Supporting Information

One-pot hydrothermal preparation of gadolinium-doped silicon nanoparticles as a dual-modal probe for multicolor fluorescence and magnetic resonance imaging

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Experimental

Stability of D-Si_{Gd}NPs. There were three aspects to evaluate the stability of D-Si_{Gd}NPs, including the pH stability, salt concentration effect and anti-photobleaching ability.

pH stability. The pH of the D-Si_{Gd}NPs solution was adjusted from 2 to 12 by adding HCl (1M) or NaOH (1M) dropwise. Afterwards, the PL intensity of the D-Si_{Gd}NPs solution with different pH values was measured via a fluorescence spectrophotometer.

Salt concentration effect. The equivalent D-Si_{Gd}NPs solution was dropped into the same volume of NaCl solution with various concentration (0, 20, 40, 60, 80, 100 mM). After ultrasonic dispersion for 5min, the PL of the mixture was measured via a fluorescence spectrophotometer.

Anti-photobleaching ability. As a contrast, FITC and D-Si_{Gd}NPs were carried out the "Time-Scan measurement" under continuous excitation at 450 nm and 488 nm for 3 h by a fluorescence spectrophotometer respectively.

Biotoxicity of the D-Si_{Gd}NPs.

The MTT assay of D-Si_{Gd}NPs. Cytotoxicity of D-Si_{Gd}NPs was evaluated by MTT (3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide) biochemical assay

(M2128, Sigma–Aldrich, USA). All cells were seeded in 96-well plates at 1×104 cells/well for 24 h followed by culture medium removal and subsequently addition of culture medium containing D-Si_{Gd}NPs with different concentrations (100 μg/mL, 300 μg/mL, 500 μg/mL, 700 μg/mL). At designated time of 48 hours, 10 μL MTT solution (5 mg/mL) was added to each well and incubated at 37℃ for another 4 h, then 100 μL of DMSO was added to stop the reduction reaction and dissolve the purple formazan, and the optical density of the solution was measured at 490 nm using a microplate reader (Bio-RAD iMarkTM, America). The cytotoxicity assay was performed 3 times and the average value of the three measurements was taken.

Trypanblue staining. All cells were seeded in 6-well plates and added different concentrations (300 μg/mL, 500 μg/mL) of the as-prepared D-Si_{Gd}NPs to incubate 4 h, 8 h, 12 h, 16 h, and 24 h. Cells viability was determined by trypanblue staining, and cells were counted in trypanblue solution with the Countess® Automated Cell Counter (Invitrogen, Carlsbad, CA, USA).

The toxicity assessment for mice. To evaluate the in vivo toxicity of D-Si_{Gd}NPs, the nude mice (14-17 g, n = 3 per group) was treated by tail intravenous injection of D-Si_{Gd}NPs (200 μL, 4 mmol Gd mL−1) with 4% chloral hydrate (180 μL), and the control group was injected with normal saline at the same conditions. And the histological sections were stained by hematoxylin and eosin (H&E) at a week after injection. The body weight of the mice was measured with a counter balance once a week for a period of 28 days.

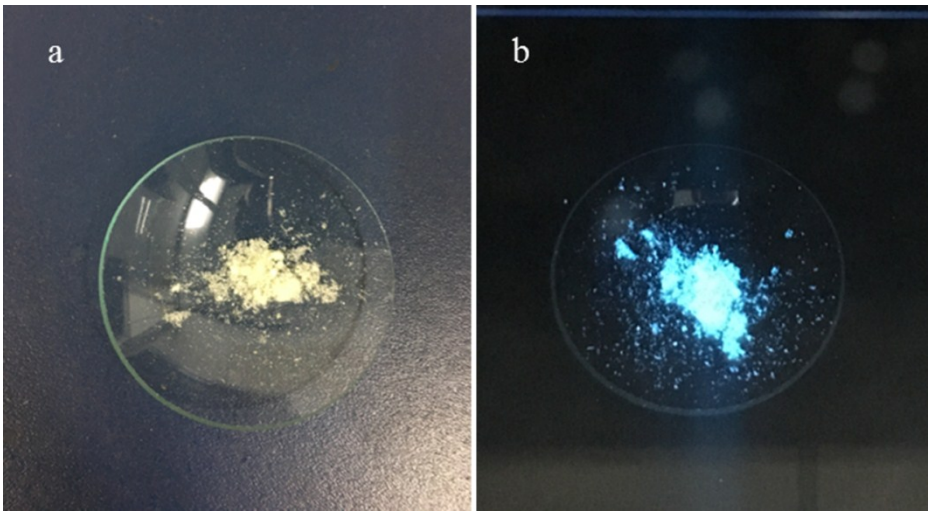

Fig. S1. The photographs of the D-Si_{Gd}NPs powder via lyophilization after dialysis under ambient light (a) and 365 nm UV irradiation (b).

