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Article

Keywords: Kinetics of Hydrogenation, Self-assembly, Directional Hydrogenation, Energy Storage, Hydrogen Detection

Posted Date: October 16th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-88509/v1>

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***In situ* wide-field visualization of palladium hydrogenation**

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ABSTRACT:

Visualizing hydrogenation processes in metals in real-time is important to various hydrogen-involved applications. However, observing hydrogen diffusion was limited by transmission electron microscopy, and the kinetics of hydrogenation in the interior of the metals was not reported. Here we proposed an optical microscopy-based visualization of palladium hydrogenation from diffusion surface to the interior by introducing a fast-response mechanical platform that transforms the hydrogen diffusion into self-organized ordered wrinkles with sharp optical contrast. This platform is an Au/Pd double layer on elastomer which results in directional hydrogenation from sidewall to the interior. The kinetics of hydrogenation in the interior of the palladium along the diffusion direction was monitored in real-time. This platform will enable in-situ visualization of atom/ion diffusion on metals that are crucial in energy storage and hydrogen detection.

The study of atom and ion diffusion in solids and related phase transitions is crucial to a wide range of applications, including energy storage¹, lithiation in batteries^{2,3}, hydrogen detection and sensing⁴⁻⁶. Direct visualization of these diffusion processes will

not only help to understand the solute intercalation mechanisms but also improve the system's cyclability by avoiding catastrophic structural failure including lattice dislocations and fractures⁷⁻⁹. In particular, metal hydrides such as palladium (Pd) hydride are receiving increasing attention due to their fast hydrogenation kinetics at comparatively more accessible reaction conditions¹⁰⁻¹², but this also poses a great challenge to the in-time monitoring of the transient processes.

Hydrogenation of palladium has been under intensive studies to resolve the kinetics of diffusion-induced phase transitions, which constitutes a representative class of atom and ion diffusion in solids and is closely related to the physics of lithiation of batteries^{10,13}. The fast kinetics of palladium-hydrogen reaction along with accessibly environmental conditions make palladium an extraordinary choice of material for rapid absorption of a large amount of hydrogen. For example, palladium membranes received great interest with their potential to separate and purify hydrogen at high flux and exclusive selectivity. In these Pd membrane based gas separation systems, molecular hydrogen first dissociates at the palladium membrane surface followed by diffusing through the membrane and then emerges as molecular hydrogen upon rebinding of the atoms. The absorption and desorption of hydrogen in palladium is accompanied by significant volume change¹⁴, and monitoring strain evolution associated with the metal lattice during hydrogenation at real time could potentially provide insights into the coupling between strain-induced hydride formation and transport of hydrogen flux. Yet a direct observation of the phase transition between α - and β -phases remains a challenge, because the planar geometry of thin films often fails to translate the microscopic structural change induced by hydrogen flux permeating through the film thickness into experimentally observable quantities at a macroscopic scale.

Several visualization techniques such as the switchable mirror devices leverage on the large optical and electrical properties changes in selective metal hydrides including magnesium and rare-earth elements¹⁵⁻¹⁷. However, the switchable-mirror approach works on planar thin films and heavily relies on the intrinsic optical properties of mirror

material to achieve large optical contrast, thus limiting its applicability. On the other hand, scanning transmission electron microscopy (STEM)¹⁰, electron energy loss spectroscopy (EELS)^{11,18} and plasmonic nanoantenna⁴ have demonstrated to be effective tools for the study of phase transformation behavior of palladium hydride on the particle level. Although they provide the capability of insights into individual nanocrystals, they inevitably require convoluted experimental setups that involve highly material-specific procedures and are not always readily accessible. A fast and effective *in situ* monitoring and observation of the hydrogenation process in real-time still remains highly desirable.

Figure 1 illustrates our proposed approach for *in situ* real-time visualization of local stress evolution during palladium hydrogenation. Without loss of generality, we chose palladium films of thickness 30 – 67 nm as our model system. Instead of directly depositing the palladium film on a rigid substrate, our model system used a soft and deformable substrate of polydimethylsiloxane (PDMS). More importantly, an impermeable gold nano-layer covers on top of the deposited palladium film and thus hydrogen can only diffuse into the Pd film laterally from the sidewall, which enforces directional hydrogenation. Such an Au/Pd double layer on PDMS is named as a GPDP.

