**Electronic Supplementary Information for:**

# Dehydrocoupling – An Alternative approach to Functionalizing Germanium Nanoparticle Surfaces

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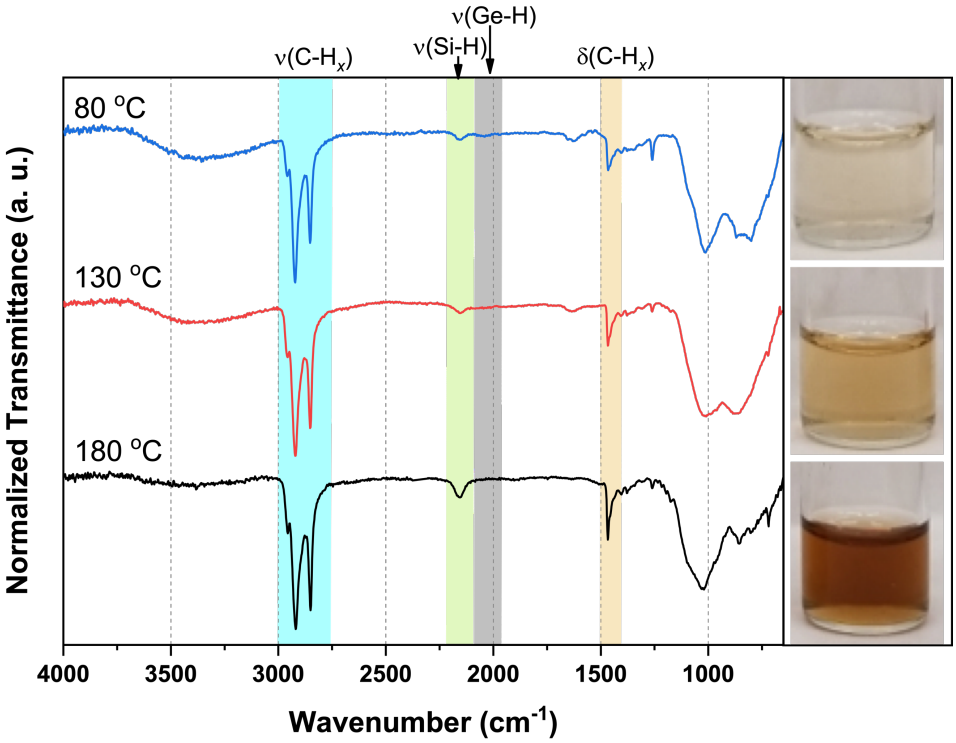


**Figure S1.** Fourier Transform Infra-red (FTIR) spectra and photographs of corresponding octadecylsilyl-GeNPs samples obtained from reactions at the indicated temperatures for 48 h.

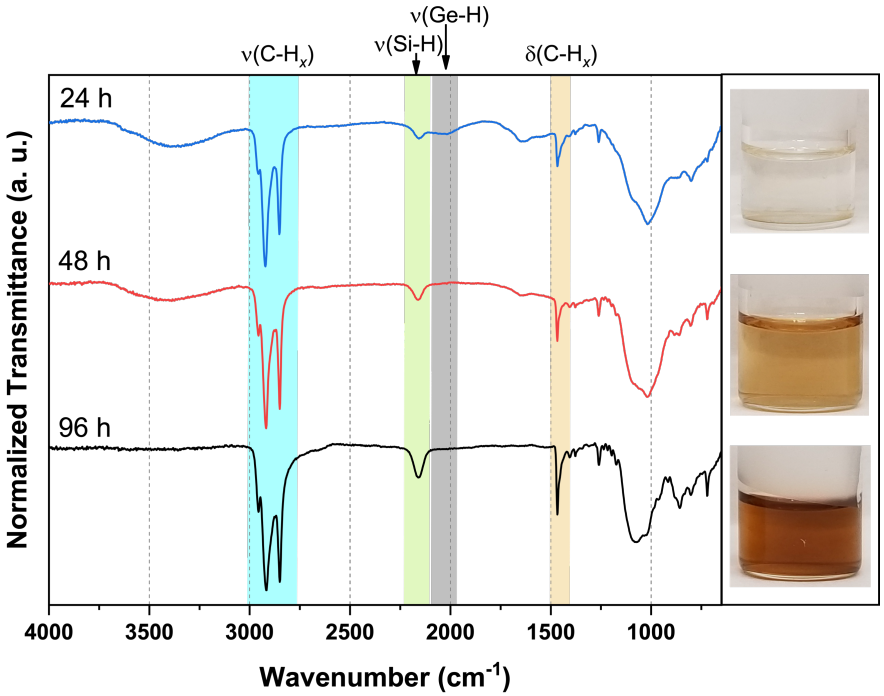


**Figure S2.** FTIR spectra and photographs of octadecylsilyl-GeNP samples obtained by reactions at 180 °C for the indicated times.

