Supporting Information

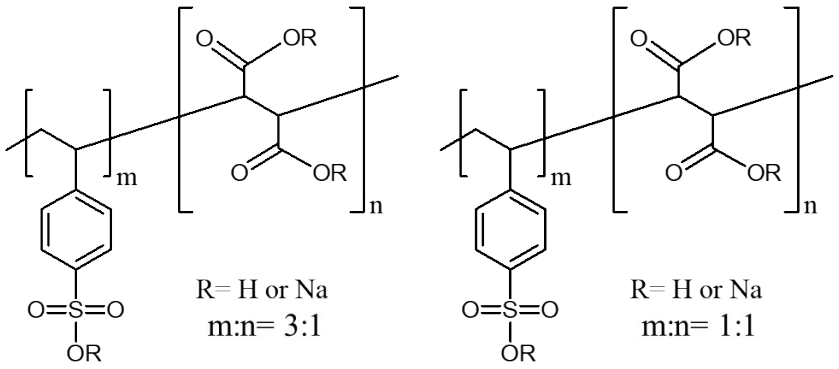
Robust Synthesis of Highly Charged Superparamagnetic Fe_3O_4 Colloidal Nanocrystal Clusters for Magnetically Responsive Photonic Crystals

Liting Pan,[#1] Zhuo Peng,[#1] Hairong Yu,[1] Ting Liang[1] and Changjing Cheng,[*1,2]

1. Key Laboratory of Basic Chemistry, the National Ethnic Affairs Commission, No.16 South Section 4, Yihuan Road, Chengdu, Sichuan, 610041, P. R. China. *Email*: chengcj@swun.edu.cn

2. College of Chemistry and Environment, Southwest Minzu University, No.16 South Section 4, Yihuan Road, Chengdu, Sichuan, 610041, P. R. China. *Email*: chengcj@swun.edu.cn

[#] These authors contributed equally to this work.



PSSMA (3:1) **PSSMA (1:1)**

Fig. S1 The chemical structures of PSSMA (3:1) and PSSMA (1:1).

Table S1. Synthesis recipes of the highly charged CNCs in this work.

Sample	EG (mL)	PSSMA (3:1) (g)	$FeCl_3 \cdot 6H_2O$ (g)	$NaAc \cdot 3H_2O$ (g)	Molar ratio of Ac^-/Fe^{3+}
CNCs0.5	40	0.5	1.080	3.0	5.5
CNCs1.0	40	1.0	1.080	3.0	5.5
CNCs1.5	40	1.5	1.080	3.0	5.5
CNCs2.0	40	2.0	1.080	3.0	5.5
CNCs2.5	40	2.5	1.080	3.0	5.5
CNCs3.0	40	3.0	1.080	3.0	5.5
CNCs-5	40	2.5	1.192	3.0	5
CNCs-6	40	2.5	0.993	3.0	6
CNCs-8	40	2.5	0.745	3.0	8
CNCs-10 (CNCs-1X)	40	2.5	0.596	3.0	10
CNCs-12	40	2.5	0.497	3.0	12
CNCs-2X	80	5	1.192	6.0	10
CNCs-5X	200	12.5	2.98	15.0	10
CNCs-10X	400	25	5.96	30.0	10
CNCs-20X	800	50	11.92	60.0	10

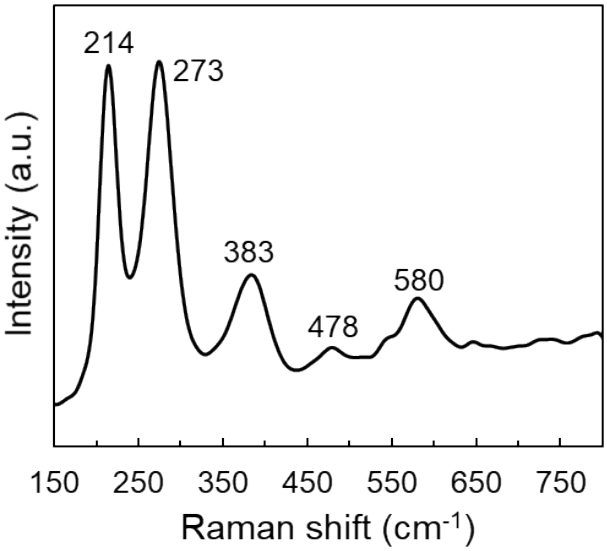


Fig. S2 Raman scattering spectrum of 131-nm CNCs with a laser power of 10 mW.

