

Supporting information for: Radical-Initiated and Thermally-Induced Hydrogermylation of Alkenes on the Surfaces of Germanium Nanosheets

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Material

All reagents were purchased from *Sigma-Aldrich* and used without further purification unless otherwise stated. All solvents, except acetone, were dried using an Innovative Technology, Inc. Grubbs-type solvent purification system. Acetone was dried over molecular sieves (3 Å), degassed *via* 3 freeze-pump-thaw cycles using an argon charged double manifold. All solvents and liquid reagents were degassed *via* 3 freeze-pump-thaw cycles using an argon charged double manifold and stored in MBraun glove box with nitrogen working gas.

Material Synthesis

Synthesis of CaGe_2

A stoichiometric mixture of calcium (Sigma, 99.0 %) and germanium (Sigma, 99.999 %) was pressed to a pellet and subsequently melted together in an arc furnace installed in an argon-filled glove box (MBraun, H_2O and O_2 levels < 0.1 ppm). To ensure effective homogenization,

the resulting silver, metallic regulus was melted upon simultaneous heating from the top and bottom in the arc furnace, ground thoroughly in an agate mortar, pressed again to a pellet, melted from both sides in the arc furnace and ground into a powder again.¹ The resulting product was evaluated using X-ray powder diffraction and XPS.

Synthesis of HGe-flakes

All manipulations were performed in an argon atmosphere. A standard Schlenk flask was charged with 100 mL of concentrated HCl. After cooling to -30 °C in a low temperature freezer, CaGe₂ (1.00 g) was added. The mixture was maintained at -30 °C for at least 7 d and shaken 10 times per day at regular intervals.² Then the reaction mixture was filtered using a glass frit under nitrogen to provide shiny metallic shiny flakes that were washed with 3 times dry, degassed acetone followed by drying in vacuum on the Schlenk line. The resulting HGe-flakes were characterized using XRD and FTIR and stored in a nitrogen filled glove box until further use.

Radical-initiated hydrogermylation

In a nitrogen charged glove box, HGe-flakes (5 mg) were transferred into a dry 5 mL Biotage[®] microwave tube. Dry degassed toluene (2 mL), AIBN (10 mg) and 1-dodecene (1 mL, 4.5 mmoles) were added and the tube was sealed. The reaction mixture was subsequently ultrasonicated in a bath sonicator (Fisher Scientific FS30) for 3-hours after which it was heated to and maintained at 65 °C and stirred for 12 hours. The resulting red suspension was transferred to a PTFE centrifuge tube, methanol (40 mL) was added and the mixture was centrifuged (12,000 rpm for 10 min) to yield a deep red pellet. The solid was redispersed in a minimal amount of toluene (2 mL). Methanol (40 mL) was added and the mixture was centrifuged (12,000 rpm for 10 min). This suspension/precipitation procedure was repeated twice after which the dodecyl-GeNSs were freeze dried from benzene and finally dispersed in toluene.

Thermally-Induced Hydrogermylation

In a nitrogen charged glovebox, HGe-flakes (5 mg) were transferred into a dry 5 mL Biotage[®] microwave tube. 1-dodecene (2 mL, 9.0 mmol) was added and the tube was sealed. The reaction mixture was subsequently ultrasonicated in a bath sonicator (Fisher Scientific FS30) for 3-hours after which it was heated to and maintained at 190 °C for 12 hours. After the reaction, the dark brown mixture was transferred to a PTFE centrifuge tube, methanol (40 mL) was added and the mixture was centrifuged (12,000 rpm for 10 min). The solid was redispersed in a minimal amount of toluene (2 mL). Methanol (40 mL) was added and the mixture was centrifuged (12,000 rpm for 10 min). This suspension/precipitation procedure was repeated twice after which the dodecyl-GeNSs were freeze dried from benzene and finally dispersed in toluene.

Materials Characterization

Fourier Transformed Infrared (FT-IR) Spectroscopy

FT-IR Spectra were acquired using a Thermo Nicolet Magna 750 IR Spectrometer. Samples were prepared by drop coating a toluene dispersion of the material of choice onto an electronic-grade Si-wafer (N-type, 100 surface, 100 mm thickness and 10 ohm·cm resistivity) and dried under nitrogen atmosphere.

Electron Microscopy

Bright-field transmission electron microscopy (TEM) images were acquired using a Hitachi-9500 or JEOL JEM-ARM200CF S/TEM electron microscope at accelerating voltages of 300 kV or 200 kV, respectively. HRTEM images obtained from a Hitachi-9500 were processed using Gatan Digital Micrograph software (Version 3.22.1461.0). HRTEM images were enhanced with commercial software HREM-Filters Pro/Lite v.2.5.1 equipped in Gatan Digital Micrograph. The CrystalKitX was employed for the selected area electron diffraction (SEAD) pattern simulation.

The crystallographic data used for the simulation is from Cultrara *et al.*³ TEM samples were prepared by depositing a drop of GeNS suspensions in toluene onto a holey/lacey carbon coated copper grid (Electron Microscopy Inc.) The grid was kept in a vacuum chamber for at least 24 h prior to data collection.

Atomic Force Microscopy (AFM)

AFM was performed using a Bruker Dimension EdgeTM system with NanoDrive version 8.02 software. The tapping mode cantilever was purchased from Bruker (Resonance frequency: 300 kHz, force constant 42 N/m). Thin films of GeNSs (5 mg of exfoliated sheets in 2 mL of toluene) were spin coated (90 seconds, 1000 rpm) onto a Si (111) wafer substrate that had been cleaned using a standard Piranha protocol.

X-ray Photoelectron Spectroscopy (XPS)

XPS was performed using a Kratos Axis Ultra instrument operating in energy spectrum mode at 210 W. Samples were prepared by depositing a suspension of the material of choice onto a copper foil substrate followed by drying in air. Prior to analysis, the Ge (111) wafer reference was cleaned by immersing in 30% v/v H₂O₂ for 90 s followed by 10 minutes etching in 10% v/v HF. The base and operating chamber pressure were maintained at 10⁻⁷ Pa. A monochromatic Al K source ($\lambda = 8.34\text{\AA}$) was used to irradiate the samples, and the spectra were obtained with an electron take-off angle of 90°. CasaXPS software (VAMAS) was used to interpret high-resolution spectra. All spectra were internally calibrated to the C1s emission (284.8 eV). After calibration, a Shirley-type background was applied to remove most of the extrinsic loss structure.

Thermogravimetric Analysis (TGA)

TGA was performed using a Mettler Toledo Star TGA/DSC system. The sample being evaluated was placed in a Pt pan and heated under N₂ atmosphere from 35 to 700 °C at a rate of 10 °C/min.

