

SUPPLEMENTARY INFORMATION

Ultrasmall and monodisperse colloidal amorphous Nd-Fe-B-Na nanoparticles with high T_C

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Experimental section

Materials: Nd(acac)₃·xH₂O (99.99 %), Fe(acac)₃ (99 %), NaBH₄ (99 %) are adopted. Oleylamine (OM, C18:80~90%, Alfa Aesar), oleic acid (OA, 90 %, Alfa Aesar), and 1-Octadecene (ODE, > 90 %, Alfa Aesar) are used as starting materials without further purification. Tetrabutylammonium borohydride and triethylamine borane are selected as reducing agents.

Synthesis of colloidal Nd-Fe-B-Na nanoparticles with different size: In a typical synthesis for 3 nm nanoparticles, 0.25 mmol Nd(acac)₃ and 1.5 mmol Fe(acac)₃ are added to mixed solvent composed of 4 mL of oleylamine (OM), 2 mL oleic acid (OA), and 10 mL 1-Octadecene (ODE) at room temperature. The mixture is heated to 100 °C in a vacuum for 30 min to remove water and oxygen. Then, the powder of 2.5 mmol NaBH₄ is swiftly added in under Ar atmosphere. The mixture is heated to 310 °C over approximately 4.5 min under Ar atmosphere, aging for 6 min. After air cooling the three-necked flask by taking off the temperature-controlled electromantle, the nanosheets are precipitated with ethanol, redispersed in cyclohexane for the transmission electron microscopy (TEM) characterizations and dried in a vacuum overnight for other measurements. One batch allows us to obtain about 0.3 g colloidal nanoparticles. For the nanoparticles with 1 nm or 2 nm, the temperature and aging time are selected as 300 °C and without aging or aging for 6 min, respectively.

For the synthesis for 5 nm nanoparticles, the mixed solvent composed of 2 mL of oleylamine (OM), 1 mL oleic acid (OA), and 5 mL 1-Octadecene (ODE) is selected, while other parameters are kept identical. The mixture is heated to 320 °C, aging for 10 min.

Characterization: XRD patterns are recorded with a Bruker D8 diffractometer using Cu K α radiation with 40 mA and 40 kV. Transmission electron microscope (TEM), energy-dispersive X-ray spectroscopy (EDS), and selected the selected area electron diffraction (SAED) are carried out on a JEOL JEM-2010F electron microscope operated at 200 kV. XPS experiments were carried out on a Perkin Elmer PHI-5000C ESCA system with Mg K α radiation ($h\nu=1253.6$ eV) under a base pressure of 10⁻⁹ Torr.

The analysis of Nd, Fe, B, and Na is performed on the Perkin Optima 2100DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The magnetic properties at temperature lower than 400 K are measured with a SQUID-VSM system (MPMS, Quantum), which adopts the new FastLab data acquisition technique and the QuickSwich magnetic control technique. The magnetic properties at temperature higher than 400 K are measured with a LakeShore 7407 vibrating sample magnetometer (VSM) with Hall probe. X-ray absorption fine structure (XAFS) spectra are measured at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) with a ring current of 200-300 mA at 3.5 GeV. Data are recorded in transmission mode using a Si(111) double crystal monochromator. Fe K-edge XAFS data are analyzed using standard procedures with the program IFEFFIT. ⁵⁷Fe Mössbauer spectra are measured under constant acceleration transmission mode with a ⁵⁷Co/Rh source. The velocity is calibrated by a 25 μ m thick α -Fe foil, and the Isomer Shift (I.S.) is relative to the center of α -Fe foil at 300 K. The spectra are analyzed using MossWinn.^[2] Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are simultaneously performed on a Netzsch STA 409 at a heating rate of 5 K/min under nitrogen atmosphere. Dynamic light scattering (DLS) measurement is analyzed on a Nanotrac 250 analyzer by dispersing the 3 nm Nd-Fe-B-Na nanoparticles in hexane.

