Supporting Information

Precursor-directed synthesis of quasi-spherical barium ferrite particles with good dispersion and magnetic properties

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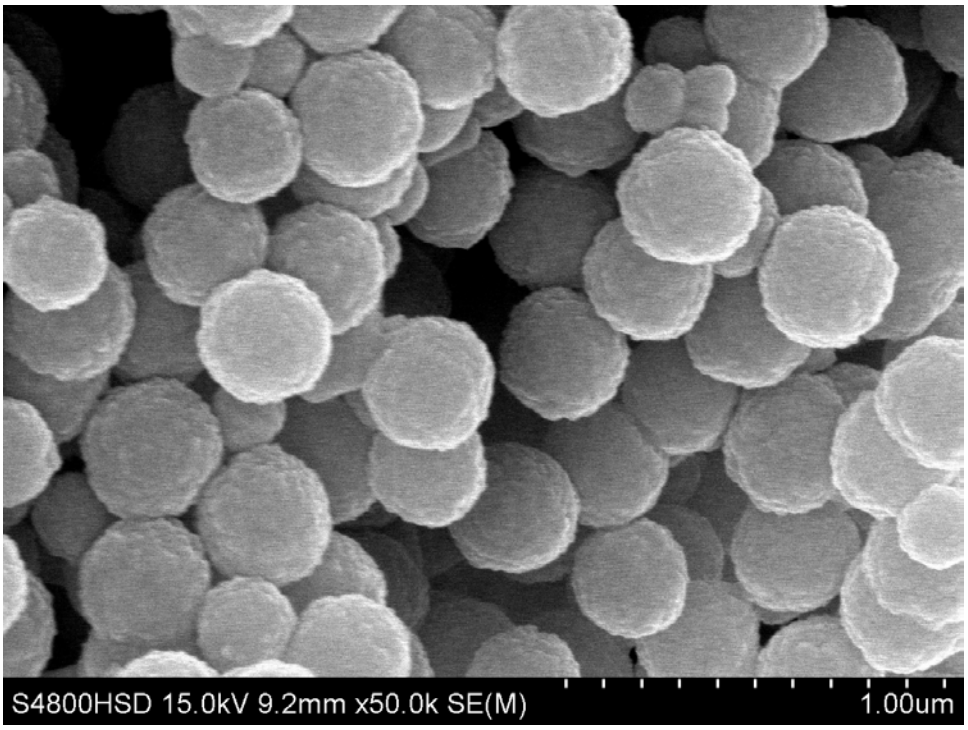

Figure S1 SEM image of the composite of $BaCO_3$ and Fe_3O_4.

