Supporting Information

Carbon nanotube growth catalyzed by metal nanoparticles formed via seed effect of metal clusters

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This file includes:

Supplementary Note 1

Synthesis of $Co^{II}(TFA)_2(aq)_4$

Trifluoroacetic acid (1.3 mL) was added to a dispersion of $CoCO_3$ (1.00 g) in water (1 mL) and the mixture was stirred for 10 min. After the evolution of CO_2 gas, the solution turned bright pink and transparent. The solvent was then removed by heating at 150 °C on a hot-plate. The resulting solid was dried in vacuo to affording $Co(TFA)_2(aq)_4$ as a pink powder. The product was stored under inert atmosphere because of its hygroscopic nature. $C_4H_8F_6O_8Co$: Calcd: C, 13.44; H, 2.24; F, 31.93; Co, 16.5. Found: C, 13.41; H, 2.37; F, 33.56; Co, 15.88.

Supplementary Note 2

Synthesis of $Fe^{II}(TFA)_2(aq)_4$

Trifluoroacetic acid (1.5 mL) and degassed water (1.28 mL) were added to the iron nanopowder (500 mg) in a two-necked recovery flask under inert atmosphere (Ar), and the mixture was stirred for 2–3 h. After the evolution of H_2 gas, the solution turned pale, turquoise, and transparent. The solution and the unreacted iron powder were separated using a powerful magnet. The separated solution was evaporated under Ar flow while stirring for 1 d without heating to avoid thermal decomposition. The obtained pale-turquoise solid was dried in vacuo to afford a pale-gray powder of $Fe(TFA)_2(aq)_4$. The product was stored under inert atmosphere because it is hygroscopic and oxygen sensitive. $C_4H_8F_6O_8Fe$: Calcd: C, 13.56; H, 2.26; F, 32.27; Fe, 15.78. Found: C, 13.53; H, 2.29; F, 32.07; Fe, 14.84.

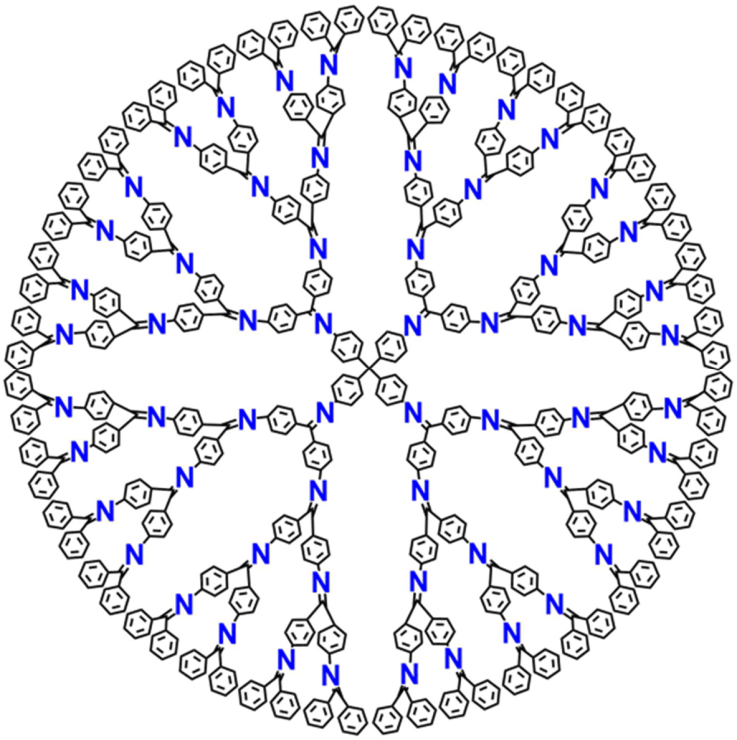

Figure S1. Molecular structure of the dendrimer (tetraphenylmethane-cored dendritic poly-phenylazomethines) used in this work.

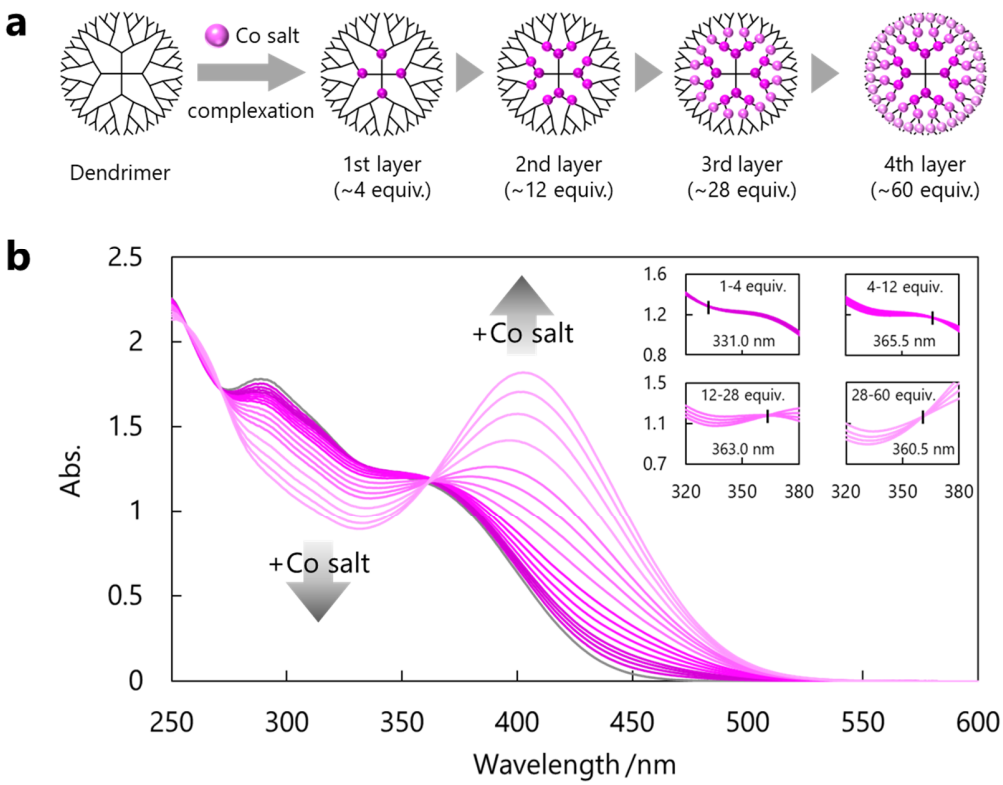

Figure S2. Accumulation of $Co^{II}(TFA)_2$ using the dendrimer as a molecular template. (**a**) Reaction scheme for stepwise complexation of $Co^{II}(TFA)_2$ with dendrimer. (**b**) UV-vis absorption spectral changes during addition of $Co^{II}(TFA)_2$ to the dendrimer, and (inset) isosbestic points observed for each layer.

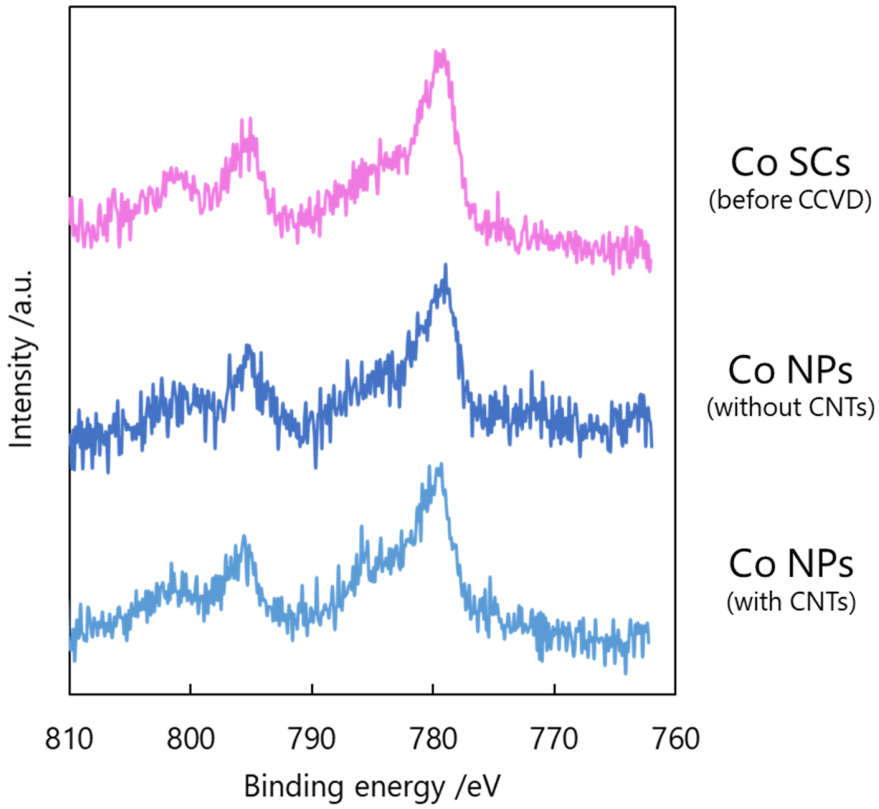

Figure S3. Co 2p core level XPS profiles of Co SCs (Co_{60}) before CCVD, Co NPs after CCVD using only H_2 at 600 °C for 60 min (no CNT growth), and Co NPs after CCVD using CO + H_2 at 600 °C for 60 min (CNT growth progressed).

