Supporting Information for:

Surface Modification of Gadolinium Oxide Thin Films and Nanoparticles using Polyethylene glycol-phosphate

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Gd_2O_3 thin film characterization: The flatness of electron beam-deposited Gd_2O_3 thin films (Figure S1a) was confirmed with both SEM and AFM (Figure S1b and c). AFM-measured surface roughness was of only 1 nm over a surface area of 20 × 20 μm^2 (Figure S1c). The XRD pattern revealed, at $2\theta \approx 28.6°$, the 222 peak characteristic of body-centered cubic Gd_2O_3 (Figure S2). This result is very similar to that obtained with US-Gd_2O_3 nanoparticles.[1] The most intense peaks detected were from the SiO_2/Si substrate[2]; the absence of other Gd_2O_3 peaks is an indication of the thinness of the oxide layer.

No contribution from Si was found in Angle Resolved XPS data (Figure S3a), even at 90° (higher penetration), suggesting that thin films are probably slightly thicker than 10 nm. As expected, higher amounts of C (organic contamination) were detected at grazing angles whereas O and Gd reached their highest values at deeper angles (Figure S3a). The composition of Gd_2O_3 thin films was further studied by XPS depth profiling (Figure S3b). After only 1 min of argon sputtering, the contaminating organic adlayer was largely eliminated (2). From 5 min (3) to 20 min (4), O and Gd contents appeared rather constant, revealing the presence of both gadolinium hydroxide and oxide. After 20 min of sputtering, the silicon substrate was hit. Organic contamination at the surface is reflected by a large amount of C-O bonds at 532 eV (Figure S3c, (1)). At (2), most of the organic contamination is gone; however, the residual peak at 532 eV is attributed to gadolinium hydroxide.[3] From (2) to (4), this contribution gradually decreases whereas the contribution at 529.7 eV, assigned to gadolinium oxide (Gd_2O_3)[3], increases.

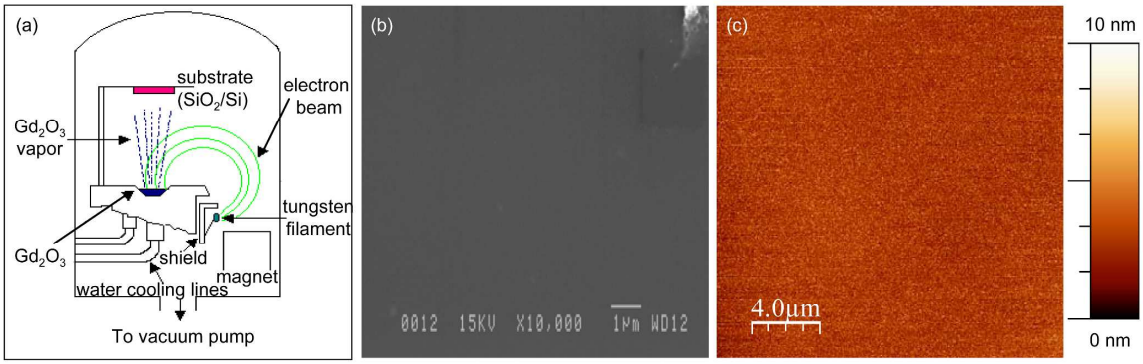

Figure S1. Electron-beam evaporation system (a); SEM (b) and AFM (c) images of the as-deposited Gd_2O_3 thin film on silicon substrate

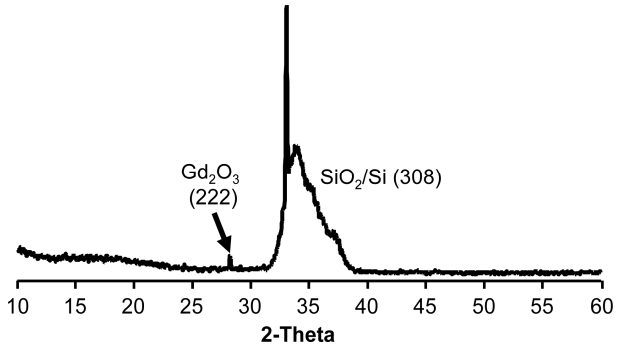

Figure S2. XRD spectrum of the as-deposited Gd_2O_3 thin film on silicon substrate