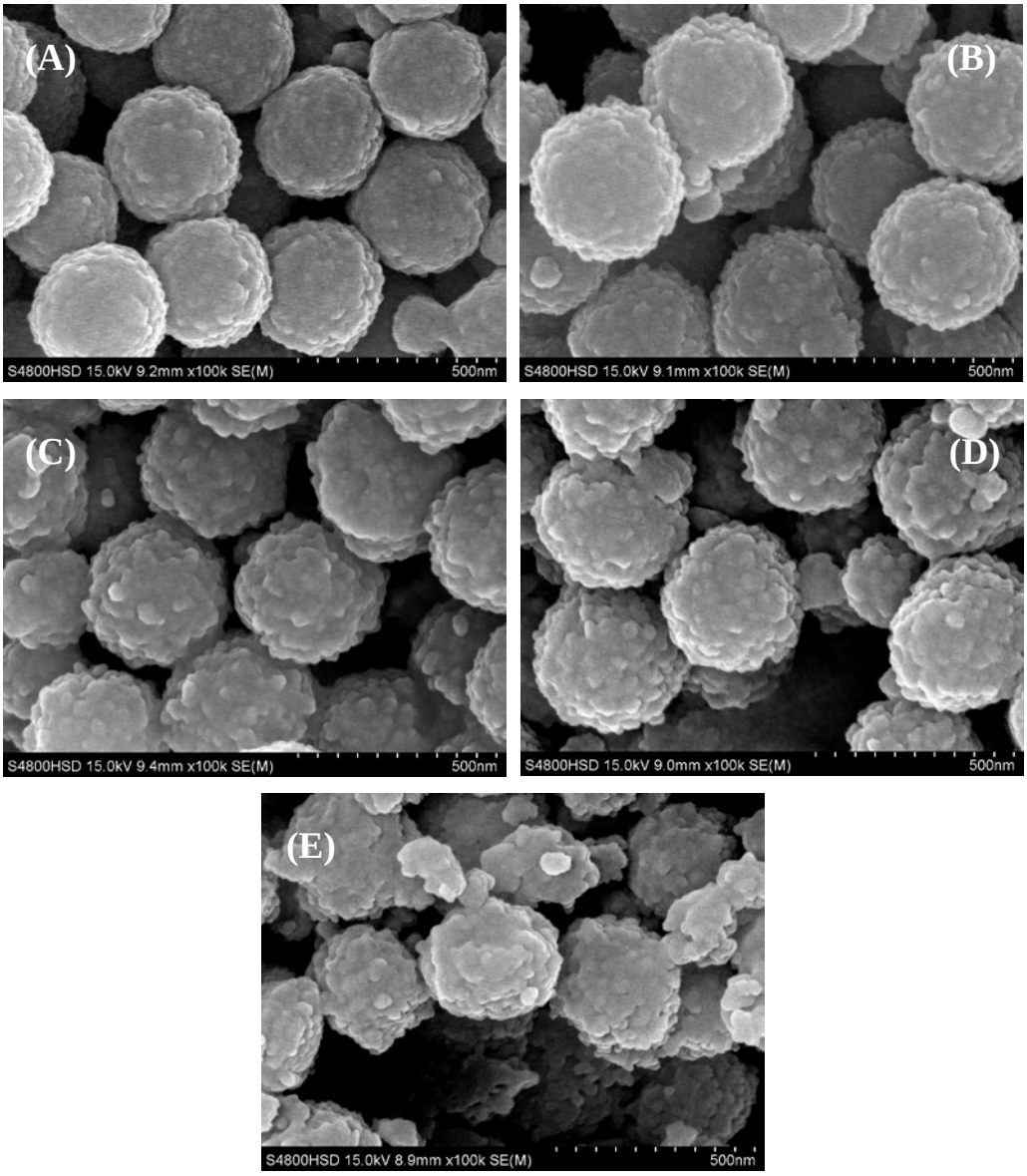

Figure S2 SEM images of Fe_3O_4 (A), $(CoTi)_{0.0625}Fe_{2.875}O_4$ (B), $(CoTi)_{0.125}Fe_{2.75}O_4$ (C), $(CoTi)_{0.1875}Fe_{2.625}O_4$ (D), and $(CoTi)_{0.25}Fe_{2.5}O_4$ (E).

