Supporting Information

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Stabilizing $\gamma$-MgH$_2$ at Nanotwins in Mechanically Constrained Nanoparticles

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SI-1. Full Dehydrogenation ESI Series (movie)

Supplementary Movie SM1. Complete ESI image series of the electron beam induced dehydrogenation of a MgH$_2$ nanoparticle (NP) from electron beam lithography. Exposure time and cumulated electron dose are indicated for each image. Contrast / signal range was adjusted for maximum dynamic range within the particles and kept constant throughout the image series.

SI-2. Diffraction from MgO

The diffraction pattern in Figure 1c, main text, does not contain the expected MgO reflection from the native oxide belt. Figure S1 shows the corresponding radial profile with simulated MgO reflections.$^{[1]}$ Only a small, insignificant shoulder might be observed at the position of the 002$_{\text{MgO}}$ peak. The weakness or absence of the MgO peaks can be explained by the small volume of MgO within the field of few during electron diffraction. The diffraction pattern is formed by four 350 nm nanoparticles (NPs) within a total field of view of $1.76\cdot 10^6$ nm$^2$. A Mg layer of about 42 nm in thickness yields a Mg volume of $16.1\cdot 10^6$ nm$^3$ for four particles. The membrane thickness of 15 nm yields a Si$_3$N$_4$ volume of $26.4\cdot 10^6$ nm$^3$. With a mean thickness of 5 nm for the MgO belt, the MgO volume of four NPs adds up to $0.5\cdot 10^6$ nm$^3$. The two layers of Ti with a total thickness of 5 nm yield about $1.9\cdot 10^6$ nm$^3$ and a 3 nm thick Pd layer yields about $1.2\cdot 10^6$ nm$^3$ for four NPs. This makes a volume fraction of 57% for Si$_3$N$_4$, 35% for Mg, 4% for Ti, 3% for Pd, and 1% for MgO. The latter three are hardly observed in the diffraction pattern due to their small diffracting volume.
Supplementary Figure S1: Radial averaged line profile of the diffraction pattern in Figure 1e, main text, and simulated MgO reflections.

SI-3. Influence of the Objective Aperture on ESI

Figure S2 shows the influence of an objective aperture (OA) on electron spectroscopic imaging (ESI). The OA introduces diffraction contrast, which is superimposed with the electron energy loss signal. The stronger a volume diffracts, the more electrons are filtered out by the OA and the darker is the corresponding area. However, it also maintains spatial and energetic resolution\(^2\) and avoids scattering angle dependent artefacts during ESI. The energy resolution without OA (d) is for example not sufficient to separate the Mg surface from the Mg volume when imaging at 8.0±0.5 eV – both appear equally bright. This is not the case with OA (a). The energy resolution is sufficient to separate the electrons, which excite the Mg volume plasmon, from those which excite the Mg surface plasmon. Furthermore, a tail is visible on the left of the particle when imaging at 9±0.5 eV (e). This tail reduces spatial resolution and is absent when imaging with OA (b). Only when the signal to noise ratio (SNR) is high due to intense Mg volume plasmon signal at 10.6 eV (f), spatial resolution seems equal for both cases. However, when the signal is less intense and SNR lower, i.e. the
signal originates from a smaller volume, spatial resolution is drastically reduced. Danaie et al.\textsuperscript{[3]} used no OA when imaging Mg and MgH\textsubscript{2} to avoid the superimposition of the electron energy loss signal and diffraction contrast. However, we however found that the reduced spatial and energetic resolution without OA is not suitable to sufficiently distinguish between the signals of Mg surface, Mg volume and MgH\textsubscript{2} volume plasmons – especially when imaging small amounts of Mg and MgH\textsubscript{2}.

**Supplementary Figure S2.** Comparison of electron spectroscopic imaging (ESI) of a pristine NP with (a-c) and without (d-f) objective aperture; contrast adjusted, scale 100 nm.
SI-4. EELS and ESI Analysis of MgO and Si₃N₄

The EELS background spectrum of Si₃N₄ (Figure S3a) shows a volume plasmon peak at about 22 eV. Due to the broadness of the peak, a considerable Si₃N₄ signal is visible when imaging MgH₂ at 15 eV energy loss (cf. Figure 2, main text).

