# Nanoscale Hydrogenography on Single Magnesium Nanoparticles

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**Supporting Information** 

**ABSTRACT:** Active plasmonics is enabling novel devices such as switchable metasurfaces for active beam steering or dynamic holography. Magnesium with its particle plasmon resonances in the visible spectral range is an ideal material for this technology. Upon hydrogenation, metallic magnesium switches reversibly into dielectric magnesium hydride (MgH<sub>2</sub>), turning the plasmonic resonances off and on. However, up until now, it has been unknown how exactly the hydrogenation process progresses in the individual plasmonic nanoparticles. Here, we introduce a new method, namely nanoscale hydrogenography, that combines near-field scattering microscopy, atomic force microscopy, and single-



particle far-field spectroscopy to visualize the hydrogen absorption process in single Mg nanodisks. Using this method, we reveal that hydrogen progresses along individual single-crystalline nanocrystallites within the nanostructure. We are able to monitor the spatially resolved forward and backward switching of the phase transitions of several individual nanoparticles, demonstrating differences and similarities of that process. Our method lays the foundations for gaining a better understanding of hydrogen diffusion in metal nanoparticles and for improving future active nano-optical switching devices.

**KEYWORDS:** active plasmonics, hydrogen, magnesium, magnesium hydride, palladium, nanoparticles, nanodisks, absorption, desorption, hydrogenation, hydrogenography, optical near-field, scanning near-field optical microscopy, atomic force microscopy, dielectric function, refractive index, dark-field spectroscopy, far-field scattering, crystallinity

Recently, it was shown that hydrogen-absorbing metals can be employed to realize active plasmonic systems in which the plasmon resonance of metal nanoantennas can be switched off in the presence of hydrogen gas. This was, for example, demonstrated for yttrium<sup>1</sup> and magnesium nanostructures.<sup>2</sup> Magnesium, which offers the significant advantage of plasmon resonances in the visible wavelength range, was also employed in switchable chiral structures<sup>3</sup> as well as dynamic color displays.<sup>4,5</sup> To engineer switchable nanostructures with a short response time and a reproducibility over many absorption desorption cycles, it is very important to understand the mechanism of hydrogen absorption and diffusion in the metal.

Furthermore, tailoring of the hydrogen absorption– desorption kinetics of metal–hydride systems by nanostructuring has gained significant interest in recent years<sup>6–9</sup> because the hydrogen absorption and desorption kinetics at the nanoscale may differ significantly from the corresponding bulk materials, especially on the size scale of individual metal crystallites. This scientific interest is, in part, fueled by the potential application of metal hydrides as solid-state hydrogen storage systems, which can significantly outperform pressurized or even liquefied  $H_2$  in terms of volumetric energy density.<sup>10–12</sup>

Extensive studies have been performed on hydrogen kinetics in the model system of palladium nanoparticles, <sup>13–15</sup> and even a direct visualization of hydrogen absorption in Pd by means of

in situ transmission electron microscopy (TEM) was demonstrated.<sup>16-19</sup> However, studies on nanostructured systems of other metal hydrides such as MgH<sub>2</sub> mainly rely on a one-dimensional nanostructuring, i.e., the use of thin films. In addition to analysis techniques such as X-ray diffraction and other ion-beam techniques,<sup>20-24</sup> a plethora of studies on thin film systems have been carried out using the high-throughput optical characterization method termed hydrogenography.<sup>23</sup> This method exploits the contrast between the dielectric functions of a metal and its hydride by recording the optical transmittance through a film, which is directly related to the local ratio of metallic and hydrogenated domains. While such an optical analysis can be applied to materials that show only a small change in dielectric function upon hydrogenation, such as Pd, the full metal-insulator transition of the Mg-H system leads to a very strong optical contrast. This was, for example, applied for investigating the role of nucleation and growth in the (de)hydrogenation of Pdcapped Mg films<sup>26-28</sup> and Mg-based alloys<sup>29</sup> as well as the influence of elastic constraints of Mg films.<sup>30,31</sup> Investigating the dynamics of such films is possible on a scale down to

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several nanometers in the direction perpendicular to the substrate. However, the resolution in the horizontal plane remains limited by the optical diffraction limit. This prevents a direct investigation of the hydrogen diffusion on the size scale of individual Mg crystallites, which is typically on the order of 100 nm.<sup>22,32</sup>