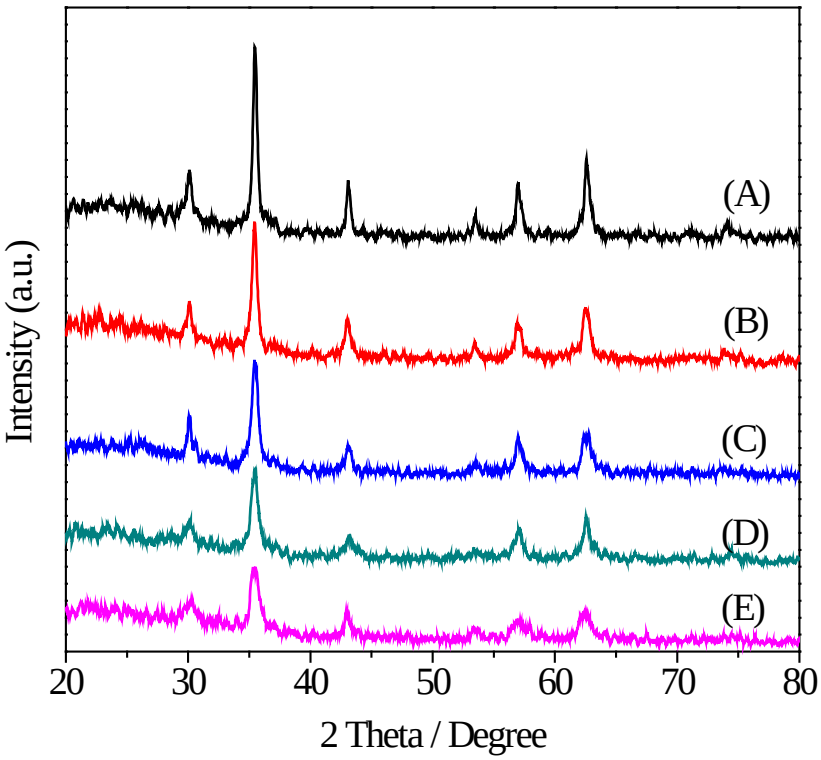

Figure S3 XRD patterns of Fe_3O_4 (A), $(CoTi)_{0.0625}Fe_{2.875}O_4$ (B), $(CoTi)_{0.125}Fe_{2.75}O_4$ (C), $(CoTi)_{0.1875}Fe_{2.625}O_4$ (D), and $(CoTi)_{0.25}Fe_{2.5}O_4$ (E).

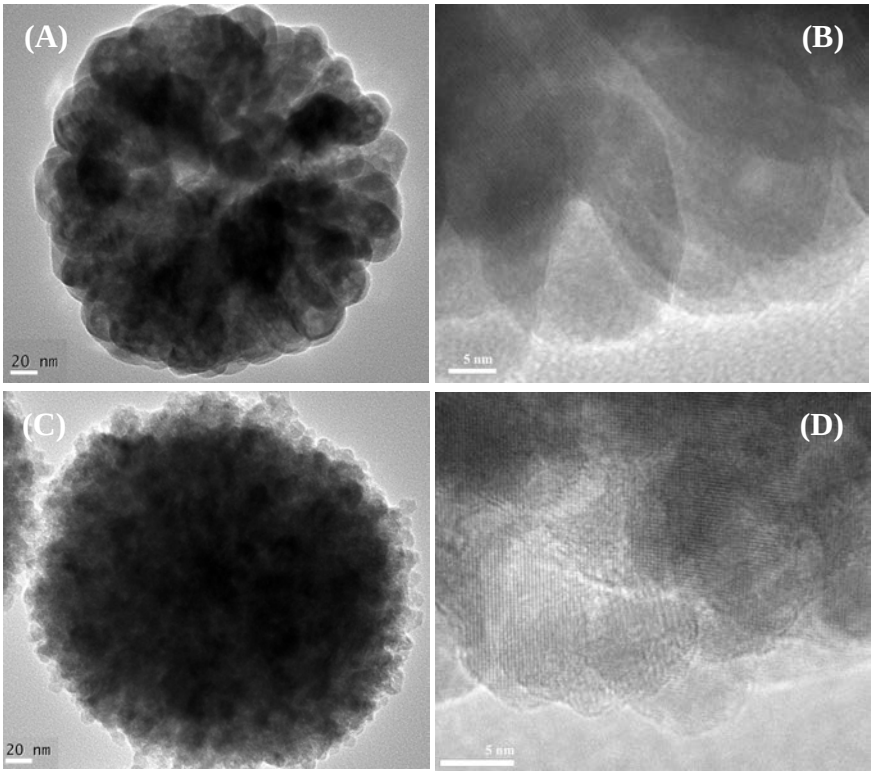

Figure S4 TEM images of Fe_3O_4 and $(CoTi)_{0.1875}Fe_{2.625}O_4$.