Powder X-ray Diffraction (XRD)

PXRD data were collected using an Inel MPD MultiPurpose Diffractometer equipped with a CPS 120 curved position sensitive X-ray detector and Cu $K\alpha$ (8.047 KeV energy) source or Stoe STADI P diffractometer equipped with a Ge(111) monochromator for Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) and a Dectris MYTHEN DCS 1K solid-state detector. CaGe_2 was ground in an agate mortar and filled into 0.3 mm glass capillaries which were then sealed. The sample was measured within a 2θ -range of $5\text{--}87.5^\circ$ (PSD steps, 1.5° ; time/step, 15 s). GeH powders were deposited on an amorphous silica holder.

Diffuse Reflective Spectroscopy

Diffuse Reflective spectroscopy data was collected using an Agilent TechnologiesTM Cary Series (Model# 5000) UV-Vis-NIR spectrophotometer. Samples were prepared by drop coating a toluene dispersion of the material of choice onto an electronic- grade Si-wafer (N-type, 100 surface, 100 mm thickness and 10 ohm-cm resistivity) and dried under nitrogen atmosphere.

Raman Spectroscopy

Raman spectroscopy was performed using a Renishaw inVia Raman microscope equipped with a 514 nm diode laser operating at a power of 3.98 mW on the sample. Samples were prepared by mounting the suspension on gold-coated glass.

Surface Coverage

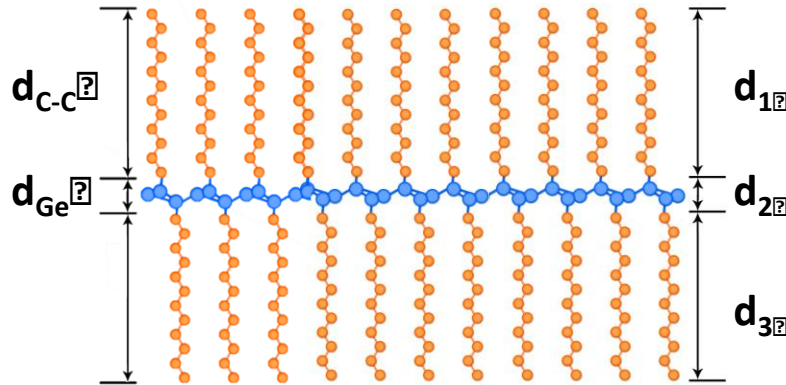
The thickness of the carbon overlayer can be calculated using the overlayer model described in literature:⁴⁻⁶

$$\left(\frac{I_{Ov}}{I_{Ge}}\right)\left(\frac{SF_{Ge}}{SF_{Ov}}\right)\left(\frac{r_{Ge}}{r_{Ov}}\right) = \left(\frac{1 - e^{-\frac{d_{Ov}}{l_{Ov}\cos q}}}{e^{-\frac{d_{Ov}}{l_{Ge}\cos q}}}\right) \quad (S1)$$

where I is the peak intensity, ρ is the atomic volume density, SF is the sensitivity factor, d_{Ov} is the overlayer thickness, λ is the photoelectron escape length, and θ is the photoelectron take-off angle determined by the surface orientation relative to the analyzer. The subscript Ov signifies an overlayer component; the subscript Ge signifies a Ge component. The take-off angle (θ) is 0° for this work, and atomic volume density is assumed identical where each Ge atom is bonded to one alkyl chain and three other Ge atoms, giving Equation S2:

$$\left(\frac{I_{Ov}}{I_{Ge}}\right)\left(\frac{SF_{Ge}}{SF_{Ov}}\right) = \left(\frac{1 - e^{-\frac{d_{Ov}}{\lambda_{Ov}}}}{e^{-\frac{d_{Ov}}{\lambda_{Ge}}}}\right) \quad (S2)$$

Extending this structure to a NS provides a Ligand-Sheet-Ligand Model for functionalized Ge NSs:



This model describes a nanosheet that is covalently bonded to two overlayers at both sides, where the thickness of the each carbon overlayer can be determined using Equation S3:

$$\left(\frac{I_{Ov}}{I_{Ge}}\right)\left(\frac{SF_{Ge}}{SF_{Ov}}\right) = \frac{\left(1 - e^{-\frac{d_{C-C} + d_{Ge}}{\lambda_{C-C}}}\right)\left(1 + e^{-\frac{(d_{C-C} + d_{Ge})}{\lambda_{C-C}}}\right)}{\left(1 - e^{-\frac{d_{Ge}}{\lambda_{Ge}}}\right)\left(e^{-\frac{d_{C-C}}{\lambda_{Ge}}}\right)} \quad (S3)$$

From Equation S3, $\left(1 - e^{-\frac{d_{C-C} + d_{Ge}}{\lambda_{C-C}}}\right)$ describes signal generated in d_{C-C} layer, $\left(1 + e^{-\frac{(d_{C-C} + d_{Ge})}{\lambda_{C-C}}}\right)$ describes signal collected from $d_1 (= 1)$ and d_2 layers, $\left(1 - e^{-\frac{d_{Ge}}{\lambda_{Ge}}}\right)$ describes signal generated from d_{Ge} layer, and $\left(e^{-\frac{d_{C-C}}{\lambda_{Ge}}}\right)$ describes signal collected from d_2 layer. While Equation S3 describes the relationship

between carbon and germanium intensities collected from a single GeNSs ($n = 1$), photoelectrons generated from the sheets stacked beneath can also reach the detector and must be considered. When two layers of functionalized GeNSs are involved ($n = 2$), the correlation of carbon layer thickness d_{C-C} and germanium layer thickness d_{Ge} can be expressed as Equation S4:

$$\left(\frac{I_{C-C}}{I_{Ge}}\right)\left(\frac{SF_{Ge}}{SF_{C-C}}\right) = \frac{\left(1 - e^{-\frac{d_{C-C}+d_{Ge}}{l_{C-C}}}\right)\left(1 + e^{-\frac{(d_{C-C}+d_{Ge})}{l_{C-C}}} + e^{-\frac{(2d_{C-C}+d_{Ge})}{l_{C-C}}} + e^{-\frac{(2d_{C-C}+2d_{Ge})}{l_{C-C}}}\right)}{\left(1 - e^{-\frac{d_{Ge}}{l_{Ge}}}\right)\left(e^{-\frac{d_{C-C}}{l_{Ge}}} + e^{-\frac{2d_{C-C}}{l_{Ge}}}\right)} \quad (S4)$$

