

Electronic Supporting Information

Gd³⁺ doped CoCr₂O₄ nanoparticles: Tuning of physical properties and optimizing the hyperthermia efficacy

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Synthesis of chromite nanoparticles

The preparation of Gd-doped nanocrystalline Co-chromite (CCO) nanoparticles involved the use of a conventional co-precipitation method.^{1,2} The chemical composition of the nanoparticles was denoted as CoCr_{2-x}Gd_xO₄, where x varied (0.00, 0.04, 0.08, and 0.12). High-purity chemicals, namely Co(NO₃)₂·6H₂O, Cr(NO₃)₃·9H₂O, and Gd(NO₃)₃·6H₂O were used without additional purification in the synthesis process. The chemical reagents used for nanoparticle preparation in their respective molar concentration are shown in the table below

Chemical reagents	Molar concentration
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	(mM)
Co(NO ₃) ₂ .6H ₂ O	25
Cr(NO ₃) ₃ .9H ₂ O	50
Gd(NO ₃) ₃ .6H ₂ O	50
NaOH	50

These chemicals, in stoichiometric quantities, were dissolved in 200 ml of distilled water. The resulting solution in the beaker underwent continuous stirring on a magnetic stirrer at 700 rpm to achieve homogeneity. The precipitating reagent, sodium hydroxide (NaOH) solution, was added drop-wise under identical stirring conditions to raise the mixture's pH to 11, facilitating precipitation. After reaching a pH of 11, the solution was digested for two hours at a constant temperature of 80°C with continuous stirring to ensure complete reaction. The mixture was then cooled to room temperature and washed multiple times with distilled water and methanol to achieve a neutral pH of 7. The resulting precipitate was air-dried and ground into a fine powder. Subsequently, the pure and doped powder samples underwent calcination at 500°C for 5 hours in a furnace to enhance nanocrystallinity. To prevent quenching effects during calcination, the furnace temperature was raised to 500°C, maintained for 5 hours, and then gradually lowered. The prepared samples were named Gd-00 (CCO), Gd-04 (CCO), Gd-08 (CCO), and Gd-12 (CCO) corresponding to increasing percentages of Gd ions. The prepared chromite samples were subjected to various characterizations.

Characterization techniques

The physical characterizations of the Gd-doped Co-Chromite samples were comprehensively conducted using various techniques. The room temperature XRD profiles were obtained with a Bruker D8 Advance powder X-ray diffractometer employing Cu-K α radiation (wavelength

1.5406 Å). The powder samples were scanned at a rate of 0.02°/sec over the range of 20° to 80°. The X-ray diffractometer operated at 40 kV voltage and 40 mA current. Morphology, shape, and mean size of both pristine and doped ferrite nanoparticles were investigated through HRTEM (JEM-2100F, JEOL, Japan), operating at an accelerating voltage of 200 kV. FTIR spectra for all samples were recorded at 300 K using the Perkin-Elmer FTIR spectrophotometer. Room temperature vibrational Raman active modes were identified using a Raman spectrometer (Renishaw, UK) within the span of 100-1000 cm⁻¹ with a monochromatic laser (473 nm). Magnetic properties at different temperatures were measured using a SQUID (Quantum design) magnetometer. The specific surface area of each sample was determined through N₂ adsorption-desorption isotherms utilizing the Brunauer–Emmett Teller (BET) method with the Quanta chrome iQ auto sort analyzer, USA. Average pore size was assessed using the Barrett–Joyner–Halenda (BJH) approach. For additional characterizations, including absorption data, antibiotic degradation, antioxidant properties, and antidiabetic activities, a UV DRS spectrometer (UV-2550, Shimadzu, USA) was employed. Dielectric properties were investigated at room temperature for all prepared samples using an LCR meter (HIOKI, IM 3536). Hyperthermia application was tested for all synthesized chromite samples through an induction heating experiment using Ambrell equipment (Scottsville, USA).

Measurement of dielectric properties

Impedance spectroscopy (Novocontrol, Alpha) was employed to acquire both the AC conductivity and dielectric characteristics of each sample at room temperature. The dielectric properties were measured at 300 K within a frequency range of 4 Hz to 10 MHz. Utilizing the samples in powder form, thin circular pellets with a diameter of 13 mm were created for the measurements.³ To ensure proper contact, all pellets were coated with silver paste on both sides. Furthermore, dielectric measurements of the entire chromite samples were conducted using the prepared pellets.

