of active catalysts.

	Matching Structure	Measured d-Spacing (nm)	Reference d-Spacing (nm)	Error (%)	Miller Plane	Angle Between Planes (°)	Reference Angle (°)	Error (%)	Zone Axis
1	Co ₂ C	0.2177	0.2213	1.627	(020)	51.36	56.676	9.38	[100]
		0.2362	0.2432	2.858	(011)	75.18	66.648	12.801	
		0.2389	0.2432	1.748	(0-11)	126.54	123.324	2.608	
2	Co ₂ C	0.2345	0.2439	3.838	(101)	109.56	113.859	3.776	[0 1 0]
		0.2328	0.2439	4.535	(10-1)				
3	Co ₂ C	0.2141	0.2185	2.027	(002)	91.66	90	1.844	[100]
		0.2203	0.2223	0.913	(020)				
4	Co ₂ C	0.2771	0.2427	14.164	(110)	71.35	66.169	7.831	[0 0 1]
		0.2545	0.2427	4.853	(1-10)				

5	Co ₂ C	0.2234	0.2213	0.949	(020)	57.77	56.676	1.93	[100]
		0.2234	0.2432	8.123	(011)	69.94	66.648	4.939	
		0.2436	0.2432	0.185	(0-11)	127.71	123.324	3.556	
6	Co ₂ C	0.2342	0.2213	5.829	(020)	126.23	123.324	2.356	[100]
		0.2342	0.2432	3.681	(0 -1 1)				
7	Co ₂ C	0.2303	0.2223	3.585	(020)	58.67	56.916	3.082	[0 0 1]
		0.2502	0.2427	3.082	(110)	67.9	66.169	2.617	
		0.2499	0.2427	2.958	(1-10)	126.57	123.084	2.832	
8	Co ₂ C	0.216	0.2185	1.158	(002)	57.03	56.464	1.003	[0 1 0]
		0.2502	0.2415	3.615	(101)	72.49	67.073	8.077	
		0.242	0.2415	0.219	(10-1)	129.52	123.536	4.844	
9	Co ₂ C	0.2264	0.2213	2.305	(020)	58.4	56.676	3.042	[100]
		0.2554	0.2432	5.038	(011)	69.32	66.648	4.009	
		0.2395	0.2432	1.501	(0 -1 1)	127.72	123.324	3.565	
10	Co ₂ C	0.2279	0.2213	2.982	(020)	57.44	56.676	1.348	[100]
		0.2581	0.2432	6.148	(011)	69.52	66.648	4.309	
		0.251	0.2432	3.228	(0 -1 1)	126.96	123.324	2.948	
11	Co ₂ C	0.2086	0.2213	5.739	(020)	52.7	56.676	7.015	[100]
		0.2373	0.2432	2.406	(011)	69.19	66.648	3.814	
		0.2507	0.2432	3.105	(0 -1 1)	121.89	123.324	1.163	

 Table S4
 Obtained structure and data of deactivated nanoparticles.

						Angle			
		Measured	Reference			Between			
	Matching	d-Spacing	d-Spacing	Error	Miller	Planes	Reference	Error	Zone
	Structure	(nm)	(nm)	(%)	Plane	(°)	Angle (°)	(%)	Axis
1	Co ₃ C	0.2344	0.2265	3.488	(002)	62.48	60.769	2.816	[0 1 0]
		0.2188	0.2212	1.094	(201)	56.3	58.463	3.7	
		0.2164	0.2212	2.179	(20-1)	118.78	119.231	0.379	
2	Co₃C	0.2188	0.2102	4.086	(211)	69.4	68.198	1.762	[0-1 1]
		0.2221	0.2102	5.656	(2-11)	55.9	55.901	0.001	

		0.198	0.1875	5.617	(022)	125.3	124.099	0.968	
3	Co ₂ C	0.2678	0.2439	9.817	(101)	51.77	56.93	9.063	[0 1 0]
		0.2138	0.2235	4.319	(200)				
4	Co ₃ C	0.2812	0.3016	6.773	(111)	71.02	67.035	5.945	[-1 -2 3]
		0.258	0.2379	8.463	(-121)	52.19	46.364	12.566	
		0.227	0.2371	4.26	(-210)	123.21	113.399	8.652	
5	Co₃C	0.2824	0.3016	6.375	(111)	76.01	83.496	8.966	[-1 1 0]
		0.2763	0.3016	8.398	(11-1)	55.15	48.252	14.296	
		0.2339	0.2265	3.267	(002)	131.16	131.748	0.446	
6	Co₃C	0.2043	0.2026	0.829	(220)	107.19	105.915	1.204	[0 0 1]
		0.1958	0.2026	3.366	(-220)				
7	Co₃C	0.2954	0.3016	2.059	(111)	49.98	56.714	11.873	[0-1 1]
		0.1963	0.1759	11.617	(-1 2 2)	54.3	69.733	22.131	
		0.2622	0.2538	3.289	(-2 0 0)	104.28	126.447	17.53	
8	Co₃C	0.334	0.3016	10.732	(111)	50.7	63.243	19.834	[-1 0 1]
		0.3152	0.335	5.91	(020)	69.34	63.243	9.64	
		0.3109	0.3016	3.073	(-1 1 -1)	120.04	126.487	5.097	
9	Co₃C	0.2035	0.2101	3.123	(211)	55.02	55.961	1.681	[011]
		0.1812	0.1876	3.432	(022)	53.77	55.961	3.915	
		0.2205	0.2101	4.97	(-2 1 1)	108.79	111.921	2.798	