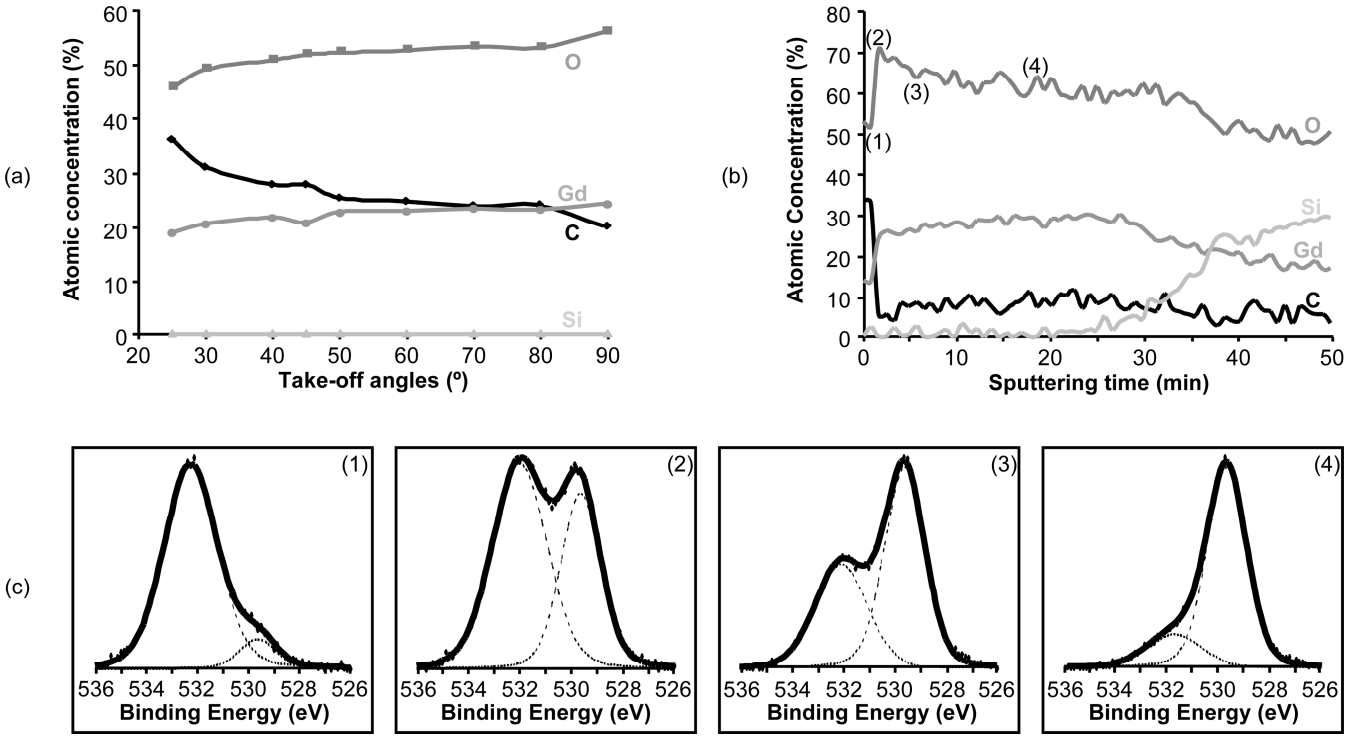

Figure S3. As-deposited Gd_2O_3 thin films characterized by (a) angle resolved XPS, (b) XPS depth profiling and (c) O1s high resolution XPS at different depths

A pretreatment of the surface is necessary to remove contaminants and to increase the number of hydroxyl groups in order to facilitate PEG grafting. In this study, Gd_2O_3 thin films were immersed in a solution of NaOH at 10^{-2} M for 15 min. The hydroxylation was confirmed by XPS, without evidence of thin film degradation (data not shown).

In order to assess the stability of Gd_2O_3 thin films, the surfaces were immersed in water or in ethanol for 24 h. XPS surveys on these samples confirmed the good retention of Gd on the surfaces submitted to ethanol (Table S1). However, after 24 h in water, a small but significant contribution of Si, together with a decrease of the Gd proportion, provided clear indications of Gd leaching. In subsequent grafting studies, the pH was therefore adjusted to 7.0 in order to limit the alteration of Gd_2O_3 films, which seems to occur in acidic water. Apparently, no evidence of degradation was noticed after this adjustment (Table S1, PEG diacid reactions).

