SUPPLEMENTARY MATERIAL FOR

Thickness-dependent Hydrogen Evolution Reaction Activity on Pd thin film: an insightful view from magnetism

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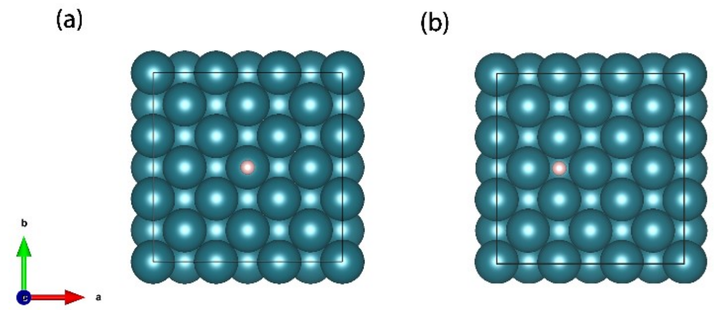

Figure S1. The optimized structure for H atom adsorption on Pd top site (a), hollow site (b), respectively.

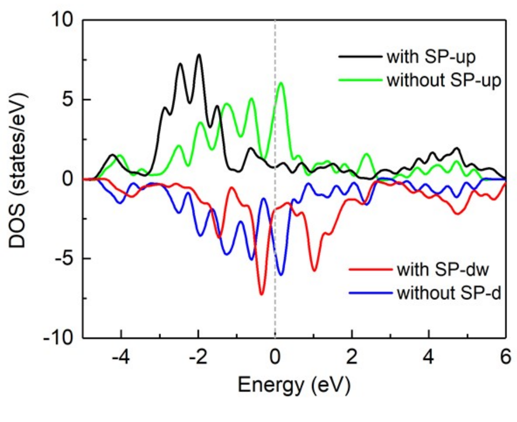

Figure S2. The PDOS of d orbital of the Pd active site for 4 ML Pd (001) thin film in FM and NM state.

Table S1 The ground states, and the ΔG_{H*} of different adsorption sites for 3~10 ML Pd (001) thin films without SOC

Thickness (ML)	The ground state	The ΔG_{H*} of top site (eV)	The ΔG_{H*} of hollow site (eV)
3	NM	-0.17	-0.45
4	FM	-0.11	-0.38
5	NM	-0.13	-0.54
6	NM	-0.15	-0.58
7	NM	-0.17	-0.60
8	NM	-0.18	-0.64
9	FM	-0.14	-0.55
10	NM	-0.19	-0.66

Table S2 The ground state, the average distance between the top to subsurface Pd (001) layer, d(Pd-Pd) (Å), and H and Surface Pd Atoms, d(H-Pd) (Å).

Thickness (ML)	Magnetic state	d(Pd-Pd) (Å)	d(H-Pd) (Å)
3	NM	2.6935	1.6301
4	FM	2.6906	1.5379
5	NM	2.6930	1.5394
6	NM	2.6937	1.5406
7	NM	2.6945	1.5410
8	NM	2.6951	1.5412
9	FM	2.6933	1.5395
10	NM	2.6954	1.5424

In table S2, one can see that the top layer to subsurface layer Pd-Pd distance (d (Pd-Pd)) varies with thickness of Pd (001) thin films. When the 4 and 9 ML Pd (001) film is ferromagnetic, the d (Pd-Pd) is 2.6906 and 2.6933 Å, respectively. They are both smaller than their adjacent nonmagnetic 3/5 and 8/10 ML Pd films, indicating that the coupling strength between the top layer and sublayer is enhanced when the Pd film is ferromagnetic. Obviously, the catalytic activity of Pd film (ΔG_{H*}) is consistent with the evolution trend of the d (Pd-Pd). In addition, it is worth noting that the same is to the equilibrium H to Pd distance **(**d(H-Pd) (Å)). This means that the structure of Pd films is also important to their HER activity.

Table S3 The ground states, and the ΔG_{H^*} of top site for 11~16 ML Pd (001) thin films

Thickness (ML)	The ground state	The ΔG_{H^*} of top site (eV)
11	NM	-0.191
12	NM	-0.195
13	NM	-0.200
14	NM	-0.205
15	FM	-0.158
16	NM	-0.211

Discussion HER activity about 9 ML Pd (001) film:

Table S4 The ground states, and the ΔG_{H*}, the d-band center and the H Bader charge for H atom of 9 ML Pd (001) film.

The ground state	The ΔG_{H*} of top site (eV)	d-band center (eV)	H Bader charge(|e|)
NM	-0.151	-1.683	0.021
FM	-0.132	-1.704	0.028

The HER performance of 9 ML Pd (001) thin films in NM conditions (MAGMOM is set as 0) is also calculated, and the corresponding results are shown in Table S4. We find that the top site is still active site for it. The calculated ΔG_{H*} under NM state is -0.151 eV, which exhibits a poor HER activity than that of ferromagnetic state (-0.132 eV). Furthermore, the calculated d-band center under NM state is -1.683 eV, which is closer to Fermi Level than that under FM state (-1.704 eV). The H Bader charge in NM state is 0.021 |e|, which is less than that in FM state (0.028 |e|), evidencing that magnetism indeed promote the transfer of the electron between substrate and adsorbate. Both the d-band center and the H Bader electron show that the ferromagnetism in Pd thin film can lead to excellent HER performance.