### Supporting Information

### Modulating the Electrocatalytic Semihydrogenation Selectivity of Alkynes from

### Water Electrolysis Using Pd-based Sulfides and Phosphides Cathode

Yibo Yan<sup>a</sup>, Peng Wang<sup>a,b</sup>, Jiangsheng Han<sup>d</sup> Aihua Wang<sup>b</sup>, Guofeng Zhang<sup>\*,b</sup>, Yingjun

Tian<sup>b</sup>, Yuyang Ge<sup>c</sup>, Wei Gao<sup>b</sup>, Ling Wang<sup>b</sup>, Zunqi Liu<sup>\*,a</sup>, Jianbin Chen<sup>\*a,b</sup>

<sup>a</sup>Chemistry and Chemical Engineering College, Xinjiang Agricultural University, Urumqi 830052, China
<sup>b</sup>School of Chemistry and Chemical Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353 China

<sup>c</sup>School of Chemistry and Chemical Engineering, Linyi University, Linyi 276000, China <sup>d</sup>ShanDongWeGo Pharmaceutical CO., LTD, Weihai 264414, China

#### **Experimental Section**

#### Preparation of Pd<sub>4</sub>S/Pd<sub>3</sub>P<sub>0.95</sub>

All the chemicals were of analytical grade purity and used as received without further purification. In a typical synthesis, 2 mL of 1-butyl-3-methylimidazolium chloride, 0.25 mmol (288.9 mg) of Tetrakis (triphenylphosphine) palladium (Pd[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub>) and 0.5 mmol of S<sub>8</sub> (16 mg) were dissolved or dispersed in 13 mL of anhydrous alcohol followed by magnetic stirring for 0.5 h, then the obtained mixture was transferred into a 20 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 30 h in an oven. Afterwards, the precipitates were collected by centrifuging, washed with dichloromethane and ethanol for several times, and dried in a vacuum at 60 °C overnight. By changing the amounts of added S<sub>8</sub> (4, 8, 16 and 24 mg), heterostructures of different compositions can be obtained. The corresponding samples were denoted to be HS4, HS8, HS16, and HS24, respectively.

### Preparation of Pd<sub>3</sub>P<sub>0.95</sub>

The synthesis procedure  $Pd_3P_{0.95}$  was similar with that of  $Pd_4S/Pd_3P_{0.95}$  but without adding  $S_8$ .

#### **Preparation of Pd<sub>4</sub>S**

The synthesis procedure of  $Pd_4S$  was also similar with that of  $Pd_4S/Pd_3P_{0.95}$ , except that the temperature was increased to 200 °C and the amount of added S8 was 24 mg.

#### Characterization

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus Diffraction system with Cu Ka radiation ( $\lambda = 0.15418$  nm) at V = 40 kV and I = 40 mA. Transmission electron microscope (TEM) images were recorded on a Tecnai G<sup>2</sup> F20 S-Twin transmission electron microscope at an accelerating voltage of 120 kV. The chemical states of the elements were determined by X-ray photoelectron spectroscopy (XPS) using Kratos Axis Ultra DLD multitechnique.

#### General procedure for electrochemical semihydrogenation of alkynes

Typically, 2 mg of Pd-based catalyst was dispersed in a suspension containing 960  $\mu$ L ethanol and 40  $\mu$ L 5% Nafion solution by sonicating for 30 min. Then the homogeneous catalyst ink was spread uniformly on carbon fiber paper (CFP) as the working electrode, on which the area was controlled to 1 cm<sup>2</sup> with the loading amount of ~ 2 mg cm<sup>-2</sup>. Electrochemical measurements were carried out in a divided three-compartment electrochemical cell consisting of a working electrode, a Pt plate counter electrode, and a Hg/HgO reference electrode. The cathode cell (10 mL) and anode cell (10 mL) containing 0.5 M KOH solution (4.0 mL Diox and 3.0 mL H<sub>2</sub>O), respectively, were separated by the membrane. 0.2 mmol of alkynes were added into the cathode and

sonicated to form a homogeneous solution. Then, chronoamperometry was carried out at a given constant potential of -1.4 V vs. Hg/HgO. After that, the products at cathode were extracted with dichloromethane (DCM). The DCM phase was removed, and the residuals were subjected to be separated either by flash column chromatography or using thin-layer chromatography (TLC) plate to give the isolated yields or was analyzed by GC to provide the GC yields. The yields were calculated by dividing the amount of the obtained desired product by the theoretical yield. The GC yields were calculated according to standard calibration curves.