When three layers of functionalized GeNSs are involved ($n = 3$) Equation S5 is used:

$$\left(\frac{I_{C-C}}{I_{Ge}}\right)\left(\frac{SF_{Ge}}{SF_{C-C}}\right) = \frac{\sum_{m=1}^3 \left(1 - e^{-\frac{d_{C-C}}{l_{C-C}}}\right) \left(\sum_{m=0}^2 e^{-\frac{(2m+1)d_{C-C}}{l_{C-C}}} + \sum_{m=0}^2 e^{-\frac{2md_{C-C}+md_{Ge}}{l_{C-C}}}\right)}{\left(1 - e^{-\frac{d_{Ge}}{l_{Ge}}}\right) \left(\sum_{m=0}^2 e^{-\frac{(2m+1)d_{C-C}+md_{Ge}}{l_{Ge}}}\right)} \quad (S5)$$

Equation S6 give photoelectrons collected from the top n layers of functionalized GeNSs:

$$\left(\frac{I_{C-C}}{I_{Ge}}\right)\left(\frac{SF_{Ge}}{SF_{C-C}}\right) = \frac{\sum_{m=1}^n \left(1 - e^{-\frac{d_{C-C}}{l_{C-C}}}\right) \left(\sum_{m=0}^{n-1} e^{-\frac{(2m+1)d_{C-C}}{l_{C-C}}} + \sum_{m=0}^{n-1} e^{-\frac{2md_{C-C}+md_{Ge}}{l_{C-C}}}\right)}{\left(1 - e^{-\frac{d_{Ge}}{l_{Ge}}}\right) \left(\sum_{m=0}^{n-1} e^{-\frac{(2m+1)d_{C-C}+md_{Ge}}{l_{Ge}}}\right)} \quad (S6)$$

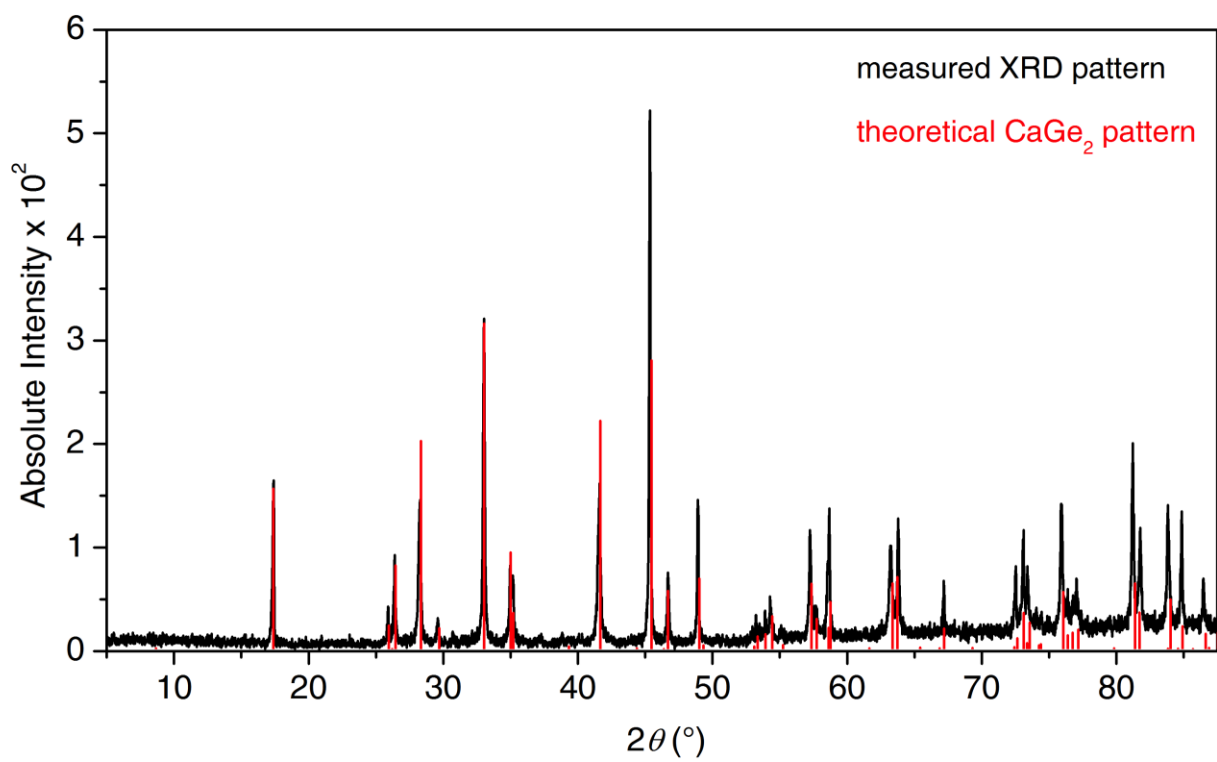


Figure S1: Experimental (black) and theoretical (red) powder diffraction patterns of CaGe_2 .

