

Magnesium as Novel Material for Active Plasmonics in the Visible Wavelength Range

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(5) Supporting Information

ABSTRACT: Investigating new materials plays an important role for advancing the field of nanoplasmonics. In this work, we fabricate nanodisks from magnesium and demonstrate tuning of their plasmon resonance throughout the whole visible wavelength range by changing the disk diameter. Furthermore, we employ a catalytic palladium cap layer to transform the metallic Mg particles into dielectric MgH₂ particles when exposed to hydrogen gas. We prove that this transition can be reversed in the presence of oxygen. This yields plasmonic nanostructures with an extinction spectrum that can be repeatedly switched on or off or kept at any intermediate state, offering new perspectives for active plasmonic metamaterials.



KEYWORDS: Magnesium, active plasmonics, hydrogen loading, nanofabrication, nanooptics, chemical reaction sensing, nanochemistry

In recent years, the field of plasmonics has become an important driving force for progress in the area of nanophotonics. Building on initial applications in chemical and biological sensing devices,^{1,2} there has been an increased focus on active plasmonics.³ Here, metamaterial structures can be actively reconfigured via temperature change,^{4,5} mechanical stress,^{6–8} optically,⁹ or electrically,^{10,11} promising interesting applications in, for example, all-optical data network switches¹² and smart solar collectors.¹³ A previously demonstrated approach for realizing reconfigurable metamaterials is via the absorption of hydrogen, which was realized for yttrium (Y)¹⁴ and palladium (Pd)^{15,16} nanoparticles.

One particular metal which has not been subject to extensive investigation regarding its plasmonic properties yet, is magnesium (Mg). Mg has several very promising properties for applications in plasmonics in general and switchable plasmonic metamaterials in particular. As mentioned by Sanz et al.,¹⁷ Mg nanoparticles support localized surface plasmon resonances at wavelengths down to the ultraviolet. Thus, Mg constitutes an ideal alternative to established materials for UV plasmonics such as aluminum,¹⁸ providing higher extinction efficiencies in the same wavelength range. This indicates that, via adequate tuning of the particle size, resonances throughout the visible spectrum can be obtained.

While the plasmonic properties of Mg are yet largely unexplored, this material has been widely investigated for applications in a different context, namely the field of solid-state hydrogen storage. Magnesium is known to be able to absorb up to 7.6 wt % of hydrogen gas,¹⁹ making it one of the most promising candidates for hydrogen storage in the advent of a hydrogen economy.^{20,21} Upon absorption of hydrogen gas, the metallic magnesium changes into dielectric magnesium hydride (MgH₂). One issue associated with magnesium, however, is the high thermodynamic stability of MgH₂ and the relatively slow hydrogen diffusion at room temperature. In order to address these challenges, several solutions have been proposed, including the fabrication of various Mg-based alloys,^{22,23} the addition of different catalysts,^{24–27} and the use of nanocrystal-line magnesium.^{19,28}

In this work, we demonstrate that magnesium nanoparticles exhibit a pronounced plasmonic response that is tunable throughout the whole visible wavelength range. The plasmon resonance vanishes upon exposure to hydrogen gas at room temperature if a catalytic layer of palladium (Pd) is added on top of the Mg layer. This happens because the dielectric MgH_{22} into which the Mg is transformed, does not support plasmonic resonances. This Pd caplayer technique has previously been applied to magnesium films²⁹⁻³² as well as small Mg nanoparticles, allowing for the observation of hydride formation via indirect nanoplasmonic sensing.³³ However, reversible switching of plasmonic Mg particles from the metallic to the dielectric state has not been demonstrated, while the presence of such a reversible chemical reaction is one of the main prerequisites for a material with potential applications in active plasmonics. We show for the first time that the hydriding

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process can be reversed by exposure to oxygen, upon which the MgH_2 dehydrogenates and returns to its metallic Mg state. This process can be repeated over multiple cycles without significant degradation and with hydrogen loading/unloading times on the order of minutes at room temperature.