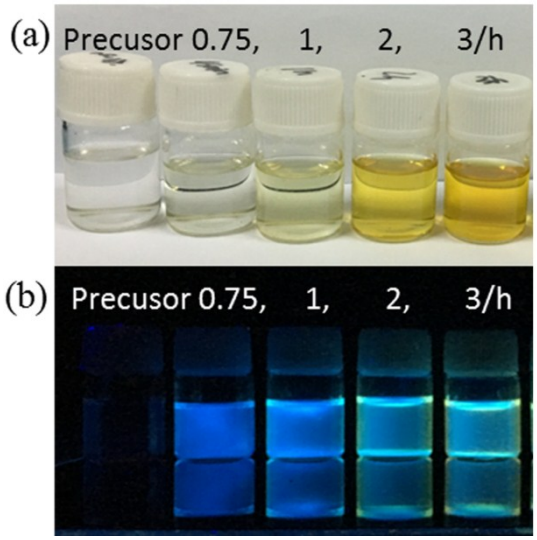

Fig. S2. The photographs of the D-Si_{Gd}NPs prepared at different reaction times (precusor, 0.75, 1, 2, 3 h) under ambient light (a) and 365 nm UV irradiation (b).

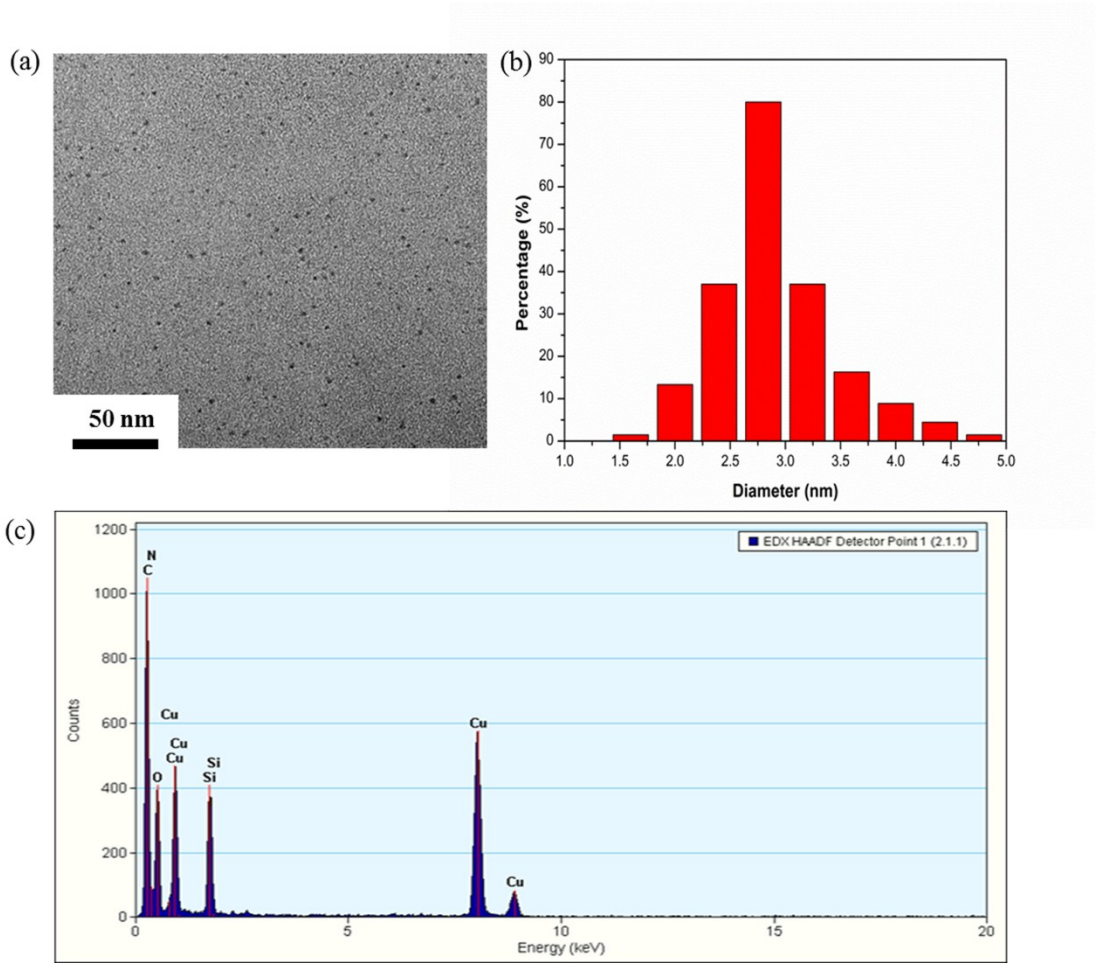