It is now established that the mobility of hydrogen atoms in metal is many orders of magnitude larger than that of other interstitially dissolved atoms at room temperature. Rapid transport of hydrogen into Pd leads to a considerable lattice expansion, and to accommodate the compressive stress applied by the Pd layer, the supporting PDMS substrate developed into self-organized strips and wrinkles triggered by linear and nonlinear elastic instabilities. Such diffusion-deformation process can be characterized by relevant time scales:

$$\frac{\tau_r}{\tau_d} = \frac{\eta_s}{E_s} \cdot \frac{D}{l^2} = \frac{10^5 Pa \cdot s}{10^6 \cdot Pa} \cdot \frac{10^{-10} m^2 \cdot s^{-1}}{(10 \mu m)^2} \sim 10^{-1} \quad (1)$$

where $\tau_r = \frac{l^2}{D}$ and $\tau_d = \frac{E_s}{\eta_s}$ are the diffusion time scale of hydrogen and relaxation time of the PDMS, η_s and E_s are the viscosity and Young's modulus of the PDMS

substrate, D is the typical diffusivity of hydrogen in palladium and l is the diffusion length. Equation (1) indicates that wrinkling instability provides a fast route for the visualization of spontaneous hydrogen diffusion with minimal lag.

For palladium at low concentration of hydrogen (known as α -phase), palladium atoms are arranged in face-centered cubic lattice of constant 3.891 Å. With the increased supply of hydrogen gas species from the environment, the hydrogen atoms will occupy randomly at the octahedral interstices in the lattice, forming a solid mixture of PdH_x. Further increasing hydrogen concentration $x > 0.60$ leads to a discontinuous change to β -phase with a new lattice parameter of 4.026 Å. At thermal equilibrium, macroscopic hydrogen concentration ratios $0.03 < x < 0.60$ reflect a mixture of α - and β -phases of palladium hydrides. Compressive stress is thus exerted by the Pd film to induce the formation of ripples and folds that can be monitored by a wide-field microscope under illumination. With proper selection of film thickness and stiffness of the PDMS substrate, the one-dimensional (1D) ripples act as optical gratings, whose amplitude depends on the local stress states during volume expansion of the Pd layer. A stronger amplitude of such ripple causes stronger diffraction, and the intensity of directly reflected light is reduced, as observed by intensity contrast in the image field. With this approach, we can clearly visualize the propagating front of α - and β -phases and determine their propagation speeds.

Coupled with our diffusion-deformation-diffraction framework, we are able to provide more quantitative insights into the hydrogenation kinetics and phase-dependent self-induced stress during phase transition. To our best knowledge, it is the first time for such a pattern generation mechanism to be implemented on a hydrogenation platform to observe the diffusion and phase transition kinetics of the hydrogen in the interior of the Palladium. This approach constitutes a general framework for *in situ* in efficient real-time visualization of generic solutes diffusion into solids.

Results

Fig. 1 Deformation process of a GPDP. **a**, Schematic of the setup for *in situ* and real-time observing the surface deformation of a GPDP exposed to H_2 . **b,c**, Schematic of the surface wrinkling of a GPDP during hydrogenation. **d**, Schematic of light reflecting on the 1D ripple. **e-h**, Microscopic images showing the evolution of the surface deformation of the GPDP with a 30-nm Pd film in the hydrogenated process. **i-l**, The magnified images of the surface deformation.

An optical microscope was used to observe the surface deformation of a GPDP, which was placed on a gas cell (Fig. 1a). Figure 1b,c show the schematic of the surface deformation of the GPDP comprised of an Au/Pd film on a PDMS slab, which changes from a planar surface to regular wrinkles during hydrogenation. The x-axis and y-axis are defined to be parallel and perpendicular to the edge on planar directions, respectively, and the z-axis is normal to the surface (Fig. 1b). The deformation of the PDMS is assumed to be viscoelastic with Kelvin-Voigt material behavior (Fig. 1c). Figure 1d shows the mechanism of the reflectance variation, where the reflected light

collected by the objective lens decreases due to the diffraction resulted from the formation of the 1D ripple. The microscopic images (Fig. 1e-h) and corresponding magnified images (Fig. 1i-l) reveal the evolution of the surface deformation of the GPDP on exposure to 4% hydrogen gas (H_2). The thicknesses of Au and Pd film in the GPDP are $h_{Au} = 10$ nm and $h_{Pd} = 30$ nm, respectively. Before loading with H_2 , the GPDP was flat with high reflectance because of the metallic property of the Au/Pd film (Fig. 1e, i). When 4% H_2 with nitrogen gas (N_2) was injected, uniform 1D ripples evolved from the edge of the GPDP along the direction of hydrogen diffusion (in the y-direction from the graph) and extended to the center of the film, resulting in a drastic change of reflected light intensity (Fig. 1f, j). We found that merging of the 1D ripples (Fig. 1f), which is induced by topological defects such as elementary dislocations and disclinations¹⁹. Surprisingly, a sharp contrast of brightness is observed in different zones of the film (Fig. 1j), which can be attributed to the phase transition of Pd film during hydrogenation. As the hydrogen diffused from the edge to the center of the GPDP, the 1D ripple at the inner region became dark as well (Fig. 1g, k) and then transformed into two-dimensional (2D) herringbones (Fig. 1h, l). Meanwhile, the deformed area with saturated hydrogenation remained stable in the hydrogen environment. The two ongoing processes which involve the diffusion of hydrogen in palladium and deformation of the film-substrate hybrid are coupled within the GPDP. The lattice expansion induced by the diffusion of hydrogen leads to surface wrinkle, which consequently affects the hydrogen diffusion as the stress field of the Pd/Au double layer is disturbed by the deformation patterns and becomes non-uniform and anisotropic. More details of the surface deformation are recorded in Supplementary Video 1, 2 and 3. This process is reversible by introducing N_2 to the flow cell to remove H_2 (Supplementary Video 4). To test the cycle performance of the GPDP after successive treatment with H_2 , we measured the response time at the place with a distance of 100 μm to the edge under 10 hydrogenation/ dehydrogenation cycles. As shown in Supplementary Fig. 1, the response time of the first cycle is much longer than that of others and becomes stable after the third cycle. This is similar to the hydrogenation process of a flat Pd film on PDMS²⁰. After several cycles of hydrogen