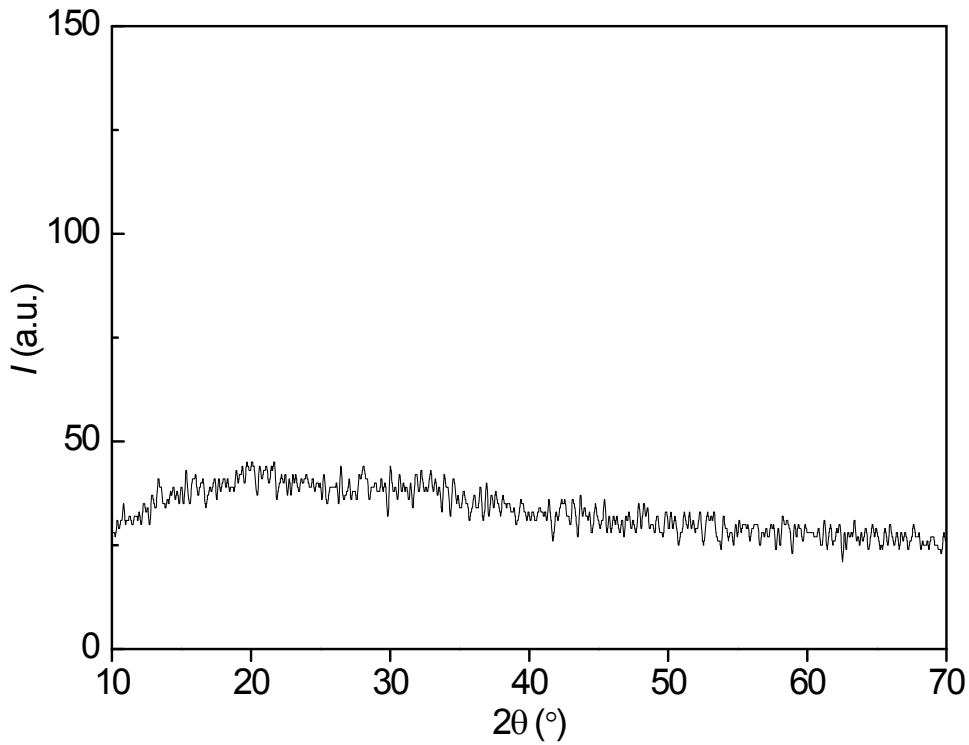


Figure S1 XRD pattern of the 3-nm Nd-Fe-B-Na nanoparticles.

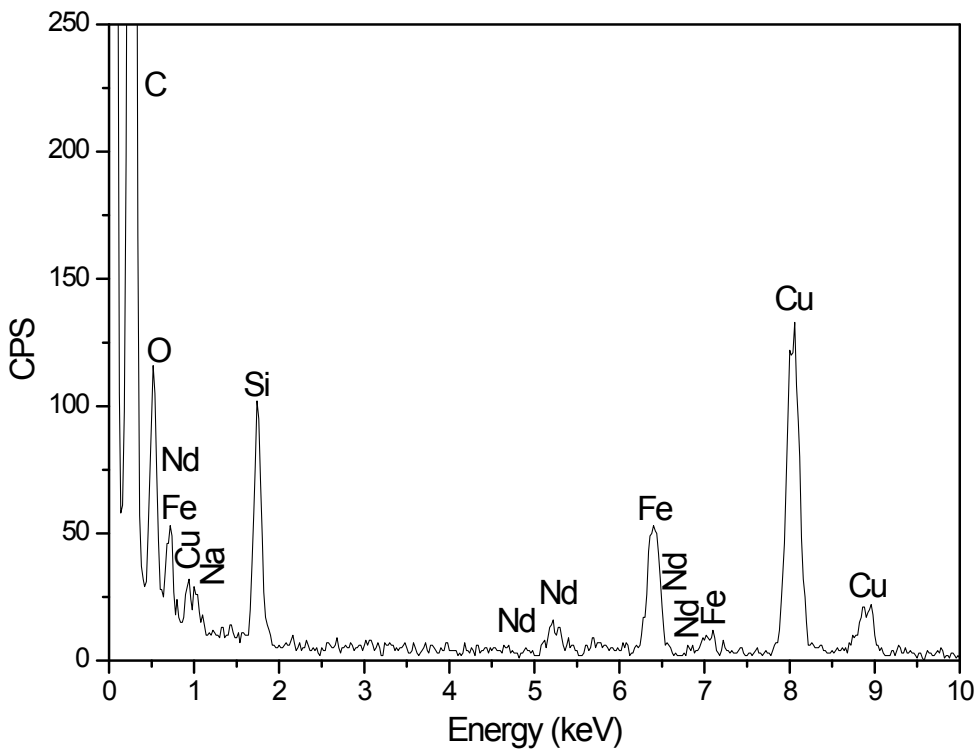


Figure S2 EDS of colloidal Nd-Fe-B-Na nanoparticles with 3 nm diameter, corresponding to the TEM image in Figure 1c in the main text. Cu and carbon elements are coming from the holey carbon film coated Cu grid supporting sample during EDS measurement. The signal of B is overlapped with that of carbon element. Si and O signals are probably from SiO₂ contaminant, for

no signals of Si element in XPS spectrum in Figure S3.

