Supporting Information

X-ray Photoelectron Spectroscopy of Metal Oxide Nanoparticles: Oxidation State, Functional Group Content and Impurities

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Table S1. Atomic composition data obtained from high resolution scans of NiO NPs. The bold number is the average of 3 measurements on the sample with the number below the standard deviation. Blank entries indicate no peak was observed above the background. A group of samples of the same size from the same supplier are indicated by the shaded region.

	Ni 2p	O 1s	C 1s	N 1s	Si 2p	Ni/O	C/Ni
Ni-01 **Skyspring, bare**	**37.4** 0.9	**50.3** 0.4	**12.2** 0.6			**0.74** 0.02	**0.33** 0.02
Ni-02 **mkNano, bare**	**46.7** 1.1	**43.8** 0.8	**9.5** 0.3			**1.07** 0.04	**0.20** 0.01
Ni-03 **Sigma, bare**	**49.3** 0.7	**42.6** 0.7	**8.0** 0.1	**0.10** 0.05		**1.16** 0.04	**0.16** 0.003
Ni-04 **USRN, bare**	**45.1** 1.5	**42.9** 0.7	**11.8** 0.8	**0.2** 0.1		**1.05** 0.05	**0.26** 0.03
Ni-04-NRC **USRN, PVP**	**27.4** 2.8	**33.3** 1.7	**35.7** 3.6	**3.7** 0.4		**0.82** 0.07	**1.33** 0.28
Ni-05 **USRN, PVP**	**41.8** 1.3	**42.3** 0.4	**15.0** 1.2	**0.8** 0.1		**0.99** 0.03	**0.36** 0.04
Ni-06 **USRN, SA**	**15.2** 0.4	**24.4** 0.6	**60.4** 0.9			**0.62** 0.02	**3.99** 0.17
Ni-07 **USRN, APTES**	**18.2** 2.0	**36.9** 1.4	**32.5** 1.5	**6.2** 0.2	**6.2** 0.4	**0.49** 0.07	**1.81** 0.27
Ni-08 **USRN, bare**	**42.9** 0.2	**43.0** 0.3	**14.1** 0.4			**1.00** 0.01	**0.33** 0.01

Table S2. Atomic composition data obtained from high resolution scans of Fe_2O_3 NPs. The bold number is the average of 3 measurements on the sample with the number below the standard deviation. Blank entries indicate no peak was observed above the background. A group of samples of the same size from the same supplier are indicated by the shaded region.

	Fe 2p	O 1s	C1s	N 1s	Si 2s	Fe/O	C/Fe
Fe-01 **Sigma, bare**	**36.4** 1.2	**45.4** 1.5	**18.2** 1.2			**0.80** 0.05	**0.50** 0.04
Fe-02 **USRN, bare**	**33.8** 1.1	**45.6** 0.5	**20.6** 0.5			**0.74** 0.03	**0.61** 0.03
Fe-03 **USRN,PVP**	**33.5** 0.4	**44.8** 0.3	**21.3** 0.1	**0.3** 0.1		**0.75** 0.02	**0.64** 0.01
Fe-04 **USRN, NH2**	**29.2** 0.5	**45.0** 0.7	**25.1** 0.8	**0.7** 0.06		**0.65** 0.02	**0.86** 0.04
Fe-05 **USRN, APTES**	**29.3** 1.7	**44.8** 0.8	**21.7** 0.7	**2.3** 0.1	**2.0** 0.1	**0.65** 0.05	**0.74** 0.07
Fe-06 **USRN, SA**	**9.5** 0.2	**30.3** 0.3	**60.2** 0.4			**0.31** 0.004	**6.35** 0.09
Fe-07 **Lanxess**	**18.4** 2.1	**55.6** 0.6	**16.8** 2.5		**9.2** 0.7	**0.33** 0.04	**0.93** 0.24

Table S3. Atomic composition data obtained from high resolution scans of CeO_2 NPs. The bold number is the average of 3 measurements on the sample with the number below the standard deviation. Blank entries indicate no peak was observed above the background. A group of samples of the same size from the same supplier are indicated by the shaded region. For Ce-10 HR scans were only obtained for one area.