Induction heating experiment

The efficacy of the synthesized chromite samples for hyperthermia applications was assessed through induction heating. Each synthesized chromite sample, at a consistent concentration of 1 mg/ml, was dispersed in distilled water and positioned at the center of a solenoid having a specified diameter and number of turns. The induction heating data for all samples were collected at 300 K, applying an AC magnetic field with a frequency of 337 kHz and an amplitude of 14.92 kA/m.³

Sample-Id	Gd-00 (CCO)	Gd-04 (CCO)	Gd-08 (CCO)	Gd-12 (CCO)
Space group	<i>Fd-3m</i>	<i>Fd-3m</i>	<i>Fd-3m</i>	<i>Fd-3m</i>
Unit cell parameters				
a (Å)	8.332	8.346	8.353	8.359
Density (g/cm³)	5.211	5.332	5.449	5.584
D (nm)	18.2 ± 0.1	7.6 ± 0.1	7.1 ± 0.1	6.8 ± 0.1
Compressive microstrain (X 10⁻³)	0.31	1.81	1.88	1.72
Refinement parameters				
R_{wp} (%)	2.63	2.32	2.33	2.29
R_p (%)	2.03	1.78	1.82	1.77
χ²	1.08	1.03	1.11	1.07

Table S1. Displays unit cell parameters and refinement parameters of all the samples

Sample-Id	r_A (Å)	r_B (Å)	a_{th} (Å)	u	L_A (Å)	L_B (Å)
Gd-00 (CCO)	0.580	0.615	8.087	0.3856	3.607	2.945
Gd-04 (CCO)	0.580	0.622	8.104	0.3853	3.613	2.950
Gd-08 (CCO)	0.580	0.628	8.122	0.3850	3.616	2.952
Gd-12 (CCO)	0.580	0.634	8.138	0.3847	3.619	2.955

Table S2. Contains cationic radii, theoretical lattice constant, oxygen positional parameters and hopping lengths of all the samples

Sample-Id	$\frac{I_{220}}{I_{222}}$	$\frac{I_{422}}{I_{222}}$	θ_1 (degree)	θ_2 (degree)
Gd-00 (CCO)	3.23	1.02	121.89	138.91
Gd-04 (CCO)	2.13	0.91	122.01	139.30
Gd-08 (CCO)	1.98	0.73	122.07	139.64
Gd-12 (CCO)	1.63	0.70	122.11	140.02

Table S3. Contains intensity ratio of diffracted x-rays from specific crystallographic planes and bond angles of entire synthesized chromite samples

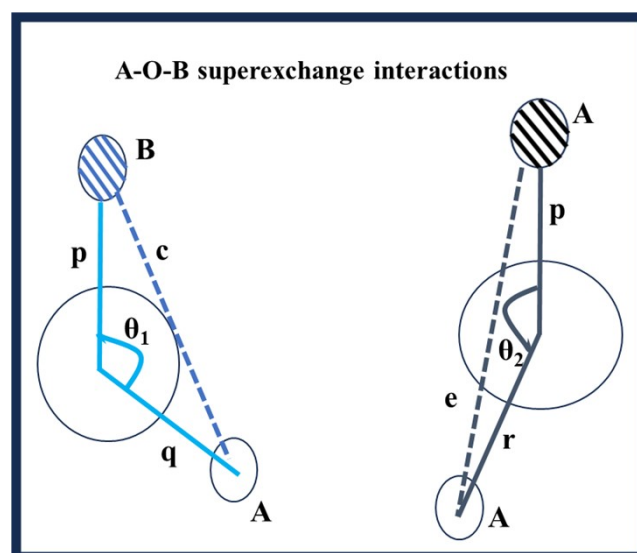


Fig. S1 Schematic representation of A-O-B superexchange interactions for spinel cubic chromite nanoparticles

Sample Id	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	k_t (N/m)	k_o (N/m)	K (N/m)	C_{11} (GPa)	V_1 (m/s)	V_s (m/s)	V_m (m/s)
Gd-00	856.1	455.1	329.1	114.3	221.7	266.0	7141	4123	4578

(CCO)									
Gd-04 (CCO)	841.3	454.3	317.8	118.6	218.2	261.4	7007	4045	4491
Gd-08 (CCO)	857.8	461.6	330.4	127.2	228.8	273.9	7089	4093	4544
Gd-12 (CCO)	854.8	464.7	328.1	133.7	230.9	276.2	7032	4060	4507

Table S4. Displays several elastic parameters of all the chromite samples

Sample Id	G (GPa)	B (GPa)	E (GPa)	θ_D (K)
Gd-00 (CCO)	88.6	266.0	239.2	613
Gd-04 (CCO)	87.2	261.4	235.4	616
Gd-08 (CCO)	91.3	273.9	246.5	623
Gd-12 (CCO)	92.0	276.2	248.4	620

