Electronic Supplementary Information

Highly dispersed palladium nanoclusters anchored on nanostructured hafnium(IV) oxide as highly efficient catalysts for the Suzuki–Miyaura coupling reaction

Xiaoxue Wu, a Wenting Lin, a Li Wang, a Nan Li, a Gaomei Tu, a Yanghe Fu, a De-Li Chen, a
Weidong Zhu, a Guihua Chen b and Fumin Zhang a

aKey Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, 321004 Jinhua, People’s Republic of China
bSchool of Pharmaceutical and Material Engineering, Taizhou University, 318000 Jiaojiang People’s Republic of China

[*] Corresponding Author: E-mail: zhangfumin@zjnu.edu.cn
1. Experimental

1.1. Chemicals

All chemicals are commercially available and used directly without any treatment: hafnium (IV) chloride (HfCl$_4$, Strem, 99.9%), zirconium (IV) tetrachloride (ZrCl$_4$, Strem, 99.9%), 2-aminoterephthalic acid (NH$_2$-BDC, TCI, ≥98%), palladium chloride (PdCl$_2$, TCI, 98%), hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd., 37%), N, N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., ≥99.5%), methanol (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%), ethanol (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%), acetic acid (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%), acetonitrile (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%), acetone (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%), ethyl acetate (Sinopharm Chemical Reagent Co., Ltd., ≥99.5%), phenylboronic acid (C$_6$H$_7$BO$_2$, J&K, 99%), bromobenzene (C$_6$H$_5$Br, damas-beta, 98%), iodobenzene (C$_6$H$_5$I, Aldrich, 99%), chlorobenzene (C$_6$H$_5$Cl, Mreda, ≥99%), 2-bromobenzaldehyde (C$_7$H$_5$BrO, Meryer, 98%), 3-bromobenzaldehyde (C$_7$H$_5$BrO, Aldrich, 97%), 4-bromobenzaldehyde (C$_7$H$_5$BrO, Aldrich, 99%), 4-bromotoluene (C$_7$H$_7$I, Aldrich, 99%), 2-bromotoluene (C$_7$H$_7$I, Meryer, 99%), 4-iodotoluene (C$_7$H$_7$I, Aldrich, 99%), 4-bromoanisole (C$_7$H$_7$I, Aldrich, 99%), potassium carbonate (K$_2$CO$_3$, Aldrich, 99.5%), caesium carbonate (Cs$_2$CO$_3$, Meryer, 99.9%), sodium hydroxide (NaOH, Kermel, >96%), sodium carbonate (Na$_2$CO$_3$, Sinopharm Chemical Reagent Co., Ltd., ≥99.8%), natrium bicarbonate (NaHCO$_3$, Sinopharm Chemical Reagent Co., Ltd., ≥99.8%), and triethylamine (C$_6$H$_{15}$N, Aldrich, ≥99%). Deionized water with a resistance >18.2 MΩ was obtained from a Millipore

1.2. Characterization

The X-ray powder diffraction (XRD) patterns were obtained on a Philips PW3040/60 diffractometer using Cu Kα radiation (λ=0.1541 nm, 40 kV, 30 mA).

N₂ adsorption isotherms were measured at -196 °C on a Micromeritics ASAP 2020 instrument. The samples were outgassed under vacuum at 200 °C for 12 h before adsorption measurement. The surface area was determined using the Brunauer-Emmett-Teller (BET) method.

The morphology of the samples were obtained by field emission SEM on a scanning electron microscope (a Hitachi S-4800 microscope) and TEM on a transmission electron microscope (JEM2100F, JEOL, Japan) working at 200 kV.

X-ray photoelectron spectroscopy (XPS) data were collected on an ESCALAB250 electron spectrometer from VG Scientific using 300 W Al-Kα radiation. The XPS data were internally calibrated, fixing the binding energy of C 1s at 284.8 eV.

The surface properties of the catalysts were measured by temperature-programmed desorption of ammonia (NH₃-TPD, a Micro-meristics AutoChem II 2920 instrument). The sample (150 mg) was purged under a flow of He of 30 mL/min at 350 °C for 2 h. After purging, the sample was cooled to 110 °C, and the feed composition was switched to a mixture containing 20% NH₃ in He (30 mL/min) for 30 min. The physisorbed ammonia was flushed out with He flow for 1 h. Afterward, the sample cell was heated at
10 °C/min under He to 900 °C. The concentration of the desorbed ammonia was monitored continuously with a TCD detector.

The amounts of the metal Pd species in the different samples were determined by an IRIS Intrepid II XSP inductively coupled plasma-atomic emission spectrometer (ICP-AES).

