Supplementary Information

# Chemomechanical effect of reduced graphene oxide encapsulation on hydrogen storage performance of Pd nanoparticles

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# Additional experimental data



**Fig. S1** TEM image at high magnification (left) and size distribution (right) of (a)  $PdH_x$  in hydrided rGO/PdH<sub>x</sub>/rGO nanolaminates (3.42±0.44 nm diameter), (b) bare-Pd (4.49±0.54 nm diameter) nanoparticles.



**Fig. S2** Cross-section TEM image of rGO/Pd/rGO nanolaminates; Pd nanoparticle is wrapped by rGO multilayer on either sides.



**Fig. S3** C1s XPS spectra of (a) neat GO, (b) rGO/Pd/rGO; XPS was performed to confirm the reduction of graphene oxide (GO) to rGO in the as-synthesized rGO/Pd/rGO nanolaminates. GO was reduced to rGO where the sp<sup>2</sup> bonding is recovered, and the intensities of sp<sup>3</sup>, C–O and C=O bond, are decreased.



**Fig. S4** XPS spectra of Pd 3d for rGO/Pd/rGO; two strong peaks indicate an elemental Pd without any Pd<sup>2+</sup> peaks that correspond to PdO.



**Fig. S5** XRD patterns of rGO/Pd/rGO and rGO/PdH<sub>x</sub>/rGO nanolaminates; XRD was performed on rGO/Pd/rGO nanolaminates in which a characteristic of rGO stacking peak was presented at 20 of 25° and also the (111) and (200) reflections of Pd were observed at 20 of 40.1° and 46.7°, respectively as shown in Table S1. The peak at 20 of 33.9° and 54.8° that correspond to PdO were not found. Pd peak can be found in rGO/PdH<sub>x</sub>/rGO nanolaminates where the Pd peak is denoted with a dashed line, indicating that the Pd hydride nanoparticle has been partially dehydrided.



**Fig. S6** Set of energy-dispersive spectroscopy (EDS) data of rGO/Pd/rGO nanolaminates. EDS mapping was performed to determine the composition of the synthesized nanoparticles. The nanoparticles are elemental Pd and the positions for high intensity Pd peak corresponds to the location of the Pd particle as seen in the high-angle annular dark-field (HAADF) image. Oxygen elements were found to be uniformly distributed rather than concentrated around the Pd particle, indicating that no significant formation of oxide in Pd nanoparticles has occurred.



**Fig. S7** (a) HRTEM image and (b) intensity profile of the Pd nanoparticle; the intensity profile recorded from the area indicated by the rectangular green box in HRTEM images. Average interplanar spacing was determined from multiple atomic planes.



Fig. S8 PCT profiles of bulk Pd at three different temperatures; each isotherm shows flat plateau pressures and the wider coexistence phase ( $\alpha$  and  $\beta$  phases) than that of rGO/Pd/rGO nanolaminates.



**Fig. S9** A schematic illustration describing the procedure for determining the equilibrium pressure ( $P_{eq}$ ). Gray dots represent PC isotherm of rGO/Pd/rGO nanolaminates for H desorption at 385 K.  $\alpha$ ,  $\beta$  phase and transformation regions are fitted through linear regression, subsequently finding the intersection points of each line. By averaging the intersection values of pressures,  $P_{eq}$  was obtained.



**Fig. S10** van't Hoff plots obtained from PC isotherms of bulk Pd and rGO/Pd/rGO nanolaminates for (a) absorption and (b) desorption reactions.



**Fig. S11** Projection of bulk moduli *K* of Pd (left) and PdH (right) nanoparticles. The trend away from the bulk properties as a function of particle size (black dashed lines) obtained from the interatomic distance prediction (Fig. 3) is combined with the calculated bulk moduli of 1.6 nm Pd and 1.4 nm PdH nanoparticles (red  $\times$  markers).



**Fig. S12** XPS spectra of Pd 3d from rGO/Pd/rGO (black line) and bare-Pd (blue line). Binding energies of  $3d_{3/2}$  shifted from 340.3 eV (bare-Pd) to 340.8 eV (rGO/Pd/rGO) and that of  $3d_{5/2}$  shifted from 335.0 eV (bare-Pd) to 335.5 eV (rGO/Pd/rGO).

hkl	2 Theta [°]	d-value [Å]
(111)	40.12	2.246
(200)	46.66	1.945
(220)	68.12	1.375
(311)	82.10	1.173

