

Supporting Information

Bimetallic Pd/Co Embedded in Two-Dimensional Carbon-Nitride For Z-Scheme Photocatalytic Water Splitting

*Liyan Xie, Xiyu Li, Xijun Wang, Wanying Ge, Jinxiao Zhang, Jun Jiang, Guozhen Zhang**

Hefei National Laboratory for Physical Sciences at the Microscale, *iChEM* (Collaborative Innovation Center of Chemistry for Energy Materials), CAS Center for Excellence in Nanoscience, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.

**Corresponding author.*

E-mail: guozhen@ustc.edu.cn

Part 1: Supporting Figures

1.1 Atomic models

The $\text{Pd}(\text{OH})_2@\text{CN}$ and $\text{Co}(\text{OH})_2@\text{CN}$ systems are built by loading $\text{Pd}(\text{OH})_2^-$ or $\text{Co}(\text{OH})_2^-$ onto vacancies formed by CN atoms in a $2\times 2\times 1$ g-CN, with OHs located at the most stable configuration (Figure S1). The C–C and C–N bond lengths are measured to be 1.50 ± 0.02 Å and 1.33 ± 0.02 Å, respectively, while the N–Pd and N–Co bond lengths are 2.07 ± 0.02 Å and 2.06 ± 0.02 Å, respectively.

The above two then were merged on the same g-CN platform so as to form the integrated ($\text{Pd-Co}@\text{CN}$) configuration. It is a $2\times 2\times 1$ supercell of g-CN containing 24 carbon atoms and 24 nitrogen atoms, in which $\text{Pd}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ were embedded in two neighboring vacancy holes surrounded by C and N atoms (Figure S2). The lattice parameter is 7.13 Å. Bond lengths of C–C, C–N, N–Pd and N–Co are 1.50 ± 0.02 Å, 1.33 ± 0.02 Å, 2.07 ± 0.02 Å and 2.06 ± 0.02 Å, respectively, which have smaller uncertainties compared to isolated $\text{Pd}(\text{OH})_2@\text{CN}$ and $\text{Co}(\text{OH})_2@\text{CN}$.

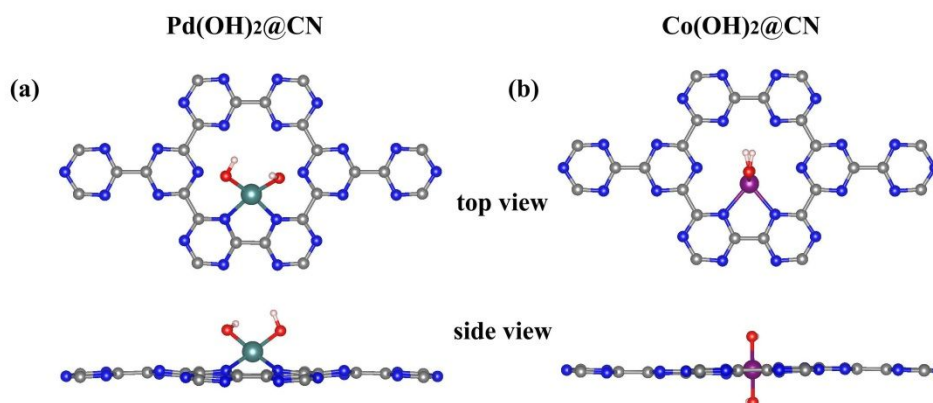


Figure S1. The optimized atomic structure of $\text{Pd}(\text{OH})_2@\text{CN}$ and $\text{Co}(\text{OH})_2@\text{CN}$

Our previous study¹ found that loading the two OHs in $\text{Pd}(\text{OH})_2$ on the same side of the CN network is more stable, whereas loading the two OHs on opposite sides of $\text{Co}(\text{OH})_2$ is more stable.