Figure S1. Local magnified XRD pattern of P-doped Pd<sub>4</sub>S.



**Figure S2.** a) XPS survey spectra, b) Pd 3d, c) S 2p, and d) P 2p high-resolution XPS spectra for P-doped Pd<sub>4</sub>S.



Figure S3. a, b) TEM images of P-doped Pd<sub>4</sub>S.



Figure S4. Elemental mapping images for P-doped Pd<sub>4</sub>S.



Figure S5. Elemental mapping images for Pd<sub>3</sub>P<sub>0.95</sub>.



Figure S6. Elemental mapping images for Pd<sub>4</sub>S.



Figure S7. Elemental mapping images for HS8.



Figure. S8 (a) XPS survey spectra, (b) Pd 3d, (c) P 2p, and (d) S 2p high-resolution

XPS spectra for  $Pd_4S$ ,  $Pd_3P_{0.95}$  and HS8.

X-ray photoelectron spectroscopy (XPS) spectra in Figure S8b showed the Pd 3d high-resolution spectra of Pd<sub>3</sub>P<sub>0.95</sub>, Pd<sub>4</sub>S and H8. Apparently, the binding energies of Pd<sup>0</sup> and Pd<sup>II</sup> species in these samples all positively shifted compared with that of palladium powder (Figure S9, Supporting Information) in the order of Pd<sub>3</sub>P<sub>0.95</sub>, Pd<sub>4</sub>S/Pd<sub>3</sub>P<sub>0.95</sub> and Pd<sub>4</sub>S from high to lower for the shift degree. These phenomena indicated that the electronic interaction between Pd and P(S), which induced electron transfer from Pd to P(S), weakening the 3d electron density of Pd.<sup>[1-3]</sup> In the S 2p and P 2p spectra (Figure S8c and 8d), the relative contents of SO<sub>x</sub><sup>-2</sup> and P-O species of HS8 were all lower than that of pure Pd<sub>4</sub>S and Pd<sub>3</sub>P<sub>0.95</sub>, indicating our synthesized Pd<sub>3</sub>P<sub>0.95</sub>/Pd<sub>4</sub>S heterostructures possessing stronger antioxidant capacity, which might be benefit to the electrochemical hydrogenation process.



Figure S9. Pd 3d high-resolution XPS spectra for Palladium powder.



Figure S10. Proposed mechanisms for semihydrogenation of: a) diphenylacetylene over  $Pd_3P_{0.95}$  cathode, b) 4-acetylene biphenyl over  $Pd_3P_{0.95}/Pd_4S$  cathode.



Scheme S1. [(E)-2-phenylethenyl] benzene as the substrate in the standard conditions



Figure S11. Failed substrates scope.



**Figure S12.** Selectivity profiles of  $P_3Pd_{0.95}$  catalysts for the products 4-ethylbiphenyl and 4-vinylbiphenyl in 1-4 hours.

### <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra (2a) 4-Vinylbiphenyl

<sup>1</sup>**H NMR** (400 MHz, CDCl3): $\delta$  7.63 (dd, J = 12.5, 7.6 Hz, 4H), 7.50 (dd, J = 23.0, 8.0 Hz, 4H), 7.39 (t, J = 7.4 Hz, 1H), 6.81 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (d, J = 17.6 Hz, 1H), 5.32 (d, J = 10.8 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  140.66, 140.51, 136.52, 136.35, 128.74, 127.27, 127.18, 126.91, 126.60, 113.86. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[4]</sup>

(2b) 4-(Trifluoromethyl)styrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.58 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (d, J = 17.4 Hz, 1H), 5.39 (d, J = 10.8 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  141.03, 135.71, 129.56, 126.48, 125.65, 125.63, 125.61, 125.57, 125.53, 116.58. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[4]</sup>

(2c) 4-Bromostyrene



<sup>1</sup>H NMR (400 MHz, CDCl3): $\delta$  7.45 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.65 (dd, J = 17.6, 10.9 Hz, 1H), 5.74 (d, J = 17.5 Hz, 1H), 5.28 (d, J = 10.9 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl3):  $\delta$  136.42, 135.68, 131.59, 127.73, 121.56, 114.58. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[5]</sup> (2d) 4-Fluorostyrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.42 – 7.34 (m, 2H), 7.05 – 6.99 (m, 2H), 6.69 (dd, J = 17.6, 10.9 Hz, 1H), 5.67 (d, J = 17.5 Hz, 1H), 5.23 (d, J = 10.9 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  162.55 (d, J = 247.0 Hz), 135.77, 133.81 (d, J = 3.4 Hz), 127.82 (d, J = 8.1 Hz), 115.49 (d, J = 21.6 Hz), 113.59. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[5]</sup>