 Table S5
 Obtained structure and data of inactive nanoparticles.

		Measured	Reference			Angle			
	Matching	d-Spacing	d-Spacing	Error	Miller	Between	Reference	Error	
	Structure	(nm)	(nm)	(%)	Plane	Planes (°)	Angle (°)	(%)	Zone Axis
1	Co ₃ C	0.252	0.2382	5.785	(121)	57.73	58.164	0.746	[-2 1 0]
		0.2161	0.2258	4.296	(002)	52.91	58.164	9.033	
		0.2515	0.2382	5.575	(-1 -2 1)	110.64	116.328	4.889	
2	Co₃C	0.334	0.3016	10.732	(111)	50.7	63.243	19.834	[-1 0 1]
		0.3152	0.335	5.91	(020)	69.34	63.243	9.64	
		0.3109	0.3016	3.073	(-1 1 -1)	120.04	126.487	5.097	

3	Co ₂ C	0.205	0.2213	7.366	(020)	53.41	56.676	5.762	[100]
		0.2418	0.2432	0.555	(0 -1 1)	73.63	66.648	10.476	
		0.2455	0.2432	0.966	(011)	127.04	123.324	3.013	
4	Co₃C	0.1936	0.1868	3.662	(131)	54.74	50.549	8.29	[1-25]
		0.2317	0.2382	2.737	(-1 2 1)	73.64	79.109	6.913	
		0.233	0.2375	1.895	(-2 -1 0)	128.38	129.659	0.986	
5	Co₃C	0.2105	0.2068	1.789	(102)	41.1	48.145	14.633	[0 1 0]
		0.2131	0.2068	3.046	(-1 0 2)	41.27	36.696	12.465	
		0.2091	0.2212	5.479	(-2 0 1)	82.37	84.841	2.913	
6	Co₃C	0.1317	0.1349	2.358	(042)	87.93	90	2.3	[0-1 2]
		0.2647	0.238	4.274	(200)	57.89	62.017	6.655	
		0.2316	0.2382	2.779	(1 -2 -1)	145.82	152.017	4.077	

4. Computational Details

For both Co₂C and Co₃C, the surfaces were obtained by cleaving the initial structure of the carbide along the planes observed experimentally, obtaining the different surface chemistries (i.e. the C, Co, or C/Co termination in the top layer) possible for each case. We proceeded to calculate the surface formation energy for each one of the cleaved surfaces evaluated for their respective terminations. The surface energy can be defined as the energy needed to cleave the bulk crystal^{8,9}, it is a critical factor in the development of surface morphologies and can highlight some important surface characteristics. Fig. S2 and S3 summarize the average surface energy for all cleaved surfaces and their possible terminations for Co₂C and Co₃C, respectively. After analyzing the surface energy and the internal structure of the different surfaces, it was found that some of the surfaces evaluated have similar energetic and geometrical properties. For that

below is available upon request.



Surface energy comparison for Co₃C surfaces

Fig. S2 Surface energies calculated for Co₂C cleaved surfaces evaluated. A lesser value for surface energy implies the formation of the respective cleaved surface is more likely to occur, compared with others.



Surface energy comparison for Co₂C surfaces

Fig. S3 Surface energies calculated for Co₃C cleaved surfaces evaluated.

Before running the main simulations to calculate the work of adhesion, preliminary simulations were done to find the ideal graphene initial distance to the top layer in the slab. Below are the

three different behavior obtained due to the surface chemistries evaluated, summarized in Figure S4 from Co_2C (101) cleaved surface as an example.

Energy behavior in Fig. S4 a finds a stabilization value at a relatively long distance from the surface (i.e. at around 0.335 nm from the top layer). This behavior matches with all cases where the termination of the top layer is found to be C-terminated. Comparing the stabilization distance with a graphite system demonstrates that the behavior is quite similar and the main interaction taking place is the C-C graphite-like interaction. For those systems, the initial distance was defined as 0.245 nm, based on previous work¹⁰.