**Table S1** Reference value of interplanar spacing  $d_{hkl}$  of bulk Pd (ICSD: 00-046-1043).

#### **Computational details**

#### Interatomic distance prediction

Pd nanoparticles in rGO/Pd/rGO nanolaminates are expected to have combinatorial effects of surface tension, *i.e.* change in the interatomic distance upon nanosizing, and rGO encapsulation. In order to extract the strain solely induced by rGO encapsulation, atomistic simulations were performed to assess the effect of surface tension. First, free standing spherical Pd and PdH nanoparticles were created with 1-7 nm sizes, and the dynamic evolution of their morphology and atomic positions was simulated at 500 K within the embedded-atom method (EAM) potential<sup>1</sup> using the LAMMPS code<sup>2</sup> under the non-periodic and shrink-wrapped boundary condition. MD simulations using an NVT ensemble with 1 fs timestep were performed (i) for 50 ps to anneal the system to 500 K, (ii) for 50 ps to equilibrate at 500 K, (iii) for 50 ps to quench from 500 K to 300 K, and (iv) finally for 80 ps to equilibrate and produce data at 300 K. During the equilibration at 500 K (step (ii)), more than 10 structures were sampled and independently quenched to 300 K and equilibrated (steps (iii) and (iv)). The 1 fs of timestep is a little stride for light hydrogen in PdH, but we confirmed hydrogen atoms do not move away from their original octahedral sites.

Considering the limitations of the Pd-H EAM potential we used, which is not trained for nanoparticles, we employed the density functional theory (DFT) calculations to predict the structure changes in nanoparticles smaller than 2 nm. First, MD simulations with the EAM potential were conducted for aforementioned steps (i), (ii) and (iii), and the quenched structures were optimized within DFT. Vienna *ab initio* Simulation Package (VASP)<sup>3</sup> and the generalized gradient approximation (GGA) parametrized by Perdew-Burke- Ernzerhof (PBE)<sup>4</sup> were used with the projector-augmented wave (PAW) potentials.<sup>5</sup> The plane-wave energy cutoff was 300 eV, and the k-point was sampled at Gamma only. Nanoparticles were placed in a

25 Å×25 Å×25 Å cell ensuring enough space between periodic images, and their atomic positions were optimized until the energy and force converged within  $10^{-6}$  eV and  $10^{-2}$  eV/Å·atom, respectively. Various geometries, such as spheres, cubes, and Wulff shapes were constructed to assess the impact of particle morphology.

The final structures were used to calculate average Pd-Pd interatomic distance ( $d_{nano}$ ), and the reduction in the interatomic distance induced by surface tension was calculated using the bulk counterpart ( $d_{bulk}$ ). MD simulations using an NPT ensemble at 300K and 1 bar within the EAM potential and DFT structure optimization were performed for the reference  $d_{bulk}$  prediction. In the nanoparticles simulated in the classical MD, due to the large deformation near the surface and temperature-induced kinetics, the average  $d_{nano}$  is critically influenced by the cutoff radius  $r_{cutoff}$ . We employed  $r_{cutoff} = 3.2$  Å for Pd and  $r_{cutoff} = 3.5$  Å for PdH, while the uncertainty from the  $r_{cutoff}$  setting is accounted by introducing the error bars using the average interatomic distance calculated using  $r_{cutoff} = 3.1-3.3$  Å (Pd) and 3.4-3.6 (PdH). The change in interatomic distance, ( $d_{nano} - d_{bulk}$ )/  $d_{bulk} \times 100$  (%), predicted from the DFT calculation for particles smaller than 2 nm is interpolated with that from the classical MD simulation for larger particles.

## Elastic properties of PdH<sub>x</sub> nanoparticles

Mechanical strain can tune the thermodynamic parameters by shifting the stability of nanoparticles. To compute the strain energies contributing to the reaction enthalpy, the elastic properties of PdH<sub>x</sub> nanoparticles, such as elastic stiffness tensor, should be known. As the EAM potential is not designed for nanoparticles, the DFT computation is desired for the prediction of elastic constants of PdH<sub>x</sub> nanoparticles. Due to the extensive computing resources needed to simulate the full anisotropic response of nanoparticles under external stress, the bulk modulus for the bulk ( $K_{bulk}$ ) and the nanoparticles ( $K_{nano}$ ) was predicted based on the DFT computation, and we assumed other elastic properties scale proportionally to the bulk modulus change, for

example, the stiffness tensor of the nanoparticles  $C_{\text{nano}} = C_{\text{bulk}} \cdot K_{\text{nano}} / K_{\text{bulk}}$ .