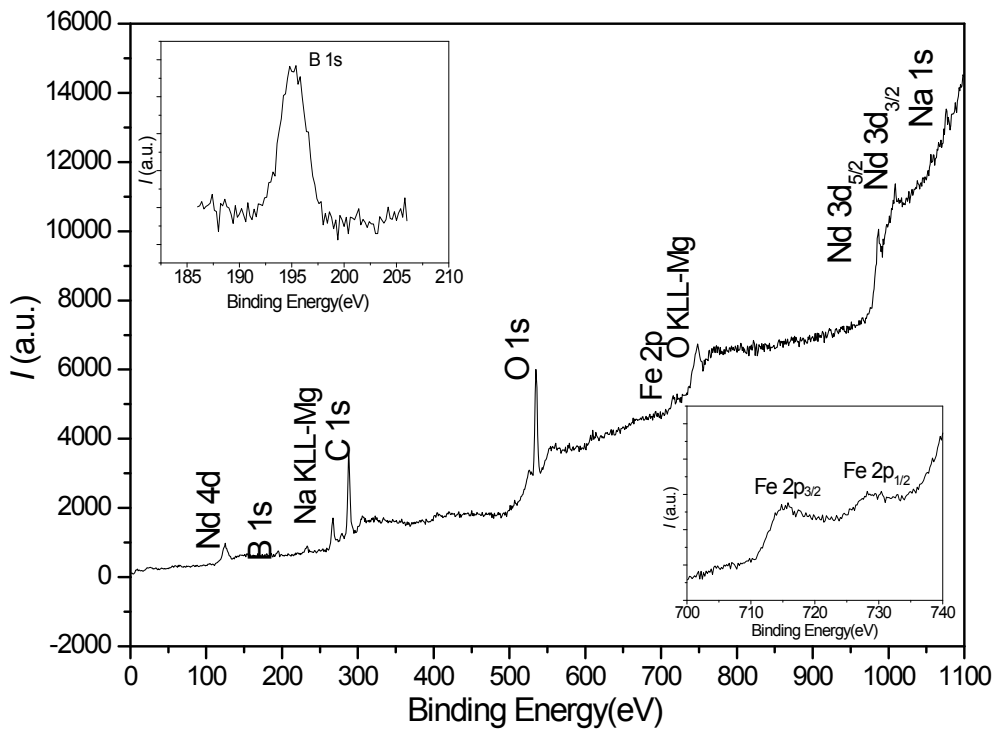


Figure S3 XPS spectrum of colloidal Nd-Fe-B-Na nanoparticles with 3 nm diameter.

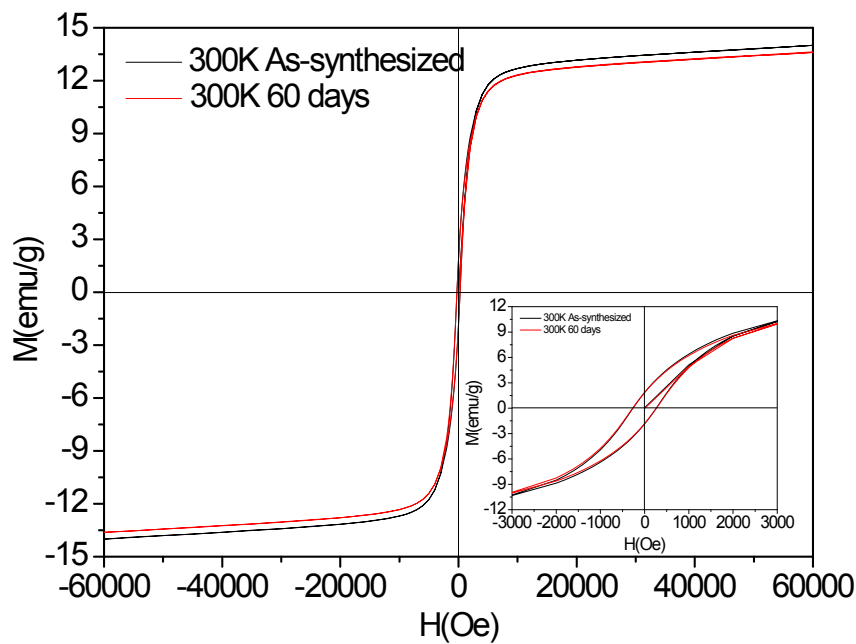


Figure S4 Magnetic properties of colloidal Nd-Fe-B-Na nanoparticles with 3 nm diameter.

