

Supporting Information

Engineering Ni/Pd Heterojunctions for Dehydrogenation of Ammonia Borane: Improving the Catalytic Performance with 3D Mesoporous Structure and External N Doped C Layer

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1. Experimental detail

1.1 Materials

Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98.5%), 4-Picolinic acid ($\text{C}_6\text{H}_5\text{NO}_2$, 99%), sodium tetrachloropalladate(II) (Na_2PdCl_4 , 99.95%) were purchased from Shanghai Haiyi Co. All reagents were used as received without further purification.

1.2 Preparation of Ni coordination complex:

In a typical synthesis, nickel nitrate (0.0291 g, 0.1 mmol) and isonicotinic acid (0.0123 g, 0.1 mmol) were dissolved in the mixed solvent of DMF, ethanol, and deionized water (volume ratio = 9:5:1). Then the mixed solution was ultrasonicated for 10 minutes, and transferred to a 25 mL Teflon-lined steel autoclave. After the reaction

at 150 °C for 6 hours in the oven, the products were collected via centrifugation and washed several times with deionized water and ethanol, then dried at 60 °C overnight.

1.3 Preparation of NiO@N-C micro-spheres:

NiO@N-C porous microsphere particles were synthesized via calcination of the obtained coordination compound at 450 °C for 2 h in N₂ gas atmosphere with a heating rate of 2 °C·min⁻¹.

1.4 Preparation of Ni@N-C micro-spheres:

Ni@N-C microsphere were synthesized via calcination of the obtained NiO@N-C porous microsphere particles at 400 °C for 2 h in H₂/Ar (H₂: 10%) atmosphere with a heating rate of 2 °C·min⁻¹.

1.5 Preparation of Ni/Pd@N-C micro-spheres:

Ni/Pd@N-C microsphere were synthesized via a reduction reaction. The obtained Ni@N-C porous microsphere particles (0.0150 g) and sodium tetrachloropalladate(II) (0.0075 g) were dissolved in deionized water (5 ml). Then the dispersion was ultrasonicated for 10 minutes. After the reaction at 60 °C for 3 hours in the oven, the products were collected via centrifugation and washed several times with deionized water and ethanol, then dried at 60 °C overnight.

1.6 Preparation of Pd particles :

Sodium tetrachloropalladate(II) (0.10 g) and sodium borohydride (0.20 g) were dissolved in the deionized water (15 ml). Then the dispersion was ultrasonicated for 10 minutes. After the reaction at 30 °C for 3 hours, the products were collected via centrifugation and washed several times with deionized water and ethanol, then dried

at 60 °C overnight.

1.7 Preparation of Ni/Pd microspheres

NiO microsphere were synthesized via calcination of the obtained NiO@N-C porous microsphere nanoparticles at 450 °C for 2 h in O₂ atmosphere with a heating rate of 2 °C·min⁻¹. Ni microspheres were synthesized via calcination of the obtained NiO@N-C porous microspheres at 400 °C for 2 h in H₂/Ar (H₂: 10%) atmosphere with a heating rate of 2 °C·min⁻¹. Ni/Pd microspheres were synthesized by a process similar to Ni/Pd@N-C. The obtained Ni porous microspheres (0.0100 g) and sodium tetrachloropalladate(II) (0.0150 g) were dissolved in the deionized water (5 ml). Then the mixed solution was ultrasonicated for 10 minutes. After the reaction at 60 °C for 3 hours in the oven, the products were collected via centrifugation and washed several times with deionized water and ethanol, then dried at 60 °C overnight.

1.8 Synthesis conditions of series of Ni/Pd@N-C samples with different palladium contents

Sample	Ni@N-C	Na ₂ PdCl ₄	H ₂ O
Ni/Pd-1@N-C	10 mg	7.5 mg	10 ml
Ni/Pd-2@N-C	10 mg	15 mg	10 ml
Ni/Pd-3@N-C	10 mg	20 mg	10 ml

1.9 Characterization

The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Panalytical X-pert diffractometer with CuK α radiation. The morphology and crystal structure of the as-prepared products were

observed by scanning electron microscopy (SEM, SU8010), and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai-F30) with an acceleration voltage of 300 kV. All TEM samples were prepared from depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid. The solid states UV-Vis spectra were acquired using the Thermo Scientific Evolution 220 spectrophotometer equipped with integrating sphere and recorded in absorbance vs. wavelength modes using appropriate baseline correction (Zero/baseline correction). The surface areas (S) of samples were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. PHI QUANTUM2000 photoelectron spectrometer (XPS) was used to characterize the surface compositions of the products. NMR spectra were taken on a Bruker AV400 at room temperature.