Bulk moduli of Pd and PdH nanoparticle were evaluated using the Environ<sup>6,7</sup> code within the Quantum ESPRESSO code.<sup>8</sup> Environ allows to compute the quantum volume of a particle under external pressure and its energy. The second derivative of the energy-volume plot corresponds to the bulk modulus of the system. For general setting, the ultrasoft Rappe-Rabe-Kaxiras-Joannopoulos (rrkjus) pseudopotentials<sup>9</sup> kinetic energy cutoff of 50 Ry for wavefunctions and 230 Ry for charge density and potential; cubic box fixed to 60 bohr (=3.2 nm) length; Gamma-only *k*-point; and parabolic point-counter-charge (PCC) correction were used.

A series of pressures from 10 GPa (compression) to -6 GPa (tension) were applied on the 1.6 nm Pd and 1.4 nm PdH particle structures we used for the interatomic distance prediction. It results in the volumetric strains  $\Delta V/V \approx 3\varepsilon = -10.0$  to -11.8%, corresponding to  $\varepsilon = -3.3$  to -3.9%. The atomic positions under the given pressure were optimized within the DFT, and the final quantum volume and energy were fitted to the Murnaghan equation of state.<sup>10</sup> The calculated bulk moduli of 1.6 nm Pd and 1.4 nm PdH particles are 66.6 and 65.7 GPa, respectively. To estimate the bulk moduli of 3 nm Pd and PdH particles comparable to the particle size examined in the TEM, the trend away from the bulk properties as a function of particle size (dashed lines in Fig. 3) is combined with the bulk moduli of 1.6 nm Pd and 1.4 nm PdH nanoparticles (66.6 and 65.7 GPa) as shown in Fig. S11. The bulk moduli of 3 nm Pd and PdH nanoparticles are projected to reduce by 42.0 and 41.5% from the bulk values (173.0 and 183.0 GPa in Table S2). Other elastic properties, namely, elastic stiffness tensor and shear modulus, scaled to 3 nm Pd and PdH nanoparticles are displayed in Table S3.

	Elastic stiffness tensor			Bulk	Shear
In GPa	$C_{11}$	$C_{12}$	$C_{44}$	modulus K	modulus G
Bulk Pd	209.9	154.6	66.4	173.0	46.6
Bulk PdH	211.1	168.9	65.0	183.0	41.4

Table S2 Calculated elastic constants of bulk Pd and PdH.

**Table S3** Projected elastic constants of 3 nm Pd and PdH nanoparticles based on the calculated bulk values in Table S2 and scaling ratio obtained from Fig. S11.

	Elastic stiffness tensor			Bulk	Shear
In GPa	$C_{11}$	$C_{12}$	C <sub>44</sub>	modulus K	modulus G
3nm Pd	121.8	89.7	38.4	100.4	27.0
3nm PdH	123.4	98.8	38.0	107.0	24.2

#### Modeling the rGO-PdH<sub>x</sub> nanoparticle interface and its chemical interaction energy

Chemical interaction between rGO and PdH<sub>x</sub> nanoparticle is another factor determining the hydrogen storage thermodynamics and kinetics. More adhesive interactions between rGO and PdH<sub>x</sub> nanoparticle would stabilize the dangling bonds on the surface of PdH<sub>x</sub> nanoparticle, minimizing the contributions of the surfaces to the hydrogen storage performance. The chemical interaction between rGO and PdH<sub>x</sub> nanoparticle is simplified and modeled by the interface structure between graphene and spherical PdH<sub>x</sub> nanoparticles (1.6 nm Pd and 1.4 nm PdH). The same DFT computational setting was used in the prediction of interatomic distance other than the plane-wave energy cutoff = 400 eV. The van der Waals interaction is accounted by the vdW-DF2 functional<sup>11,12</sup> as implemented in VASP.



**Fig. S13** Model system used to assess the rGO and PdH<sub>x</sub> nanoparticle interactions. C, Pd, and H atoms are denoted by brown, gray, and red spheres. (a) Top-view, and side-view of fully optimized interface between graphene and (b) Pd nanoparticle and (c) PdH nanoparticle. Charge density difference before and after creating graphene-nanoparticle interface for (d) Pd nanoparticle, and (e) PdH nanoparticle. Electron gain and loss are denoted by yellow and cyan cloud. Figures are generated using VESTA.<sup>13</sup>

