Supporting Information

Graphitically Encapsulated Cobalt Nanocrystal Assemblies

Experimental Section

Synthesis: All chemicals and solvents are used as received. Typically, 4-mmol $CoCl_2 \cdot 6H_2O$ reacted with 8-mmol sodium oleate to form Co(II) oleate in the mixed hexane/ethanol/water solvents (40 mL/24 mL/16 mL). After thorough purification, the as-formed 4-mmol Co(II) oleate was dissolved in a mixture solution of 20-mL hexane and 20-mL oleic acid followed by rotary evaporation to remove lower boiling-point solvents. The resulting Co(II) oleate solution in oleic acid was degassed in vacuum at 120 ^{o}C for 1 h. It took ~30 min to heat the reaction system to boiling at 360 ^{o}C in argon atmosphere. After this temperature was remained for 1 h, it started to increase steadily. After reaching ~380 ^{o}C, the reaction solution burst out to form dense gas clouds and black products, accompanying a fast increase in temperature up to 395 ^{o}C. The reaction temperature then fell down quickly and dwelled at 385 ^{o}C for 1 h before removing heating mantle for cooling. With the addition of dichloromethane/ethanol, the black precipitates were magnetically separated for three times, and stored in dichloromethane for further studies. For comparison purpose, similar synthesis procedure was adopted by employing extra 40-mmol sodium oleate together with 20-mL oleic acid in the starting reaction mixture in order to study the role of oleate in the formation of graphitically encapsulated cobalt products.

Characterization: TEM images were obtained with a Zeiss 912 Omega transmission electron microscope operating at an accelerate voltage of 120 kV and a FEI Tecnai F20 transmission electron microscope operating at an accelerate voltage of 200 kV, respectively. EEL spectral mapping was recorded on a Zeiss 912 microscope operated with an in-column Omega energy filter. Magnetic studies were carried out using a Quantum Design MPMS-5S SQUID magnetometer with a magnetic field up to 50 KOe and a temperature from 5 to 390 K. The Raman measurements were performed on a JYT64000 micro-Raman set up using 514.5 nm line from an Ar^+ laser. The incident laser power was kept very low to avoid sample heating. The X-ray powder diffraction patterns were collected from a high resolution X-ray diffractometer at Singapore Synchrotron Light Source, using 6.9303 keV photons (Co Kα1 equivalent) that were selected by a Si (111) channel-cut monochromator.

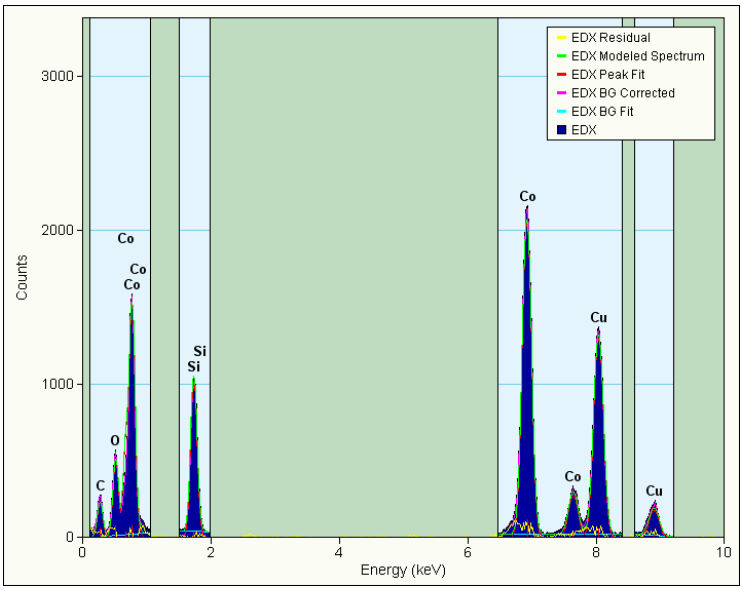


Figure S1. Quantitative EDX analysis result of graphitically encapsulated cobalt nanocrystal assemblies on a silica-coated copper grid.