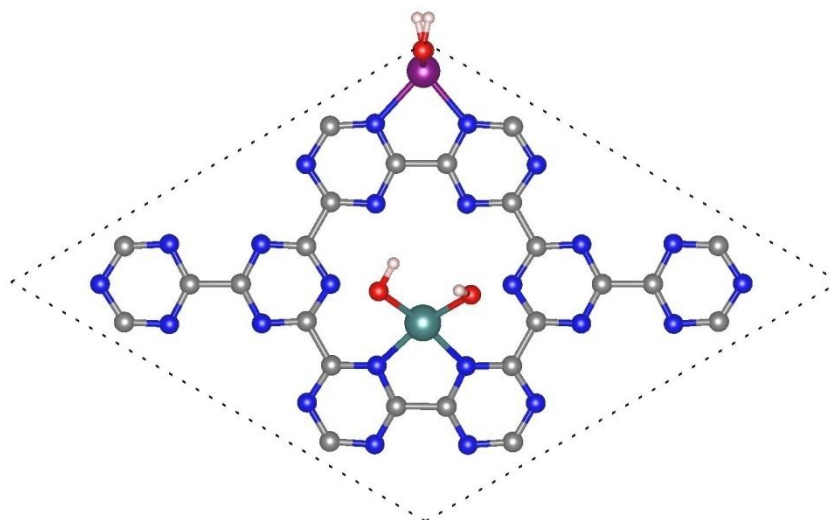


Figure S2. The optimized atomic structure of $\text{Pd}(\text{OH})_2+\text{Co}(\text{OH})_2@\text{CN}$

We made a model using a $2\times 2\times 1$ supercell of g-CN by loading $\text{Pd}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ simultaneously at two different pockets formed by CN atoms, with the OHs placed at their most stable positions ($\text{Pd-Co}@\text{CN}$).

1.2 Investigation of size effect of adopted models

In order to investigate how model size and transition metal placement affect the density of states (DOS), we constructed two models as shown in Figure S3a and Figure S3c. Then, we used the PBE method to calculate the density of states (DOS). Figure S3b is the DOS corresponding to the Figure S3a structure and Figure S3d is the DOS corresponding to the Figure S3c structure. It is very encouraging to see that the CBM of both structures is on the Co-fragment (atoms in the red dotted ellipses and OHs), and in each case their VBM is on the Pd-fragment (atoms in the blue dotted ellipses and OHs). Moreover, the shapes of the two model's DOS are similar, indicating that the model's size and transition metal placement have little affection on the DOS. Therefore we can use the small model to calculate DOS by using HSE06 functional.