2.0 Computational details.

All of the density functional calculations were performed using plane-wave pseudopotential method, as implemented in the Cambridge Sequential Total Energy Package (CASTEP) code.¹ The local density approximation (LDA)² and ultrasoft pseudopotential³ were used to describe the exchange-correlation effects and electron-ion interactions, respectively. A Monkhorst-Pack mesh⁴ of k-points, Γ points was used to sample the two-dimensional Brillouin zone for the geometry optimization. The self-consistent convergence accuracy was set at 2×10^{-6} eV/atom, the convergence criterion for the force between atoms was 5.5×10^{-2} eV/Å, and the maximum displacement was 2×10^{-3} Å. The Ni (111), Pd (111) and N-doped graphite (001) surfaces were simulated using a slab model with $12.52 \text{ Å} \times 12.52 \text{ Å}$, $13.66 \text{ Å} \times 13.66 \text{ Å}$, and $12.30 \text{ Å} \times 12.30 \text{ Å}$, respectively. All these four slab models were separated by a vacuum spacing of 15 Å to wipe out the interactions between periodic images.

The adsorption energy for H₂O molecular adsorbing on surface was calculated by:

$$E_{ad} = E_{(H_2O+surface)} - E_{(H_2O)} - E_{surface}$$

where $E_{(H_2O+surface)}$ was the total energy of the surface containing the adsorbed H₂O molecular, $E_{(H_2O)}$ was the total energy of H₂O molecular, and $E_{surface}$ denoted the total energy of pure surface without the adsorbed H₂O molecular.

2. The experimental results

Figure S1 (a) SEM image of Ni precursor, and (b-f) the corresponding elemental mapping of Ni precursor.

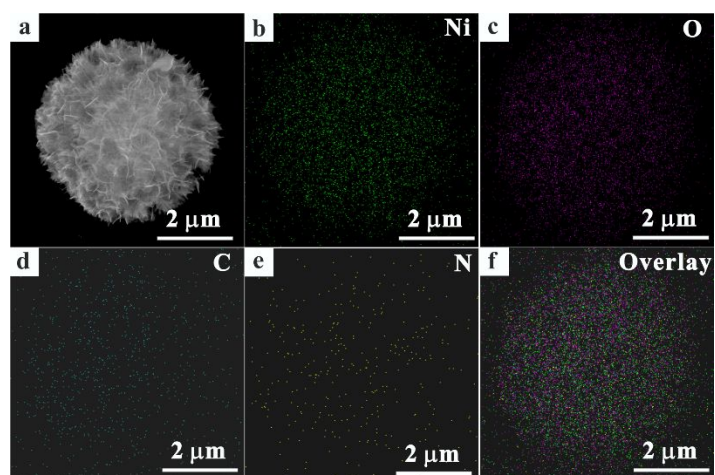


Figure S2 XRD pattern of the NiO@N-C hierarchical mesoporous micro-spheres.

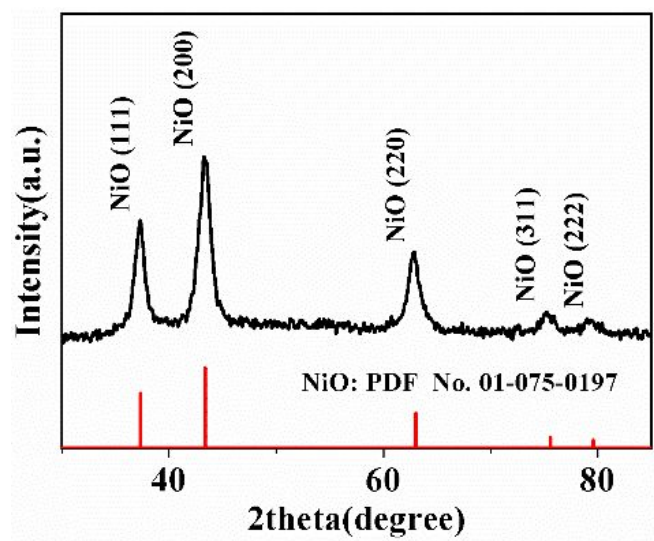


Figure S3 (a) SEM image of NiO@N-C micro-spheres, and (b-f) the corresponding elemental mapping.

