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Supplementary Information

PdZn Alloy Nanoparticles Encapsulated within Few layers of Graphene for Efficient Semi-Hydrogenation of Acetylene

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Experimental

Synthesis of ZnO nanowire

The ZnO nanowires were synthesized by a modified physical vapor deposition process under atmosphere pressure.[1] The source materials (a mixture of 0.5 g of ZnO powder and 0.5 g of active carbon) were loaded into a ceramic boat that was positioned in the middle of a quartz tube. The silica wafer was used as the substrate to collect samples, which was placed downstream from the source material in the temperature zone of 700 ^{o}C. Prior to heating, the quartz tube was purged with Ar gas (30 ml min^{-1}) for 30 min. Then, it was heated up to 1000 oC under the mixture of Ar (50 ml min^{-1}) and O_2 (ml min^{-1}) for 1 h. The surface of silica substrate appeared white after the reaction, indicating the deposition of ZnO nanowires.

Synthesis of Pd/ZnO and PdZn/ZnO

Pd nanoparticles (NPs) supported on the ZnO nanowire were obtained by the deposition-precipitation method. The as-prepared ZnO nanowire was dipped into an aqueous solution containing $Pd(NO_3)_2$ as precursor salts. The pH value of the aqueous solution was maintained, by adding NaOH, between 8 and 9. Then, the mixture was stirred at the temperature of 70 °C for 2 h, filtered, washed and dried at room temperature under vacuum overnight. Finally, the resulting material was reduced under H_2 at 200 °C for 2h to obtain the Pd/ZnO catalyst. The 2 wt% weight loading of Pd was confirmed by the ICP analysis. The PdZn/ZnO was obtained by reducing the Pd/ZnO catalyst at 400 °C under H_2 for 2h.

Synthesis of PdZn@C/ZnO

The synthesis strategy of PdZn alloy NPs encapsulated within few layers of graphene (PdZn@C/ZnO) was illustrated in Figure S1. The PdZn/ZnO catalysts (500 mg) were employed as the substrate for the in situ growth of graphene layer by a chemical vapor deposition (CVD) process using ethylbenzene (5ml) as the precursor. The process of coating the graphene layer on PdZn/ZnO at 700 °C was just for 2 min, and then the as-prepared sample was cooled down to room temperature in Ar atmosphere and denoted as PdZn@C/ZnO.

Catalyst characterization

Transmission electron microscopy (TEM), was performed by a Tecnai G2 F20 operated at 200 kV. X-ray diffraction (XRD) measurement was conducted on a Philips diffractometer using Cu Ka radiation. Raman spectroscopy was performed on a LabRam HR 800 using a 533 nm laser. XPS characterization was conducted by ESCALAB 250 instrument with Al Kα X-rays (1489.6 eV, 150 W, 50.0 eV pass energy).

Catalyst performance test

The selective hydrogenation activity of the catalysts was conducted in a quartz-bed flow reactor for acetylene hydrogenation with 5 mg catalysts mixed with 200 mg quartz sand. A gas mixture of 1 vol% C_2H_2, 10 vol% H_2, 20 vol% C_2H_4, with He balance (flow rate = 15 ml min^{-1}, GHSV = 180000 mL g^{-1} h^{-1}) was introduced into the reactor. The reactants and products were analyzed by GC (Agilent 7890A) equipped with a flame ionization detector (FID).The selective hydrogenation activity of the catalysts was conducted in a quartz-bed flow reactor for acetylene hydrogenation with 5 mg catalysts mixed with 200 mg quartz sand. A gas mixture of 1 vol% C_2H_2, 10 vol% H_2, 20 vol% C_2H_4, with He balance (flow rate = 15 ml min^{-1}, GHSV = 180000 mL g^{-1} h^{-1}) was introduced into the reactor. The reactants and products were analyzed by GC (Agilent 7890A) equipped with a flame ionization detector (FID).

The conversion and selectivity of the reaction were calculated as follows:

$$\text{Conversion (\%)} = \frac{Acetylene\ feed\ (mol) - Acetylene\ residue(mol)}{Acetylene\ feed\ (mol)} \times 100\% \tag{1}$$

$$\text{Selectivity (\%)} = \left(1 - \frac{Ethane\ product\ (mol)}{Acetylene\ feed\ (mol) - \ Acetylene\ residue\ (mol)}\right) \times 100\% \tag{2}$$

DFT Calculations.

