Electronic Supplementary Information for

Germanium-Regulated Adsorption Site Preference on Ruthenium Electrocatalyst for Efficient Hydrogen Evolution

Meihong Fan, a,b Bo Zhang, c Lina Wang, a Zhenyu Li, a Xiao Liang, a Xuan Ai a and Xiaoxin Zou* a

a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China
b State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun, 130012, China
c International Center of Future Science, Jilin University, Changchun, 130012 China

* E-mail: xxzou@jlu.edu.cn
1. Theoretical Section

1.1. Computation Details.

All the calculations were performed by using the Perdew-Burke-Ernzerhof (PBE)[1] exchange-correlation functional within the generalized gradient approximation (GGA) in the framework of Vienna *ab initio simulation package* (VASP)[2-3] based on the density functional theory (DFT). For all the structural relaxations and electronic structure calculations, the cut off energy of plane-wave set[4] was 400 eV, while the convergence threshold was set as 0.02 eV/Å in force and 10⁻⁴ eV in energy. For the bulk calculations, the Brillouin zones were sampled by Monkhorst-Pack 11×11×7 and 5×5×5 k-point grid for Ru and RuGe, respectively. For the slab models, the appropriate Monkhorst-Pack k-point meshes 5×5×1 for Ru and 3×3×1 for RuGe were employed. A 5×5×1 Monkhorst-Pack grid was used for the DOS calculations of slab models.[5] During the surface calculations, the symmetrization was switched off and the dipolar correction was included. The DFT-D2 method[6] was used to correct the *van der Waals* interaction. The crystal orbital Hamiltonian population (COHP) was obtained by LOBSTER code.[7-10]

For the slab models, we constructed 2 × 2 supercells for Ru and RuGe by cleaving the bulk structure along the (001) direction, and both of them contain 4 metal atom layers. A vacuum layer of 15 Å between slabs was added to avoid inter-layer interactions, and the upper half of atom layers were relaxed while the remaining were kept frozen during the slab calculations.


The Gibbs free-energy ($\Delta G_{H^*}$) of the hydrogen adsorption for different sites was calculated by the formula: $\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T \Delta S$. $\Delta E_{H^*}$ is the adsorption energy, which is defined as $\Delta E_{H^*} = E(\text{surface} + \text{H}) - E(\text{surface}) - 1/2 E(\text{H}_2)$, where $E(\text{surface} + \text{H})$ and $E(\text{surface})$ are the energy of one hydrogen atom adsorbed on the surface and the bare surface, while $E(\text{H}_2)$ is the energy of a gas phase H₂ molecule. $\Delta ZPE$ and $\Delta S$ are the zero point energy and entropy change.[11] $\Delta ZPE$ can be calculated by using the equation $\Delta ZPE = ZPE(\text{H}^*) - 1/2 ZPE(\text{H}_2)$, and $T \Delta S$ can be obtained from the equation $T \Delta S \approx -1/2 TS(\text{H}_2)$. Since $TS(\text{H}_2)$ is 0.41 eV for H₂ at 298K and 1atm, the corresponding $T \Delta S \approx -0.205$ eV.
Table S1 The energy $E$ (eV) and formation enthalpy $\Delta H$ (eV) per formula unit for various structures.

<table>
<thead>
<tr>
<th>Formula</th>
<th>RuGe</th>
<th>MgCl$_2$</th>
<th>RuCl$_3$</th>
<th>Ru</th>
<th>Mg</th>
<th>Ge</th>
<th>Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(eV)</td>
<td>$-15.370$</td>
<td>$-10.779$</td>
<td>$-16.771$</td>
<td>$-9.204$</td>
<td>$-1.536$</td>
<td>$-4.480$</td>
<td>$-3.594$</td>
</tr>
<tr>
<td>Formation enthalpy (eV)</td>
<td>$-1.326$</td>
<td>$-5.649$</td>
<td>$-2.176$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The formation enthalpies per formula unit of RuGe, MgCl$_2$ and RuCl$_3$ were calculated by

$\Delta H_f$(RuGe) = [E(RuGe) − E(Ru) − E(Ge)].

$\Delta H_f$(MgCl$_2$) = [E(MgCl$_2$) − E(Mg) − E(Cl$_2$)].

$\Delta H_f$(RuCl$_3$) = [E(RuCl$_3$) − E(Ru) − 1.5E(Cl$_2$)].