Table S1. XPS survey data of Gd_2O_3 thin films following their immersion in different solutions for 24 h

Sample	Solvent	Atomic concentrations (%)				
		C1s	O1s	Si2p	N1s	Gd4d
unmodified Gd_2O_3/Si (control)	Water	41.3 ± 0.6 4.5% C-O 2.4% COO	41.0 ± 0.5	4.9 ± 0.2 SiO_2/Si	-	12.9 ± 0.1
	Ethanol	41.5 ± 1.0 8.0% C-O 2.9% COO	43.4 ± 0.5	-	-	15.1 ± 0.5
PEG-silane[a] on Gd_2O_3/Si	Water pH 7.0	39.7 ± 2.8 3.9% C-O	46.0 ± 1.4	~ 0.3[b] silane	< 0.1[b]	14.1 ± 1.0
	Ethanol	36.0 ± 2.6 15.0% C-O	50.4 ± 1.6	~ 0.1[b] silane	~ 0.2[b]	13.3 ± 1.4
PEG diacid[b] on Gd_2O_3/Si	Water pH 7.0	42.8 ± 3.6 3.4% C-O 3.2% COO	43.8 ± 2.0	-	-	13.4 ± 1.6
	Ethanol	32.8 ± 3.0 16.6% C-O 6.7% COO	53.0 ± 1.7	-	-	14.3 ± 1.3

Theoretical compositions and ratios:
[a] CH_3O-$(CH_2CH_2O)_n$-$(CH_2)_2$-NH-CO-NH-$(CH_2)_3$-$Si(OCH_2CH_3)_3$: 65.8% C (64.9% C-O and C-N), 33.3% O, 0.3% Si and 0.6% N; (C-O + C-N)/Si: 216
[b] HOOC-CH_2-$(OCH_2CH_2)_n$-O-CH_2-COOH: 61.9% C (57.1% C-O) and 38.1% O; C-O/COOH: 12

PEG-silane and PEG diacid graftings on Gd_2O_3 thin films: Gd_2O_3 thin films were also incubated with PEG-silane and PEG diacid, followed by XPS analyses, in order to compare the reactivity of these molecules with that of PEG-phosphate. Since the silicon and the COO percentages did not increase drastically after reaction with PEG-silane and PEG diacid respectively (Table S1), the PEG grafting efficiency on Gd_2O_3 thin films was measured by HRXPS. Indeed, on C1s spectra, the presence of PEG on thin films can be clearly confirmed by the peak at 286.5 eV, which is attributed to the C-O links. In PEG-silane and PEG diacid samples, the characteristic band of PEG was predominant for the surfaces grafted in ethanol (Figure S4g and h), whereas it was similar to that of the control (Figure S4a) in the

case of samples grafted in water (Figure S4c and d). Moreover, the PEG diacid grafting in ethanol (Figure S4h) was clearly evidenced with the band at 289 eV, attributed to COO groups.