DFT calculations were performed with VASP 5.3.5 code.[2] The revised Perdew-Burke-Ernzerh of (revPBE)[3] exchange-correlation functional was adopted as the generalized-gradient approximation functional. The valence orbital of involved atoms was described by plane-wave basis sets with cutoff energies of 400 eV.[4] A Gaussian smearing with the width of 0.2 eV was used. The convergence criteria for the energy and force were set to 10^{-4} eV and 0.05 eV/Å. Additionally, the weak van der Waals (vdW) interactions were corrected via DFT-D2 method.

A 16.48×16.48 Å Pd (111) supercell was used to model the Pd catalyst. The PdZn alloy was modeled by a unit cell of 1:1 intermetallic PdZn with a space group of P4/mmm, and a 16.61×16.61 Å PdZn (111) surface was used to simulate PdZn catalyst structure. The graphene-coated PdZn (PdZn@C) catalyst was modeled by a covering a single layer of graphene to PdZn (111). The relaxed structures of the above models are shown in Fig.S6. In order to model the catalytic hydrogenation of acetylene, the adsorption energy (E_{ad}) of relevant intermediates and reaction energy (E_r) of each elementary step were calculated. $E_{ad} = E_{slab*A} - E_{slab} - E_A$, where the E_{slab*A}, E_{slab} and E_A are the total energy of substrate with the adsorbate, clean slab and isolated intermediate, respectively. $E_r = E_{fs} - E_{is}$, where the E_{is} and E_{fs} represent the total energy of the corresponding initial state and final state, respectively. To evaluate the energy barriers (E_a) of some key steps, the transition states were computed with the climbing image nudged elastic band

(CI-NEB) method.[5, 6] $E_a = E_{ts} - E_{is}$, where E_{ts} is the energy of transition states.

As known, the linear scaling relation between the adsorption energy of complex intermediates and some certain molecules has been proved widely. Herein, the adsorption energy of intermediates in hydrogenation of acetylene were described as a function of the adsorption energy of CH_3 over Zn (0001), Ag (111), Pd (111) and Pt (111) surface. The results are shown in Fig.S7 and the function can be written as:

$E_{ad}(Int) = k \bullet E_{ad}(CH_3) + b$ (3)

where the $E_{ad}(Int)$ and $E_{ad}(CH_3)$ represent the adsorption energy of the intermediates and CH_3, respectively.

Then, the reaction energy of each elementary step can be calculated via $E_{ad}(Int)$. For example, for elementary step $A^*+B^* \rightarrow AB^*$,

$E_r=E_{ad}(AB)-E_{ad}(A)-E_{ad}(B)$ (4)

where the $E_{ad}(AB)$, $E_{ad}(A)$ and $E_{ad}(B)$represent the adsorption energy of A, B and AB, respectively, and they are referenced to a same criterion. Combined (3) and (4), we can construct the linear scaling relation between E_r of each elementary steps and E_{ad} of CH_3.

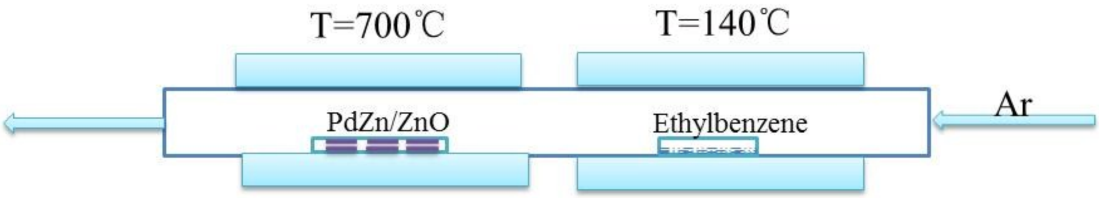


Figure S1. The synthesis strategy of PdZn@C/ZnO catalyst.