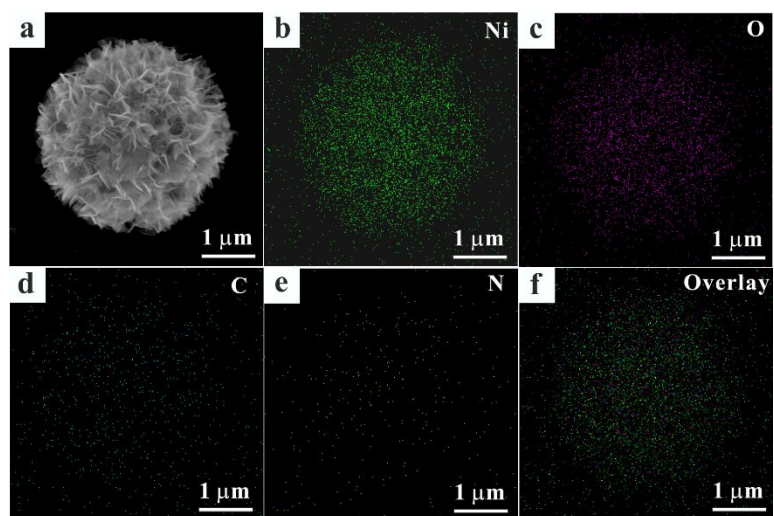


Figure S4 (a) XRD pattern of Ni@N-C, (b-c) SEM image of Ni@N-C, and (d-f) the corresponding elemental mapping.

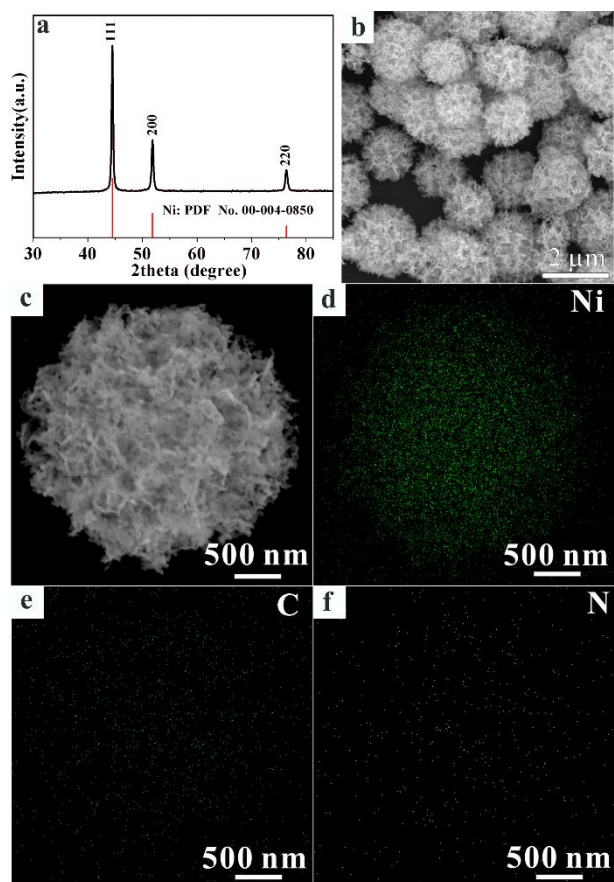


Figure S5 XPS survey spectrum of Ni/Pd-2@N-C hierarchical mesoporous spheres.

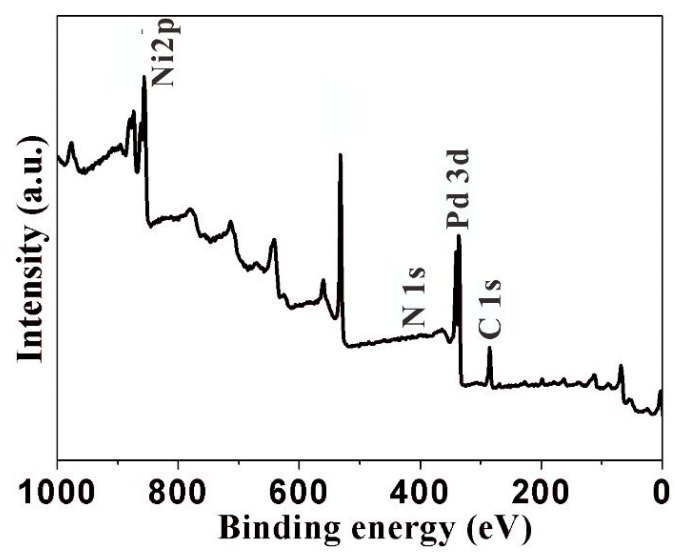


Figure S6 (a) XRD pattern of Ni/Pd-2 hierarchical mesoporous spheres, (b-c) SEM image of Ni/Pd-2, and (d-e) the corresponding elemental mapping of hierarchical mesoporous spheres.