	Ce 3d	O 1s	C 1s	N 1s	Si 2s	Ce/O	C/Ce	%Ce+4
Ce-01 **USRN, bare**	**25.5** 2.1	**53.3** 2.8	**21.1** 4.9			**0.48** 0.01	**0.84** 0.25	**80.7** 2.4
Ce-02 **USRN, bare**	**21.6** 0.7	**50.2** 0.8	**28.2** 1.0			**0.43** 0.02	**1.31** 0.08	**79.6** 2.7
Ce-03 **USRN, bare**	**31.6** 0.8	**59.9** 1.4	**8.5** 0.7			**0.53** 0.03	**0.27** 0.01	**71.7** 2.4
Ce-03-NRC **USRN, SA@NRC**	**10.6** 0.6	**33.2** 0.6	**56.2** 1.0			**0.32** 0.02	**5.29** 0.38	**71.9** 1.6
Ce-04 **USRN, PVP**	**29.5** 0.5	**57.5** 0.5	**13.1** 0.3			**0.51** 0.01	**0.44** **0.01**	**73.6** 2.0
Ce-05 **USRN, SA**	**12.3** 0.8	**33.1** 1.7	**54.6** 2.6			**0.37** 0.01	**4.42** 0.44	**77.9** 1.4
Ce-06 **NAM, bare**	**18.4** 0.4	**58.6** 1.1	**23.0** 1.3			**0.31** 0.01	**1.10** 0.05	**41.5** 1.6
Ce-07 **mkNano, bare**	**18.9** 0.7	**48.7** 0.8	**32.4** 1.2			**0.39** 0.01	**1.72** 0.13	**76.9** 0.9
Ce-08 **mkNano, bare**	**29.2** 1.9	**59.1** 0.5	**11.7** 1.4			**0.49** 0.04	**0.40** 0.07	**72.1** 4.4
Ce-09 **USRN, APTES**	**12.3** 0.7	**43.4** 1.2	**29.8** 0.9	**5.9** 0.4	**8.6** 0.5	**0.28** 0.01	**2.42** 0.21	**62.3** 2.4
Ce-10 **USRN, PVP**	**23.0**	**51.0**	**25.4**	**0.6**		**0.45**	**1.10**	

Table S4. Atomic composition data obtained from high resolution scans of Mn_2O_3 NPs. The bold number is the average of 3 measurements on the sample with the number below the standard deviation. Blank entries indicate no peak was observed above the background. A group of samples of the same size from the same supplier are indicated by the shaded region.

	Mn 2p	O 1s	C 1s	Mn/O	C/Mn
Mn-01 USRN, bare	**18.8** 0.6	**38.9** 0.6	**42.3** 1.2	**0.48** 0.01	**2.25** 0.14
Mn-02 USRN, PVP	**17.4** 0.5	**37.2** 0.7	**45.4** 1.1	**0.47** 0.006	**2.62** 0.13
Mn-03 USRN, SA	**12.2** 0.5	**26.1** 0.4	**61.7** 0.9	**0.47** 0.01	**5.05** 0.28
Mn-04 USRN, APTES	**17.5** 0.8	**40.0** 0.8	**42.6** 1.5	**0.44** 0.01	**2.45** 0.20
Mn-05 USRN, bare	**20.0** 1.3	**40.1** 1.6	**39.9** 2.8	**0.50** 0.01	**2.00** 0.26
Mn-06 mKNano, bare	**18.0** 0.4	**38.6** 0.1	**43.4** 0.3	**0.47** 0.01	**2.42** 0.07
Mn-07 Am. Elem., bare	**16.6** 1.7	**37.0** 2.3	**46.4** 4.0	**0.45** 0.02	**2.84** 0.52
Mn-08 Nanografi, bare	**22.9** 1.2	**43.2** 0.7	**33.9** 1.9	**0.53** 0.02	**1.48** 0.16

Table S5. Parameters (peak position and fractional contribution) obtained for the NiO samples by fitting five peaks in the Ni 2p3/2 region, following the approach of Beisinger et al. (ref. 42). The bold values represent the average for spectra taken at three different points on the sample with the corresponding standard deviation shown in the line below. Note that only one point was measured on sample Ni-04. The last line in the table shows the fitting parameters for NiO in ref. 42.

