

Electronic Supplementary Information

Transformation of Co_3O_4 Nanoparticles to CoO Monitored by In-Situ TEM and Predicted Ferromagnetism at the $\text{Co}_3\text{O}_4/\text{CoO}$ Interface from First Principles

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Supporting Tables

Table S1. Results of the DFT calculations conducted on the {100}/{100} CoO/Co₃O₄ interface. The interface designation refers to the various magnetic and nonmagnetic input configurations displayed in Figure 2. Supercell dimensions and interface energies are listed, as well as the lattice mismatch between the two constituent phases in the plane of the interface. All interface supercells contain the same number of atoms.

Interface	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	A_{int}	γ_{int}	γ_{int}	Mismatch
Co ₃ O ₄ /CoO	(Å)	(Å)	(Å)	(°)	(°)	(°)	(Å ²)	(eV/Å ²)	(J/m ²)	(%)
AFM2/AFM1	8.238	8.238	33.39	88.5	88.5	88.5	67.84	0.024	0.38	4.2
AFM1/AFM1	7.974	7.974	36.26	90.0	90.0	89.7	63.58	0.050	0.80	4.4
FM/FM	7.992	7.992	36.34	90.0	90.0	89.8	63.87	0.047	0.75	4.8
NM/NM	7.924	7.924	35.20	90.0	90.0	89.4	62.78	0.239	3.82	2.1

Table S2. Lattice reflections and corresponding lattice spacings of Co₃O₄ and CoO.

Co ₃ O ₄			CoO		
No.	(h k l)	lattice spacings (Å)	No.	(h k l)	lattice spacings (Å)
1	(1 1 1)	4.67	1*	(1 1 1)	2.45
2	(0 2 2)	2.86	2*	(0 0 2)	2.12
3	(1 1 3)	2.43	3*	(0 2 2)	1.50
4	(0 0 4)	2.02			
5	(2 2 4)	1.65			
6	(1 1 5)	1.55			
7	(0 4 4)	1.42			

Supporting Figures

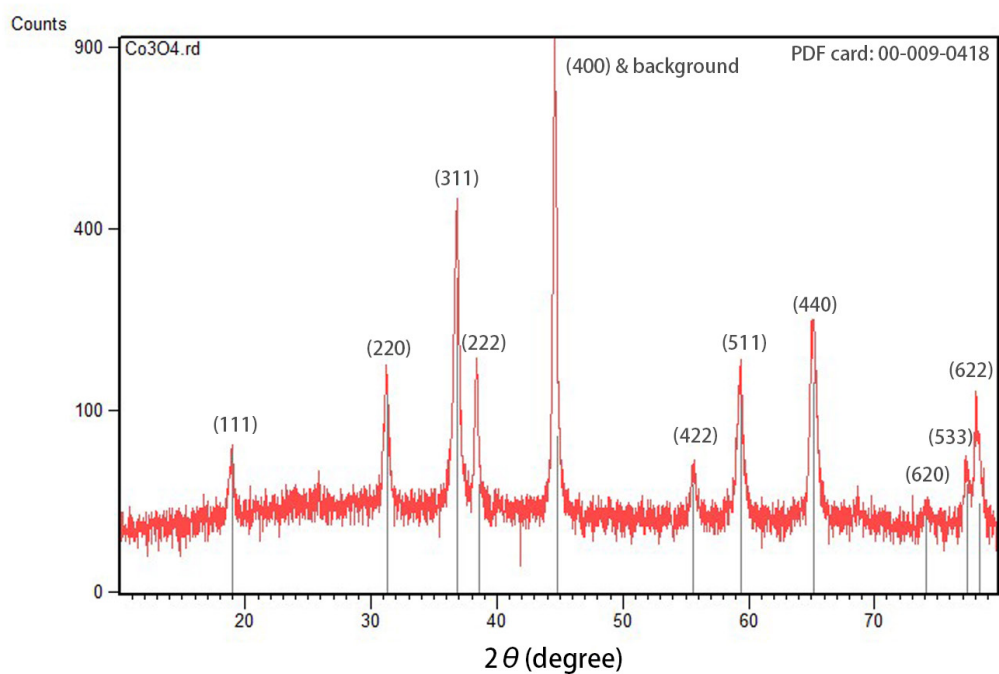


Figure S1. X-ray diffraction spectrum of the as-received Co_3O_4 nanoparticles, confirming the Co_3O_4 crystallographic phase.