treatment, some slight surface corrugations form on the Pd film surface, which decreases the constraint of the substrate on the deformation of the Pd film. It is easy to distinguish various deformation regions through the brightness contrast, where the 1D ripples are brighter than the 2D herringbones (Fig. 1h). In contrast, the surface wrinkling of a single Pd film with the same thickness on PDMS upon exposure to 4% H₂ is subject to isotropic stress which manifests aperiodic labyrinth patterns (Supplementary Fig. 2). This indicates that the Au film capped on the top of the Pd film plays a key role on the ordered self-organization, which provides a platform to visualize the diffusion of hydrogen in Pd film.

Figure 2 Microscopic visualization of phase transition. **a**, Snapshot images showing the phase transition of a 30-nm Pd film during hydrogenation. The region between the white and red dash line is at the β phase, which is fully hydrogenated. The region marked by the black dash line is the wrinkling front which indicates the tipping point of the transition from α -phase to β -phase. The α - and β -phase coexist in the region between the black and red dash line. l_β and l_α are the distance between the edge to the red line and the black line, respectively. **b**, l_β and l_α as functions of the hydrogenated time. The experimental and fitting results are marked by the dotted and solid lines, respectively. t_L is the time intervals from the beginning of α -phase to the stability of the 1D wrinkling β -phase marked by the blue dash line. y_0 is the distance of the measuring position to the edge. **c**, Real-time optical responses of the GPDP on different monitoring positions during hydrogenation. The inset is the real-time optical response of a single Pd film on PDMS and the GPDP, where the y_0 is 55 μm . t_R is the time intervals from the beginning of the decreasing of reflected light intensity (marked by a blue dot) to the inflection point before termination (marked by a blue cross). **d**, Response time of the t_L and t_R on different monitoring areas. Scale bars: 20 μm .

To further elaborate the physical mechanism behind the phenomenon of Fig. 1, we observe the propagation of the self-organized 1D ripples at the first 100 s by taking snaps of the Supplementary Video 2 in which the GPDP has treated by several hydrogenation/dehydrogenation cycles, as shown in Fig. 2a. The GPDP is divided into three areas based on surface morphology and apparent brightness changes, separated by red and black dash lines, respectively. Such a large reduction of the reflected light intensity is enhanced by a simple geometric effect, that is, the transition of the flat surface into the undulated pattern induced by the surface deformation of the GPDP during hydrogenation²⁰. While the phase transition of PdH_x from α - to β -phase may also contribute to the change of optical properties illuminated by white light²¹, the wrinkled GPDP greatly enhanced the contrast, therefore making such system ideal choice to visualize the transformation of α - to β -phase under illumination. The Pd/Au film

between the white and red dash lines is dark and fully hydrogenated with stable 1D ripples, representing the β -phase region. The red line can be thought as β -phase front. The region between the red and black dash lines, where both the surface wrinkles and brightness change rapidly, corresponds to the $\alpha \rightarrow \beta$ -phase transition. The wrinkling front of the Pd film marked by the black dash line can be approximately treated as the end of pure α -phase, in other words, transition front between $\alpha \rightarrow \beta$ -phase. The distance from the edge (white dash line) to transition front (black dash line) and β -phase front (red dash line) are defined as l_α and l_β , respectively. Figure 2b presents the relations of l_α and l_β with the H_2 ventilation time. It is clear that these relations can be fitted by parabolic equations as follows:

$$l_i^2 = K_i(t - t_i) \quad (2)$$

where K_i and t_i are the front mobility²² and the formation time of two phases on the edge respectively, i represents α or β . Through fitting of the experimental curves, we can obtain $K_\alpha = 3.13 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $t_\alpha = 1.1 \text{ s}$ and $K_\beta = 1.87 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $t_\beta = 5.1 \text{ s}$. The time interval of the phase formation time t_i is defined as $t_\beta - t_\alpha = 4 \text{ s}$, a timescale comparable to our report on the response time of hydrogenation in a single Pd film on PDMS²⁰. It can be found that $K_\alpha > K_\beta$, this verifies that the H_2 dissolution rate in α -phase is higher than in β -phase. Due to the different front mobilities of α -phase and β -phase, as the phase front moves further into the center of the film, the separation between β -phase front and transition front is also getting longer, and the corresponding time interval becomes longer as well. Furthermore, depending on the front mobility K_i , we can calculate the diffusion constants D_i of two phases $D_\alpha = 0.94 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $D_\beta = 4.50 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The calculation procedure is outlined in the next section.

Based on the quantitative reflected light intensity, we further analyzed the phase transition in the deep inner region of the GPDP *in situ* and real-time. We monitored the optical response of the specific areas with different y_0 (marked by the black dash line

in Supplementary Fig. 3) varying from 55 μm to 112 μm (Fig. 2c). t_R is defined as the time duration between the onset of curve inflection and the flattened trailing region (marked by the blue dot and cross, respectively). Compared to a single Pd film on PDMS, the real-time optical response of the GPDP at the position of 55- μm away to edge becomes slow, as shown in the inset of Figure 2c. As the monitoring distance y_0 grows, t_R also increases. Please note that the spatial variation of optical reflectance observed in the phase-transition process can be characterized by two linear regions inside the Pd film, in which the slope of the declining reflectance is initially small at the first stage and abruptly becomes steep at the second stage. With the distance y_0 increasing, the first linear stage extends over longer regions in the film and the slope reduces, which indicates that the resistance (stress) increases to prevent from the diffusion of hydrogen atoms. To our best knowledge, this phenomenon was observed for the first time. This might be related to the accumulated stress induced by the hydrogenation and the slow diffusion rate in the inner of the GPDP. As shown in Figure 2d, the response time t_R is consistent with the time intervals t_L . In other words, this also confirms that the definition of phase fronts is reasonable. Therefore, we have developed a simple but effective route to visually observe the diffusion of hydrogen in Palladium from the surface to the inside along the diffusion direction *in situ*. Furthermore, due to the high reflectance change induced by the surface wrinkling on the GPDP, the hydrogen diffusion can also be directly observed by naked eye (Supplementary Fig. 4).

Figure 3 Theoretical framework of diffusion-induced 1D self-organized patterns. **a**, Distribution of stress component σ_x in the GPDP resulting from hydrogen diffusion. **b**, Schematic of the reflected light intensity variation plotted against hydrogen concentration and diffusion-induced 1D ripple. Enabled by this platform, quantitative information such as H_2 concentration, stress distribution, and surface undulation can be extracted from the reflected light intensity. **c**, Curve fitting of the relationship between stress (derived from experimental data) and concentration (related to Equation (6)). The generalized concentration-stress relation shows a strong correlation with phase conditions (logarithmic growth across the α -phase boundary and consequently piecewise linear in $\alpha + \beta$ and β phases). **d**, Combining solutions from the Fickian model (Equation (6)) and Figure 3c leads to the change of the reflected light intensity at a 550-nm wavelength on the GPDP during hydrogenation.

The generation of 1D/2D patterns of the GPDP can be explained by the mechanical deformation of a thin stiff film on an elastic substrate. We first focus on the 1D ripple pattern, which is characterized by the distance between adjacent ripples defined by ripple wavelength λ_1 and ripple amplitude A_I (Fig. 1c). In the case of a freestanding substrate with uniform exposure, the absorption of H₂ results in an isotropic volume expansion of Pd film. On the other hand, when the Au cladding forces H₂ to diffuse unilaterally into the film constrained on a substrate, the diffusion-induced stress becomes anisotropic with two orthogonal components denoted as σ_x along the x-axis and σ_y along the y-axis. As the GPDP is exposed to 4% H₂, with the volume inflation during the hydrogenation, the component σ_x first exceeds the critical stress of 1D ripple buckling σ_{c_1} in the x-direction, and the 1D ripple occurs to release the stress σ_x . Whereas the component σ_y , because of the short hydrogenated length in the y-direction, has yet to reach the critical stress of 2D herringbone buckling σ_{c_2} , no 2D herringbone feature appears. At low H₂ concentration (0.4%), the stress component σ_x is not enough to form regular ripple patterns, in which the wrinkles are aperiodic and twisted (Supplementary Fig. 5).