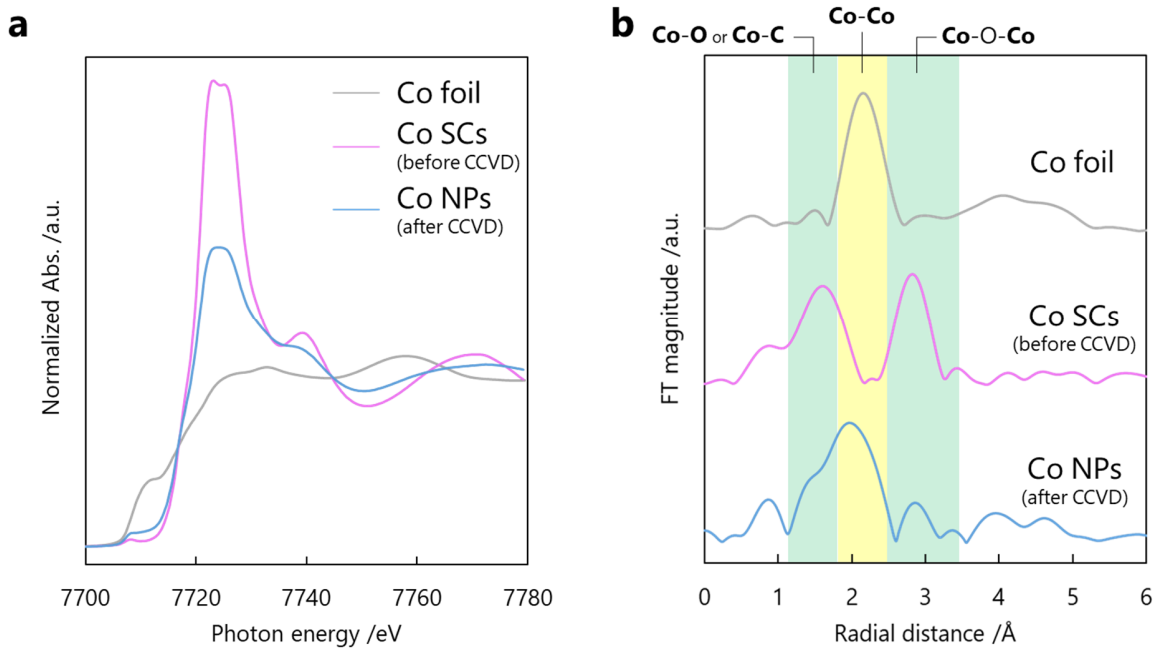

Figure S4. (**a**) Normalized XANES spectra and (**b**) Fourier-transform of k^3-weighted EXAFS data ($3 \leq \Delta k \leq 12$ Å^{-1}) for Co foil, Co SCs (Co_{60}) before CCVD, and Co NPs after CCVD. Co NP is the sample after CO-CCVD reaction at 600 °C for 60 min.

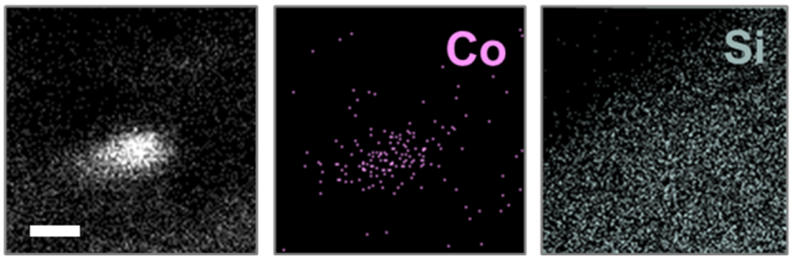

Figure S5. EDS elemental mapping images of a Co SC on silica focusing on Co-Kα and Si-Kα (scale bar: 1 nm).

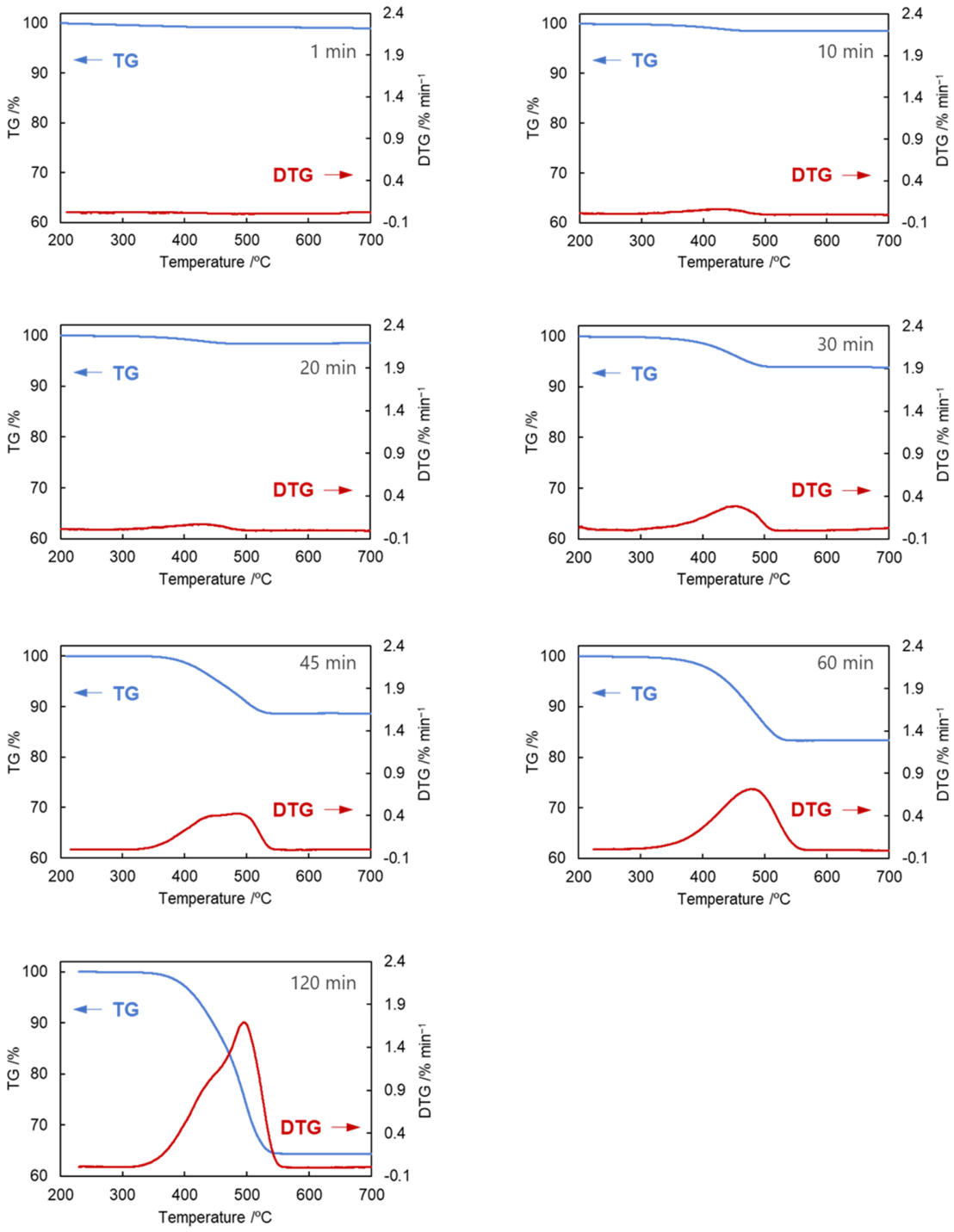

Figure S6. TG profiles of the sample (Co SCs) under ambient atmosphere after the CO-CCVD reaction using mixture of CO/H_2 = 1 at 600 °C for various times (1, 10, 20, 30, 45, 60, 120 min).