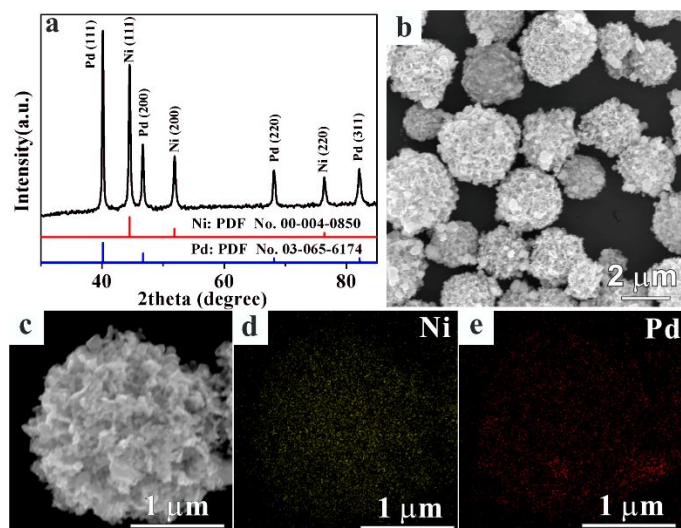


Figure S7 (a) XRD pattern and (b) SEM image of Pd nanoparticles.

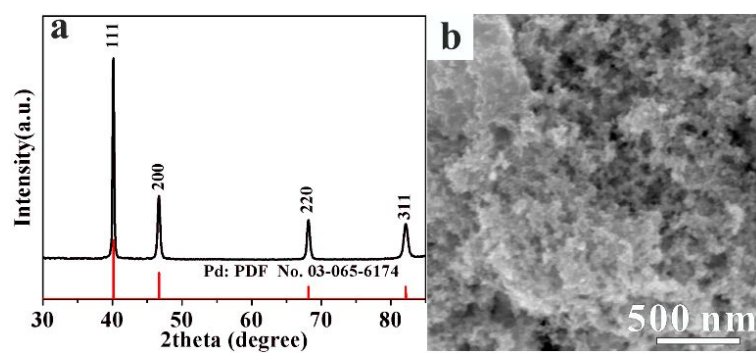


Figure S8 (a) XRD pattern of Ni/Pd-2@N-C after catalytic reaction, (b,c) SEM image of Ni/Pd-2@N-C after catalytic reaction, and (d-h) the corresponding elemental mapping.

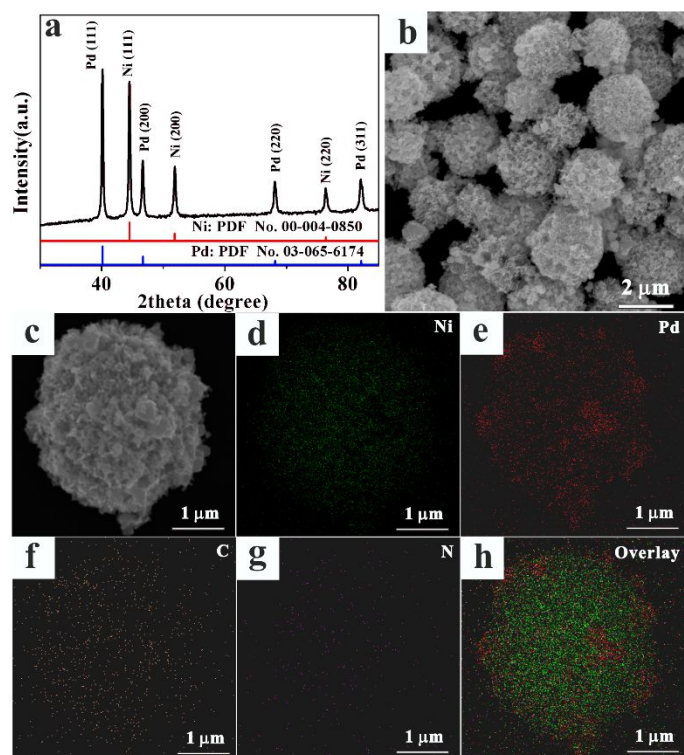


Figure S9 (a) XRD pattern of Ni/Pd-1@N-C, (b,c) SEM image of Ni/Pd-1@N-C, and (d-h) the corresponding elemental mapping.