Upon increasing the laser power from 1 to 10 mW, two typical peaks at 214 and 273 cm^{-1} assigned to α-Fe_2O_3 were observed, indicating that the magnetite (Fe_3O_4) was transformed into hematite (α-Fe_2O_3) because of the local heating induced oxidation from laser irradiation.[1]

Table S2. ζ potentials of CNCs synthesized with PSSMA (3:1), PSSMA (1:1) and PSS as the ligands.

Sample	Ligand	ζ potential (mV)
CNCs-PSSMA (3:1)	PSSMA (3:1)	-51.0±1.3
CNCs-PSSMA (1:1)	PSSMA (1:1)	-26.6±1.5
CNCs-PSS	PSS	-20.2±2.5

Note: The CNCs were synthesized by using 2.5 g of PSSMA (3:1) for CNCs-PSSMA (3:1), of PSSMA (1:1) for CNCs-PSSMA (1:1), and of PSS for CNCs-PSS, while keeping other conditions unchanged (0.596 g of $FeCl_3 \cdot 6H_2O$ and 3.0 g of $NaAc \cdot 3H_2O$ in 40 mL of EG for 10 h at 200 °C).

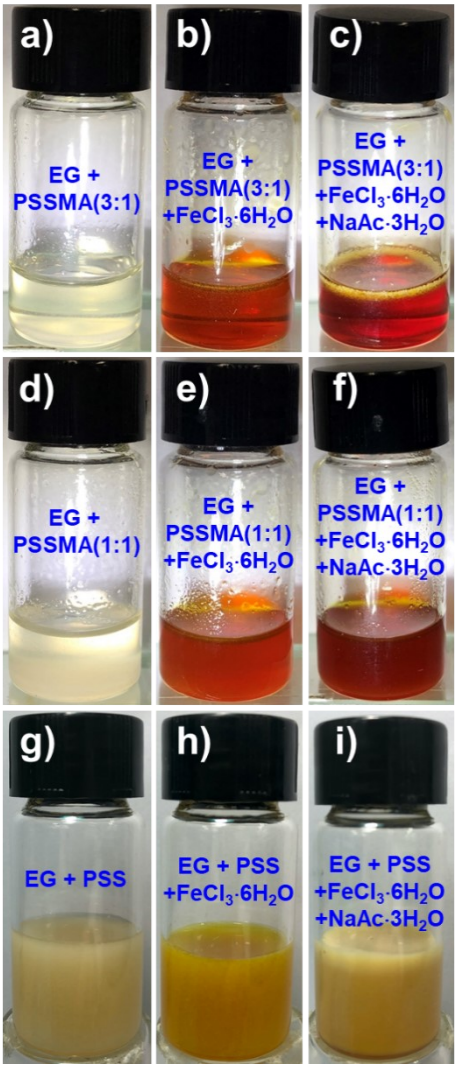


Fig. S3 Digital pictures of the reaction mixtures dissolved different ligands: PSSMA (3:1) (a-c), PSSMA (1:1) (d-f), and PSS (g-i).

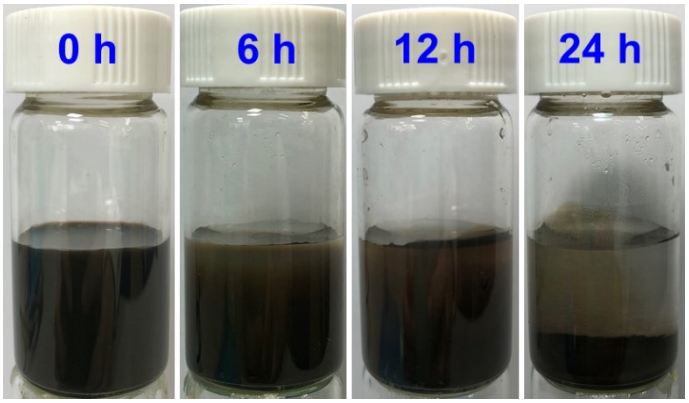


Fig. S4 Digital pictures of PSS-stabilized CNCs (CNCs-PSS) in water after storing different time.