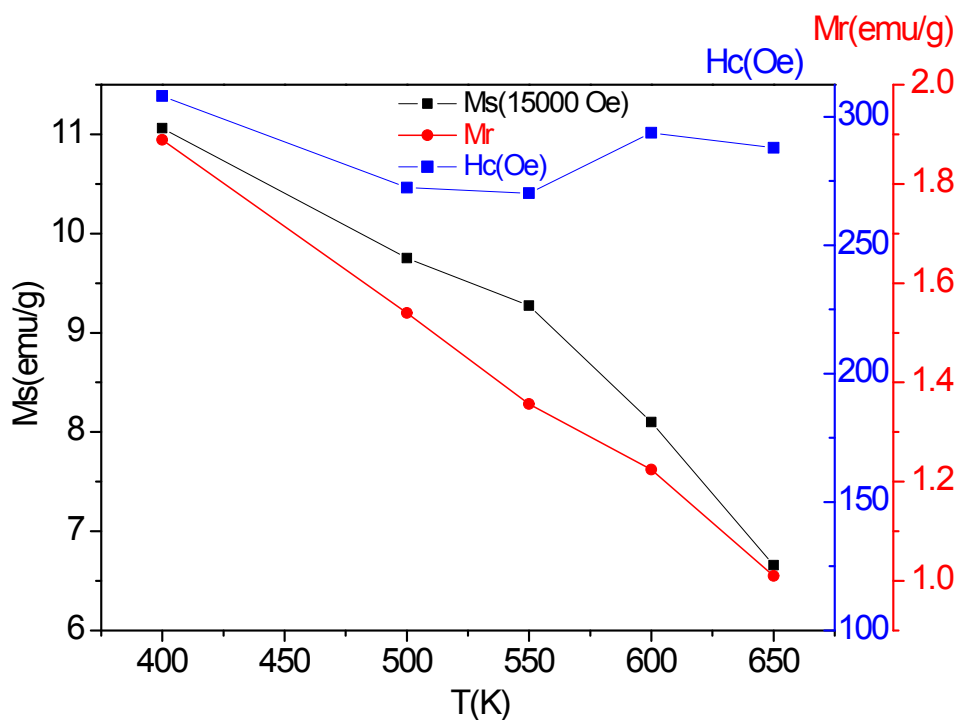


Figure S5 Graphic presentation of the magnetic parameters in Figure 3 in the main text.

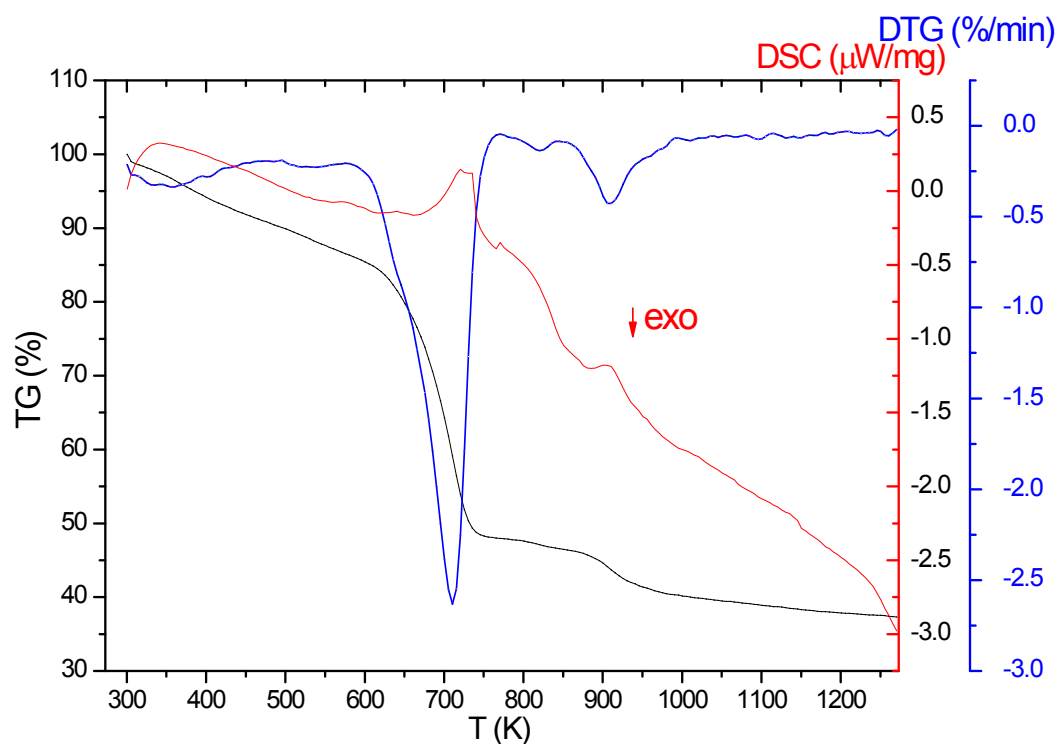


Figure S6 The thermogravimetric analysis (TG) (black curve), differential scanning calorimetry (DSC) (red curve) and differential thermogravimetric analysis (DTG) (blue curve) for colloidal Nd-Fe-B-Na nanoparticles with 3 nm diameter under N₂ atmosphere.