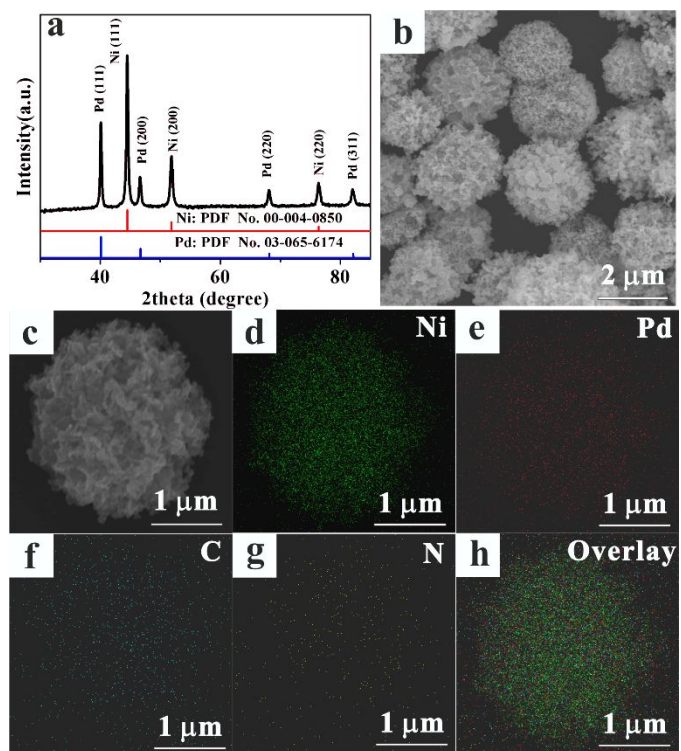


Figure S10 (a) XRD pattern of Ni/Pd-3@N-C, (b,c) SEM image of Ni/Pd-3@N-C, and (d-h) the corresponding elemental mapping.

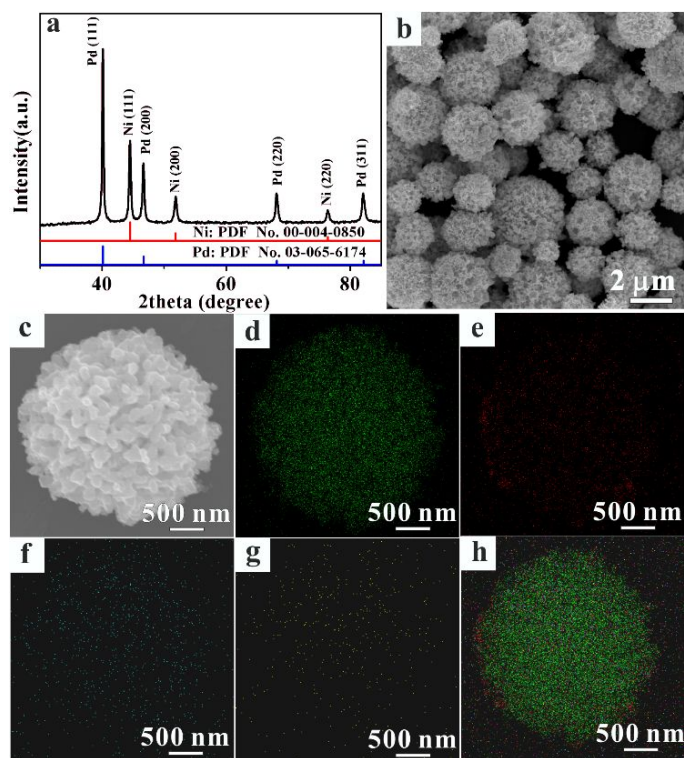


Table S1 Element amounts of Ni/Pd-1@N-C, Ni/Pd-2@N-C, Ni/Pd-3@N-C, and Ni/Pd-2 measured by EDS.

Element Sample	C,N (Atomic%)	Ni (Atomic%)	Pd (Atomic%)	Ni/Pd
Ni/Pd-1@N-C	26.70	60.88	12.42	4.90
Ni/Pd-2@N-C	34.60	46.55	18.86	2.46
Ni/Pd-3@N-C	42.37	29.59	28.04	1.05
Ni/Pd-2	-----	70.68	29.32	2.41

Figure S11 (a) XRD pattern of Ni microspheres, (b,c) SEM image of Ni microspheres, and (d) the corresponding elemental mapping.