A simple model has been developed to characterize the 1D ripple of the GPDP at saturation of hydrogenation. The 1D ripple pattern is described by a sinusoidal vertical deflection of the film²³ :

$$z(x) = A_1 \sin \frac{2\pi x}{\lambda_1} \quad (3)$$

The ripple wavelength λ_1 can be estimated by minimizing the system energy, including film and bending energy of the Au/Pd film and elastic energy of the PDMS substrate, which can be expressed as²⁴ :

$$\lambda_1 = 2\pi(h_{Au} + h_{Pd}) \left(\frac{E_{eff}/(1-\nu_{eff}^2)}{3E_s/(1-\nu_s^2)} \right)^{\frac{1}{3}} \quad (4)$$

where E_{eff} and ν_{eff} are the effective Young's modulus²⁵ and the effective Poisson's ratio of Au/Pd film, E_s and ν_s are the Young's modulus and the Poisson's ratio of PDMS, respectively. Then the ripple amplitude A_I is given by²⁶ :

$$A_1 = (h_{Au} + h_{Pd}) \sqrt{\frac{\sigma_x - \sigma_{c1}}{\sigma_{c1}}} \quad (5)$$

We also conduct finite element analysis using software package COMSOL to directly solve the solid mechanics equation under plane strain condition for the displacement field of a 30-nm Pd film in the form of 1D ripple, as illustrated by Supplementary Fig. 6, which is well consistent with the experiment. According to equation (4), the 1D wavelength λ_1 is proportional to the thickness of the Pd film h_{Pd} . As shown in Supplementary Fig. 7, the λ_1 increases with an increasing h_{Pd} from 30 to 67 nm, showing a good match with the model. We also measured the formation time of the β -phase t_β of the GPDP with various h_{Pd} in which the l_β is 100 μm . As shown in Supplementary Fig. 8, the t_β increases with the increase of the h_{Pd} . Besides the thickness modulation, equation (4) also suggests that the λ_1 can be adjusted by varying the Young's modulus of the substrate E_s . The λ_1 decreases on the hard PDMS (Supplementary Fig. 9) with higher Young's modulus. The tunable wavelength of the GPDP points to potential applications in optical devices such as switchable diffraction gratings as well.

The schematic of reflected light variation on the GPDP during hydrogenation was shown in Figure 3a, b. The hydrogen diffusion generates a stress gradient in the y-direction (Fig. 3a), which leads to the varied light scattering of the GPDP based on the undulation amplitude of 1D self-organized patterns (Fig. 3b). To establish a more quantitative characterization of this novel visualization platform for phase transition during hydrogenation, we develop a complete framework incorporating a 1D Fickian diffusion model in solids coupled with surface reflectance simulation of a sinusoidal diffraction grating. A diagram of the breakdown structure of the framework is illustrated in Supplementary Fig. 10. It begins with the upper branch of the chart where front mobilities from experimental data are substituted into the Fickian diffusion model, which assumes a binary diffusivity on account of the observation that hydrogen diffusion rates differ in α and β phases²⁷. Hence, we can write the section-wise diffusion equations as:

$$\frac{\partial C_i(y,t)}{\partial t} = D_i \frac{\partial^2 C_i(y,t)}{\partial y^2} \quad (6)$$

Using phase front mobilities obtained in Figure 2b, diffusion constants D_i and concentration profile $C_i(y, t)$ can be readily deduced by solving equation (6). Details of the calculation are shown in Supplementary Fig. 11a. The solved values of the diffusion constants D_i are $D_\alpha = 0.94 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $D_\beta = 4.50 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which are consistent with previously reported results^{27,28}. Based on this diffusion model, we graphed hydrogen concentration profiles at different positions of the Pd film as time increases (Supplementary Fig. 11b). In order to gain more insights into the concentration-induced stress, we traced the other half branch of the diagram featuring the variation of the reflected light intensity with time at one particular position ($y_0 = 112 \text{ } \mu\text{m}$). The steep descent portion of that variation was converted into stress information through diffraction simulation (Supplementary Fig. 12a) and wrinkling amplitude Equation (5). Eventually, the information gathered from two branches led to the concentration-stress relation, which was deduced from experimental data at one particular point. However, it can be applied to any arbitrary position of the field (Fig. 3c). The fitting results suggest that H_2 absorption-induced stress initially exhibits a logarithmic growth when the ratio of hydrogen atoms is low, followed by two piecewise linear increasing relations in $\alpha + \beta$ and β phases, respectively. This indicates that the palladium's uptake of hydrogen solutes may trigger a different elastic response of lattice depending on the solute concentration. After acquiring this essential relation, we once again exploited the relationship between the amplitude of the 1D ripples with various Pd thicknesses and the stress ratios σ_x/σ_{c_1} (Supplementary Fig. 12b) according to equation (5). The strictly monotonic relation ensures a well-defined one-to-one mapping when the stress profile is converted to the undulation's amplitude and vice versa. The data flow was directed into the sinusoidal grating simulation to obtain light intensity change at the wavelength of 550 nm illumination on a 5- μm period grating. Again the reflected light collection was cut off at the 3rd diffraction order on account of the numerical aperture of the objective lens. Finally, we established the quantitative