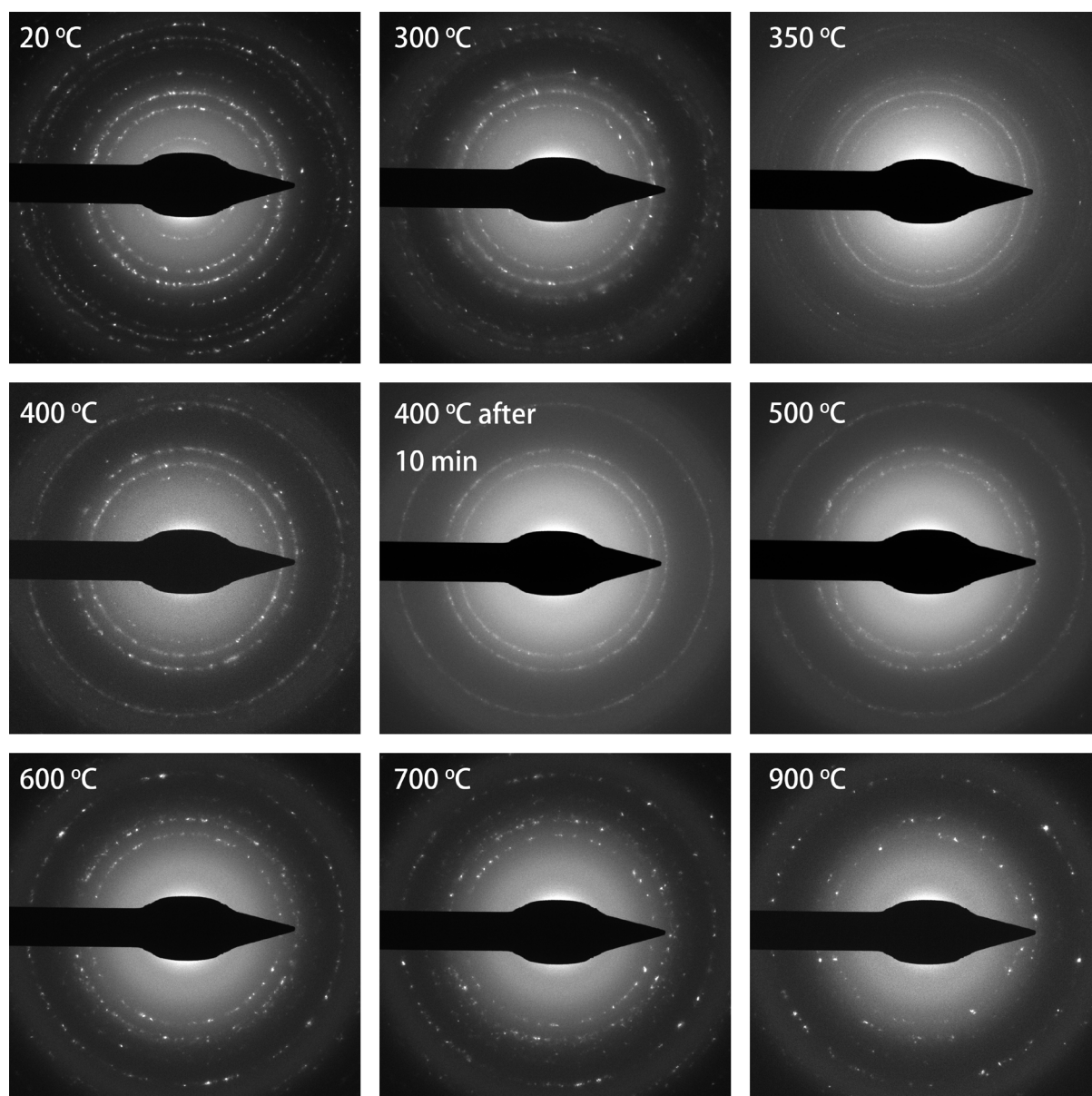


Figure S2. Selected area diffraction patterns (SAED) of Co_3O_4 NPs after in situ annealing at the indicated temperatures in the temperature range from 20 °C to 900 °C. At 20 °C, the rings in the DP correspond to Co_3O_4 . During annealing at 350 °C, the pattern started to change. After keeping the sample at 400 °C for 10 minutes, only three rings remained, that are indicative of the CoO phase. From 600 °C onwards, there are fewer spots on the rings due to coalescence and alignment of the nanocrystals, which consequently became fewer in number but larger. The transformation took place everywhere, also in areas that were not examined with the electron beam prior to heating, which means that the reduction is not due to electron beam exposure.