	Peak 1 (eV)	Peak 2 (eV)	Peak 3 (eV)	Peak 4 (eV)	Peak 5 (eV)	Peak 1 (%)	Peak 2 (%)	Peak 3 (%)	Peak 4 (%)	Peak 5 (%)
Ni-01	**853.9** 0.0	**855.6** 0.1	**861.0** 0.0	**864.1** 0.0	**866.5** 0.0	**11.2** 0.4	**45.4** 0.3	**34.8** 0.2	**4.9** 0.2	**3.8** 0.1
Ni-02	**853.6** 0.0	**855.3** 0.0	**860.8** 0.0	**863.9** 0.0	**866.2** 0.0	**12.5** 0.2	**44.4** 0.1	**35.9** 0.1	**3.4** 0.5	**3.8** 0.6
Ni-03	**853.5** 0.1	**855.2** 0.1	**860.7** 0.1	**863.9** 0.0	**866.1** 0.1	**11.7** 0.3	**45.2** 0.5	**35.9** 0.4	**3.7** 0.3	**3.6** 0.1
Ni-04	**853.8**	**855.6**	**861.0**	**864.1**	**866.2**	**11.8**	**45.0**	**36.6**	**2.4**	**4.2**
Ni-04-NRC	**853.3** 0.1	**855.1** 0.1	**860.5** 0.0	**863.6** 0.0	**865.9** 0.0	**11.6** 0.6	**45.7** 0.9	**36.5** 1.0	**3.2** 0.7	**3** 0.6
Ni-05	**853.9** 0.1	**855.6** 0.2	**861.1** 0.1	**864.3** 0.4	**866.5** 0.3	**11.2** 0.9	**44.9** 0.3	**37.6** 2.5	**2.6** 0.1	**3.7** 1.2
Ni-06	**853.9** 0.0	**856.0** 0.1	**860.2** 0.2	**863.7** 0.1	**866.9** 0.2	**6.9** 0.3	**46.6** 2.9	**31.4** 3.9	**13.9** 1.8	**1.0** 0.6
Ni-07	**853.4** 0.0	**855.1** 0.0	**860.6** 0.0	**863.7** 0.0	**865.9** 0.2	**10.6** 2.1	**48.6** 3.0	**35.8** 1.0	**2.1** 1.5	**3.1** 0.4
Ni-08	**853.5** 0.0	**855.3** 0.0	**860.7** 0.0	**863.9** 0.1	**866.1** 0.1	**12.8** 0.4	**43.8** 0.3	**36.6** 0.2	**2.8** 0.1	**4.1** 0.4
NiO Ref. 42	**853.7**	**855.4**	**860.9**	**864**	**866.3**	**14.3**	**44.2**	**34**	**3.6**	**3.9**

Table S6. Parameters (peak position and fractional contribution) obtained for the Fe_2O_3 samples by fitting five peaks in the Fe 2p3/2 region. The bold values represent the average for spectra taken at three different points on the sample with the corresponding standard deviation shown in the line below. Note that only one point was measured on sample Ni-04. The last line in the table shows the fitting parameters for Fe_2O_3 from ref. 37.

