Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

Core-shell nanoparticles by silica coating of metal oxides in a dual-stage hydrothermal flow reactor

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Content of supporting information

Experimental Setup

An outline of the configuration of the dual-stage continuous flow reactor is shown in Figure S1

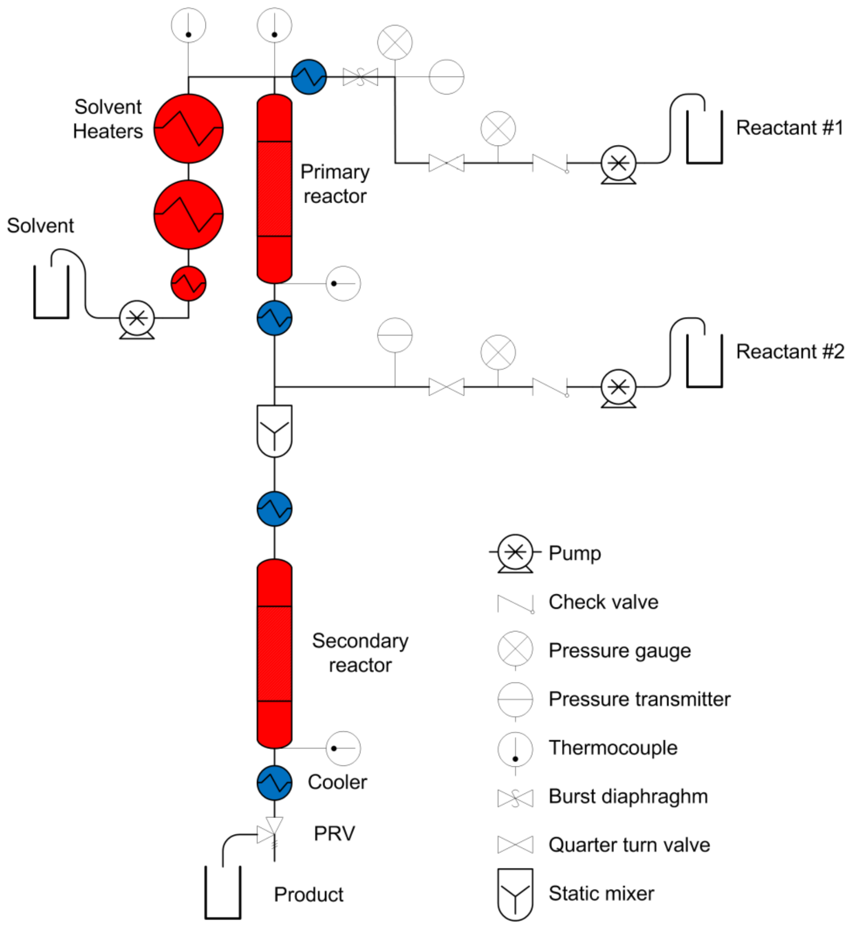

Figure S1: Diagram of dual-stage flow reactor. TEOS was used for Reactant #2 and mixed with the nanoparticle suspension synthesized in the primary reactor. The mixture is subsequently heated in the secondary reactor.

PXRD and Rietveld Refinements

α-Fe_2O_3 was synthesized at temperatures of 250°C and above. Diffraction patterns are shown in Figure S2. Figure S3 shows the hematite crystal size for different temperatures. Parameters from the Rietveld refinements are listed below. SiO_2 is amorphous, and all cell parameters are of the metal oxide.

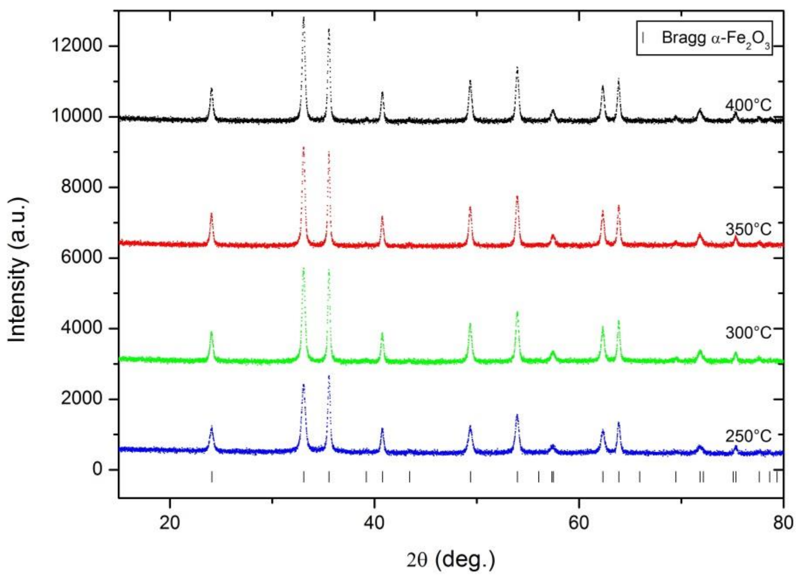

Figure S2: Diffraction patterns for α-Fe_2O_3 synthesized at different temperatures.

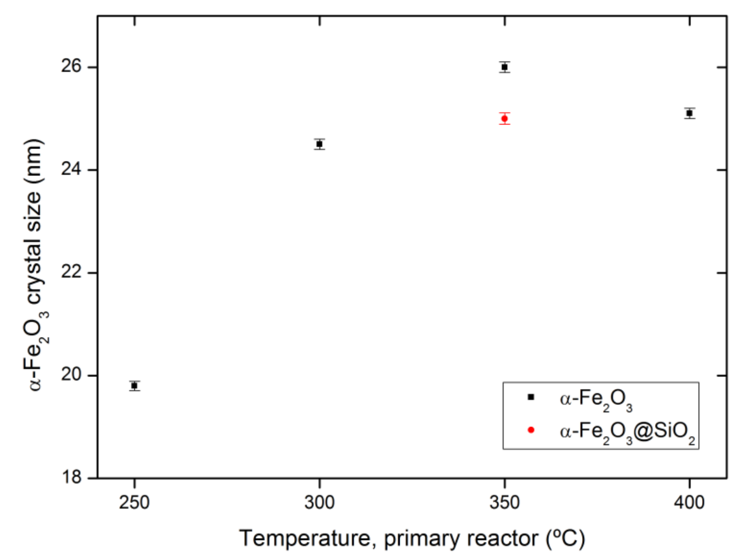

Figure S3: Calculated Fe_2O_3 crystal sizes. The deposition of a silica shell has no significant effect on the core crystal size. The effect of increased reaction rates at higher temperatures is offset by the decrease in residence time caused by the solvent expansion in the supercritical region.

Table S1: Parameters from Rietveld refinements.

α-Fe_2O_3, 250°C		α-Fe_2O_3, 300°C	
$a = b$ (Å)	5.0450(2)	a (Å)	5.0448(1)
c (Å)	13.786(6)	c (Å)	13.7774(4)
$x = y$ (Fe1)	0	$x = y$ (Fe1)	0
z (Fe1)	0.3525(1)	z (Fe1)	0.3532(1)
x (O1)	0.315(2)	x (O1)	0.314(2)
y (O1)	0	y (O1)	0
z (O1)	0.25	z (O1)	0.25
B_{iso} (Fe1) / Å^2	0.25	B_{iso} (Fe1) / Å^2	0.25
B_{iso} (O1) / Å^2	0.5	B_{iso} (O1) / Å^2	0.5
X	0	X	0
Y	0.284(1)	Y	0.2295(9)
Size (nm)	19.8(1)	Size (nm)	24.5(1)
R_{Bragg}	8.16	R_{Bragg}	6.48
R_F	7.48	R_F	5.37

α-Fe_2O_3, 350°C		α-Fe_2O_3, 400°C	
$a = b$ (Å)	5.0446(1)	$a = b$ (Å)	5.0451(1)
c (Å)	13.7774(4)	c (Å)	13.7779(4)
$x = y$ (Fe1)	0	$x = y$ (Fe1)	0
z (Fe1)	0.3532(1)	z (Fe1)	0.3533(1)
x (O1)	0.316(2)	x (O1)	0.315(2)
y (O1)	0	y (O1)	0
z (O1)	0.25	z (O1)	0.25
B_{iso} (Fe1) / Å^2	0.25	B_{iso} (Fe1) / Å^2	0.25
B_{iso} (O1) / Å^2	0.5	B_{iso} (O1) / Å^2	0.5
X	0	X	0
Y	0.2158(9)	Y	0.2239(9)
Size (nm)	26.0(1)	Size (nm)	25.1(1)
R_{Bragg}	7.71	R_{Bragg}	7.35
R_F	6.08	R_F	6.18

α-Fe_2O_3@SiO_2	
a = *b* (Å)	5.0452(1)
c (Å)	13.7793(4)
x = *y* (Fe1)	0
z (Fe1)	0.3528(1)
x (O1)	0.3122(2)
y (O1)	0
z (O1)	0.25
B_{iso} (Fe1) / Å^2	0.25
B_{iso} (O1) / Å^2	0.5
X	0
Y	0.225(1)
Size (nm)	25.0(1)
R_{Bragg}	5.95
R_F	4.73

