Supplementary Materials: Cobalt-iron Oxide, Alloy and Nitride: Synthesis, Characterization and Application in Catalytic Peroxymonosulfate Activation for Orange II Degradation

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Figure S1. XPS spectra of CFA-500 in different regions (a) survey, (b) O 1s, (c) Co 2p, (d) Fe 2p.



Figure S2. XPS spectra of CFN-500 in different regions (a) survey, (b) Co 2p, (c) Fe 2p, and (d) C 1s.



Figure S3. TG-DSC (a) and the TG-MS (b) curves of the as-prepared cobalt-iron nanomaterials under Ar atmosphere.



Figure S4. XPS spectra of CFNH-500 in different regions (a) survey, (b) Co 2p, (c) Fe 2p, (d) C 1s, (e) N 1s and (f)O 1s.



Figure S5. XRD patterns of the used CFA-600, CFN-600 and CFNH-600.



Figure S6. S2p XPS spectrum of the CFN-600 before and after reaction.

| Sample | BET (m ² g ⁻¹) | Pore Volume (cm ³ g ⁻¹) |
|----------|---------------------------------------|--|
| CFA-500 | 66.0 | 0.126 |
| CFA-600 | 17.7 | 0.044 |
| CFN-500 | 174.1 | 0.144 |
| CFN-600 | 52.7 | 0.094 |
| CFNH-500 | 108.1 | 0.040 |
| CFNH-600 | 13.04 | 0.019 |

Table S1. The BET surface area and pore volume of prepared samples.

| | δ (mm s ⁻¹) | ∆ (mm s ⁻¹) | Bhf,0 (T) | B _{hf} (T) | Δ <i>B</i> hf (T) | W _G (mm s⁻¹) | WL (mm s ⁻¹) | σ(B _{hf}) (T) | $\mathrm{d} \delta / \mathrm{d} B_{\mathrm{hf}}$ | Relative abundance (%) | Assign ment |
|---|----------------------------|----------------------------|--------------|------------------------|----------------------|----------------------------|-----------------------------|-------------------------|--|---------------------------|--|
| CFA-500 <i>c</i> (Co _A) 0 250(4) | 0.346(7) | | 51.0(1) | | -3.9(1) | 0.46(2) | 0.28(1) | | | 62.1(8) | Fe ³⁺ (B) |
| 0.200(1) | 0.281(4) | | | 48.1(4) | | | 0.28(1) | 1.62(4) | 0.028(3) | 37.3(3) | Fe ³⁺ (A) |
| | 0.32(2) | 0.39(3) | | | | | 0.28(1) | | | 0.6(2) | Fe ³⁺ doublet |
| CFA-600 <i>c</i> (Coa) | 0.359(2) | | 51.83(2) | | -3.82(3) | 0.32(1) | 0.291(5) | | | 57.2(3) | Fe ³⁺ (B) |
| 0.145(2) | 0.274(2) | | | 49.07(2) | | | 0.29(1) | 1.15(2) | 0.050(2) | 42.7(2) | Fe ³⁺ (A) |
| | 0.23(2) | 0.39(4) | | | | | 0.29(1) | | | 0.15(8) | Fe ³⁺ doublet |
| CFA-600 after | 0.359(2) 0.274(2) | | 51.83(2) | 49.07(2) | -3.82(3) | 0.32(1) | 0.291(5) 0.29(1) | 1.15(2) | 0.050(2) | 56.8(6) 40.7(3) | Fe ³⁺ (B) Fe ³⁺ (A) |
| с(Соа) 0.165(3) | 0.23(2) | 0.39(4) | | | | | 0.29(1) | | | 2.5(3) | Fe ³⁺ doublet |

Table S2. ⁵⁷Fe Mössbauer parameters of the samples CFA-500 and CFA-600 as well as CFA-600-after reaction derived on the basis of Mössbauer spectra recorded at room temperature. Numbers in parentheses denote the statistical uncertainty (1 σ) of the last digit(s).