relation between diffusion time and reflected light intensity at any location (Fig. 3d). The variation of simulated reflected light intensity with time shows similar trends as Figure 2c, which successfully recovers the abrupt change of slope in the middle of transition observed at reference lines further away from the H₂ entry. The hydrogen-induced stress illustrated by Figure 3c not only shows pronounced phase dependency and drastic changing of slopes across phase boundaries, consistent with mechanical stress measurements in literature²⁹⁻³¹, but also reveals unique details about the logarithmic rate of hydride growth at low concentration regime. Our study bridges stress evolution of the thin palladium film with the absorption kinetics of hydrogenation. Historically such measurement of mechanical stress on metal hydrides would require highly specific precision instruments, including electrochemical quartz crystal microbalance²⁹, X-ray diffractometry³⁰, and laser scanning technique³¹. However these methods can't reveal the diffusion of hydrogen in the interior along the diffusion direction *in situ* in real time. While our GPDP platform overcomes these limitations by extracting phase transition information from scattered light of the self-assembly 1D ripples, and opens up new avenues to visualize the effects of hydrogen diffusion and phase transition in metal from sidewall to the interior.

Thick Pd films and membranes are prone to catastrophic structural failure including lattice dislocations and fractures during hydrogenation. In contrast, there is no evidence of cracks in sub-70-nm Pd films constructed on wrinkled surfaces, even after severe tensile deformation. As the hydrogen atoms diffuse from the edge into the center of Pd film, the growing stress component σ_y disrupts the stabilized system to deviate from the preferential wrinkling direction, and the GPDP may take various new equilibrium states depending on the perturbation type³². Multiple wrinkling morphologies on a 2D stress map are illustrated in Figure 4a, namely the unwrinkled flat surface, small and large 1D ripples, herringbone type, the checkerboard type and labyrinth type. Since the phase transition of Pd film favors 1D ripple when the hydrogenation progresses relatively unboundedly along the y-direction at first, the next favored pattern will be the herringbone type as the stress along y keeps increasing, and the critical boundary lies on the red dashed line given by competing stresses along two directions and film's Poisson's Ratio³³. As shown in Figure 4b, the 2D herringbone is characterized by the short wavelength λ_1 , the long-wavelength λ_2 , amplitudes in the z-direction A_1 and in the y-direction A_2 , and jog angle θ . Here the λ_1 is the wavelength of 1D ripple, while the λ_2 is the distance between two adjacent jogs. Compared to other wrinkling modes, the herringbone mode is easier to form because of its relatively lower elastic energy²³ and stress history. When the stress component σ_y exceeds the critical stress of 2D herringbone generation, the herringbones occur at the inner region with the jog angle θ gradually varying from 0° to $\sim 90^\circ$ (Supplementary video 3). This is further validated by our modal analysis using COMSOL assuming a pre-defined 1D ripple pattern (Fig. 4c), which agrees well with the experimental result. The long-wavelength λ_2 monotonically increases with the increasing thickness of the Pd film h_{Pd} (Fig. 4d, Supplementary Fig. 13) as that of the short wavelength λ_1 (Fig. 2b). Unlike the primary buckling, the quantitative evaluation of λ_2 tends to be challenging without knowing the values of σ_y a priori³². Further insights into the 2D stress state can be gained through the measurement of the secondary wrinkling wavelength λ_2 .

Although our study was focused on real time visualization of hydrogenation in metal membranes using local wrinkles, our methods of retrieving stress states using wide-field optical scatterometric means in real time can be applied to a more general class of reaction-diffusion systems³⁴, where the induced surface instability generates various surface patterns, as previously reported in chemical traveling waves³⁵, electrodeposition^{36,37}, and biological systems³⁸. Because the wrinkles and folds can be easily imposed on these material systems over large areas at low cost, we expect such simple and elegant geometric effect on enhanced reflection can provide deep physical insight of monitoring strain evolution associated with the host material (such as thin solid electrolyte interphases in the lithium battery) during diffusion-reaction at real time.

Discussion

In summary, we have demonstrated that an Au/Pd double layer on a PDMS substrate is a perfect platform for *in situ* observation of the Pd hydrogenation from the surface to the interior in real-time based on an optical microscope. Interestingly, we showed for the first time the hydrogen-induced self-organization of 1D ripples and 2D herringbones during the Pd hydrogenation, and we also established that the phase transition of the Pd-H system can be understood by leveraging on the analysis of the transformation of these self-organized patterns. To characterize the deformation, we investigated the relationship between the Pd thickness and related characteristics of the patterns such as wavelength and other structural parameters, in which the wavelength of the 1D ripple was in good agreement with the theoretical calculation utilizing minimum energy method. Additionally, using the GPDP as a measurement platform, we were able to track the phase transition of the Pd hydrogenation by the surface wrinkling, e.g., the diffusion of hydrogen in the α - and β -phase was vividly displayed in real-time *in situ*.

