Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Gadolinium oxide nanoplates with high longitudinal relaxivity for magnetic resonance imaging

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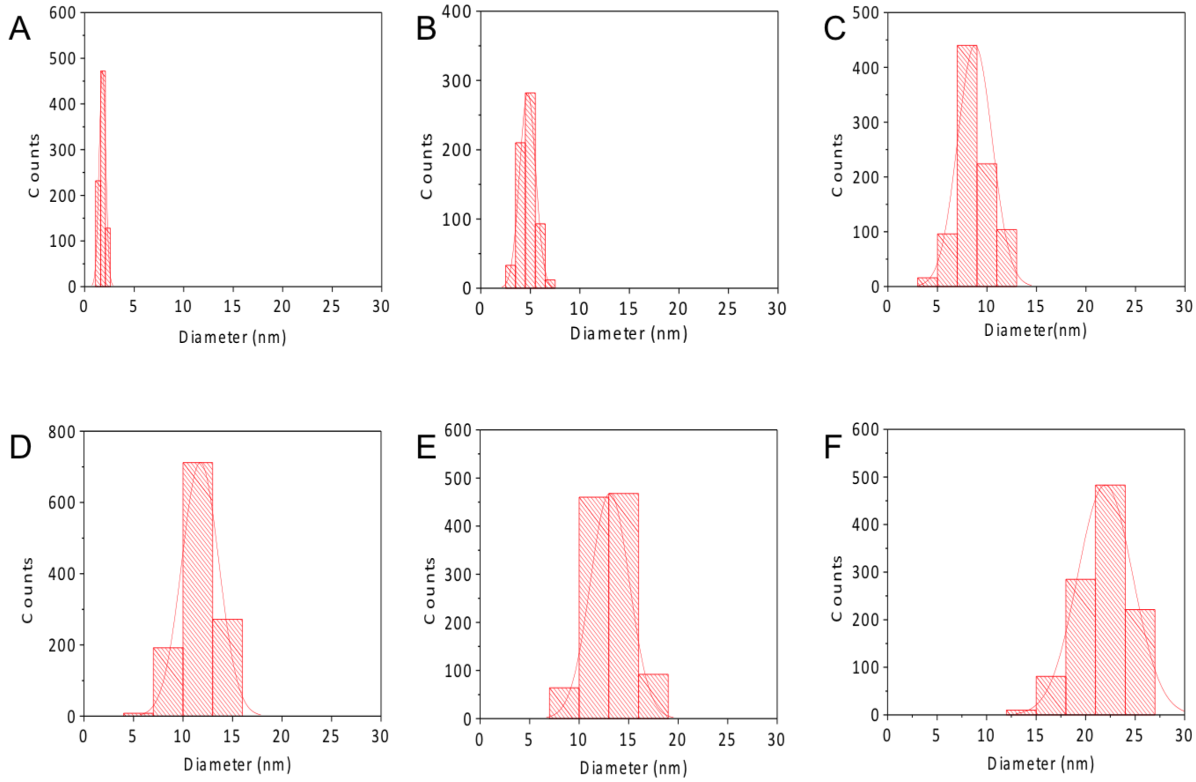

Fig. S1 The histograms of Gd_2O_3 nanoparticles ranging from 2 to 22 nm. The average diameters with standard deviation are (A) 1.79 ± 0.23 nm, (B) 5.02 ± 0.45 nm, (C) 7.95 ± 0.82 nm, (D) 10.82 ± 1.75 nm, (E) 13.18 ± 2.09 nm, and (F) 21.97 ± 2.78 nm, respectively. The averages were calculated with over 1000 individual nanoparticles.