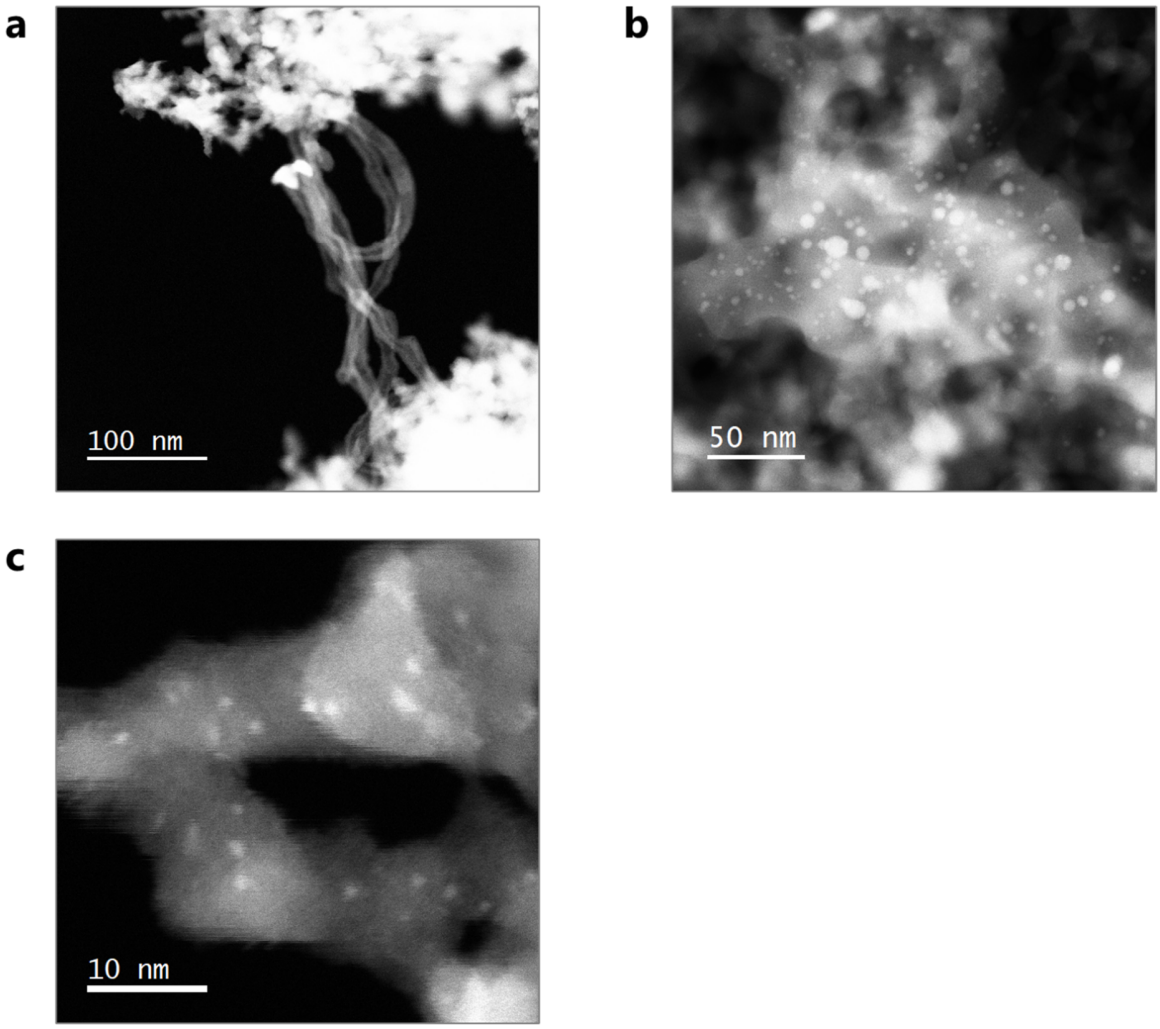

Figure S7. STEM images of the sample (Co nucleuses on silica) after the CO-CCVD reaction using mixture of CO/H_2 = 1 at 600 °C for (**a**) 30, (**b**) 10, and (**c**) 1 min.

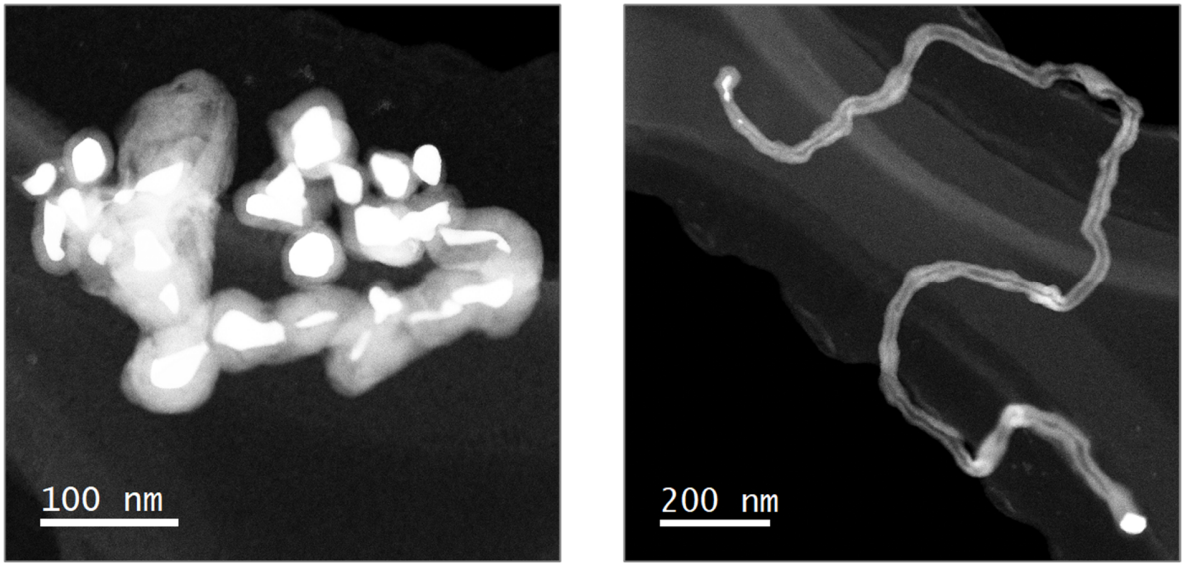

Figure S8. STEM images of the sample (Co nucleuses on an alumina) after the CO-CCVD reaction using mixture of CO/H_2 = 1 at 600 °C for 60 min.

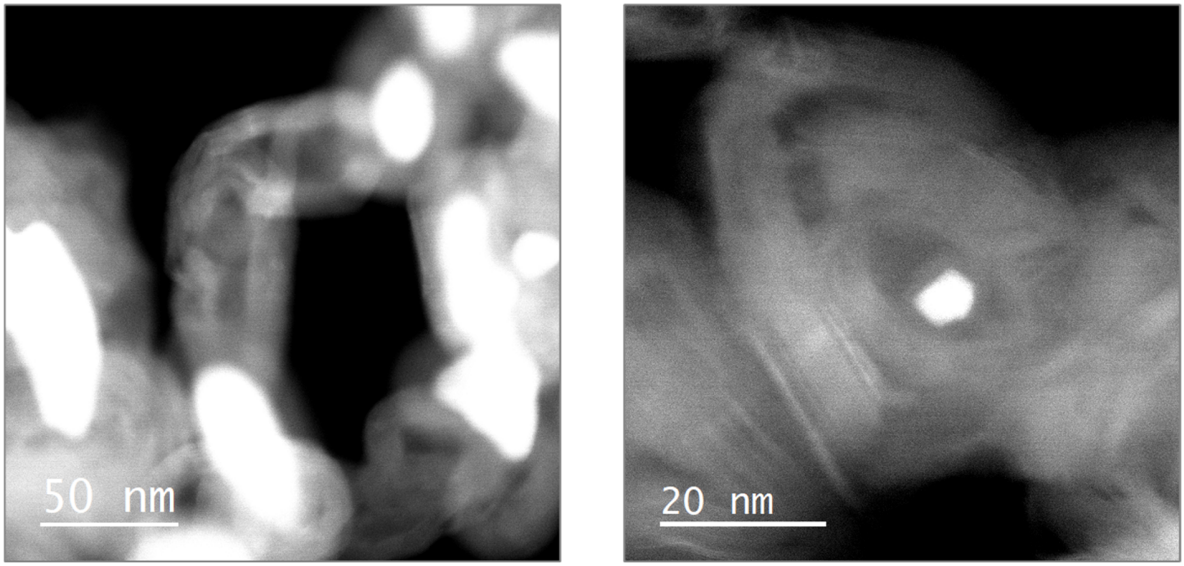

Figure S9. STEM images of the sample (Co nucleuses on silica) after the CO-CCVD reaction using mixture of CO/H_2 = 1 at 800 °C for 60 min.

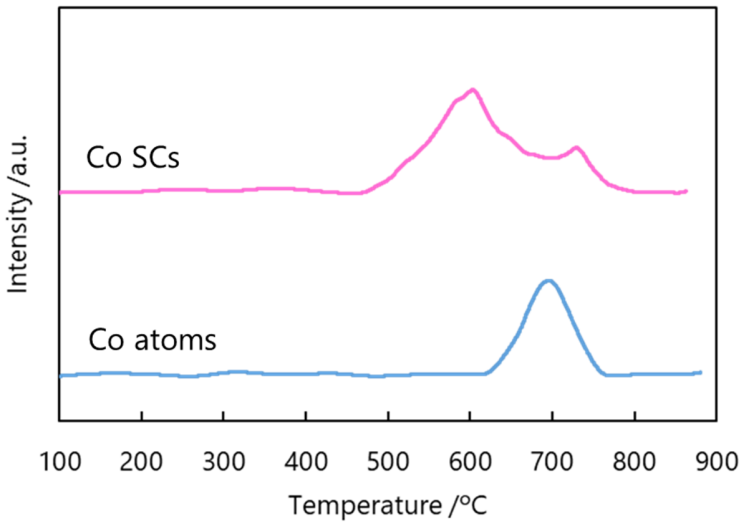

Figure S10. H_2-TPR profiles of Co SCs and Co atoms on silica. Air-oxidized Co samples are chemically reduced by H_2, and is H_2O generated accordingly. The signal is mass intensity for m/z = 18. Measurement conditions: 10% H_2 in Ar, 30 cm^3 min^{-1}, +5.0 °C min^{-1}, 1 atm, 50 mg of catalyst.

