# Time-controlled synthesis of multicore maghemite nanoflowers: structure, defects and surface chemistry optimized for reactive interfaces

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## Abstract

Multicore iron-oxide "nanoflowers" represent a distinctive class of nanomaterials where functional behavior is dictated by hierarchical architecture (core–cluster organization), defect disorder, and surface chemistry. Here, $\gamma$-$Fe_2O_3$ nanoflowers were synthesized by an aminated polyol route and systematically tuned by varying the solvothermal treatment time (2–12 h) to map composition–structure–surface relationships relevant to nanoscale interfaces. XRPD shows that 2 h is insufficient for crystallization into the target phase, yielding intermediate (oxy)hydroxide signatures, whereas ≥4 h produces patterns consistent with maghemite-type spinel ordering. Rietveld refinement (maghemite model) indicates crystallite sizes of ~23 nm for the sample prepared with a 4 h treatment (NF4) and ~29 nm for those prepared with 8 and 12 h treatments (NF8/NF12) , accompanied by a subtle increase in lattice parameter with longer treatment time.

TEM reveals a pronounced microstructural evolution: NF4 consists of well-defined flower-like assemblies built from multiple crystalline cores ($D_C \approx 12 \pm 2$ nm) arranged into ~34 ± 5 nm clusters, while NF8 exhibits larger cores (≈17 ± 3 nm) and a mixed population of nanoflowers and pseudospherical nanoparticles. NF12 shows extensive aggregation and loss of a clearly preserved nanoflower motif, preventing reliable size statistics. Comparison of XRPD-derived coherent domain sizes with TEM core sizes suggests lattice continuity across the multicore assemblies, supporting an oriented-attachment/epitaxial-growth scenario where the nanoflower behaves as a partially coherent crystalline entity rather than a loose agglomerate. Colloidal metrics (DLS, ζ-potential) further indicate increasing hydrodynamic size with synthesis time and identify NF4 as the most dispersible, least aggregated material within the series.

Surface chemistry, probed by XPS on the selected NF4 sample, evidences mixed-valence $Fe^{2+}/Fe^{3}$ contributions and a substantial fraction of non-lattice oxygen species (defect-related oxygen/hydroxyl groups), highlighting a hydroxyl-rich, defect-containing interface characteristic of reactive iron-oxide nanostructures. Magnetic measurements (300 K) show narrow hysteresis loops with low coercivity, with NF4 exhibiting markedly reduced $H_C$ relative to longer-time samples, consistent with multicore interaction-driven collective magnetization and lowered effective anisotropy in well-formed nanoflowers.

As a brief functional demonstration, the optimized NF4 material was used as a heterogeneous activator in peroxymonosulfate-based oxidation under controlled conditions, where its defect/hydroxylated surface and $Fe^{2+}/Fe^{3+}$ couples provide reactive interfacial sites for application in catalysis.

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