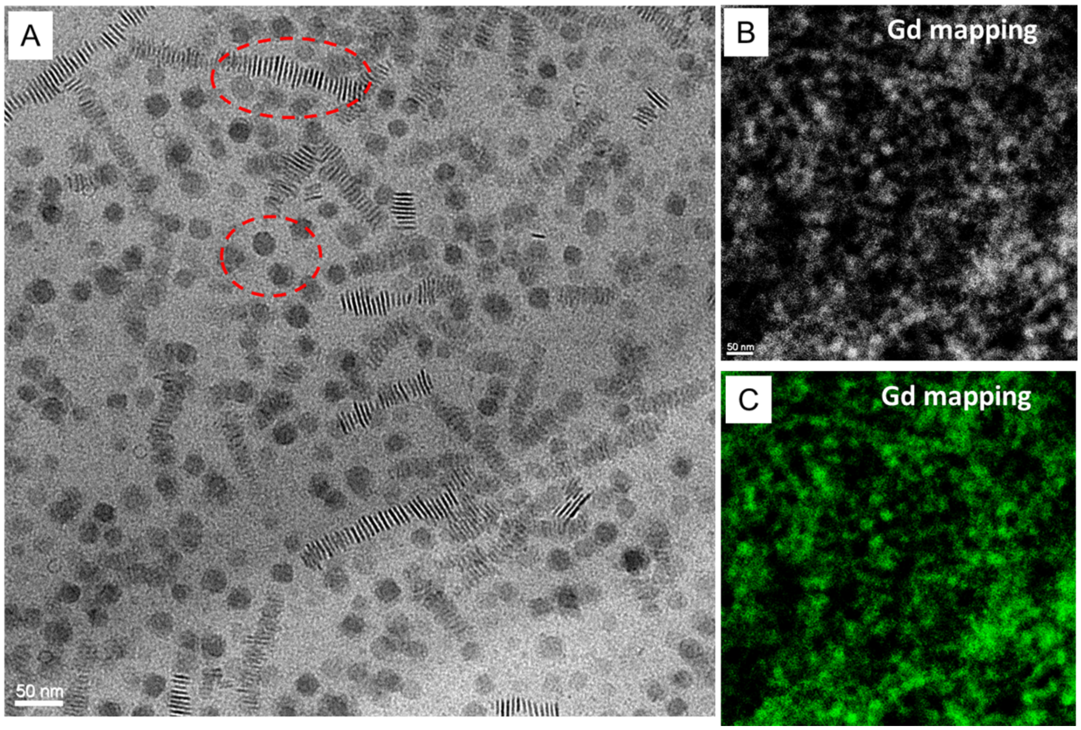

Fig. S2 The TEM image of 22 nm diameter gadolinium oxide nanoplates; In the TEM images, some ultrathin nanoplates were aligned parallel with face-to-face direction. From Gatan Image Filter (GIF) mapping, these nanoplates have gadolinium (green) in a nanoparticle**.**

