Electronic Supplementary Material (ESI) for Chemical Communications

How Hollow Structures form from Crystalline Iron/Iron Oxide Core/Shell Nanoparticles in the Electron Beam

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Supporting Information

Experimental Section

Syntheses were carried out using commercially available reagents. Bis(η^5-1,3,5-*exo*-6-tetramethylcyclohexadienyl) iron(II), [Fe(η^5-$C_6H_3Me_4)_2$] was purchased from Boutiq Nanoparticle Solutions Ltd. Oleylamine (OLA, 98%) and Toluene (99.3%) were all purchased from Sigma-Aldrich.

Synthesis of iron/iron oxide core-shell nanoparticles

All procedures were performed under standard Schlenk techniques. [Fe(η^5-$C_6H_3Me_4)_2$] (0.3 g, 0.93 mmol) and OLA (4.0 cm^3, 12 mmol) were mixed and degassed via freeze-pump-thaw method (FPT), while separately OLA (8 cm^3) was degassed via FPT in a 3-necked flask and then heated to 300°C, where the mixture containing [Fe(η^5-$C_6H_3Me_4)_2$] was injected instantly resulting in a black solution within two seconds. Upon injection the reaction temperature immediately dropped to 260°C and was left at that temperature for 2h and then cooled to room temperature before being exposed to air and separated from solution using a bar magnet and redispersed in toluene for TEM analysis.

TEM analysis

Samples for transmission electron microscopy TEM were prepared by drop-casting a solution of nanoparticles suspended in toluene onto a carbon coated copper grid. TEM images were taken on a JEOL 2010 TEM microscope at an acceleration voltage of 200 keV.

X-ray diffraction

Samples for powder X-ray diffraction were prepared by drying drops of the nanoparticles suspended in toluene onto a zero background holder. Powder XRD measurements were obtained from a Pan Analytical X'pert Pro MPD X-ray diffraction System using Cu Kα radiation.

TGA analysis

TGA analysis was performed on a TA Instruments SDT Q600. Scans were conducted from 100°C to 450°C under flowing argon (50 mL/min) at a rate of 10 °C/min.

Supplementary Figures

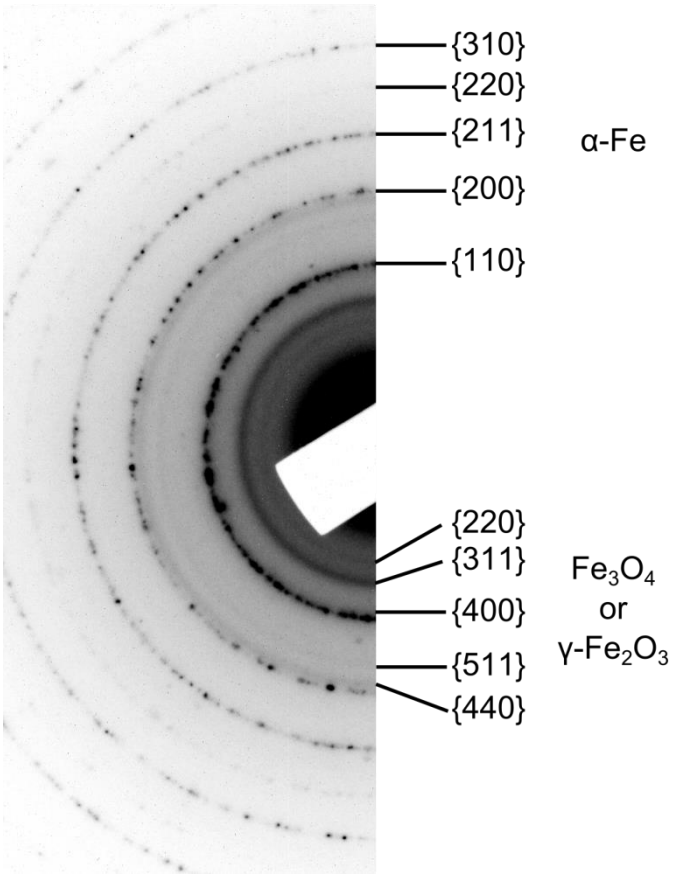


Figure S1. Selected area electron diffraction (SAED) of the iron/iron oxide core-shell nanoparticles indexed to both α-Fe and iron oxide of the spinel phase