To investigate the plasmonic properties of magnesium nanostructures, we fabricated Mg nanodisks of different sizes using colloidal hole-mask lithography³⁴⁻³⁶ and subsequent electron-beam evaporation. This low-cost method provides large-area samples of randomly distributed and well-separated nanodisks with a relatively narrow size distribution, avoiding any lattice effects in the extinction spectra. The method can easily be extended to obtain more complex nanostructure geometries such as plasmonic perfect absorbers.^{37,38} Nanodisk samples with average diameters of approximately 80, 160, and 220 nm were obtained, with a typical Mg thickness of 80 nm (see Figures S1 of the Supporting Information). Figure 1 shows exemplary SEM images of such nanodisks and their corresponding extinction spectra. Ensemble extinction measurements were performed using a white-light source and a microscope combined with a grating spectrometer (Princeton Instruments Acton Advanced SP 2500i) and a 2D CCD detector (PIXIS 256).

The measurement results displayed in Figure 1 demonstrate that the plasmonic response of Mg nanodisks can be tuned by adequate choice of the disk diameter throughout the visible wavelength range, from resonance wavelengths below 500 nm up to 800 nm and further into the near-infrared. Furthermore, the SEM micrographs in Figure 1a–c indicate that the magnesium nanoparticles take on a hexagonal monocrystalline shape at relatively small sizes (Figure 1a,b) and tend to form polycrystalline particles when the particle size increases (Figure 1c). This is consistent with findings in earlier studies on sputtered magnesium films, which show that these films consist of crystalline grains with sizes in the order of 100–200 nm, with a dominating (0002) orientation perpendicular to the substrate.³⁹

To validate the measured spectra of Mg disks, we performed numerical FDTD-based simulations on a system consisting of a single cylindrical Mg particle on a glass substrate. To accommodate for the degradation of magnesium after removal of the sample from the evaporation chamber,⁴⁰ a 5 nm thick layer of magnesium oxide (MgO) is assumed on the surface of the nanoparticle. The dielectric data of magnesium are taken from the work of Palik.⁴¹ The extinction spectra resulting from these simulations, for disks of the same diameters as the fabricated particles, are displayed in Figure 1e. Surprisingly, the measured resonances turn out to be narrower than the simulations predict, especially for the 160 and 220 nm particles. The resonance wavelengths, however, are in good agreement with the simulations. This outperformance of the measured particles compared to the simulations can possibly be attributed to the very high crystallinity of our nanodisks, whereas the dielectric data used in the simulations were obtained from measurements on extended, polycrystalline films.

Magnesium is a comparatively reactive element, which can undergo several chemical reactions when exposed to ambient concentrations of different gaseous environments. Most of these reactions produce relatively stable compounds and cannot be easily reversed to obtain pure magnesium again. Consequently, Mg nanoparticles are subject to degradation when exposed to air after they are removed from the vacuum of the evaporation chamber. As it turns out, the plasmon



Figure 1. Magnesium nanodisks as a model system for magnesium plasmonics. (a-c) Colorized SEM images of Mg nanodisks with average diameters of 80, 160, and 220 nm, respectively. (d) The resonance wavelength of such nanodisks can be tuned throughout the visible wavelength range by varying the diameter. The smaller particles (a,b) appear to be monocrystalline, while the particles with an average diameter of 220 nm (c) appear to take on a polycrystalline shape. (e) Extinction spectra obtained from numerical (FDTD) simulations on cylindrical Mg particles with different diameters, encapsulated in a 5 nm thick layer of magnesium oxide (MgO), and placed on a SiO₂ substrate.