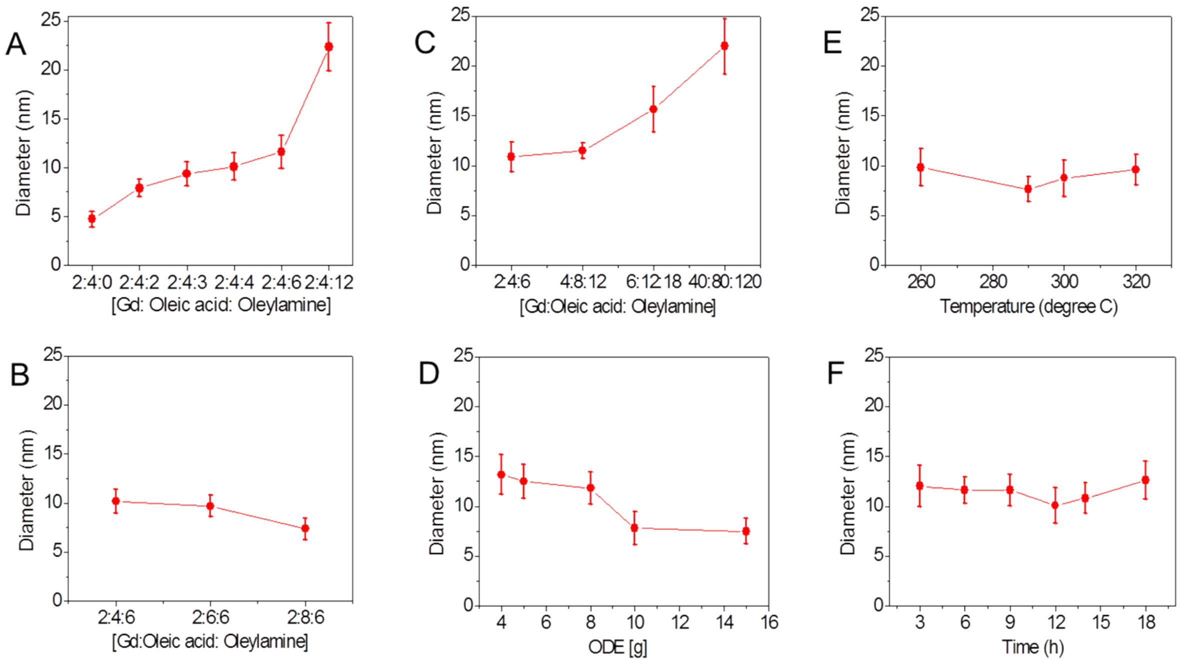

Fig. S3 The size controllable Gd_2O_3 nanoparticles by changing synthetic parameters (A) oleylamine, (B) oleic acid, (C) concentration of precursors, (D) ODE, (E) temperature, and (F) reflux time; As increasing the amounts of oleylamine (A), the particle sizes were increased from 5 to 22 nm. As increasing the amounts of oleic acid (B), the particle sizes were decreased from 10 to 7 nm. When increasing the concentration of precursors or reducing ODE amounts, the particle sizes were increased due to high monomer concentration. The temperature (E) and (F) did not show any significant size changes.

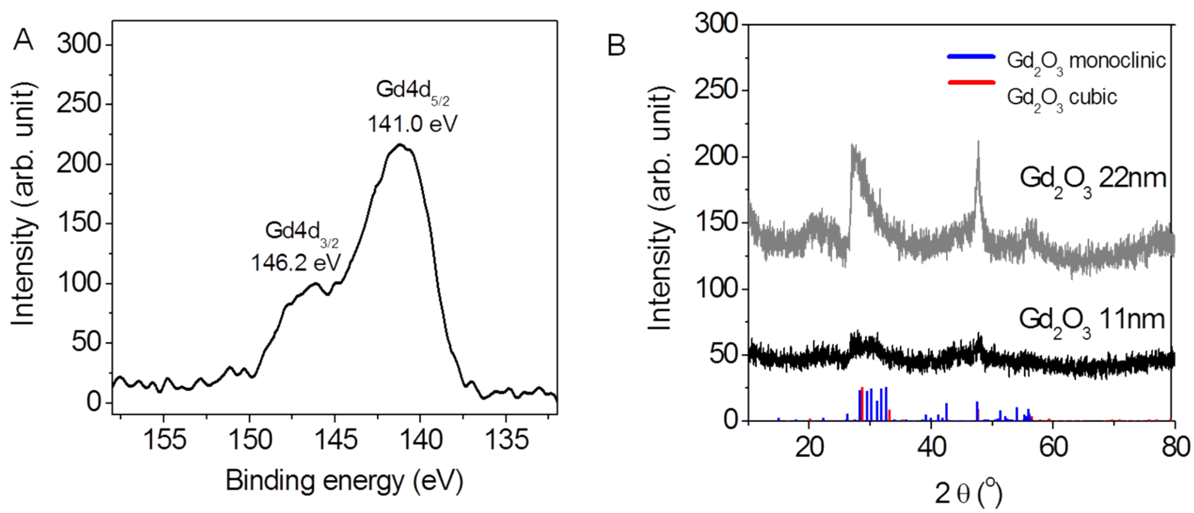

Fig. S4 XPS and XRD data of Gd_2O_3 nanoparticles (A) XPS data of Gd_2O_3 nanoparticles (11 nm diameter) showing Gd $4d_{3/2}$ at 146.2 eV and (B) XRD Data of Gd_2O_3 nanoparticles with diameter 11 nm and 22 nm. For the references, JCPDS Gd_2O_3 monoclinic (# 43-1015) and cubic (# 43-1014) were used.