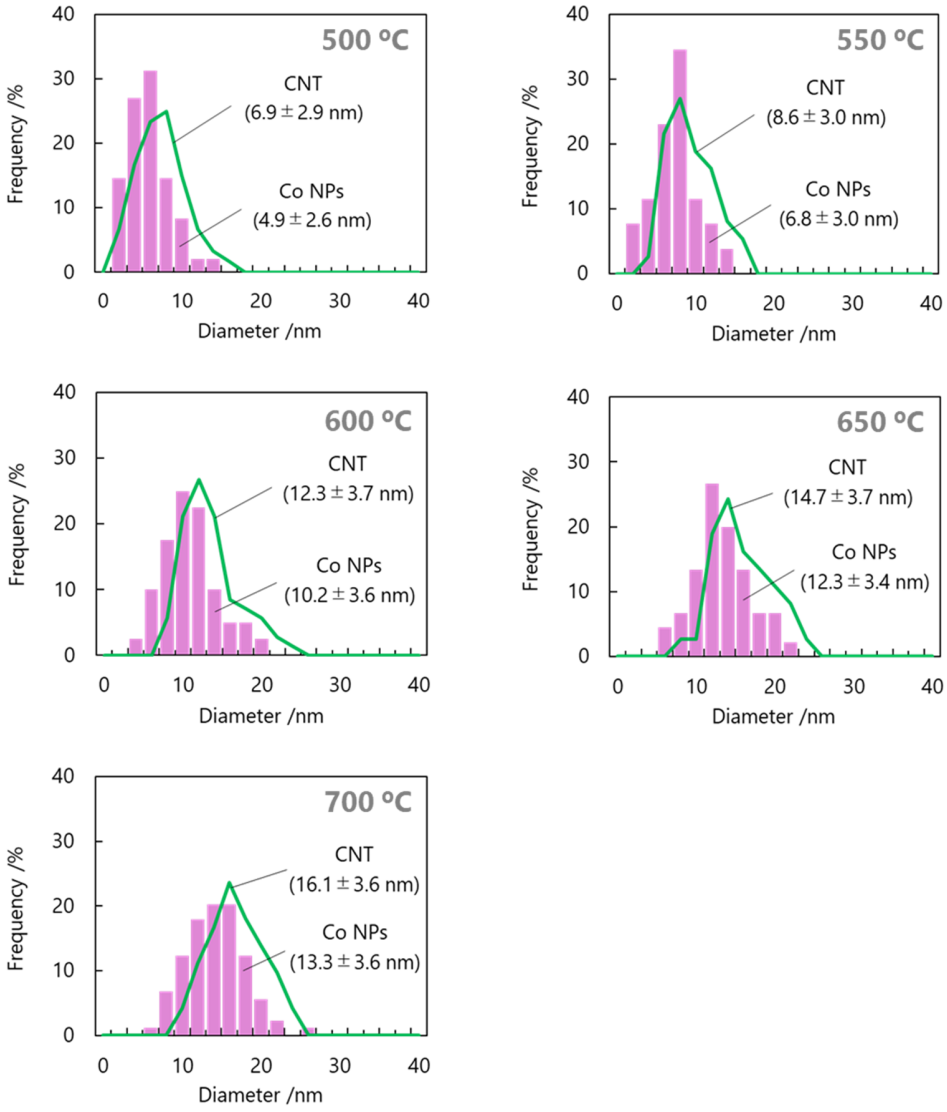

Figure S11. Histogram of the diameter of Co nucleuses (pink bar) and grown CNTs (green line) after the CO-CCVD reaction using mixture of CO/H_2 = 1 at various temperatures for 60 min. Diameter of grown CNTs changed according to the size of Co nucleuses.

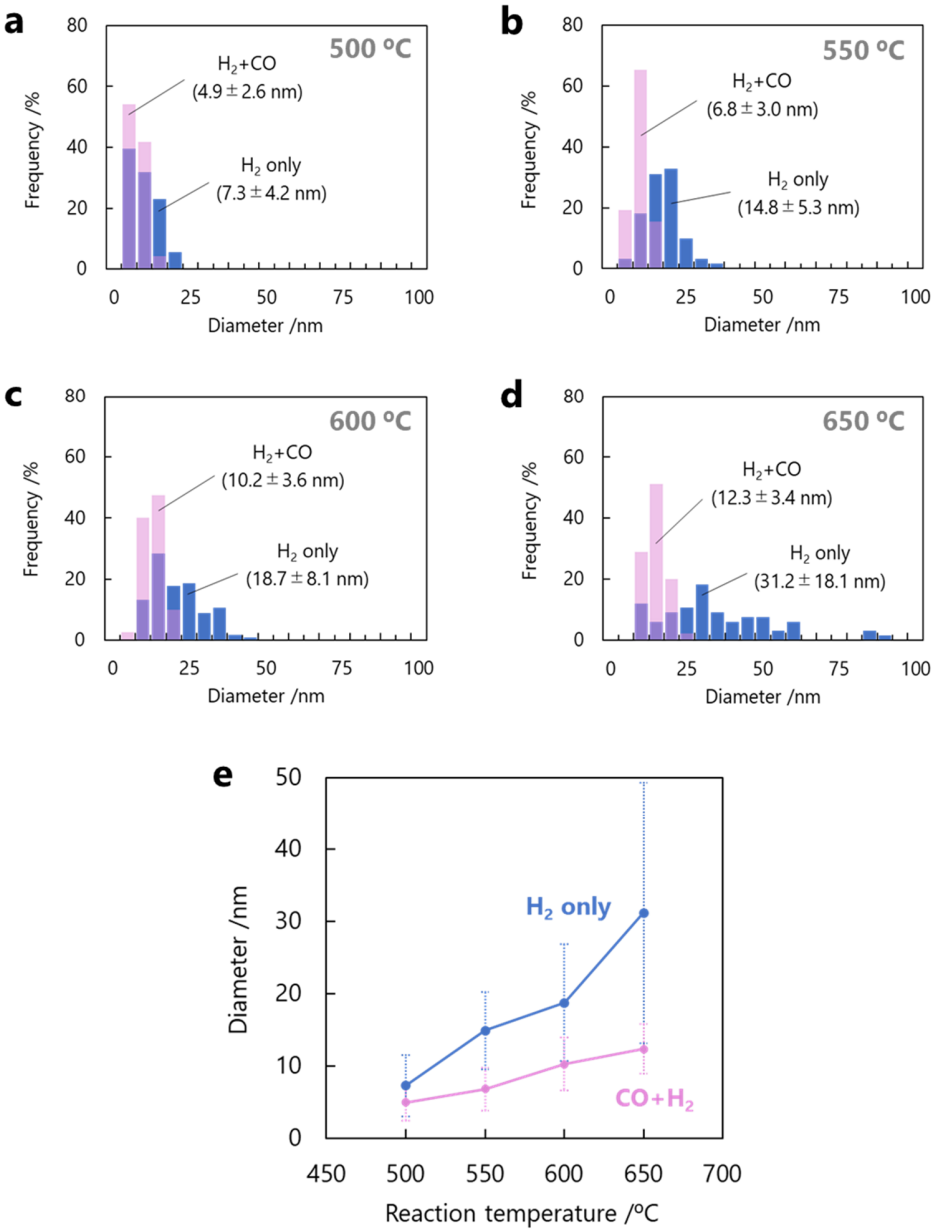

Figure S12. Histogram of diameter of Co nucleuses after the reaction using mixture of CO/H_2 = 1 or H_2 only at (**a**) 500 °C, (**b**) 550 °C, (**c**) 600 °C, and (**d**) 650 °C for 60 min. (**e**) Relationship between diameter of Co nucleuses and reaction temperature depending on the gas species (CO/H_2 = 1 or H_2 only).