Table S5. Contains various modulus and Deby temperatures of all the samples

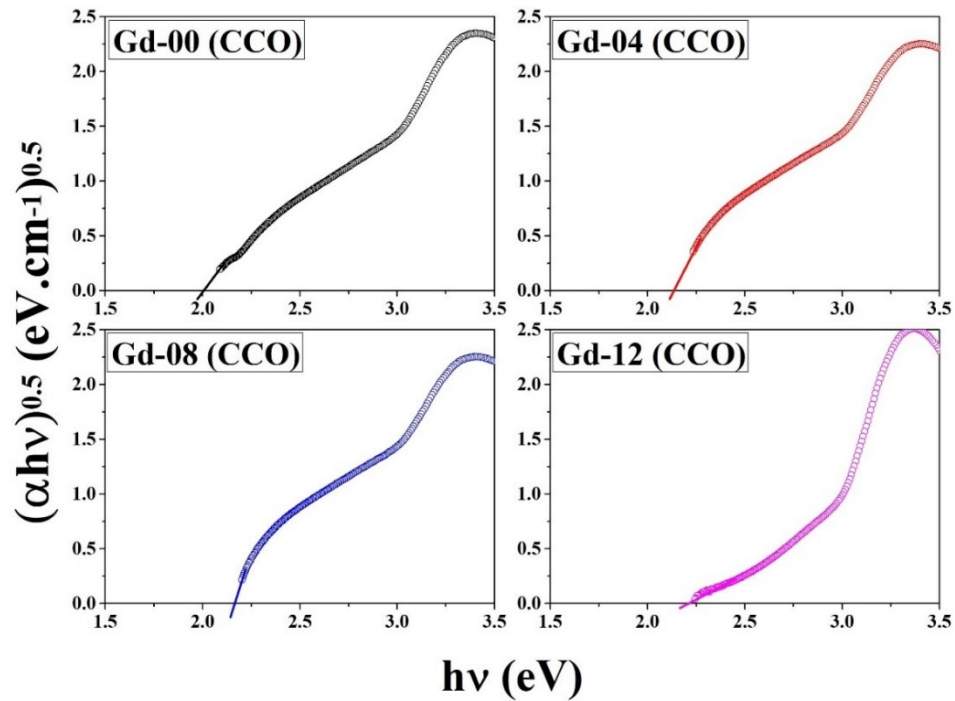


Fig. S2 Tauc plot of all the chromite samples at 300 K

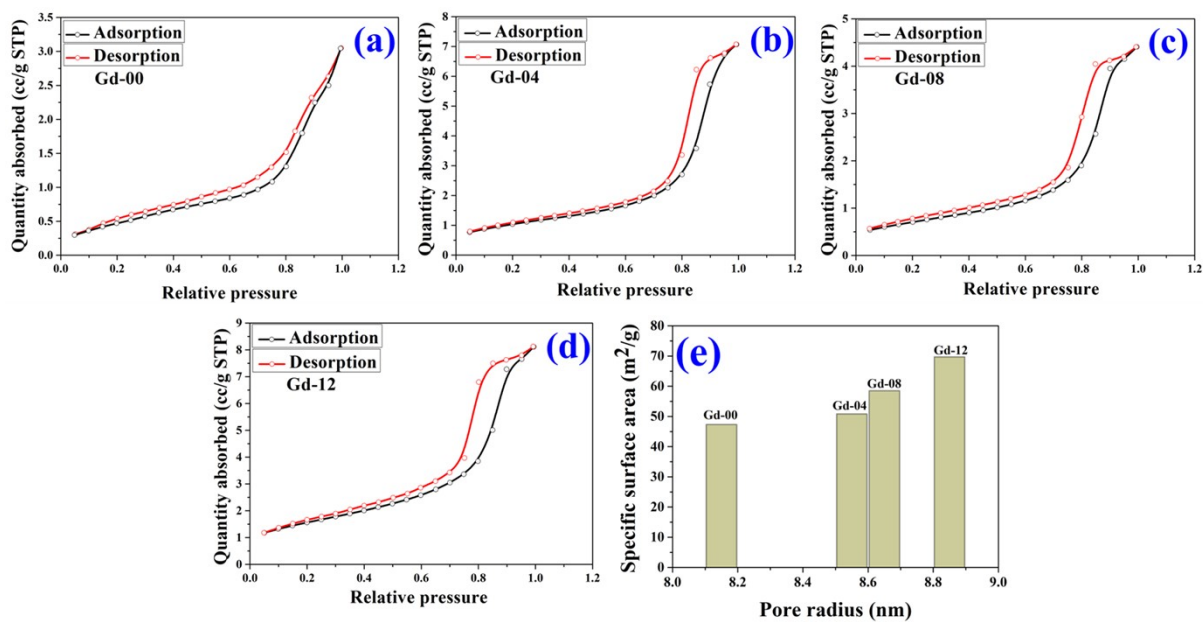


Fig. S3 (a-d) N₂ gas adsorption-desorption isotherms of all the samples and (e) Plot of specific surface area vs pore radius