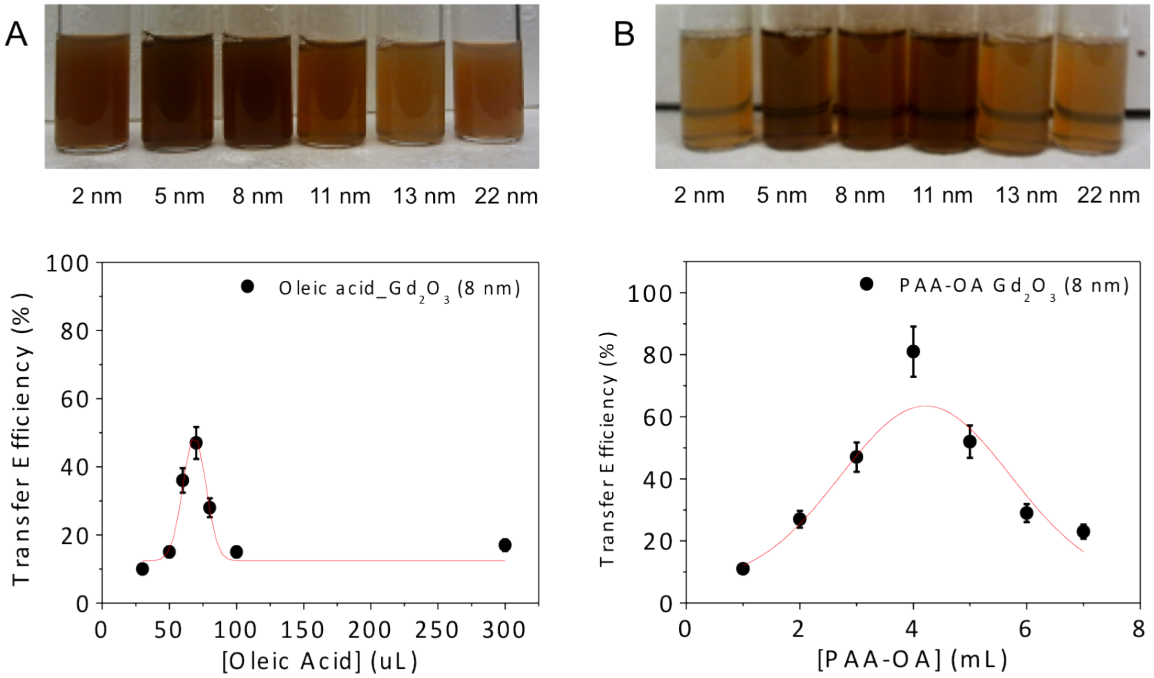

Fig. S5 The photographs of oleic acid bilayer coated Gd_2O_3 nanoparticles with different sizes from 1.8 nm to 22 nm and phase transfer efficiency (%) when using various amounts of oleic acid (30-300 μL, 0.95 X 10^{-4} to 9.5 X 10^{-4} mol) in 1 ml Gd_2O_3 nanoparticle/ethyl ether solution (1.5~4 mg/ml) (C) The photographs of PAA-OA coated Gd_2O_3 nanoparticles ranging from 1.8 nm to 22 nm diameters and phase transfer efficiency (%) using various amounts of PAA-OA solutions (1-7 mL, 4 X 10^{-4} to 26 X 10^{-4} mol) with 1 mL Gd_2O_3 nanoparticle/ethyl ether solution (1.5~4 mg/ml). The concentrations of Gd in a particle were analyzed by inductive coupled plasma-optical emission spectroscopy (ICP-OES).

