Title: TiO_2/polymeric Supported Silver Nanoparticles Applied as Superior Nanocatalyst in Reduction Reactions

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Highlight

- This study focused on synthesis of tailored bi-magnetic clusters to induce unique magnetic characteristics for self-bias magnetoelectric (ME) composites.

- The self-bias magentoelectric effect is very promising phenomenon, which can provide a feasible ME voltage over 50 mV/cmOe under no-applied DC magnetic field.

- Two types of bi-magnetic materials were synthesized with magnetical combinations of ferromagnetic[FM]/ferrimagnetic[FiM] and ferromagnetic[FM]/antiferromagnetic[AFM] to induce built-in magnetic bias for large strain change at zero DC magnetic field.

- Size optimizations of clusters (over 100 nm) and primary particles (under 20 nm) were successfully conducted to enhance effective strain transfer in ME composites and to improve magnetic properties, respectively.

Hydrothermal Synthesis of Bi-magnetic Clusters for Magnetoelectric Composites

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Abstract

Bi-magnetic materials possess unique magnetic characteristics combining hysteretic and built-in responses for self-bias magnetoelectric applications. In this work, two bi-magnetic clusters of Co/MFe$_2$O$_4$(M=Co and Zn) were hydrothermally synthesized for relative comparison of magnetic characteristics between ferromagnetic/ferrimagnetic (Co/CoFe$_2$O$_4$) and ferromagnetic/antiferromagnetic (Co/ZnFe$_2$O$_4$) complexes. Both bi-magnetic clusters were found to exhibit clear two-phases with random morphology and average cluster size of 110 nm via physical complexation. Magnetic characteristics of the Co/CoFe$_2$O$_4$ and Co/ ZnFe$_2$O$_4$ illustrated M-H slope of 0.02 emu/g· Oe at H_{dc} = 0 Oe with different remanent magnetization of 15.16 emu/g and 0.22 emu/g, respectively. As a magnetostritive phase in the magnetoelectric composites, two bi-magnetic clusters were formed with uniform cluster size for effective strain transfer between magnetostrictive-piezoelectric phases in the magnetoelectric system.

Keywords: Bi-magnetic, Clusters, Magnetostriction, Self-bias, Magnetoelectric

Introduction

Magnetoelectric effect is one candidate among several promising phenomena for effective energy harvesting, which can induce an electrical voltage by applying a bias magnetic field. The magnetoelectric responses were fundamentally obtained by applying a small AC magnetic field (H_{ac} = 1 Oe) under constant DC magnetic field, which can cause a reliable electrical displacement with effective strain change in magnetoelectric materials. Therefore, many research groups have attracted the magnetoelectric effect to develop potential applications such as transducers, magnetic/electric sensors, memory storage devices and even medical devices. [1, 2]

In recent, the magnetoelectric materials have been studied with two-phase composites consisting piezoelectric and magentostrictive materials respectively due to strong piezoelectricity and magentostriction given by each separated phase. The multi-phase magnetoelectric composites (PZT/$CoFe_2O_4$, $BaTiO_2$/$La_xBa_{1-x}MnO_4$, PZT/Ni/PZT) were found to exhibit high magnetoelectric coefficients of ~ 500 mV/cm·Oe under a bias magnetic fields by an optimum complexation of large strain change at magnetostrictive phase and high piezoelectric property at piezoelectric phase. [2] Further, focused studies on effective strain transfer at interface between magentostrictive and piezoelectric phases have been performed for ME enhancement via microstructure investigation, post heat treatment and hardness control of interfacial rooms respectively in each type of 3-0, 2-2 and 1-3 composite structures. [3-6]

Even though magnetoelectric voltage improvement have been successfully conducted, there is still a critical issue to be used in magnetoelectric applications, which is related with a required driving force of DC magnetic field over 100 Oe. That means the magnetoelectric responses cannot be obtained due to its non-effective strain change ($\Delta\lambda/\Delta H_{ac}$) at low DC magnetic field under 100 Oe even if AC magnetic field was applied with constant magnitude of H_{ac} = 1 Oe, f = 1 kHz. Yang et al reported a feasible characteristic of self-bias magnetoelectric effect, which is a remanent magnetoelectric responses under applying AC magnetic field (H_{ac} = 1 Oe, f = 1 kHz) at zero DC magnetic field. [7] They have revealed that reliable magnetoelectric responses were existed with meaningful magnetoelectric magnitudes of 20 mV/cm·Oe from an effective strain change ($\Delta\lambda/\Delta H_{ac}$) generated by coupling effect between structural bending configuration and built-in magnetic bias field ($H_{built-in}$). [7-9] Herein, exchanging bias of adjusting magnetic hysteresis have been developed via applying graded system between ferromagnetic and antiferromagnetic materials. [10, 11] Moreover, impact researches on shift of optimum DC magnetic field have been investigated to obtain feasible magnetoelectric voltage at low DC magnetic field under 100 Oe. [12, 13]