δ - ⁵⁷Fe isomer shift relative to α-Fe at room temperature, Δ - quadrupole splitting, WL - Lorentzian FWHM width of absorption peaks, WG - Gaussian FWHM width of Voigt-shaped absorption peaks, $B_{hf,0}$ - hyperfine magnetic field sensed by Fe³⁺ nuclei at octahedral sites with no Co atom at nearest neighbor (n.n.) tetrahedral sites, ΔB_{hf} change in the hyperfine magnetic field sensed by Fe³⁺ nuclei at octahedral sites when the number of Co atoms at n.n. tetrahedral sites increases by one, c(CoA) - concentration of Co atoms at tetrahedral sites, B_{hf} - mean value of the hyperfine magnetic field sensed by Fe³⁺ nuclei at tetrahedral sites, σ (B_{hf}) - standard deviation of the Gaussian shaped distribution in the Bhf values. VBF refers to "Voigt Based Fitting" that is explained in references.[1,2]

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Note that *x* in $(Co_xFe_{1-x})[Co_{1-x}Fe_{1+x}]O_4$ also determines the relative occurrence of A-site and B-site Fe³⁺ ions as Fe_A/Fe_B = (1-x)/(1+x). By assuming that the difference between the recoilless fractions of A-site and B-site Fe³⁺ ions can be neglected, the same ratio can be used to constrain the spectral area (*A*) associated with A-site Fe³⁺ on the basis of that of B-site Fe³⁺: $A(Fe_A) = A(Fe_B) \cdot (1-x)/(1+x)$. The parameter values listed in Table 1a were derived by applying this constraint. The quadrupole shift of the fitted sextet components were assumed to be zero, which is a reasonable approximation on the basis of previous results concerning CoFe₂O₄.[3]

Table S3. ⁵⁷Fe Mössbauer parameters of the samples CFN-500 and CFN-600 as well as CFN-600-*after reaction* derived on the basis of Mössbauer spectra recorded at room temperature. Numbers in parentheses denote the statistical uncertainty (1σ) of the last digit(s). Parameter values denoted with (F) were fixed during the fit.

| | δ (mm s ⁻¹) | δ (mm s ⁻¹) | ∆ (mm s⁻¹) | WL (mm s ⁻¹) | Bhf,0 (T) | 2ɛº (mm s ⁻¹) | Δ <i>δ</i> (T) | Δ <i>B</i> hf (T) | Δ2ε (mm s ⁻¹) | Relativea bundanc e (%) | Assignment |
|---|----------------------------|----------------------------|---------------|---|--------------|------------------------------|-------------------|----------------------|------------------------------|-------------------------------|--------------------------|
| CFN-500 <i>c</i> (Fe) 0.647(6) | 0.0064(8) | | | 0.258(3) | 28.59(6) | 0.046(9) | 0.0025(F) | 0.771(F) | -0.0045(9) | 54(4) | Fe in Co-Fe alloy |
| | | 0.36(2) | 0.85(3) | 0.82(6) | | | | | | 6.8(5) | Fe ³⁺ doublet |
| | | Peak cente 0.0064(8) | er | 11.2(1.5) Magnetic component with relaxation broadening | | | | | | | |
| CFN-600 <i>c</i> (Fe) 0.717(6) | 0.0064(8) | | | 0.258(3) | 28.59(6) | 0.046(9) | 0.0025(F) | 0.771(F) | -0.0045(9) | 98.1(2) | Fe in Co-Fe alloy |
| | | 0.36(2) | 0.85(3) | 0.82(6) | | | | | | 1.9(2) | Fe ³⁺ doublet |
| CFN-600 after | 0.0064(8) | | | 0.258(3) | 28.59(6) | 0.046(9) | 0.0025(F) | 0.771(F) | -0.0045(9) | 91.0(5) | Fe in Co-Fe alloy |
| <i>c</i> (Fe) 0.699(6) | | 0.36(2) | 0.85(3) | 0.82(6) | | | | | | 9.0(6) | Fe ³⁺ doublet |