The reaction enthalpies of route I and route II were calculated according to the reaction equations of

**Route I:** Ru + Ge = RuGe

**Route II:** RuCl$_3$ + Ge + 1.5Mg = RuGe + 1.5MgCl$_2$

Their reaction enthalpies were calculated according to the formula:

$$\Delta H_R = \Delta H_f(R) - \Delta H_f(S)$$  \hspace{1cm} (1)

$\Delta H_f(S)$ and $\Delta H_f(R)$ are formation enthalpies of the starting and resulting compounds, which are listed are listed in **Table S1**.
2. Experimental Section

2.1. Chemicals and Reagents.
Ruthenium(III) chloride (RuCl$_3$), molybdenum(V) chloride (MoCl$_5$, 99.6%), palladium chloride (PdCl$_2$, 99.9%), platinum tetrachloride (PtCl$_4$, 99.9%), ruthenium oxide (RuO$_2$, 99.9%), germanium powder (Ge, 99.9%), ruthenium powder (Ru, 99.9%) were purchased from Aladdin Chemistry Co., Ltd. Magnesium powder (Mg) was purchased from Shantou Xilong Chemical Factory. Isopropanol ((CH$_3$)$_2$CHOH) and Sulfuric acid (H$_2$SO$_4$) were purchased from Beijing Chemical Factory. Nafion$^\text{®}$ perfluorinated resin solution were purchased from Sigma-Aldrich. Highly purified water (> 18 MΩ cm resistivity) was obtained from a PALL PURELAB Plus system.

2.2 Materials Synthesis.

**Synthesis of RuGe.** RuCl$_3$ (51.9 mg, 0.25 mmol), Ge (7.0 mg, 0.25 mmol) and Mg (14.6 mg, 0.5 mmol) were transferred into a quartz tube, which was then sealed in a vacuum atmosphere (1.0 Pa). Next, the sealed quartz tube was heated at 800 °C for 4 h. The obtained product was treated in a 0.5 M H$_2$SO$_4$ solution to remove redundant Mg and by-product (i.e., MgCl$_2$). Finally, the resulting sample was washed several times with deionized water and ethanol, and vacuum dried at 80 °C.

**Synthesis of MoGe$_2$.** MoCl$_5$ (68.3 mg, 0.25 mmol), Ge (36.3 mg, 0.5 mmol) and Mg (15.2 mg, 0.63 mmol) were transferred into a quartz tube, which was then sealed in a vacuum atmosphere (1.0 Pa). Next, the sealed quartz tube was heated at 800 °C for 4 h. The obtained product was treated in the same method as the RuGe.

**Synthesis of PtGe.** PtCl$_4$ (84.2 mg, 0.25 mmol), Ge (18.2 mg, 0.25 mmol) and Mg (14.6 mg, 0.5 mmol) were transferred into a quartz tube, which was then sealed in a vacuum atmosphere (1.0 Pa). Next, the sealed quartz tube was heated at 800 °C for 4 h. The obtained product was treated in the same method as the RuGe.

**Synthesis of Pd$_2$Ge.** PdCl$_2$ (44.3 mg, 0.25 mmol), Ge (18.2 mg, 0.25 mmol) and Mg (7.3 mg, 0.25 mmol) were transferred into a quartz tube, which was then sealed in a vacuum atmosphere (1.0 Pa). Next, the sealed quartz tube was heated at 700 °C for 4 h. The obtained product was treated in the same method as the RuGe.

**Synthesis of Ru.** RuCl$_3$ (51.9 mg, 0.25 mmol) and Mg (14.6 mg, 0.6 mmol) were transferred into a quartz tube, which was then sealed in a vacuum atmosphere (1.0 Pa). Next, the sealed quartz tube was heated at 700 °C for 4 h. The obtained product was treated in the same method as the RuGe.

**Synthesis of Pt.** PtCl$_4$ (84.2 mg, 0.25 mmol) and Mg (24.3 mg, 1.0 mmol) were transferred into a quartz tube, which was then sealed in a vacuum atmosphere (1.0 Pa). Next, the sealed quartz tube was heated at 500 °C for 4 h. The obtained product was treated in the same method as the RuGe.