Fig. S3. (a) TEM image, (b) corresponding size distribution histogram and (c) EDX pattern of the D-Si_{Gd}NPs prepared at reaction time of 1 h.

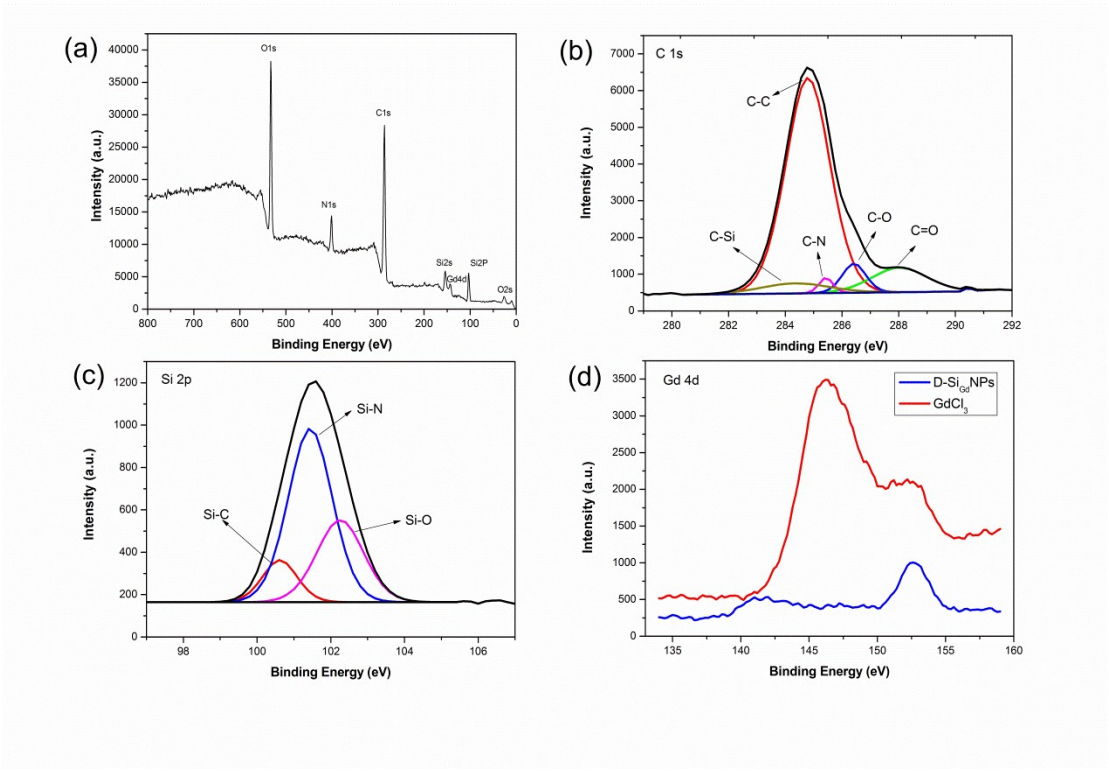

Fig. S4. The XPS spectra of the D-Si$_{Gd}$NPs: (a) full range, (b) C 1s, (c) Si 2p, (d) Gd 4d.

