Supporting Information

Molten Salt Growth and Magnetic Properties of Octahedral $CoFe_2O_4$ Crystals:effects of synthesis conditions

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Experimental Details

1. Chemicals

$Co(Ac)_2•4H_2O$, $FeCl_3•6H_2O$, NaX (X=F, Cl, Br), Na_2SO_4, KCl, NaOH and ethanol (C_2H_5OH) were purchased from Sinopharm Chemical Reagent Co., All the chemical reagents and solvents are analytical grades and used without further purification. Self-made distilled water was used in the present work.

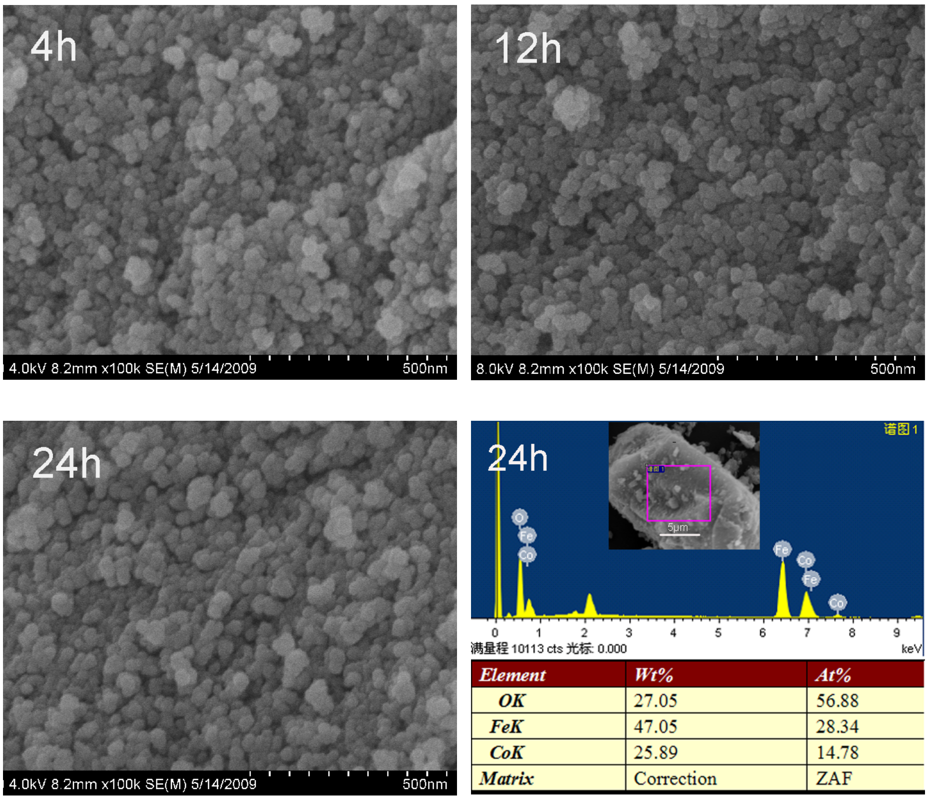
2. Preparation of the $CoFe_2O_4$ precursor

For a typical synthesis, 0.1 g/mL NaOH was added into a mixture of $Co(Ac)_2•4H_2O$ and $FeCl_3•6H_2O$ solution (mol ratio Co^{2+}: Fe^{3+}=1:2) slowly to form a pH >12 suspension, then the suspension was transferred into a 100 mL Teflon-lined autoclave, sealed and kept statically at 150 ^{o}C for 4 h, 12 h, 24 h hydrothermal treatment respectively.

3. Characterization

Powder X-ray diffraction (XRD) patterns were measured on a Bruker D8 Advance X-Ray diffractionmeter using Cu-Kα (λ=1.540562Å, 40 kV, 40 mA,) as X -ray source. The scanning electron microscopy images were taken on a HITACHI S-4800 field emitting scanning electron microscope (FESEM). The transmission electron microscopy (TEM) images and selective area electron diffraction (SAED) patterns of the CoFe2O4 particles were obtained on a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 200 kV.

Magnetic properties were measured by a Lakeshore Model 7400 series vibrating sample magnetometer (VSM) at room temperature (300 K). Fourier transform infrared spectra (FTIR) were measured with a Bruker Vertex 70 Spectrophotometer within the wave number range of 4000-360cm^{-1} using KBr pressed pellet technique.