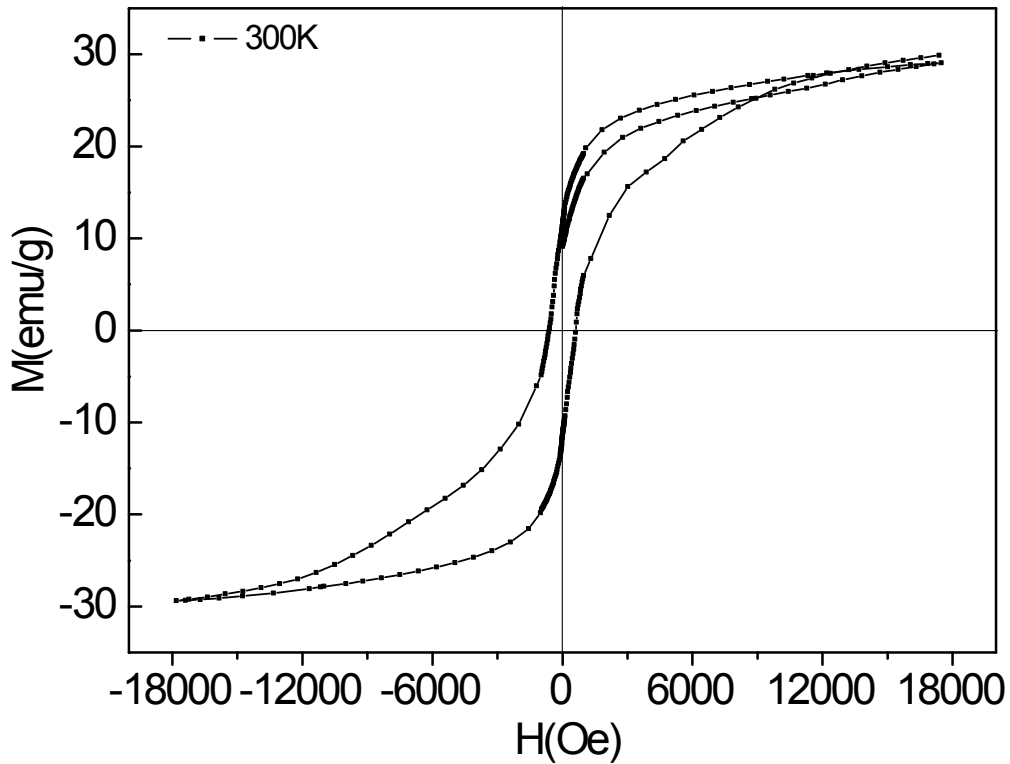


Figure S7 Magnetic properties of colloidal Nd-Fe-B-Na nanoparticles with 5 nm diameter at 300 K measure by LakeShore 7407 vibrating sample magnetometer (VSM).

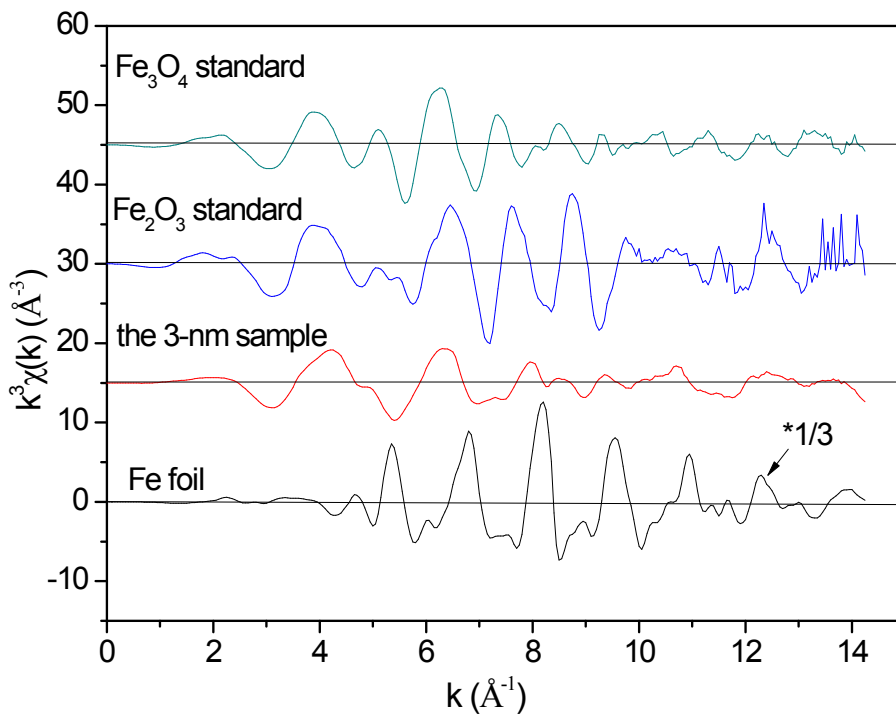


Figure S8 Fe *K*-edge k^3 -weighted experimental EXAFS spectra of the Fe foil, the 3-nm sample, Fe_2O_3 standard, and Fe_3O_4 standard.