Because plasmonic resonances sensitively rely on the dielectric properties of the host material, plasmonic spectroscopy is ideally suited to study the absorption and desorption dynamics of metal nanoparticles.<sup>33–36</sup> Plasmonic dark-field spectroscopy enables the investigation of individual nanoparticles, which has been used to address single Pd nanocrystals.<sup>37–39</sup> This method can be used to probe the amount of hydride in Mg particles smaller than the diffraction limit, thus outperforming thin-film hydrogenography. However, although previous studies have highlighted the importance of the crystallinity of Mg films,<sup>20–22</sup> a visualization of the hydrogen diffusion inside a single Mg nanoparticle or crystallite has, to our knowledge, not yet been demonstrated.

In this Letter, we present a novel approach to performing hydrogenographic measurements on submicron-sized particles of Mg, with a spatial resolution on the order of a few tens of nanometers. In contrast to conventional hydrogenography, we do not rely on transmission measurements but rather probe the change of the local optical properties at the material surface. Overcoming the optical diffraction limit is possible via the use of scattering-type scanning near-field optical microscopy (s-SNOM), which, in parallel, allows us to monitor topographical changes.<sup>40</sup> The system we use to demonstrate this method consists of disk-shaped Mg nanoparticles with a nominal thickness of 40 nm on top of a 10 nm thick catalytic Pd layer, as illustrated in Figure 1a. Both layers are separated by a 5 nm thick Ti layer, which serves as a buffer to prevent the formation of a Mg/Pd alloy layer.<sup>41,42</sup>

The strong contrast between metallic and dielectric materials is regularly exploited for imaging by means of s-SNOM. By excitation with mid-infrared or terahertz radiation, free-carrier concentrations and distributions can be visualized that can be used to analyze the doping of semiconductors or the carrier injection mechanism.<sup>43</sup> Temperature-induced Mott transitions have recently been monitored as well.44,45 Alternatively, a strong contrast can be obtained by the resonant excitation of vibrational modes. This has, for example, been used to visualize the phase transition associated with the (de)lithiation of LiFePO<sub>4</sub> taking place during the charging and discharging of Li-ion batteries<sup>46</sup> and reversible switching in optical phasechange materials.<sup>47</sup> In other approaches, s-SNOM measurements have been combined with scanning and transmission electron microscopy.<sup>48,49</sup> This combination of methods has for example been employed to observe metal-dielectric phase transitions in phase-change materials.<sup>50</sup> However, to the best of our knowledge, imaging by means of s-SNOM has not yet been employed to investigate the phase transition from a metal to a dielectric associated with the absorption of hydrogen.

**Sample Fabrication.** The Pd/Ti/Mg nanodisks are situated in a grid with a spacing of 10  $\mu$ m next to Au structures, which are used for reference measurements in both near-field and far-field measurements (see the Supporting Information). The samples are fabricated using two-step electron beam lithography and electron-beam assisted evaporation. First, plasma-cleaned CaF<sub>2</sub> substrates were covered with resist (PMMA) through spin-coating. The pattern of the Au structures, along with alignment markers,

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Figure 1. Measurement principle. (a) The nanostructures consist of a 40 nm thick Mg layer on top of a 10 nm thick Pd layer, separated by a 5 nm thick Ti buffer layer. The Mg particles have a nominal diameter of 240 nm. The Pd layer acts as a catalyst for the splitting of H<sub>2</sub> and, thus, as a gate for the hydrogen diffusion into the Mg layer. (b) In the s-SNOM setup, a laser beam with a wavelength of 4  $\mu$ m is focused onto a Pt-coated atomic force microscopy tip that is raster-scanned over the sample surface. The light scattered back from the sample surface is recorded with a liquid nitrogen-cooled IR detector, producing a map of the local scattering amplitude. (c) To monitor the hydrogenation of the Pd/Ti/Mg nanodisks, dark-field spectroscopy is employed to record the far-field scattering spectra of individual particles during hydrogen exposure. The total scattered intensity can be used as a measure of the amount of metallic Mg in the nanostructure because the metallic Mg particles can sustain a plasmon resonance in the visible wavelength range. This resonance vanishes when the particle is hydrogenated to MgH<sub>2</sub>, which is a dielectric and, thus, scatters much less light (inset).