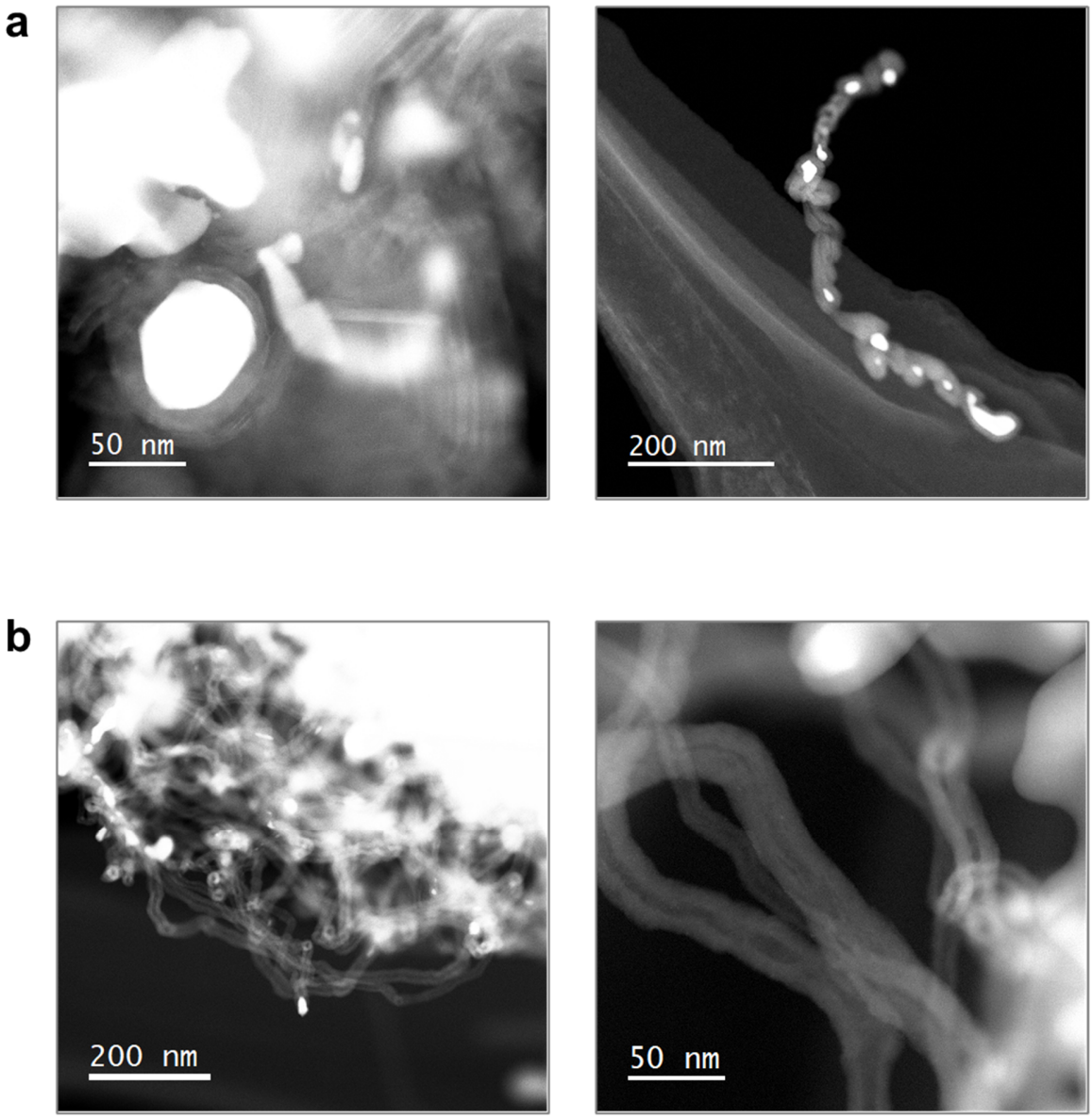

Figure S13. STEM images of the sample (Co nucleuses on silica) after the CO-CCVD reaction using mixture of CO/H_2 = 2 at (**a**) 700 °C and (**b**) 600 °C for 60 min.

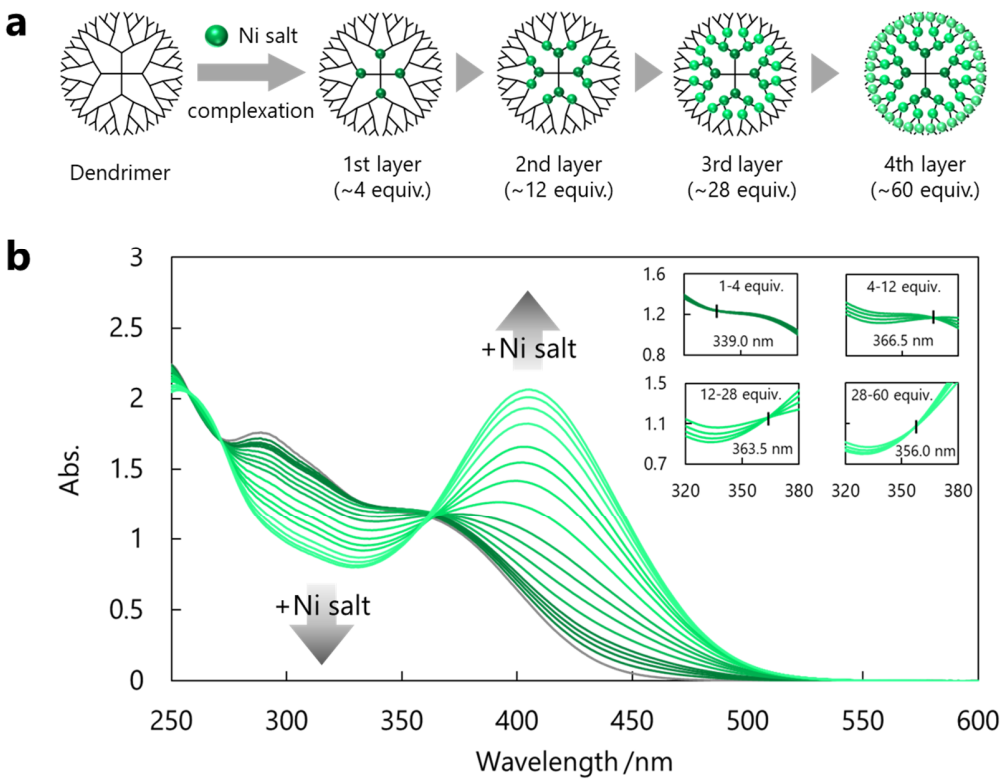

Figure S14. Accumulation of $Ni^{II}(TFA)_2$ using dendrimer as a molecular template. (**a**) Reaction scheme for stepwise complexation of $Ni^{II}(TFA)_2$ with dendrimer. (**b**) UV-vis absorption spectral changes during addition of $Ni^{II}(TFA)_2$ to the dendrimer, and (inset) isosbestic points observed for each layer.

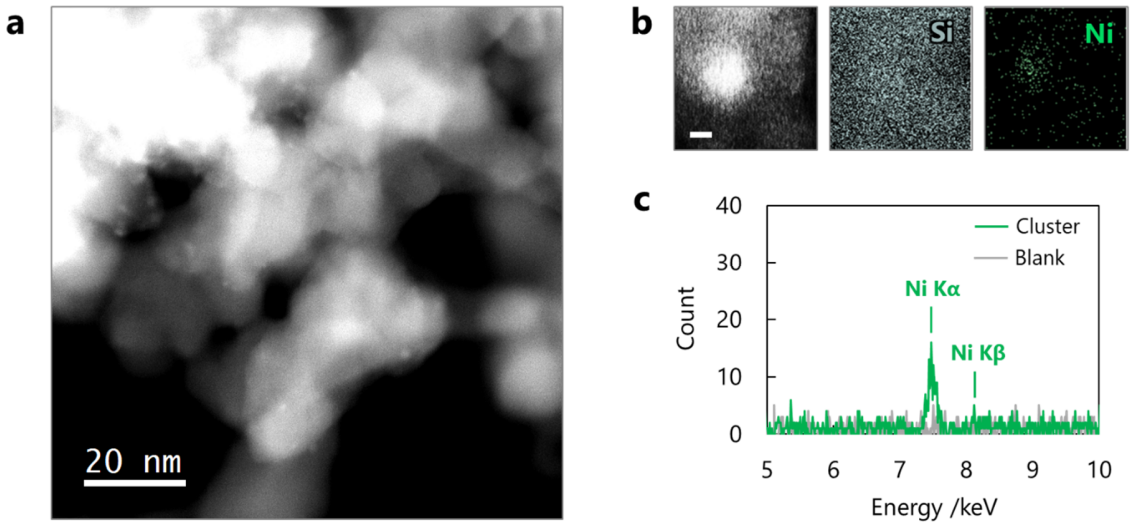

Figure S15. (**a**) STEM images of Ni SCs (Ni_{60}) supported on silica. (**b**) EDS elemental mapping images of a Ni SC on silica focusing on Ni-Kα and Si-Kα (scale bar: 1 nm). (**c**) EDS profile of a Ni SC on silica.

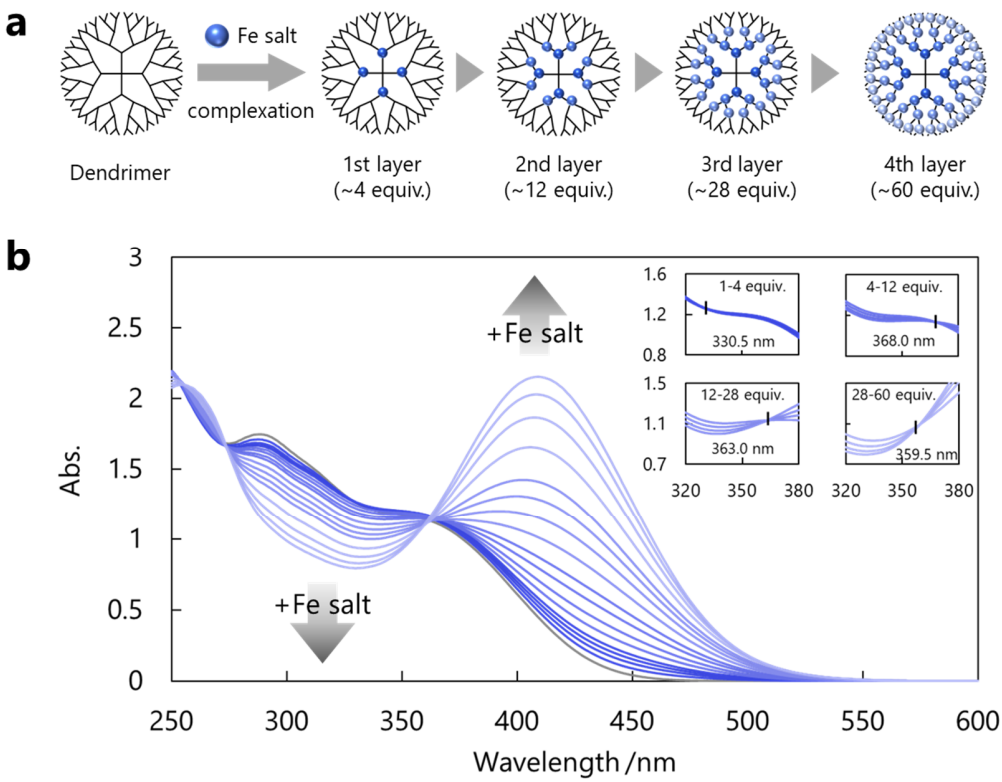

Figure S16. Accumulation of $Fe^{II}(TFA)_2$ using dendrimer as a molecular template. (**a**) Reaction scheme for stepwise complexation of $Fe^{II}(TFA)_2$ with dendrimer. (**b**) UV-vis absorption spectral changes during addition of $Fe^{II}(TFA)_2$ to the dendrimer, and (inset) isosbestic points observed for each layer.