resonance of Mg disks, when exposed to air at room temperature, slowly shifts into the red by approximately 10-20 nm while slightly increasing in extinction. This behavior can be attributed to the high refractive index of a slowly growing outer layer of corrosion products. This shift takes place over the course of days, after which it saturates and the particles can remain stable over several months (see Figure S3 of the Supporting Information). If the sample is exposed to an atmosphere of pure oxygen, however, no shift is visible at all. This is consistent with previous studies on the oxidation of Mg films, which show that a layer of MgO with a thickness of several nm is formed on the Mg surface, which then prevents the underlying material from further oxidation.⁴²⁻⁴⁴ In a humid environment, this oxide surface can become hydroxilated, forming brucite $(Mg(OH)_2)$.⁴⁵ Ambient concentrations of CO₂ also contribute to the degradation of the Mg particles, forming



Figure 2. (a) Switching of magnesium particles to magnesium hydride and vice versa with the aid of a 10 nm catalytic Pd layer and a 5 nm Ti buffer. (b) Extinction spectra of 160 nm Mg/Ti/Pd particles (Mg thickness 80 nm) in the different stages of a typical hydrogenation/dehydrogenation cycle. As the initial Mg/Ti/Pd particles (blue curve) are exposed to hydrogen gas ($4 \text{ vol } \% \text{ H}_2 \text{ in N}_2$), the Pd layer performs catalytic splitting of molecular H₂ into single hydrogen atoms, which diffuse into the Mg lattice, forming MgH₂. During hydrogenation, the Mg, Ti and Pd lattices expand by different factors (32%, 25%, and 11%, respectively). Due to the dielectric nature of MgH₂, these hydrogenated particles do not exhibit any plasmonic resonances (red curve). Upon termination of the H₂ exposure, the Pd dehydrogenates, inducing a small increase in extinction (green curve), while the Mg remains in its hydrogenated state. Upon exposure to oxygen, however, the MgH₂ also dehydrogenates, and the particles return to their initial Mg/Ti/Pd state (black dashed curve). The small redshift and increase in extinction after completion of the cycle can be attributed to the increasing thickness of the magnesium oxide (MgO) layer.

a magnesium hydroxy carbonate on the surface.⁴⁶ In principle, such reactions could form the basis for magnesium-based nanoplasmonic sensors for different gases; applications like this would however suffer from the chemical stability of magnesium-based compounds and the irreversibility of the associated chemical reactions.

As mentioned above, the chemical reaction of magnesium which is subject to most extensive investigation is the absorption of hydrogen, which yields magnesium hydride (MgH₂). The high hydrogen content of MgH₂ is the major reason for the long-lasting interest in Mg as a hydrogen storage medium. Simply exposing the particles to an ambient concentration of hydrogen gas is, however, not sufficient to induce this reaction: the hydride formation in bulk Mg only takes place at temperatures of several hundred degrees Celsius and pressures of tens of atmospheres, ^{19,20,28} and even then it takes several hours. The dehydrogenation of magnesium hydride requires even higher temperatures.⁴⁷ Due to the relatively low melting point of bulk Mg (923 K),⁴⁸ such temperatures would threaten the stability of nanostructured magnesium.

The main limiting factor in these reactions is the impossibility of absorption of molecular hydrogen, which requires a means of splitting the hydrogen molecules at the surface of the nanodisk. To circumvent this problem, the use of several catalysts (which aid the dissociation of molecular hydrogen into single hydrogen atoms) has been investigated. Most importantly, several studies have been published on the hydrogenation of extended Mg films with the aid of a thin layer of palladium.^{30,31,49–51}

Palladium nanoparticles, which are also able to sustain plasmonic resonances themselves, have previously been employed as plasmonic hydrogen sensors,^{16,52} utilizing the transformation of palladium into palladium hydride (with a relative hydrogen content depending on the external hydrogen concentration) and the associated shift of the plasmonic resonance. The atomic hydrogen present in the palladium can be used to hydrogenate other materials, such as Mg. For this reason, we fabricated magnesium nanodisks with a 10 nm thick Pd layer on top. As shown by Baldi et al.,³¹ simply capping the Mg with a Pd layer has the disadvantage that a Mg–Pd alloy is formed in the interfacial region, which significantly hinders the diffusion of hydrogen through the Mg/Pd interface into the Mg. This can be avoided by separating the Mg and Pd layers from each other by 5 nm of titanium acting as a buffer layer. This buffer layer has two functions: not only does it prevent the Mg and Pd layers from alloying, but it also elastically decouples the two layers, releasing the mechanical stress induced when magnesium and palladium expand laterally at different rates. A slight drawback of the titanium layer is that it causes some damping of the plasmonic resonance of the Mg particle.⁵³