γ-Fe_2O_3		γ-Fe_2O_3@SiO_2	
a = *b* = *c* (Å)	8.3850(1)	*a* = *b* = *c* (Å)	8.3893(1)
x = *y* = *z* (Fe1)	1/8	*x* = *y* = *z* (Fe1)	1/8
x = *y* = *z* (Fe2)	1/2	*x* (Fe2)	1/2
x = *y* = *z* (O1)	0.2548(4)	*x* (O1)	0.2547(4)
B_{iso} (Fe1) / Å^2	0.25	B_{iso} (Fe1) / Å^2	0.25
B_{iso} (Fe2) / Å^2	0.25	B_{iso} (Fe2) / Å^2	0.25
B_{iso} (O1) / Å^2	0.5	B_{iso} (O1) / Å^2	0. 5
X	0	X	0
Y	0.299(1)	Y	0.302(2)
Size (nm)	18.81(9)	Size (nm)	18.6(1)
R_{Bragg}	2.41	R_{Bragg}	2.85
R_F	1.81	R_F	2.31

Anatase TiO_2		$TiO_2@SiO_2$	
a = *b* (Å)	3.7929(1)	*a* = *b* (Å)	3.7924(1)
c (Å)	9.5038(4)	*c* (Å)	9.4956(4)
x (Ti1)	0	*x* (Ti1)	0
y (Ti1)	1/4	*y* (Ti1)	1/4
z (Ti1)	3/8	*z* (Ti1)	3/8
x (O1)	0	*x* (O1)	0
y (O1)	1/4	*y* (O1)	1/4
z (O1)	0.1672(2)	*z* (O1)	0.1684(2)
B_{iso} (Ti1) / Å^2	0.125	B_{iso} (Ti1) / Å^2	0.125
B_{iso} (O1) / Å^2	0.5	B_{iso} (O1) / Å^2	0.5
X	0	X	0
Y	0.773(3)	Y	0.864(3)
Size (nm)	7.26(3)	Size (nm)	6.51(3)
R_{Bragg}	2.96	R_{Bragg}	1.72
R_F	1.18	R_F	0.758

STEM analyses

α-Fe_2O_3 nanoparticles without SiO_2

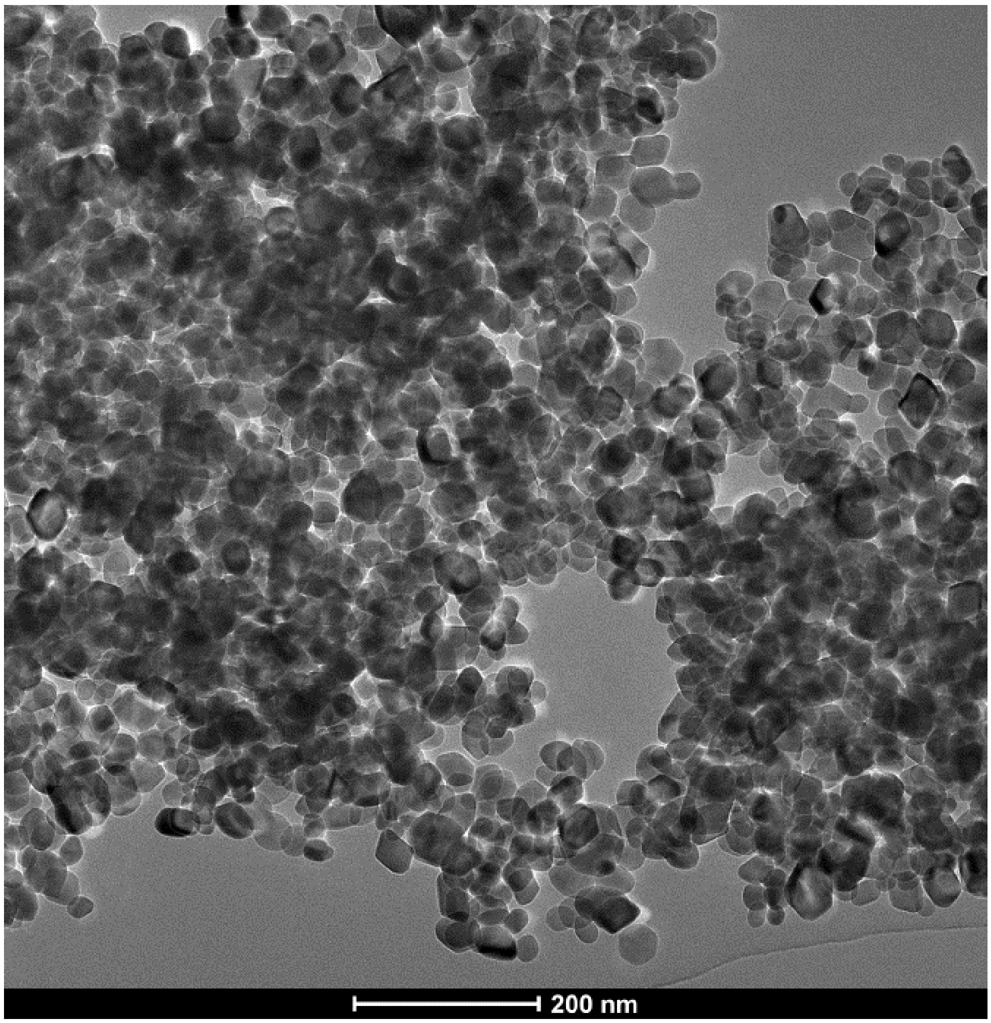

Figure S4: TEM of α-Fe_2O_3. Hematite forms nanoparticles around 20-30 nm of narrow size distribution. Scale bar is 200 nm

