**Silicon Nanoparticles as Hyperpolarized Magnetic Resonance Imaging Agents**

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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 0.01 mT, $f_{\text{mod}} = 100$ 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 Pb defects at the silicon-silicon dioxide interface [1]. ESR spectra of ball milled silicon particles with sizes $0.17 \, \mu m$ and $1.6 \, \mu m$ 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 [2].

![ESR Signal Amplitude vs B (mT)](image)

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

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 S1: DLS size measurements showing size before and after pegylation.

<table>
<thead>
<tr>
<th>Silane</th>
<th>PEG^a</th>
<th>Size after pegylation (nm)</th>
<th>Measured in MeOH</th>
<th>Measured in PBS</th>
<th>After two days in PBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTES only</td>
<td>None</td>
<td>220 ± 88</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amine</td>
<td>Aggregated</td>
<td>271 ± 84</td>
<td>260 ± 70</td>
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<td></td>
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<tr>
<td>SMB</td>
<td>360 ± 127</td>
<td>396 ± 126</td>
<td>371 ± 140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPM</td>
<td>240 ± 95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APTES &amp; BTEOSE</td>
<td>None</td>
<td>235 ± 100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amine</td>
<td>Aggregated</td>
<td>314 ± 165</td>
<td>520 ± 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMB</td>
<td>300 ± 151</td>
<td>271 ± 84</td>
<td>260 ± 70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPM</td>
<td>255 ± 100</td>
<td>396 ± 126</td>
<td>371 ± 140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>APTES &amp; THPMP</td>
<td>None</td>
<td>235 ± 100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amine</td>
<td>Aggregated</td>
<td>295 ± 139</td>
<td>295 ± 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMB</td>
<td>490 ± 200</td>
<td>295 ± 126</td>
<td>360 ± 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPM</td>
<td>295 ± 126</td>
<td></td>
<td>295 ± 200</td>
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^aAmine refers to mPEG-Amine, SMB refers to mPEG-SMB, NPM refers to NHS-PEG-MAL

FIG. 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.

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.
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