is then transferred into a resist mask, after which a 2 nm thick adhesion layer of Cr is deposited, followed by 20 nm of Au. A Pfeiffer Vacuum PLS 500 system is used for this at a typical evaporation chamber pressure in the range of  $10^{-3}$  mbar. After lift-off, the substrate is again covered with resist, and the Au alignment markers are used to realign the sample. After the mask for the second layer is written, the same evaporation system is used to deposit 10 nm of Pd, 5 nm of Ti, and 40 nm of Mg, respectively, at a chamber pressure in the range of  $10^{-7}$ 



**Figure 2.** Hydrogen absorption in magnesium nanoparticles. (a-g) Far-field scattering spectra of four individual nanoparticles (particles P1–P4, top to bottom: green, red, yellow, and purple, respectively) before and after discrete hydrogen exposures at 60 °C. The graph captions indicate the total H<sub>2</sub> exposure time. (h-n) Near-field scattering maps of the same particles as investigated in panels a–g, covering an area of 600 nm × 600 nm. The s-SNOM images are recorded between the hydrogen exposures. A high scattering amplitude (red colors) in the s-SNOM images and a strong far-field scattering due to plasmon resonances indicate metallic Mg, whereas the dielectric MgH<sub>2</sub> does not support particle plasmon resonances and leads to a weak near-field scattering signal. (o-u) Cross-sections of the topography of the same particles as in panels a–n. The cross-section curves are obtained by averaging along the *x* direction over all 200 scan lines, omitting pixels with a height lower than 5 nm. The underlying topography is recorded in parallel to the near-field scattering maps presented in panels h–n. The individual particles are indicated by the different colors of the cross-sections (P1–P4: green, red, yellow, and purple, respectively).

mbar. The different material layers are deposited subsequently without breaking the vacuum in between to prevent the formation of intermediate oxide layers.  $CaF_2$  substrates were chosen to ensure optical transparency at both the visible wavelength used for dark-field spectroscopy and the infrared wavelengths used for s-SNOM measurements. Exemplary SEM micrographs of the nanodisks can be found in Figure S2.

**Scattering Scanning Near-Field Microscopy.** In the s-SNOM measurement setup (NeaSNOM, NeaSpec), an oscillating platinum-iridium coated silicon atomic force microscopy (AFM) tip with a nominal radius below 30 nm and a resonance frequency of 250 kHz is raster-scanned across the sample surface, thus producing a topographic map of the sample. At the same time, a laser beam with a wavelength of 4  $\mu$ m is focused onto the AFM tip, as illustrated in Figure 1b. A parametric frequency converter system (Alpha-HP, Stuttgart Instruments)<sup>51</sup> is used to generate this excitation beam with a 1/*e* bandwidth of approximately 130 nm. A liquid nitrogencooled infrared (IR) detector records the intensity of the light scattered between the sample surface and the tip.<sup>40,52,53</sup> This

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signal is then demodulated at the fourth harmonic of the tip oscillation frequency, which allows for discrimination of the optical near-field scattering from the total amount of scattered light.<sup>54</sup> To enhance the generally weak scattered light, interferometric enhancement is employed.<sup>55,56</sup> To this end, the AFM tip is positioned at the end of one arm of an asymmetric Michelson interferometer. Thus, the backscattered light is superimposed on the detector with the reflected light from the reference arm. The position of the reference mirror is kept fixed in such a way that all spectral components simultaneously interfere constructively (white-light position), thus maximizing the detector signal.<sup>55,56</sup> An approach curve confirming the background-free measurement of the optical near field<sup>57</sup> can be found in Figure S1. By this, the local optical properties of the sample surface in the nanometer vicinity of the tip can be resolved, which, in turn, depend on the local dielectric properties of the material.<sup>58</sup> An s-SNOM image therefore provides a map of the local dielectric properties alongside the topography, which is ideally suited for visualizing the distribution of Mg and MgH<sub>2</sub> because of the strong dielectric contrast between the two materials.

For each nanoparticle, an s-SNOM image is recorded with a scan size of 800 nm  $\times$  800 nm at a resolution of 200 pixels  $\times$  100 pixels. To image the exact same particles before and after each hydrogen exposure or heating period, the lithographically defined Au reference structures are detected by AFM imaging before imaging the Mg nanoparticles. The Au structures are simultaneously used as a height reference for the separate measurement sequences.