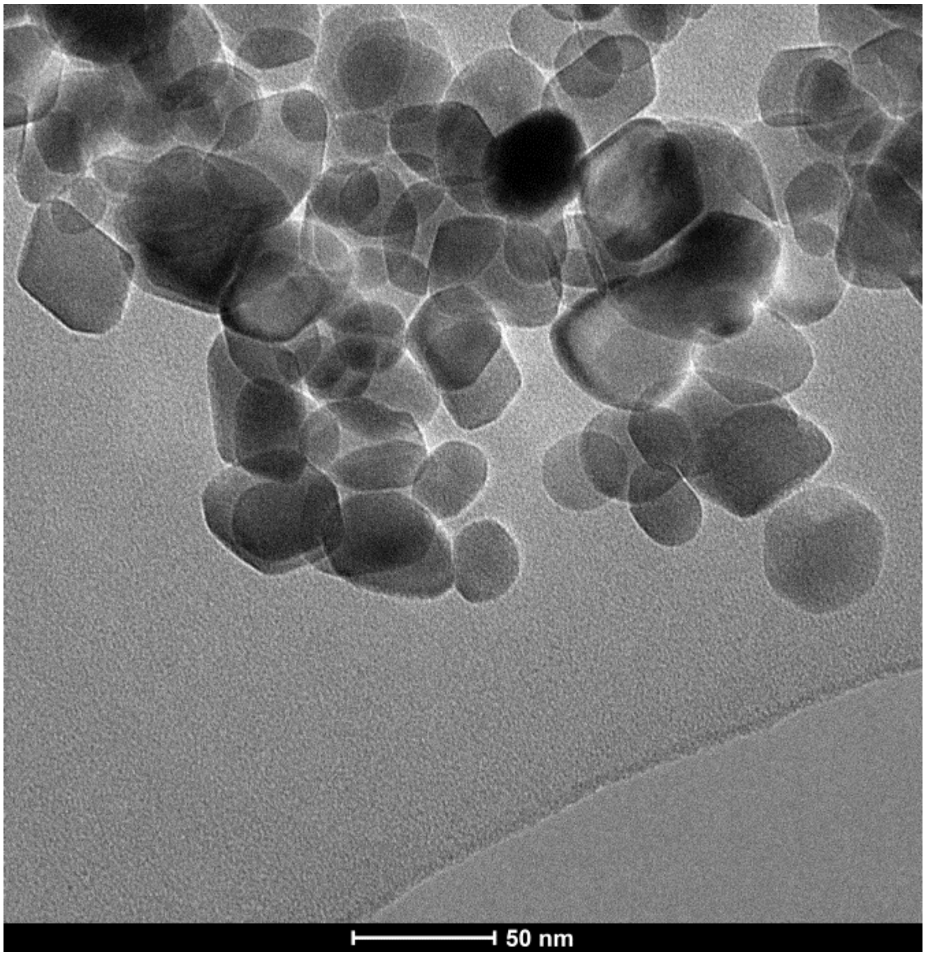

Figure S5: TEM of α-Fe_2O_3. Scale bar is 50 nm

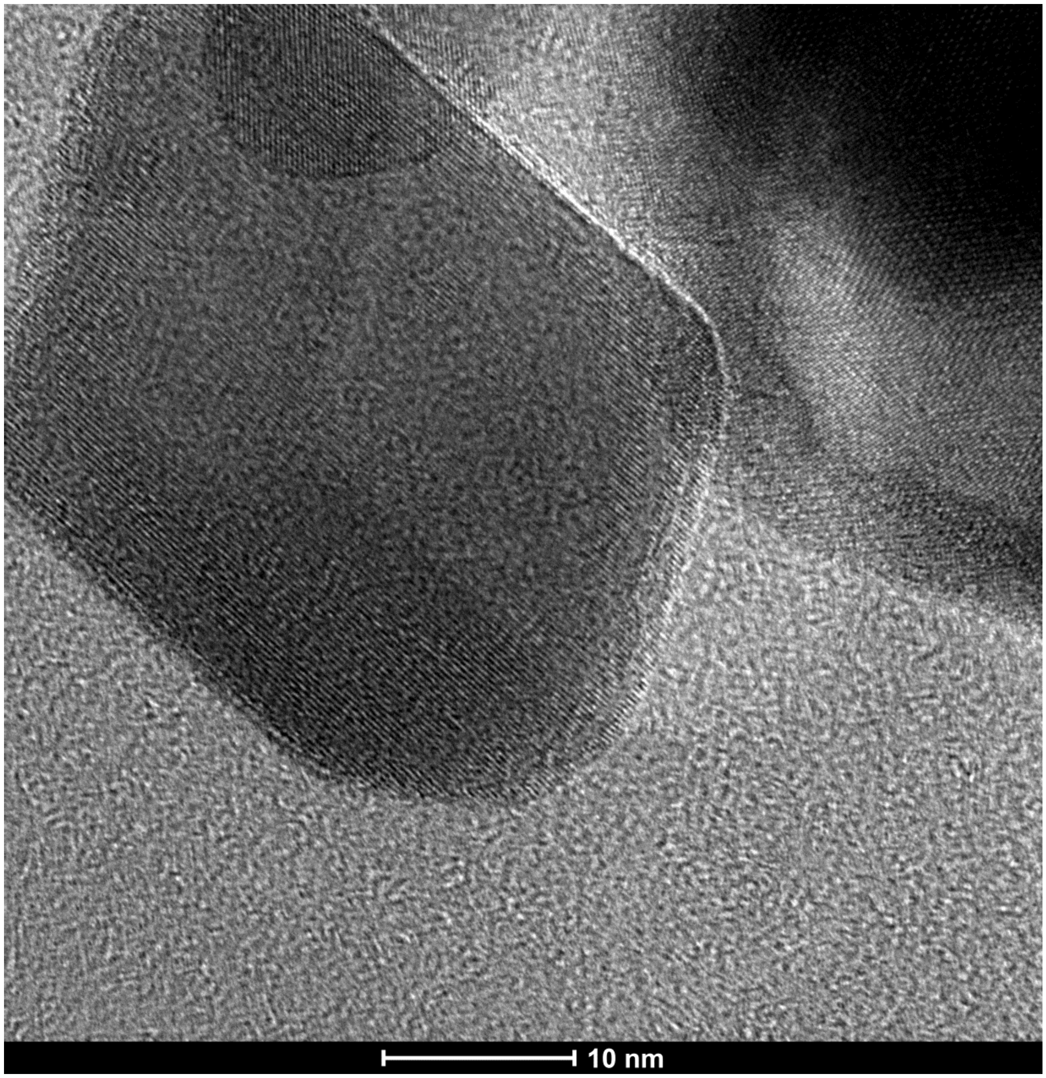

Figure S6: HR-TEM image of hematite at high magnification. Crystalline planes can be seen. Scale bar 10 nm

α-Fe_2O_3@SiO_2 nanocomposites

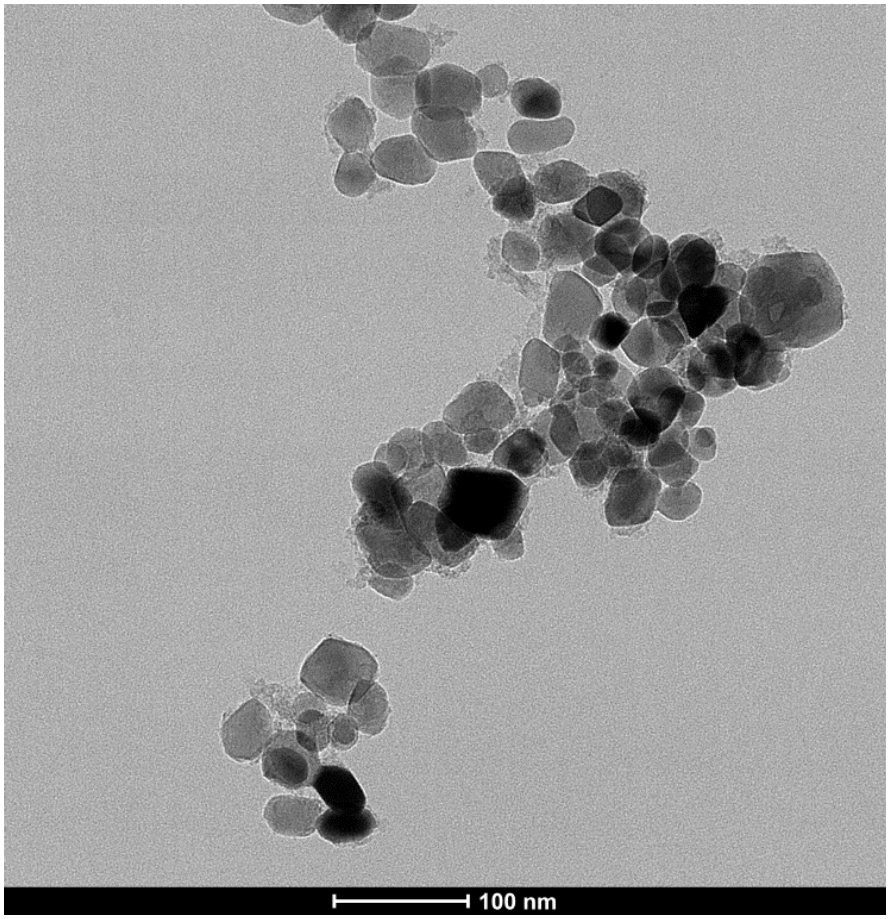

Figure S7: TEM image of α-Fe_2O_3@SiO_2. The size distribution of core particles is in agreement with that of the uncoated hematite nanoparticles.

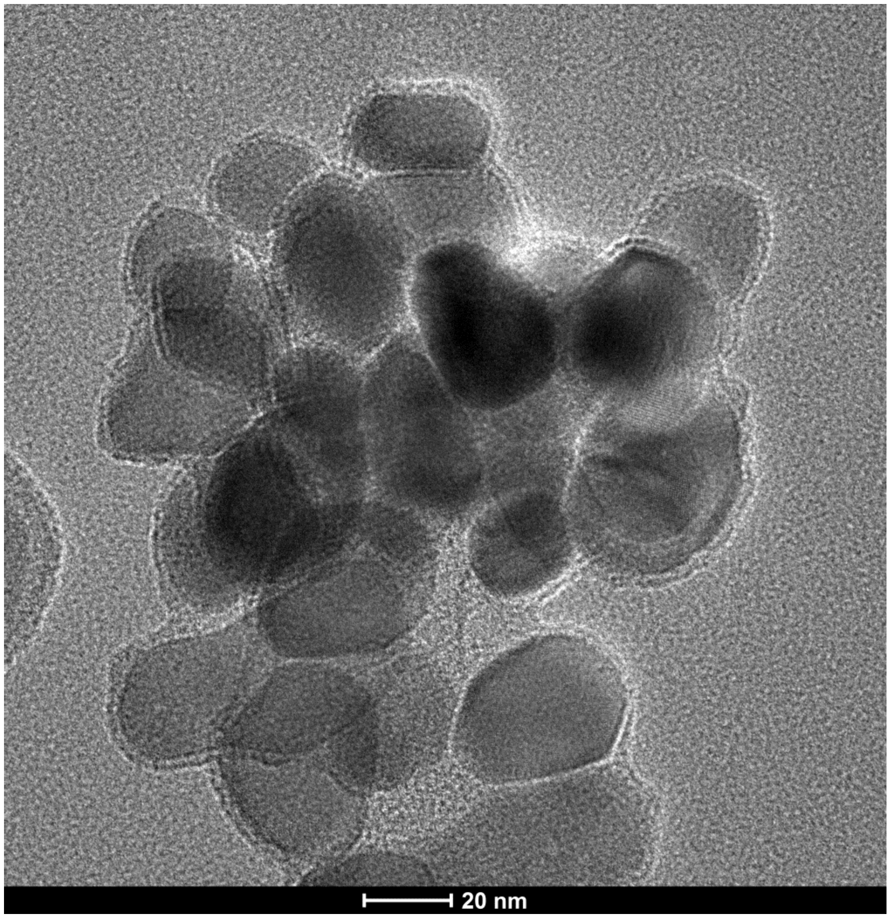

Figure S8: TEM of α-Fe_2O_3@SiO_2. A thin amorphous silica shell surrounds the hematite nanoparticles