The spectrum of MgO powder⁴ is composed of several minor peaks below 20 eV energy loss and a major volume plasmon peak at 22.4 eV. The MgO spectrum in specular geometry was recorded via reflection EELS (REELS) from the 004_MgO reflection of a MgO surface.⁵ Specular REEL spectra are mainly composed of surface excitations and allow to distinguish these surface from volume excitations. The MgO EELS signal within the ESI energy windows at 8, 11.6 and 15 eV is dominated by surface excitations. Volume excitations remain weak. Thus, the volume of the MgO belt appears dark during ESI and its surface is surrounded by a bright halo from the surface signal (cf. Figure 2, main text).

**Supplementary Figure S3.** Comparison of the EEL spectra of the Si₃N₄ membrane, MgO powder⁴ and the MgO surface recorded in specular geometry⁵. The bars indicate the energy windows for electron spectroscopic imaging (ESI) in the work at hand.
SI-5. Richardson-Lucy Deconvolution to Remove Si₃N₄ Background from EELS

The EELS signal of the Si₃N₄ support film can be removed from the EEL spectra with the Richardson-Lucy deconvolution⁶. We used 6 iterations. In the case of smaller particles, where the contribution of the Si₃N₄ support film is stronger, a higher number of iterations (14) was necessary.

Supplementary Figure S4. EELS spectra from the center of a NP and of the Si₃N₄ background. a, Bright field TEM image of the investigated NP after radiolytic dehydrogenation. Dashed circle indicates the area of spectrum acquisition; scale 100 nm. b, Spectra in the hydrogenated state before (black) and after (red) Richardson-Lucy deconvolution with the Si₃N₄ spectrum (blue) as kernel. c, Corresponding spectra in the dehydrogenated state.

SI-6. Morphological changes due to void formation by Mg diffusion

Figure S5 shows voids in NPs after radiolytic dehydrogenation (a-f) and after dehydrogenation through air exposure⁷ (g-m). After the last images of the dehydrogenation series (a-c), the first ESI images (d-f) were recorded four days later without further beam exposure in between. The network ripened and larger voids grew at the expense of smaller ones.
We observe similar voids after the dehydrogenation of the NPs by air exposure on a hotplate at 80 °C. For more information on the dehydrogenation in air see Duan et al.[7] Fewer, but comparably larger voids form, which makes faceting better visible. This is a result of the enhanced Mg diffusion at elevated temperatures and the different nucleation behavior during radiolytic dehydrogenation.[3] This and the ripening of the void network without further beam exposure excludes beam damage as underlying mechanism for void formation. The finer morphology of the radiolytic dehydrogenated NPs is a result of the different *in-situ* and *ex-situ* dehydrogenation mechanisms.[8]

**Supplementary Figure S5.** Morphological changes due to void formation as a result of Mg diffusion. a-f, ESI images of the NP for electron tomography (see Figure 3, main text) at the
end of dehydrogenation image series at 60 kV (a-c), and four days later without further beam exposure at 200 kV (d-f). **g-m**, Two NPs dehydrogenated by air exposure at about 80 °C on a hotplate. **l-m**, Lower part of the particle in **j, k**; contrast adjusted, scale 100 nm.

**SI-7. Void Formation in Smaller NPs**

The size, shape and distribution of voids within the NPs is comparable within the examined size range of NP sizes between 100 and 400 nm. **Figure S6** shows the reconstruction of a small NP with about 120 nm diameter from electron tomography. It contains two voids of similar size compared to the larger particle with about 350 nm in the main text. The voids are also wider at the bottom of the particle, but do not tend to accumulate at the MgO belt ring.