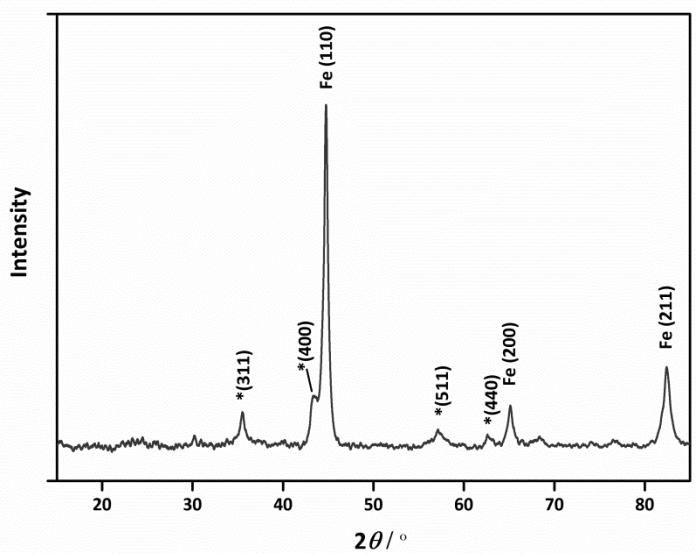


Figure S2. X-ray diffraction of the as synthesised iron/iron oxide core-shell nanoparticles with diffraction peaks indexed to α-Fe and spinel iron oxide phase (*)

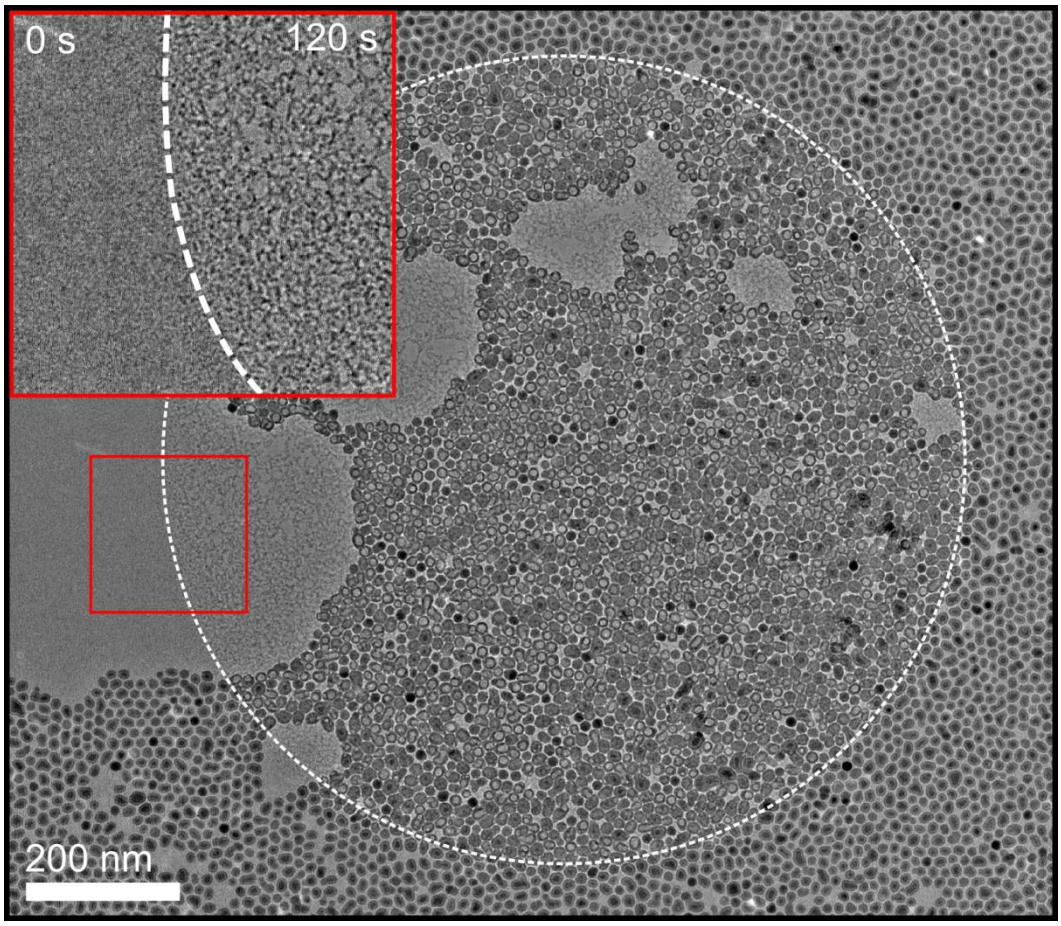


Figure S3. Low magnification TEM image of the area exposed to the electron beam. White dashed circle indicates electron beam perimeter. (Inset) Magnification of red boxed area of sample not exposed to the electron beam (0 s) and area exposed to electron beam (120 s). After 120 s, the typical carbonaceous species formed as a result of the excess oleylamine melting under electron beam is evident.