The functionality of these particles is illustrated in Figure 2. When the Mg/Ti/Pd particles are exposed to an atmosphere of hydrogen gas (4 vol % H_2 in N_2 carrier gas), the Pd layer catalyzes the splitting of the hydrogen molecules into atomic hydrogen, which easily diffuses into the titanium layer and further into the magnesium. The formation of dielectric magnesium hydride causes the plasmonic resonance to disappear almost completely. When the hydrogen flow is switched off and the particles are exposed to pure N_2 , the palladium layer releases its stored hydrogen in tens of seconds, causing the extinction of the particles to increase slightly. The pronounced resonance peak of magnesium does, however, not come back, since the magnesium remains in its hydrogenated state.

As it turns out, the dehydrogenation of the MgH₂/Ti/Pd particles only takes place in the presence of oxygen: when the system is exposed to oxygen diluted in nitrogen, or even simply to dry air, the resonance is fully restored in tens of minutes, after which the cycle can start over. This oxidative dehydrogenation has been observed before in magnesium-based films.^{13,51} The extinction resonance of the dehydrogenated system is slightly enhanced and red-shifted after one gas cycle (see Figure 2b). This is likely due to cracking of the oxide shell around the Mg layer during hydrogenation, since the Mg expands by more than 30% in volume, so that some additional oxidation can take place when the particle is exposed to oxygen for dehydrogenation. This does, however, not greatly compromise the stability of the Mg/Ti/Pd system, as our experiments indicate that the plasmon resonance can be reliably switched off and back on over 10 or more gas cycles. All measurements were carried out at room temperature.

The switching dynamics of the palladium-capped magnesium nanodisks are investigated by placing the respective samples into a custom gas cell and continuously recording optical spectra in transmission. The gas cell is continuously purged with nitrogen to which hydrogen and oxygen are added at predefined intervals, while keeping the total gas flow rate constant at a value of 1 nL/min. Particularly, we focus on the changing extinction spectrum of Mg nanodisks of 220 nm in diameter with a Pd cap during a typical gas cycle measurement, both for the case where the Ti buffer layer is present, and the case where the Pd is in direct contact with the Mg. Figure 3



Figure 3. (a,b) Color-coded plots of extinction spectrum vs time upon repeated hydrogen and oxygen exposure for magnesium—palladium disks (diameter 220 nm, thicknesses 80 and 10 nm) without and with an additional 5 nm titanium buffer layer. (c) Relative extinction at the spectral location of the initial peak (indicated by the dashed gray lines in a and b). Gray and black curves indicate the disks without and with the 5 nm Ti buffer, respectively. For both the structures with and without the Ti buffer layer, the hydrogenation takes place within a few minutes. For the Mg/Pd nanodisks, the dehydrogenation process takes over 2 h, while for the Mg/Ti/Pd disks, dehydrogenation is completed in 15–30 min. The buffer layer also increases the stability of the system after several gas cycles. All experiments were conducted at room temperature.

presents color-coded plots in which the extinction spectrum on the vertical wavelength axis is plotted as a function of time on the horizontal axis for both of these geometries. The measurements displayed here illustrate that the plasmon resonance of Mg/Ti/Pd disks can be switched off within a few minutes, while the dehydrogenation is completed in approximately 15 min. This behavior is reproducible for nanodisks of different diameters (see Figure S5 of the Supporting Information).