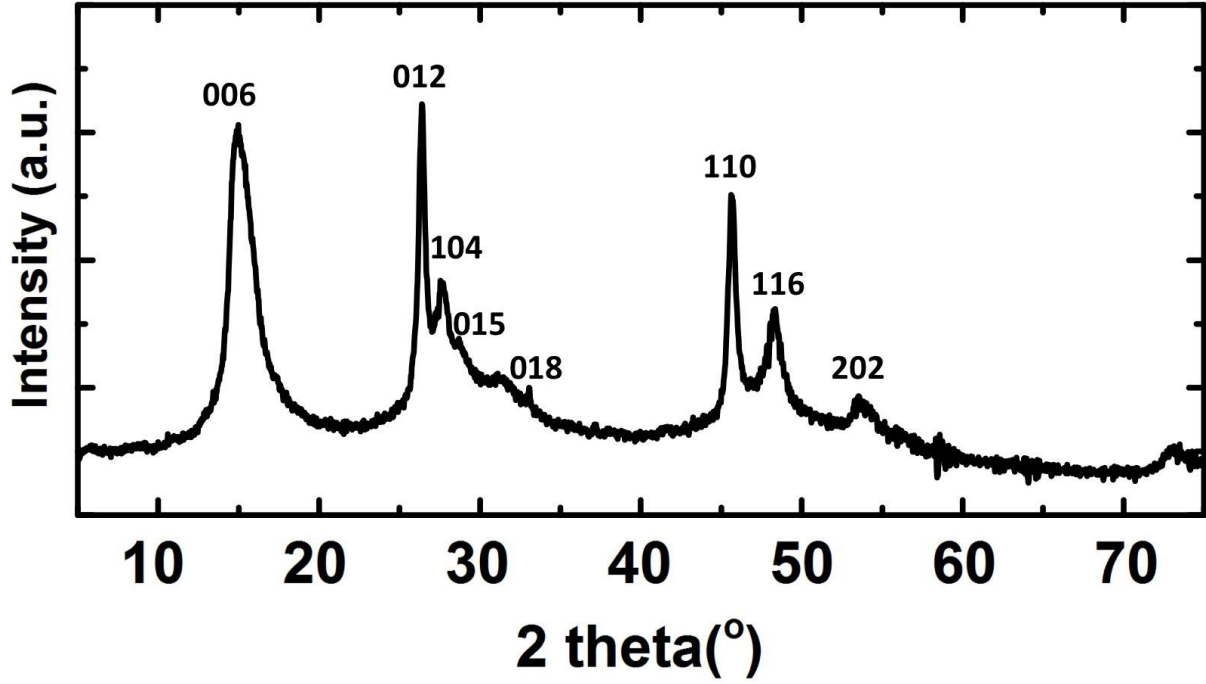


Figure S2: XRD patterns of as-synthesized HGe-flakes. The reflections of the regularly stacked sheets can be indexed by $\text{tr}6$ CaGe_2 unit cell with $a = 3.99 \text{ \AA}$ and $c = 33.0 \text{ \AA}$.

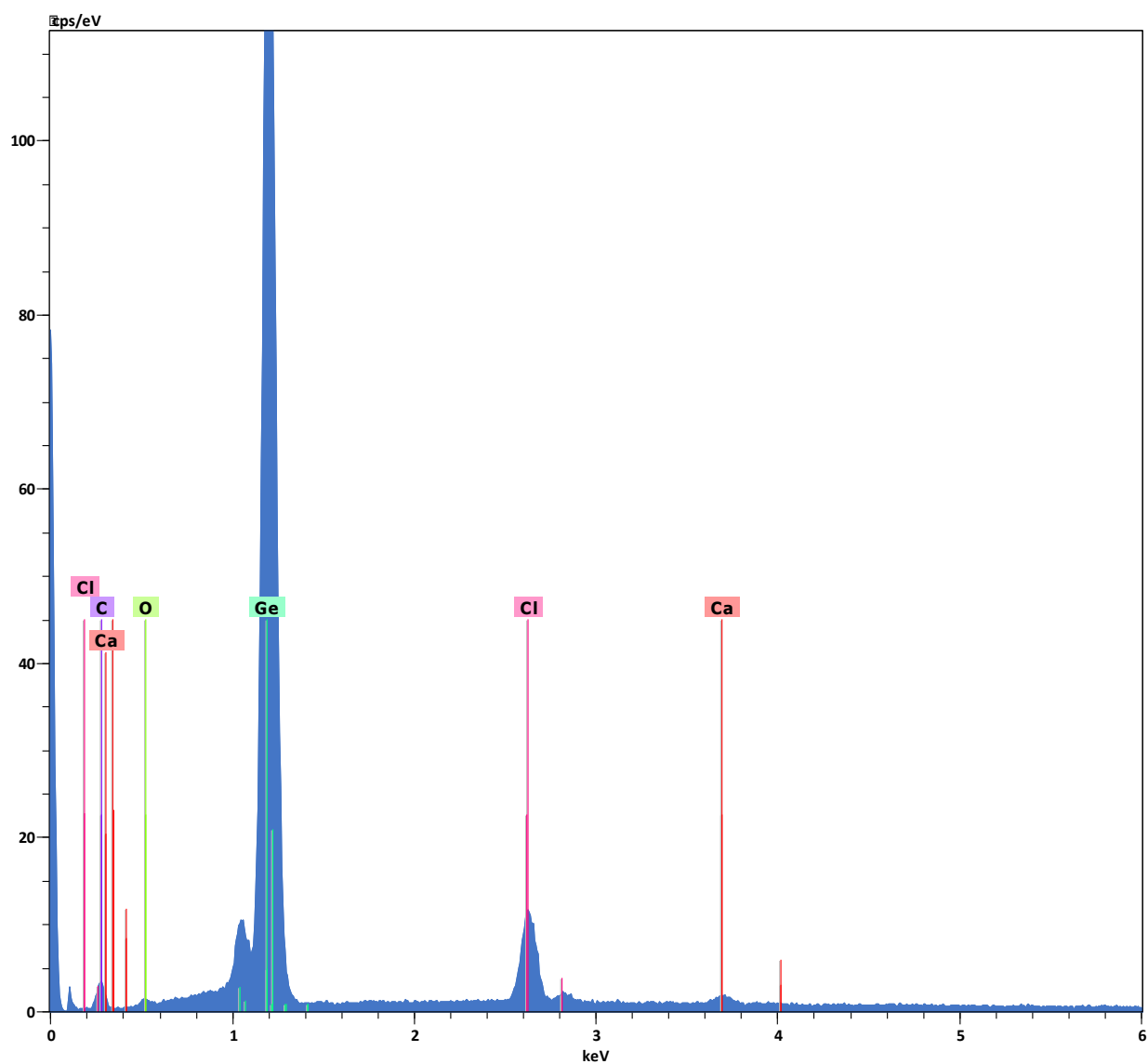


Figure S3: EDX output for HGe-flakes.