To the best of our knowledge, this is the first time the double-inflection in the reflectance curve is used to derive the local stress states of palladium hydride at increasing hydrogen flux. A theoretical framework combining 1D Fickian diffusion model, deformation theory and grating diffraction was developed to offer new insights

into the physical processes, and the simulated hydrogen-induced reflectance variation showed trends consistent with the experimental result. These suggest that such a platform has great potential applications in conforming to various surface topographies and readily applicable to the *in situ* studies of real-time phase transition in more generic diffusion-deformation systems.

Author contributions

C.J.J. conceived the idea. C.J.J. and N.X.F. guided the research. C.J.J., X.Y.S. and Y.S. designed the experiments. X.Y.S. fabricated the structures. X.Y.S. measured the surface deformation of the structures and analyzed the data. H.F.D. and N.X.F. performed mechanical modeling and contributed to the studies on deformation mechanism. R.H.X. extracted the grayscale changes at the pixels to obtain the reflectance change. C.J.J., N.X.F., X.Y.S. and H.F.D. co-wrote the paper.

Acknowledgement

The authors thank the fruitful discussion with Prof. Guowei Yang (Sun Yat-Sen University) and Dr. Yiwan Zhong (Massachusetts Institute of Technology). The authors C.J.J., X.Y.S. and Y.S. acknowledge the financial support from the National Natural Science Foundation of China (91850106, 11974438, 11874436), and the Fundamental Research Funds for the Central Universities (No.17lgpy07). H.F.D. and N.X.F. acknowledge the financial support provided by the Centers for Mechanical Engineering Research and Education at MIT and SUSTech (MechERE Centers at MIT and SUSTech).

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Methods

GPDP fabrication. To make an elastic PDMS substrate, firstly, we placed a clean silicon wafer and a little tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane (TFOCS, Sigma-Aldrich) dropped on a petri dish together in a vacuum desiccator for 40 min, in which a single layer of TFOCS molecules would be coated on the silicon to prevent the cured PDMS from sticking on the silicon wafer. A mixture of the base and curing agent of PDMS (Sylgard 184, Dow Corning, USA) with a weight ratio of 10 : 1 in a petri dish was coated on the silicon wafer and then placed in the desiccator to remove the bubble. After cured at 70 °C for 1h in an incubator, the PDMS slab was peeled from the silicon wafer as the elastic substrate. Finally, the GPDP was fabricated by using magnetron sputtering to deposit an Au/Pd dualayer onto PDMS with base and deposition pressure under Ar flow of 6×10^{-4} and 0.01 mbar, respectively.

Optical measurement. The sample was placed in a gas chamber with an optically transparent window and two gas channels (Fig. 1a) at room temperature. Surface wrinkling of the GPDP during hydrogenation was observed by an optical microscope system with 10X and 50X objectives (MPLFLN10x and SLMPLN50x, Olympus, Japan), which were utilized to focus the probe light of a tungsten halogen light source on the sample and collect the backscattered light. The numerical aperture (N.A.) and work distance (W.D.) of the 50X objectives are 0.35 and 18 mm, respectively. A COMS camera (Zyla-4.2P-USB3, Andor, UK) was utilized to record the deformation process. The concentration and flow rate of H₂ are 4% and 1000 sccm, respectively.

Theoretical calculation of the 1D wavelength. Based on the minimum energy method, the wavelength of 1D deformation λ_1 on the system of a stiff thin film on an elastic substrate can be expressed as³⁹ :

$$\lambda_1 = 2\pi h \left(\frac{E_f/(1-\nu_f^2)}{3E_s/(1-\nu_s^2)} \right)^{\frac{1}{3}} \quad (1)$$

Where E and ν are the Young's modulus and Poisson's ratio, and the subscript f and s represent the thin film and substrate, respectively. For the GPDP, we assume that the

Young's modulus and Poisson's ratio of the Pd film have no significant variation during hydrogenation. The stiff thin film consists of an Au and Pd film with the effective Young's modulus E_{eff} , defined by :

$$E_{eff} = \frac{1+m^2n^2+2mn(2n^2+3n+2)}{(1+n)^3(1+mn)} E_{Pd} \quad (2)$$

Here $m = \frac{E_{Pd}}{E_{Au}}$ and $n = \frac{h_{Pd}}{h_{Au}}$ are the modulus and thickness ratio of the Au/Pd bilayer film, respectively. The Young's modulus of Au and Pd are $E_{Au} = 70$ GPa and $E_{Pd} = 126$ GPa, respectively^{40,41}. Since the Pd film dominates the bilayer, the Poisson's ratio of Pd⁴⁰, $\nu_{Pd} = 0.39$, is used as the effective Poisson's ratio of the Au/Pd bilayer. The Young's modulus and Poisson's ratio of PDMS are $E_s = 3.5$ Mpa and $\nu_s = 0.48$, respectively⁴².