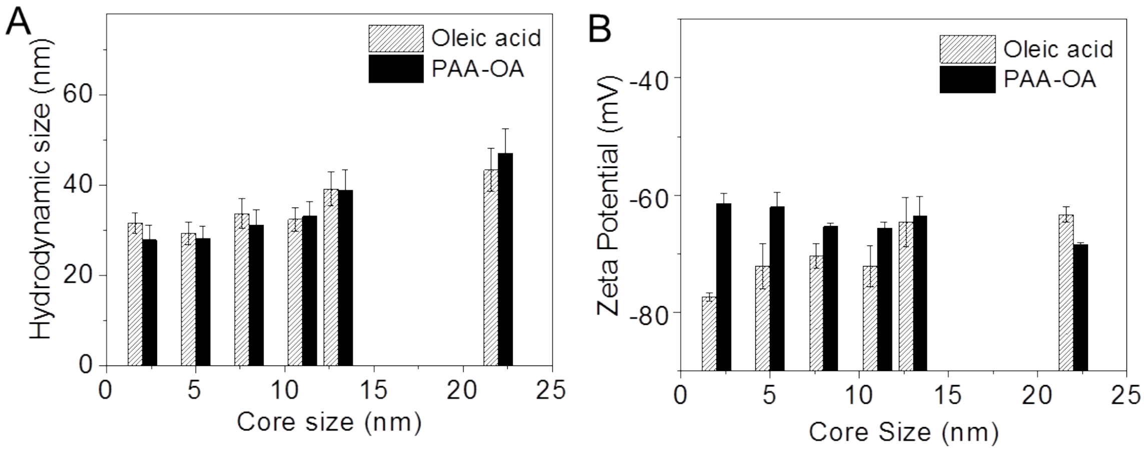

Fig. S6 (A) The hydrodynamic sizes of oleic acid bilayer and PAA-OA coated Gd_2O_3 nanoparticles with different core diameters (2 to 22 nm) using dynamic light scattering (DLS) analysis; The measurement was repeated 5 times and the average diameters with errors were shown. (B) Zeta Potential (mV) of oleic acid bilayer and PAA-OA coated Gd_2O_3 nanoparticles. Due to carboxylic acid (COOH) and basic solution, the zeta potential was around -60 ~-80 mV. The measurement was repeated five times for the average and standard deviation.

Table S1. The average hydrodynamic sizes (nm) and zeta potentials (mV) of oleic acid bilayer and PAA-OA coated Gd_2O_3 nanoparticle

	Hydrodynamic size (nm)		Zeta Potential (mV)	
Core Size (nm)	Oleic acid bilayer	PAA-OA	Oleic acid bilayer	PAA-OA
2	31.6 ± 2.3	27.8 ± 3.3	-77.4 ± 0.7	-61.5 ± 1.7
5	29.3 ± 2.5	28.1 ± 2.8	-72.1 ± 3.9	-62.0 ± 2.4
8	33.7 ± 3.2	31.2 ± 3.2	-70.4 ± 2.2	-65.3 ± 0.5
11	32.4 ± 2.6	33.0 ± 3.4	-72.2 ± 3.5	-65.6 ± 1.0
13	39.1 ± 3.7	38.9 ± 4.5	-64.7 ± 4.2	-63.6 ± 3.4
22	43.4 ± 4.8	47.1 ± 5.4	-63.3 ± 1.3	-68.5 ± 0.5

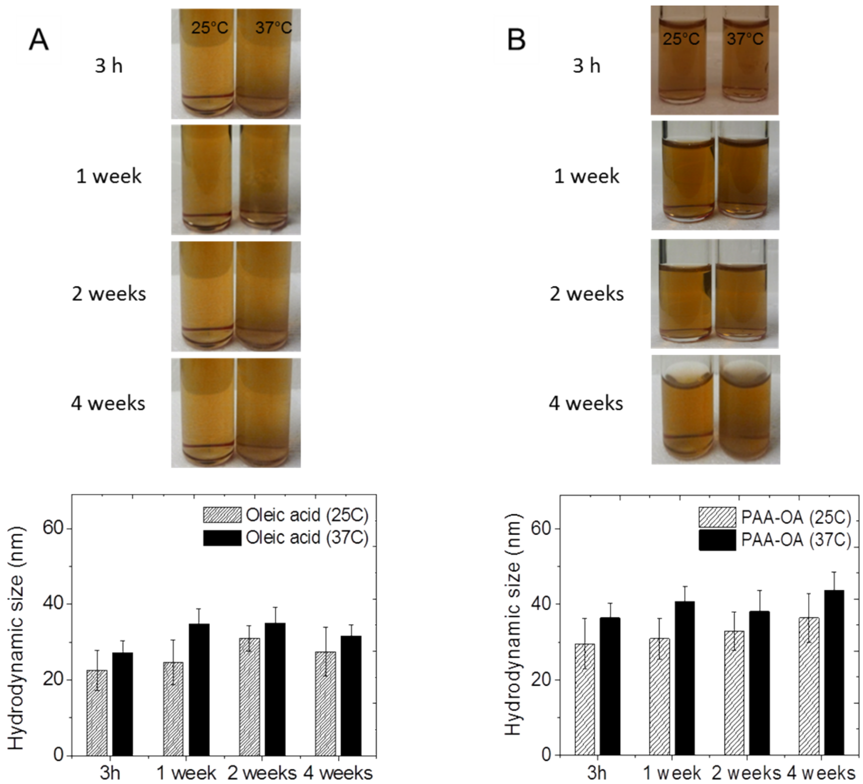

Fig. S7 The stability test of (A) oleic acid bilayer and (B) PAA-OA coated Gd_2O_3 nanoparticles at room temperature (25 °C) and body temperature (37 °C) from 3 h to 4 weeks. The stability data were based on the photographs and the changes of hydrodynamic size (nm) for long-term duration.