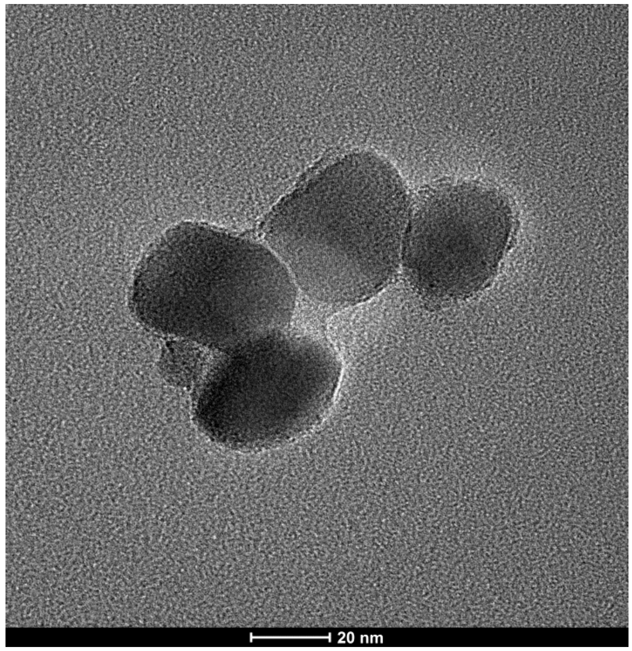

Figure S9: TEM of α-Fe_2O_3@SiO_2. The silica shell is likely connected to neighboring composites.

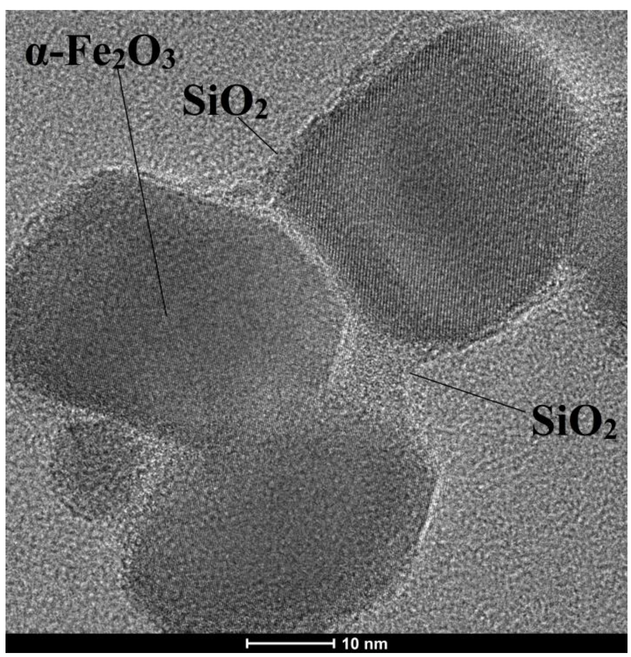

Figure S10: HR-TEM of α-Fe_2O_3@SiO_2. An amorphous material of low scattering power surrounds the heavier crystalline core.

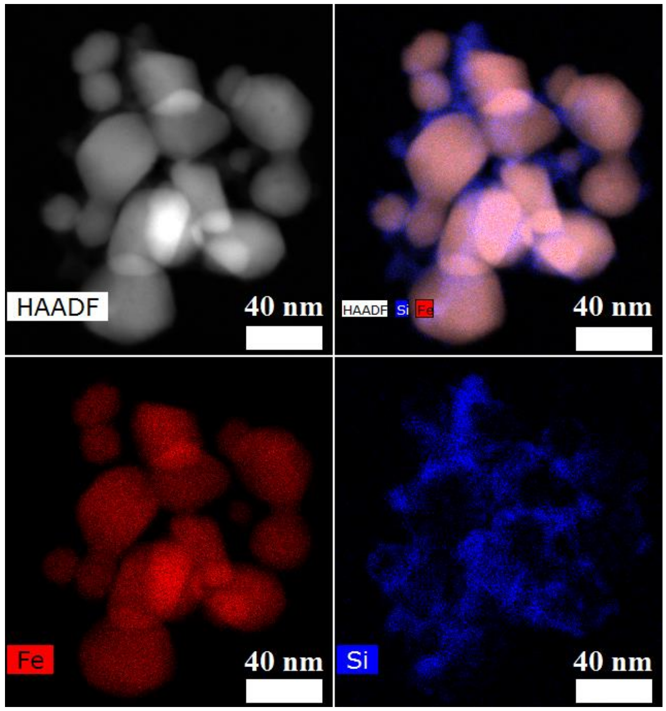

Figure S11: HAADF and EDX images of α-Fe_2O_3@SiO_2 nanocomposites

γ-Fe_2O_3 nanoparticles without SiO_2

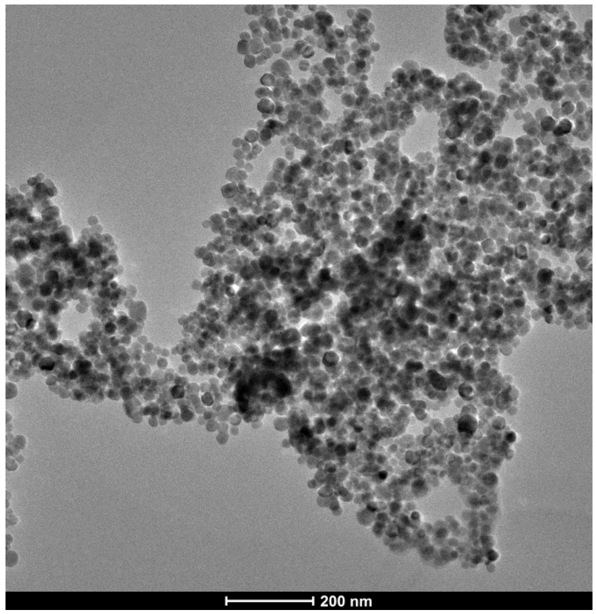

Figure S12: TEM of γ-Fe_2O_3 nanoparticles synthesizes in the primary reactor stage. The nanoparticles have a narrow size distribution. Scale bar is 200 nm

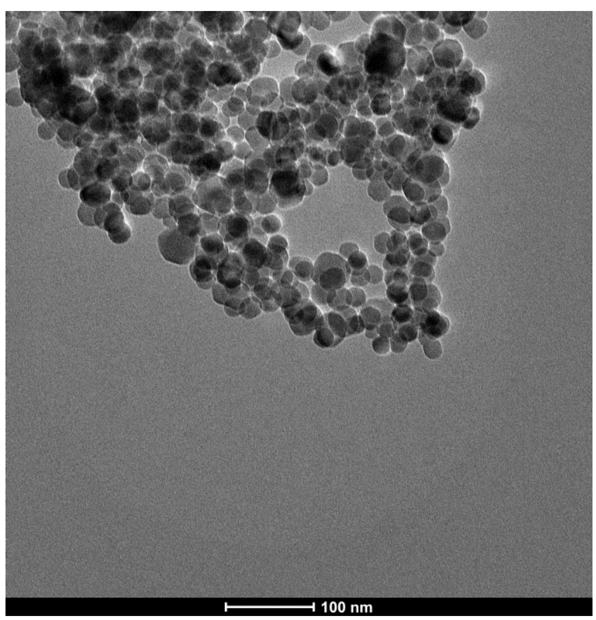

Figure S13: TEM of γ-Fe_2O_3 nanoparticles. Particle size is around 20-30 nm. Scale bar is 100 nm

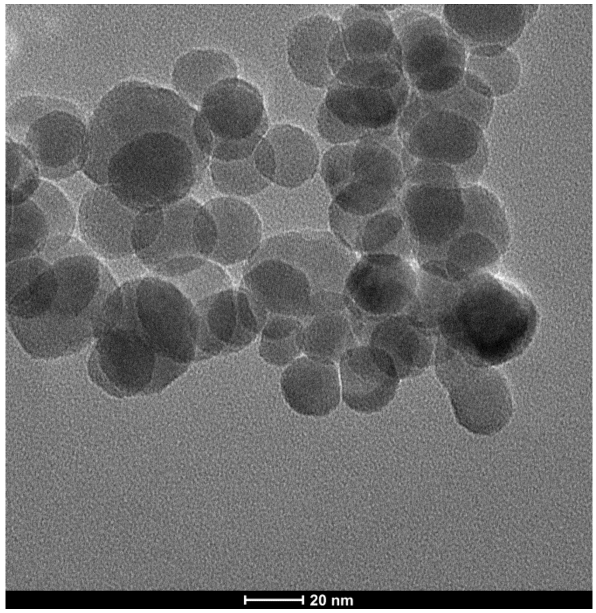

Figure S14: TEM of γ-Fe_2O_3 nanoparticles. The particles are isotropic in shape. Scale bar is 20 nm

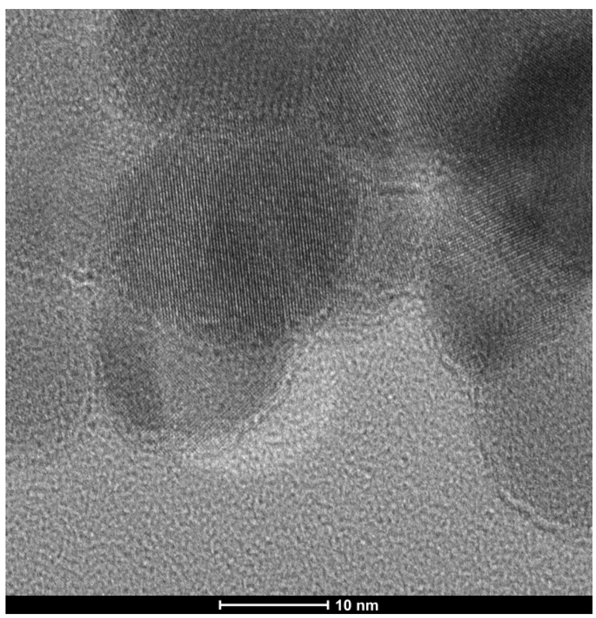

Figure S15: HR-TEM of γ-Fe_2O_3 nanoparticles. Visible lattice planes indicate high crystallinity.