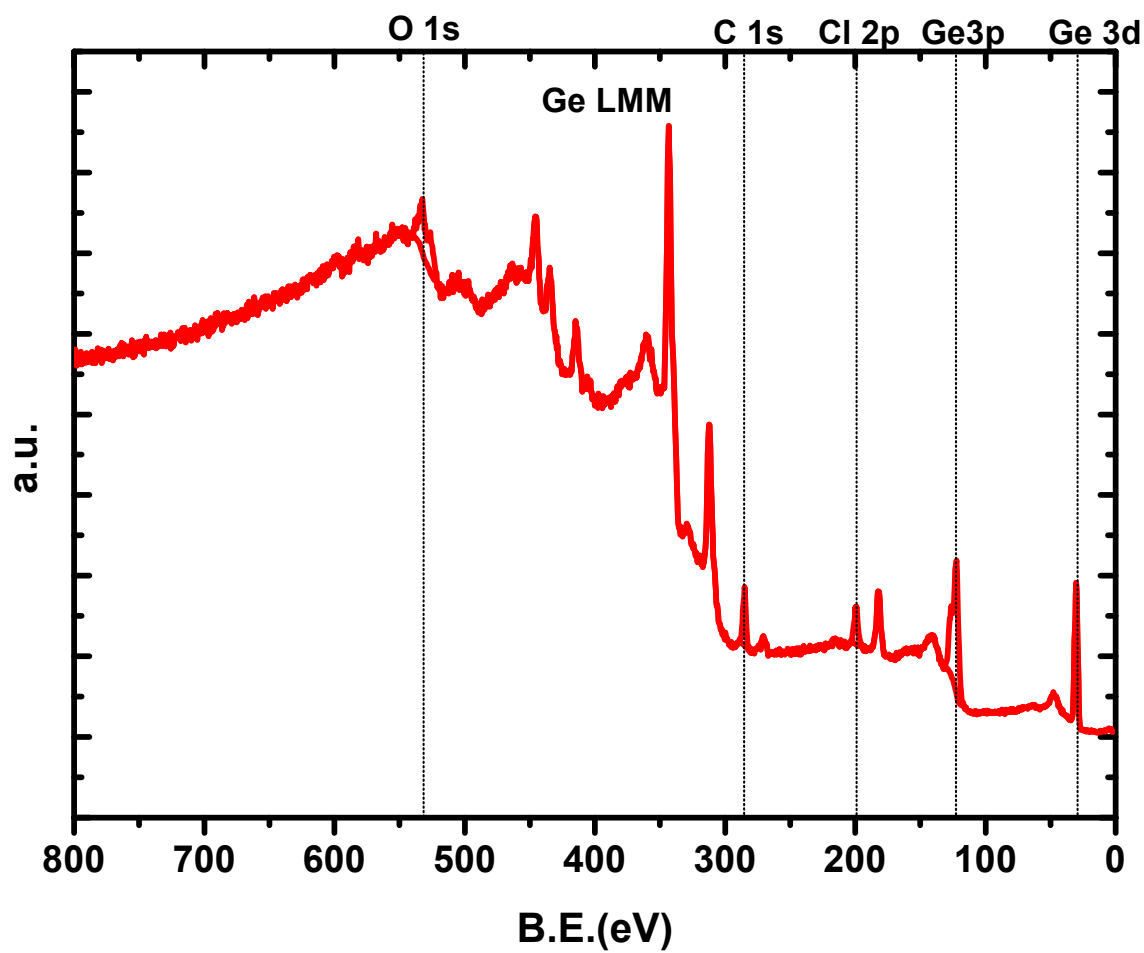


Figure S4: Survey X-ray photoelectron spectrum of HGe-flakes.

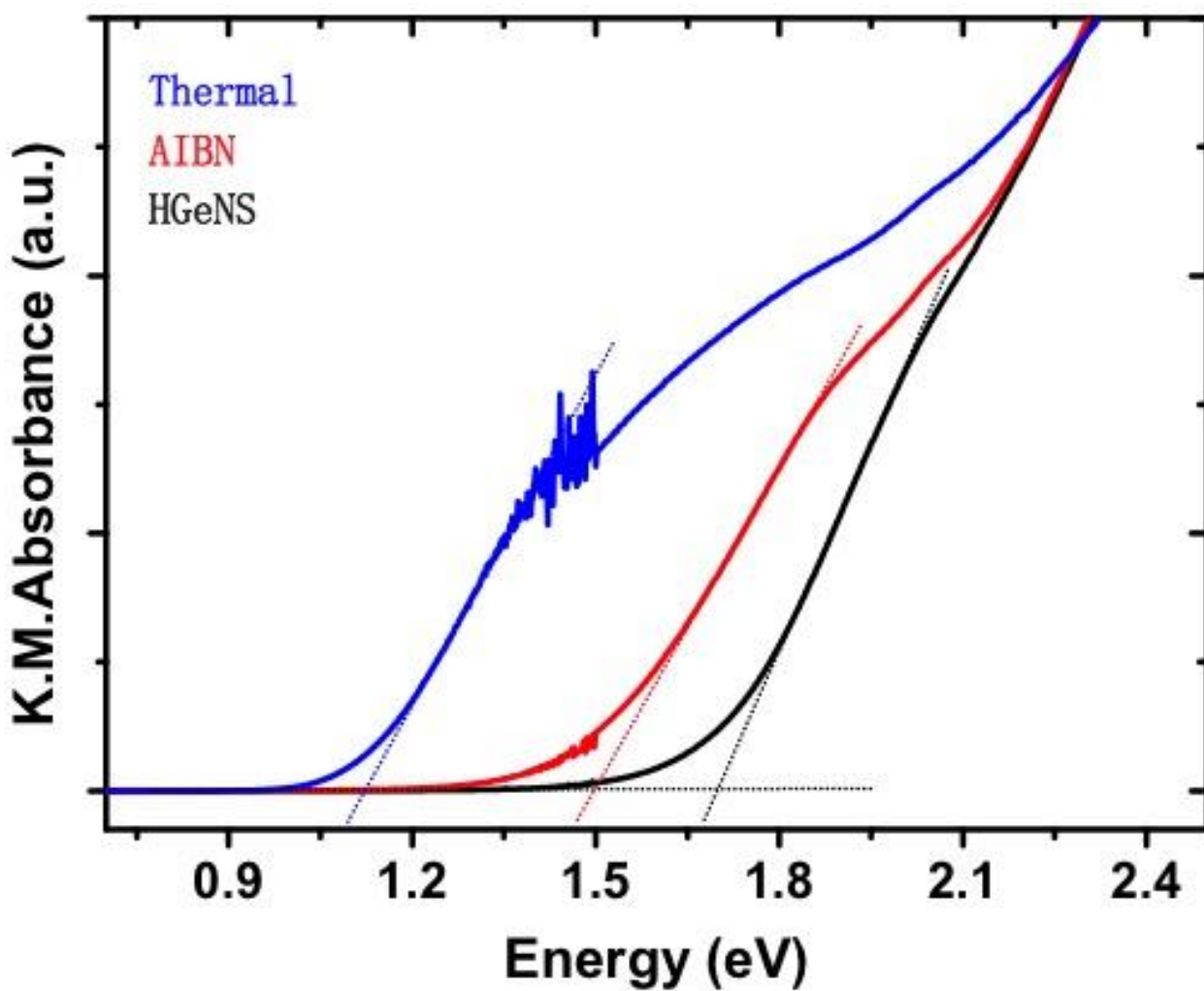


Figure S5: Diffuse reflectance spectroscopy of HGe flakes (black), radical- induced functionalized (red) and thermally-induced functionalized (blue) dodecyl-GeNSs.