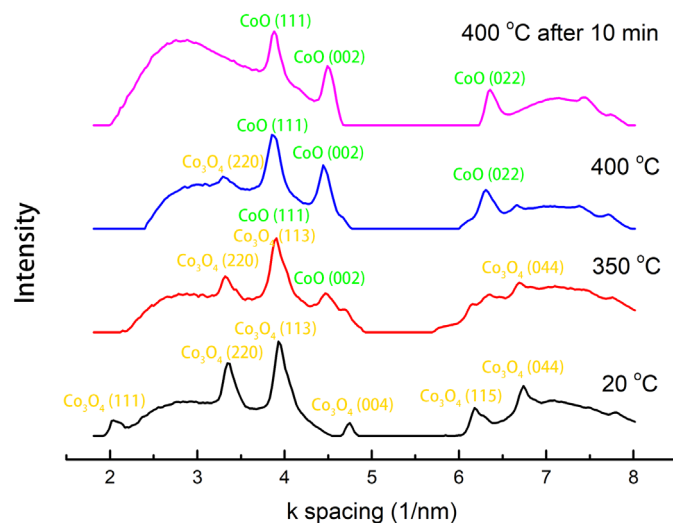


Figure S3. Circularly integrated diffraction patterns obtained after heating at 20 °C, 350 °C, 400 °C, and 400 °C after 10 minutes. The corresponding lattice reflections are indicated above the peaks with Co_3O_4 reflections marked in yellow and CoO reflections marked in green. Please note that the (hkl) indexing of the diffraction rings refers to reflections at {hkl} families of lattice planes. At 20 °C, all peaks corresponded to the Co_3O_4 structure. At 350 °C, the (111) peak of Co_3O_4 disappeared and the (004) reflection became very weak, while the (002) reflection of CoO appeared. This trend continued to 400 °C, and finally only three peaks corresponding to reflections of CoO remained.