2.3. Characterizations.
Powder X-ray diffraction (XRD) were collected using a Rigaku D/Max 2550 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscope (SEM) images were obtained with a JEOL JSM 7800F electron microscope. The transmission electron microscope (TEM) and high
resolution TEM (HRTEM) images were recorded on a Philips-FEI Tecnai G2STwin microscope equipped with a field emission gun operating at 200 kV. X-ray photoemission spectroscopy (XPS) studies were performed on a Thermo Fisher Scientific ESCALAB 250Xi with photoelectron spectroscopy system using a monochromatic Al Ka (1486.6 eV) X-ray source.

2.4. Electrochemical Measurements.

Electrochemical measurements were carried out using a CH Instrument (Model 660E) with a conventional three-electrode system: glassy carbon electrode (GCE) loaded with catalyst as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and carbon rod as the counter electrode. The electrolyte was 0.5 M H\textsubscript{2}SO\textsubscript{4} solution.

The calomel electrode calibration was performed according to the method used by our group previously,[14] and the calibrated value (\(E\text{vs.SCE}\)) was 0.267 V. Calibrations were performed using a reversible hydrogen electrode (RHE), which was made up of two Pt as working electrode and counter electrode, and SCE as reference electrode, respectively. H\textsubscript{2} is bubbled over the working electrode. Two Pt electrodes were cleaned and cycled in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution (about ± 2 V) prior to use. The electrolyte was saturated with hydrogen before use and hydrogen was bubbled over the working electrode during the test. The wide-ranged Linear sweep voltammetry (LSV) was measured in a cathode to determine possible zero-current potential. Then controlled potential chronoampermetric tests were performed to further determine the zero-current potential. It was necessary to stabilize for 300 s to reach the steady state value under each potential.

The working electrode was prepared by the following steps: (1) 4 mg of catalyst was uniformly dispersed in 200 μL of isopropanol and 200 μL of conductive polymer binder (0.3% Nafion solution); (2) 4 μL of this solution was dropped onto a GCE with a diameter of 3 mm, and then dried in the air; (3) 1 μL of 0.3% Nafion solution was dropped on top and dried. The loading mass was 0.56 mg cm\textsuperscript{-2}.

LSV measurements were performed with the scan rate of 1 mV/s and 85% \(iR\)-compensation. Chronopotentiometric measurements were studied at a current density of 10 mA cm\textsuperscript{-2} without \(iR\)-compensation. The obtained potentials were converted to the potentials vs reversible hydrogen electrode (RHE) according to the formula:

\[
E\text{vs.RHE} = E\text{vs.SCE} + 0.267 \text{eV} + 0.059 \text{pH}
\]

The geometric current density \(j_{geo}\) (mA cm\textsuperscript{-2}) was normalized by the geometric area of working electrode according to the formula:

\[
j_{geo} = \frac{i \times 1000}{S}
\]

where \(i\) (A) is the obtained current, and \(S\) is the geometric area of working electrode (0.071 cm\textsuperscript{2}).

The mass activity of ruthenium \(j_{Ru}\) (A g\textsuperscript{-1}) was obtained by normalizing the measured current with respect to the mass of ruthenium according to the following equations:

\[
j_{Ru} = \frac{i \times 1000}{m \times WRu}
\]
where $i$ (A) is the obtained current, $m$ is catalyst mass loading $(4 \times 10^{-5}$ g), and $W_{R\text{u}}$ is weight percent of ruthenium (wt%) in the catalyst.

The specific activity $j_{\text{ECSA}}$ (mA cm$^{-2}$) was normalized by the electrochemical active surface area (ECSA) according to the formula:

$$j_{\text{ECSA}} = \frac{i}{1000 \frac{\text{ECSA}}{\text{mA cm}^{-2}}}$$

(5)

where $i$ (A) is the obtained current, and ECSA is the corresponding electrochemical surface area of catalyst.

The ECSA of catalyst was estimated by CO stripping experiments.$^{[15]}$ 99.99% pure CO was purged to the cells filled with 0.5 M H$_2$SO$_4$ electrolyte for 30 min, while the working electrode was held at 0.02 V vs. SCE. Before the measurements, N$_2$ was then purged to the system for 30 min to remove non-adsorbed CO. The CO stripping was performed in the potential range of -0.2~1.0 V at a scan rate of 0.5 V s$^{-1}$ (Fig. 3b). Assuming that the Coulombic charge required for the oxidation of the CO monolayer was 0.42 mC cm$^{-2}$, and the ECSA was calculated according to the formula:

$$ECSA = \frac{Q_{\text{CO}}}{m \times 0.42 \left( \frac{\text{mC cm}^{-2}}{\text{mC cm}^{-2}} \right)} = \frac{S_{\text{CO}}}{V}$$

(6)

Where $Q_{\text{CO}}$ is the CO stripping charge, $V$ is scan rate, and $m$ is catalyst mass loading $(4 \times 10^{-5}$ g).