Element	*Wt%*	*At%*
OK	27.05	56.88
FeK	47.05	28.34
CoK	25.89	14.78
Matrix	Correction	ZAF

Figure S1. SEM and EDX images of precursors with different hydrothermal time.

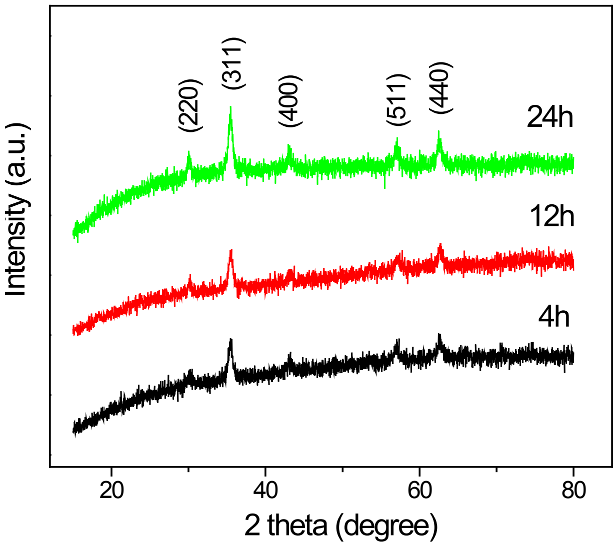


Figure S2. XRD patterns of precursors with different hydrothermal time.

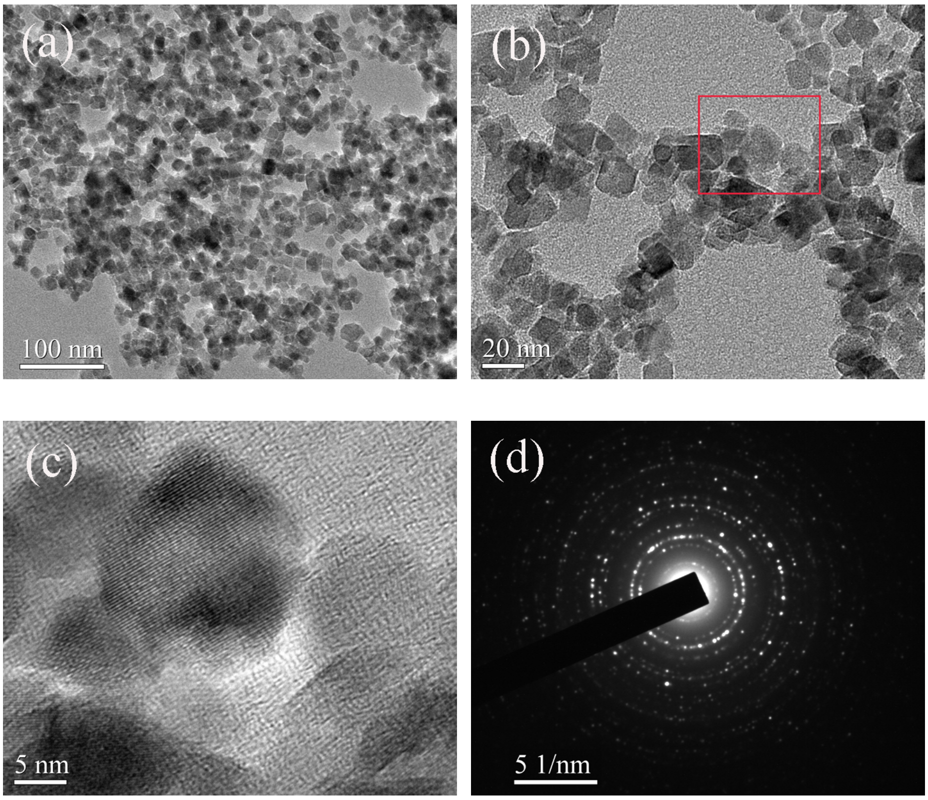


Figure S3. TEM (a, b), HR-TEM (c) and SAED (d) images of the precursor prepared through 24 h hydrothermal reaction.