γ-Fe_2O_3@SiO_2 nanocomposites

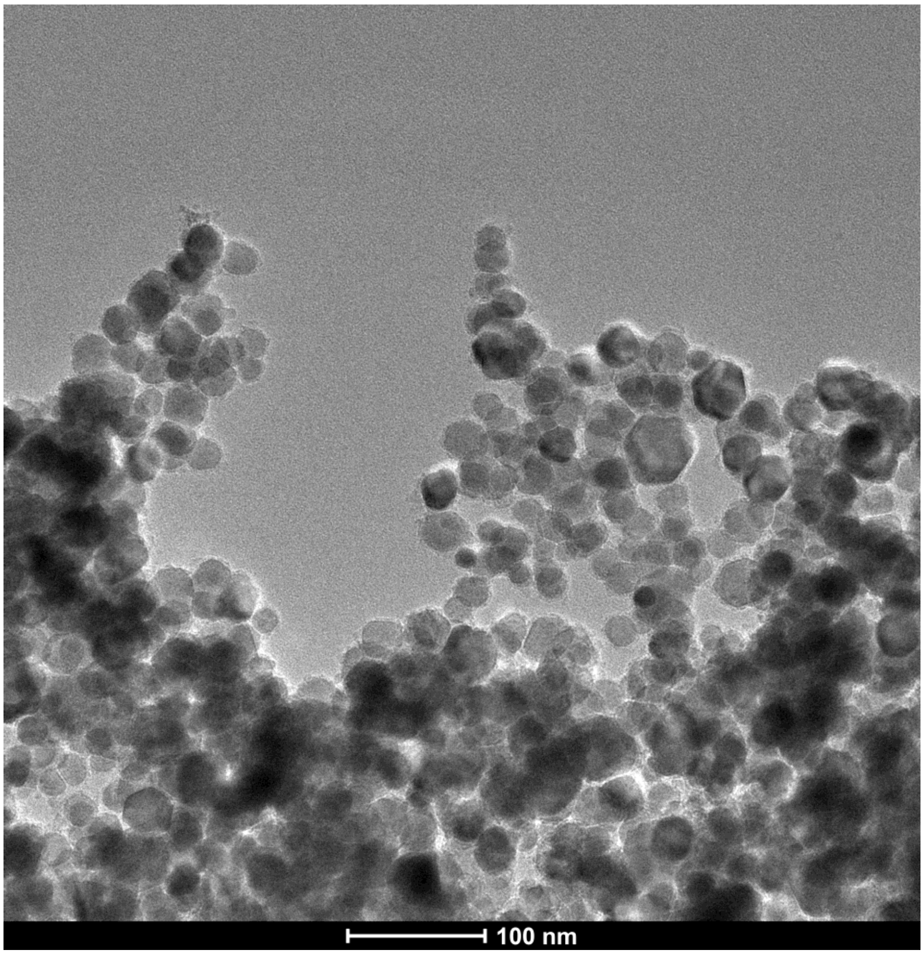

Figure S16: TEM of γ-Fe_2O_3@SiO_2. Composites are of narrow size distribution. Particle sizes are similar to the uncoated sample.

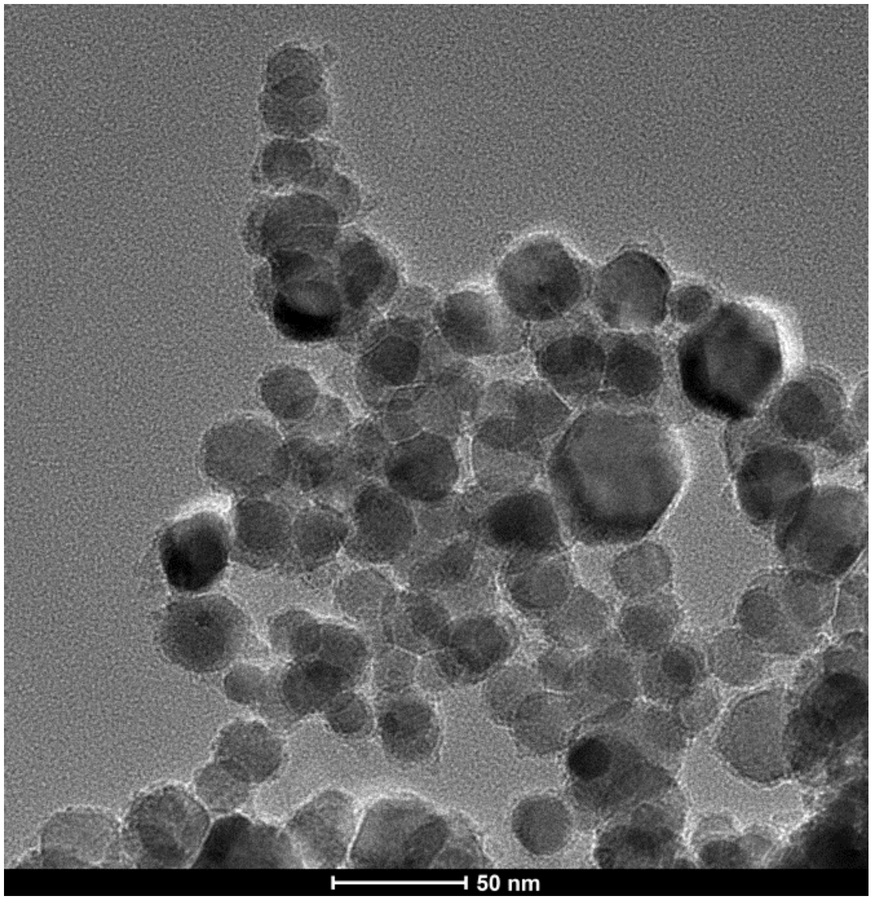

Figure S17: TEM image of γ-Fe_2O_3@SiO_2.

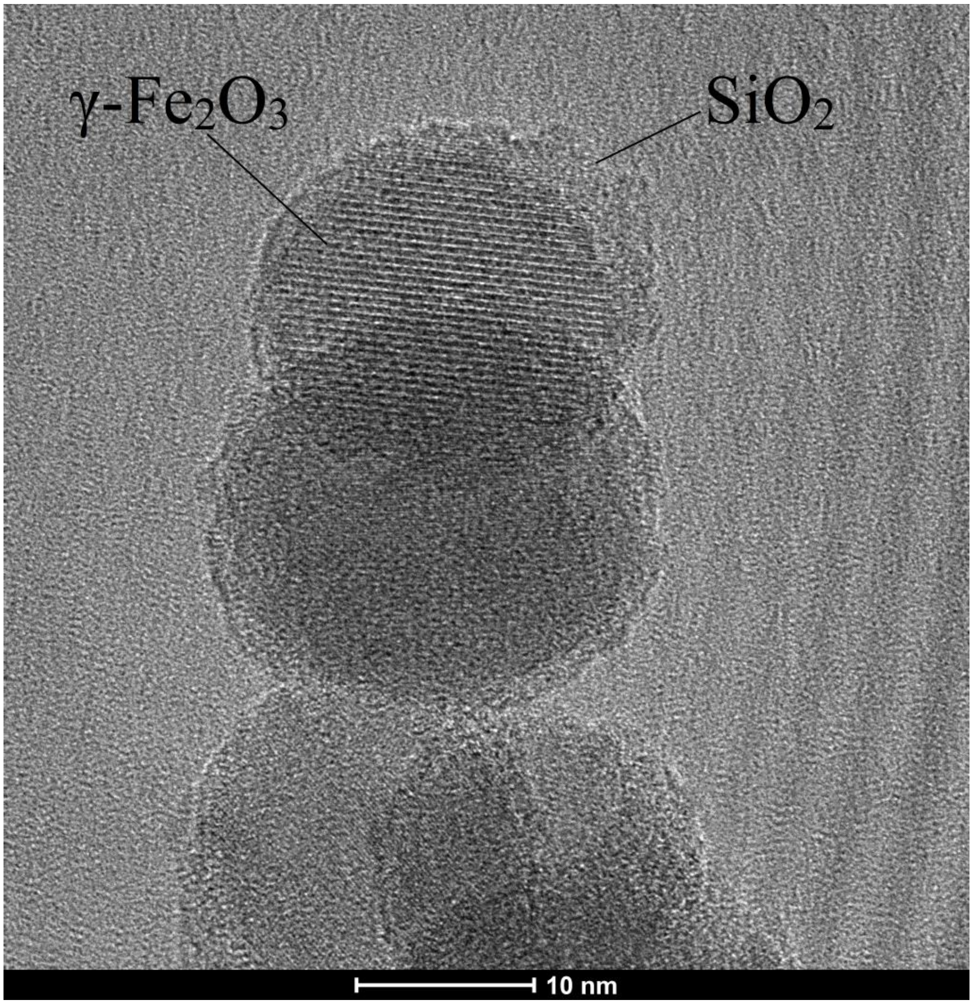

Figure S18: HR-TEM image of γ-Fe_2O_3@SiO_2.