In this study, we have investigated magnetic properties of bi-magentic clusters for self-bias magnetoelectric applications, which require effective strain changes under a limited driving condition of small AC magnetic field ($\Delta\lambda/\Delta H_{ac}$). The bi-magnetic clusters consisting antiferromagnetic (AFM), ferromagnetic (FM) and ferrimagnetic (FiM) complexations can contribute variation of built-in magnetic bias field ($H_{built-in}$). Further, particle size of magnetic cluster with sub-micron (0.1 ~ 0.4 μm) provides an effective transfer of magentostriction into piezoelectric phase. Therefore, we have hydrothermally synthesized and investigated tailored bi-magnetic clusters through two compositional combinations of Co[FM]/$CoFe_2O_4$[FiM] and Co[FM]/$ZnFe_2O_4$[AFM] as a magnetostrictive phase for self-bias magnetoelectric composites.

Experimental

Synthesis of cobalt nanoparticles: All reagents of $Co(NO_3)_2\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, $Fe(NO_3)_3\cdot 9H_2O$ $CoCl_2\cdot 6H_2O$, $NaBH_4$, NaOH were purchased from Sigma Aldrich Inc. Cobalt nanopowders were synthesized at ambient condition via reduction method. [14] First, 2g $CoCl_2·6H_2O$ was completely dissolved in 100 ml deionized water and then 1g $NaBH_4$ was added in the aqueous solution. $NaBH_4$ was added over 5 times owing to explosive reaction. After hydrogen emission stopped, a gray–black powders were collected by strong magnet. The powders were washed with deionized water and ethanol for several times to eliminate other impurities and then were collected by centrifuge at 15000 rpm for 2h. Finally, the cobalt powders were obtained after drying at 80℃ for 48h.

Synthesis of bi-magnetic clusters: Bi-magnetic clusters of $Co/CoFe_2O_4$ were synthesized by hydrothermal synthesis. [15] 1mmol $Co(NO_3)_2·6H_2O$ and 2mmol $Fe(NO_3)_3·9H_2O$ were dissolved in 10ml deionized water (molar ratio, Co:Fe = 1:2). Then pH of the solution was adjusted to pH~12 by drop-wise of 10M during virgours stirring. After stirring for 1 h, prepared Co powders 0.1178g(2mmol) were added in viscous solution and the mixed solution was sonicated for 10 min to prevent aggregation. The mixed solution was sealed in 20ml Teflon lined stainless steel autoclave and heated at 200℃ for 8h. After hydrothermal reaction, it was cooled at room temperature. Then the precipitates were washed with deionized water and ethanol for several times to decrease pH~7. The washed precipitates were centrifuged and dispersed in ethanol and dried at 80℃ for 48h. In the same process, bi-magnetic clusters of $Co/ZnFe_2O_4$ were hydrothermally synthesized with molar ratio (Zn : Fe = 1 : 2).

Characterizations: Crystallinity and crystal structure of the synthesized bi-magenetic clusters were observed by X-Ray diffraction (XRD; Miniflex600(Cu Kα radiation = 1.5406Å), RIGAKU) analysis. Fe-O bonds in the bi-magenetic clusters were confirmed by Fourier transform infrared spectra (FTIR; 4600 type A, JASCO) analysis. Primary particle size andmorphology of the bi-magnetic clusters were investigated by Transmission electron microscope (TEM; JEM 2010, 200kV, JEOL/Energy-dispersive X-ray spectroscopy, EDS; Oxford instruments co.) analysis. Average size and size uniformity of the bi-magenetic clusters were investigated under deionized water as media by dynamic light scattering measurement (Particle Size Analyzer; PSA, Multiscope, K-ONE). Magnetic properties of two bi-magenetic clusters were determined at room temperature using vibration sample magnetometer (VSM; 7404, Lake shore).