Dark-Field Spectroscopy. To monitor in situ the total amount of hydrogen absorbed by each Mg particle, we make use of the plasmon resonance of the particles, which is designed to lie in the visible to near-infrared wavelength range via the nominal particle diameter of 240 nm. The sample is situated in a temperature-controlled gas flow cell in a dark-field imaging and spectroscopy setup, in which the optical signal scattered into the far-field can be recorded for multiple particles in parallel during gas exposure, as illustrated in Figure 1c. The setup consists of a Nikon Eclipse LV100 upright microscope combined with a Princeton Instruments IsoPlane-160 spectrograph and a Pixis 256 Peltier-cooled frontilluminated charge-coupled device camera. A high-intensity laser driven light source (Energetiq eq 99) is used to illuminate the sample via a 50× dark-field condenser/objective (Nikon TU Plan ELWD). An exposure time of 10 s is used to record dark-field scattering spectra. The sample temperature is regulated by Peltier elements with an accuracy of less than 0.1 °C. The large interparticle distance of 10  $\mu$ m makes it possible to record the scattered signal of each particle individually. Because the plasmon resonance can only be sustained in a volume of metallic Mg and not in the dielectric MgH<sub>2</sub>, the strength of the plasmon resonance, and thus, the total far-field signal decreases with an increasing relative amount of MgH<sub>2</sub>.

The particle geometry with the thin Pd bottom layer leads to a relatively small exposed Pd surface area, which acts as a "gate" for the hydrogen absorption and desorption. This small exposed surface leads to a relatively slow absorption and desorption, with hydrogenated particles showing virtually no desorption when exposed to air at room temperature. This geometry was deliberately chosen because it enables us to remove a sample from the gas cell in the dark-field spectroscopy setup and transfer it to the s-SNOM setup to record a "snapshot" of the optical near field. In this way, we can monitor the changing distribution of Mg and  $MgH_2$  as well as the particle morphology during both hydrogen absorption and desorption.

**Hydrogen Absorption in Magnesium.** To drive the hydrogenation process of the Pd/Ti/Mg nanodisks, the pristine sample is placed in the gas flow cell, which is initially flooded with pure nitrogen. The sample is then heated to a temperature of 60 °C, after which H<sub>2</sub> is mixed with the nitrogen at a partial H<sub>2</sub> pressure of 20 mbar, while the total flow rate is kept at a constant value of 1  $l_n$ /min (liter normal per minute). The far-field scattering spectra of four selected particles are continuously monitored in parallel so that the H<sub>2</sub> exposure can be stopped at chosen times to record an intermediate s-SNOM image of the very same particles. The results of such a measurement run are displayed in Figure 2.

Figure 2a–g shows the recorded far-field scattering spectra of four selected particles at different stages of hydrogenation. Panel a depicts the spectra of the particles in their pristine state, and panels b–g show the spectra recorded just before H<sub>2</sub> exposure was terminated and the sample was taken out of the gas-flow cell. The corresponding s-SNOM images are shown in Figure 2h–n. The near-field scattering amplitude has been normalized to the signal from the dielectric CaF<sub>2</sub> substrate for each frame. Furthermore, Figure 2o–u show height profiles of all particles, obtained by averaging along the *x*-direction over the AFM data recorded simultaneously with the s-SNOM images.

Although the four particles are fabricated in the same way, the recorded far-field scattering spectra reveal a difference in the dynamics of the hydrogen absorption of the four individual particles. After 25.7 min of  $H_2$  exposure, the far-field spectra of particles P1 and P3 do not show any changes anymore, indicating that they are fully hydrogenated. In contrast, particle P2, which exhibits a comparable change of its spectrum in the beginning, still does not appear completely hydrogenated after 36.5 min, as indicated by the region with a high near-field scattering amplitude in panel m and the difference in far-field scattering between panels f and g. The same holds true for particle P4, which additionally shows a much-slower response in the beginning, as a significant change with respect to the pristine particle only starts occurring after 14.7 min (panels c and j).