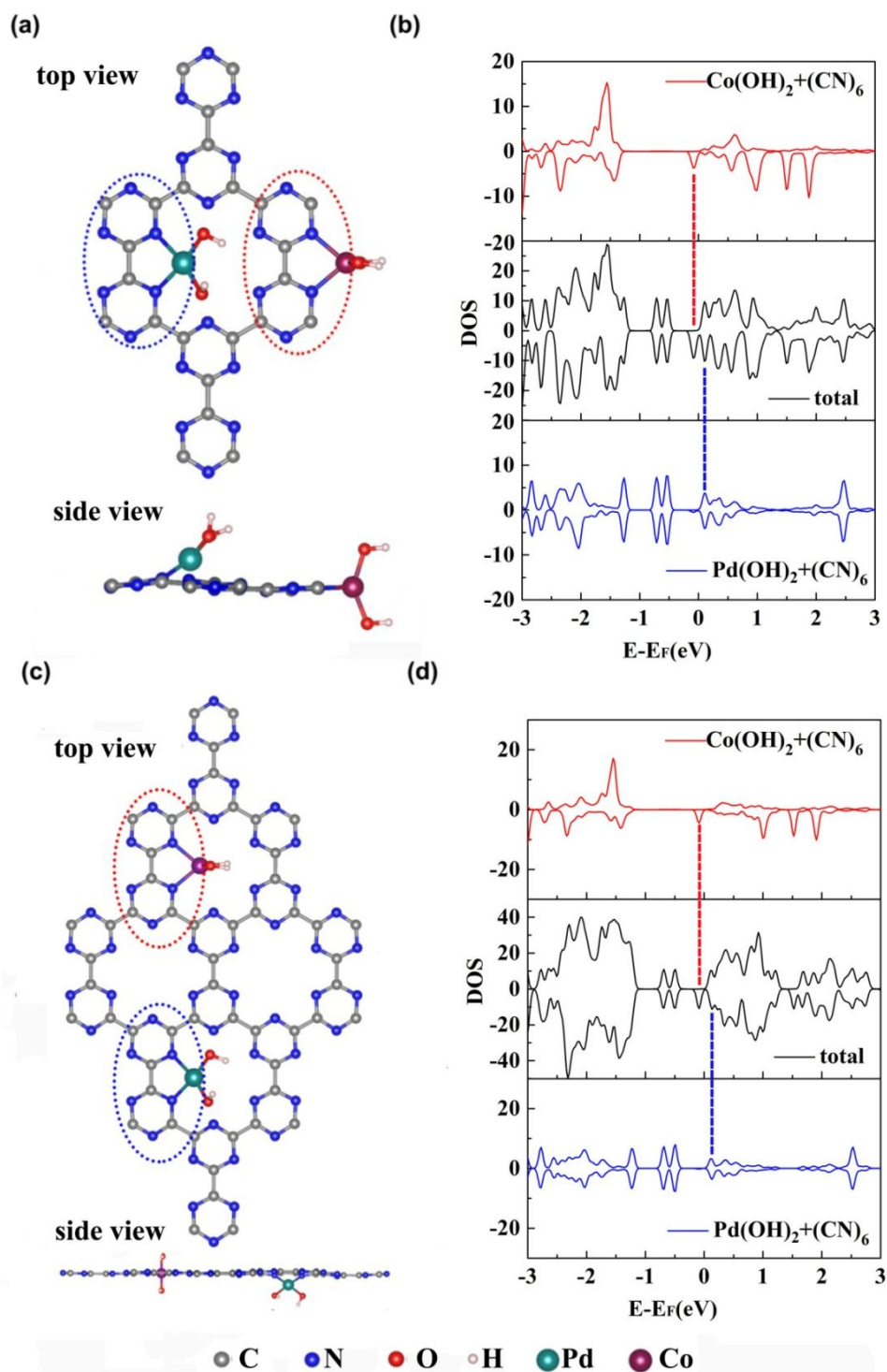


Figure S3. The optimized atomic structures (top and side views) of (a) 2x2, and (c) 4x4 Pd-Co@CN models. Pd-fragment: blue dotted ellipse zone and OHs; Co-fragment: red dotted ellipse zone and OHs. (b) and (d): The density of states (DOS) corresponding respectively to models (a) and (c). In each case, the black line is the TDOS, the blue line is the PDOS of the Pd-fragment, and the red line is the PDOS of the Co-fragment.

1.3

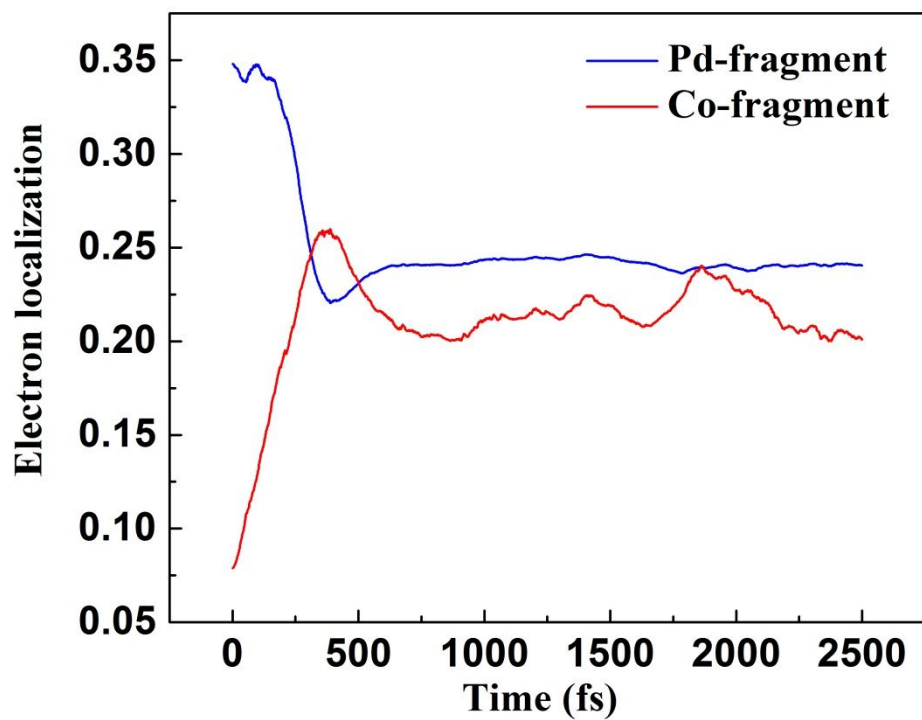


Figure S4. Spatial evolution of photo-excited electrons originating from the Pd-fragment as a function of time at T=300K.