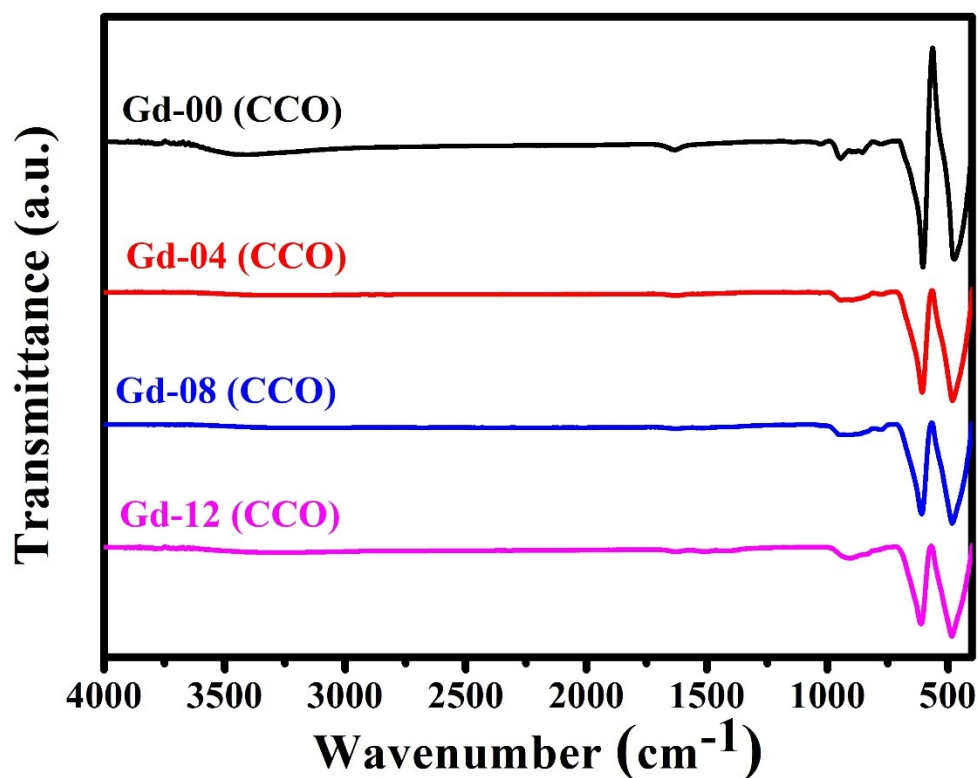


Fig. S4 FTIR spectra of CoGd_xCr_{2-x}O₄ nanoparticles

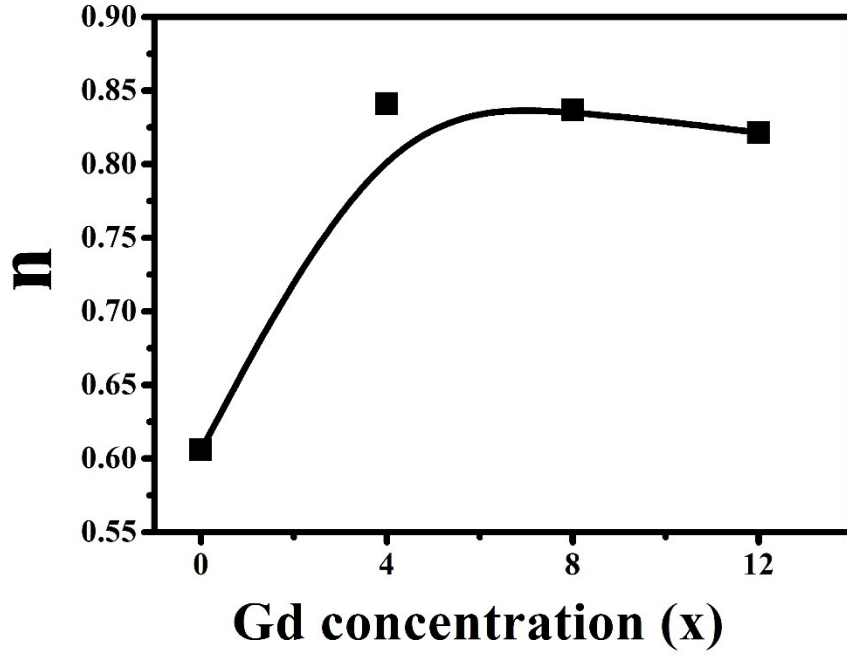


Fig. S5 Plot of the index (n) vs Gd concentration (x)