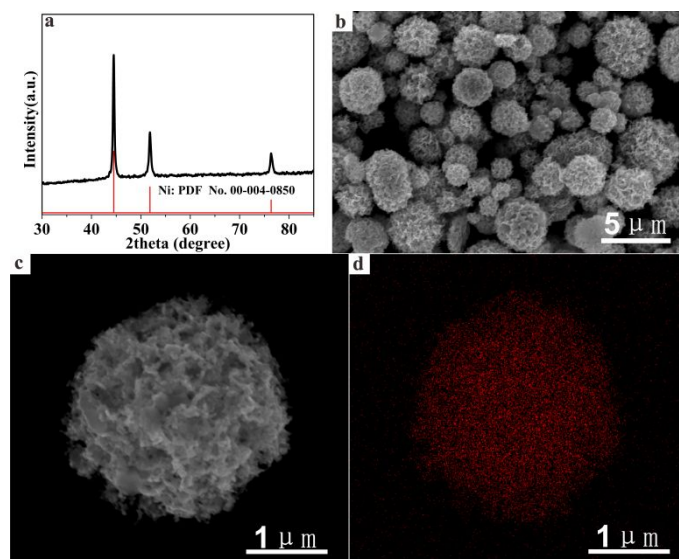


Figure S12 Comparison of catalytic activities of Ni/Pd-2, Pd nanoparticles and Ni microspheres toward the dehydrogenation of AB.

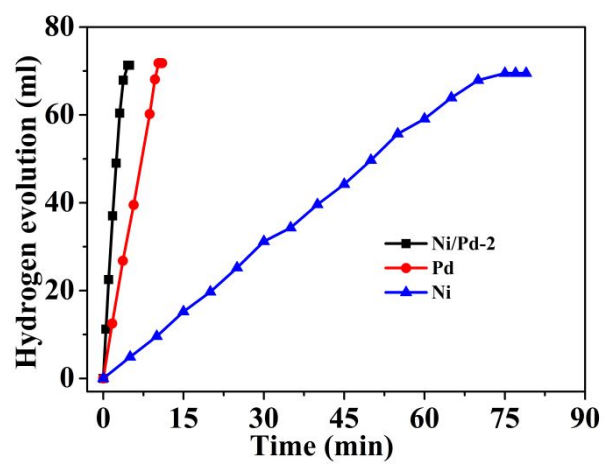


Figure S13 Time course plots for the hydrolysis of AB at different temperatures by using Ni/Pd-2 catalysts.

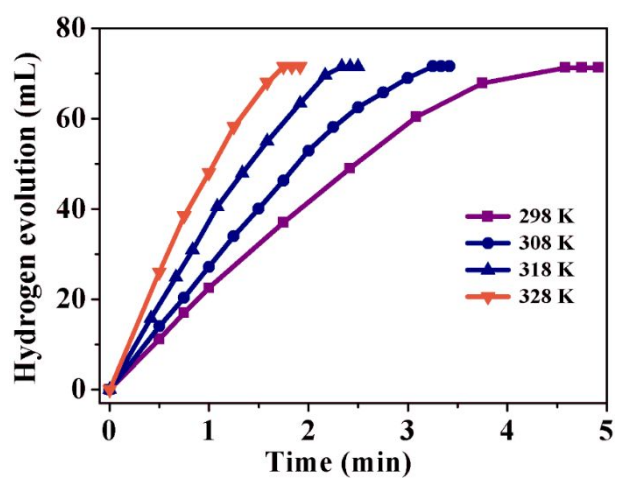
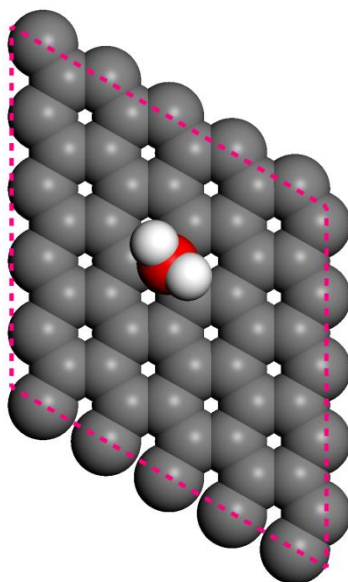


Figure S14 The geometry of H₂O adsorbed on graphite (001) surface. The bluish violet, deep green, gray, red and white balls represent Ni, Pd, C, O and H atoms, respectively.



References

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