### (2e) 4-Chlorostyrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.37 – 7.27 (m, 4H), 6.67 (dd, J = 17.6, 10.9 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.8 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  136.14, 135.77, 133.53, 128.77, 127.53, 114.56. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[5]</sup>

### (2f) 4-Vinylaniline



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.28 – 7.19 (m, 2H), 6.67 – 6.60 (m, 3H), 5.56 (d, J = 17.7 Hz, 1H), 5.05 (d, J = 10.9 Hz, 1H), 3.69 (s, 2H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  146.14, 136.48, 128.28, 127.30, 114.95, 109.96. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[6]</sup>

### (2g) 4-Methoxystyrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.32 – 7.19 (m, 2H), 7.03 – 6.94 (m, 2H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 9.9 Hz, 1H), 3.83 (s, 3H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  159.75, 138.99, 136.73, 129.48, 118.88, 114.13, 113.40, 111.46, 55.19. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[5,10]</sup>

### (2h) 3-Methylstyrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.26 – 7.22 (m, 3H), 7.09 (t, J = 4.4 Hz, 1H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 5.75 (d, J = 16.5 Hz, 1H), 5.24 (d, J = 10.9 Hz, 1H), 2.37 (s, 3H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  138.16, 137.60, 137.04, 128.68, 128.51, 127.03, 123.43, 113.69, 21.49. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[9]</sup>

### (2i) 3-Fluorostyrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.30 – 7.24 (m, 1H), 7.20 – 7.06 (m, 2H), 6.94 (td, J = 8.4, 2.6 Hz, 1H), 6.67 (dd, J = 17.6, 10.9 Hz, 1H), 5.75 (d, J = 18.4 Hz, 1H), 5.29 (d, J = 10.9 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  163.20 (d, J = 245.3 Hz), 139.99 (d, J = 7.6 Hz), 135.90 (d, J = 2.5 Hz), 130.04 (d, J = 8.3 Hz), 122.24 (d, J = 2.7 Hz), 115.28, 114.69 (d, J = 21.5 Hz), 112.70 (d, J = 21.7 Hz). <sup>1</sup>H and <sup>13</sup>C NMR spectrum of

the product were identical to that of the reference.<sup>[8]</sup> (2j) 3-Chlorostyrene



<sup>1</sup>**H NMR** (400 MHz, DMSO-d6):  $\delta$  7.30 (d, J = 1.2 Hz, 1H), 7.17 (dd, J = 2.7, 1.7 Hz, 1H), 7.15 (s, 1H), 7.13 (t, J = 2.4 Hz, 1H), 6.56 (dd, J = 17.6, 10.9 Hz, 1H), 5.66 (dd, J = 17.5, 0.7 Hz, 1H), 5.20 (d, J = 10.9 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, DMSO-d6)  $\delta$  139.48, 135.69, 134.59, 129.84, 127.84, 126.26, 124.55, 115.43. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[8]</sup> (2k) 3-Vinylanisole



<sup>1</sup>**H NMR** (400 MHz, CDCl3): $\delta$  7.26 (t, J = 7.9 Hz, 1H), 7.08 – 6.94 (m, 2H), 6.83 (dd, J = 8.7, 2.1 Hz, 1H), 6.71 (dd, J = 17.6, 10.8 Hz, 1H), 5.76 (dd, J = 17.6, 0.9 Hz, 1H), 5.27 (dd, J = 11.0, 0.9 Hz, 1H), 3.83 (s, 3H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  159.91, 139.13, 136.88, 129.62, 119.02, 114.25, 113.54, 111.62, 55.31, 30.43. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[8]</sup>

(2l) 2-Vinylnaphthalene



<sup>1</sup>**H** NMR (400 MHz, CDCl3):  $\delta$  7.86 – 7.74 (m, 4H), 7.65 (dd, J = 8.6, 1.8 Hz, 1H), 7.51 – 7.42 (m, 2H), 6.90 (dd, J = 17.6, 10.8 Hz, 1H), 5.89 (d, J = 17.6 Hz, 1H), 5.35 (d, J = 10.9 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl3):  $\delta$  137.02, 135.10, 133.64, 133.24, 128.25, 128.14, 127.76, 126.47, 126.33, 126.01, 123.26, 114.28. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[5]</sup>