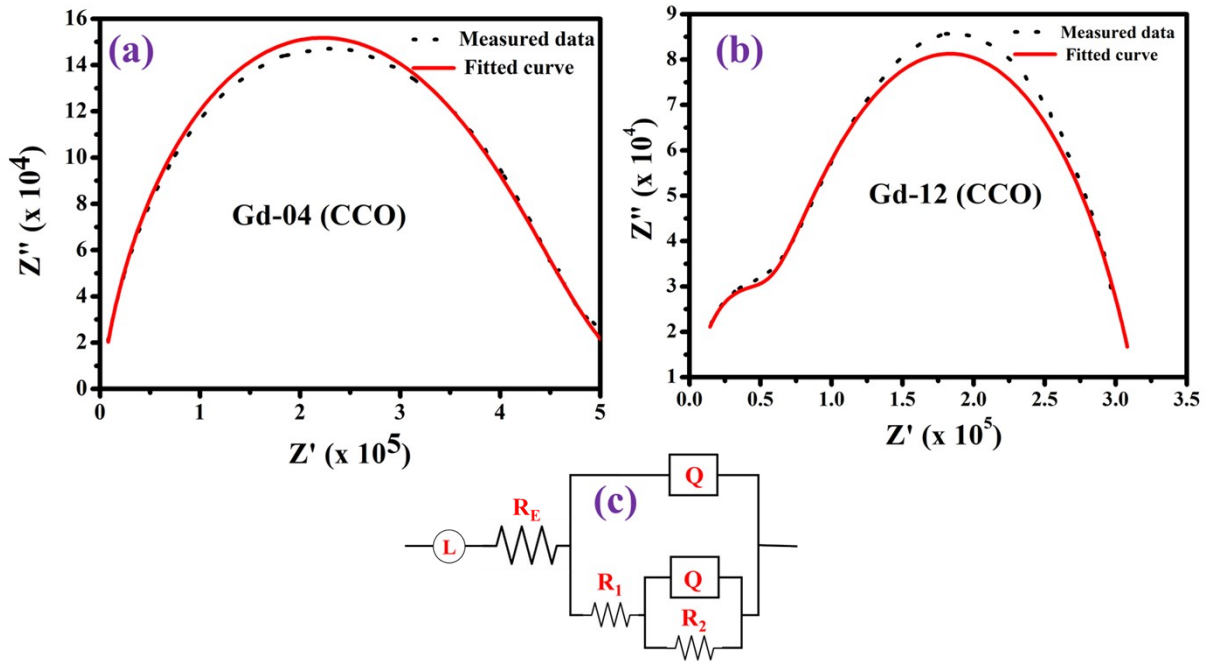


Fig. S6 (a-b) Cole-Cole plots (Z'' vs Z') of Gd-04 (CCO) and Gd-12 (CCO) samples (c) diagram of corresponding circuit