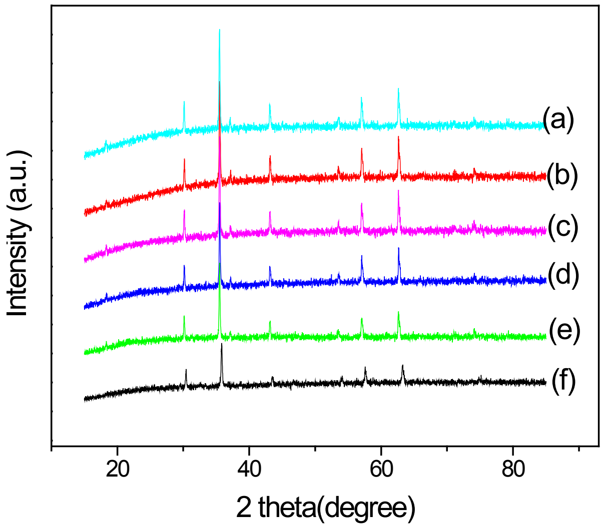


Fig. S4. XRD patterns of $CoFe_2O_4$ crystals prepared by molten salt growth method using different kinds of salts(a) Na_2SO_4 (b) NaCl (c) NaCl-KCl (d) NaBr (e) $NaCl/Na_2SO_4$ (f) Na_2CO_3.

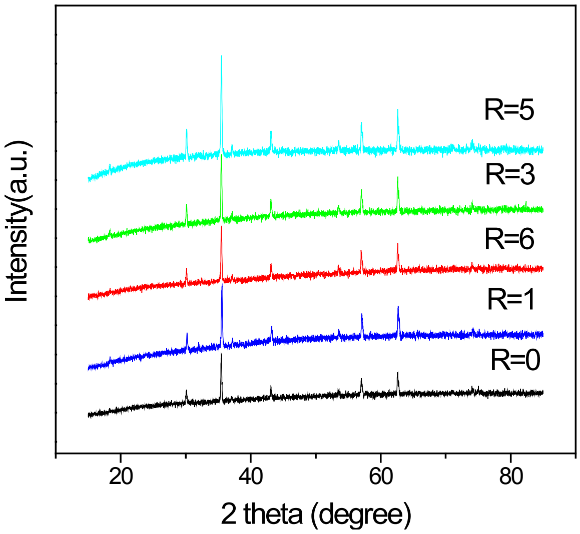


Fig. S5. XRD patterns of $CoFe_2O_4$ crystals prepared in NaCl/KCl (24 h precursors) with different mass ratio R=0, 1, 3, 5, 6.

Table S6. The main magnetic parameters precursor and samples after molten salt reaction

samples	Hc/(Oe)	σs/(emu/g)	σr/(emu/g)	σr/ σs
P4	661.51	66.97	17.59	0.263
P12	705.20	62.61	17.71	0.283
P24	773.80	58.60	17.55	0.299
MP4	252.20	74.17	18.16	0.245
MP12	248.70	75.53	19.40	0.257
MP24	298.60	81.06	25.41	0.313
MT700	957.07	68.44	28.47	0.416
MT800	563.29	79.17	37.98	0.480
MT1000	366.51	83.16	36.07	0.434
MT0.5	388.50	70.11	25.89	0.369
MT3	350.94	80.86	35.05	0.433
MT5	366.51	83.16	36.07	0.434
MR1	279.70	82.90	16.40	0.198
MR3	262.40	78.03	18.72	0.240
MR5	298.60	81.06	25.41	0.313
MR6	253.20	80.68	22.96	0.285
MNaF	323.79	35.33	12.98	0.367
MNaCl	334.79	81.46	26.34	0.323
MNaBr	496.06	85.40	25.93	0.304
MNaCl/KCl	298.60	81.06	25.41	0.313
MNa_2SO_4	380.87	88.08	26.56	0.302
MNaCl/Na_2O_4	349.73	71.53	21.37	0.299