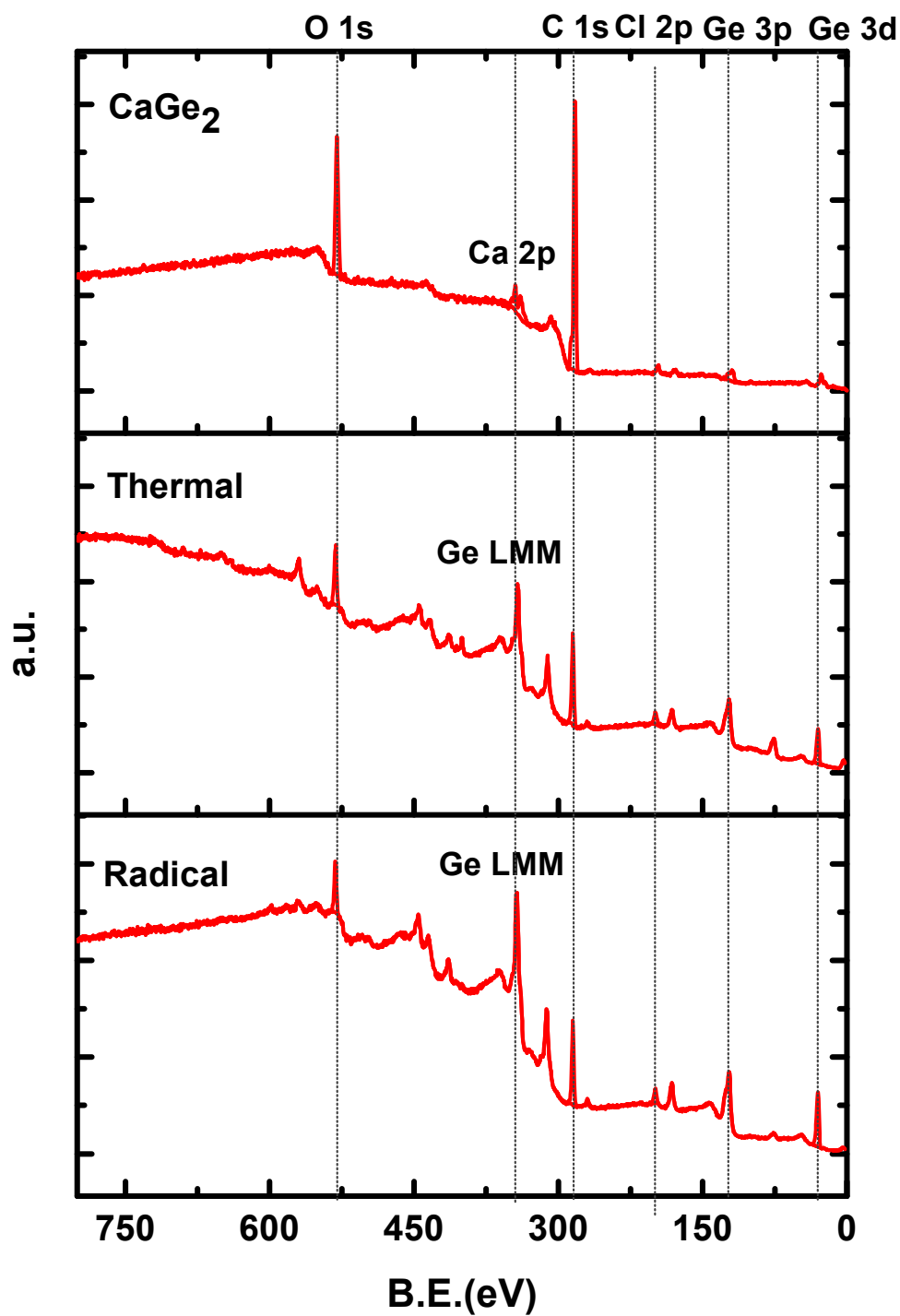


Figure S6: Survey X-ray photoelectron spectra of CaGe_2 (top), dodeceyl-terminated GeNSs prepared by thermally-induced hydrogermylation (middle) and dodeceyl-terminated GeNSs prepared by radical-initiated hydrogermylation (bottom).