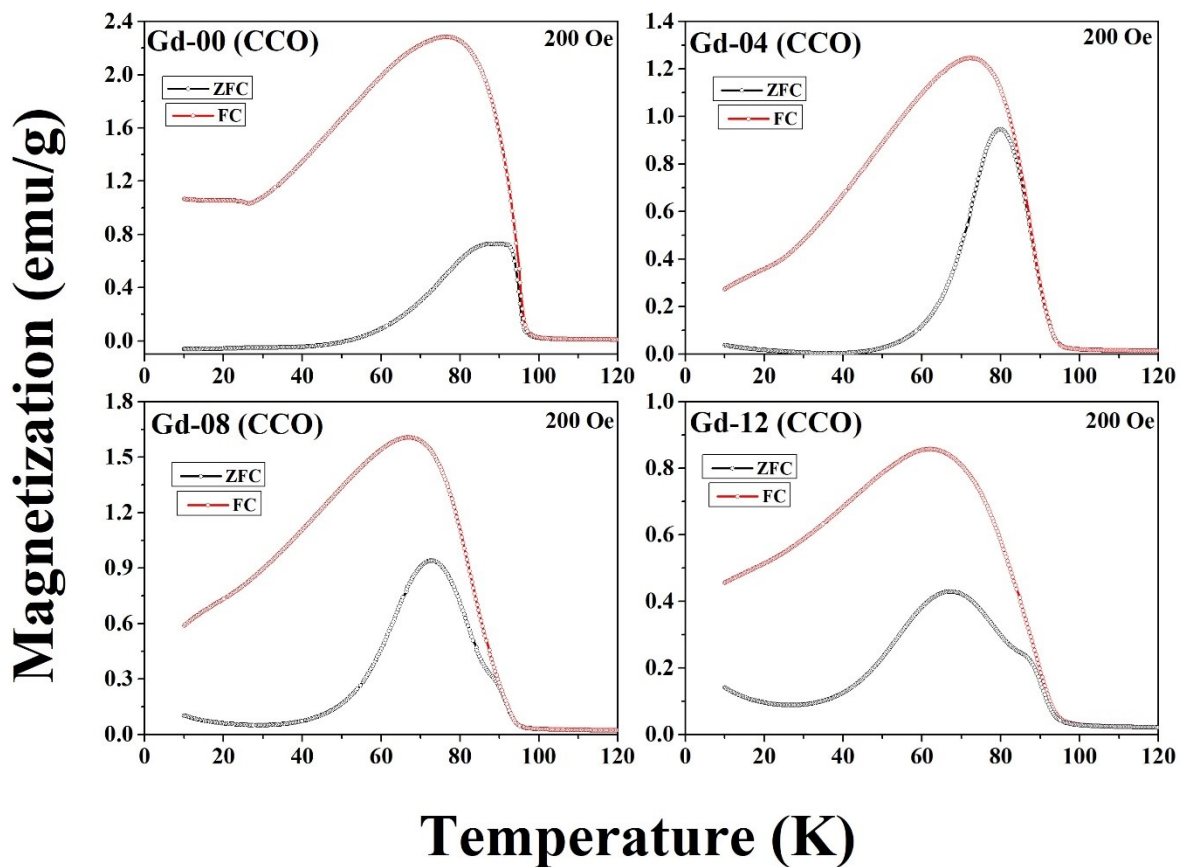


Fig. S7 M(T) plots of entire synthesized chromite samples

Sample-Id	Magnetic Parameters			
	5 K			150 K
$\text{CoGd}_x\text{Cr}_{2-x}\text{O}_4$	M_S (emu/g)	H_C (kOe)	K_{eff} (kOe.emu/g)	M_{7T} (emu/g)
Gd-00 (CCO)	5.08	4.88	25.29	3.06
Gd-04 (CCO)	15.43	1.24	19.52	4.17
Gd-08 (CCO)	33.63	0.78	26.76	6.14
Gd-12 (CCO)	37.86	0.63	24.33	6.73