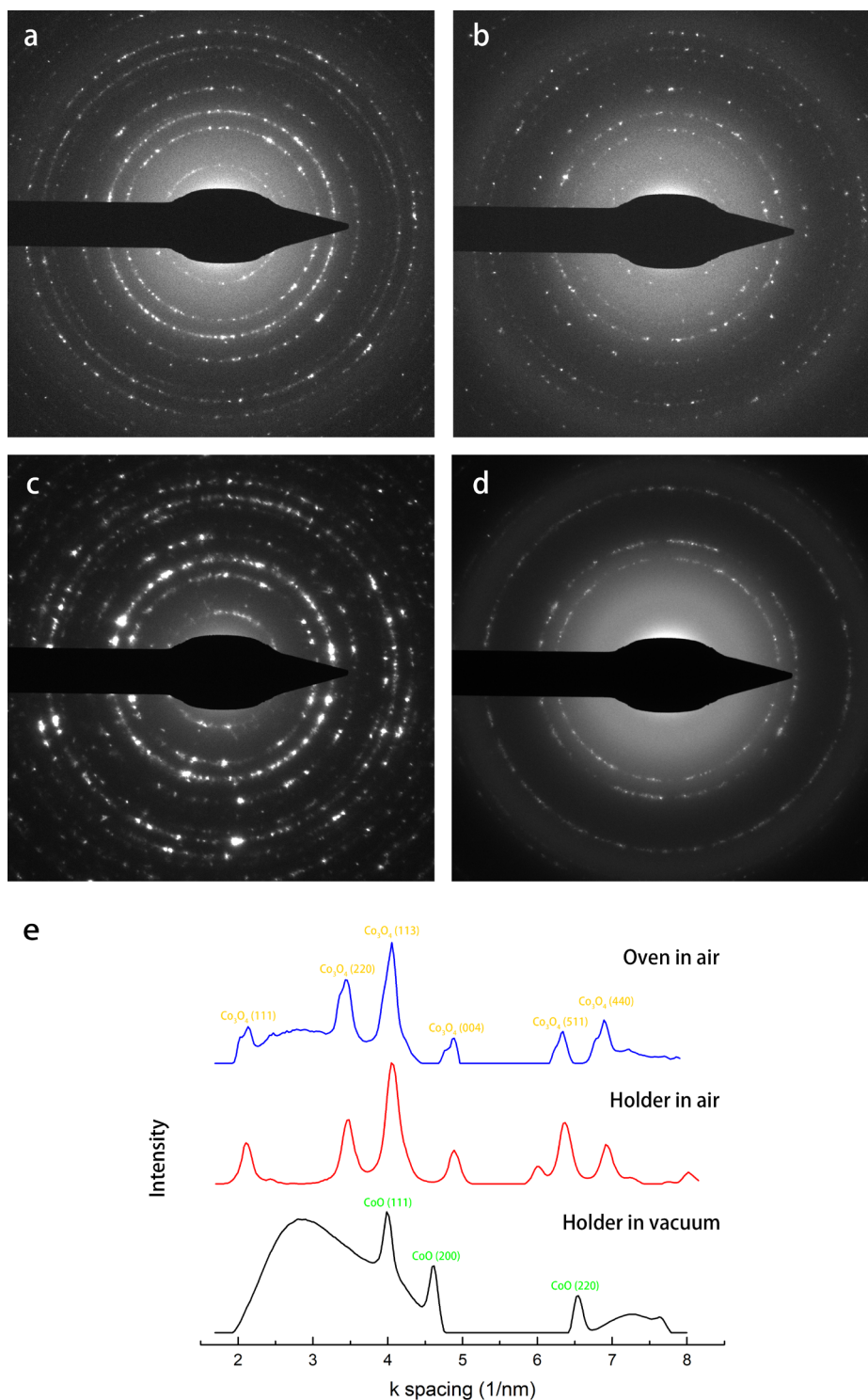


Figure S4. SAED of Co_3O_4 NPs after ex-situ heating. (a) and (b) are DPs of the sample heated in the oven in air and under N_2 flow, respectively. (c) and (d) are DPs obtained after heating inside the heating holder in air and in a high vacuum chamber following the same temperature profile as in the in-situ experiments. (e) Integrated image of (a, c, d). Please note that the (hkl) indexing of the diffraction rings refers to reflections at {hkl} families of lattice planes. Different intensities between panels are due to different amounts of particles in the selected areas (SA).