Results & Discussion

Crystal structures of Co, Co/CFO and Co/ZFO powders were identified by XRD patterns shown in Figure 1. XRD peak of the Co particles were observed in a broad region around 45°, which might be merged from two Co crystal structures confirmed by face centered cubic (111) at 38^o and hexagonal close packed (101) at 47^o (*fcc* Co, PDF Card No.: 00-015-0806, JCPDS and *hcp* Co, PDF Card No.: 01-089-4308, JCPDS). [14] The two bi-magnetic clusters of Co/CFO and Co/ZFO were found to exhibit 1st peak (311), 2nd peak (440) and 3rd peak (220) ($CoFe_2O_4$, PDF Card No.: 01-079-1744, JCPDS and $ZnFe_2O_4$, PDF Card No.: 01-077-0011, JCPDS) corresponding to spinel structure. Even though the bi-magnetic clusters include Co particles, Co peak disappeared in Fig 1 (b) and (c) due to its low crystallinity.

FT-IR analysis between 400 and 4000 cm^{-1} was conducted to confirm chemical or physical bonding between magnetostrictive phases in the two clusters of Co/CFO and Co/ZFO as shown in Figure 2. Since the spinel structure is normally composed of two site with tetrahedral and octahedral site, it is unambiguously observed two peaks of divided into Fe-O, Metal-O bands due to their different vibration bands. [16] The most important peaks are strong Fe-O band of symmetrical stretching vibration at tetrahedral site 579cm^{-1} and 586cm^{-1} in Co/CFO(blue line) and Co/ZFO(green line), respectively. All broad peaks at 3396, 3401, 3423 cm^{-1} are O-H stretching vibrations. The peaks at 2921cm^{-1}, 1631 cm^{-1}, 1384 cm^{-1} and 1068 cm^{-1} indicate sp^{3}C-H stretch, C=O stretch, C-H bend, C-O bonding, respectively.

Primary particle size and morphology of the synthesized Co, Co/CFO and Co/ZFO powders were investigated by TEM analysis. Figure 3 (a) and (b) illustrates that the as-prepared Co particles were found to exhibit particle size of 20 ~ 80 nm with weak selected area electron diffraction (SAED) image related to its low crystallinity. EDS analysis shown in Figure 3 (c) exactly described that the as-prepared Co particles were consist of pure Co ions without any impurities. The hydrothermally synthesized bi-magnetic clusters of Co/CFO and Co/ZFO were found to exhibit no impurities, random morphology as a cluster and spinel crystal structure with clear ring SAED patterns of (311), (440) and (220) as shown in Figure 3 (d) ~ (i). Table 1 illustrates that Co, CFO and ZFO after hydrothermal synthesis for bi-magnetic clusters were found to exhibit average primary particle sizes of 45 nm (standard deviation 19 nm), 16 nm (standard deviation 4 nm) and 9 nm (standard deviation 4 nm) respectively but average cluster size cannot be measured due to its local scope region.

Dynamic light scattering measurement was performed under deionized water as media to observe average cluster size of the synthesized Co/CFO and Co/ZFO clusters. It was inferred that Co/CFO and Co/ZFO clusters have sufficient stability in deionized water illustrating reliable results of average size and size distribution during dynamic light scattering measurement for 30 minute. Figure 4 shows that average cluster sizes of Co/CFO and Co/ZFO bi-magnetic clusters were found to exhibit cluster size of 110 nm, which is smaller than 121 nm of Co particles. The reason might be that the Co particles have aggregated form due to its stronger attraction of metallic natures in deionized water compared with mixed bi-magnetic clusters of Co/CFO and Co/ZFO.As shown in figure 4 (b) and 4 (c), it was described that the Co/ZFO bi-magnetic clusters have narrow size distribution with suppressed particle aggregation over 1μm size compared with the Co/CFO clusters. That is very important roles for effective magnetoelectric composites because micron-sized magnetic particles disturb effective magnetoelectric coupling between piezoelectric and magnetostrictive phases. [17]

Magnetic properties of bi-magnetic clusters were investigated by VSM analysis. From the Figure 5, highlight point for self-bias magnetoelectric effect is a sharp slope($\Delta M/\Delta H$) at H_{dc} = 0 Oe, which induces strong deformation from bi-magnetic materials under only applying H_{ac} = 1 Oe, f = 1 kHz.[18] That makes a large strain change transferring to piezoelectric phase, which directly related to root $\Delta\lambda/\Delta H$ inducing self-bias magnetoelectric effect. The Co/CFO [FM/FiM] and Co/ZFO [FM/AFM] bi-magnetic clusters possess M-H slope of 0.02 emu/g·Oe at H_{dc} = 0 Oe with remanent magnetization of 15.16 emu/g and 0.22 emu/g, respectively. In order to induce self-bias magnetostriction from magnetoelectric composites, bending configuration will be required due to shifting strain-stress curve to make asymmetric strain. Hence, the synthesized bi-magnetic clusters are very promising candidates for self-bias magnetostriction for magnetoelectric applications.