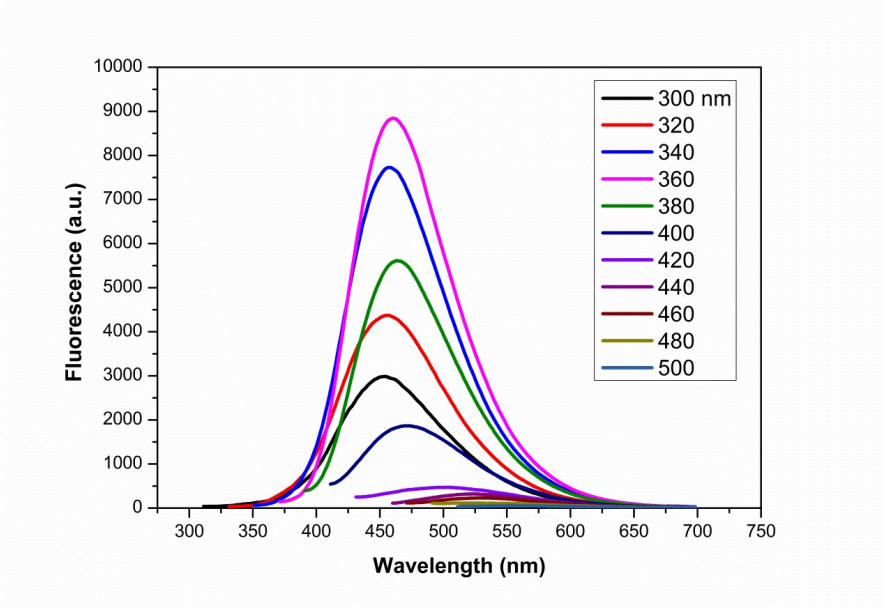

Fig. S5. PL spectra of SiNPs at different excitation wavelength from 300 nm to 500 nm.

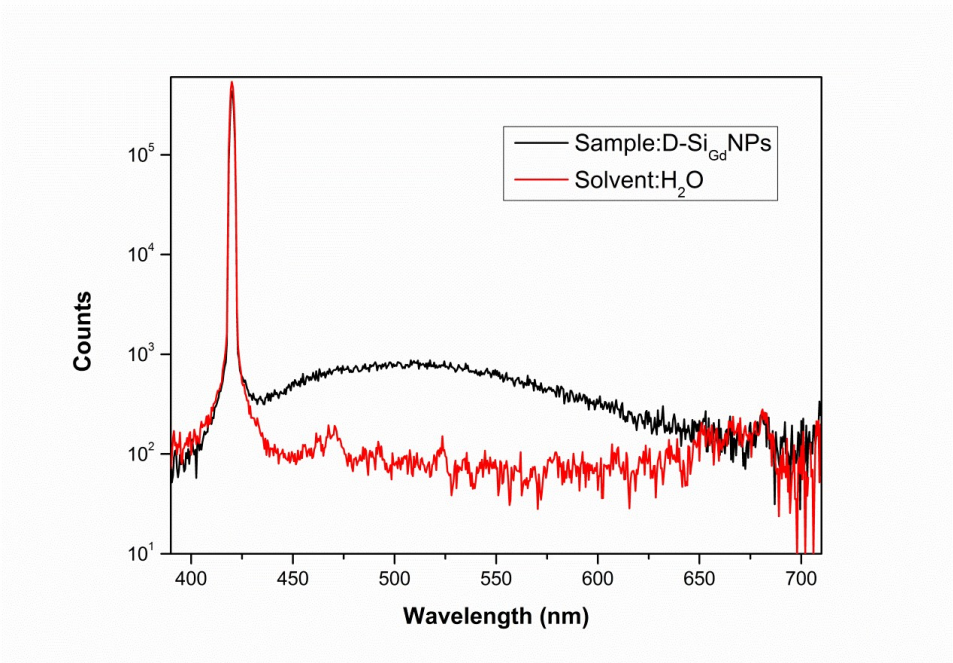

Fig. S6. APLQY spectra of the as-prepared D-Si$_{Gd}$NPs. The APLQY value was measured by FLS-920 instrument equipped with an integrating sphere.