**Table S1.** Determination of Surface Coverage of Octadecyl-GeNPs Using $^{1}$H NMR

| NMR peak | Ligand to TMS Proton ratio | Moles of ligand[#] | % Surface coverage[$] |
|---|---|---|---|
| **a** (-$CH_3$) | 6.23 | $3.29 \times 10^{-5}$ | 157 |
| **b** (-$(CH_2)_{16}$-) | 61.12 | $2.85 \times 10^{-5}$ | 182 |

[#] 0.03% v/v of TMS in 0.6 mL of $CDCl_3$ solvent has been defined as $1.32 \times 10^{-6}$ moles.
[$] Per 7.3 mg of functionalized GeNPs (d = 8 nm) contain $1.81 \times 10^{-5}$ moles considering *ca.* 18% of atoms on the surface.

**Table S2.** Determination of Surface Coverage of Octadecylsilyl-GeNPs Using $^{1}$H NMR

| NMR peak | Ligand to TMS Proton ratio | Moles of ligand[#] | % Surface coverage[$] |
|---|---|---|---|
| **a** (-$CH_3$) | 1.53 | $8.08 \times 10^{-6}$ | 163 |
| **b** (-$(CH_2)_{16}$-) | 12.91 | $6.39 \times 10^{-6}$ | 129 |
| **c** Si-$(CH_2)$- | 0.78 | $6.18 \times 10^{-6}$ | 125 |

[#] 0.03% v/v of TMS in 0.6 mL of $CDCl_3$ solvent has been defined as $1.32 \times 10^{-6}$ moles.
[$] Per 2.0 mg of functionalized GeNPs (d = 8 nm) contain $4.96 \times 10^{-6}$ moles considering *ca.* 18% of atoms on the surface.

**Table S3.** Determination of Surface Coverage of Dimethyloctadecylsilyl-GeNPs Using $^{1}$H NMR

| NMR peak | Ligand to TMS Proton ratio | Moles of ligand[#] | % Surface coverage[$] |
|---|---|---|---|
| **a** (-$CH_3$) | 2.27 | $1.20 \times 10^{-5}$ | 89.6 |
| **b** (-$(CH_2)_{16}$-) | 22.55 | $1.12 \times 10^{-5}$ | 83.3 |
| **c** Si-$(CH_2)$- | 1.36 | $1.08 \times 10^{-5}$ | 80.6 |
| **d** -Si-$(CH_3)_2$-) | 3.50 | $9.24 \times 10^{-6}$ | 68.9 |

[#] 0.03% v/v of TMS in 0.6 mL of $CDCl_3$ solvent has been defined as $1.32 \times 10^{-6}$ moles.
[$] Per 5.4 mg of functionalized GeNPs (d = 8 nm) contain $1.34 \times 10^{-5}$ moles considering *ca.* 18% of atoms on the surface.