Conclusion

In this study, two bi-magnetic clusters of Co/CFO [FM/FiM] and Co/ZFO [FM/AFM] were hydrothermally synthesized as a magnetostrictive phase for self-bias magnetoelectric composites. The bi-magnetic clusters were found to exhibit clear two-phases with random morphology by physical complexation. The Co/CFO and Co/ZFO bi-magnetic clusters were found to exhibit M-H slope of 0.02 emu/g·Oe at H_{dc} = 0 Oe and different remanent magnetizations of 15.16 emu/g and 0.22 emu/g, respectively. Both bi-magnetic clusters with uniform submicron cluster size can be used as magnetostrictive phase in magnetoelectric composites by inducing effective strain transfer between magnetostrictive-piezoelectric phases. In particular, high M-H slope at H_{dc} = 0 Oe in both bi-magnetic clusters can provide a potential to generate self-bias magnetoelectric effect.

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Fig. 1 X-ray diffraction patterns of (a) as-prepared Co particles, (b) Co/CFO clusters and (c) Co/ZFO clusters.

Fig. 2 FT-IR spectra of as-prepared Co particles (red), Co/CFO clusters (blue) and Co/ZFO clusters (green).

Fig. 3 TEM images, SAED patterns and EDS analysis of (a-c) as-prepared Co particles, (d-f) Co/CFO clusters and (g-i) Co/ZFO clusters.

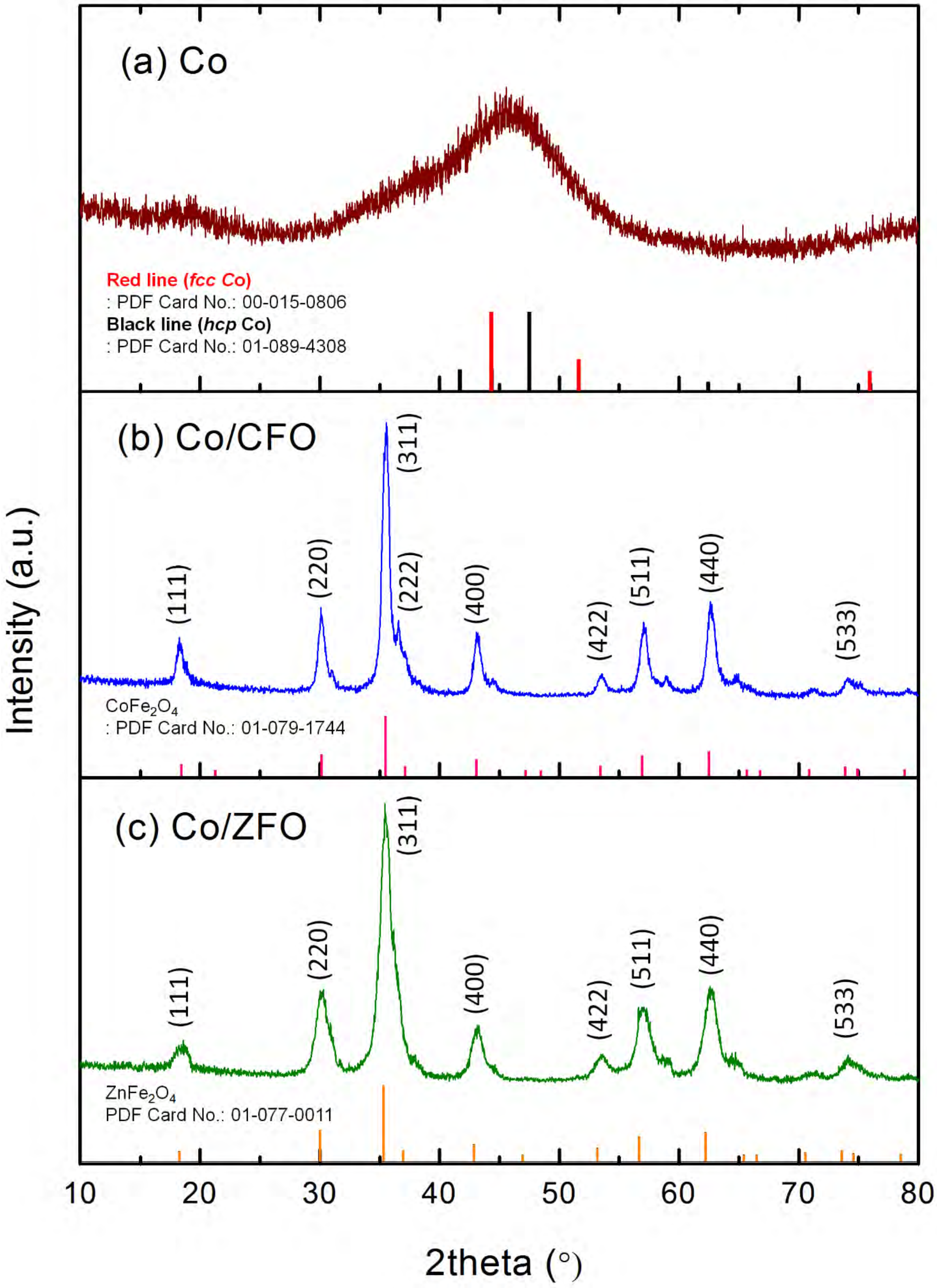
Fig. 4 Dynamic light scattering analysis of (a) as-prepared Co particles, (b) Co/CFO clusters and (c) Co/ZFO clusters.