Electron Paramagnetic Resonance (EPR) measurement was obtained on the Bruker EPR EMXplus-9.5/12 at room temperature. The frequency and power of the microwave were set to 9.847226 GHz and 2.0000 mW, respectively. Gauss field modulation at 100 kHz and a time constant of 20 ms was used for detection.

The nuclear magnetic resonance (NMR) spectra of the products were recorded on a Bruker Avance 600 MHz spectrometer at 297 K using CDCl₃ (δ H=7.26, δ C=77.0) as an internal standard for ¹H NMR and 125 MHz for ¹³C NMR.

1.3. Catalyst preparation

Synthesis of Pd@NH₂-UiO-66(Hf)

Pd@NH₂-UiO-66(Hf) was synthesized by a one-pot strategy according to the procedure reported in the previous papers with some slight modification.¹ Briefly, HfCl₄ (4.7 mmol) and NH₂-BDC (4.7 mmol) were dissolved in DMF (200 mL) in a round-bottom flask (500 mL in capacity) and then added acetic acid (36 mL), deionized water (5.0 mL), and PdCl₂ precursor (0.5 mL, 10 mg/mL) to the solution. The mixture was treated under ultrasound for 10 min to form a homogeneous solution. Afterward, the mixture was heated at 75 °C for 20 h. Subsequently, the temperature was raised to 130 °C, and the mixture was allowed to stir for another 4 h, and then cooled to room
temperature. The product was centrifugated at 9000 rpm for 4 min, washed with DMF and methanol three times, respectively, and finally dried under vacuum at 120 °C for 12 h. Other control samples, including Pd@NH2-UiO-66(Zr), NH2-UiO-66(Zr), and NH2-UiO-66(Hf), were also synthesized by a similar method.

**Synthesis of Pd/HfO2@CN**

The Pd/HfO2@CN powders were fabricated directly via one-step pyrolysis strategy. Typically, the Pd@NH2-UiO-66(Hf) precursor (0.1 g) was transferred into a tube furnace. The furnace was heated at 600 °C at a rate of 3 °C/min with nitrogen gas flow (flow rate: 100 ml/min). The furnace was held at this temperature for 3 h and then allowed to cool to room temperature. Before use, the obtained powder was further reduced in a stream of hydrogen (H2)/N2 (10:40 mL/min) at 250 °C for 4 h. Pd/ZrO2@CN was prepared following the same procedure.
Fig. S1 XRD patterns of simulated UiO-66, the synthesized Pd@NH₂-UiO-66(Hf) and Pd@NH₂-UiO-66(Zr).

Fig. S2 N₂ adsorption–desorption isotherms of NH₂-UiO-66(Zr), Pd@NH₂-UiO-66(Zr), NH₂-UiO-66(Hf), and Pd@NH₂-UiO-66(Hf).
Fig. S3 TEM images of Pd@HfO$_2$ (a and b) and Pd@ZrO$_2$ (c and d).

Fig. S4 XRD pattern of Pd/HfO$_2$(Im).
Fig. S5 SEM (a), TEM (b), and HRTEM (c) images of Pd/HfO$_2$(Im).
Fig. S6 XRD pattern of Pd@HfO$_2$(air).

Fig. S7 N$_2$ adsorption–desorption isotherms of Pd@HfO$_2$(air).
Fig. S8 SEM (a), TEM (b), and HRTEM (c) images of Pd@HfO$_2$(air).
Fig. S9 XRD patterns of the fresh and used Pd@HfO$_2$ catalyst.

Fig. S10 N$_2$ adsorption isotherms of the spent Pd@HfO$_2$ catalyst.
Fig. S11 High resolution XPS spectrum of Pd 3d for the spent Pd@HfO₂ catalyst.

Fig. S12 TEM (a) and HRTEM (b) images of the spent Pd@HfO₂ catalyst.
The Pd@HfO$_2$ has more oxygen vacancies in comparison with that of Pd/HfO$_2$(Im), likely owning to the strong interaction between HfO$_2$ and Pd formed during the two-step thermal treatment, which is beneficial for forming a highly stable catalyst.
Table S1  Suzuki-Miyaura cross-coupling reaction of bromobenzene and arylboronic acids using palladium catalysts

![Reaction Scheme](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>R</th>
<th>Products</th>
<th>T</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Pd@HfO₂</td>
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<td><img src="image" alt="Product" /></td>
<td>50</td>
<td>&gt;99</td>
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<td>2</td>
<td>Pd@NH₂-UiO-66(Hf)</td>
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<td><img src="image" alt="Product" /></td>
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<td>41</td>
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<td>Pd/HfO₂@CN</td>
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<td><img src="image" alt="Product" /></td>
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<td>Pd/ZrO₂@CN</td>
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<tr>
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<td>4-CH₃</td>
<td><img src="image" alt="Product" /></td>
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<td>2-CH₃</td>
<td><img src="image" alt="Product" /></td>
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<td>70</td>
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</table>

Reaction conditions: bromobenzene (0.32 mmol), arylboronic acid (0.38 mmol), K₂CO₃ (0.38 mmol), Ethanol/H₂O = 1:1 (4.0 mL), catalyst (0.1 mol%), 2 h.
Table S2 Comparison of catalytic activity for the Suzuki-Miyaura coupling reaction over different catalysts.