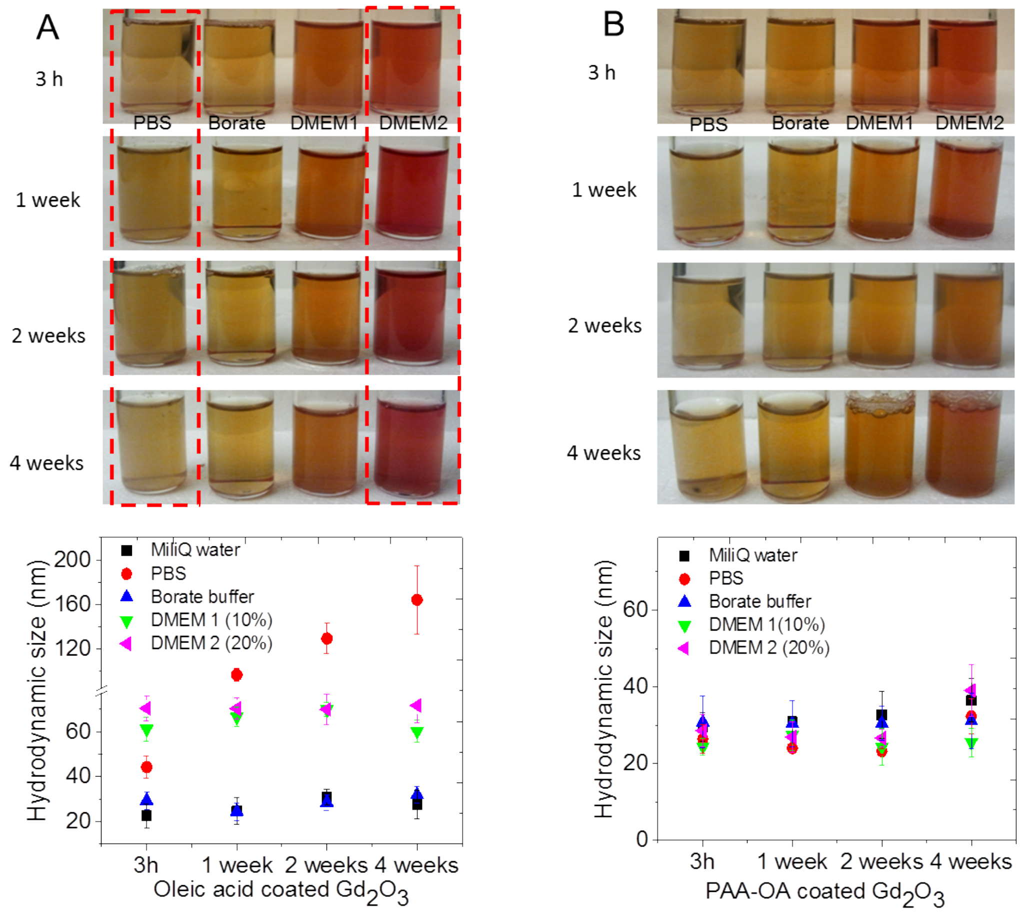

Fig. S8 The stability test of (A) oleic acid bilayer and (B) PAA-OA coated Gd_2O_3 nanoparticles at different buffer conditions including phosphate buffer saline (PBS), borate buffer (BB), DMEM 1 (10 %), and DMEM2 (20 %) cell media solution. The stability data were based on the visible change (photographs) and the changes of hydrodynamic sizes (nm) for long-term duration (up to 4 weeks).