Fig. 5 M-H curves of (a) as-prepared Co particles, (b) Co/CFO clusters and (c) Co/ZFO clusters.

Table 1 Average, minimum, maximum and standard deviation of crystalline size of as-prepared Co particles, Co/CFO clusters and Co/ZFO clusters.

	Co	**CFO**	**ZFO**
Avg. Crystalline Size (nm)	45	16	9

Min. Crystalline Size (nm)	24	12	5
Max. Crystalline Size (nm)	77	17	10
Standard Deviation (nm)	19	4	4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Red line (fcc Co)
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Black line (hcp Co)
: PDF Card No.: 01-089-4308
(b) Co/CFO
(111)
(220)
(311)
(222)
(400)
(422)
(511)
(440)
(533)
CoFe2O4
: PDF Card No.: 01-079-1744
(c) Co/ZFO
(111)
(220)
(311)
(400)
(422)
(511)
(440)
(533)
ZnFe2O4
PDF Card No.: 01-077-0011
Intensity (a.u.)
10
20
30
40
50
60
70
80
2theta (°)

Figure. 1 | X-ray diffraction patterns of (a) as-prepared Co particles, (b) Co/CFO clusters and (c) Co/ZFO clusters.

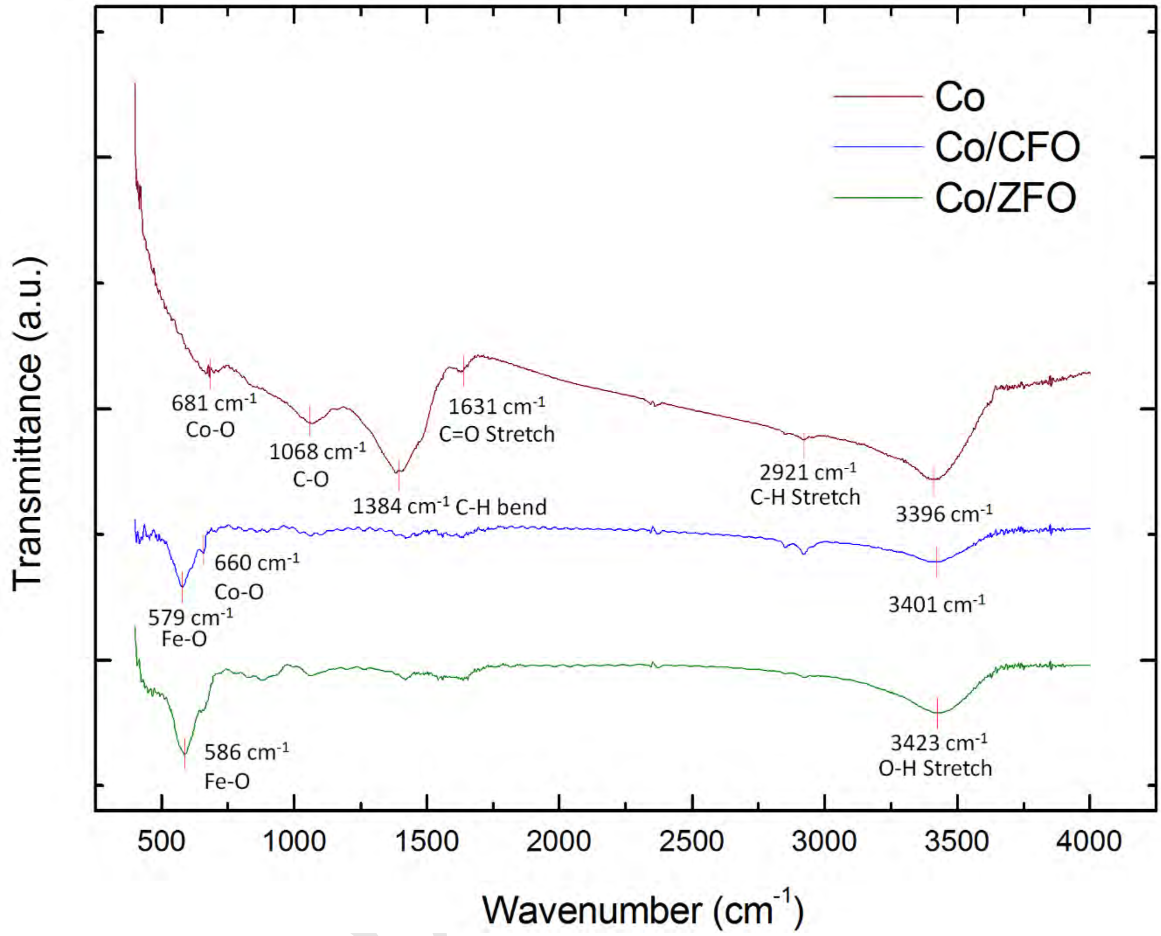

Figure. 2 | FT-IR spectra of as-prepared Co particles (red), Co/CFO clusters (blue) and Co/ZFO clusters (green).