Table S6. Displays magnetic parameters of entire chromite samples

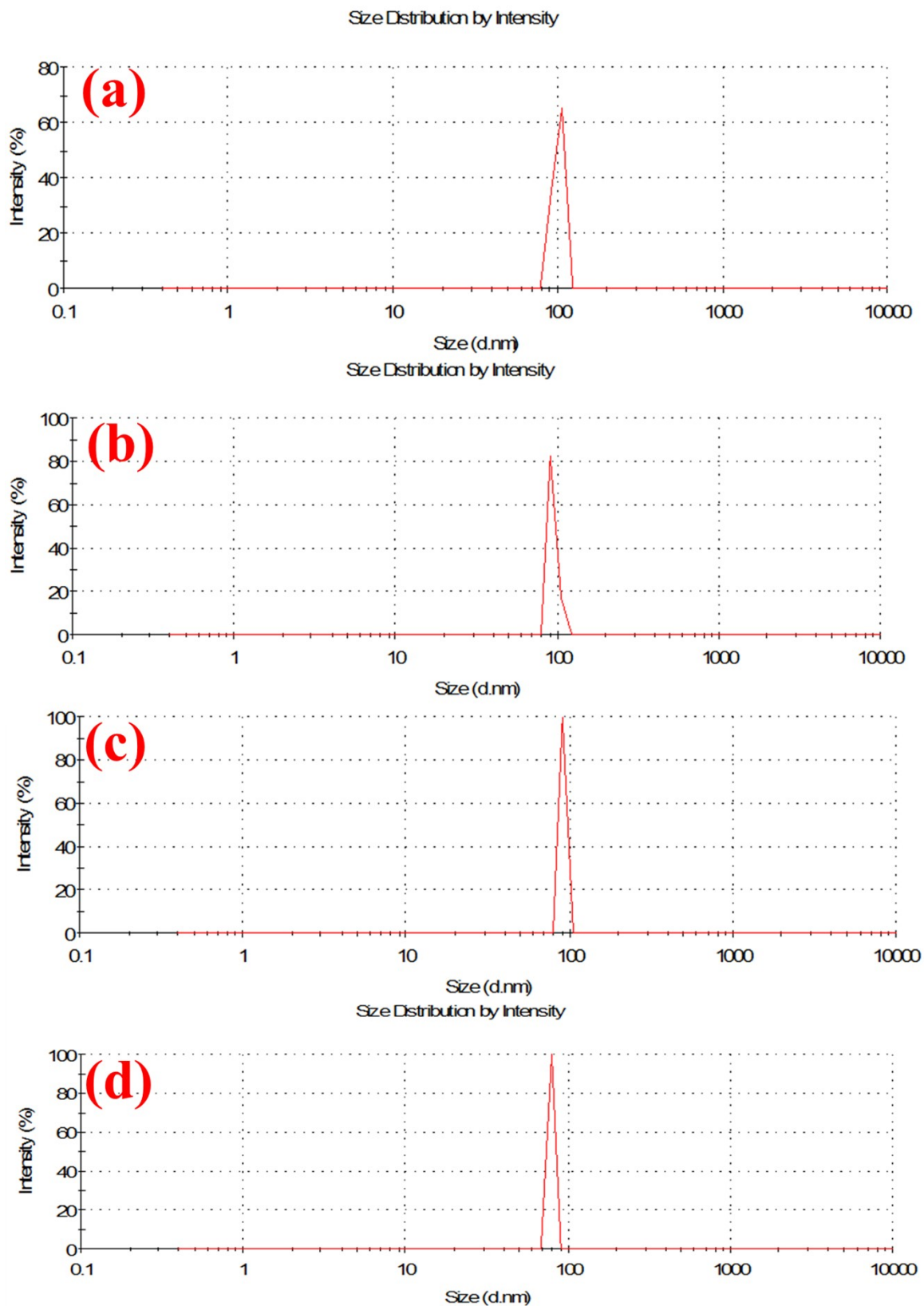


Fig. S8 DLS size distribution curve of (a) Gd-00 (CCO), (b) Gd-04 (CCO), (c) Gd-08 (CCO) and (d) Gd-12 (CCO) samples at 1 mg/mL concentration.

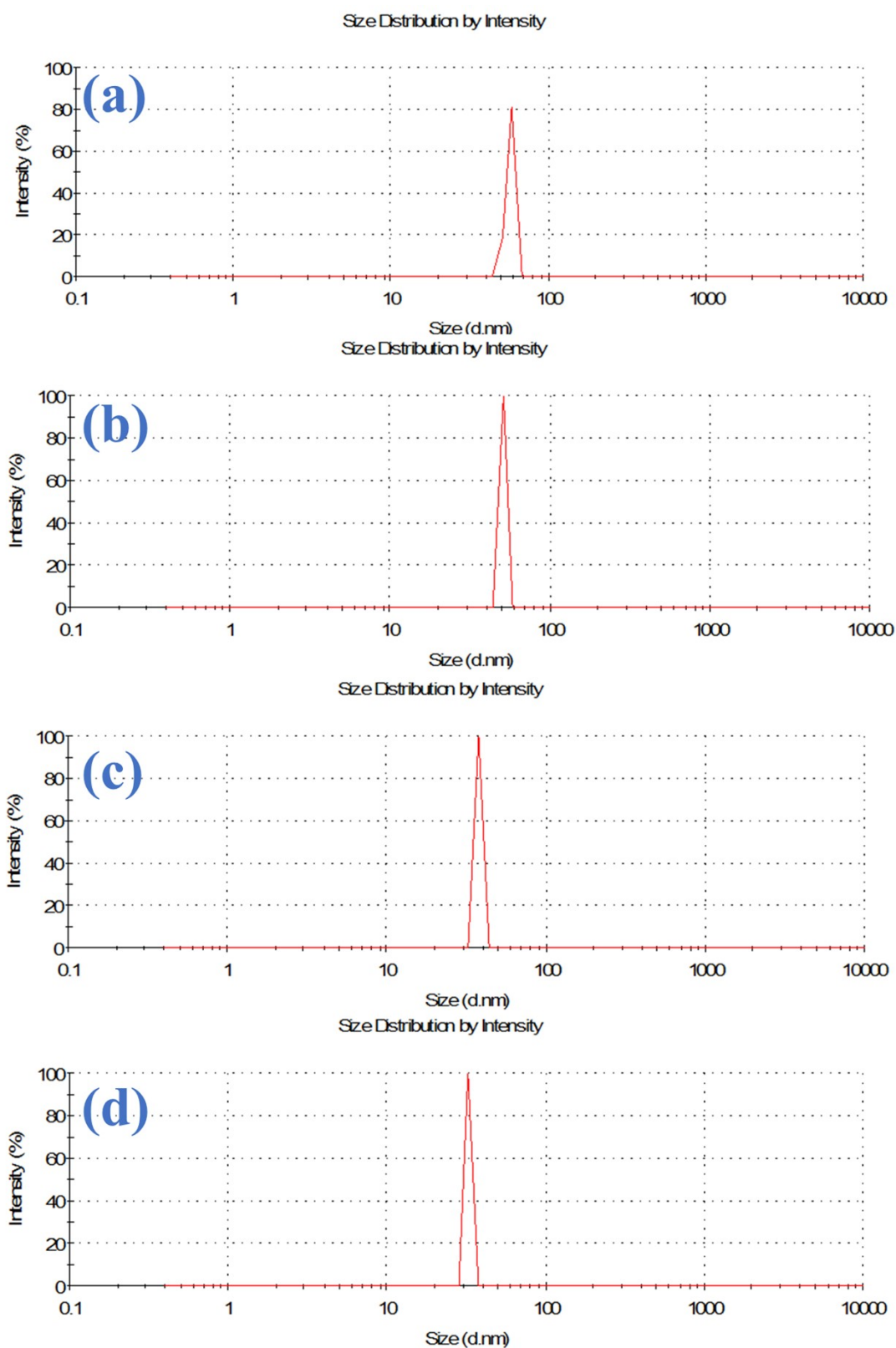


Fig. S9 DLS size distribution curve of (a) Gd-00 (CCO), (b) Gd-04 (CCO), (c) Gd-08 (CCO) and (d) Gd-12 (CCO) samples at 0.5 mg/mL concentration.