The s-SNOM images of the pristine particles (Figure 2h) show that the scattering amplitude recorded on the metallic Mg surface is approximately 5 to 7 times as high as the signal recorded on the bare substrate. To verify this signal, a comparison of the Pd/Ti/Mg disks with gold structures of similar size was performed (see Figure S2). The scattering amplitudes arising from both materials are virtually the same, as one would expect from the very similar dielectric functions of Mg and Au at a wavelength of 4  $\mu$ m. The s-SNOM images exhibit structural features as well: in particular, on particles P1 and P4, one can recognize edges with a lower scattering amplitude indicating roughly hexagonal shapes. These features are visible not only in the near-field signal but also in the raw AFM data (see Figure S3). Because Mg has a hexagonal crystal lattice,<sup>32</sup> these features most likely arise from individual Mg crystallites protruding from the particle surface.

The s-SNOM images recorded after different  $H_2$  exposure periods (Figure 2i–n) exhibit in great detail how the strongly scattering metallic Mg particles are transformed into dielectric particles, whose near-field scattering amplitude is almost



**Figure 3.** Hydrogen desorption of magnesium hydride nanoparticles. (a-g) Far-field scattering spectra of four individual nanoparticles (particles P1-P4, top to bottom: green, red, yellow, and purple, respectively) before and after discrete annealing periods at 95 °C in argon atmosphere. The graph captions indicate the total heating time. (h-n) Near-field scattering maps of the same particles as investigated in panels a-g, covering an area of 600 nm × 600 nm. The s-SNOM images are recorded between the annealing periods. (o-u) Cross-sections of the topography of the same particles as in panels a-n. The underlying topography is recorded in parallel to the near-field scattering maps presented in panels h-n. The individual particles are indicated by the different colors of the cross-sections (P1-P4: green, red, yellow, and purple, respectively).

uniform and similar to that of the dielectric substrate. However, the near-field scattering amplitude does not decrease in a spatially uniform way. Instead, nucleation sites with a nearfield scattering amplitude similar to that of the dielectric substrate become visible at early stages of the  $H_2$  exposure. These nucleation sites expand throughout the entire particle during hydrogen absorption. This growth appears not to progress continuously through the particle, but instead, it appears as if individual regions of a particle change one after another. Of course, one has to keep in mind that our ex situ measurements cannot resolve the entire temporal evolution of the hydrogen absorption. Furthermore, the images indicate a correlation between the material transition and the particle topography. This effect is most pronounced in particles P1 and P4, where the hydrogenated areas in panels i and j overlap with the hexagonal features observed in panel h.

A comparison between the s-SNOM images and the far-field scattering spectra reveals a correlation between the total intensity scattered into the far-field and the portion of the particle with high near-field scattering amplitude, which corroborates the validity of our measurement method. For example, as the near-field scattering amplitude of particle P1 has become almost uniformly similar to that of the substrate (panel 1), its far-field scattering has diminished as well (panel e). The same comparison can be carried out for the other particles. Furthermore, the AFM measurements represented by

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the cross-sections in Figure 20–u reveal an increasing particle thickness. This can be attributed to the strong lattice expansion in Mg of around 30% upon hydrogenation. The expansion appears to be anisotropic, taking place mostly in the vertical direction, which could be caused by the presence of an oxide shell that prevents a strong lateral expansion. The measured expansion further validates the full hydrogenation indicated by the vanishing far-field as well as near-field scattering of the metallic Mg.

**Hydrogen Desorption of Magnesium Hydride.** A similar measurement routine was applied to visualize the morphology and material composition during hydrogen desorption. The sample was placed in the gas cell and heated to a temperature of 95 °C in an argon atmosphere, at which point the Pd/Ti/Mg nanoparticles dehydrogenate over the course of several hours. Dehydrogenation by heating was favored over oxygen exposure to avoid potential corrosion, which could form Mg(OH)<sub>2</sub>. At chosen times, the dehydrogenation process was stopped by cooling down the sample to room temperature to record an s-SNOM image. The far-field scattering spectra and corresponding s-SNOM images and AFM profiles are shown in Figure 3 for the exact same particles as in Figure 2.