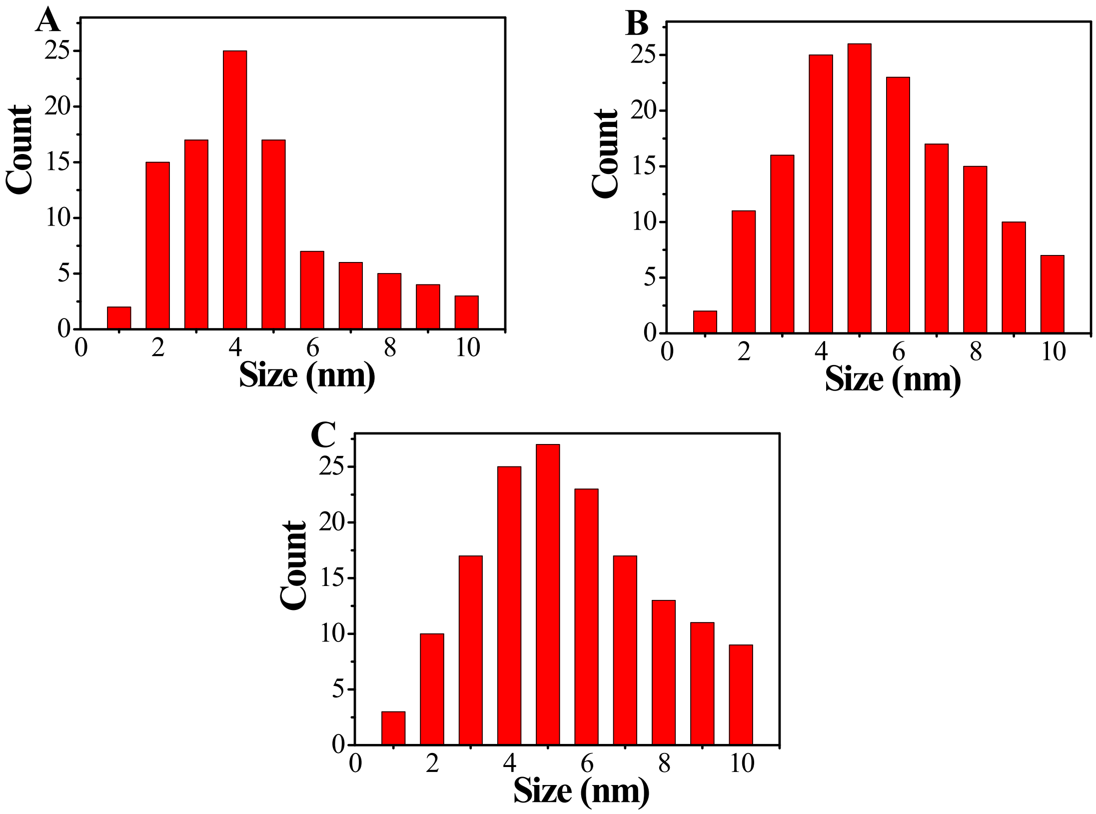


Figure S2. The size distribution of Pd NPs in (A) Pd/ZnO cataly, the size distribution of PdZn intermetallic alloy NPs in (B) PdZn/ZnO catalyst, (C) PdZn@C/ZnO catalyst.

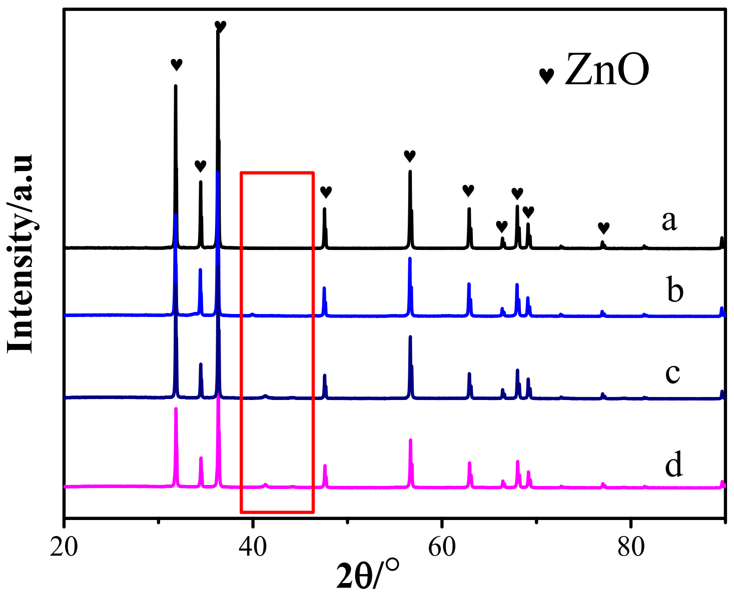


Figure S3. XRD patterns of (a) ZnO, (b) Pd/ZnO, (c) PdZn/ZnO and (d) PdZn@C/ZnO.