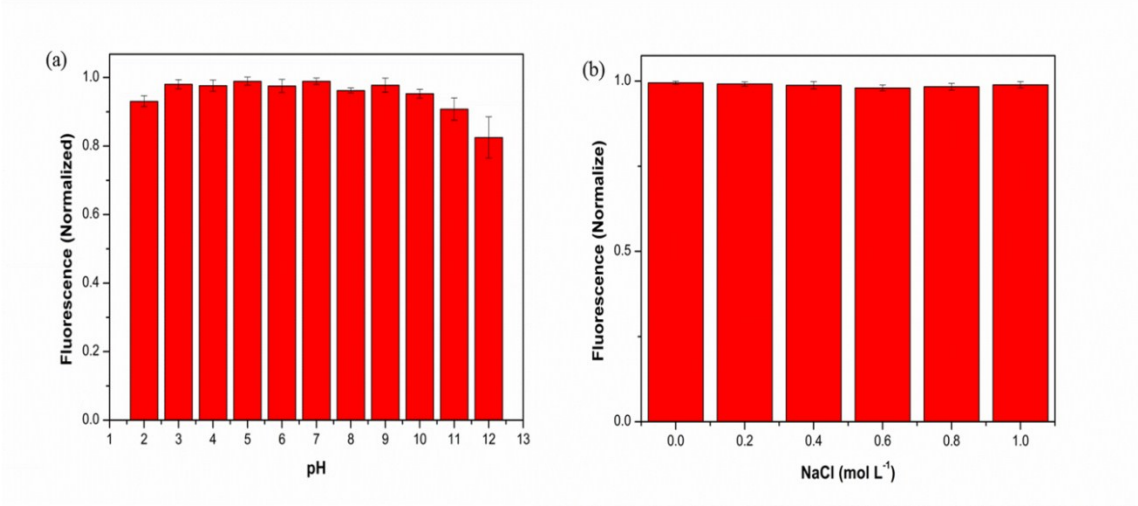

Fig. S7. The stability of the as-prepared D-Si$_{Gd}$NPs. (a) pH stability in water; (b) Salt effect.

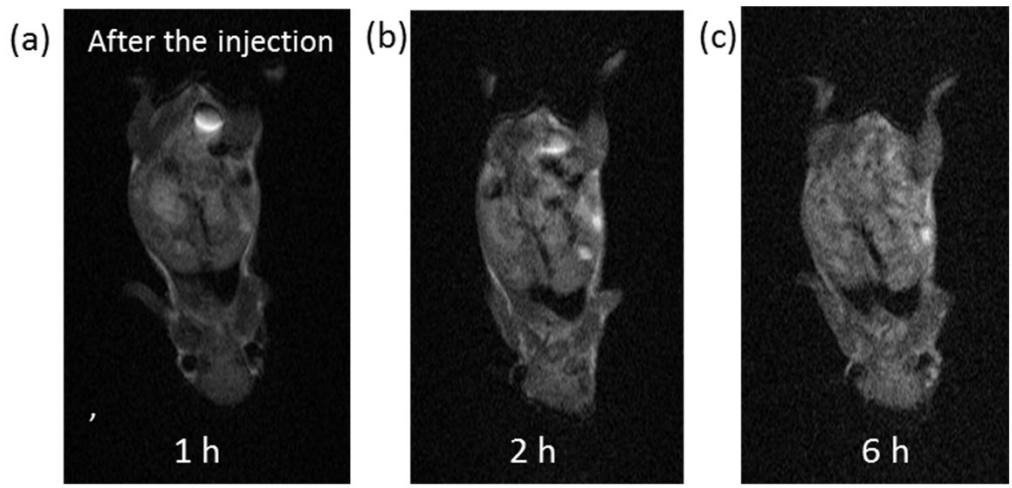

Fig. S8. In vivo MR images of mice after tail-vein injection of D-Si_{Gd}NPs (200 μL, 4 mmol Gd mL^{-1}) at 1 h (a), 2 h (b) and 6 h (c).