Deformation of graphene to maximize its contact area with the nanoparticle was quantified by the displacement of carbon atoms from their mean positions ( $\Delta z$  in Fig. S13b). The maximum  $\Delta z$  is +0.53 Å (at the center of the nanoparticle) and -0.11 Å (at the edge of the nanoparticle) for PdH. On the other hand, the graphene sheet deformed more in contact with Pd by  $\Delta z = +0.63$  Å and -0.16 Å. Along with the high wettability of the Pd nanoparticle as shown in Fig. S13b, our modeling demonstrates more deformation (higher strain) of the hydrogen-poor phase in contact with graphene (or its derivatives). We further confirmed that the average  $d_{Pd}$ - <sub>Pd</sub> in Pd nanoparticle is 3.92% longer compared to the bare Pd particle when it comes to contact with graphene, while the elongation effect is smaller as 3.48% in PdH. This cohesive adhesion explains the larger in-plane strain observed in rGO/Pd/rGO nanolaminates than the hydrided ones despite of their similar bulk moduli.

The interface energy was computed by subtracting the energies of  $PdH_x$  nanoparticles and graphene from the energy of the interface model,

$$\Delta H_{\text{interface}} = H(\text{deformed PdH}_{x} \text{ nanoparticle-deformed C}) - H(\text{bare PdH}_{x} \text{ nanoparticle}) - H(\text{pristine C}), \qquad S(1)$$

where H(system) indicates the energy of the system. The calculated  $\Delta H_{\text{interface}} = -3.27$  eV for Pd nanoparticle containing 141 Pd atoms, and -2.44 eV for PdH nanoparticle containing 87 Pd atoms. However, large deformation of both PdH<sub>x</sub> nanoparticles and graphene sheet contribute *mechanical* interface energy to  $\Delta H_{\text{interface}}$  besides the chemical interaction energy,  $\Delta H_{interface} = \Delta H_{interface}^{mech} + \Delta H_{chem}$ . Therefore, we revisited equation S(1) and calculated the chemical interaction energy by accounting for the deformation of PdH<sub>x</sub> nanoparticles and graphene sheet,

$$\Delta^{H_{chem}} = H(\text{deformed PdH}_{x} \text{ nanoparticle-deformed C}) - H(\text{deformed PdH}_{x} \text{ nanoparticle}) - H(\text{deformed C}).$$

and obtained  $\Delta H_{chem} = -3.80 \text{ eV}$  for 1.6 nm Pd nanoparticle containing 141 Pd atoms, and -2.87 eV for 1.4 nm PdH nanoparticle containing 87 Pd atoms.

Now, in order to assess  $\Delta\Delta H_{rxn}^{chem}$ , which is proportional to  $\Delta H_{chem}(Pd)$ -  $\Delta H_{chem}(PdH)$ , the  $\Delta H_{chem}$  of PdH nanoparticle containing 87 Pd atoms is scaled to the PdH nanoparticle energy with 141 Pd atoms: From the equilibrium molar volume of PdH, 10.57 cm<sup>3</sup>/mol, the size of a spherical PdH nanoparticle containing 141 Pd atoms is derived to be 1.7 nm (radius = 0.866 nm). As can be seen in Fig. S13d-e, chemical interactions between graphene and PdH<sub>x</sub> nanoparticles are originated from the charge transfer from the entire surface of PdH<sub>x</sub> nanoparticles, not only from the contact area with graphene. Hence, the  $\Delta H_{chem}$  of 1.7 nm PdH particle is scaled from the  $\Delta H_{chem}$  of 1.4 nm PdH particle (radius = 0.700 nm) by their surface energy ratio:

$$\Delta H_{chem}(141 \text{ Pd atoms PdH}) = \frac{\Delta H_{chem}(87 \text{ Pd atoms PdH}) \frac{4\pi \times 0.866^2}{4\pi \times 0.700^2} = -4.39 \text{ eV}}{4\pi \times 0.700^2}$$

The chemical interaction of PdH<sub>x</sub> nanoparticles with rGO encapsulant will be at least double of the graphene interface model given the sandwich architecture (Scheme 1), which results in  $\Delta$  $H_{chem}$ = -7.61 eV for 1.6 nm Pd nanoparticle containing 141 Pd atoms, and -8.78 eV for 1.7 nm PdH nanoparticle containing 141 Pd atoms. Therefore, the reaction enthalpy change due to the chemical interaction is:

$$\Delta \Delta H_{rxn}^{chem} = \Delta H_{chem}^{Pd} - \Delta H_{chem}^{PdH} = \frac{-7.61 - (-8.78) \text{ eV}}{141 \text{ Pd atoms}} \cdot 2 \mod \text{Pd per}$$
  
mol H<sub>2</sub> = 1.61 kJ (mol H<sub>2</sub>)<sup>-1</sup>.