Finite element simulation of the wrinkled patterns. Finite element software COMSOL Multiphysics and its Solid Mechanics Module is used to solve for the displacement field as well as eigenmodes of deformations in the modal analysis. For Supplementary Fig. 6, we assume plane strain condition and solve the static solid mechanics equations with bottom and sides of substrate fixed, while using the same material parameters as we calculate the theoretical solution of 1D ripple. For Figure 4c eigenmode analysis computes the possible deformation patterns of a fully 3D structure with a pre-defined 1D ripple pattern. Only the herringbone type of wrinkle has been listed for direct comparison with experimental observation.

Diffusion-reflection simulation: The concentration profile $c = C(x, t)$ was solved from equation (6) using a MATLAB code, and surface elevation was found with equation (5) assuming a linear relation in concentration-induced stress. The reflection coefficient of a composite sinusoidal grating was obtained using COMSOL Multiphysics (Electromagnetic Waves Module, Frequency Domain). We calculated reflected light intensity up to the diffraction order of 3 in consideration of the numerical aperture of the objective lens. The simulated reflected light intensity against time was outputted at the same locations as optical measurement.

Figures

Figure 1

Deformation process of a GPDP. a, Schematic of the setup for in situ and real-time observing the surface deformation of a GPDP exposed to H₂. b,c, Schematic of the surface wrinkling of a GPDP during hydrogenation. d, Schematic of light reflecting on the 1D ripple. e-h, Microscopic images showing the evolution of the surface deformation of the GPDP with a 30-nm Pd film in the hydrogenated process. i-l, The magnified images of the surface deformation.

Figure 2

Microscopic visualization of phase transition. a, Snapshot images showing the phase transition of a 30-nm Pd film during hydrogenation. The region between the white and red dash line is at the β phase, which is fully hydrogenated. The region marked by the black dash line is the wrinkling front which indicates the tipping point of the transition from α -phase to β -phase. The α - and β -phase coexist in the region between the black and red dash line. l_β and l_α are the distance between the edge to the red line and the black line, respectively. b, l_β and l_α as functions of the hydrogenated time. The experimental and fitting

results are marked by the dotted and solid lines, respectively. t_L is the time intervals from the beginning of α -phase to the stability of the 1D wrinkling β -phase marked by the blue dash line. y_0 is the distance of the measuring position to the edge. c, Real-time optical responses of the GPDP on different monitoring positions during hydrogenation. The inset is the real-time optical response of a single Pd film on PDMS and the GPDP, where the y_0 is 55 μm . t_R is the time intervals from the beginning of the decreasing of reflected light intensity (marked by a blue dot) to the inflection point before termination (marked by a blue cross). d, Response time of the t_L and t_R on different monitoring areas. Scale bars: 20 μm .

Figure 3

Theoretical framework of diffusion-induced 1D self-organized patterns. a, Distribution of stress component σ_x in the GPDP resulting from hydrogen diffusion. b, Schematic of the reflected light intensity variation plotted against hydrogen concentration and diffusion-induced 1D ripple. Enabled by

this platform, quantitative information such as H₂ concentration, stress distribution, and surface undulation can be extracted from the reflected light intensity. c, Curve fitting of the relationship between stress (derived from experimental data) and concentration (related to Equation (6)). The generalized concentration-stress relation shows a strong correlation with phase conditions (logarithmic growth across the α -phase boundary and consequently piecewise linear in $\alpha+\beta$ and β phases). d, Combining solutions from the Fickian model (Equation (6)) and Figure 3c leads to the change of the reflected light intensity at a 550-nm wavelength on the GPDP during hydrogenation.

Figure 4

2D self-organized patterns. a, wrinkling diagram on a stress map with as the critical stress to allow 1D ripple pattern aligning with y-direction. As stress builds up along the x-direction, film morphology

transforms from the initial flat state to small and large undulations, each being related to the α , $\alpha+\beta$ and β phases. Secondary wrinkling pattern (herringbone) emerges when the stress state crosses the red reference line. More isotropic shapes undergoing different stress history and perturbation types are also predicted before^{32,33}. b, Microscopic images showing the typical 2D herringbone pattern of the GPDP, which can be described by these geometric parameters: short wavelength λ_1 , long wavelength λ_2 , amplitude A_2 , and jog angle θ . The herringbone length is defined as L . c, Modal analysis results showing herringbone pattern for fully 3D geometry with predefined 1D ripples. d, The long-wavelength λ_2 of the GPDP with various thicknesses of Pd films. Error bars are obtained by measuring the λ_2 at various positions of the GPDPs.

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