1.4

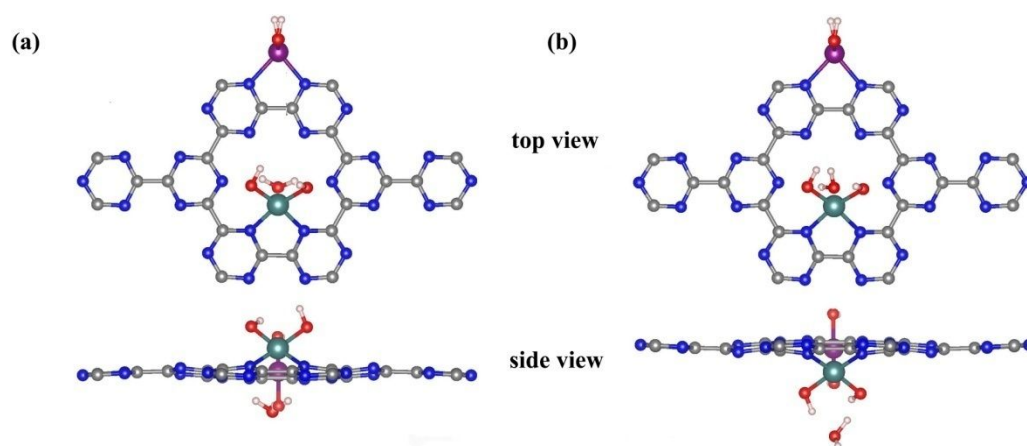


Figure S5. The optimized atomic structure of H₂O adsorbed on the Pd-Co@CN surface.

(a) different (b) same side of loading Pd(OH)₂.

1.5

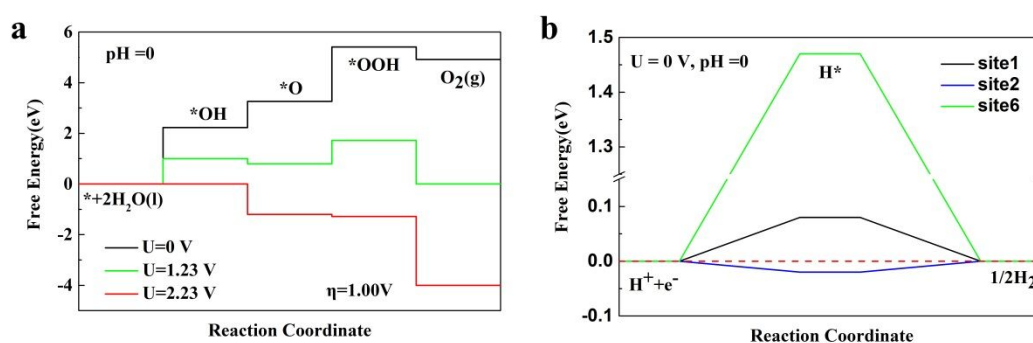


Figure S6. (a) Schematic diagram of the Gibbs free energy changes for the four elementary OER steps on Pd-Co@CN, where pH=0. (c) Schematic diagram of the Gibbs free energy changes for HER on Pd-Co@CN with H positioned at site 1, site 2 or site 6, red dot line: ideal value for HER. Where pH = 0, U = 0V (U vs Reversible Hydrogen Electrode).

1.6

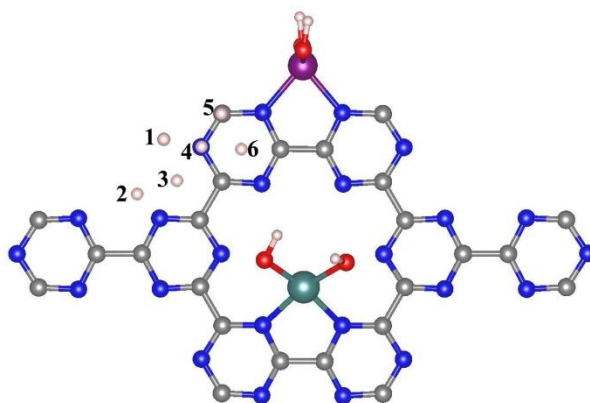


Figure S7. The optimized atomic structure of Pd-Co@CN, showing sites 1-6 for H atom adsorption.