### 2.5. TOF calculation.

The turnover frequency (TOF, H$_2$ s$^{-1}$) can be estimated by using the following equation:

$$\text{TOF} = \frac{i}{2nF}$$

(7)

where $i$ is the current during the LSV measurement; the factor, 2, is the number of electron involved in HER reaction; $F$ is the Faraday constant (96485 C mol$^{-1}$); $n$ is the number of active sites on corresponding electrode.

It is difficult to accurately estimate the number of active sites ($n$) in heterogeneous catalysis. There are usually two methods: (i) only quantifying the number of surface active sites on catalyst ($n_1$) to give a upper limit of TOF (TOF$_1$)$^{[15]}$ (ii) considering all metal atoms loaded on the electrode as active sites ($n_2$) to give a lower limit of TOF (TOF$_2$)$^{[16]}$. The calculated TOF$_1$ and TOF$_2$ values are shown in Table S2.

#### $n_1$ calculation. The CO stripping method was used for quantifying the number of surface active sites on catalysts.$^{[17,18]}$ In this method, $n_1$ (mol) was calculated on basis of the CO stripping charge ($Q_{\text{CO}}$) with the following equation:

$$n_1 = \frac{Q_{\text{CO}}}{2F}$$

(8)
where \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), and \( Q_{CO} \) is the CO stripping charge.

**n\(_2\) calculation.** \( n_2 \) (mol) was the number of whole metal loading in the catalyst.

\[
\frac{m}{M} = n_2
\]

(9)

where \( m \) is catalyst mass loading (4×10\(^{-5}\) g), and \( M \) is the relative molecular mass of catalyst.

**Table S2.** Comparison of \( Q_{CO} \), the number of active sites and TOF values (at the overpotential of 30 mV) of our synthesized RuGe, Ru and Pt catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>( Q_{CO} ) (mC)</th>
<th>Number of active sites (mol), ( n_1 )</th>
<th>TOF(_1) at the overpotential of 30 mV (H(_2) s(^{-1}))</th>
<th>Number of active sites (mol), ( n_2 )</th>
<th>TOF(_2) at the overpotential of 30 mV (H(_2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuGe</td>
<td>0.06</td>
<td>3.1×10(^{-10})</td>
<td>5.2</td>
<td>2.3×10(^{-7})</td>
<td>0.007</td>
</tr>
<tr>
<td>Ru</td>
<td>1.13</td>
<td>5.8×10(^{-9})</td>
<td>0.1</td>
<td>4.0×10(^{-7})</td>
<td>0.001</td>
</tr>
<tr>
<td>Pt</td>
<td>0.23</td>
<td>1.2×10(^{-9})</td>
<td>5.4</td>
<td>2.1×10(^{-7})</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**Fig. S1** The XRD patterns of MoGe\(_2\), PtGe, and Pd\(_2\)Ge. For comparison, their standard XRD cards are included.
Fig. S2 (a) SEM, (b) TEM, and (b, inset) high-resolution TEM images of Ru. The sample is composed of particles of 100-500 nm size.

Fig. S3 Steady-state current density as a function of applied voltage during HER over MoGe$_2$, Pd$_2$Ge and PtGe in 0.5 M H$_2$SO$_4$ solution. The required overpotentials at a current density of 10 mA/cm$^2$ are 236 mV, 140 mV, and 54 mV, respectively.
**Fig. S4** (a) XRD, (b) SEM, (c) TEM, and (d) high-resolution TEM images of Pt. The particle size distribution is uneven ranging from 10 nm to 1 μm.