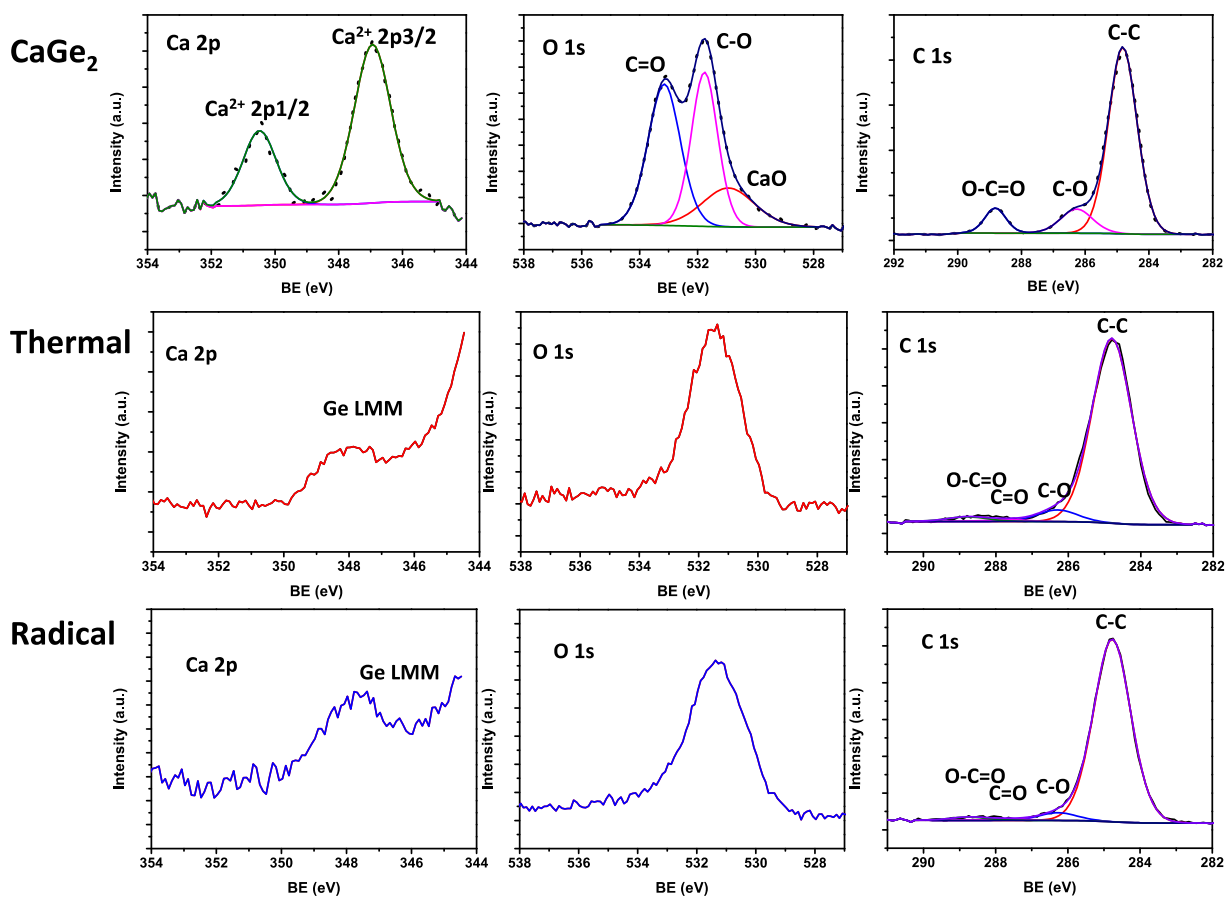


Figure S7: High-resolution X-ray photoelectron spectra of CaGe_2 (top), dodecyl-terminated GeNSs prepared by thermally-induced hydrogermylation (middle) and dodecyl-terminated GeNSs prepared by radical-initiated hydrogermylation (bottom).

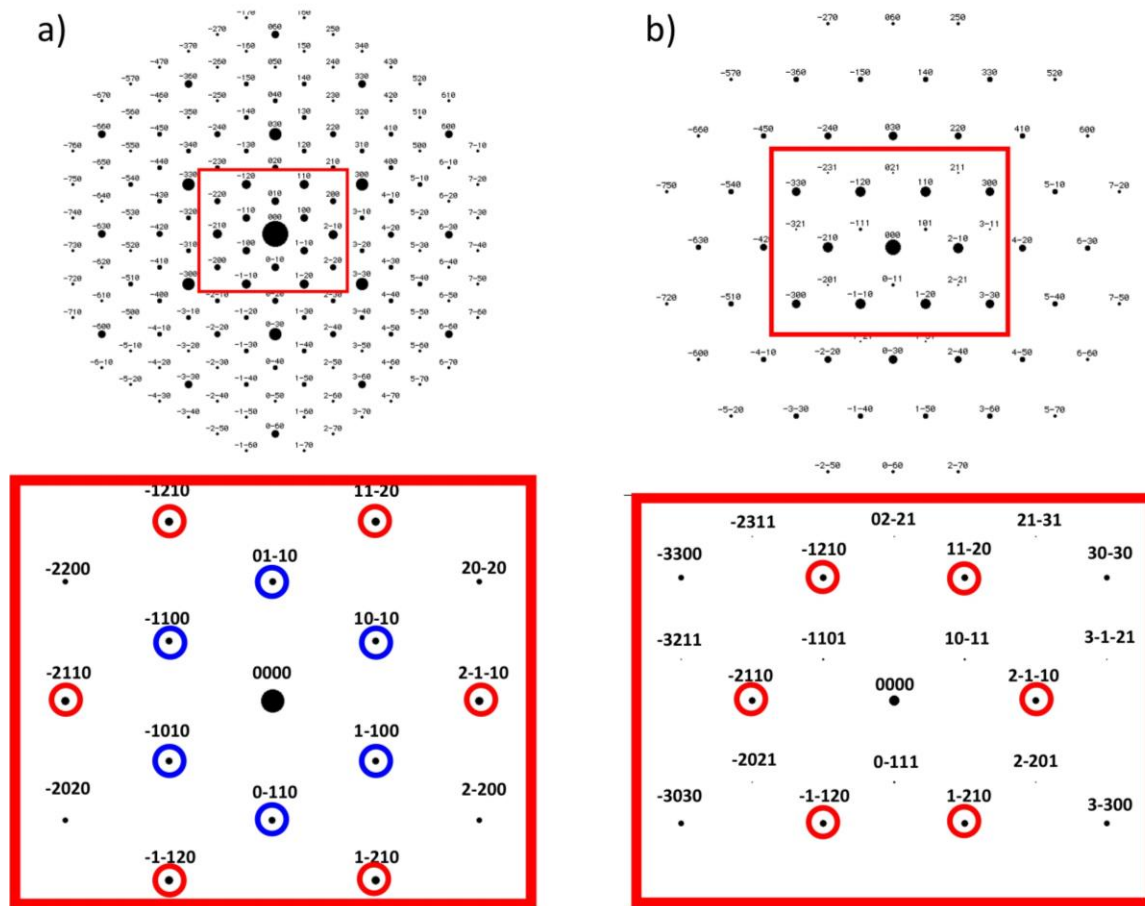


Figure S8. Electron diffraction pattern simulation results for non-fully exfoliated GeNSs using a) *h2* and b) *tr6* unit cell parameters. The diffraction patterns shown in the red boxes are enlarged by changing camera height during simulation.