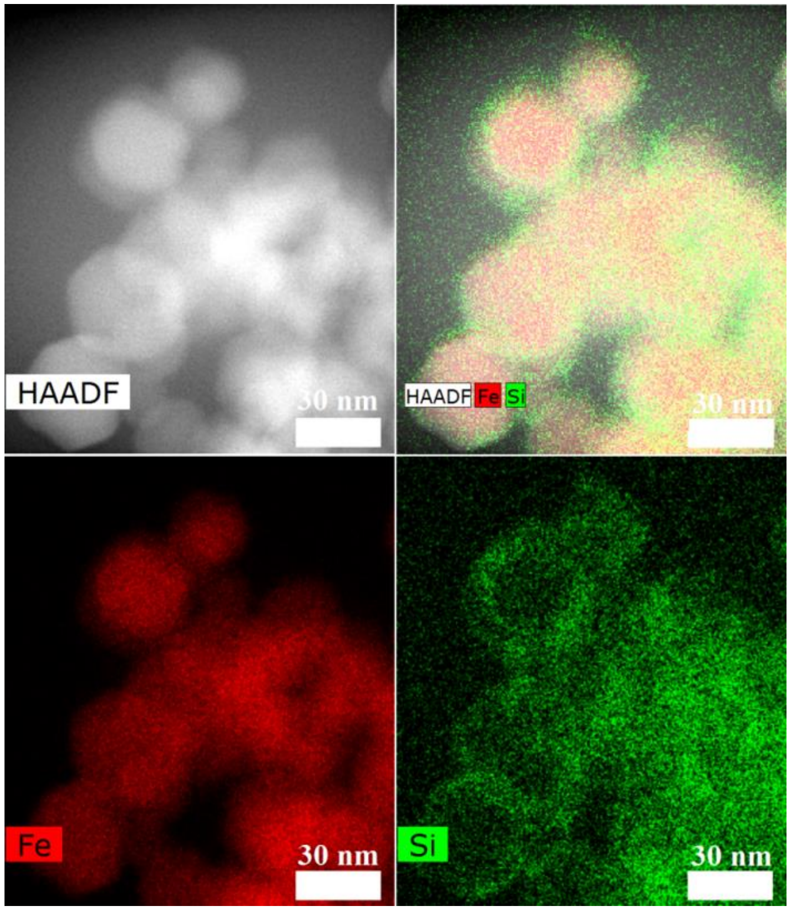

Figure S19: HAADF and EDX images of γ-Fe_2O_3@SiO_2 nanocomposites

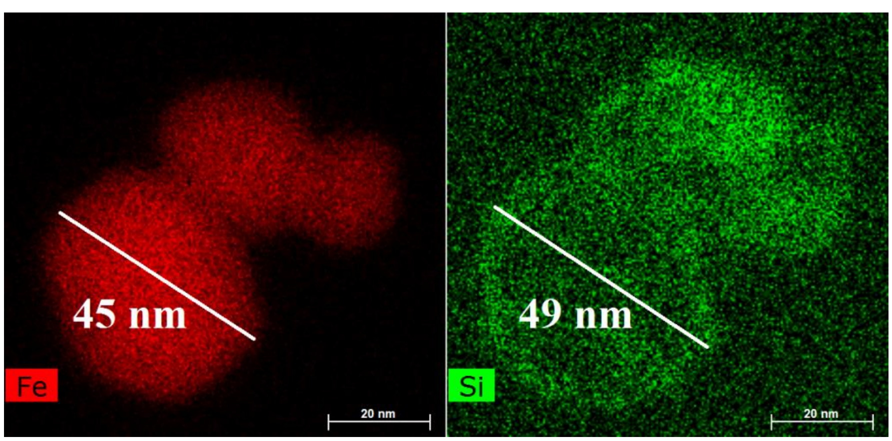

Figure S20: The maghemite core particle is 4 nm smaller than the silica shell and thus the shell layer is 2 nm.

TiO_2 nanoparticles without SiO_2

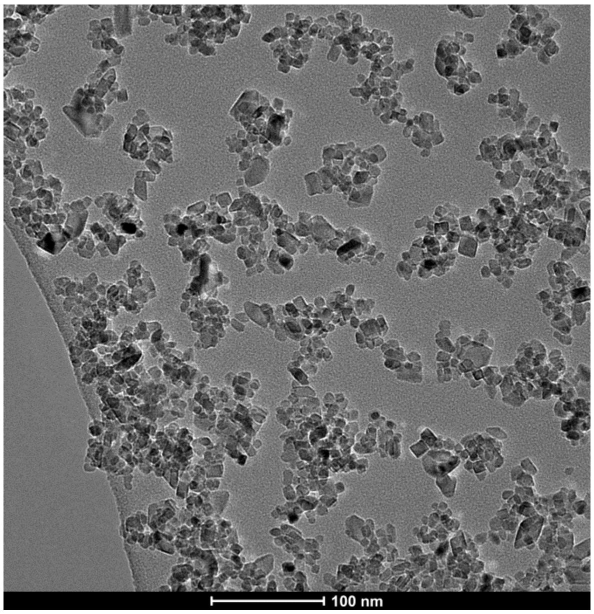

Figure S21: TEM of anatase nanoparticles. Scale bar is 100 nm

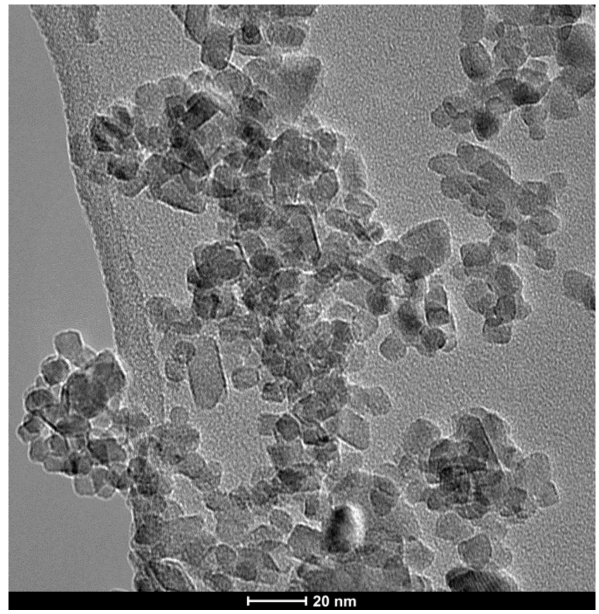

Figure S22: TEM of anatase nanoparticles. Scale bar is 20 nm. The nanoparticles are mainly isotropic in shape but a few are slightly elongated.