The comparison of the measurements on Mg/Ti/Pd disks with the measurements on Mg/Pd disks elucidates the necessity of the Ti buffer layer. In the absence of this layer, the dehydrogenation of the hydrogenated particles takes over 2 h instead of only 15 min, while the rate of hydrogenation (as represented by the relative change in extinction at the original peak wavelength in Figure 3c) decreases from cycle to cycle. This indicates a severe degradation of the particles during one hydrogenation/dehydrogenation sequence, which can most likely be attributed to the alloying of magnesium and palladium and to mechanical stress caused by the lateral expansion of the two materials.³³

The influence of an Mg-Pd alloy layer on the hydrogen diffusion into and out of the Mg disk is supported by onedimensional simulations on the diffusion dynamics of a multilayer system based on the model developed by Pasturel et al.,⁵⁴ where a Mg/Ti/Pd system is compared to a Mg/Mg-Pd/Pd system. In this model, the hydrogen diffusion coefficients and the enthalpies of hydride formation in the different materials are used as input parameters. Specifically, it can be shown that the relatively high hydrogen affinity of the Ti buffer layer compared to the low hydrogen affinity of the Mg-Pd alloy leads to a significantly higher hydrogen unloading rate for the buffered system, if one assumes that the Ti layer alloys with the Pd layer but not with the Mg. Meanwhile, the hydrogen loading rate is hardly affected, which is in good agreement with the measurement results (Figure 3c). The results of these simulations can be found in Figure S6 of the Supporting Information.

One very intriguing aspect of these switchable Mg nanodisks is the fact that both the hydrogenation and the dehydrogenation of magnesium are active processes: the plasmonic resonance can only be switched off by introducing ambient concentrations of hydrogen and can only be switched back on by adding oxygen to the system. In an atmosphere of pure nitrogen, the state of the particles remains fixed. This behavior stands in stark contrast to the hydrogenation of other commonly used materials, such as yttrium¹⁴ and palladium,¹ which automatically release the stored hydrogen as soon as the hydrogen pressure in the environment drops off. This makes it possible to keep Mg nanoparticles not only in their fully metallic or fully nonmetallic state, but also at any state in between, where the Mg disk is only partially hydrogenated, simply by means of regulating the duration and concentration of hydrogen and/or oxygen exposure.

A closer investigation of the spectral shift during hydrogenation and dehydrogenation of the magnesium nanodisks reveals a large hysteresis between the two switching directions. Figure 4 illustrates this for the example of nanodisks with an average diameter of 160 nm. As shown in Figure 4a, the magnesium resonance undergoes a rapid decrease while redshifting over more than 50 nm, after which the peak position slowly blueshifts while decreasing further in intensity. During dehydrogenation (Figure 4b), the plasmonic resonance follows a completely different pathway: it reemerges at a position which is blueshifted with respect to the original peak and returns to its initial position and intensity via a gradual redshift. This behavior occurs for all measured particle sizes and is not limited to the first hydrogenation/dehydrogenation cycle, but appears reproducibly over several gas cycles (see Figure S7 of the Supporting Information). The hysteresis, which is more pronounced in the resonance position than in the peak extinction value, becomes evident if one tracks the resonance wavelength of the plasmon peak over time alongside the extinction value at the original peak position (see Figure 4c). The resonance wavelength (solid curve) is obtained by fitting a Lorentzian function to the measured spectrum, with an estimated error (gray area) of 0.2% of the line width of the Lorentzian. The measured extinction at 560 nm is displayed as a dashed line.



Figure 4. Hysteresis between hydrogen loading and unloading of Mg/Ti/Pd nanodisks with a diameter of 160 nm at room temperature. (a) During hydrogenation, the plasmonic resonance shifts into the red while decreasing in intensity, and subsequently experiences a slight blueshift until it vanishes completely. The black curve indicates the trajectory of the resonance peak over time. (b) During dehydrogenation, the resonance peak reemerges at a lower wavelength, experiencing a constant redshift until the original spectrum is restored. It thereby follows a different trajectory than during hydrogenation (gray line). (c) This hysteresis can be clearly observed if one tracks the resonance wavelength over time (solid curve) along with the extinction measured at the original peak wavelength (560 nm; dashed curve). As the plasmon resonance is disappearing, the accuracy of the peak detection decreases (gray area). This hysteresis most likely indicates an asymmetry in the hydrogen distribution within the particle during hydrogen loading and unloading.