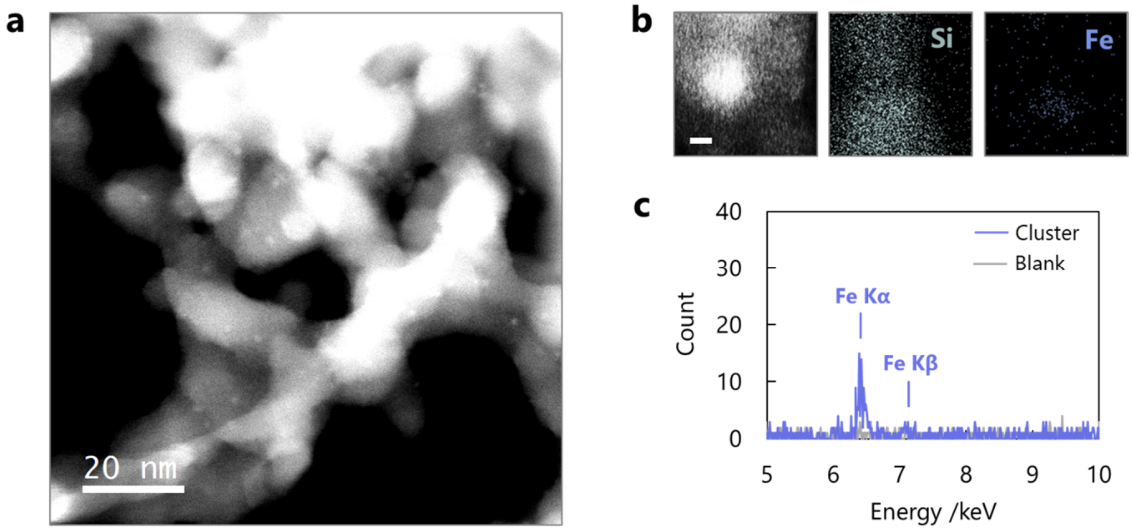

Figure S17. (**a**) STEM images of Fe SCs (Fe_{60}) supported on silica. (**b**) EDS elemental mapping images of a Fe SC on silica focusing on Fe-Kα and Si-Kα (scale bar: 1 nm). (**c**) EDS profile of a Fe SC on silica.

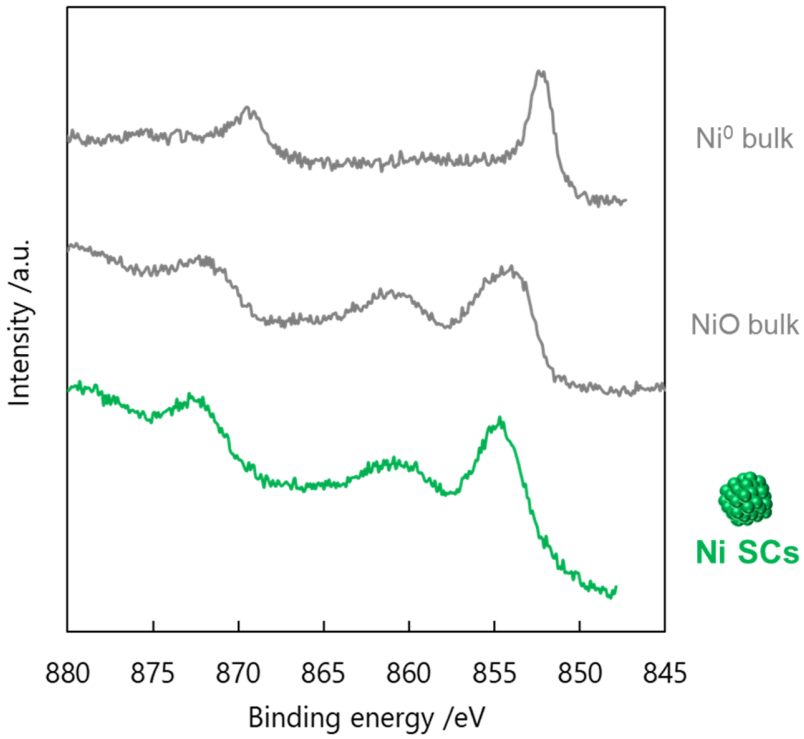

Figure S18. Ni 2p core level XPS profiles of Ni^0 bulk, NiO bulk, and Ni SCs (Ni_{60}).

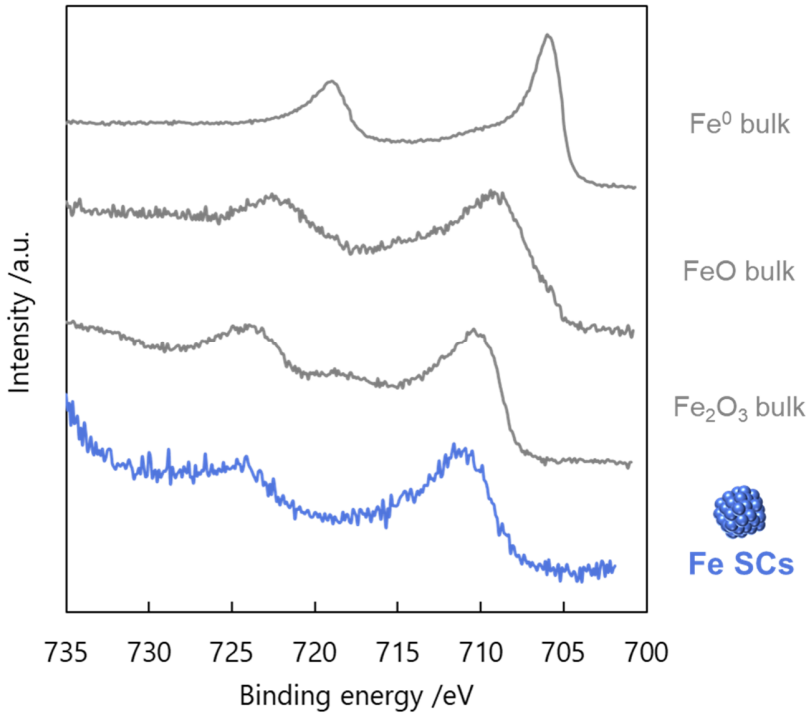

Figure S19. Fe 2p core level XPS profiles of Fe^0 bulk, FeO bulk, Fe_2O_3 bulk, and Fe SCs (Fe_{60}).

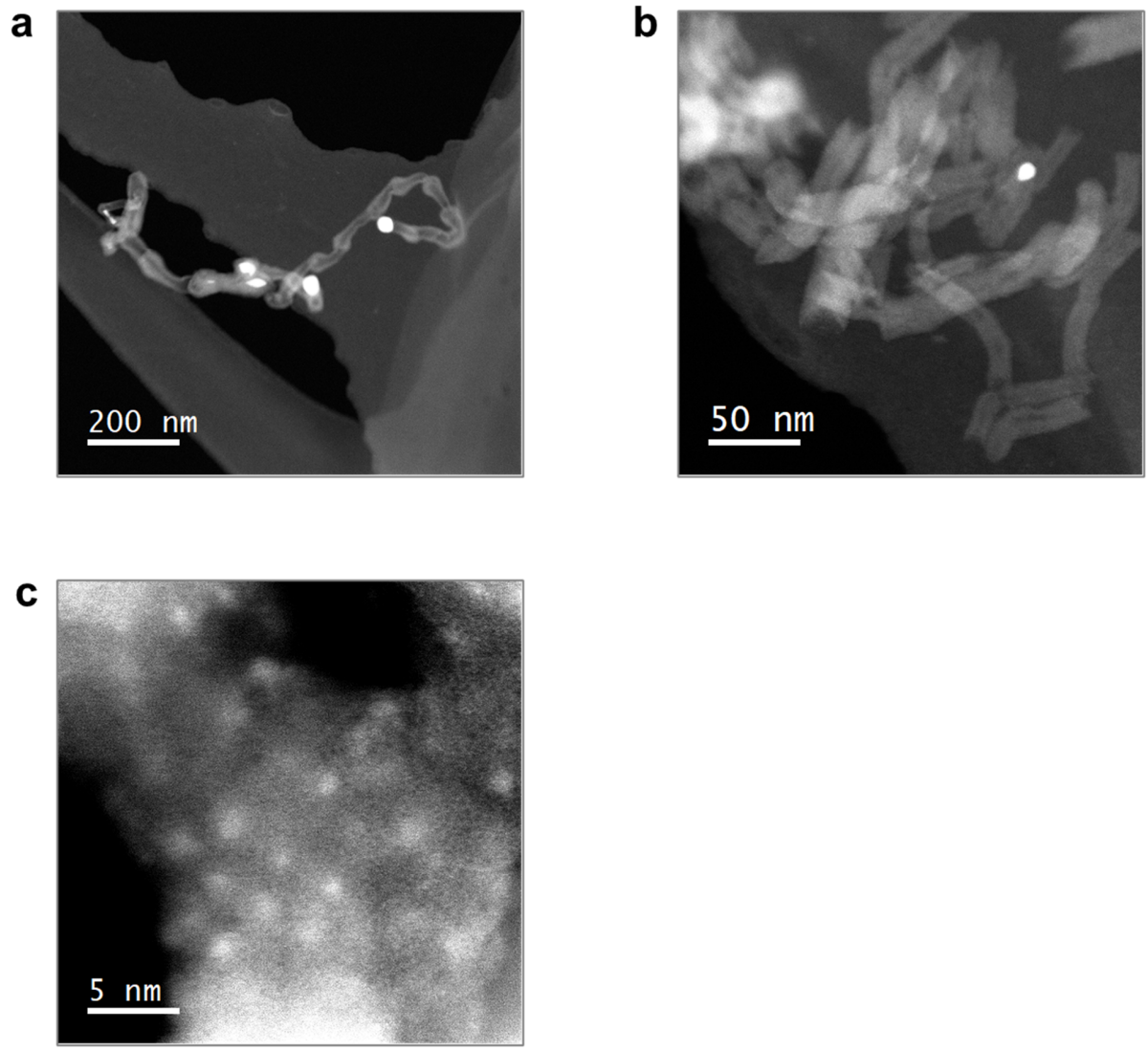

Figure S20. STEM images of sample from CO-CCVD reaction using mixture of CO/H_2 = 1 for 60 min using (**a, b**) Ni SCs and (**c**) Fe SCs on silica. Reaction temperature: (**a, c**) 700 °C and (**b**) 500 °C.