Table S1 Structural parameters obtained by fitting the Fe *K*-edge EXAFS data shown in Figure 4 in the main text.^a

Sample	Terms	N	R (Å)	σ^2 (Å ²)	R_f
3nm Nd-Fe-B-Na NPs	Fe-B ^b	3.5	1.99	0.004	0.026
	Fe-Fe	1.2	2.91	0.008	

^a N is the coordination number, R is the coordination distance, σ^2 is the Debye Waller (disorder) term, and R_f is a measure of the goodness of fit. ^b There are the Fe-O and Fe-N chemical bonds on the surface of the nanoparticles by Fe coordinating with oleate, oleic acid, and oleylamine.

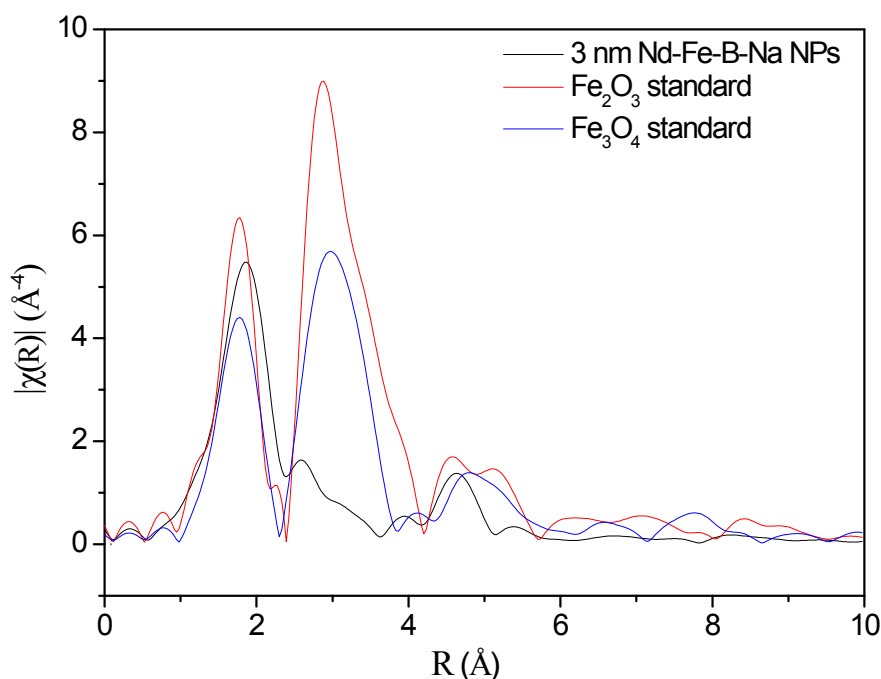


Figure S9 RDF's of the 3-nm Nd-Fe-B-Na nanoparticles, standard Fe₂O₃, and Fe₃O₄ transformed from the data from Figure S8.

Table S2. ⁵⁷Fe Mössbauer hyperfine parameters for the 3-nm Nd-Fe-B-Na nanoparticles at 300 K.^a

Sample (Nd-Fe-B-Na NPs)	Temp (K)	Subspectra	Isomer shift δ^b (mm/s)	quadrupolar splitting, ΔE_q (mm/s)	hyperfine field median value, (B_{hf}) (T)	Area _{subspectrum} (%)
3nm	300	1	0.36 (1)	0.94(1)	-	40.2
		2	0.00(1)	-	33.3(1)	24.6
		3	0.32(4)	-	21.0(3)	30.0
		4	0.39(7)	-0.52(1)	12.2(3)	5.2

^a Errors on the last digits are given within parentheses. ^b Referred to metallic iron, α -Fe.