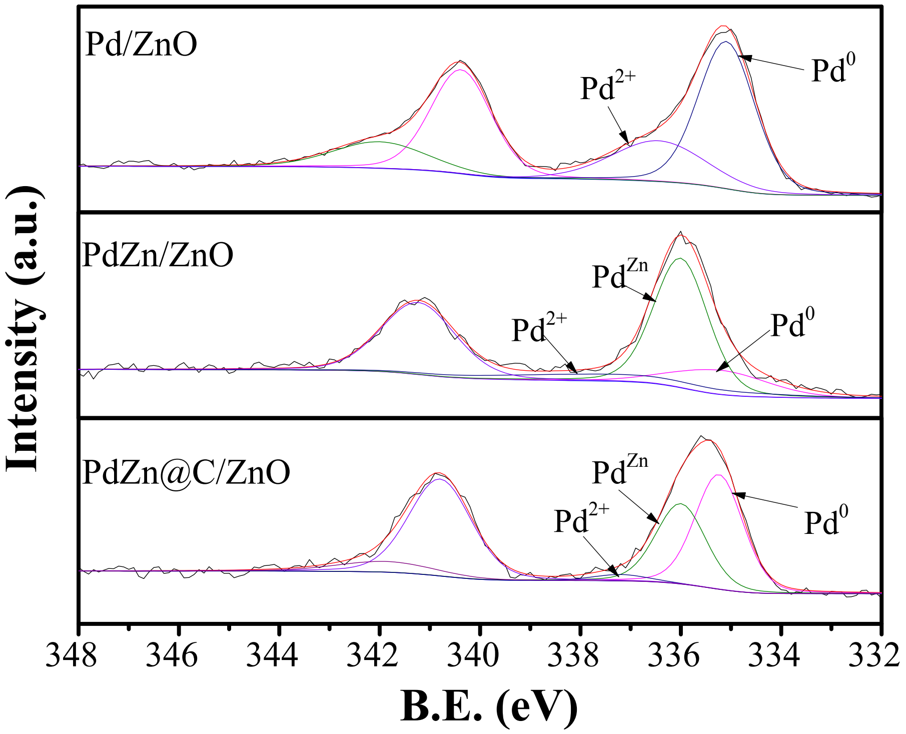


Figure S4. XPS spectra of Pd/ZnO, PdZn/ZnO and PdZn@C/ZnO.

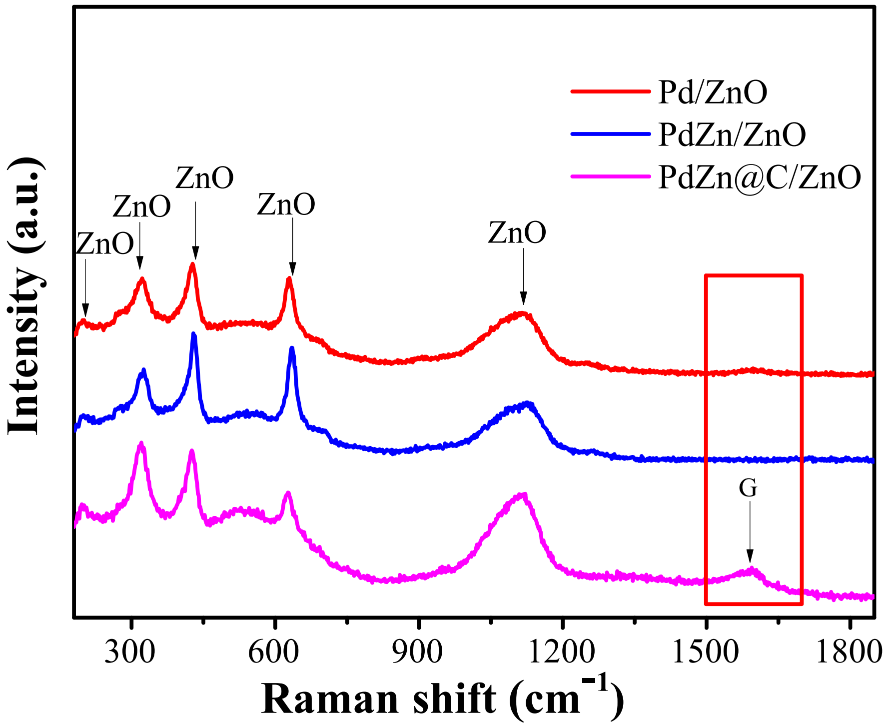
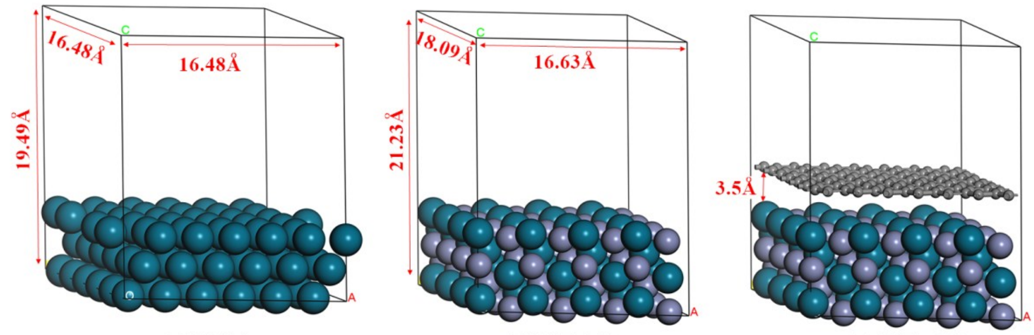


Figure S5. Raman spectra of the Pd/ZnO, PdZn/ZnO and PdZn@C/ZnO catalysts.