Peak Fitting Results

Peak	Integrated Intensity	Uncertainty
C-K	4409.495	400.853
O-K	10016.448	562.425
Si-K	23542.748	777.003
Co-K	69249.932	1274.280
Co-L	25362.086	619.624
Cu-K	46387.135	1037.470

Input FWHM = 150 eV @ 5.9 keV
Measured FWHM = 150.000 eV @ 5.9 keV
Calibration: 4.99742 eV/ch, 1.42828 eV at channel 0
Accelerating voltage: 200 kV
Alpha tilt: 15 degrees

Quantification Results
Correction method: None

Element	Weight %	Atomic %	Uncertainty %	Detector Correction	k-Factor
C(K)	10.578	30.661	0.192	0.173	6.279
O(K)	7.580	16.493	0.085	0.514	1.980
Si(K)	8.994	11.148	0.059	0.977	1.000
Co(K)	41.709	24.638	0.153	0.995	1.576
Cu(K)	31.137	17.057	0.139	0.997	1.757

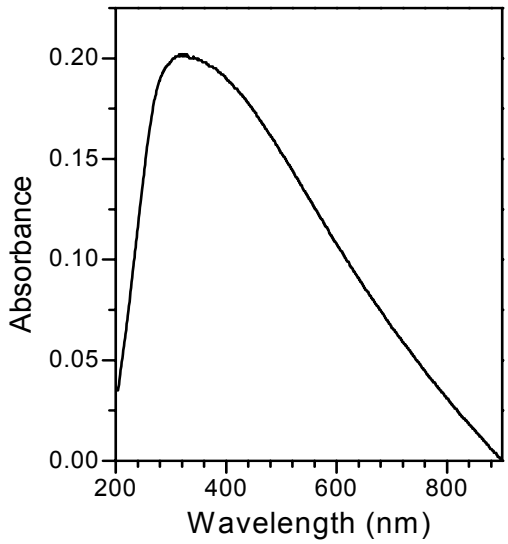


Figure S2. UV-vis spectrum of HCl-etched graphitically encapsulated cobalt nanocrystal assemblies.

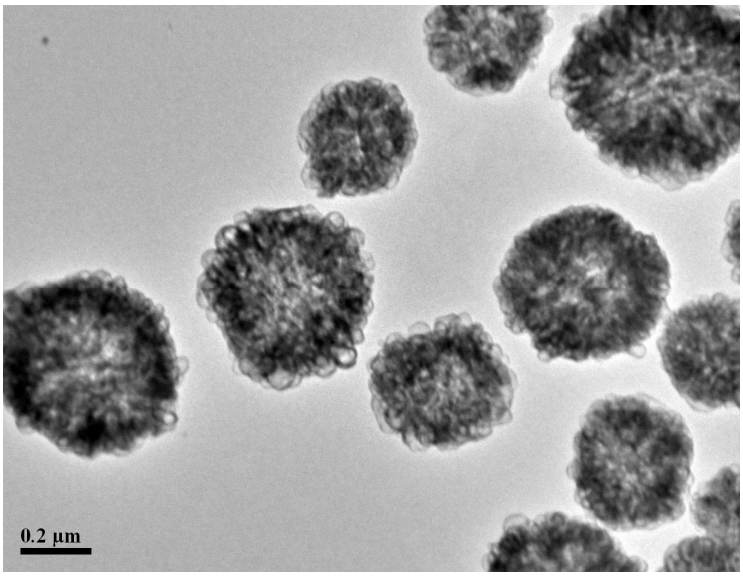
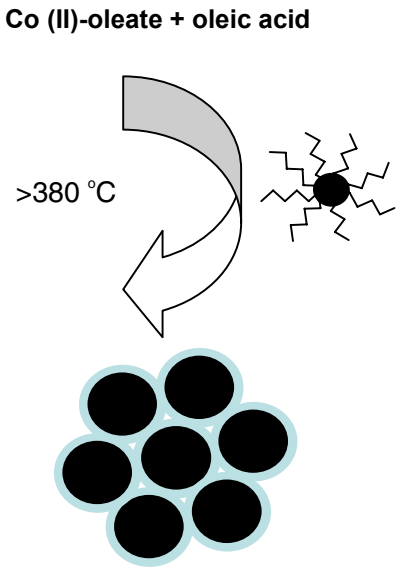


Figure S3. TEM image of HCl-etched graphitically encapsulated cobalt nanocrystal assemblies.



Scheme 1. Schematic illustration for the burst formation of graphitically encapsulated cobalt nanocrystal assemblies in the presence of excessive oleic acid at a temperature of >380 ^{o}C.