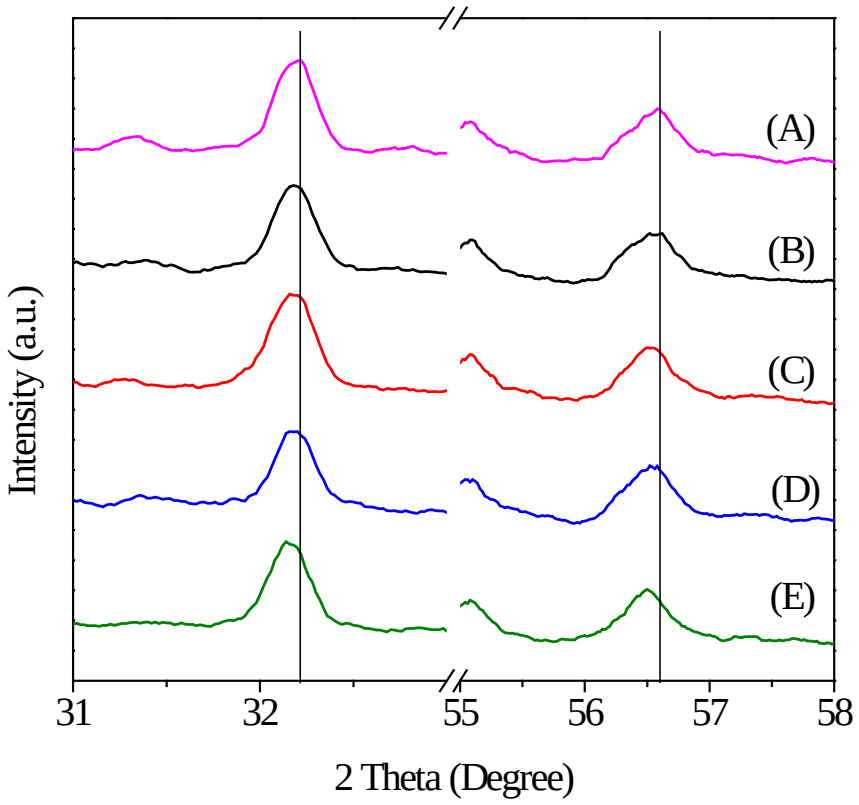

Figure S5 The local enlargement of XRD patterns of $BaFe_{12}O_{19}$ (A), $Ba(CoTi)_{0.25}Fe_{11.5}O_{19}$ (B), $Ba(CoTi)_{0.50}Fe_{11.0}O_{19}$ (C), $Ba(CoTi)_{0.75}Fe_{10.5}O_{19}$ (D), and $Ba(CoTi)_{1.00}Fe_{10.0}O_{19}$ (E).