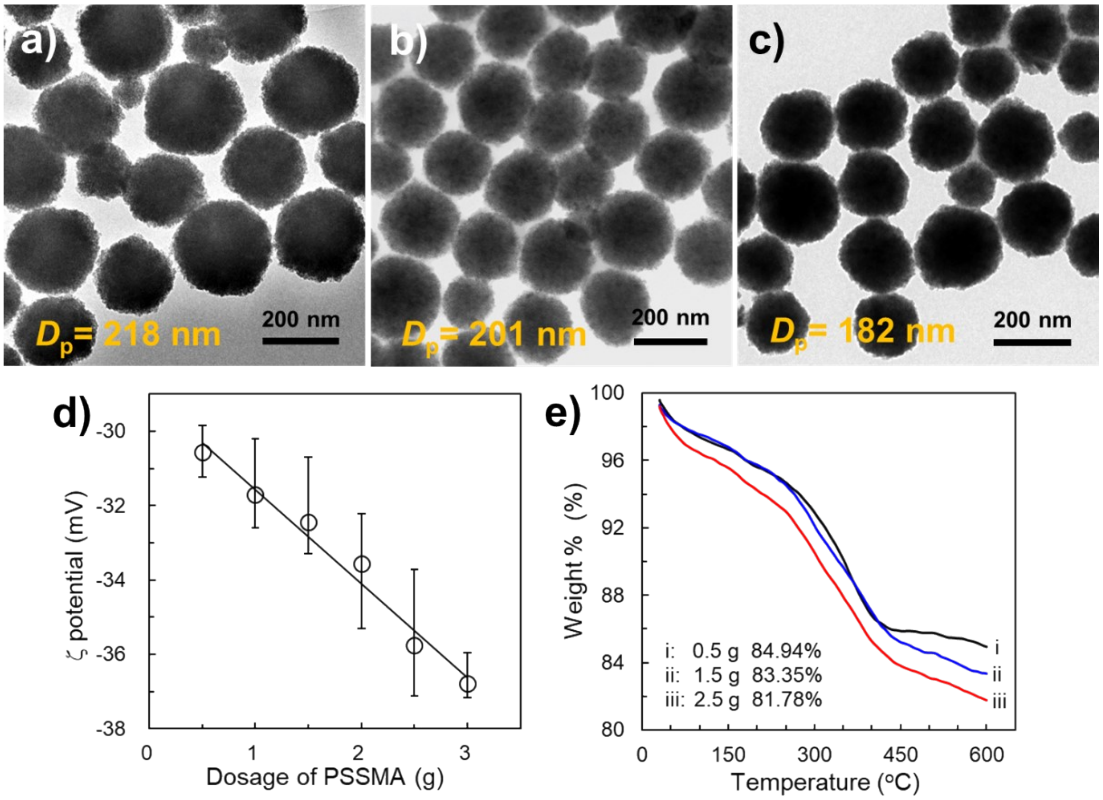


Fig. S5 (a-c) TEM images, (d) ζ potentials, and (e) TGA curves of CNCs synthesized with different dosages of PSSMA (3:1), while keeping other conditions unchanged (1.08 g of $FeCl_3 \cdot H_2O$ and 3.0 g of $NaAc \cdot 3H_2O$ were in 40 mL of EG for 10 h at 200 °C). The average sizes were obtained by measuring over 100 particles for each sample.

In TGA graph, the weight loss at temperature of 30-210 °C is ascribed to the evaporation of the adsorbed water on the particles, the decomposition of the bound PSSMA (3:1) at 210-430 °C, and the gradual oxidation of Fe_3O_4 into α-Fe_2O_3 at temperature over ~430 °C.

$$2HOCH_2CH_2OH \longrightarrow 2CH_3CHO + 2H_2O$$

$$3CH_3COONa + 3H_2O \longrightarrow 3CH_3COOH + 3OH^-$$

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$$

$$2Fe(OH)_3 + 2CH_3CHO \longrightarrow CH_3COCOCH_3 + 2Fe(OH)_2 + 2H_2O$$

$$2Fe(OH)_3 + Fe(OH)_2 \longrightarrow Fe_3O_4 + 4H_2O$$

Fig. S6 The formation process of primary magnetite (Fe_3O_4) nanocrystals.