### (2m) 2-Chlorostyrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3): $\delta$  7.57 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.25 – 7.08 (m, 3H), 5.75 (d, J = 17.5 Hz, 1H), 5.39 (d, J = 12.3 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  135.79, 133.28, 133.19, 129.73, 128.91, 126.92, 126.65, 116.64. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[9]</sup> (2n) 4-tert-Butylstyrene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.36 (s, 4H), 6.76 – 6.67 (m, 1H), 5.72 (dd, J = 17.6, 1.0 Hz, 1H), 5.20 (dd, J = 10.9, 1.0 Hz, 1H), 1.33 (s, 9H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  151.04, 136.74, 134.99, 126.07, 125.58, 113.15, 34.72, 31.43. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[6]</sup> (20) 2-Vinylthiophene



<sup>1</sup>**H NMR** (400 MHz, CDCl3):  $\delta$  7.18 (dd, J = 4.8, 1.6 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.83 (dd, J = 17.4, 10.8 Hz, 1H), 5.58 (d, J = 17.3 Hz, 1H), 5.15 (d, J = 10.8 Hz, 1H); <sup>13</sup>**C NMR** (101 MHz, CDCl3):  $\delta$  143.15, 129.96, 127.41, 125.90, 124.42, 113.35. (2p) (Z)-1, 2-diphenylethene



<sup>1</sup>H NMR (400 MHz, CDCl3): $\delta$  7.28 (dt, J = 16.5, 7.9 Hz, 10H), 6.66 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl3):  $\delta$  137.30, 130.31, 128.94, 128.28, 127.16. <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[4]</sup>

(2q) (Z)-1, 2-bis (4-fluorophenyl) ethene



<sup>1</sup>H NMR (400 MHz, CDCl3): $\delta$  7.23 – 7.15 (m, 4H), 6.97 – 6.89 (m, 4H), 6.54 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl3):  $\delta$  161.80 (d, J = 246.9 Hz), 133.52 – 132.78 (m), 130.44 (d, J = 7.8 Hz), 129.05, 115.44 (d, J = 64.5 Hz). <sup>1</sup>H and <sup>13</sup>C NMR spectrum of the product were identical to that of the reference.<sup>[7]</sup>

# Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Products (2a) 4-Vinylbiphenyl



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)





# (2b) 4-(Trifluoromethyl)styrene









# (2c) 4-Bromostyrene



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)



# (2d) 4-Fluorostyrene



(<sup>1</sup>H NMR, CDCl<sub>3</sub>, 400 MHz)





# (2e) 4-Chlorostyrene







# (2f) 4-Vinylaniline



# (2g) 4-Methoxystyrene



# (2h) 3-Methylstyrene



(<sup>13</sup>C NMR, CDCl<sub>3</sub>, 101 MHz)

# (<sup>13</sup>C NMR, CDCl<sub>3</sub>, 101 MHz)

50

40

30





(2i) 3-Fluorostyrene

7,228 7,229 7,229 7,229 7,229 7,229 7,229 7,229 7,229 7,220 7,200

# (2j) 3-Chlorostyrene



(<sup>1</sup>H NMR, DMSO-d6, 400 MHz)

- 130.48 - 135.69 - 126.26 - 124.59 - 124.59 - 124.55 - 115.43



(<sup>13</sup>C NMR, DMSO-d6, 101 MHz)

# (2k) 3-Vinylanisole



# (2l) 2-Vinylnaphthalene









# (2m) 2-Chlorostyrene









# (2n) 4-tert-Butylstyrene





# (20) 2-Vinylthiophene







160 150 140 150 120 110 100 90 50 70 60 50 40 30 20 10 6 Chemical Shift (ppm)

# (2p) (Z)-1, 2-diphenylethene









# (<sup>13</sup>C NMR, CDCl<sub>3</sub>, 101 MHz)



(2q) (Z)-1, 2-bis (4-fluorophenyl) ethene

Gas Chromatography-Mass Spectrometry (GC-MS) of the corresponding products

# (2a) 4-Vinylbiphenyl



### (2c) 4-Bromostyrene



# (2d) 4-Fluorostyrene



# (2e) 4-Chlorostyrene



# (2f) 4-Vinylaniline







# (2h) 3-Methylstyrene



# (2i) 3-Fluorostyrene







# (21) 2-Vinylnaphthalene



# (2m) 2-Chlorostyrene







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