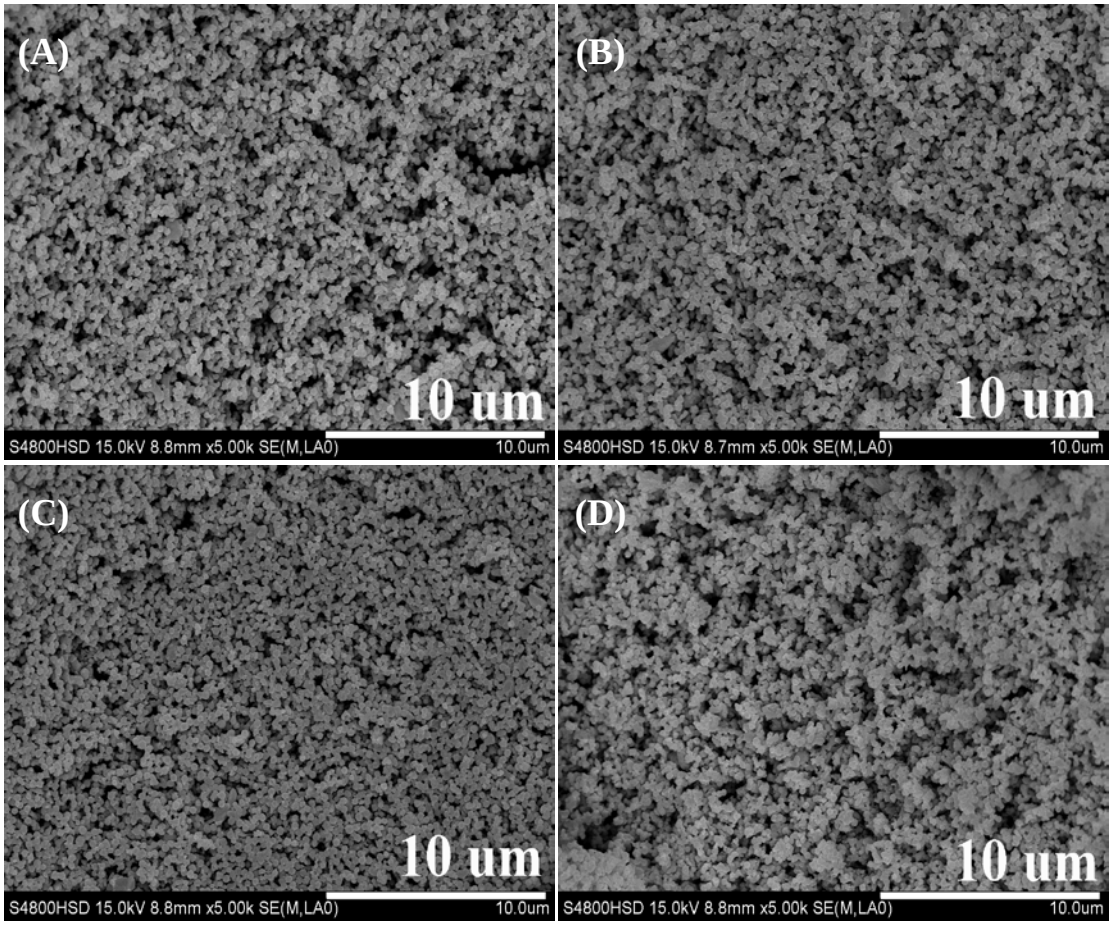

Figure S6 Low-magnification SEM images of $Ba(CoTi)_{0.25}Fe_{11.5}O_{19}$ (A), $Ba(CoTi)_{0.50}Fe_{11.0}O_{19}$ (B), $Ba(CoTi)_{0.75}Fe_{10.5}O_{19}$ (C), and $Ba(CoTi)_{1.00}Fe_{10.0}O_{19}$ (D).

To prove the uniform dispersion of barium, titanium and cobalt atoms in ferrite matrix, EDS taken by TEM is used to characterize the chemical composition of $Ba(CoTi)_{0.75}Fe_{10.5}O_{19}$ in different areas. As shown in Fig. S7 and Table S1, these areas show quite similar chemical composition, implying that Co^{2+} and Ti^{4+} prefer to enter the $BaFe_{12}O_{19}$ lattice rather than form separate oxides, which are coincident with the results of XRD.

It has to mention that the molar ratios of Fe/Co (avg. 11.9) and Fe/Ti (avg. 12.5) are close to those designed values (14.0), but the molar ratio of (Fe+Co+Ti)/Ba (avg. 6.85) is much lower than 12.0. According to previous work, a certain barium surplus is quite beneficial to yield barium ferrite particles with crystalline phase and improve magnetic properties (*J. Phys. Chem. C* 2007, *111*, 5866; *J. Alloys Compd.* 2005, *399*, 245), thus the ratio of Fe/Ba in barium ferrite materials always keeps between 10.0~11.0. In our typical case, 0.5 g Co-Ti substituted Fe_3O_4 microspheres and 0.153 g $Ba(NO_3)_2$ were ultrasonically mixed, and then the solvent was slowly evaporated and the resultant solid mixture was calcined at high temperature. That is to say, there is little loss for various metal species, and the molar ratio of (Fe+Co+Ti)/Ba should be close to 10.0~11.0 but not to 6.85. If the molar ratio given by TEM is true, there must be some other crystalline phase, such as $BaFe_2O_4$ and BaO (*J. Alloys Compd.* 2007, *428*, 17), while XRD does not show the existence of any other phases.

By considering that the overlapping of Ti peak and Ba peak may affect the results of EDS, thus we measure chemical composition of pure barium ferrite, as shown in Fig. S8 and Table 3-1. The results give the molar ratio of Fe/Ba at ~ 6.73, which is quite similar to the ratio of (Fe+Co+Ti)/Ba in $Ba(CoTi)_{0.75}Fe_{10.5}O_{19}$, indicating that the presence of Ti species does not impact the results of EDS. In order to make clear this issue, we also used EDS taken by SEM to characterize pure barium ferrite, as shown in Fig. S9. Interestingly, EDS of SEM gives similar Fe/Ba ratio from 10.2 to 10.6 in different areas, which is quite different from the results of TEM. Additionally, ICP result also shows that the molar ratio of Fe/Ba in pure barium ferrite is about 10.5. All results imply that the low Fe/Ba ratio in TEM is not true, and the reason may arise from the fact that the sensitivity factor for Ba atoms in our TEM is

on the high side. **Anyway, these results can prove that barium, titanium and cobalt atoms are highly dispersed in the ferrite matrix.**