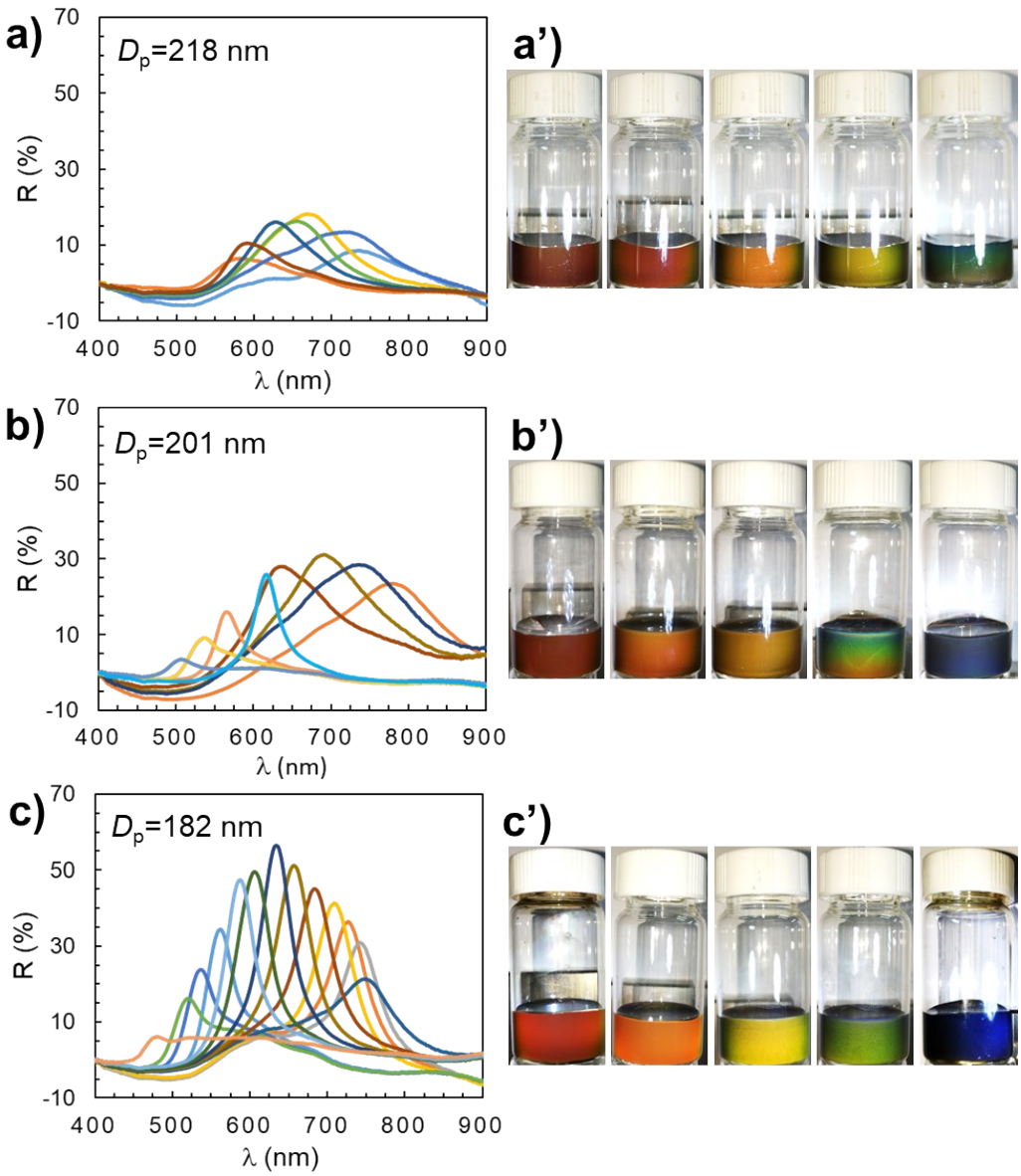


Fig. S7 Reflection spectra (a-c) and digital pictures (a'-c') of aqueous dispersions of CNCs synthesized with PSSMA (3:1) dosages of (a, a') 0.5 g, (b, b') 1.5 g and (c, c') 2.5 g upon changing the magnet-sample distances from 10.0 to 4.0 cm (a, a'), from 8.5 to 5.0 cm (b, b'), and from 9.5 to 5.0 cm (c, c').