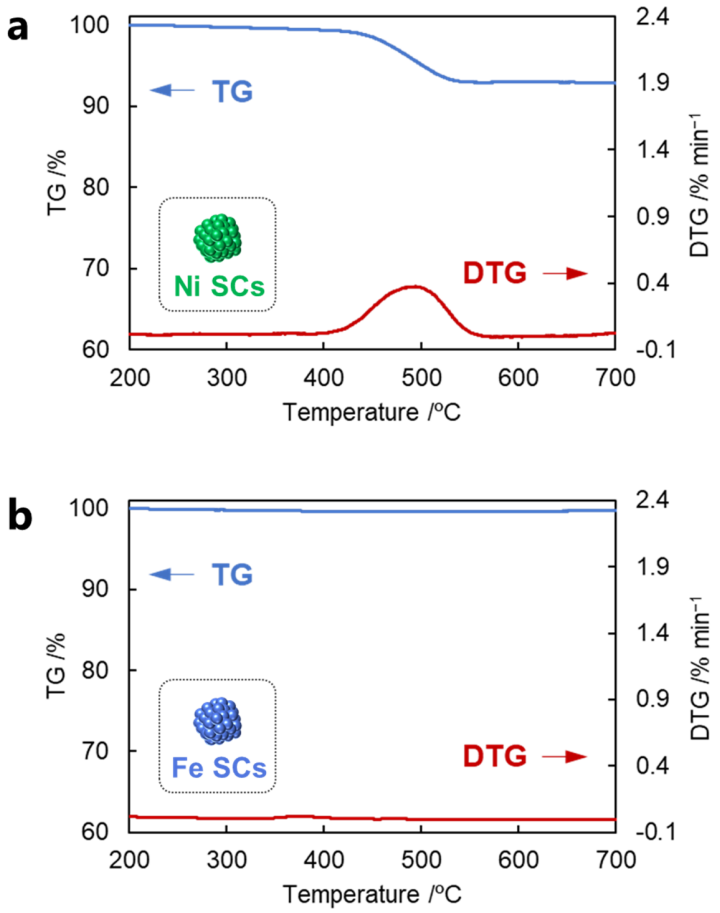

Figure S21. TG profiles of the sample measured under ambient atmosphere after the CNT growth reaction using mixture of CO/H_2 = 1 at 700 °C for 60 min using (**a**) Ni SCs and (**b**) Fe SCs on silica.

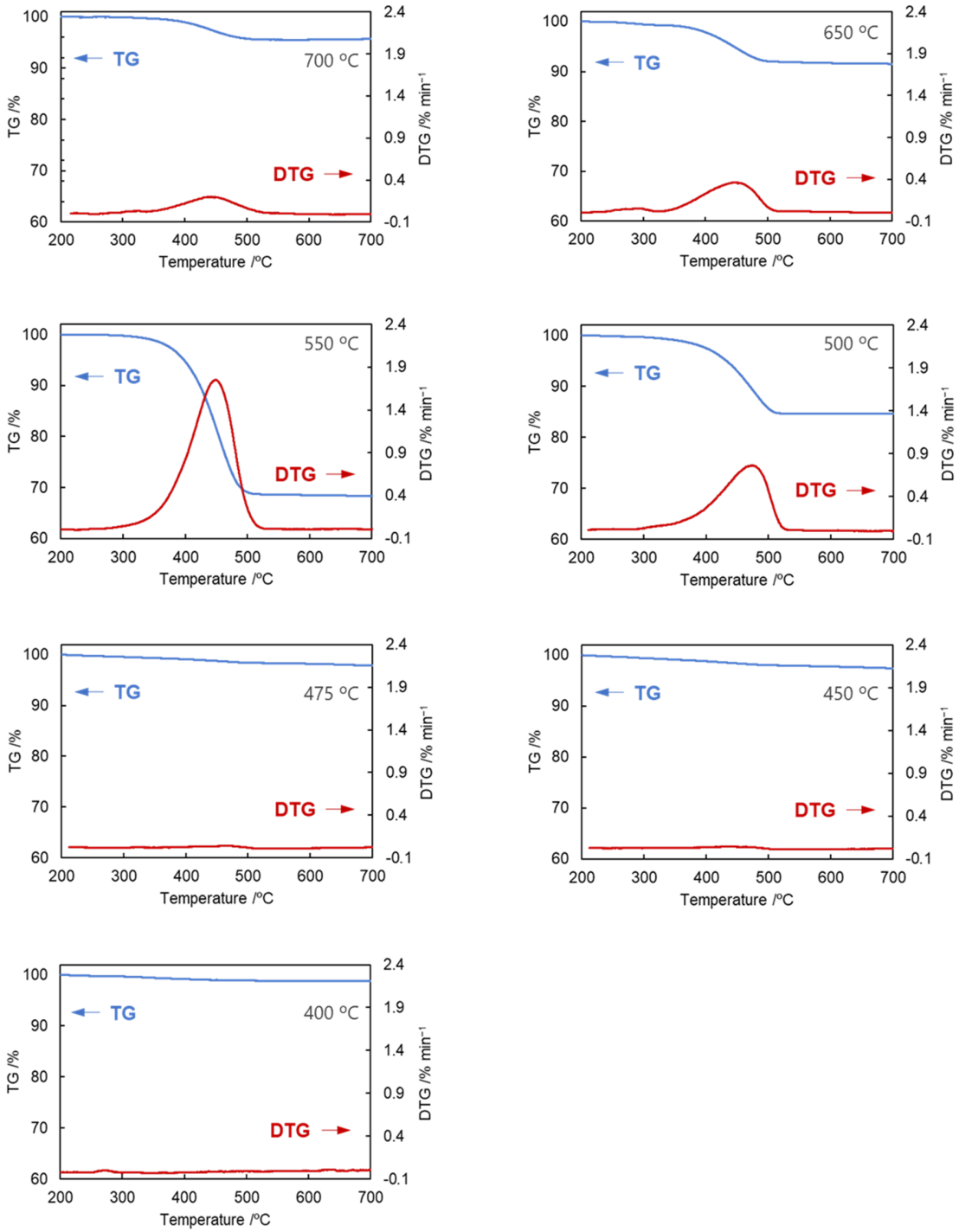

Figure S22. TG profiles of the sample (Co SCs) measured under ambient atmosphere after the CO-CCVD reaction using mixture of CO/H_2 = 1 for 1 h at various temperatures (700, 650, 550, 500, 475, 450, 400 °C).