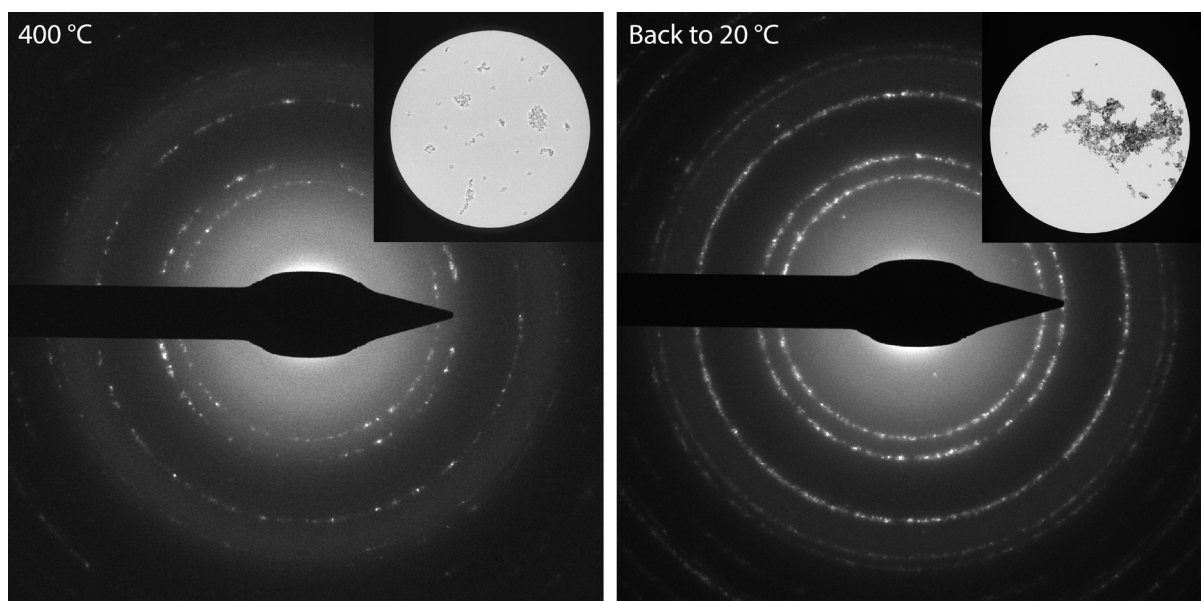


Figure S5. SAED of Co_3O_4 NPs at 400 °C (left), and after cooling down to 20 °C (right). Both DPs correspond to the crystal structure of CoO. The inset images at the top-right show the selected areas which form the diffraction patterns were taken. The intensity of the DP after cooling down is higher because there are more particles in the selected area.

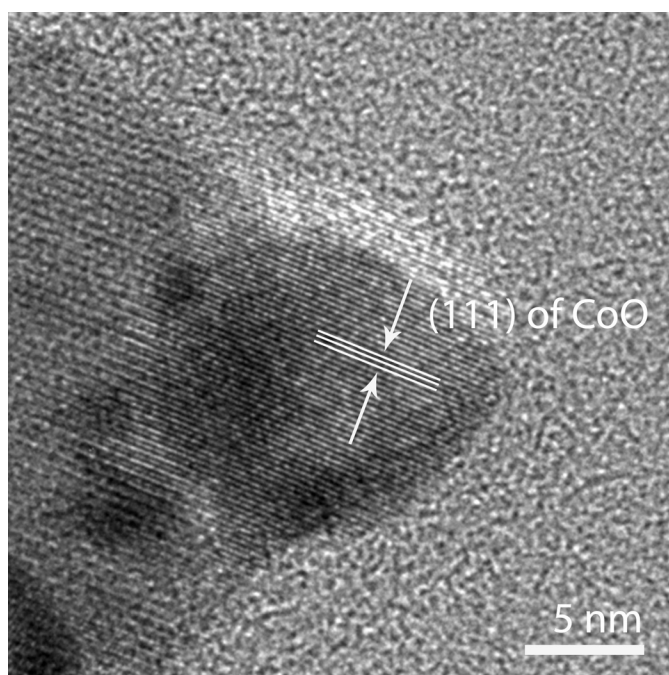


Figure S6. TEM image obtained after in-situ heating to 400 °C and subsequent slow cooling down.

