

Supporting Information - Silicon Nanoparticles as Hyperpolarized Magnetic Resonance Imaging Agents

Jacob W. Aptekar,^{†,‡} Maja C. Cassidy,^{†,‡} Alexander C. Johnson,[†]
Robert A. Barton,[†] Menyoung Lee,[†] Alexander C. Ogier,[†] Chinh Vo,[†]
Melis N. Anahtar,[¶] Yin Ren,[¶] Sangeeta N. Bhatia,^{¶,§,||}
Chandrasekhar Ramanathan,[⊥] David G. Cory,[⊥] Alison L. Hill,[#] Ross W. Mair,[#]
Matthew S. Rosen,^{†,#} Ronald L. Walsworth,^{†,#} and Charles M. Marcus^{*,†}

Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA, These authors contributed equally to this work, Harvard-MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology E19-502D Cambridge, MA 02139, USA, Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA, Division of Medicine, Brigham and Women's Hospital, Boston, Massachusetts 02115, USA, Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA, and Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, MS 59, Cambridge, MA 02138, USA

E-mail: marcus@harvard.edu

S1. Electron Spin Resonance Measurements

Continuous wave electron spin resonance (cw-ESR) measurements were taken on bulk samples of particles using a JEOL **FE-3XG** X-Band spectrometer at a frequency of 9.106 GHz. The a.c. field (amplitude 0.01mT, $f_{mod} = 100$ kHz) was swept from 315 mT to 335 mT over a period of 30 s. For each sample, a single peak at $B = 324$ mT, corresponding to a g-factor of 2.006 was recorded. This is consistent with the reported g-factor of P_b defects at the silicon-silicon dioxide interface.² ESR spectra of ball milled silicon particles with sizes $0.17 \mu\text{m}$ and $1.6 \mu\text{m}$. are shown in Fig. S1. Curves are scaled vertically by sample weight, giving a measure of density of electron spins. Smaller particles have greater defect density, scaling roughly as the inverse diameter (inset, Fig. S1), suggesting that the defects are on the surface of the nanoparticle.¹

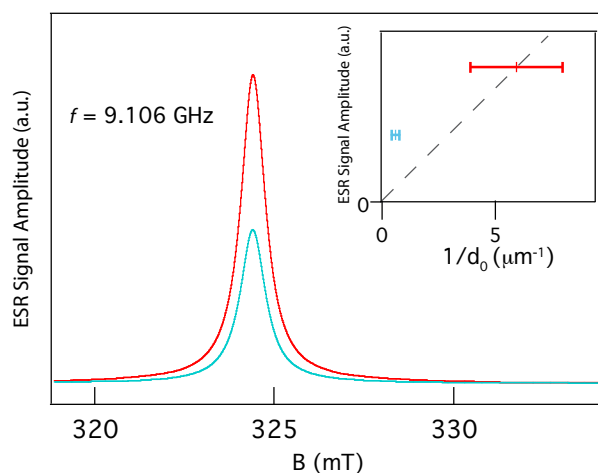


Figure S1 - Electron spin resonance measurements of silicon particles. Weight adjusted ESR spectra of ball milled silicon particles with sizes $0.17 \mu\text{m}$ and $1.6 \mu\text{m}$. Inset: ESR peak area vs inverse particle diameter.

*To whom correspondence should be addressed

†Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA

‡These authors contributed equally to this work

¶Harvard-MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology E19-502D Cambridge, MA 02139, USA

§Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

||Division of Medicine, Brigham and Women's Hospital, Boston, Massachusetts 02115, USA

⊥Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

#Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, MS 59, Cambridge, MA 02138, USA

S2. Evidence of Peylation via Stability of Particles

The aminated particles in this experiment were pegylated with either mPEG-SMB or NHS-PEG-MAL. Both SMB and NHS are reactive with amines on the particle surface. As a negative control, mPEG-Amine polymer was used because it does not contain amine-reactive groups and therefore should not conjugate to the nanoparticle surface. The stability of nanoparticles in solution was assessed using both dynamic light scattering (DLS) and visual determination of flocculation and sedimentation. The DLS-based size measurements of aminated and pegylated particles are shown in Table S1. As expected, the aminated particles treated with mPEG-Amine aggregated after centrifugation and resuspension in phosphate-buffered saline (PBS). However, the particles treated with mPEG-SMB and NHS-PEG-MAL were both stable in PBS.

Table 1: DLS size measurements showing size before and after pegylation.

Silane	PEG ¹	Size after pegylation (nm)		
		Measured in MeOH	Measured in PBS	After two days in PBS
APTES only	None	220 ± 88	-	-
	Amine	Aggregated	Aggregated	Aggregated
	SMB	360 ± 127	271 ± 84	260 ± 70
	NPM	240 ± 95	396 ± 126	371 ± 140
APTES & BTEOSE	None	235 ± 100	-	-
	Amine	Aggregated	Aggregated	Aggregated
	SMB	300 ± 151	314 ± 165	520 ± 200
	NPM	255 ± 100	Aggregated	326 ± 117
APTES & THPMP	None	235 ± 100	-	-
	Amine	Aggregated	Aggregated	Aggregated
	SMB	490 ± 200	295 ± 200	360 ± 200
	NPM	295 ± 126	295 ± 139	295 ± 200

Particle stability was also assessed visually, as shown in Fig. S2. These particles were pegylated in methanol, washed, and re-suspended in PBS. The particles treated with mPEG-Amine could not be re-suspended, as they had formed a large aggregate at the bottom of the tube. After two days in solution, some of the particles pegylated with mPEG-SMB and NHS-PEG-MAL had settled but immediately re-dispersed after gentle flicking.







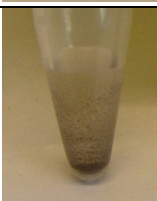


Silane	mPEG-Amine	mPEG-SMB	NHS-PEG-MAL
(a) APTES only			
(b) APTES & BTEOSE			
(c) APTES & THPMP			

Figure S2 - Stability of pegylated silicon nanoparticles. Stability of pegylated particles after two days in PBS and gentle flicking, post amination with (a) APTES, (b) APTES and BTEOSE, and (c) APTES and THPMP.

References

- (1) Dementyev, A. E., Cory, D. G., Ramanathan, C. Dynamic Nuclear Polarization in Silicon Microparticles. *Phys. Rev. Lett.* **2008**, 100, 127601.
- (2) Nishi, Y. Study of Silicon-Silicon Dioxide Structure by Electron Spin Resonance I. *Jpn. J Appl. Phys.* **1971**, 10, 52-62.