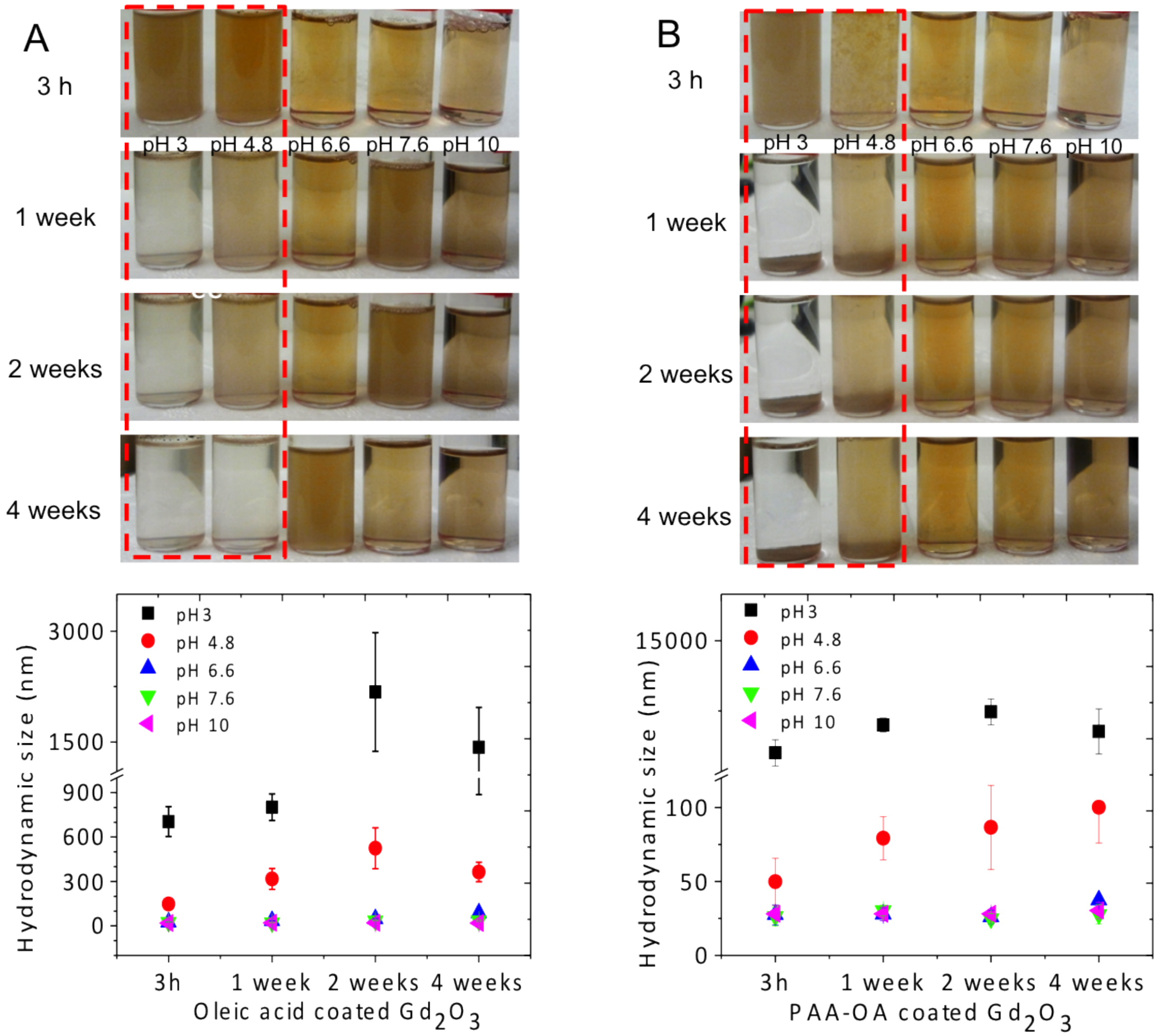

Fig. S9 The stability test of (A) oleic acid bilayer and (B) PAA-OA coated Gd_2O_3 nanoparticles at different pH conditions at 3, 4.8, 6.6, 7.6, and 10. The stabilities were determined from the photographs and changes of hydrodynamic sizes (nm) for long-term duration (up to 4 weeks).