![Supplementary Figure S6](image_url)

**Supplementary Figure S6.** Three-dimensional reconstructions of pristine and dehydrogenated nanoparticles. **a**, Slice through a reconstruction showing the top of a pristine particle. **b**, Volume rendering of the whole particle. **c, f**, To visualize inner voids, the particle is divided into slices (yellow). **d-f**, Corresponding slice, rendering, and extracted segments from a dehydrogenated particle; scale for all panels: 50 nm.
SI-8. Different Modes of the Mg Surface Plasmons during ESI

Notably, the Mg surface plasmon is composed of two modes. One is excited at about 7.4 eV (cf. Figure S5l, imaged at 7.4 ± 0.5 eV energy loss), and primarily at faces (of the voids). A second mode with slightly higher energy is primarily excited at the edges (cf. Figure S5m, imaged at 8.8 ± 0.5 eV energy loss). The former corresponds to the surface plasmon of Mg with the excitation energy $\hbar\omega_{sp} \approx \hbar\omega_{vp}/\sqrt{2}$ related to Magnesium volume plasmon energy $\hbar\omega_{vp}$. With 8 ± 0.5 eV the ESI window to image the Mg surface was chosen to cover both modes and image the whole Mg surface.

SI-9. Unidentified Surface Compound in the Hydrogenated NPs.

After hydrogenation of the NPs, additional reflections from an unidentified compound appear (cf. Figure 5, main text). The reflections are more diffuse and less discrete as for the MgH2 reflections, leading to smooth rings within the artificial diffraction pattern, indicating nanosized grains. We determined the lattice distances as 0.160, 0.139, and 0.090 nm. We assume that a surface compound forms during hydrogenation either by alloying of the present evaporated elements, or by contamination of the hydrogen chamber with air, water or organic compounds. Thus, we compared the observed lattice spacings to several compounds from Mg, Ti, Pd, O, H and C without satisfying agreement: PdTi$_2$[10], PdTi$_2$[11], Pd$_3$Ti$_2$[12], Pd$_3$Ti$_2$[13], Pd$_5$Ti$_3$[13], Pd$_{3.6}$Ti$_{0.4}$[14], Pd$_{0.2}$Ti$_{0.8}$[15], Mg$_3$Pd$_2$[16], Mg$_5$Pd$_2$[17], MgPd$_2$[18], Mg$_{1.8}$Pd$_{2.2}$[19], MgPd$_3$[20], MgCO$_3$[21], Mg(OH)$_2$[22,23], Mg$_3$H$_2$O$_5$[24], Mg$_3$H$_8$O$_9$[24], Mg$_2$O$_4$Ti$_2$[25], MgO$_4$Ti$_2$[26], MgO$_5$Ti$_2$[27], Mg$_3$TiH$_8$[28], Mg$_7$TiH$_{12.7}$[29], Mg$_7$TiH$_{16}$[30], Mg$_6$TiH$_{16}$[31], MgTiH$_4$[28], MgTi$_3$H$_8$[28] and MgTi$_7$H$_{16}$[28].
SI-10. Determination of Lattice Parameters from NBD

Due to the complexity of the artificial ring pattern, the lattice parameters of the observed phases were determined from single, identifiable peaks. We determined the lattice parameters as $a = 0.451$ nm and $c = 0.297$ nm for $\beta$-MgH$_2$ from the 110$_\beta$ and 121$_\beta$ reflections, and $a = 0.456$ nm, $b = 0.543$ nm, and $c = 0.484$ nm for $\gamma$-MgH$_2$ from the 020$_\gamma$, 111$_\gamma$, and 112$_\gamma$ reflections. The lattice parameter of cubit TiH$_2$ was determined as $a = 0.437$ nm from the 111 reflection.