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Yield</th>
<th>Ref.</th>
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</thead>
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<td></td>
<td></td>
<td>Catalyst/solvent/base/temperature/time</td>
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<tr>
<td>1</td>
<td>Pd@HfO$_2$</td>
<td>0.1 mol% catalyst/EtOH: H$_2$O (1:1)/K$_2$CO$_3$ (1.2 equiv)/50 °C/2 h</td>
<td>&gt;99</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>Pd-Pt Nanodendrites</td>
<td>4 mg catalyst/EtOH: H$_2$O (1:1)/Cs$_2$CO$_3$ (1.2 equiv)/80 °C/2 h</td>
<td>98</td>
<td>2</td>
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<td>3</td>
<td>Pd@porous SiO$_2$</td>
<td>0.003 mol% catalyst/DMF: H$_2$O (21:1)/Cs$_2$CO$_3$ (2.0 equiv)/200 °C/1 h</td>
<td>100</td>
<td>3</td>
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<tr>
<td>4</td>
<td>Pd/Porous-nanorods-CeO$_2$</td>
<td>0.3 mol% catalyst/DMF: H$_2$O (1:1)/K$_2$CO$_3$ (3.0 equiv)/90 °C/1 h</td>
<td>72.3</td>
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<tr>
<td>5</td>
<td>Pd@Mesoporous Carbon</td>
<td>2 mol% catalyst/EtOH: H$_2$O (1:1)/Na$_2$CO$_3$ (2.0 equiv)/80 °C/1 h</td>
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<td>6</td>
<td>Pd@Fluorescent Material</td>
<td>0.05 mol% catalyst/H$_2$O/K$_2$CO$_3$ (2.0 equiv)/80 °C/10 h</td>
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<td>7</td>
<td>Pd-TiO$_2$/Carbon Nanofibers</td>
<td>10 mg catalyst/H$_2$O/K$_2$CO$_3$ (2.0 equiv)/50 °C/5 h</td>
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<td>8</td>
<td>SiO$_2$/(Tetraethylene glycol)/Pd</td>
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<td>9</td>
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<tr>
<td>No.</td>
<td>Catalyst System</td>
<td>Initial Conditions</td>
<td>% Yield</td>
<td>Reaction Time</td>
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<td>Pd/Pr</td>
<td>0.4 mol% catalyst/DMF: H₂O (1:3)/K₂CO₃ (3.0 equiv)/85 °C/10 h</td>
<td>86</td>
<td>10</td>
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<tr>
<td></td>
<td></td>
<td>Coordination Polymers</td>
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</tr>
<tr>
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<td>(1:1)/K₂CO₃ (2.0 equiv)/70 °C/3 h</td>
<td></td>
<td></td>
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<tr>
<td>11</td>
<td>Pd@gel-Fe₃O₄</td>
<td>1 mol% catalyst/MeOH/Na₂CO₃ (3.0 equiv)/60 °C/5 h</td>
<td>89</td>
<td>11</td>
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<tr>
<td>12</td>
<td>Pd/TiO₂</td>
<td>0.7 mol% catalyst/NMP: H₂O (2.5:1)/Na₂CO₃ (1.5 equiv)/120 °C/4 h</td>
<td>91</td>
<td>12</td>
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<tr>
<td>13</td>
<td>Pd/Fe₃O₄ NPs</td>
<td>0.2 mol% catalyst/MeOH/K₂PO₄ (3.0 equiv)/60 °C/18 h</td>
<td>91</td>
<td>13</td>
</tr>
</tbody>
</table>
Reference
Analytical data of the products

biphenyl

![biphenyl structure]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta=7.89–7.73$ (m, 1H), 7.71–7.58 (m, 1H), 7.61–7.40 (m, 1H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta=141.41$ (s), 128.96 (s), 128.78 (s), 127.40 (d, $J=14.0$).