Similar to the data recorded during hydrogenation, the farfield scattering spectra (Figure 3a-g) display a similar trend as the corresponding s-SNOM images (Figure 3h-n). The farfield scattering spectra furthermore do not fully return to their original shape after more than 15 h of heating. The decreased overall scattering intensity of the dehydrogenated particles (Figure 3g) compared to the pristine particles (Figure 2a) indicates that only partial dehydrogenation has taken place before the particles settle in a stable state. This behavior can be recognized in the s-SNOM images as well. While regions with a higher near-field scattering amplitude, indicating the presence of metallic Mg, start to emerge along the particle rim after dehydrogenation for 30 min, the central part of the particle surface maintains its low scattering amplitude. A comparison to Figure 2 furthermore shows that the particles that have become fully dielectric within the shortest time span are also the first ones to reach a stable state after dehydrogenation (P1 and P3), while the slower particles (P2 and P4) also dehydrogenate last. This indicates that the time needed for the absorption as well as desorption process is largely determined by the structure and morphology of the particle. Depending on the number, size, and arrangement of the crystallites that compose a particle, different pathways for hydrogen diffusion might form, which determines the speed of both processes alike.

A quantitative comparison of the spectrally integrated farfield scattering and the spatially integrated near-field scattering is exemplarily shown for particles P1 and P2 in Figure 4, for hydrogen absorption as well as desorption. Because the particles undergo a full metal-dielectric transition upon hydrogenation, the total far-field scattered intensity decreases dramatically and thus constitutes a very clear measure of the progress of the hydrogenation. These same data can be found in Figure S7 for all four particles together with the relative particle expansion calculated from the AFM data.

Alongside the far-field and near-field optical responses, the particle shape undergoes a strong change as well, as evidenced by the AFM profiles. While the fully hydrogenated particles (Figure 30) feature an increased thickness with respect to the pristine particles, the particle caps remain relatively flat. As the dehydrogenation progresses, however, the particles adopt a



**Figure 4.** Total optical far field and near field vs time. The total farfield and near-field signals are exemplarily shown for particles P1 and P2 during  $H_2$  (a) absorption and (b) desorption. The solid lines show the total far-field scattered signal during  $H_2$  exposure or heating, obtained by integrating the recorded far-field spectra from 620 to 870 nm. The vertical dashed lines indicate the times at which the absorption–desorption process was interrupted to record s-SNOM images. The hydrogen exposure and heating periods between the dashed lines include 50 s of  $N_2$  purging at the start and at the end. The circles display the total near-field scattering amplitude recorded at each of these instances, obtained by integrating over all of the pixels of the corresponding s-SNOM image after subtraction of the substrate signal.

more rounded shape. Overall, this demonstrates that our nanoscale hydrogenography method based on s-SNOM imaging also provides valuable information on topographical changes alongside the optical properties, which will be correlated in the following.

**Correlation between Topography and Optical Properties.** In Figure 5, the color-coded relative optical near-field scattering amplitude has been overlaid onto a three-dimensional representation of the measured AFM thickness at selected stages of hydrogen absorption and desorption of particle P1. Projections of the particle geometry onto the *XZ* and *YZ* plane are displayed in gray, while contour lines are shown in white at 10 nm intervals. Several interesting observations can be made from these images.

Most importantly, one can clearly see how individual crystallites switch from Mg to  $MgH_2$  independently one after another. This effect is most pronounced in Figure 5a–c. In panel a, the two roughly hexagonal protrusions (which were already visible in Figure 2h–j) both feature a strong near-field scattering amplitude in the middle, with a slightly lower scattering amplitude along the edges. In panel b, the rightmost of these protrusions has turned dark and, at the same time, has increased in thickness. The left protrusion shows the same change in panel c. In panel d, the protrusion on the back of the particle has slightly increased in height and the near-field scattering amplitude has partly decreased, whereas in panel e, it has grown to the same height as the rest of the particle and its



**Figure 5.** Overlay of the color-coded near-field scattering amplitude on the topography (x, y, z data) of particle P1 at different stages of (a-e) hydrogenation and (f-j) dehydrogenation. The white lines depict contour lines with a vertical distance of 10 nm. The gray areas show the projections of the particle onto the XZ and YZ plane. Note that the view in panels f-j has been rotated by 180° with respect to panels a-e.

near-field scattering amplitude is likewise indistinguishable from the rest of the particle and the substrate. This apparently subsequent hydrogen loading of individual crystallites is comparable to the observations of Narayan et al. in mono- and polycrystalline palladium nanoparticles.  $^{17}\,$ 