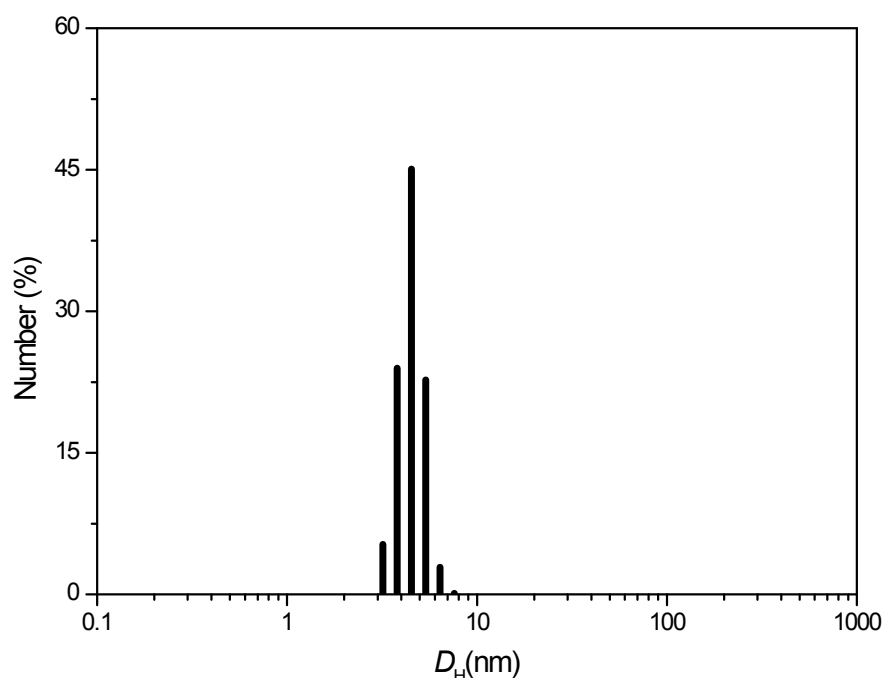
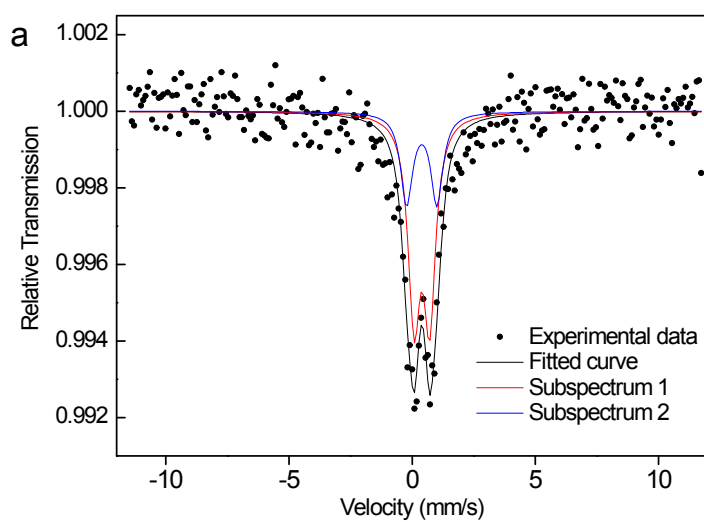


Figure S10 Hydrodynamic diameters measured by dynamic light scattering (DLS) for the 3-nm Nd-Fe-B-Na nanoparticles dispersed in hexane.