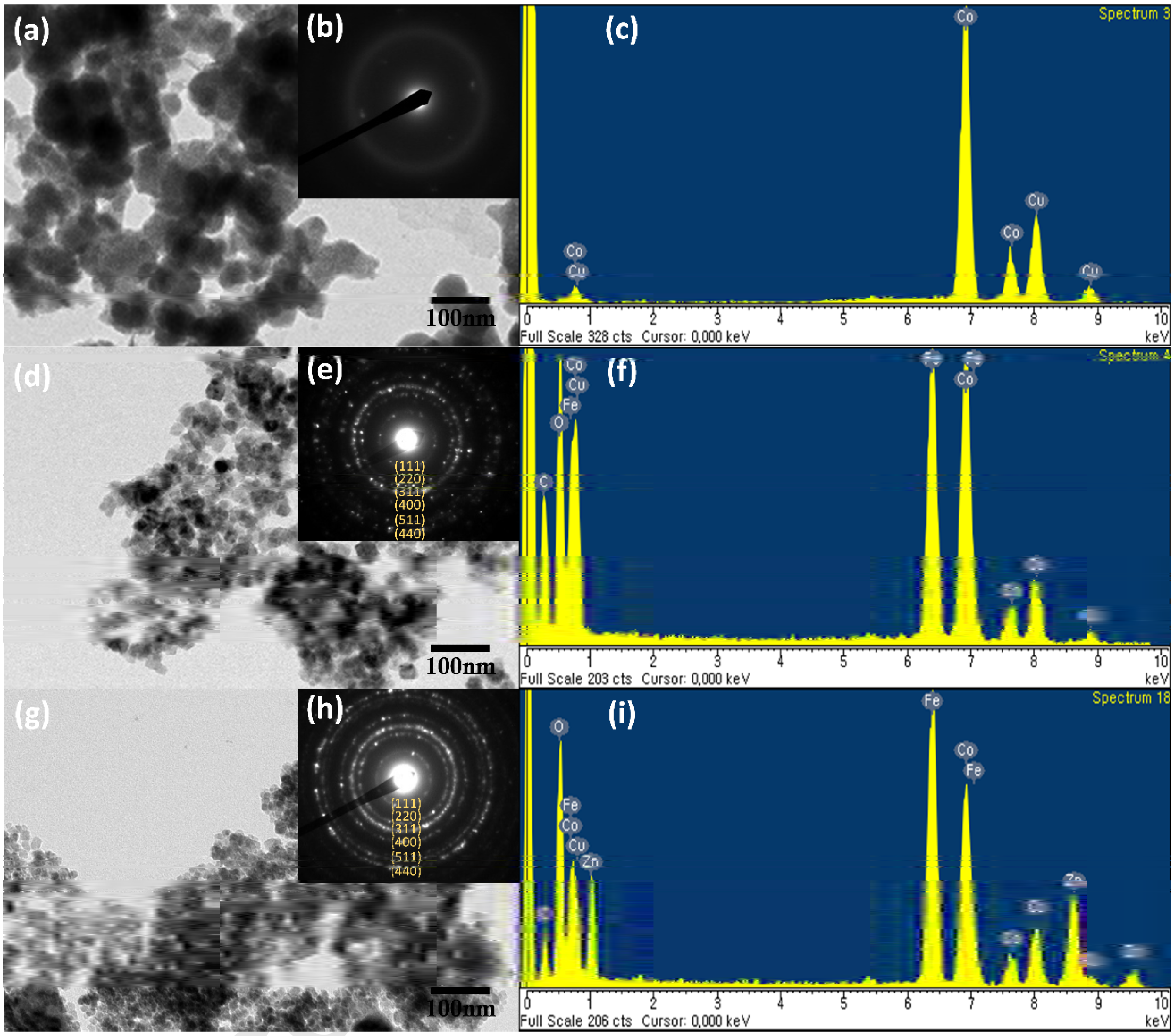

Figure. 3 | TEM images, SAED patterns and EDS analysis of (a-c) as-prepared Co particles, (d-f) Co/CFO clusters and (g-i) Co/ZFO clusters.