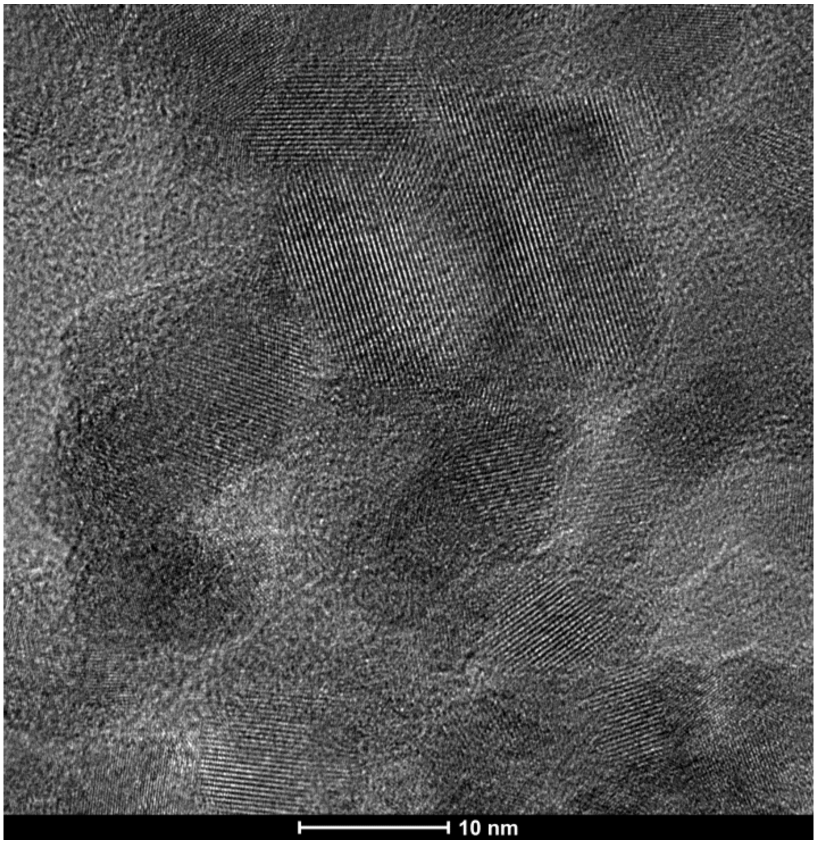

Figure S23: HR-TEM of titania nanoparticles. Particle size are around 10 nm

$TiO_2@SiO_2$ nanocomposites

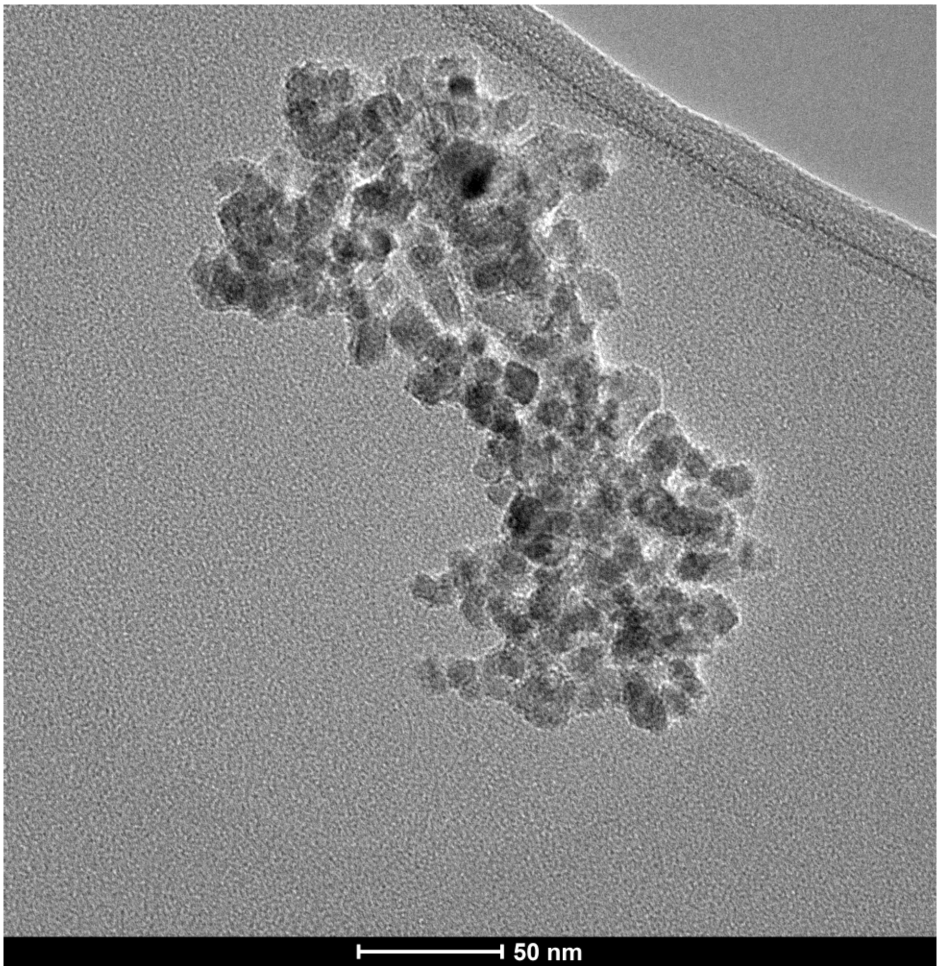

Figure S24: TEM of $TiO_2@SiO_2$. Particle shape is isotropic and sizes are comparable to uncoated titania

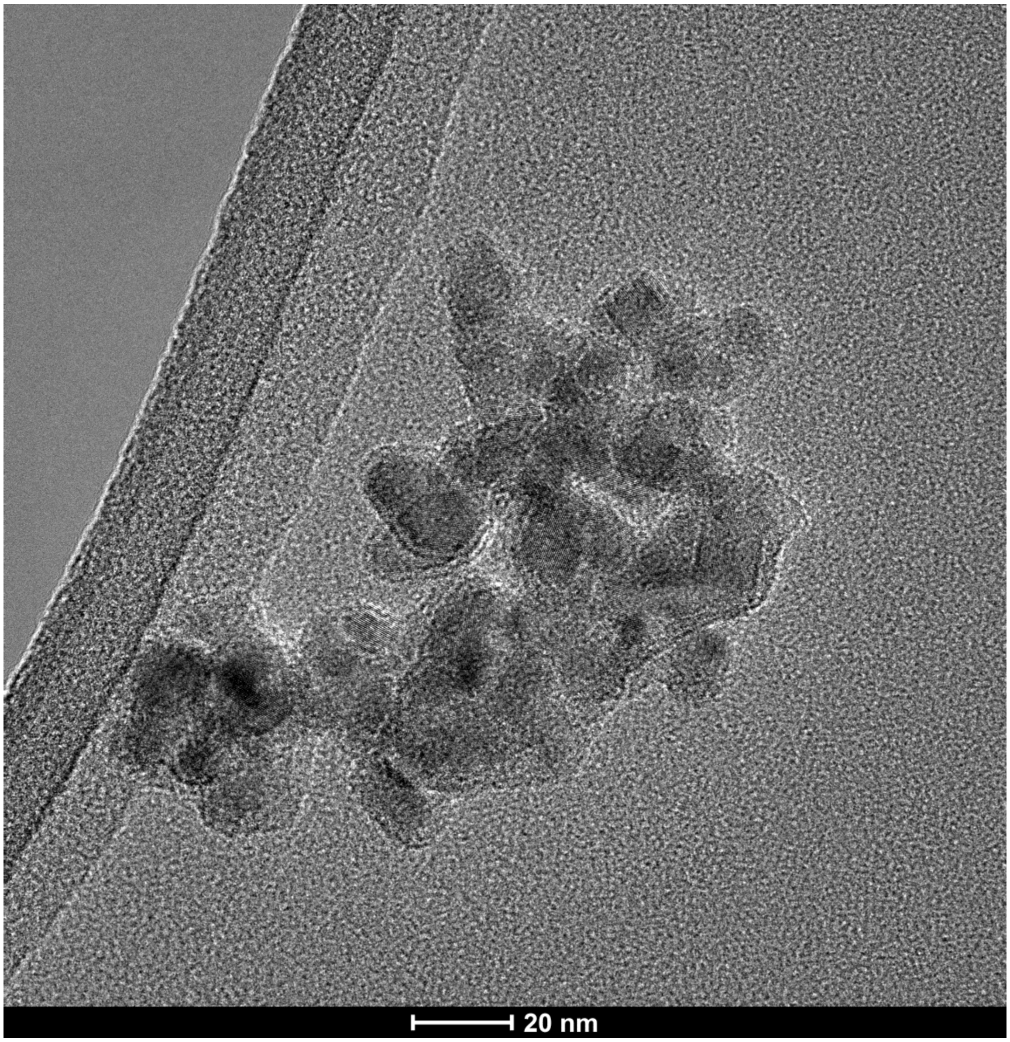

Figure S25: TEM of TiO_2@SiO_2.

