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#### **Supplementary Information**

#### Morphology-dependent reactivity of cobalt oxide nanoparticles in N<sub>2</sub>O decomposition

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#### Raman

Additional Raman spectroscopic results.



Fig. S1 Raman spectra obtained with a 785 nm laser.

#### Desorption during work function in-situ measurements

A quadrupole mass spectrometer (RGA 200, SRS) mounted onto the vacuum chamber was used to monitor the gas phase composition during thermal conditioning of the samples P4, H4 and S4. The gases followed were:  $CO_2$  (m/z = 44), N<sub>2</sub> (m/z = 28), O<sub>2</sub> (m/z = 32) and H<sub>2</sub>O (m/z = 18). Similar desorption patterns were obtained for all the samples. A representative graph is presented in the Fig. Desorption for the H4 sample. Only signals from  $CO_2$  and H<sub>2</sub>O were recorded during the heat treatment process.

**Fig. S2** Desorption of the  $CO_2$  and  $H_2O$  during thermal conditioning of the H4 sample prior the *in-situ* work function measurements.



### TEM

Additional TEM images of the investigated samples.

Fig. S3 TEM images taken at lower magnifications.



#### Nanoparticle tracking analysis, NTA

Nanoparticle tracking and analysis was carried out on a NanoSight LM10-HS (NanoSight Ltd., UK, 405 nm laser beam), using a version of NTA 3.0 software (Malvern Instruments Ltd). Three videos, each 60 s long, were recorded and analyzed in batch mode to ensure better statistics. Powder samples were thoroughly ground in an agate mortar prior the dispersion in water. Next, a small amount of powder was put in a glass beaker with 100 ml of water and sonicated for 5 min. Despite grinding, some of the material underwent sedimentation. The transparent brown liquid from the middle of its volume was further diluted by transferring 2-4 ml of suspension into 50 ml of water. Each time before recording a video the suspension was sonicated again, for 1 min.

The combined reports of the investigated materials are presented below (Fig. S4 - S8)

### Fig. S4 Combined experiment P4 report



Combined experiment S6

## Fig. S5 Combined experiment P6 report



Averaged FTLA Concentration / Size for Experiment: Combined experiment S6 Error bars indicate + / -1 standard error of the mean

500 60 Size (nm)

700 800 900

1000

Included Files		Results		
Capture 2015-06-19 15-09-40		Stats: Merced Data		
Capture 2015-06-19 15-14-39		Mean:	186.4 nm	
Capture 2015-06-19 15-	18-05	Mode:	137.0 nm	
		SD:	72.4 nm	
Details		D10:	110.4 nm	
		D50:	168.1 nm	
NTA Version:	Unknown	D90:	278.3 nm	
Script Used:				
Time Captured:	Time Captured:		Stats: Mean +/- Standard Error	
Operator:		Mean:	184.4 +/- 4.7 nm	
Pre-treatment:		Mode:	138.3 +/- 3.2 nm	
Sample Name:		SD:	72.8 +/- 1.8 nm	
Diluent:		D10:	109.3 +/- 3.3 nm	
Remarks:	Created from combined experiments: Capture	D50:	165.4 +/- 8.5 nm	
	2015-06-19 15-09-26.nano, Capture 2015-06-19	D90:	279.9 +/- 6.3 nm	
	15-14-28.nano, Capture 2015-06-19	Concentration:	6.04e+008 +/- 1.33e+008 particles/ml	
			30.7 +/- 6.8 particles/frame	
Capture Settings			40.2 +/- 8.6 centres/frame	
Camera Type:	sCMOS			
Camera Level:	6 - 8			
Slider Shutter:	86 - 317			
Slider Gain:	15			
FPS	25.0			
Number of Frames:	1499			
Temperature:	24.0 - 24.4 °C			
Viscosity:	(Water) 0.901 - 0.909 cP			
Dilution factor:	Dilution not recorded			
Analysis Settings				
Detect Threshold:	2			
Blur Size:	Auto			
Max Jump Distance:	Auto: 10.2 - 12.0 pix			

## Fig. S6 Combined experiment H4 report



		D50:	167.8 nm	
NTA Version:	Unknown	D90:	290.9 nm	
Script Used:				
Time Captured:		Stats: Mean +/- Standard Error		
Operator:		Mean:	189.0 +/- 7.8 nm	
Pre-treatment:		Mode:	160.0 +/- 4.7 nm	
Sample Name:		SD:	76.8 +/- 2.0 nm	
Diluent:		D10:	115.5 +/- 1.1 nm	
Remarks:	Created from combined experiments: Capture	D50:	169.6 +/- 7.7 nm	
	2015-06-19 14-24-34.nano, Capture 2015-06-19	D90:	275.9 +/- 25.9 nm	
	14-27-52.nano, Capture 2015-06-19	Concentration:	4.48e+008 +/- 1.59e+007 particles/ml	
			22.7 +/- 0.8 particles/frame	
Capture Settings			29.9 +/- 2.2 centres/frame	
Camera Type:	sCMOS			
Camera Level:	8			
Slider Shutter:	317			
Slider Gain:	15			
FPS	25.0			
Number of Frames:	1499			
Temperature:	23.6 - 23.9 °C			
Viscosity:	(Water) 0.911 - 0.918 cP			
Dilution factor:	Dilution not recorded			
Analysis Settings				
Detect Threshold:	2			
Blur Size:	Auto			
Max Jump Distance:	Auto: 10.1 - 11.5 pix			
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### Fig. S7 Combined experiment H6 report



FTLA Concentration / Size graph for Experiment: Combined experiment\_H6



Averaged FTLA Concentration / Size for Experiment: Combined experiment\_H6 Error bars indicate + / -1 standard error of the mean

Included Files		Results	
Capture 2016-01-15 15-11-55		State: Margard Data	
Capture 2016-01-15 15	Capture 2016-01-15 15-11-55		258.7 nm
Capture 2016-01-15 15	-24-19	Mode:	244.3 nm
Capitile 2010-01-13 13-24-18		SD:	98.1 nm
Details		D10:	132.2 nm
		D50:	251.5 nm
NTA Version:	Unknown	D90:	383.4 nm
Script Used:			
Time Captured:		Stats: Mean +/- Standard Error	
Operator:		Mean:	260.9 +/- 10.8 nm
Pre-treatment:		Mode:	220.9 +/- 17.3 nm
Sample Name:		SD:	93.0 +/- 7.0 nm
Diluent:		D10:	138.7 +/- 14.7 nm
Remarks:	Created from combined experiments: Capture	D50:	254.4 +/- 8.8 nm
	2016-01-15 15-11-47.nano, Capture 2016-01-15	D90:	378.7 +/- 13.3 nm
	15-17-04.nano, Capture 2016-01-15	Concentration:	1.14e+009 +/- 2.88e+008 particles/ml
			57.9 +/- 14.6 particles/frame
Capture Settings			89.1 +/- 26.5 centres/frame
Camera Type:	sCMOS		
Camera Level:	7		
Slider Shutter:	165		
Slider Gain:	15		
FPS	25.0		
Number of Frames:	1499		
Temperature:	22.3 - 22.8 °C		
Viscosity:	(Water) 0.935 - 0.946 cP		
Dilution factor:	Dilution not recorded		
Analysis Settings			
Detect Threshold:	5		
Blur Size:	Auto		
Max Jump Distance:	Auto: 8.2 - 9.4 pix		

### Fig. S8 Combined experiment N4 report