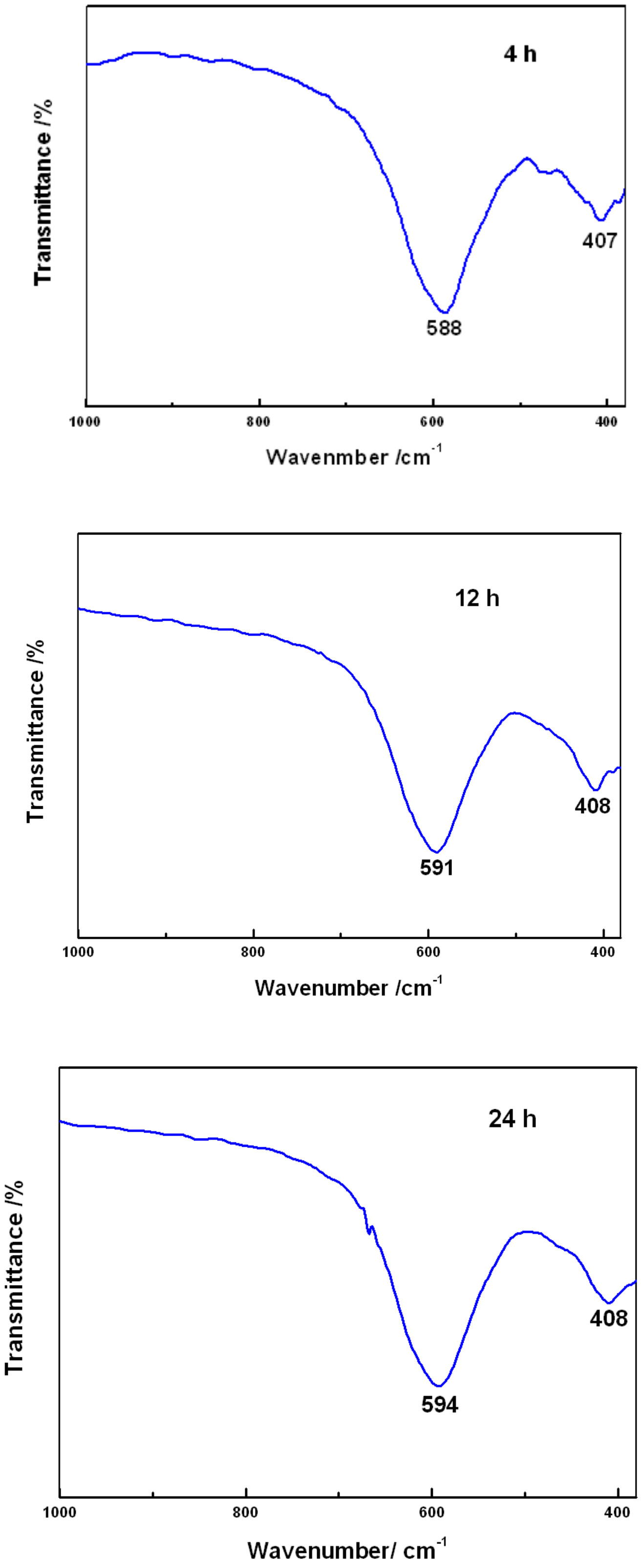


Fig. S7. FTIR spectra of precursors with different hydrothermal time.

Explanatory note：We probably determine the iron ions contents on A- and B-sites from the FTIR spectra of the precursors (see Fig. S7). The bands at 407 and 408 cm^{-1} are assigned to the vibration modes of octahedral groups (Fe^{3+}–O^{2-}), while bands at 588, 591 and 594 cm^{-1} are due to the stretching vibrations of the tetrahedral groups (Fe^{3+}–O^{2-}). Compared to the precursor that prepared through 4 h hydrothermal reaction, the band corresponding to A-sites for the precursors that prepared through 12 and 24 h hydrothermal reaction shift to high wave numbers. We all know that the ionic radius of Fe^{3+} is smaller than that of Co^{2+}, so the content of Fe^{3+} ions on A-sites increases with prolonging in hydrothermal time. However, the content of Fe^{3+} on B-sites changed slightly because no significant change can be found from the FT-IR. By above FT-IR results, we can estimate the content of Fe^{3+} ions on A and B-sites.

Magnetic properties can be evaluated non-quantitatively, because the distribution of metals ions on A- and B-sites decides the magnetic properties of $CoFe_2O_4$. The total magnetic moment ($\sigma s = \sigma_B - \sigma_A$) can be calculate by the magnetic moment on the B-sites (octahedral) minus subtract the A-sites (tetrahedral). The hydrothermal time affects directly the cationic distributions on A- and B-sites, from 4 to 24 h, the content of Fe^{3+} ions on A-sites increases, resulting in the high σ_A, however, σ_B do not obviously change. We can see that with extending time of hydrothermal treatment, σs decreased slightly.