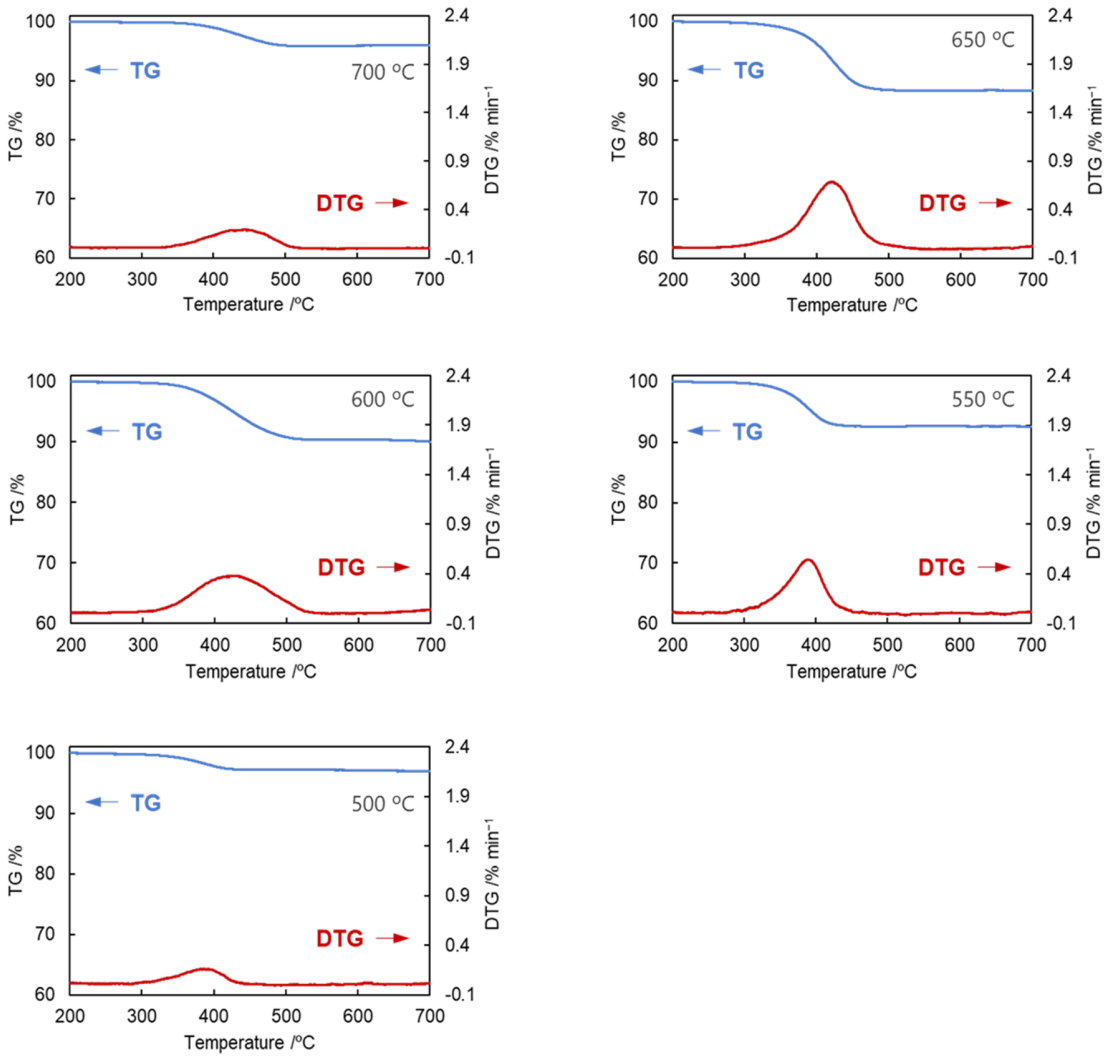

Figure S23. TG profiles of sample (Co SCs) measured under ambient atmosphere after the CO-CCVD reaction using mixture of CO/H_2 = 2 for 1 h at various temperatures (700, 650, 600, 550, 500 °C).

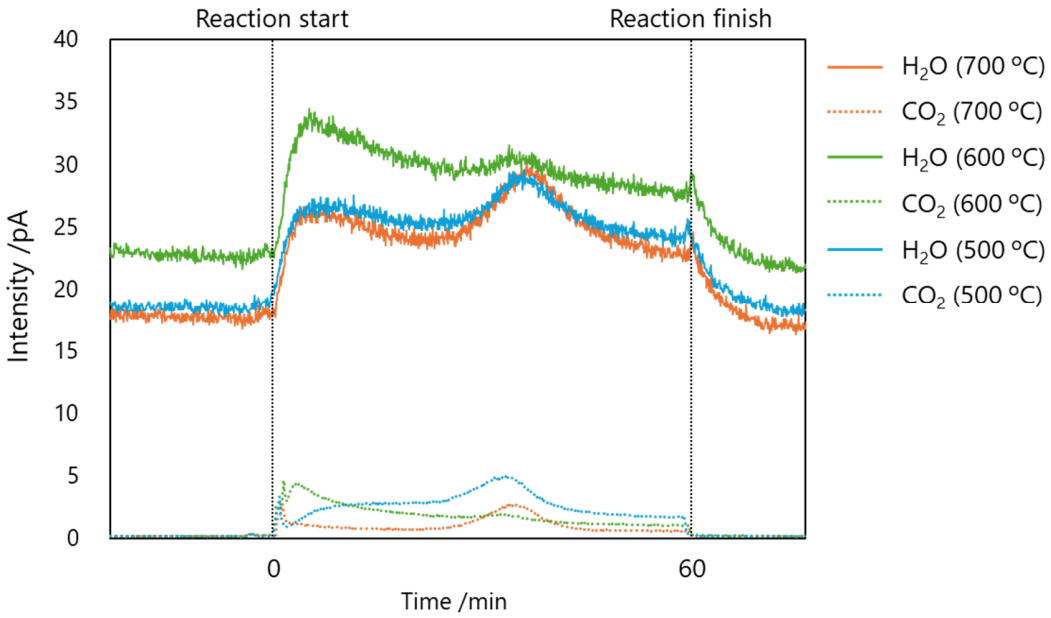

Figure S24. Mass intensity of *m*/*z* = 18 (H_2O) and *m*/*z* = 44 (CO_2) signals during CO-CCVD using mixture of CO/H_2 = 1 at 700, 600, and 500 °C for 60 min.

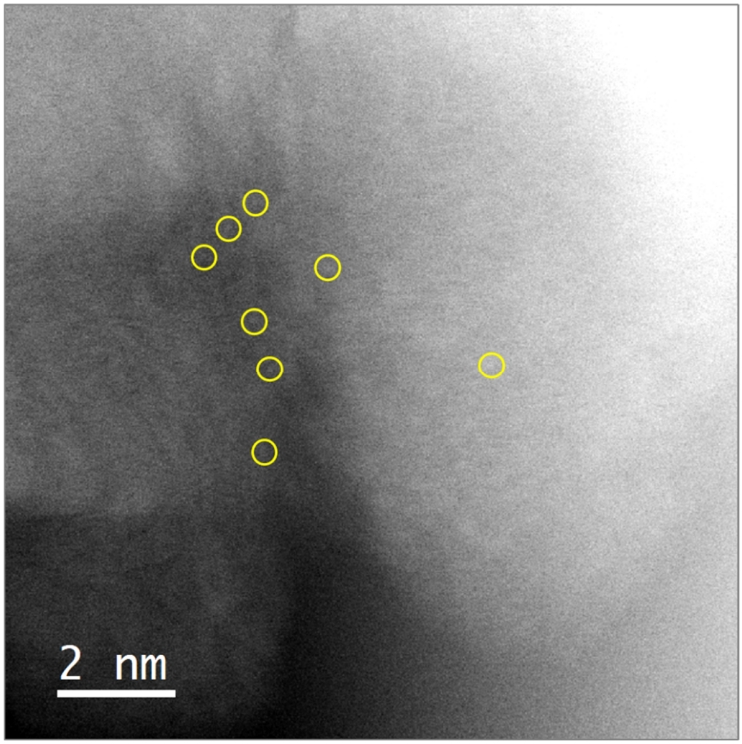

Figure S25. STEM image of Co atoms on silica. The atoms are highlighted by yellow circles. This sample was prepared using the same procedure as that used for Co SCs, without the dendrimer.

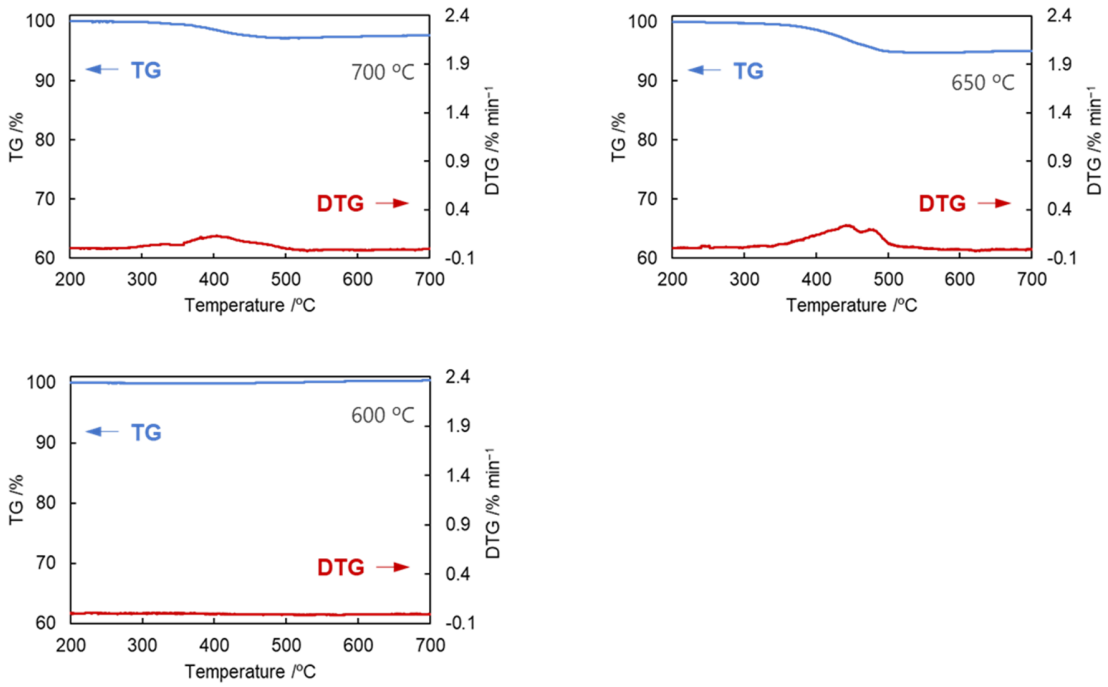

Figure S26. TG profiles of the sample (Co atoms) measured under ambient atmosphere after CO-CCVD reaction using mixture of CO/H_2 = 1 for 1 h at various temperatures (700, 650, 600 °C).