 δ - ⁵⁷Fe isomer shift relative to α-Fe at room temperature, δ - ⁵⁷Fe isomer shift of iron nuclei with only Co atoms as nearest and next-nearest neighbor, $\Delta\delta$ - change in the ⁵⁷Fe isomer shift when the number of Fe atoms at n.n. and n.n.n. sites increases by one, 2ε₀ - double of the first-order quadrupole shift characterizing iron nuclei with only Co atoms as nearest and next-nearest neighbor, $\Delta2\epsilon$ - change in the double of the first-order quadrupole shift when the number of Fe atoms at n.n. and n.n.n. sites increases by one, $2\epsilon_0$ - double of the first-order quadrupole shift when the number of Fe atoms at n.n. and n.n.n. sites increases by one, $B_{hf,0}$ - hyperfine magnetic field sensed by ⁵⁷Fe nuclei with only Co atoms as nearest and next-nearest neighbor, ΔB_{hf} - change in the hyperfine magnetic field sensed by ⁵⁷Fe nuclei with only Co atoms as nearest and next-nearest neighbor, ΔB_{hf} - change in the hyperfine magnetic field sensed by ⁵⁷Fe nuclei with only Co atoms as nearest and next-nearest neighbor, ΔB_{hf} - change in the hyperfine magnetic field sensed by ⁵⁷Fe nuclei with only Co atoms as nearest and next-nearest neighbor, ΔB_{hf} - change in the hyperfine magnetic field sensed by ⁵⁷Fe nuclei with only Co atoms as nearest and next-nearest neighbor, ΔB_{hf} - change in the hyperfine magnetic field sensed by ⁵⁷Fe nuclei with only Co atoms as nearest and next-nearest neighbor, ΔB_{hf} - change in the hyperfine magnetic field sensed by ⁵⁷Fe nuclei when the number of Fe atoms at n.n. and n.n.n. sites increases by one, Δ - quadrupole splitting, W_L - Lorentzian FWHM width of absorption peaks, c(Fe) - concentration of Fe atoms($\equiv x$ in Fe_xCo_{1-x}).

Table S4. ⁵⁷Fe Mössbauer parameters of the samples CFNH-500 and CFNH-600 derived on the basis of Mössbauer spectra recorded at room temperature. Numbers in parentheses denote the statistical uncertainty (1σ) of the last digit(s). See Table S3 for notations.

| | δ (mm s ⁻¹) | δ (mm s ⁻¹) | ∆ (mm s 1) | WL (mm s ⁻¹) | Bhf,0 (T) | 2ε₀ (mm s ⁻¹) | Δ δ (T) | ΔB _{hf} (T) | Δ2ε (mm s ⁻¹) | Relative abundance (%) | Assignment |
|--|----------------------------|----------------------------|---------------------------|-----------------------------|--------------|------------------------------|-------------------|-------------------------|------------------------------|------------------------------|----------------------------|
| CFNH-500 <i>c</i> (Fe) 0.676(2) | 0.0064 (F) | | | 0.29 (1) | 28.59(F) | 0.046(F) | 0.0025(F) | 0.771(F) | -0.0045(9) | 43(1) | Fe in Co-Fe alloy |
| | | 0.330(6) | 0.52(2) | 0.78(2) | | | | | | 46.2(1.4) | Fe in nitride (doublet) |
| | | 0.421(3) | 0.324(6) | 0.23(2) | | | | | | 10.7(1.3) | Fe in nitride (doublet) |

| CFNH-600 | | | | | |
|----------|----------|----------|----------|-----|----------------------------|
| | 0.411(2) | 0.328(2) | 0.336(4) | 100 | Fe in nitride (doublet) |

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| Elements | | CFA-600 (ppm) | CFN-600 (ppm) | CFNH-600 (ppm) |
|----------|------|------------------|------------------|-------------------|
| Со | run1 | 0.1832 | 6.068 | 0.3345 |
| | run2 | 0.1126 | 1.280 | 0.3974 |
| Fe | run1 | 0.2254 | 0.9967 | 0.5041 |
| | run2 | 0.1636 | 0.5117 | 0.6708 |

Table S5. Metal leaching concentrations detected by ICP.