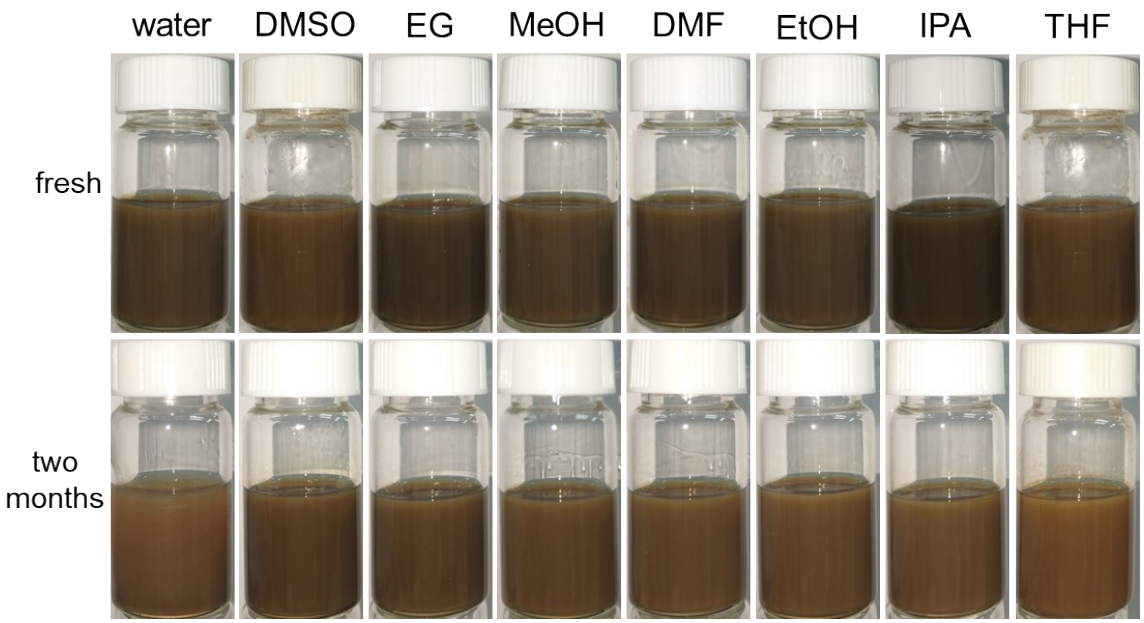


Fig. S8 Digital pictures of 131-nm CNCs dispersed in various solvents after storing different times.

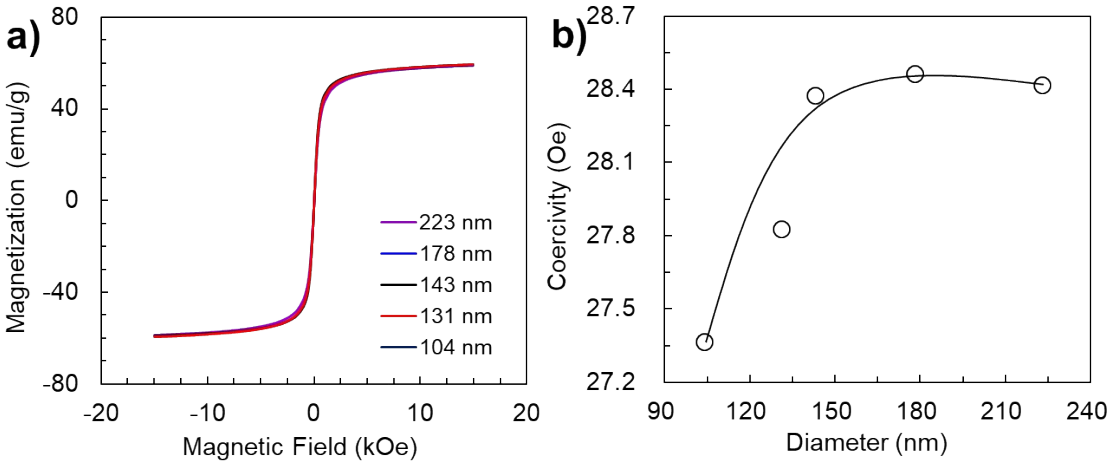


Fig. S9 Magnetic hysteresis loops (a) and coercivity of the CNCs sample with diameters ranging from 104 to 223 nm.