(a) Pd111 (b) PdZn111 (c) PdZn@C

Figure S6. Models of Pd (111) (a), PdZn (111) (b) and PdZn@C (c). The blue, purple and gray balls represent Pd, Zn and C atoms, respectively. The structure of PdZn@C is an ideal model, and the distance of 3.5 Å is an approximated average value. After the adsorption of intermediates, the distance will has a fluctuation, as shown in Fig,S7.

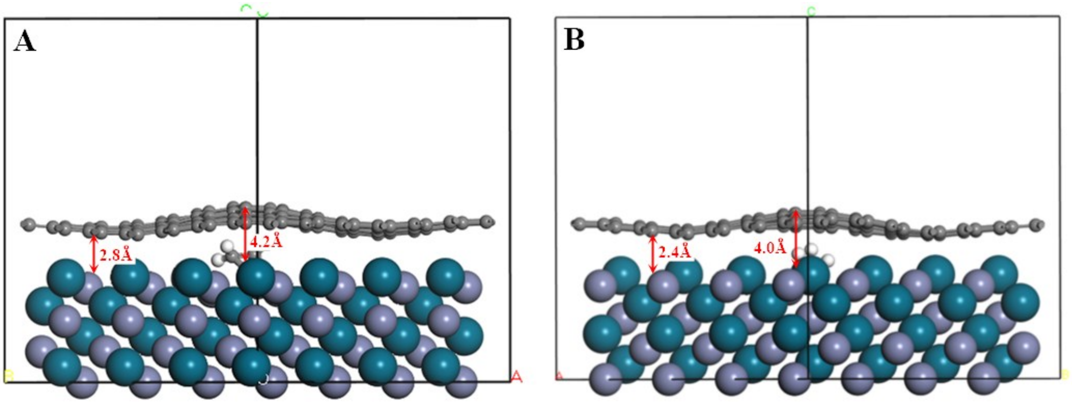


Figure S7. The adsorption structures of C_2H_4 (A) and CH_3 (B) on PdZn@Gr.

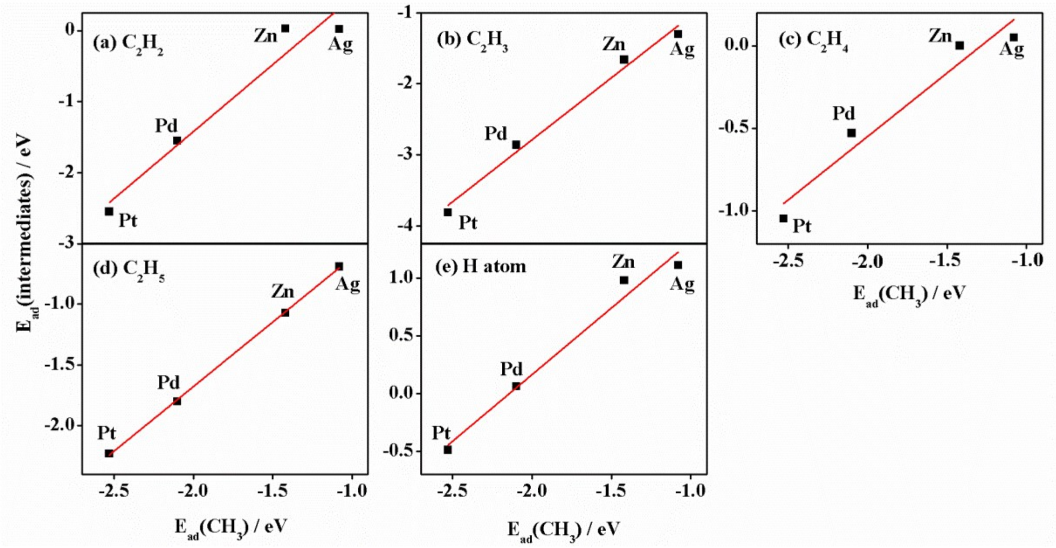


Figure S8. Scaling relation between the adsorption energy of CH_3 and that of intermediates in hydrogenation of acetylene

References

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