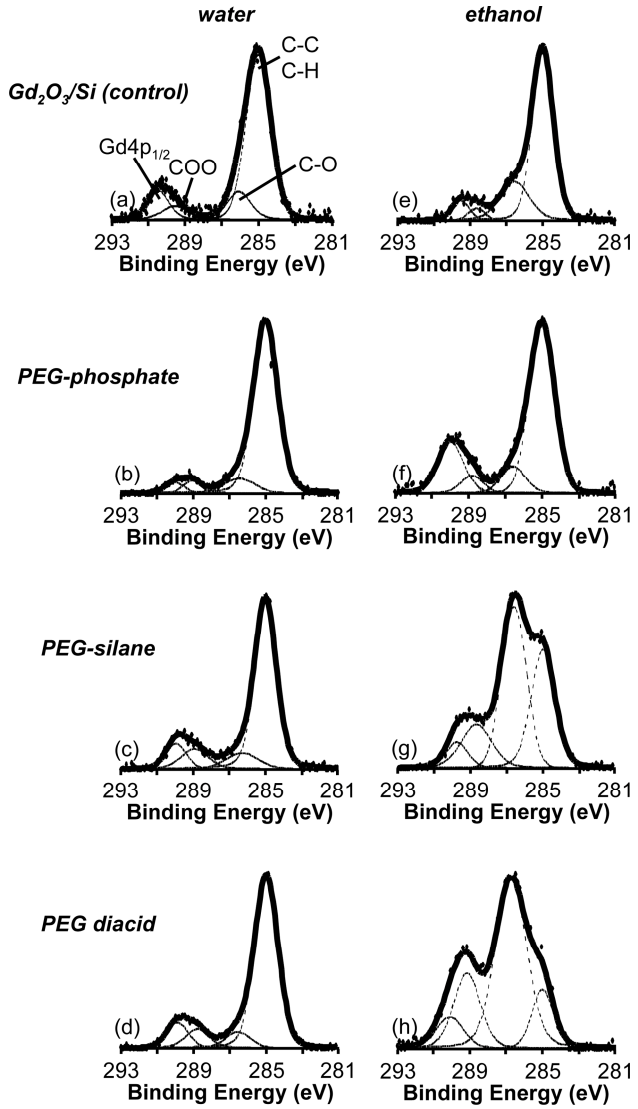

Figure S4. C1s HRXPS spectra of Gd_2O_3 thin films immersed 24 h in water (a), in PEG-phosphate (b), PEG-silane (c) or PEG diacid (d) aqueous solutions; in ethanol (e) and in PEG-phosphate (f), PEG-silane (g) or PEG diacid (h) ethanol solutions

According to the theoretical composition of PEG-silane (MW 5000 g/mol) and PEG diacid (M_n ~ 600 g/mol) used in this study, a (C-O + C-N)/Si ratio of 216 and a C-O/COOH ratio of 12 should be obtained for an ideal monolayer. For the PEG-silane-treated Gd_2O_3 surfaces, (C-O + C-N)/Si ratios of

14 and 109 were obtained after the reaction in water and in ethanol, respectively (Table S1). For the PEG diacid-treated Gd_2O_3 surfaces, C-O/COOH ratios of 1.1 and 2.5 were obtained (Table S1). After C1s peak fitting and quantification, it clearly appeared that solvent strongly influences the ligand grafting for both PEG-silane and PEG diacid (Figure S4c, d, g and h). Therefore, the grafting of PEG-silane and PEG diacid on Gd_2O_3 thin films appeared more efficient by using ethanol. However, relatively low (C-O + C-N)/Si and C-O/COOH ratios reflect the partial coverage of thin films by PEG-silane and PEG diacid molecules, possibly due to residual organic contamination. Moreover, no shift was observed in Gd4d HRXPS spectra for both Gd_2O_3 thin films treated with PEG-silane and PEG diacid in ethanol, suggesting a lower affinity of these functional groups for the rare-earth oxide compared to the phosphate (Figure S5).

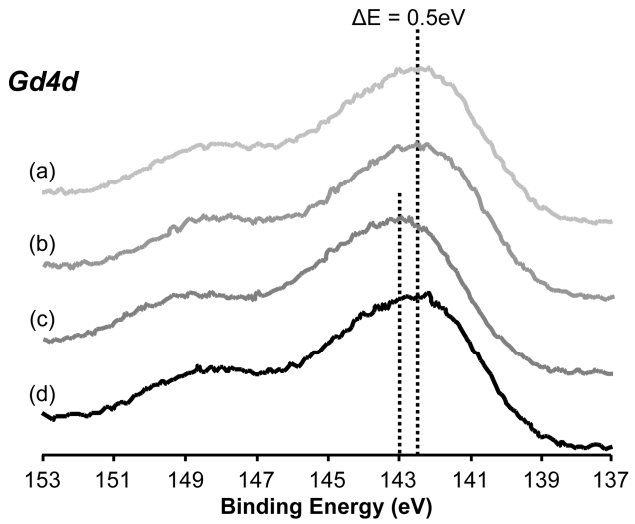

Figure S5. Gd4d HRXPS spectra of Gd_2O_3 thin films immersed in PEG diacid (a), PEG-silane (b) or PEG-phosphate (c) ethanol solutions; Gd4d of thin films immersed in ethanol only (d)

(1) Soderlind, F.; Pedersen, H.; Petoral, R. M.; Kall, P. O.; Uvdal, K. *J. Colloid Interface Sci.* **2005,** *288*, 140.
(2) Iida, S.; Abe, S. *Appl. Surf. Sci.* **1994,** *78*, 141.
(3) Wandelt, K.; Brundle, C. R. *Surf. Sci.* **1985,** *157*, 162.