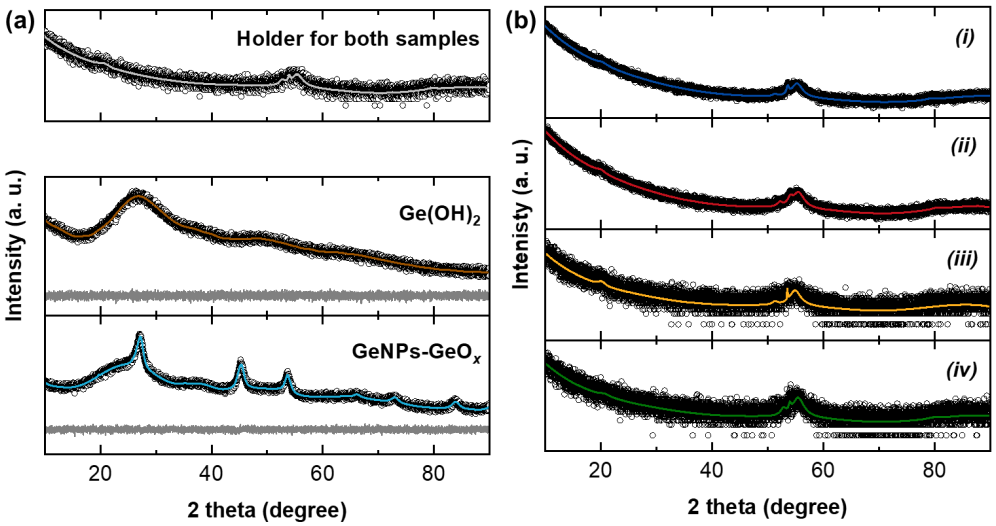


**Figure S3.** X-ray diffraction (XRD) of (a) sample holder for $Ge(OH)_2$ and GeNP/$GeO_x$, $Ge(OH)_2$, and GeNP/$GeO_x$ composite and (b) sample holders for *(i)* octadecyl-GeNPs, *(ii)* octadecylsilyl-GeNPs, *(iii)* dimethyloctadecylsilyl-GeNPs, and *(iv)* H-PDMS-GeNPs.

**Table S4.** Crystallographic Refinement Data for GeNP Samples

| Sample | Octadecyl-GeNPs | Octadecylsilyl-GeNPs | Dimethyl-octadecylsilyl-GeNPs | H-PDMS-GeNPs |
|---|---|---|---|---|
| Space group | $Fd\bar{3}m$ (No. 227) | $Fd\bar{3}m$ (No. 227) | $Fd\bar{3}m$ (No. 227) | $Fd\bar{3}m$ (No. 227) |
| $a$ (Å) | 5.6515(6) | 5.6539(2) | 5.6522(2) | 5.6561(4) |
| $T$ (K) | 296 | 296 | 296 | 296 |
| Radiation | Cu Kα, λ=1.5406 Å | Cu Kα, λ=1.5406 Å | Cu Kα, λ=1.5406 Å | Cu Kα, λ=1.5406 Å |
| 2θ limits | 10.00–80.00° | 10.00–80.00° | 10.00–80.00° | 10.00–80.00° |
| Refinement method | Pawley | Rietveld | Rietveld | Rietveld |
| No. of data collected | 4117 data points | 4117 data points | 4117 data points | 4117 data points |
| No. of Bragg reflections | 7 | 7 | 7 | 7 |
| No. of variables | 26 | 26 | 26 | 26 |
| Residuals[a] | $R_{wp}$ = 0.0468<br>$R_{exp}$ = 0.0455 | $R_{wp}$ = 0.0289<br>$R_{exp}$ = 0.0249 | $R_{wp}$ = 0.0355<br>$R_{exp}$ = 0.0309 | $R_{wp}$ = 0.0322<br>$R_{exp}$ = 0.0298 |
| Goodness of fit | 1.02 | 1.12 | 1.14 | 1.08 |
| Synthetic peaks | 19.58°<br>21.27° | 21.31° | 24.19° | 24.19° |
| Integral breadth size | 5.9(2) nm | 6.5(2) nm | 7.4(3) nm | 7.8(3) nm |
| Strain, $e_0$ | 0.00016(2) | 0.00082(3) | 0.00131(4) | 0.00155(4) |

[a] $R_{wp} = \left[\sum[w(y_o - y_c)]/\sum w y_o^2\right]^{1/2}$ $R_{exp} = [(N\text{-}P+C)/\Sigma(wy_o^2)]^{1/2}$; $R_{wp} = [\Sigma[w(y_o - y_c)] / \Sigma wy_o^2]^{1/2}$; N is the total number of observations, P is the number of parameters refined, C is the number of constraints used in the refinement.