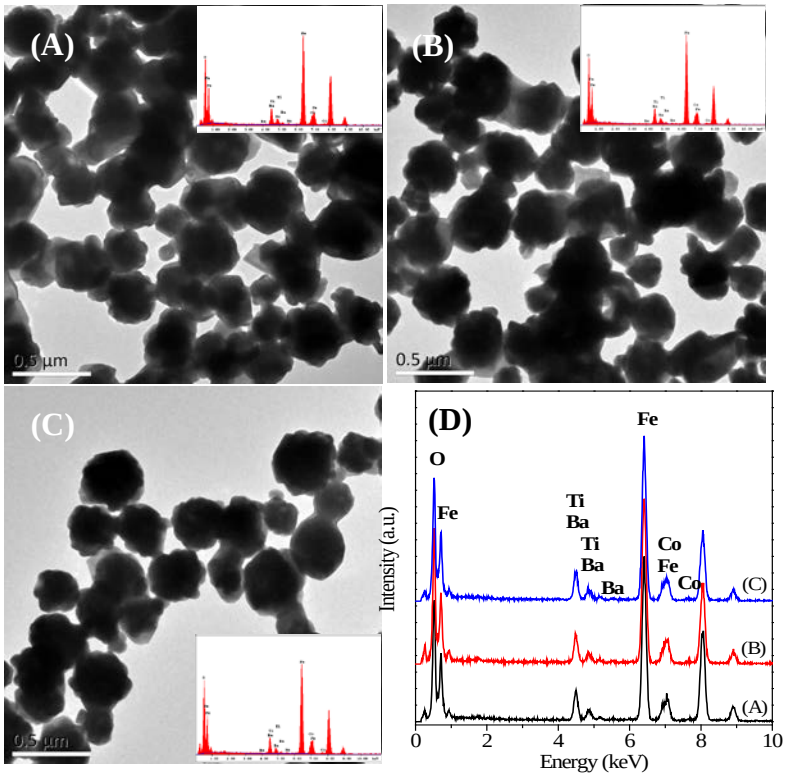

Figure S7 TEM images and EDS patterns of $Ba(CoTi)_{0.75}Fe_{10.5}O_{19}$ in different area (A~C), and normalized EDS patterns of different areas (D). The scale bar is 0.5μm.

Table S1 Chemical composition of different areas in $Ba(CoTi)_{0.75}Fe_{10.5}O_{19}$ and $BaFe_{12}O_{19}$.

Element	$Ba(CoTi)_{0.75}Fe_{10.5}O_{19}$			$BaFe_{12}O_{19}$	
	Area A	Area B	Area C	Area A	Area B
O (K)	51.2	51.1	51.3	50.5	51.3
Ba (L)	6.1	6.2	5.8	6.4	6.3
Ti (K)	2.9	2.9	2.9	-	-
Fe (K)	36.8	36.5	37.0	43.1	42.4
Co (K)	3.1	3.2	3.0	-	-
Total	100	100	100	100	100