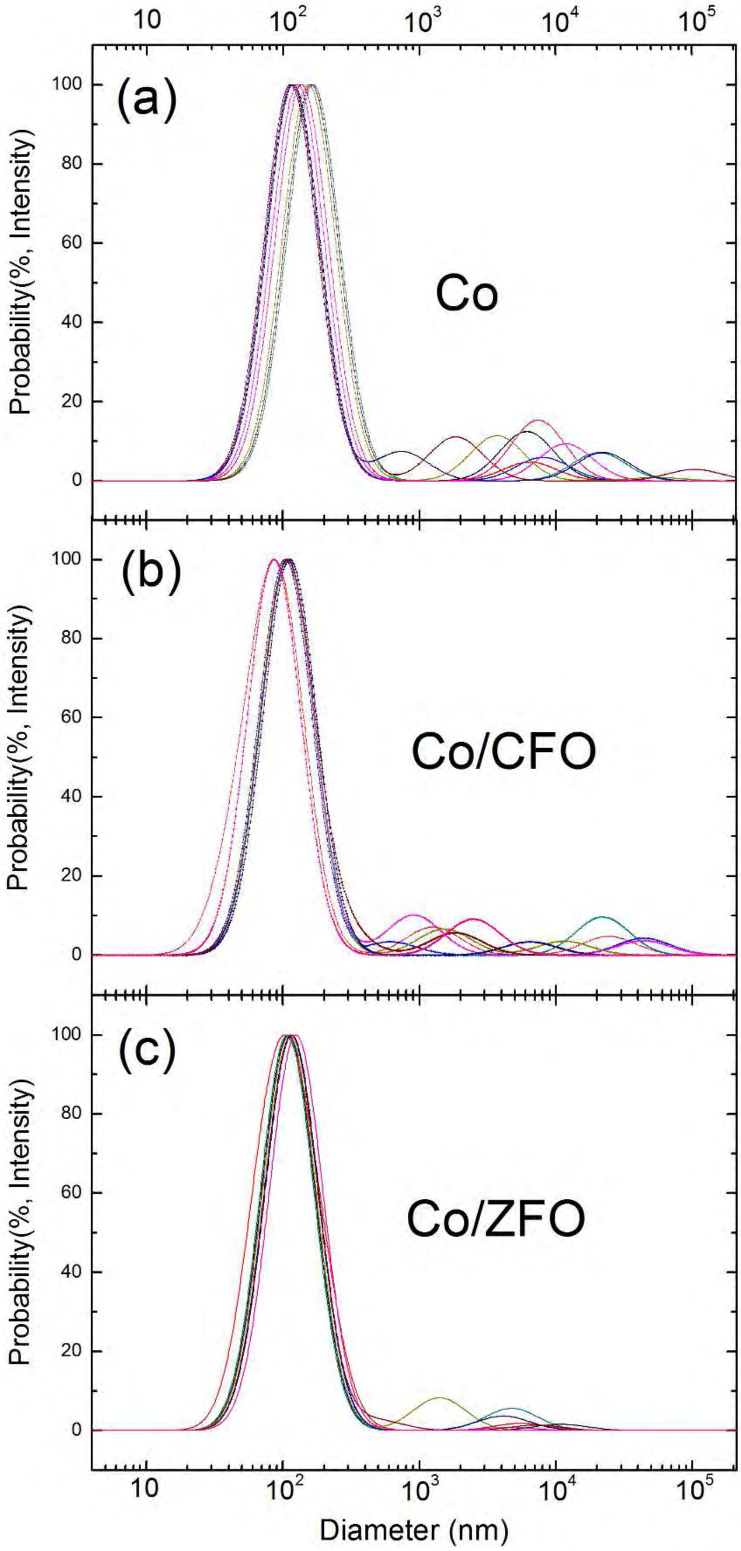

Figure. 4│ Dynamic light scattering analysis of (a) as-prepared Co particles, (b) Co/CFO clusters and (c) Co/ZFO clusters.