Table S6. XPS fitting results of surface elements for the CFA-600, CFN-600 and CFNH-600 samples before and after reaction.

| Sample | Before reaction | | | After read | Assignment | |
|----------|---------------------|----------|-------------|------------|-------------|------------------------|
| | | B.E.(eV) | Percent (%) | B.E.(eV) | Percent (%) | - |
| CFA-600 | Co2p _{3/2} | 785.9 | | 785.4 | | Satellite |
| | | 779.5 | 61.2 | 779.8 | 47 | Co ²⁺ (oct) |
| | | 781.5 | 39.8 | 781.3 | 45.8 | Co ²⁺ (tet) |
| | | | | 783.1 | 7.2 | Co ³⁺ (oct) |
| | Fe2p _{3/2} | 719.1 | | 719.1 | | Satellite |
| | | 710.0 | 52.3 | 710.3 | 44 | Fe ³⁺ (oct) |
| | | 712.7 | 47.7 | 712.6 | 56 | Fe ³⁺ (tet) |
| | O1s | 529.2 | | 529.5 | | Lattice |
| | | 531.0 | | 531.7 | | -OH |
| CFN-600 | Co2p _{3/2} | 786.6 | | 786.5 | | Satellite |
| | | 778.2 | 22.9 | - | - | Co^0 |
| | | 781.1 | 77.1 | 780.8 | 61.8 | Co ²⁺ |
| | | - | - | 783.3 | 38.2 | Co ³⁺ |
| | Fe2p _{3/2} | 719.1 | | 719.1 | | Satellite |
| | | 710.6 | 47.2 | 710.9 | 43.5 | Fe ³⁺ (oct) |
| | | 713.0 | 37.6 | 713.0 | 56.5 | Fe ³⁺ (tet) |
| | | 708.1 | 15.2 | - | - | Fe ⁰ |
| | C1s | 286.2 | 4.2 | 286.3 | 7.5 | C=O |
| | | 285.4 | 13.5 | 285.4 | 7.6 | C-O |
| | | 284.6 | 82.3 | 284.5 | 84.9 | C-C or C=C |
| CFNH-600 | Co2p _{3/2} | 786.6 | | | | Satellite |
| | | 780.4 | 60.9 | 781.0 | 74.8 | Co ²⁺ |
| | | 782.7 | 39.1 | 783.3 | 25.2 | Co ³⁺ |
| | Fe2p _{3/2} | 719.1 | | 719.1 | | Satellite |
| | | 711.2 | | 711.4 | | Fe ³⁺ |
| | C1s | 284.6 | 80.7 | 284.5 | 70.8 | C=C or C-C |
| | | 285.8 | 7.7 | 285.6 | 9.2 | C-N or C-O |
| | | 286.9 | 5.4 | 286.5 | 10.8 | C=O |
| | | 288.6 | 6.2 | 288.4 | 5.8 | O-C=O |
| | | | | 292.8 | 3.4 | π-π |

| N1s | 397.0 | 28.8 | 397 | 35.5 | pyridinic |
|-----|-------|------|-------|------|-----------|
| | 398.6 | 33.3 | 398.7 | 22.0 | N-Fe(Co) |
| | 400.1 | 23.4 | 400.1 | 27.2 | pyrrolic |
| | 402.7 | 8.8 | 402.4 | 11.5 | graphic |
| | 404.7 | 5.7 | 404.7 | 3.8 | oxidized |
| O1s | 530.0 | 45.9 | 530.0 | 24.4 | lattice |
| | 531.7 | 35.8 | 531.5 | 75.6 | -OH |
| | 536.0 | 18.2 | | | |

References:

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