	Peak 1 (eV)	**Peak 2 (eV)**	**Peak 3 (eV)**	**Peak 4 (eV)**	**Peak 5 (eV)**	**Peak 1 (%)**	**Peak 2 (%)**	**Peak 3(%)**	**Peak 4 (%)**	**Peak 5 (%)**
Fe-01	**709.9** 0.1	**711.0** 0.2	**711.9** 0.3	**712.9** 0.4	**713.8** 0.5	**38.3** 4.1	**29.5** 1.5	**17.1** 1.7	**8.3** 1.1	**6.8** 4.1
Fe-02	**709.3** 0.1	**710.5** 0.1	**711.6** 0.2	**712.5** 0.3	**713.4** 0.1	**37.0** 1.0	**32.7** 0.4	**16.3** 1.5	**9.3** 1.4	**4.8** 1.5
Fe-03	**709.3** 0.1	**710.5** 0.1	**711.5** 0.2	**712.5** 0.3	**713.5** 0.5	**28.9** 3.9	**29.2** 2.6	**20.0** 2.4	**11.0** 0.6	**11.0** 4.0
Fe-04	**709.1** 0.3	**710.2** 0.4	**711.3** 0.4	**712.3** 0.3	**713.4** 0.1	**21.0** 8.9	**31.4** 1.0	**25.1** 5.4	**13.1** 5.4	**9.5** 3.1
Fe-05	**709.4** 0.5	**710.6** 0.5	**711.5** 0.4	**712.4** 0.5	**713.0** 0.5	**33.9** 1.2	**29.9** 3.1	**16.5** 1.0	**8.9** 1.6	**9.8** 5.4
Fe-06	**709.3** 0.1	**709.9** 0.4	**710.9** 0.4	**711.9** 0.4	**713.0** 0.2	**26.5** 6.3	**20.0** 7.6	**25.7** 6.8	**13.6** 3.3	**14.2** 3.8
Fe-07	**709.8** 0.03	**710.9** 0.04	**711.8** 0.1	**712.7** 0.1	**713.6** 0.1	**30.3** 1.4	**28.3** 0.8	**17.6** 0.7	**9.2** 0.1	**14.6** 2.6
Fe2O3 ref. 37	**709.8**	**710.8**	**711.6**	**712.7**	**713.7**	**26.8**	**24.7**	**18.9**	**10.1**	**10**

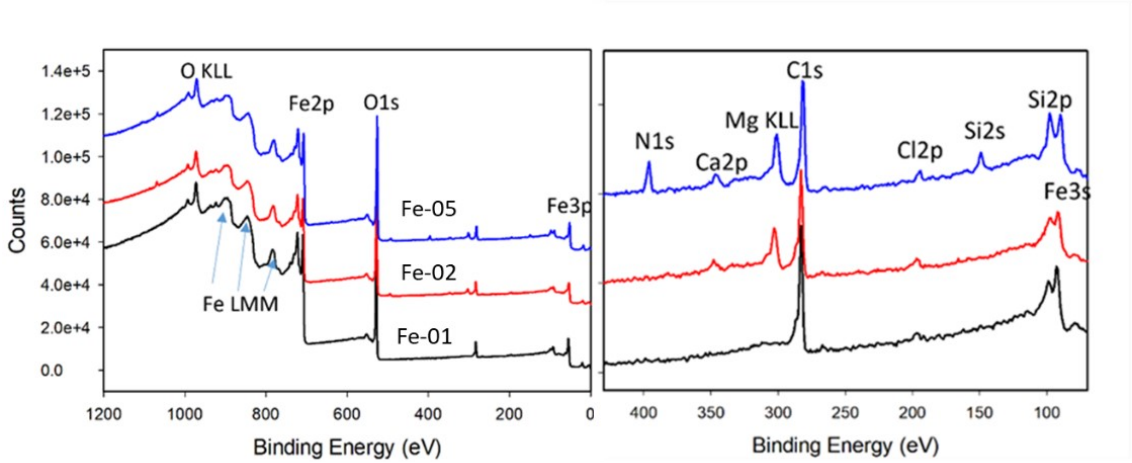

Figure S1. XPS survey data for two bare (Fe-01, Fe-02) and one APTES-modified (Fe-05) Fe_2O_3 NP sample. The binding energy range from 430 to 70eV is shown with an expanded vertical scale on the right.