We attribute this pronounced hysteresis behavior to localized changes of the Mg/Ti/Pd particle geometry and hydrogen concentration during hydrogenation and dehydrogenation. Specifically, the position, shape, and propagation direction of the Mg/MgH₂ interface will play a significant role for the optical response of the full particle. In a simple model, a layer of MgH₂ is assumed to form directly beneath the hydrogenated Ti layer³⁰ during hydrogenation, after which it expands toward the substrate while consuming the Mg particle. This is supported by the observation of an initial resonance redshift, which can be explained by an effective decrease of the thickness of the metallic Mg disk. During dehydrogenation, the lower wavelength at which the plasmon resonance emerges suggests that the magnesium layer that forms inside the MgH₂ particle grows faster in the vertical direction, after which it expands from the inside outward before returning to its original shape.

However, in a realistic system, the phase change behavior will be influenced by additional effects, such as localized strain due to different hydrogen-induced lattice expansions for Mg, Ti, and Pd. The resulting elastic constraints between the constituent materials and the forces exerted on the entire particle by the surrounding passivating MgO layer also influence its geometrical shape and thus its extinction spectrum. We believe that a more thorough investigation of this complex nanoscale system, aided by combined electromagnetic and nanomechanical simulations, will be necessary to provide more conclusive insights into the detailed hydrogenation dynamics of nanostructured Mg particles in the future.

In conclusion, we have shown that magnesium is a suitable material for nanoplasmonic applications, providing strong resonances that are tunable throughout the visible wavelength range. Magnesium nanoparticles suffer slightly from corrosion through reactions with different gaseous compounds, but the self-limiting native oxide layer of only a few nanometers prevents rapid degradation, keeping Mg nanoparticles stable over time periods of months. We have extended the use of Mg nanoparticles to the field of active plasmonics, showing that Pdcapped Mg nanodisks can be transformed into the nonmetallic magnesium hydride by simple exposure to hydrogen gas. This reaction can be reversed by exposure to oxygen. Via this reversible transformation, the plasmonic resonance of the particles can be repeatedly switched off and back on, with hydrogen loading and unloading times in the order of minutes. In combination with the abundance and low cost of magnesium, these characteristics make the material a highly promising candidate for novel applications in active plasmonic metamaterials, which can not only be held in fully metallic "on" state or a fully dielectric "off" state but can also be stable at any state in between for extended periods of time. Since all experiments presented here were conducted at room temperature, there is room for significant improvements regarding the switching times of the Mg/Pd disks when considering elevated temperatures. Our findings on the loading and unloading dynamics of Mg/Pd disks also pave the way for future investigations on the chemical processes behind the hydrogenation of magnesium, for example via single-particle spectroscopy in combination with numerical simulations on the changing extinction spectrum during hydrogen loading and unloading. In the future, magnesium-based plasmonics and metamaterials could find applications in complex active nanophotonic systems, such as wavelength-tunable perfect absorbers for tunable color filters or selective switchable mirrors for smart solar collectors, and thus contribute to the advance of smart nanoplasmonic devices. Also, reducing the size of the Mg nanodisks further, the ultraviolet spectral range could be reached which would make such a system highly attractive for

plasmonically enhanced photocatalytic and photochemical reactions, particularly when considering the high reactivity and low electronegativity of Mg.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.5b03029.

A statistical analysis of the size distribution of Mg nanodisks. More detailed information on the chemical stability of Mg particles. A comparison of extinction spectra before, during and after one H_2/O_2 cycle with and without a Ti buffer layer and a comparison of the switching dynamics for Mg/Ti/Pd particles of different sizes. A description of the 1D hydrogen diffusion simulations along with the simulation results. Spectra taken during several subsequent hydrogen loading/ unloading processes for 160 nm Mg/Ti/Pd disks (PDF)

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Notes

The authors declare no competing financial interest.

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