EDX analysis

The detection of elements that existed in the pure and Gd-doped CoCr_2O_4 nanoparticles [Gd-00 (CCO) and Gd-08 (CCO)] has been carried out using energy dispersive x-ray (EDX) analysis. The obtained EDX spectra for Gd-00 (CCO) and Gd-08 (CCO) samples are depicted in figure S10 (a-b). The presence of Co, Cr, Gd and O elements was identified in the as-prepared samples. A comparison between theoretical and obtained values of atomic % of various elements was performed, and a good agreement was reached between these two results. The existence of Gd ions in the EDX spectra of Gd-08 (CCO) nanoferrite confirmed the successful doping of Gd ions in the host system. It is noted that the reduction in the atomic percentage of Cr ions was compensated by the Gd dopants in the doped chromite sample.

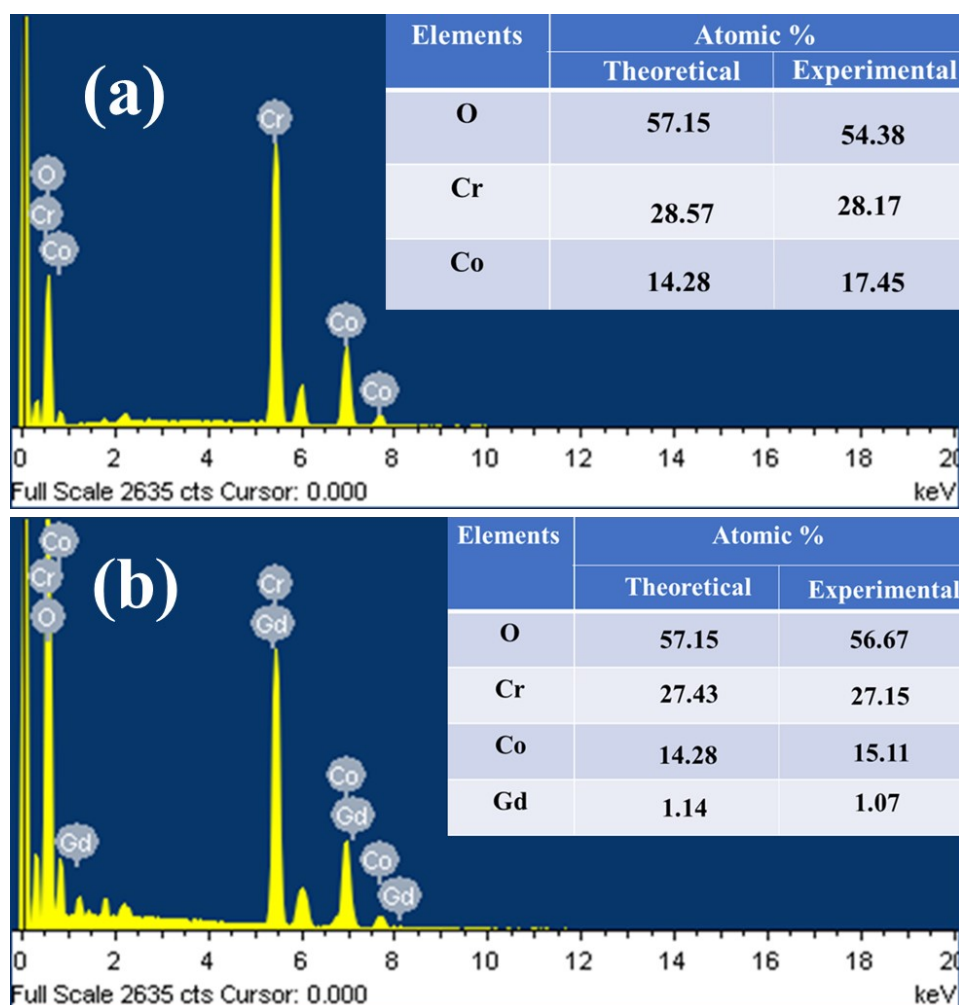


Fig. S10 EDX spectra of (a) Gd-00 (CCO) and (b) Gd-08 (CCO) samples

References

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2. M. P. Ghosh, S. Mandal and S. Mukherjee, *The European Physical Journal Plus*, 2020, **135**, 41.
3. M. P. Ghosh, N. J. Mondal, R. Sonkar, B. Boro, J. P. Borah, and D. Chowdhury, *ACS Applied Nano Materials* 2024, **7**, 7028–7042.