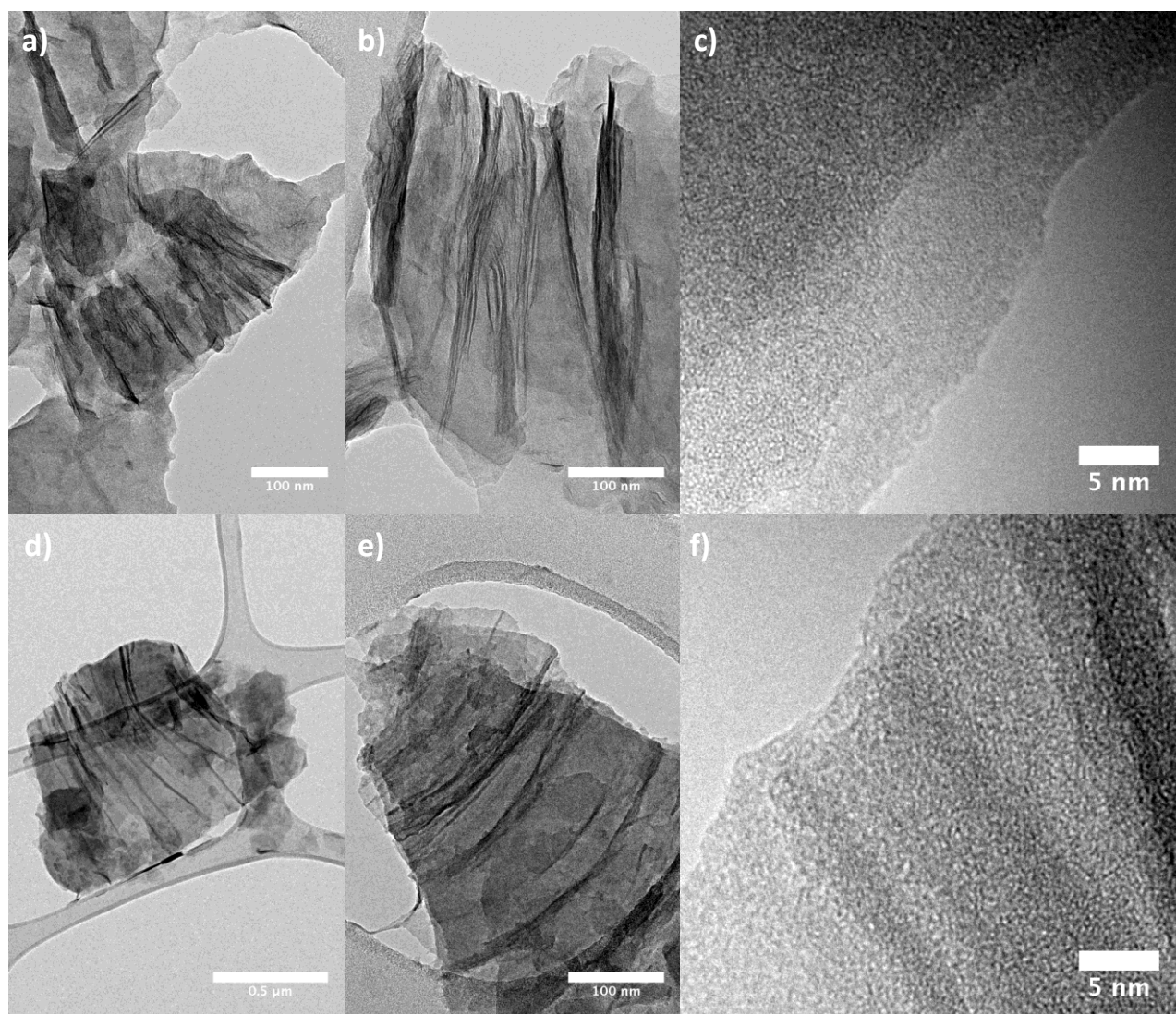


Figure S9: Top: Bright-field TEM images (a,b) and HRTEM (c) of dodecyl-terminated GeNSs prepared by thermal hydrogermylation. Bottom: bright-field TEM images (d,e) and HRTEM (f) of dodecyl-terminated GeNSs prepared by radical-initiated hydrogermylation.

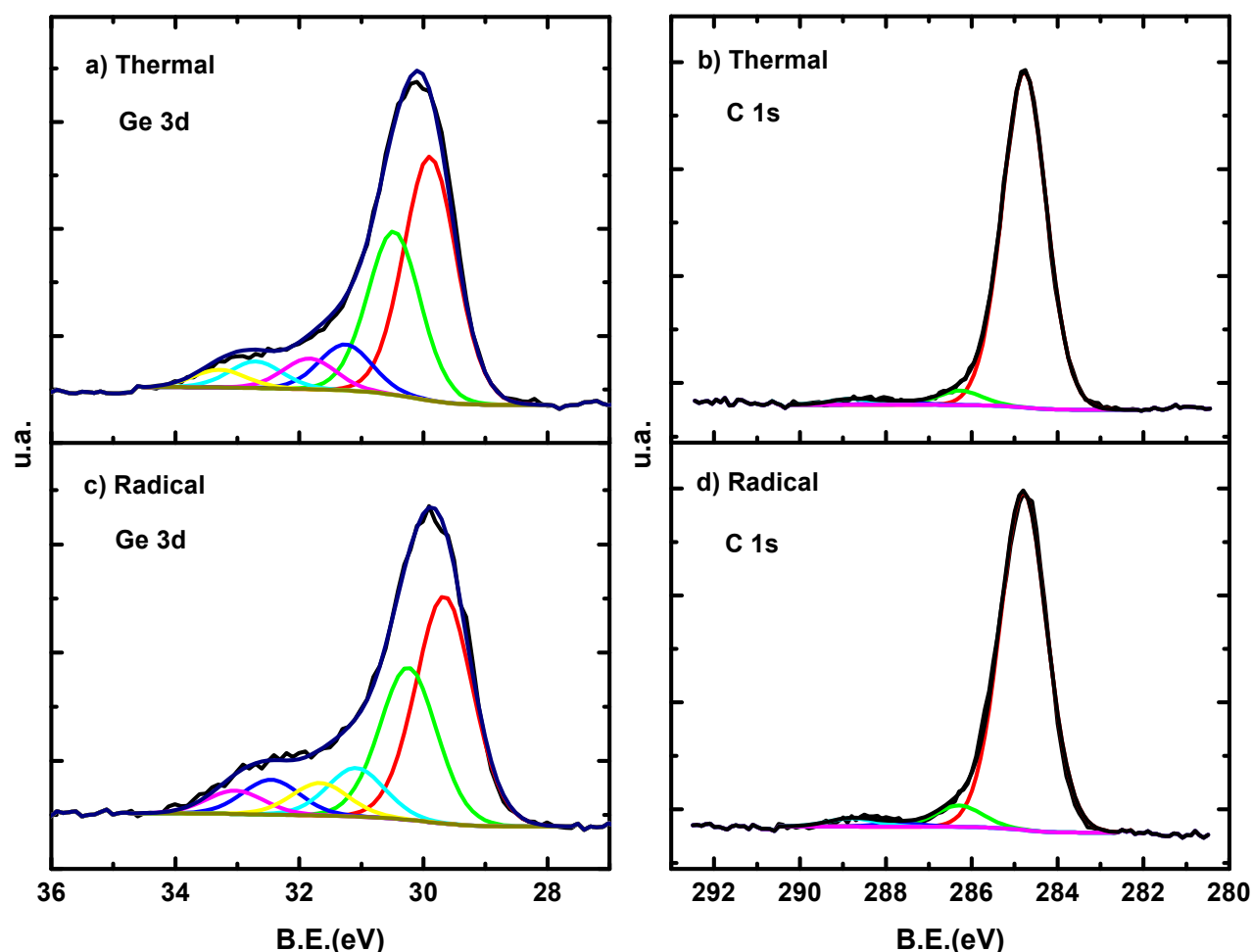


Figure S10: High-resolution X-ray photoelectron spectra of dodecyl-terminated GeNSs Ge 3d (left) and C 1s (right) signals, prepared by thermally-induced hydrogermylation (top) and dodecyl-terminated GeNSs prepared by radical-initiated hydrogermylation (bottom)

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