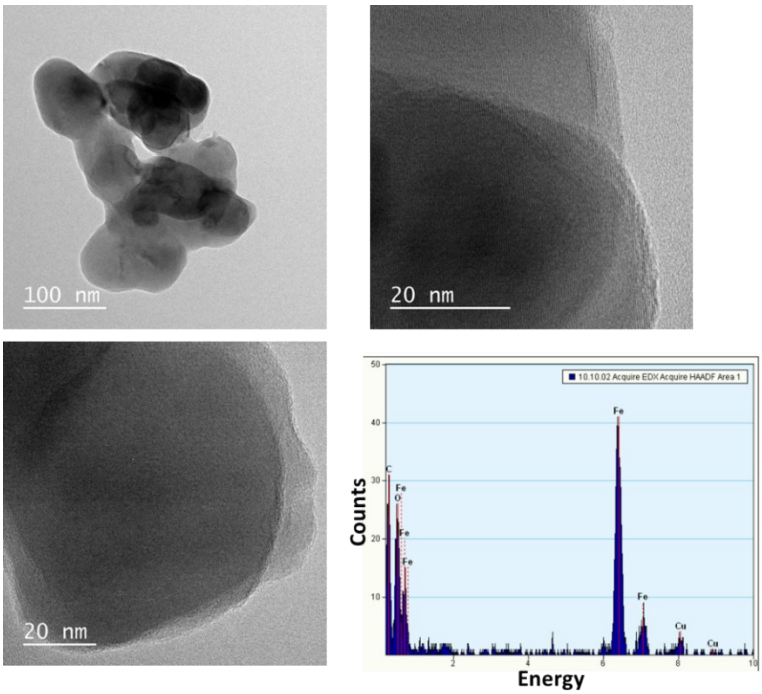

Fig. S2. TEM images of Fe-07. EDX scans show no evidence of silicon, which would be detected if the particles were composed of fayalite (Fe_2SiO_4). However, a thin (1 nm) SiO_2 layer coating the particles would likely not give a detectable Si signal.

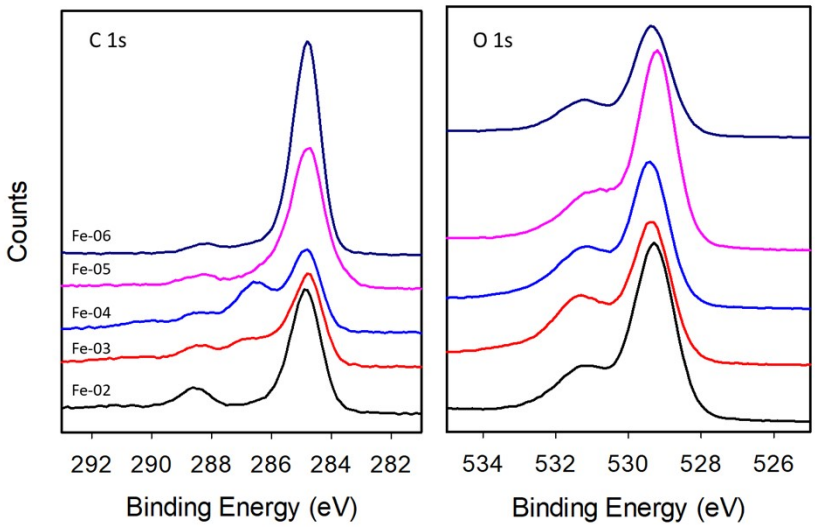

Fig. S3. HR spectra of the C 1s and O 1s regions for the bare Fe_2O_3 nanoparticle sample Fe-02 and the four corresponding nanoparticle samples modified with PVP (Fe-03), NH2 (Fe-04), APTES (Fe-05) and SA (Fe-06). The C 1s regions shows some changes due to the different modifications although interpretation of these features is complicated by the presence of adventitious carbon seen on the bare particles. The O 1s region for all the samples is very similar as the strong signal from the Fe_2O_3 particles dominates the spectra.