2-biphenylcarboxaldehyde

![2-biphenylcarboxaldehyde structure]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta=10.02$ (s, 1H), 8.07 (dd, $J=7.8$, 1.1, 1H), 7.66 (td, $J=7.5$, 1.3, 1H), 7.58–7.44 (m, 5H), 7.44–7.37 (m, 2H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta=192.44$, 145.99, 137.77, 133.74, 133.60, 130.82, 130.14, 128.47, 128.16, 127.81, 127.59.

4-biphenylcarboxaldehyde

![4-biphenylcarboxaldehyde structure]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta=10.05$ (s, 1H), 7.95 (d, $J=8.0$, 2H), 7.74 (d, $J=8.0$, 2H), 7.64 (d, $J=7.5$, 2H), 7.47 (dt, $J=33.0$, 7.3, 3H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta=191.98$ (s), 147.11 (s), 139.66 (s), 135.70 (s), 135.23 (s), 132.75 (s), 130.32 (s), 129.10 (s), 128.57 (s), 128.00 (d, $J=18.7$), 127.67 (s), 127.40 (s), 127.18 (s).

4-methoxybiphenyl

![4-methoxybiphenyl structure]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta=7.67–7.59$ (m, 1H), 7.50 (s, 1H), 7.39 (t, $J=7.4$, 1H), 7.06 (d, $J=8.7$, 1H), 3.91 (s, 1H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta=159.22$ (s), 140.89 (s), 133.83 (s), 128.81 (s), 128.23 (s), 126.78 (d, $J=9.9$), 114.28 (s), 55.39 (s).

2-phenyltoluene

![2-phenyltoluene structure]

$^1$H NMR (600 MHz, CDCl$_3$) $\delta=7.77–7.35$ (m, 1H), 2.67–2.48 (m, 1H).  
$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta=142.21$ (t, $J=5.7$), 135.53 (d, $J=2.7$), 130.55 (d, $J=4.6$), 130.05 (d, $J=4.6$), 129.43 (d, $J=4.4$), 128.98 (s), 128.31 (d, $J=4.6$), 127.50 (d, $J=4.7$), 127.00 (d, $J=4.3$), 126.03 (d, $J=5.0$), 20.73 (s).
4-phenyltoluene

\[
\text{\includegraphics[width=1cm]{4-phenyltoluene.png}}
\]

$^1$H NMR (600 MHz, CDCl$_3$) δ=7.74 (dd, $J$=8.3, 1.2, 1H), 7.66 (d, $J$=8.1, 1H), 7.58 (t, $J$=7.8, 1H), 7.48 (s, 1H), 7.40 (d, $J$=7.9, 1H), 2.55 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ=141.32 (s), 138.51 (s), 137.13 (s), 129.64 (s), 128.87 (s), 128.69 (s), 127.34–127.06 (m), 126.96 (s), 21.24 (s).

4-nitrobiphenyl

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\text{\includegraphics[width=1cm]{4-nitrobiphenyl.png}}
\]

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.35–8.30 (m, 1H), 7.78–7.74 (m, 1H), 7.67–7.64 (m, 1H), 7.55–7.45 (m, 2H), 7.28 (s, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 147.66 (s), 138.79 (s), 129.17 (s), 128.93 (s), 127.82 (s), 127.40 (s), 124.13 (s).
Figs. S14-S19 $^1$H and $^{13}$C NMR spectra of coupling products.

Fig. S14 $^1$H and $^{13}$C NMR spectra for biphenyl.
Fig. S15 $^1$H and $^{13}$C NMR spectra for 2-biphenylcarboxaldehyde.
Fig. S16 $^1$H and $^{13}$C NMR spectra for 4-biphenylcarboxaldehyde.
Fig. S17 $^1$H and $^{13}$C NMR spectra for 4-methoxybiphenyl.
Fig. S18 $^1$H and $^{13}$C NMR spectra for 2-phenyltoluene.
Fig. S19 $^1$H and $^{13}$C NMR spectra for 4-phenyltoluene.
Fig. S20 $^1$H and $^{13}$C NMR spectra for 4-nitro biphenyl.
**MS spectra**

**Fig. S21** MS spectra of the biphenyl.

**Fig. S22** MS spectra of the 2-biphenylcarboxaldehyde.
Fig. S23 MS spectra of the 3-biphenylcarboxaldehyde.

Fig. S24 MS spectra of the 4-biphenylcarboxaldehyde.
**Fig. S25** MS spectra of the 4-methoxybiphenyl.

**Fig. S26** MS spectra of the 4-phenyltoluene.
Fig. S27 MS spectra of the 2-phenyltoluene.

Fig. S28 MS spectra of the 4-nitrobiphenyl.