The second case, shown in Fig. S4 b, has a like-stabilization behavior for the system's energy at a closer distance than the previous one, but still do not have a minimum energy value as expected. For all cases that match this behavior, the presence of C atoms in the top layer is less severe without a predominant species, bringing a Co/C termination. The initial distance for each of these cases was defined as the point where the graph stabilizes and the ΔE is not significant.

Finally, for the third energy behavior in Fig. S4 c, a minimum energy point was found. Then, a second series of simulations were done, setting the new range in the area where the minimum energy system was initially found in order to accurately predict the initial distance as shown in Fig. S4 d. Table S6 shows the graphene layer's initial distance for the systems reported.



Fig. S4 Different energy profiles found for the graphene layer stabilization over the cleaved surfaces according to the different surface chemistries obtained. Behavior states for (a) all C terminations, (b) all Co/C termination, and (c) and (d) for all Co terminations evaluated.

Table S6	Initial of	listance t	for the	graphene	layer	with	respect	to the	e top	layer 1	for the	e syster	ms
(cleaved s	urface a	ind surfa	ce cher	nistry) re	ported	l.							

Co ₂ C		Co ₃ C			
	Initial		Initial		
Surface	Distance	Surface	Distance		
	(nm)		(nm)		
020	0.245	020	0.220		
101	0.245	111	0.245		
011	0.182	002	0.180		
110	0.170	201	0.142		
111	0.172	211	0.156		
-201	0.184	022	0.154		
-211	0.174	-121	0.160		
		210	0.245		
		-220	0.178		
		-122	0.202		
		113	0.160		
		131	0.154		
		042	0.182		

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The work of adhesion for each one of the cleaved surfaces was evaluated rotating each graphene layer approximately 36 degrees in order to evaluate the different possibilities for the graphene layer to interact with the surface atoms with more than one specific coordination. Hereafter, we report the characteristics for those geometries that showed the weakest, the strongest, and an intermediate value for work of adhesion in order to highlight the comparison and draw meaningful conclusions (Table S7).

Table S7	Weakest,	intermediate a	and strongest	work of	adhesion	obtained	for eac	h one	of the
cleaved su	irfaces eva	aluated after ro	otating the gra	aphene la	iyer.				

Co ₂ C			Co ₃ C				
	Work of Adhesion (eV/nm²)				Work of Adhesion (eV/nm²)		
Surface	Weakest	Intermediate	Strongest	Surface	Weakest	Intermediate	Strongest
020	-16.12	-21.97	-29.89	020	-10.83	-15.71	-28.11
101	-12.91	-15.31	-25.54	111	-10.52	-14.99	-29.23
011	-20.92	-24.8	-27.86	002	-16.99	-20.99	-25.76
110	-7.42	-28.74	-33.92	201	-19.04	-24.94	-29.33
111	-20.72	-24.22	-28.44	211	-21.64	-24.64	-27.92
-201	-17.38	-22.05	-26.84	022	-23.72	-26.74	-28.89
-211	-20.47	-23.93	-26.94	-121	-8.68	-16.9	-20.31
				210	-9.72	-16.76	-23.52
				-220	-16.48	-24.05	-29.51
				113	-12.2	-13.24	-15.69
				131	-11.28	-14.4	-16.95
				042	-10.54	-14.23	-19.66

5. Movie Descriptions

Presented are descriptions of the movies included as part of the Supporting Information. For all

movies, time is displayed on the top left with units in seconds and the movie has a rate of 30

frames per second.

Movie S1 Multiple different nanoparticles varying from 1 nm to 5 nm in diameter. Five nanoparticles are specifically labelled to better track their progress. Nanoparticles 2, 3, and 4 show SWCNT growth, while nanoparticles 1 and 5 do not show growth but become encapsulated by a graphene layer. Growth is also shown to occur at different rates.

Movie S2 An active catalyst around 2 nm in diameter on MgO support with holey carbon film during SWCNT growth. The catalyst is calculated to be in the Co_2C phase.

Movie S3 An inactive catalyst around 4 nm in diameter on MgO support with holey carbon film showing no graphene formation or SWCNT growth. The nanoparticle is calculated to be in the Co_3C phase.

Movie S4 A deactivated catalyst around 5 nm in diameter on MgO support with holey carbon film with prior SWCNT liftoff but no further growth during the period of observation. The nanoparticle is calculated to be in the Co_3C phase.

Movie S5 The deactivation of a nanoparticle around 2 nm in diameter. Initially a graphene cap forms, then subsequently lifts off and becomes a SWCNT. After which, the nanoparticle deactivates and do not show further growth.

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