Part 2: Calculation Details

2.1 Adsorption energy

2.1.1 Adsorption energy of OER

$$\Delta E_{ads} = E_{sys + H_2O} - E_{sys} - E_{H_2O}$$

Where $E_{sys + H_2O}$ is the total energy of the Pd-Co@CN system with a H_2O molecule absorbed on the surface, E_{sys} is the total energy of the Pd-Co@CN system alone, and E_{H_2O} is the energy of one H_2O molecule in the gas phase.

2.1.2 Adsorption energy of HER

We calculated the isolated H atom absorption energy as:

$$\Delta E_{ads} = E_{sys + H} - E_{sys} - 0.5E_{H_2}$$

Where $E_{sys + H}$ is the total energy of the Pd-Co@CN system with a H atom absorbed on the surface, E_{sys} is the total energy of the Pd-Co@CN system alone, and E_{H_2} is the energy of a H_2 molecule in the gas phase (-6.7eV).

2.2 Micro Kinetic Analysis

The change in Gibbs free energy (ΔG_i) was calculated by:²

$$\Delta G_i = \Delta E_i + \Delta ZPE_i - T\Delta S_i - \Delta G_{pH} - eU$$

The reaction energy (ΔE) can be obtained by analyzing the DFT total energies. Harmonic vibrational frequency calculations were performed to determine the zero point energy ΔZPE . ΔS is the entropy difference between the adsorbed state and the gas phase, and T is set to room temperature 298.15 K. $\Delta G_{pH} = 2.303k_B T \cdot pH$ is the free energy contribution depending on variations in H^+ concentration. The contribution of the applied potential was computed assuming it to be $-eU$, e representing the charge of the transferred electron, and U is the applied potential with respect to the reversible hydrogen electrode (RHE). The entropies of the free molecules (such as H_2) were taken from the NIST database³ and the energy contribution from the configuration entropy in the adsorbed state was not included.

2.2.1 Gibbs free energy for the OER

Thus, the value of the OER ΔG for steps 1-4 in the text can be calculated by the specific equations shown below:

$$1: \Delta G(1) = G(*OH) + 0.5 \times G(H_2(g)) - G(H_2O(l)) - G(*) - eU - \Delta G_{pH}$$

$$2: \Delta G(2) = G(*O) + 0.5 \times G(H_2(g)) - G(*OH) - eU - \Delta G_{pH}$$

$$3: \Delta G(3) = G(*OOH) + 0.5 \times G(H_2(g)) - G(H_2O(l)) - G(*O) - eU - \Delta G_{pH}$$

$$4: \Delta G(4) = G(*) + G(O_2(g)) + 0.5 \times G(H_2(g)) - G(*OOH) - eU - \Delta G_{pH}$$

2.2.2 Gibbs free energy for the HER

The value of ΔG can be calculated by a specific equation for each step in the HER:

$$5: \Delta G(5) = G(*H) - 0.5 \times G(H_2(g)) - G(*) - eU - \Delta G_{pH}$$

$$6: \Delta G(6) = 0.5 \times G(H_2(g)) + G(*) - G(*H) - eU - \Delta G_{pH}$$

As the contribution from the vibrational entropy of H in the adsorbed state is negligibly small, ΔZPE was set to be 0 eV. The entropy differences of H in adsorption and gas phase is $\Delta S_H \approx -0.5S_{H_2}$, where S_{H_2} is the entropy of H_2 in the gas phase under standard conditions ($130.68 \text{ J} \times \text{K}^{-1} \text{ mol}^{-1}$). So $-T\Delta S_H \approx 0.2 \text{ eV}$.

Part 3:

Table S1: The adsorption energy of a H atom on Pd-Co@CN at different sites

Adsorption site	ΔE_{ads} eV
1	-0.12
2	-0.22
3	Unstable
4	Unstable
5	Unstable
6	1.27

- (1) Li, X.; Cui, P.; Zhong, W.; Li, J.; Wang, X.; Wang, Z.; Jiang, J. Graphitic Carbon Nitride Supported Single-Atom Catalysts for Efficient Oxygen Evolution Reaction. *Chem. Commun.* **2016**, 52, 13233-13236.
- (2) Zhuo, Z.; Wu, X.; Yang, J. Two-Dimensional Phosphorus Porous Polymorphs with Tunable Band Gaps. *J. Am. Chem. Soc.* **2016**, 138, 7091-7098.
- (3) Computational Chemistry Comparison and Benchmark Database. <http://cccbdb.nist.gov/>.