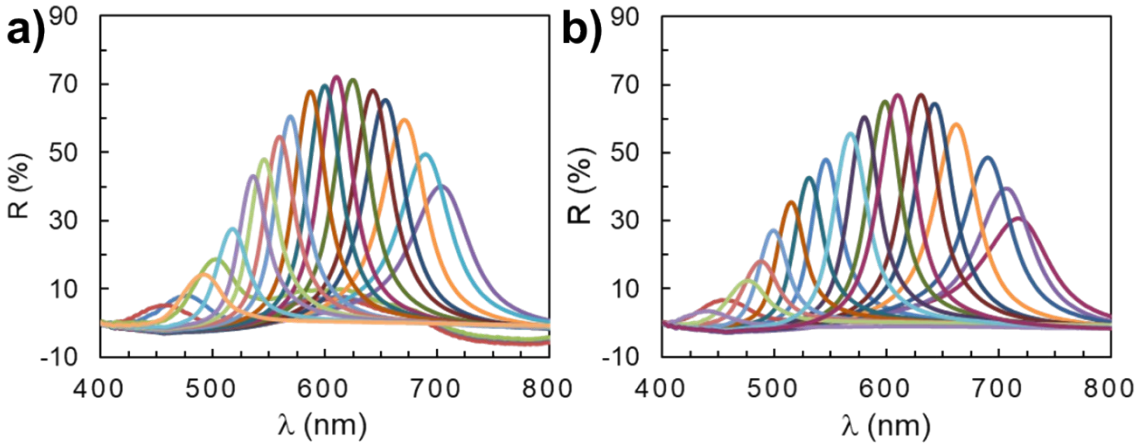


Fig. S10 Reflection spectra of an aqueous dispersion of 131-nm CNCs upon changing the magnet-sample distances from 7.0 to 3.0 cm (a) and from 3.0 to 7.0 cm (b).

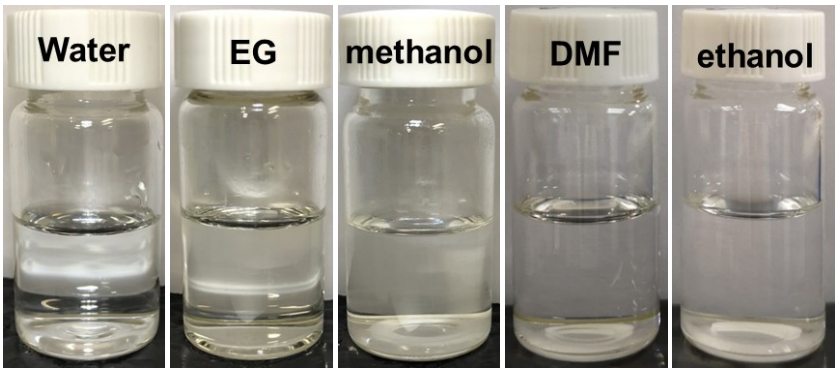


Fig. S11 Solubility of PSSMA (3:1) in various solvents. The mass content of PSSMA (3:1) in various solvents is 2.5 mg/mL.

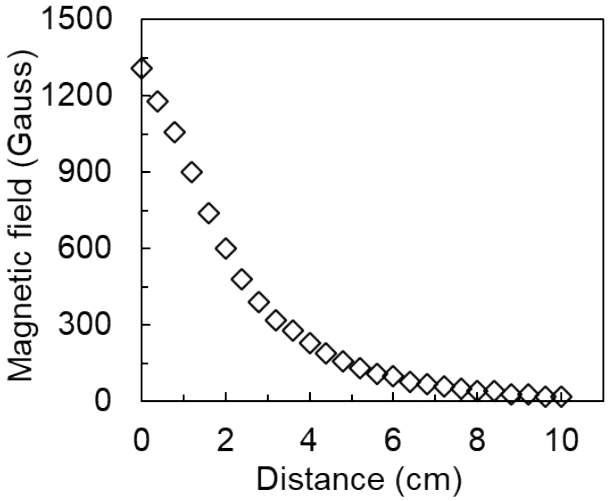


Fig. S12 Spatial distribution of the magnetic field strength measured by using a Hall probe.

Reference

1. D. L. A. de Faria, S. V. Silva and M. T. de Oliveira, *J. Raman Spectrosc.*, 1997, **28**, 873-878.