SI-11. Further Examples of Hydrogenated NPs and Assessment of $\beta/\gamma$ Orientation Relationship

Further examples of hydrogenated and twinned NPs are displayed in Figure S6 and S7. Figure S7 shows two additionally indexed NBD patterns with (301)$_\beta$ twins. The NBD patterns of the twinned areas show the same symmetry as the example in Figure 4d in the main text with a (301)$_\beta$ twin and a zone axis close to [11-3]$_\beta$. Unlike the example from the main text, the streaking is more intense and the single twin reflections cannot be separated clearly. The same applies to the $\gamma$-MgH$_2$ reflections, which are often incorporated within the streaks. Only the 020$_\gamma$ reflections can be identified unambiguously. According to the diffraction patterns in Figure S7 and the one in the main text, this plane would be parallel to the (301)$_\beta$ twin plane. Together with the two parallel $\gamma$ and $\beta$ zone axes, this would yield the orientation relationship [11-3]$_\beta$/[102]$_\gamma$, (301)$_\beta$/(010)$_\gamma$. However, this orientation relationship is likely not true, since the $\gamma$-MgH$_2$ diffraction patterns are too far out of zone axis for a precise determination. This is, for instance, evident from the asymmetric intensity distribution of the reflections and the shape asymmetry of the -201$_\gamma$ and 20-1$_\gamma$ reflections. Within the diffraction pattern in Figure S7f and 4d (main text) the individual spots of the -201$_\gamma$ and
$020_{\gamma}$ reflections are split in two diffraction points due to a large excitation error $s$, together with the inconvenient lattice transform in reciprocal space with highly elongated rel-rods in the thin direction of $\gamma$ nanolamellas and the z-direction of the particle. Thus, the highly elongated rel-rods also results in a larger possible excitation error and thus a larger tolerance to deviate from the zone axis and still observing the same reflections. This further reduces the accuracy of the determined orientation relationship.

The beam sensitivity of MgH$_2$ and the complexity of the diffraction patterns inhibit the acquisition of symmetric diffraction patterns and a tilt analysis of the lamellar defect structures. Even with such an analysis, streaking due to the small thickness of the lamella would still remain and prevent a precise determination of the parallel planes and directions. Thus, high resolution TEM is more suitable to determine the orientation relationship between the $\beta$ and $\gamma$ lamellas. Beam sensitivity can be drastically reduced at cryogenic temperatures.
Supplementary Figure S7. Further examples of hydrogenated and twinned NPs. The squares indicate the selected areas for the power spectra below. Contrast adjusted for best visibility of the twins in the zero-loss filtered bright field images and streaks within the power spectra; scale images: 100 nm; scale power spectra: 0.5 nm\(^{-1}\).
Supplementary Figure S8. Further examples of hydrogenated and twinned NPs. Within the bright field images (a, e), the volumina for nano beam diffraction are indicated by dashed circles. The upper circle in a corresponds to the NBD pattern in Figure 4f in the main text. The squares indicate the windows for the power spectra computation. b, f. Corresponding NBD patterns close to a [11-3]_β zone axis with indicated γ-MgH₂ peaks. c, g. Corresponding simulated β-MgH₂ NBD patterns of a (301)β twin with parent (red) and twin (blue) diffraction spots. * denotes twin reflections. d, h. Power spectra of the NPs; contrast adjusted, scale bright field images (a, e): 100 nm; scale diffraction pattern (b, c, f, g): 5 nm⁻¹; scale power spectra (d, h): 0.5 nm⁻¹.

SI-12. Anticorrelation of Mg surface and volume plasmon signal in dehydrogenated NPs

The excitation of the Mg surface and volume plasmons are anticorrelated. If the void transverses the NP completely in z direction, the Mg surface plasmon signal is strong and the Mg volume plasmon signal is absent (see Figure S9, arrow I). If the void does not transverse the NP completely, the Mg volume plasmon signal does not reach maximum intensity and a
considerable Mg surface plasmon signal is present in respective area (e.g., arrow II). Diffraction contrast may interfere with this correlation in rare cases (e.g., arrow III).

**Supplementary Figure S9.** Anticorrelation between Mg surface and volume plasmon signals within the dehydrogenation series in Figure 3, main text. (I) Position of a void traversing the NP completely in z direction. (II) Position of a void, which does not traverse the particle completely in z direction. (III) Superposition of the EELS signals with diffraction contrast (compare SI-3).
SI-13. References

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