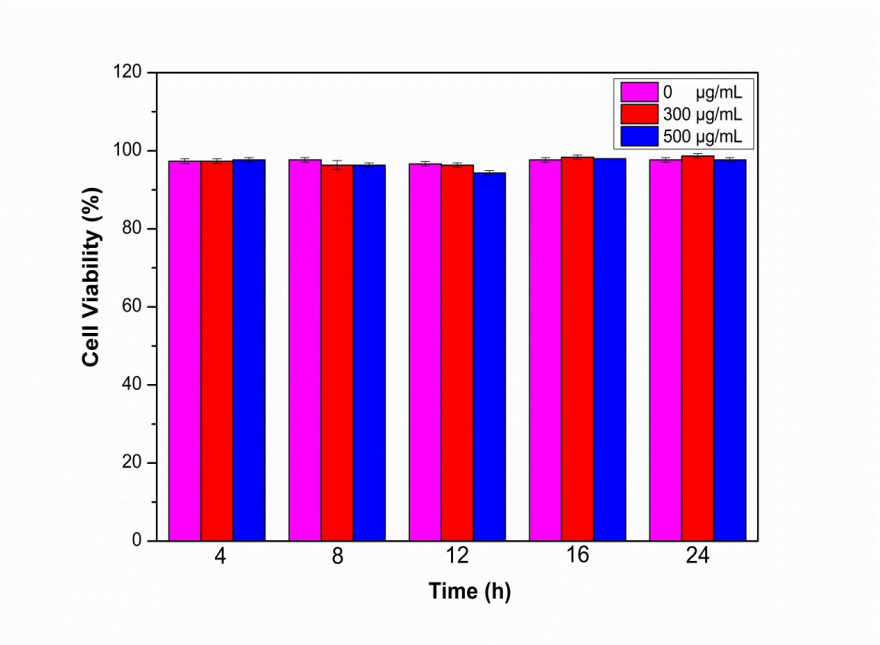

Fig. S9. The cell viability of Hela cells after incubation for 4 h, 8 h, 12 h ,16 h and 24 h with concentrations (300 and 500 μg/mL) of the as-prepared D-Si_{Gd}NPs determined by trypanblue staining.

Table S1. Comparison between the Gd-Si and Gd-C hybrid nanoparticles.

The type of hybrid nanoparticle	Reference	Longitudinal relaxivity (r_1) (mM^{-1} s^{-1})	Quantum Yield (QY) (%)
Gd-Si	In this work	5.78	38
Gd-Si	(1)	19.39	no mention
Gd-Si	(2)	2.4	no mention
Gd-C	(3)	9.805	5.76
Gd-C	(4)	57.42	40
Gd-C	(5)	56.72	5.2
Gd-C	(6)	11.356	5.4
Gd-C	(7)	5.5-6.4	2.6-8.9
Gd-C	(8)	7.36	21

References

(1) S. Sinha, W. Y. Tong, N. H. Williamson, S. McInnes, S. Puttick, A. Cifuentes-Rius, R. Bhardwaj, S. E. Plush and N. H. Voelcker, *ACS Appl. Mater. Interfaces.,* 2017, **9**, 42601−42611.

(2) F. Erogbogbo, C. W. Chang, J. L. May, L. Liu, R. Kumar,W. C. Law, H. Ding, K. T. Yong, I. Roy, M. Sheshadri, M.T. Swihart and P. N. Prasad, *Nanoscale*, 2012, **4**, 5483-5489.

(3) A. Gao, Y. F. Kang and X. B. Yin, *New J. Chem.,* 2017, **41**, 3422-3431.

(4) Y. Pan, J. Yang, Y. Fang, J. Zheng, R. Song and C. Yi, *J. Mater. Chem. B.,* 2017, **5**, 92-101.

(5) Y. Shi, Y. Pan, J. Zhong, J. Yang, J. Zheng, J. Cheng, R. Song and C. Yi, *Carbon,* 2015, **93**, 742-750.

(6) N. Gong, H. Wang, S. Li, Y. Deng, X. Chen, L. Ye and W. Gu, Langmuir, *2014*, **30**, 10933-10939.

(7) X. Ren, L. Liu, Y. Li, Q. Dai, M. Zhang and X. Jing, *J. Mater. Chem. B.,* 2014, **2**, 5541-5549.

(8) Y. Xu, X. H. Jia, X. B. Yin, X. W. He and Y. K. Zhang, *Anal. Chem.*, 2014, **86**, 12122-12129.