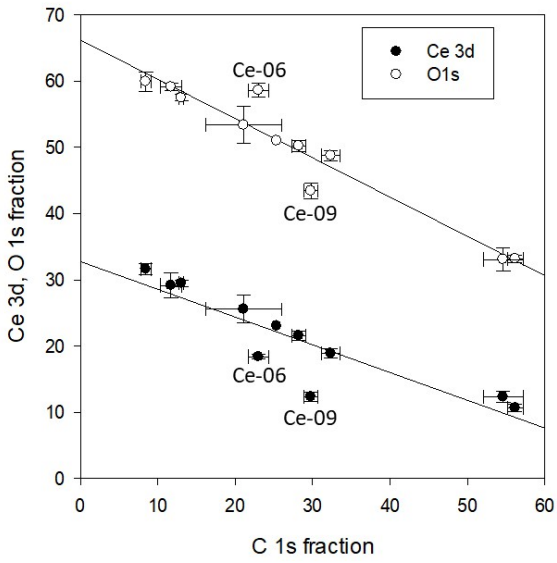

Fig S4. Ce 3d and O 1s fractions (based on HR data) as a function of the C 1s fraction for all the CeO_2 NPs. Outliers are labelled and correspond to sample Ce-06 which was unmodified but exhibited considerable P contamination and Ce-09 which was modified with APTES.

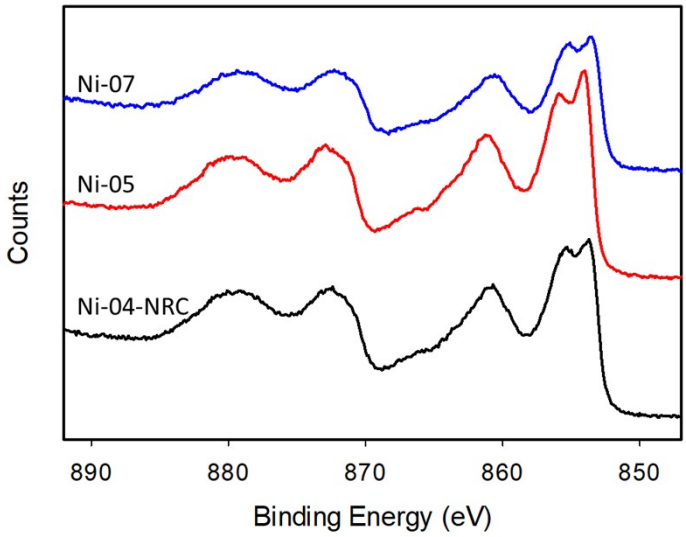

Fig. S5. Ni 2p region for three modified NiO nanoparticle samples. The three spectra are rather similar indicating that there are no significant changes in the oxidation state on these modified samples.

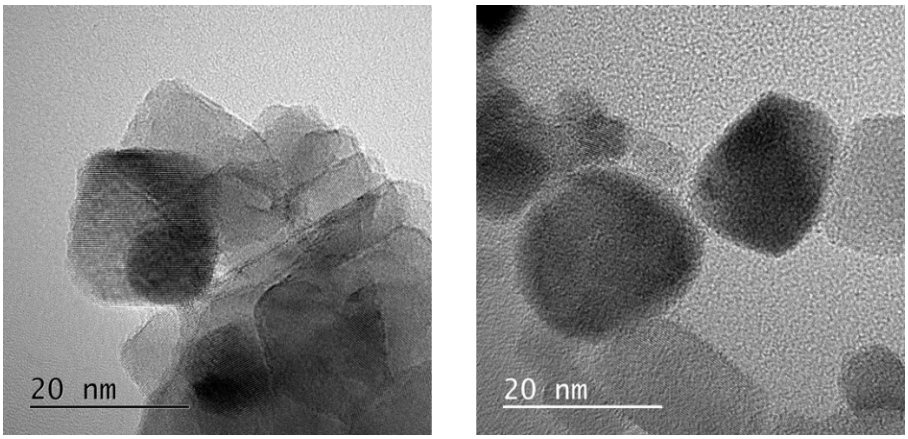

Fig. S6. TEM images of Ni-04 (left) and Ni-04-NRC (right). There is no evidence of a PVP layer coating the particles for Ni-04-NRC even though XPS shows evidence of PVP modification.