### Enthalpy shift by strain energies

We assumed that the Poisson's ratio of Pd and hydrided PdH<sub>x</sub> nanoparticles in rGO/PdH<sub>x</sub>/rGO nanolaminates is identical to that of Pd and PdH bulk,  $\nu$ =0.376 (Pd) and 0.395 (PdH) obtained from the DFT calculations. The out-of-plane components associated with the in-plane tensile strain of 4.96% and 2.99% (Fig. 4) are predicted using the Poisson's ratio under two scenarios: 1) The lateral pulling is negligible, and hence the observed in-plane strain is the response of the

clamping force,  $\varepsilon_{\text{out-of-plane, max}} = -\varepsilon_{\text{in-plane}}/\nu$ . 2) The clamping force is negligible, and hence the

in-plane strain will induce out-of-plane strain,  $\varepsilon_{\text{out-of-plane, min}} = -\frac{2\nu}{1-\nu} \times \varepsilon_{\text{in-plane. Each scenario}}$ serves an upper or lower bound of  $\varepsilon_{\text{out-of-plane, and}}$  actual  $\varepsilon_{\text{out-of-plane}}$  can be estimated by linearly interpolating these limits. The calculated ranges of  $\varepsilon_{\text{out-of-plane}}$  is from -13.19% to -5.98% for Pd, and from -7.57% to -3.90% for PdH.

By integrating the ranges of  $\varepsilon_{out-of-plane}$ , predicted elastic stiffness tensor of 3 nm Pd and PdH nanoparticles listed in Table S3, and the equilibrium molar volume V<sub>0</sub> = 9.18 cm<sup>3</sup>/mol for Pd and 10.57 cm<sup>3</sup>/mol for PdH, we calculated the ranges of strain energy according to equation (1-2). The strain energy destabilizes rGO/Pd/rGO by  $\Delta H_{strain}^{Pd} = 1.7-6.2$  kJ (mol H<sub>2</sub>)<sup>-1</sup>, while hydrided rGO/PdH<sub>x</sub>/rGO by  $\Delta H_{strain}^{PdH} = 0.9-2.5$  kJ (mol H<sub>2</sub>)<sup>-1</sup>. Their  $\Delta H_{strain}$  difference shifts the reaction enthalpy as in Fig. 6b, which range is displayed as a shaded area in Fig. 6a. Note that both equation (1-2) assume specific alignment of the PdH<sub>x</sub> lattice, for example, the *z*-direction, to the rGO interface normal. It is not a complete expression by ignoring transverse terms ( $C_{ij}$ where  $i \neq j$ ) or longitudinal terms ( $C_{ij}$  where i = j), respectively. Yet, equation (1-2) allow us to assess the ranges of stain energy and its associated reaction enthalpy changes.

**Table S4** Summary of chemical interaction and strain energies estimated for Pd and PdH nanoparticles, and their impact on the reaction enthalpy.

$\Delta H_{\rm chem}^{Pd}$	-7.61 eV (1.6 nm particle)	$\Delta H_{\rm strain}^{Pd}$	$1.7-6.2 \text{ kJ} \text{ (mol H}_2)^{-1} (3 \text{ nm particle})$
$\Delta H_{\rm chem}^{PdH}$	-8.78 eV (~1.7 nm particle)	$\Delta H_{\rm strain}^{PdH}$	0.9-2.5 kJ (mol $H_2$ ) <sup>-1</sup> (3 nm particle)
$\Delta\Delta H_{\rm rxn}^{\rm chem}$	1.61 kJ (mol H <sub>2</sub> ) <sup>-1</sup>	$\Delta\Delta H_{\rm rxn}^{\rm strain}$	1.3-2.8 kJ (mol H <sub>2</sub> ) <sup>-1</sup> in 30-70% clamping force
			1 0

# Enhanced hydrogen storage capacity

We also observed considerably enhanced hydrogen capacity as shown in Fig. 5a. We suggested the change in the electronic state due to the chemical interaction between Pd and rGO layers. As evidenced in the DFT calculations of the particle-graphene interface, as well as in the XPS data in Fig. S12, electrons in the Pd nanoparticles are transferred to rGO sheets. Consistent with an earlier report on Pd alloys,<sup>14</sup> this causes the number of holes in the 4d orbital to increase, which allows higher hydrogen concentrations in rGO/Pd/rGO nanolaminates (larger x value in PdH<sub>x</sub>).

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