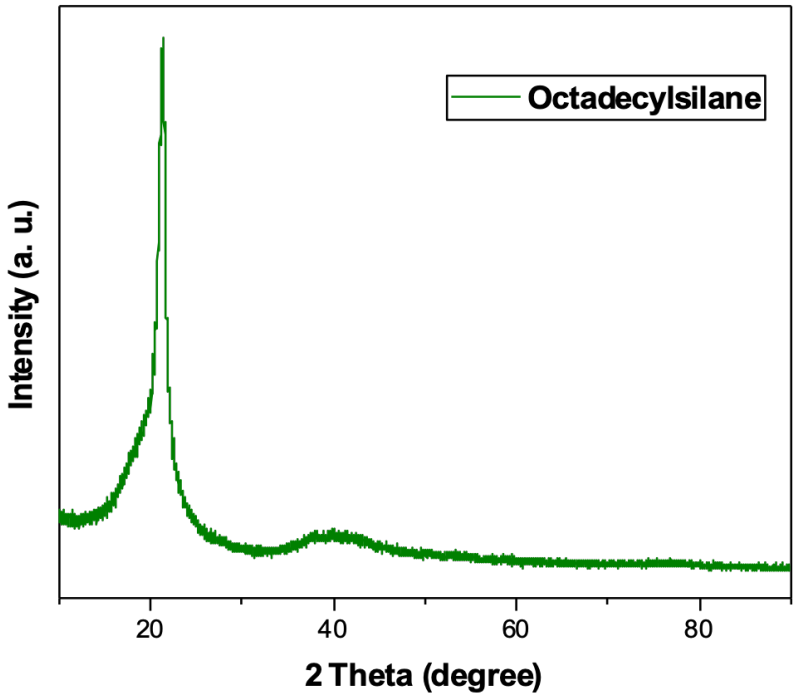


**Figure S4.** X-ray diffraction (XRD) of octadecylsilane.

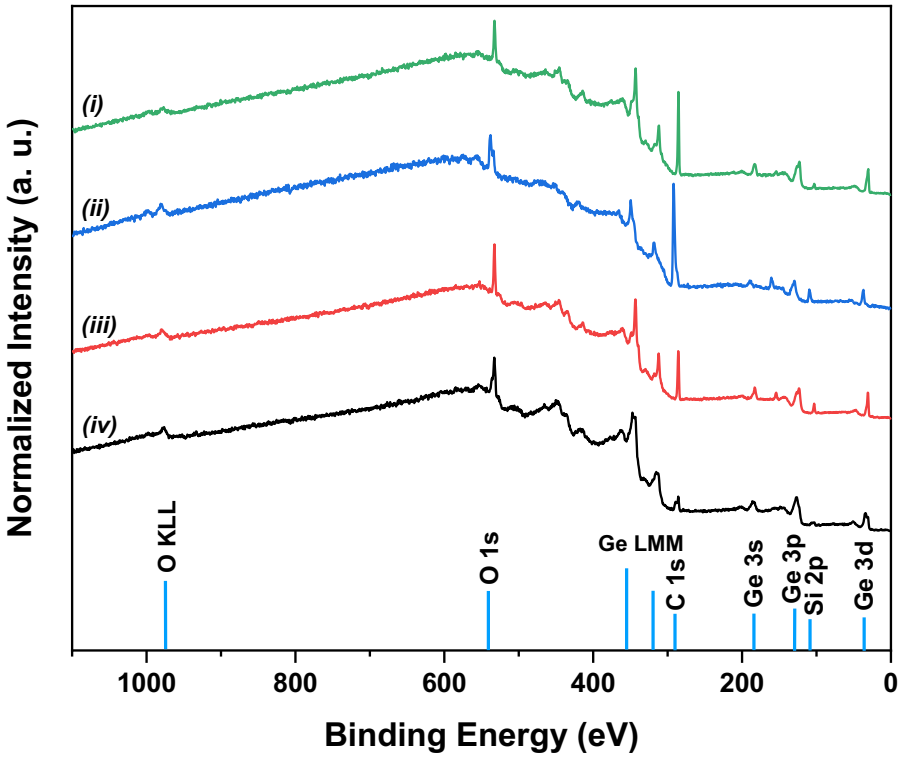


**Figure S5.** Survey X-ray photoelectron (XP) spectra of *(i)* octadecyl-GeNPs, *(ii)* octadecylsilyl-GeNPs, *(iii)* dimethyloctadecylsilyl-GeNPs, and *(iv)* H-PDMS-GeNPs.

**Table S5.** Percentage of Element in the DHC Samples

| Sample | C 1s | O 1s | Ge 3p | Si 2p |
|---|---|---|---|---|
| Octadecyl-GeNPs | 69.17% | 15.61% | 15.22% | - |
| Octadecylsilyl-GeNPs | 75.24% | 13.99% | 6.39% | 4.43% |
| Dimethyloctadecylsilyl-GeNPs | 52.90% | 19.93% | 18.73% | 8.45% |
| H-PDMS-GeNPs | 29.25% | 23.23% | 39.95% | 7.56% |