Furthermore, the shape change of the particle is clearly visible in this representation. During hydrogenation, the relatively rough particle cap becomes smooth while the particle thickness increases. During dehydrogenation, the particle evolves toward a hemispherical shape. Based on a detailed analysis of the AFM data, we argue that the change in shape can be explained via a minimization of the surface energy of the particle (see the Supporting Information). Corrosion of the particle surface as a result of air exposure in the s-SNOM setup likely plays a role as well because control experiments on pristine and hydrogenated Pd/Ti/Mg particles show a somewhat decreased near-field scattering amplitude after air exposure for several hours. These control measurements can be found in Figures S4–S6.

We can finally pool together our measurements to explain the dynamic switching behavior of the Mg plasmonic structures. The switching off of the plasmonic resonances due to hydrogen absorption is not a strictly continuous process, and they do not react linearly to hydrogen exposure, as visible when comparing Figure 2a-g as well as Figure 4a. Instead, each particle exhibits an individual hold-back time in the beginning. We attribute this to the fact that the grain boundaries of the individual crystallites in a single nanostructure act as a barrier for the hydrogen diffusion, as visible in the s-SNOM images in Figure 2h-n as well as Figure 5a-e. In the end, however, the plasmonic resonances can be completely switched off, relying on the fact that the nanoparticles are completely turned into a dielectric material. However, this process is not entirely reversible because the plasmonic resonances cannot be brought back to their original oscillator strength. This can be deducted from a qualitative comparison of the spectral shapes in Figures 2a and 3g as well as the absolute far-field scattering intensity displayed in Figure 4. Because the resonances of plasmonic nanostructures are artificially tailored by the particle geometry, it is quite clear that even minor changes of the geometry will alter their spectra. Such geometrical changes are clearly visible when comparing Figures 20 and 3u and even more in the time series displayed in Figure 5. Furthermore, the s-SNOM images in Figure 3n indicate that the particles do not become completely metallic again in the end. This thus indicates that the local conductivity, which microscopically governs the plasmonic response of a structure, has been altered after one switching cycle.

In summary, we recorded s-SNOM-image time series of four individual magnesium nanoparticles during hydrogen absorption and desorption. This allowed us to observe the phase change from metallic to dielectric of individual domains. The topographical maps recorded in parallel to the s-SNOM images show that these domains very likely correspond to separate nanocrystallites. This indicates that the phase change from Mg to MgH<sub>2</sub> occurs rapidly within a single crystalline domain before progressing toward adjacent nanocrystallites. We additionally compared the overall near-field scattering to the plasmonic far-field scattering of the particles. From the combination of both methods, it becomes clear how the properties of the individual nanoparticle change during the full forward- and backward-switching cycle: while the s-SNOM images show a change of the particle morphology, the plasmonic resonances do not regain their original strength. The insights gained from our s-SNOM measurements (namely, the formation of hydride domains during hydrogenation and the morphological change during dehydrogenation) reveal the underlying processes of the optical switching behavior. Our nanoscale hydrogenography by means of s-SNOM imaging is

thus a highly promising research tool for the investigation of the dynamics of hydrogen diffusion in single metal nanoparticles, allowing for a lateral resolution on the order of a few tens of nanometers. The technique allows for the study of a wide variety of structures and material combinations for active nanoplasmonic devices at different time and length scales. For instance, the influence of the average crystallite size on the switching behavior of different metal—hydride systems can be addressed in the future. Furthermore, our results show that the crystalline structure of individual Mg nanoparticles appears to be crucial for the speed of the hydrogen absorption and desorption processes. Our findings thus also highlight the importance of the exact fabrication conditions for the quality, reproducibility, and switching speed of future active plasmonic devices as well as magnesium-based hydrogen-storage systems.

## ASSOCIATED CONTENT

## **S** Supporting Information

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Figures and additional details on the approach curve of the s-SNOM signal, a comparison of near-field and AFM images with SEM images of the investigated particles, AFM amplitude and phase maps of the pristine particles, results of control measurements, total far-field and total near-field vs time for all particles, an explanation of the AFM data analysis, and the sample layout map and measurement routine description. (PDF)

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# Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

s-SNOM, scattering-type scanning near-field optical microscopy; AFM, atomic force microscopy

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