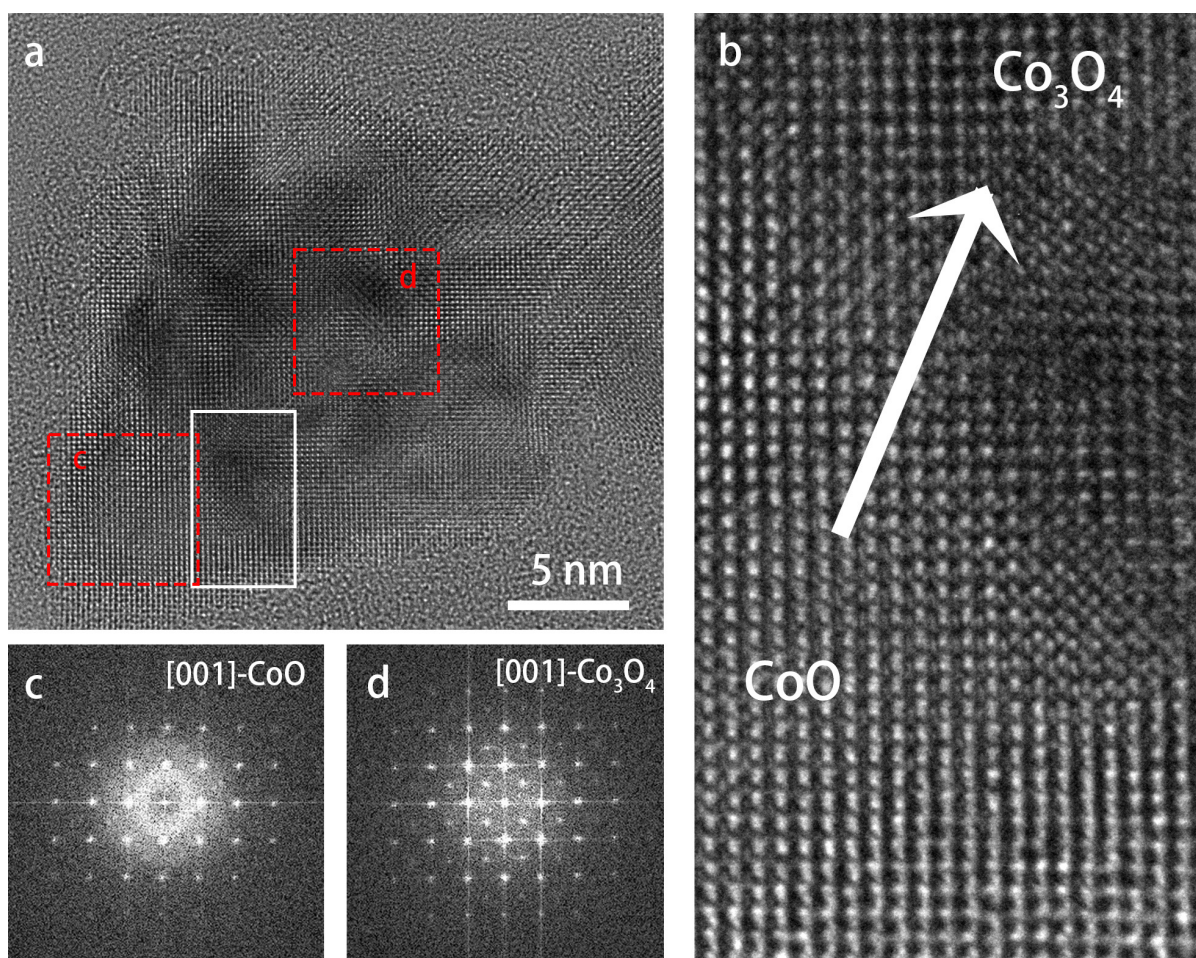


Figure S7. HRTEM images of a partially transformed nanoparticle imaged in a [001] projection. (a) Overview of the particle, left-bottom part and the surface areas are in the CoO phase while the central part of the nanoparticle is still in Co_3O_4 phase. (b) Magnified image of the area marked by white square in (a). (c) and (d) show the FFT pattern of the corresponding areas marked in panel (a), clearly indicating the crystal structures of CoO and Co_3O_4 , respectively.