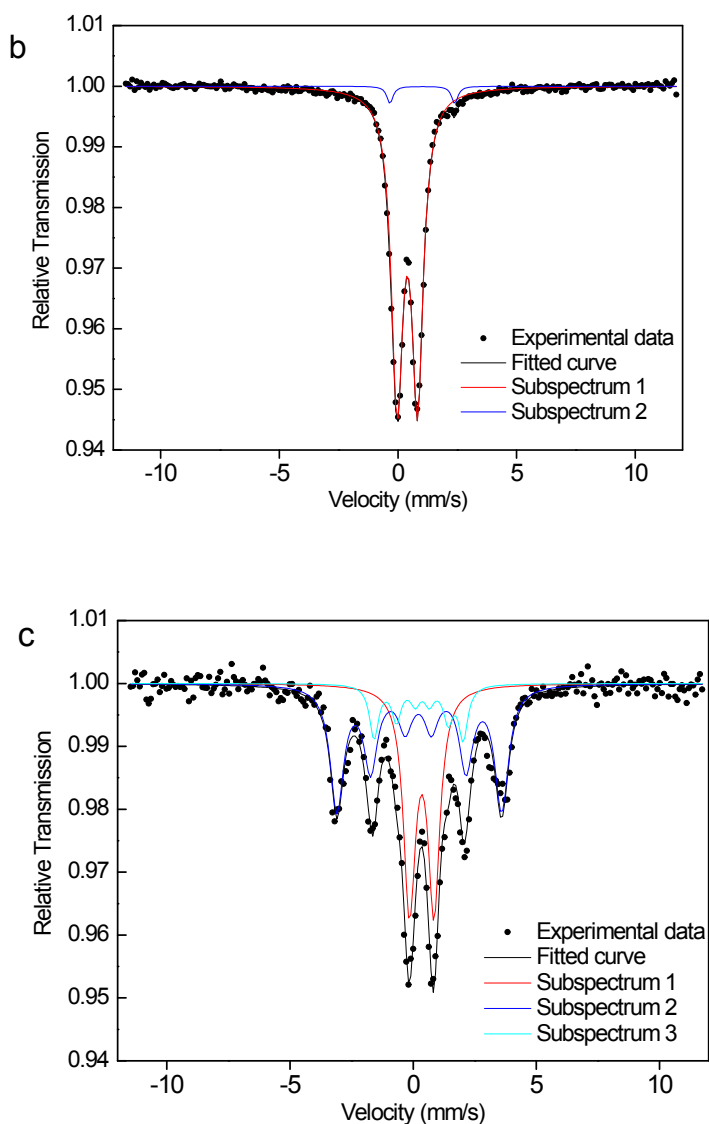


Figure S11 ^{57}Fe Mössbauer spectrum of the Nd-Fe-B-Na nanoparticles with different size measured at 300 K. a, 1 nm; b, 2 nm; c, 5 nm.

Table S3. ^{57}Fe Mössbauer hyperfine parameters for the Nd-Fe-B-Na nanoparticles with different diameter at 300 K. ^a

Sample (Nd-Fe-B-Na NPs)	Temp (K)	Subspectra	Isomer shift δ^b (mm/s)	quadrupolar splitting, ΔE_q (mm/s)	hyperfine field median value, (B_{hf}) (T)	Area _{sub spectrum} (%)
1 nm	300	1	0.40(1)	0.63(2)	-	68.4
		2	0.39(3)	1.2(1)	-	31.6
2 nm	300	1	0.397(1)	0.863(1)	-	97.0
		2	1.03(1)	2.73(2)	-	3.0
5 nm	300	1	0.35(1)	1.00(1)	-	37.4
		2	0.23(1)	0.04(1)	20.8(1)	48.6
		3	0.30(2)	-0.15(3)	11.3(1)	14.0

^a Errors on the last digits are given within parentheses. ^b Referred to metallic iron, α -Fe.

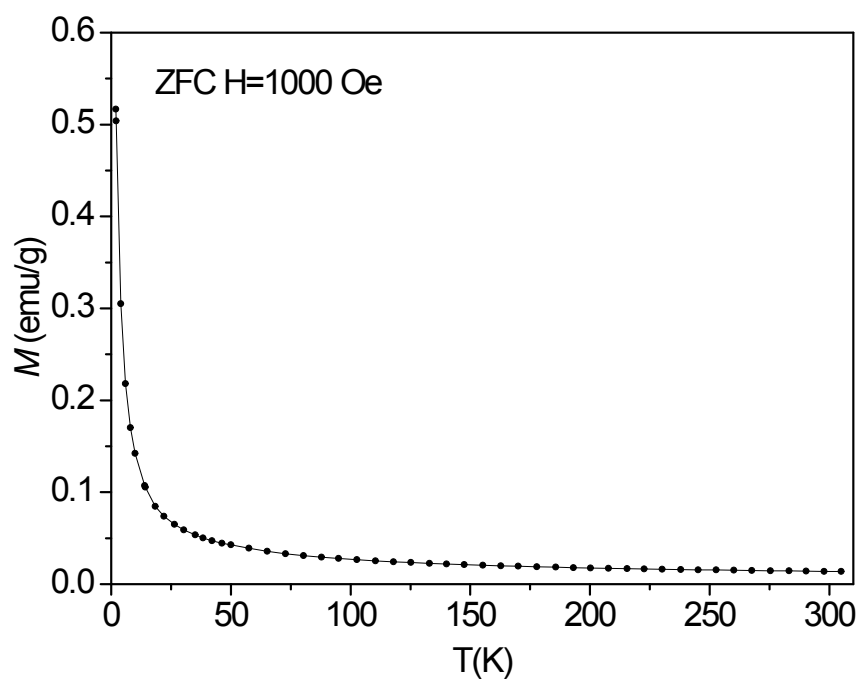


Figure S12 The zero-field-cooling (ZFC) magnetization curve of 1 nm colloidal Nd-Fe-B-Na nanoparticles under 1000 Oe magnetic field at the temperature between 2 K and 305 K.

Reference

- [1] M. Newville, IFEFFIT: interactive XAFS analysis and FEFF fitting. *J. Synchrotron Radiat.*, **2001**, *8*, 322-324.
- [2] Z. Klencsár, E. Kuzmann, A. Vértes, User-friendly software for Mössbauer spectrum analysis, *J. Radioanal. Nucl. Chem.*, **1996**, *210*, 105-118.