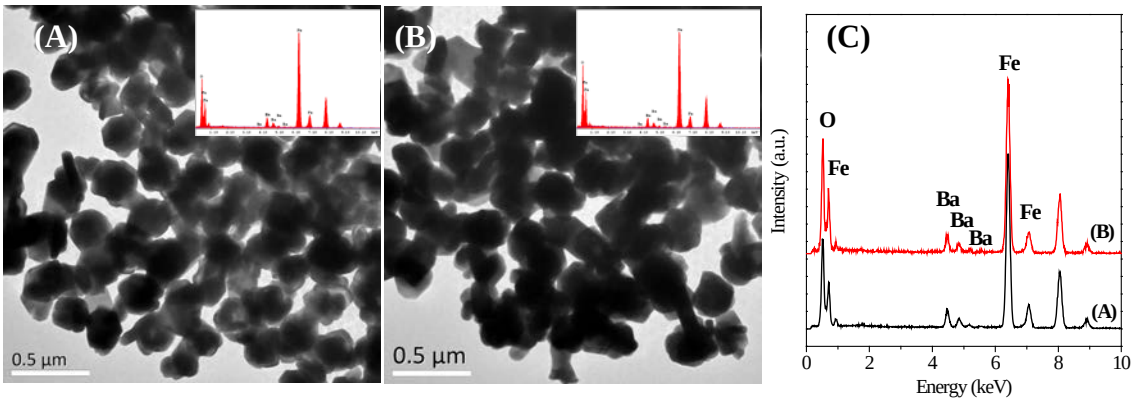

Figure S8 TEM images and EDS patterns of $BaFe_{12}O_{19}$ in different area (A and B), and normalized EDS patterns of different areas (C). The scale bar is 0.5μm.

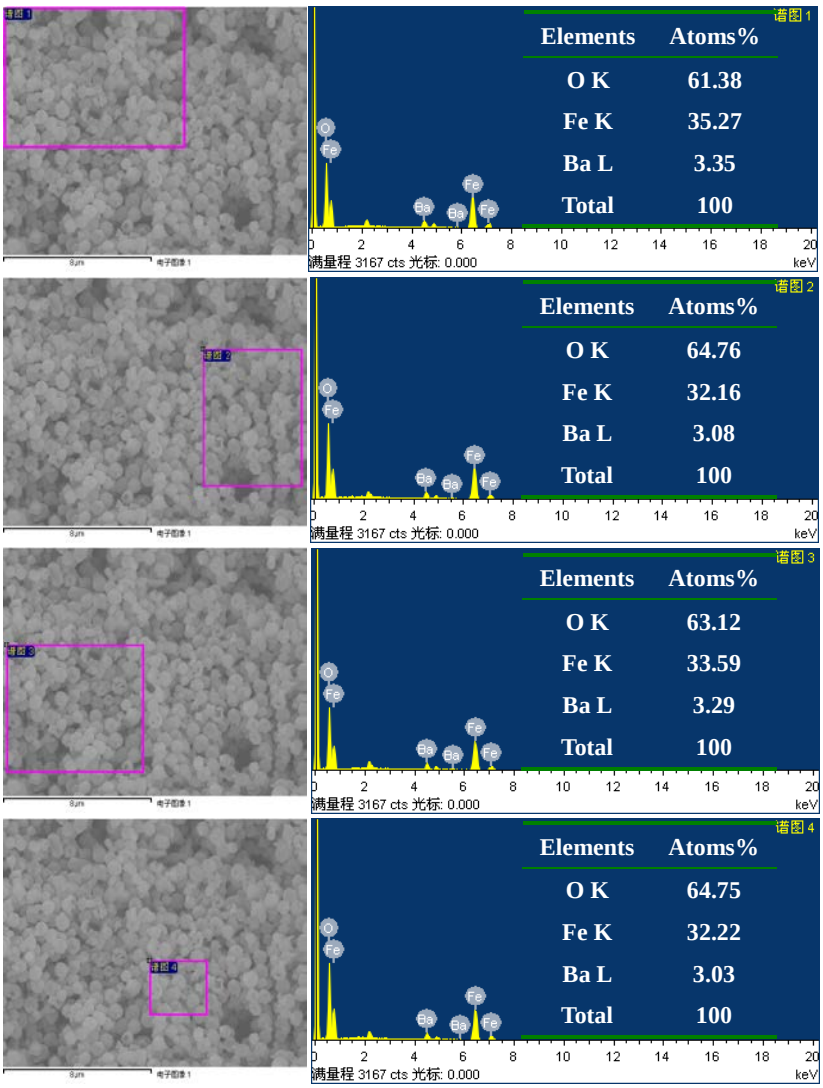

Figure S9 SEM images, EDS patterns and atoms percentage of $BaFe_{12}O_{19}$ in different area. The scale bar is 8μm.