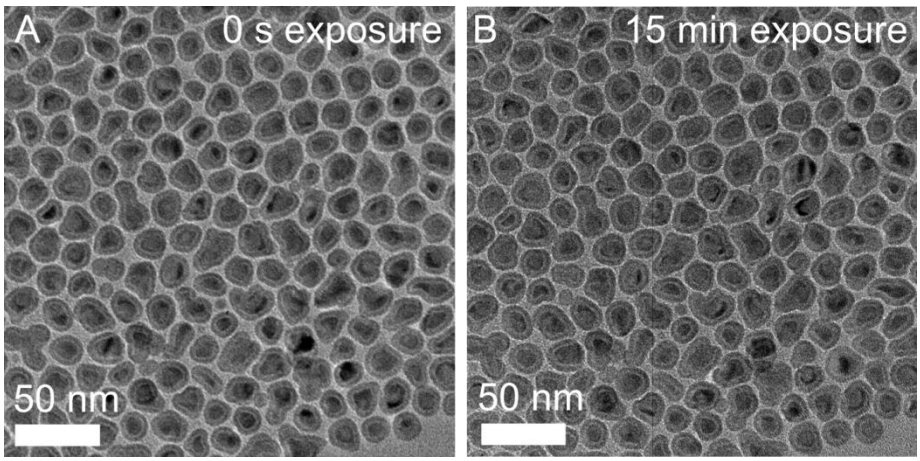


Figure S4. Control experiment of iron/iron oxide core-shell nanoparticles that were further purified A) before exposure and B) after 15 min exposure in the electron beam, where the core/shell structures remained.

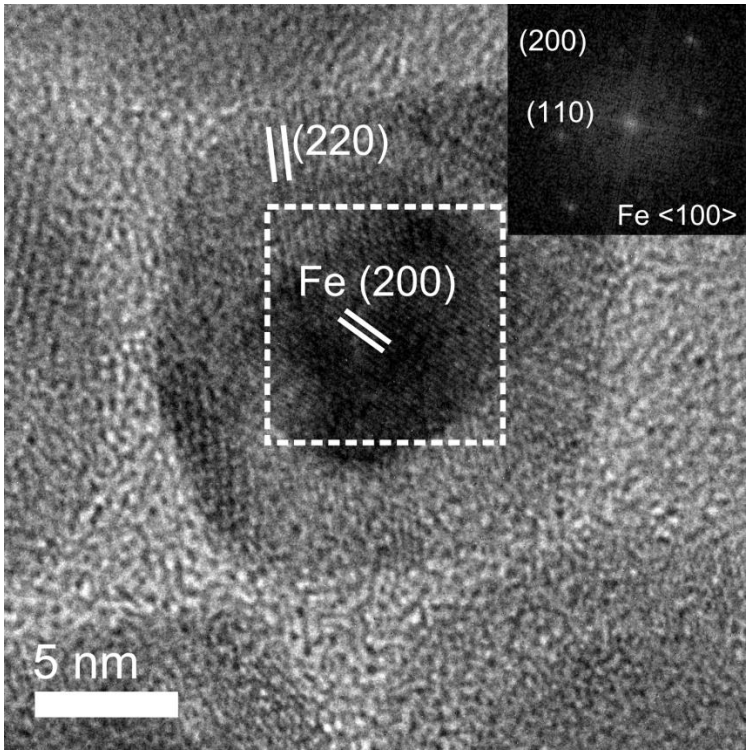


Figure S5. High resolution TEM image (HRTEM) of a core/shell nanoparticle from the further purified sample showing a single crystal α-Fe core with lattice spacings corresponding to Fe(200) planes observed in the core region. The lighter contrast shell is polycrystalline iron oxide with (220) planes observed in sections of shell. Inset shows the corresponding FFT of the α-Fe core area in white dashed box viewed down the Fe<1,0,0> zone axis.