**Fig. S5** Chronopotentiometric curves (V-t) with RuGe and Ru as catalysts at a current density of 10 mA cm$^{-2}$ in 0.5 M H$_2$SO$_4$ solution.
Fig. S6 (a) TEM and (b) HRTEM images of RuGe after electrocatalysis for HER in 0.5 M H₂SO₄ solution.
Table S3 Summary of some recently reported, representative Ru-based electrocatalysts for HER. Note that the calculated TOF\(_1\) and TOF\(_2\) values are the upper limit and lower limit of TOF, and their computation methods are shown in part 2.5 and Table S2.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mass loading (mg cm(^{-2}))</th>
<th>(\eta) at 10 mA cm(^{-2}) (mV)</th>
<th>(j_{Ru}) (A g(^{-1}))</th>
<th>TOF (s(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RuGe particles</strong></td>
<td>0.56</td>
<td>43</td>
<td>325.7 (100 mV)</td>
<td>TOF(_1)=5.2 (30 mV) TOF(_2)=0.007 (30 mV)</td>
<td>This work</td>
</tr>
<tr>
<td><strong>Ru particles</strong></td>
<td>0.56</td>
<td>98</td>
<td>18.9 (100 mV)</td>
<td>TOF(_1)=0.1 (30 mV) TOF(_2)=0.001 (30 mV)</td>
<td></td>
</tr>
<tr>
<td>RuB(_2) particles</td>
<td>0.571</td>
<td>52</td>
<td>106.3 (100 mV)</td>
<td>–</td>
<td>[19]</td>
</tr>
<tr>
<td>Ru/RuS(_2) nanosheets</td>
<td>0.849</td>
<td>45</td>
<td>&lt;192.5 (110 mV)</td>
<td>0.71 (100 mV)</td>
<td>[20]</td>
</tr>
<tr>
<td>h-RuSe(_2)</td>
<td>0.3</td>
<td>34</td>
<td>341.9 (110 mV)</td>
<td>0.34 (30 mV)</td>
<td>[16]</td>
</tr>
<tr>
<td>Cu(<em>{53})Ru(</em>{47}) alloy</td>
<td>0.306</td>
<td>15</td>
<td>199.6 (50 mV)</td>
<td>1.14 (100 mV)</td>
<td>[21]</td>
</tr>
<tr>
<td>RuTe(_2) nanorods</td>
<td>0.204</td>
<td>33</td>
<td>432 (60 mV)</td>
<td>–</td>
<td>[22]</td>
</tr>
<tr>
<td>PtPdRuTe</td>
<td>0.285</td>
<td>39</td>
<td>145.6 (46 mV)</td>
<td>0.94</td>
<td>[23]</td>
</tr>
<tr>
<td>RuNi@carbon dots</td>
<td>0.418</td>
<td>58</td>
<td>1680 (13 mV)</td>
<td>5.03 (100 mV)</td>
<td>[24]</td>
</tr>
<tr>
<td>Ru single atoms@PN nanotubes</td>
<td>1</td>
<td>24</td>
<td>6060.6 (41 mV)</td>
<td>1.67 (25 mV); 4.29 (50 mV)</td>
<td>[25]</td>
</tr>
<tr>
<td>Ru@C(_2)N</td>
<td>0.285</td>
<td>22</td>
<td>366.8 (50 mV)</td>
<td>1.95 (50 mV)</td>
<td>[26]</td>
</tr>
<tr>
<td>Ru(_2)B(_3)@B, N-doped carbon</td>
<td>0.5</td>
<td>41</td>
<td>3030.3 (41 mV)</td>
<td>7</td>
<td>[27]</td>
</tr>
<tr>
<td>RuP(_2)@N, P-doped carbon</td>
<td>1</td>
<td>38</td>
<td>42.9 (38 mV)</td>
<td>–</td>
<td>[28]</td>
</tr>
<tr>
<td>Ru single atom @Ti(_3)C(_2)T(_x)</td>
<td>1</td>
<td>76</td>
<td>833 (76 mV)</td>
<td>0.52 (100 mV)</td>
<td>[29]</td>
</tr>
<tr>
<td>Ru particles @carbon</td>
<td>0.6</td>
<td>23</td>
<td>~100 (30 mV)</td>
<td>~0.2 (40 mV)</td>
<td>[30]</td>
</tr>
<tr>
<td>N-doped RuP@NPC</td>
<td>0.4</td>
<td>20.5</td>
<td>2500 (58.9 mV)</td>
<td>1.56 (30 mV)</td>
<td>[31]</td>
</tr>
</tbody>
</table>
Supplementary References

22. J. Wang, L. Han, B. Huang, Q. Shao, H. L. Xin and X. Huang, Nat. Commun., 2019, **10**, 5692.