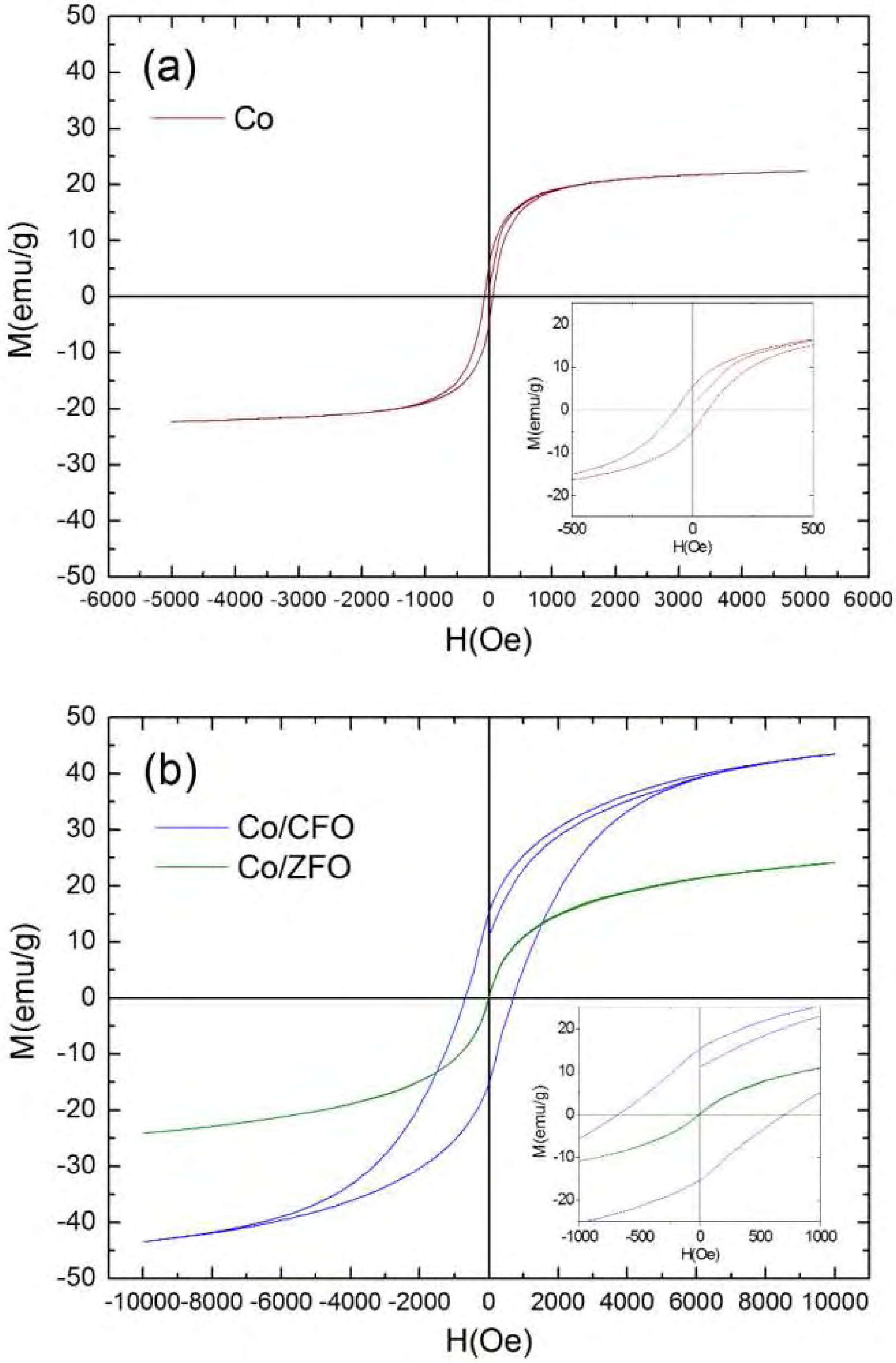

Figure. 5│M-H curves of (a) as-prepared Co particles, (b) Co/CFO clusters and (c) Co/ZFO clusters.