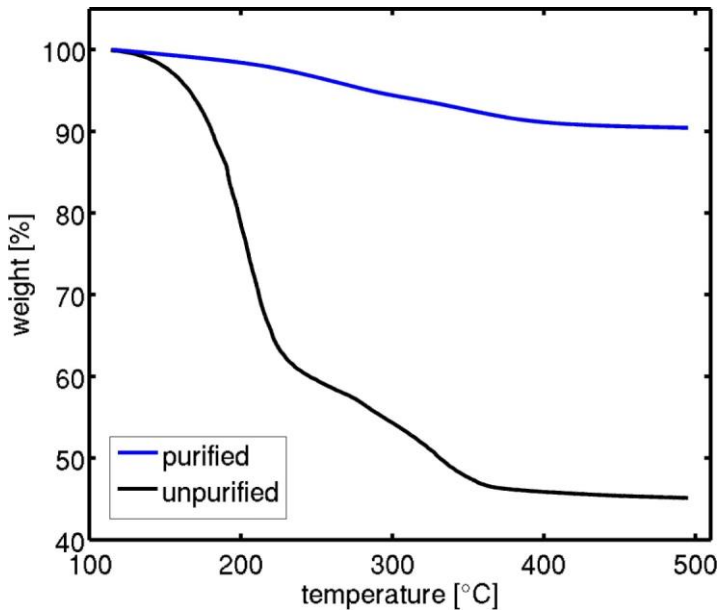


Figure S6. TGA plots of samples that were unpurified (black) and further purified (blue). Greatest weight loss is observed in the sample that was unpurified, which indicates presence of excess oleylamine compared to the further purified sample. The analysis was performed on a TA Instruments SDT Q600. Scans were conducted from 100°C to 450°C under flowing argon (50 mL/min) at a rate of 10 °C/min.

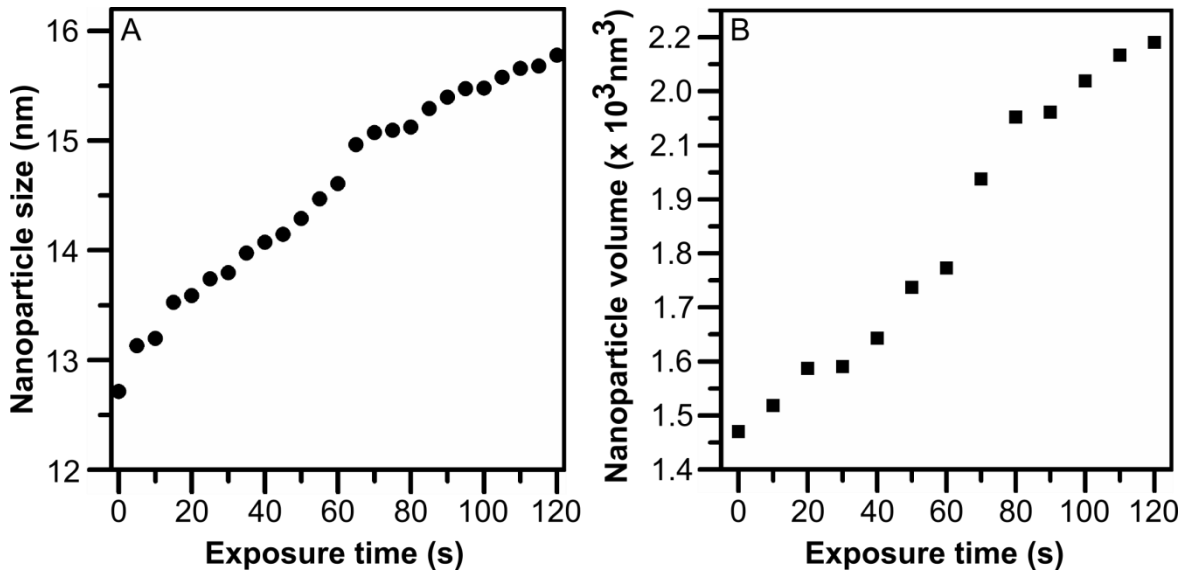
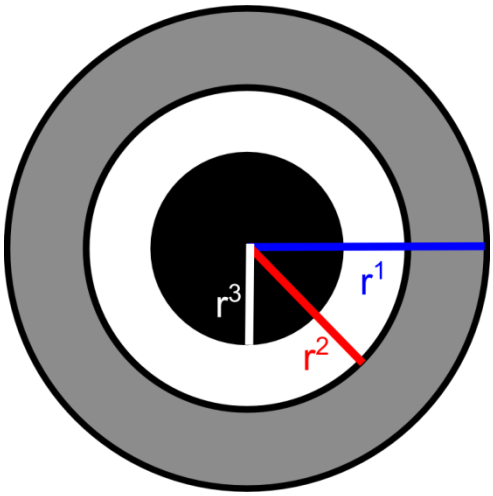


Figure S7. A) Plot showing the average size as a function of electron beam exposure for a single nanoparticle. The size of 40 individual nanoparticles was measured every 30 seconds. B) Plot showing the average nanoparticle volume as a function of electron beam exposure time. The volume of 40 individual nanoparticles was calculated (see below) every 30 seconds.

Schematic showing how nanoparticle volume was calculated is shown below.



Estimated volume = $4/3 \cdot \pi \cdot (r^1-r^2+r^3)^3$

Where r^1 = total nanoparticle radius, r^2 = void radius and r^3 = Fe core radius.