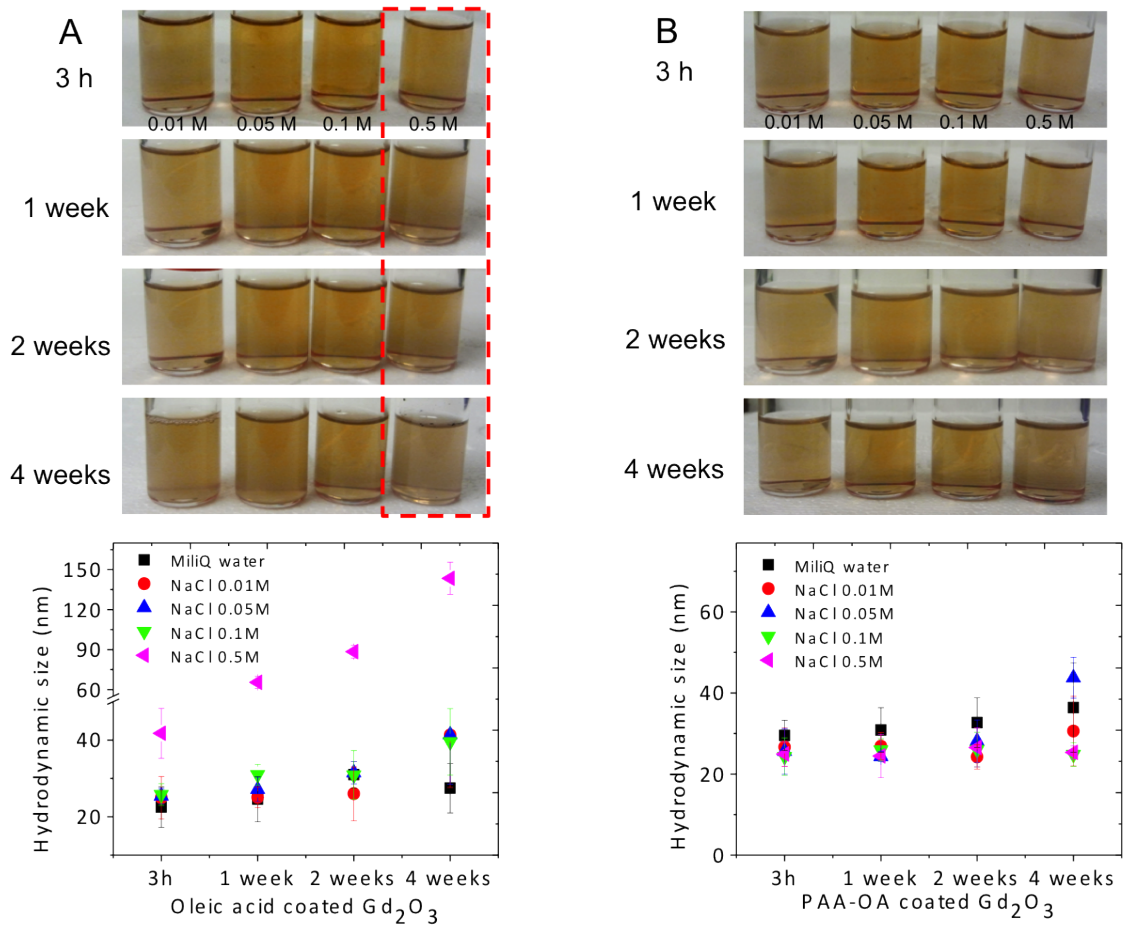

Fig. S10 The stability test of (A) oleic acid bilayer and (B) PAA-OA coated Gd_2O_3 nanoparticles at different ionic strengths (0.01 M NaCl to 0.5M NaCl). The stability data were based on the visible photographs and changes of hydrodynamic sizes (nm) for long-term duration (up to 4 weeks).

Table S2. The stabilities on the hydrodynamic sizes of gadolinium oxide suspensions under various conditions.

	The change of hydrodynamic size (√ : stable, ❐: little stable, ✗ : non-stable)														
	Temperature		Buffers				pH					NaCl (M)			
	25°C	37°C	PBS	Borate	DMEM1	DMEM2	3	4.8	6.6	7.6	10	0.01	0.05	0.1	0.5
Oleic acid	√	√	✗	√	❐	❐	✗	❐	√	√	√	√	√	√	✗
PAA-OA	√	√	√	√	√	√	✗	❐	√	√	√	√	√	√	√

Table S3. The stabilities on r_1 relaxivities of gadolinium oxide suspensions under various conditions.

	The change of r_1 relaxivity (√ : stable, ❐: little stable, ✗ : non-stable)														
	Temperature		Buffers				pH					NaCl (M)			
	25°C	37°C	PBS	Borate	DMEM1	DMEM2	3	4.8	6.6	7.6	10	0.01	0.05	0.1	0.5
Oleic acid	√	√	✗	√	√	√	✗	❐	√	√	√	√	√	√	√
PAA-OA	√	√	✗	√	❐	❐	✗	❐	√	√	√	√	√	√	√