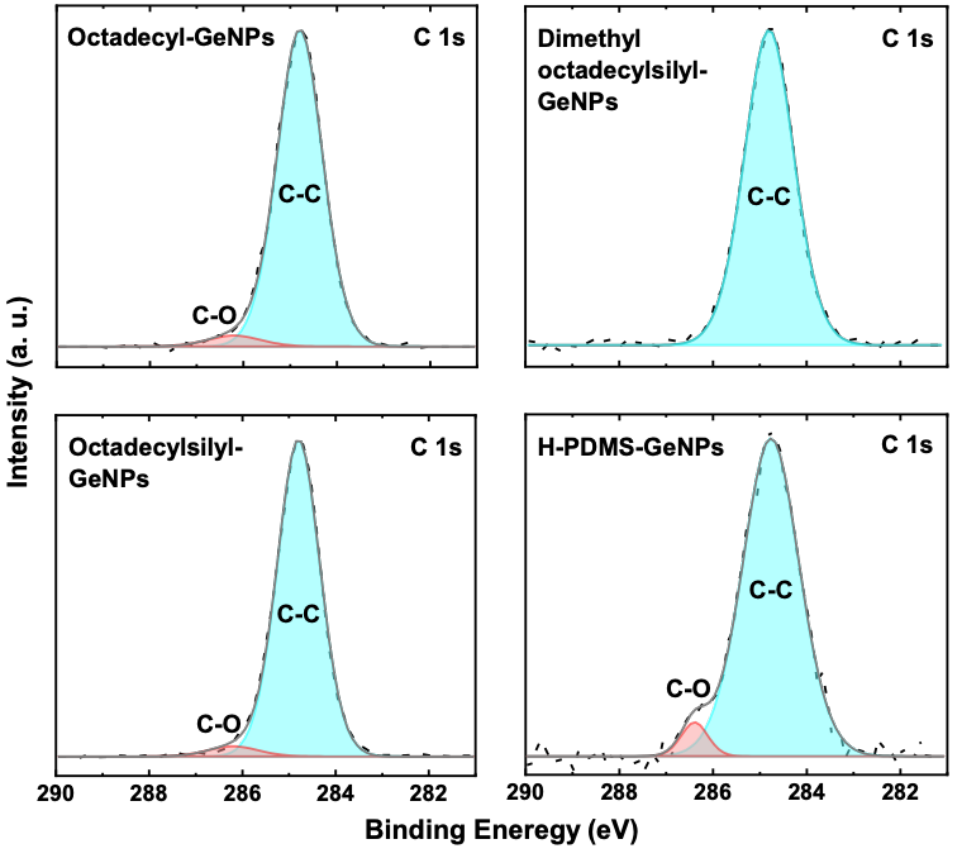


**Figure S6.** High-resolution XP spectra of C 1s of octadecyl-GeNPs, octadecylsilyl-GeNPs, dimethyloctadecylsilyl-GeNPs, and H-PDMS-GeNPs (black dashed line = experimental data, gray solid line = complete fit, blue = C-C, red = C-O).

**Table S6.** Percentage of Oxide in C 1s in DHC Samples

| Sample | C-C | C-O |
|---|---|---|
| Octadecyl-GeNPs | 96.15% | 3.85% |
| Octadecylsilyl-GeNPs | 96.3% | 3.63% |
| Dimethyloctadecylsilyl-GeNPs | 100% | - |
| H-PDMS-GeNPs | 95.20% | 4.80% |

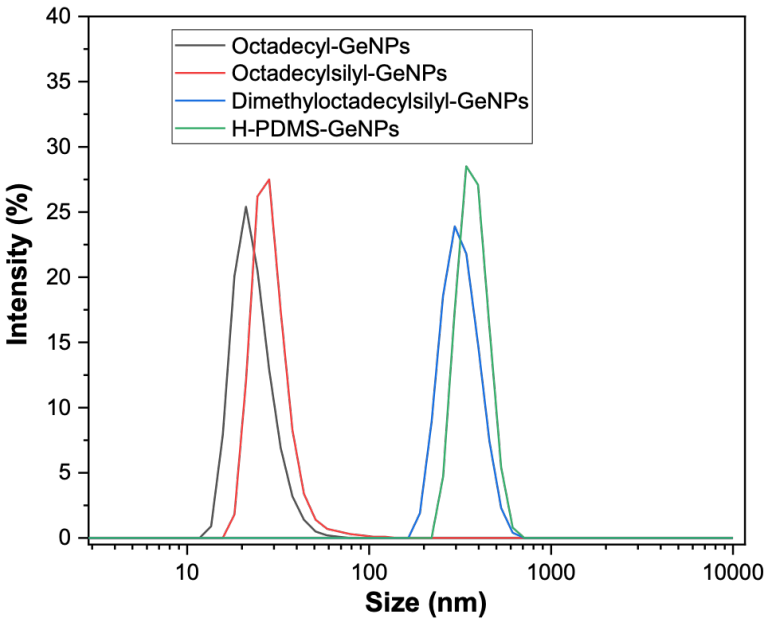


**Figure S7.** Dynamic light scattering (DLS) size distribution of octadecyl-GeNPs, octadecylsilyl-GeNPs, dimethyloctadecyl-GeNPs, and H-PDMS-GeNPs.