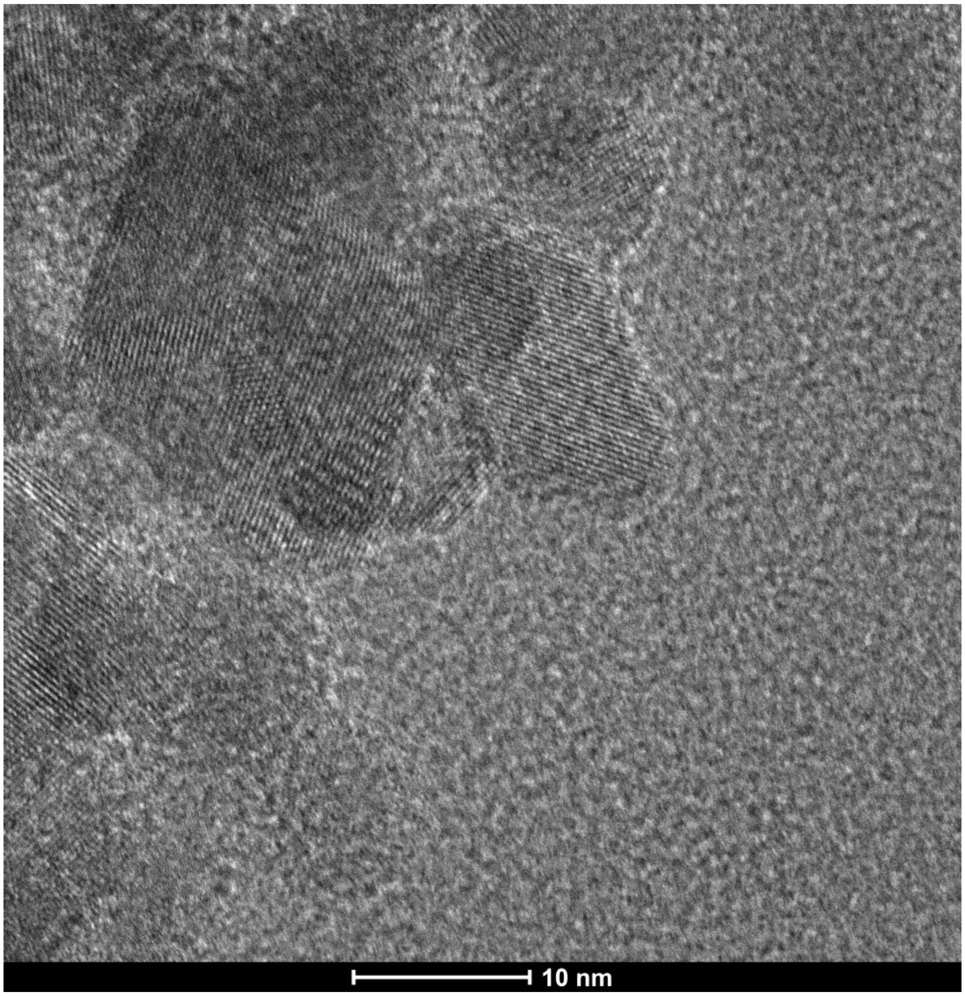

Figure S26: HR-TEM of $TiO_2@SiO_2$. The lower scattering power and particle size of titania compared to the iron oxides makes it more difficult to observe the thin silica layers by TEM and HR-TEM.

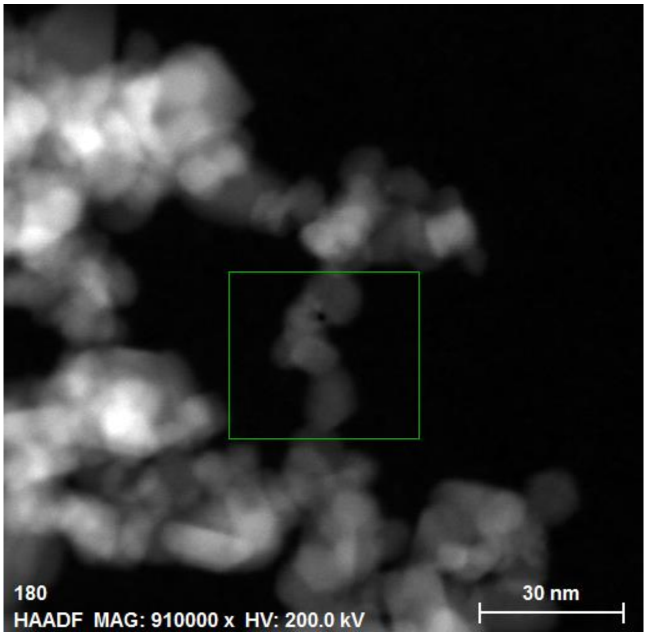

Figure S27: $TiO_2@SiO_2$, HAADF image

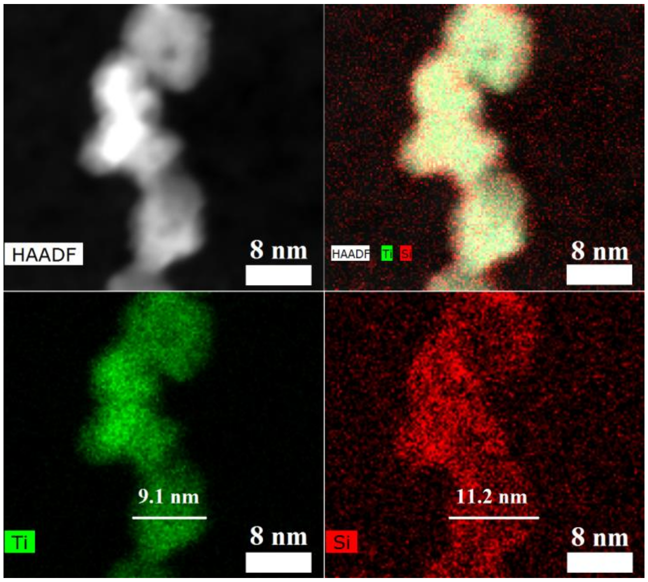

Figure S28: Close up of Figure S27. HAADF and EDX images are displayed along with their superposition. The silica shell layer is 1-2 nm.

FTIR

The Si-O-Si bands of all three composites are clearly defined near 1100/cm.

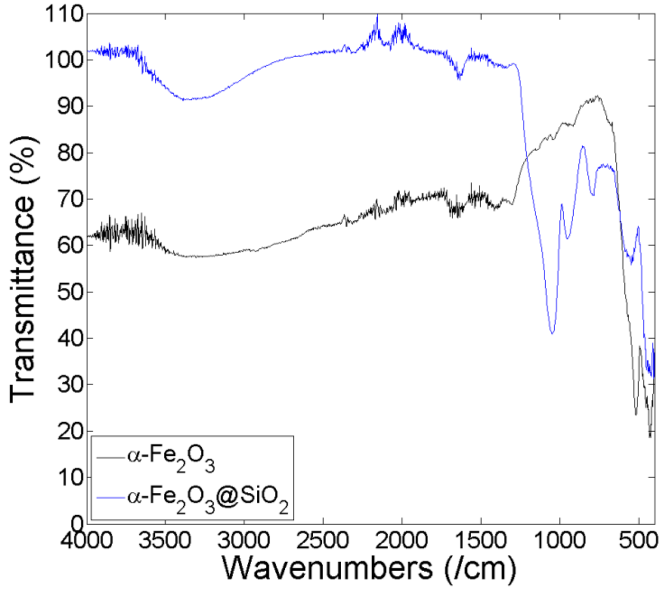

Figure S29: FTIR spectra of α-Fe_2O_3 and α-Fe_2O_3@SiO_2. The dark red hematite powder becomes a lighter red when coated by silica which increases transmittance for the composite

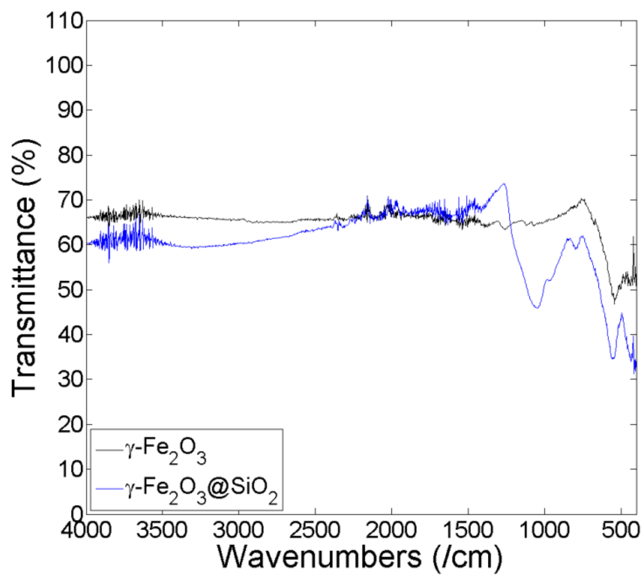

Figure S30: FTIR spectra of γ-Fe_2O_3 and γ-Fe_2O_3@SiO_2. Transmittance only around 60% due to blackness of the powder

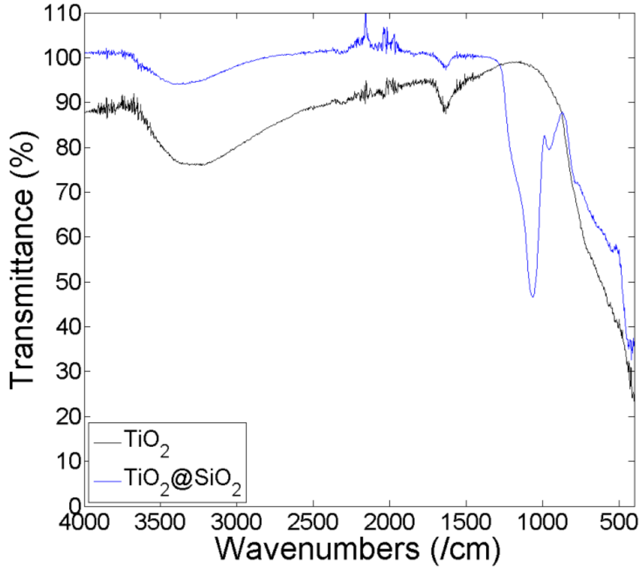

Figure S31: FTIR spectra of TiO_2 and TiO_2@SiO_2. Both powders are white.