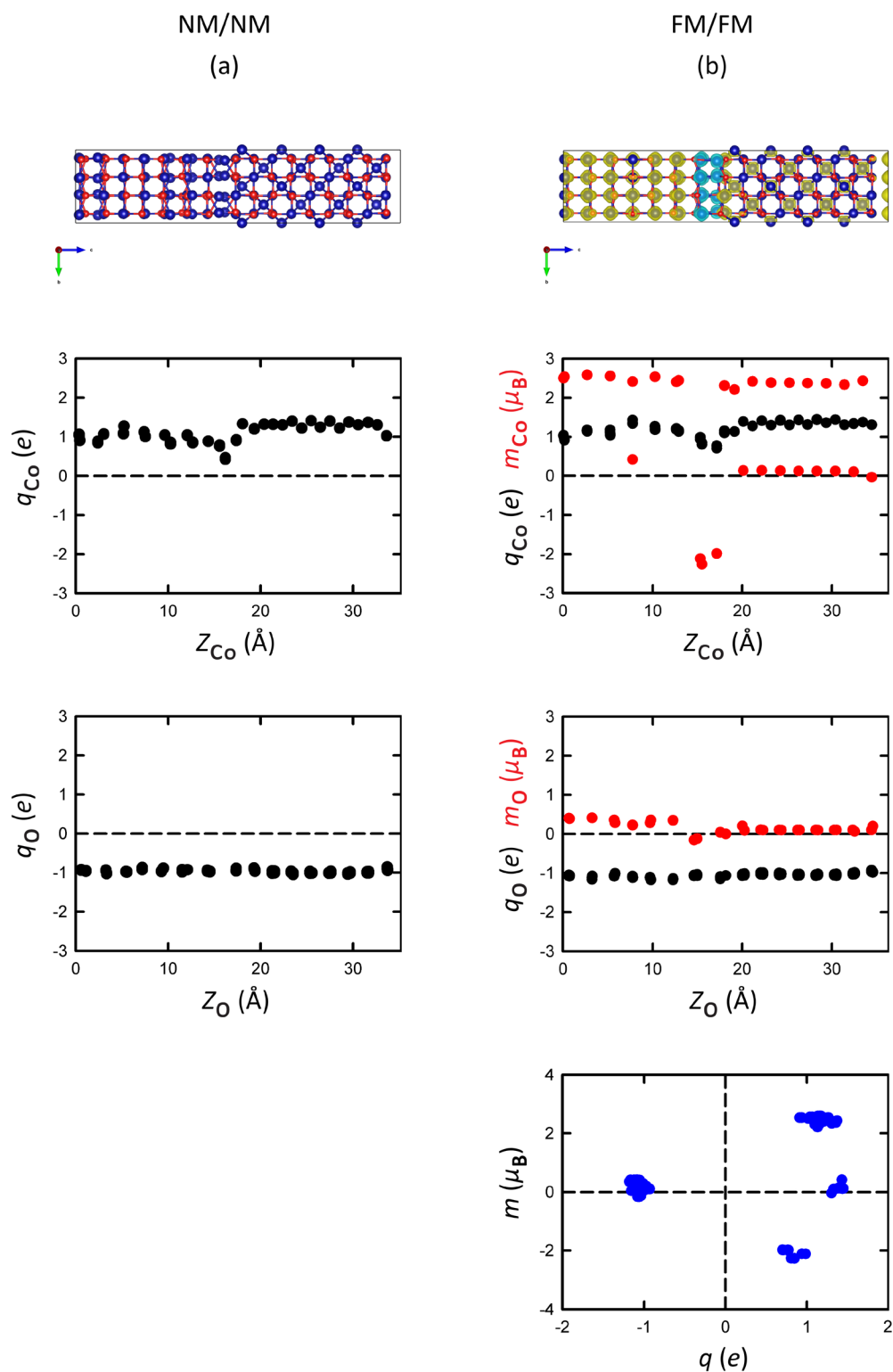


Figure S8. Top: relaxed configurations of the interface supercells, with overlaid the magnetization density, with (a) the NM/NM nonmagnetic configuration and (b) the FM/FM magnetic ordering. Co atoms are depicted in blue and O atoms in red, while yellow isosurfaces indicate excess spin-up electron density and blue isosurfaces excess spin-down electron density (isosurface levels are ± 0.24 e/ $\text{\AA}^3$). Middle: charges and magnetic moments on the Co and O atoms plotted as a function of Z-coordinate. Bottom: correlation between the charges and the magnetic moments on the atoms.

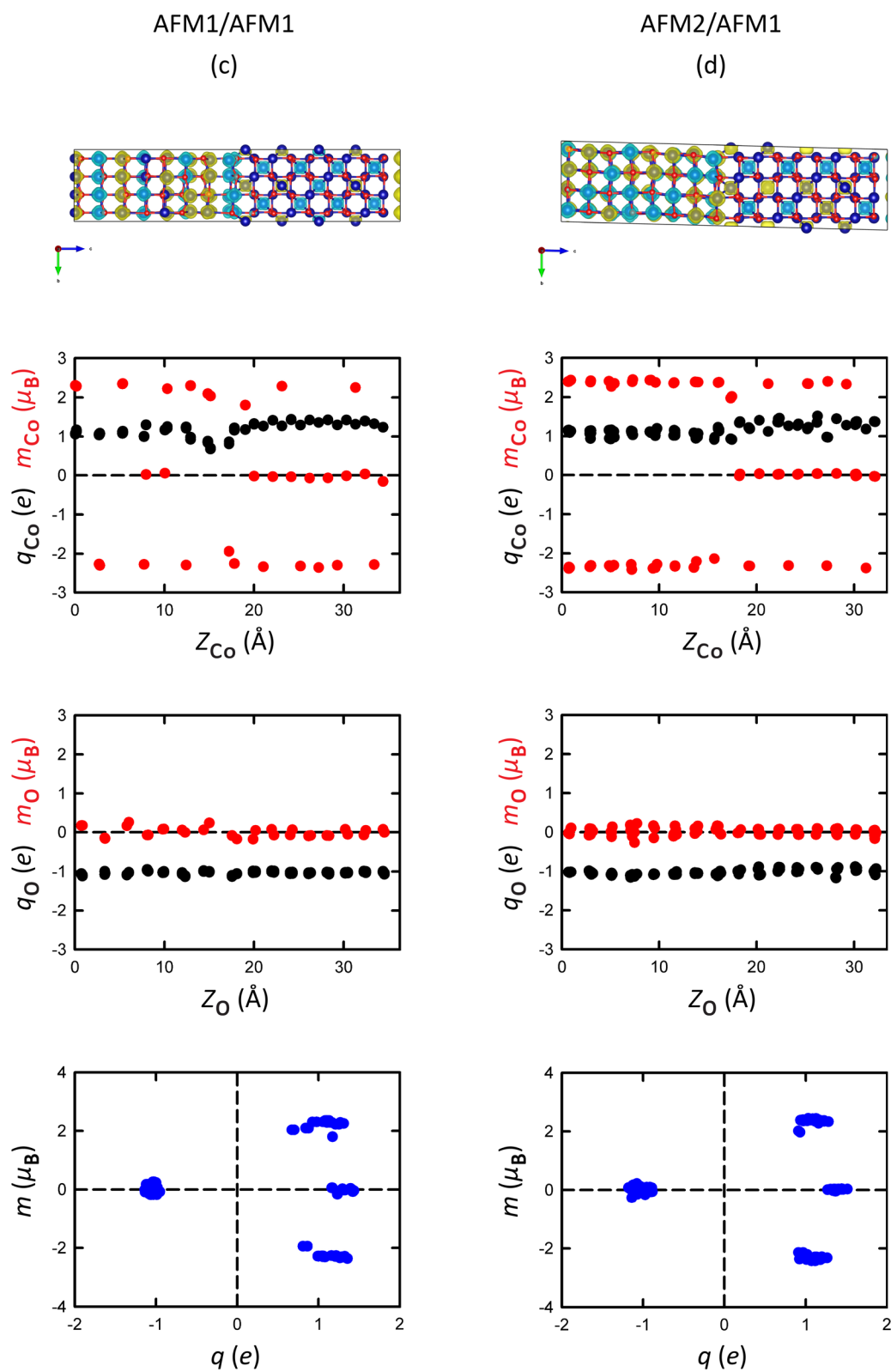


Figure S8 (continued). As previous, with (c) the AFM1/AFM1 magnetic ordering and (d) the AFM2/AFM1 magnetic ordering.