Single-atom catalyst for high-performance methanol oxidation

Zhiqi Zhang, Jiapeng Liu, Jian Wang, Qi Wang, Yuhao Wang, Kai Wang, Zheng Wang, Meng Gu, Zhenghua Tang, Jongwoo Lim, Tianshou Zhao, Francesco Ciucci

Single-atom catalysts have been widely investigated for several electrocatalytic reactions except electrochemical alcohol oxidation. Herein, we synthesize atomically dispersed platinum on ruthenium oxide (Pt/RuO₂) using a simple impregnation-adsorption method. We find that Pt/RuO₂ has good electrocatalytic activity towards methanol oxidation in an alkaline media with a mass activity that is 15.3-times higher than that of commercial Pt/C (6766 vs. 441 mA mg⁻¹Pt). In contrast, single atom Pt on carbon black is inert. Further, the mass activity of Pt/RuO₂ is superior to that of most Pt-based catalysts previously developed. Moreover, Pt/RuO₂ has a high tolerance towards CO poisoning, resulting in excellent catalytic stability. Ab initio simulations and experiments reveal that the presence of Pt–O₃f (3-fold coordinatively bonded O)–Ruₘₙ ( coordinatively unsaturated Ru) bonds with the undercoordinated bridging O in Pt/RuO₂ favors the electrochemical dehydrogenation of methanol with lower energy barriers and onset potential than those encountered for Pt–C and Pt–Ru.
Platinum is the most effective element for anodic methanol oxidation reaction (MOR) in direct methanol fuel cells1,2. The electrocatalytic activity of Pt is highly dependent on its geometrical structure and the surrounding environment. To improve MOR activity and reduce Pt loading, conventional strategies have focused on (i) tailoring the structure and/or morphology of Pt (e.g., by making hollow/framed3 or core–shell4 Pt); and (ii) hybridizing Pt with other elements (e.g., Co3, Ni4, Sn5, Bi6, etc.). However, the Pt in these catalysts is usually assembled as a nanoparticle of diameter greater than 1 nm, leading to unsatisfactory mass activity. Furthermore, in MOR, Pt nanoparticles are susceptible to poisoning by adsorbed intermediates (COads)5, resulting in activity loss. Hence, developing new types of Pt-based MOR electrocatalysts with high activity and anti-poisoning capability is of both practical and fundamental significance.

Single-atom catalysts (SACs) are now emerging as a new class of catalysts with extraordinary activity towards many electrocatalytic reactions, including oxygen and hydrogen evolution, oxygen, CO, and N2 reduction, and hydrogen and formic acid oxidation6–12. Pt SACs have utmost utilization of Pt atoms and good capability for CO oxidation13. However, the electrochemical dehydrogenation of methanol to CO in MOR requires at least three contiguous Pt atoms14. Further, it has been reported that SACs consisting of Pt single atoms supported on carbon nanotubes are inactive towards MOR15. Yet, we should note that these studies focused only on the Pt active centers rather than the entire catalysts, thereby neglecting the environment surrounding Pt. In this regard, enhancing the activity of single atomic Pt towards MOR is a scientifically significant and challenging topic.

For SACs, the atomic coordination of single atoms also plays an important role in determining the catalytic activity. It has been shown that the electronic structure and coordination of the central single atoms can be adjusted by tuning the bonds between the single atoms and the substrate17–20. Herein, we designed two types of Pt SACs. Thanks to a simple adsorption–impregnation preparation method21, single Pt atoms were immobilized on RuO2 and carbon black (VXC-72) to obtain Pt1/RuO2 and Pt1/VXC-72, respectively. The Pt1/RuO2 SACs showed superb mass activity (6766 mA mg⁻¹) and stability towards the MOR, far superior to those of most Pt-based catalysts developed to date. The MOR mechanism including the dehydrogenation of methanol and CO electrooxidation is further studied by density functional theory (DFT), confirming the experimental observation that the prepared SACs are active for the alcohol oxidation reaction. This finding suggests an approach of SACs for direct alcohol fuel cells.

Results

Structure characterization of Pt1/RuO2. RuO2 and VXC-72 supports were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) (Supplementary Fig. 1). Pt1/RuO2 and Pt1/VXC-72 catalysts with an identical Pt loading of 0.38 wt% were prepared by simple impregnation/adsorption followed by filtration and washing (for more details, see ‘Methods’ and Supplementary Fig. 2). Figure 1 shows the catalysts’ morphology and structure. As revealed by the bright spots marked as yellow circles in the high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image, individual Pt atoms were randomly dispersed on RuO2 (Fig. 1a). The magnified HAADF-STEM image of Pt1/RuO2 suggests that the Pt atoms exactly substituted Ru (Fig. 1b). The presence of Pt single atoms was further verified by the intensity profile along with the dashed rectangle in the image (the inset in Fig. 1b), where the Pt atom brightness is more intense than that of Ru due to the higher Z number. The corresponding elemental mapping shows that Pt, Ru, and O were homogeneously distributed throughout the entire Pt1/RuO2 sample (Fig. 1d–g). For Pt1/VXC-72, Pt atoms were also atomically dispersed, as shown in the HAADF-STEM image (Fig. 1c). No Pt clusters/nanoparticles on VXC-72 were observed by low-magnification HAADF-STEM and TEM imaging (Supplementary Fig. 3). Due to the single-atom structure and low Pt loading, Pt peaks were, however, not detectable by XRD (Supplementary Fig. 4).

To study the coordination and electronic configuration of Pt single atoms in the Pt1/RuO2 and Pt1/VXC-72, X-ray absorption fine structure (XAFS) spectroscopy and XPS were carried out (Fig. 2). The normalized X-ray absorption near-edge structure (XANES) spectra of Pt1/RuO2 shows stronger white-line intensity at 11,568 eV compared to the Pt foil, suggesting that Pt is positively charged in Pt1/RuO2 due to the electron transfer from Pt to the surrounding O atoms in the RuO2 support (Fig. 2a)22,23. The Pt1/VXC-72 catalyst is characterized by a similar Pt-to-VXC-72 electron transfer. However, the white-line peaks suggest that the Pt in Pt1/VXC-72 has a lower charge state than the one observed for Pt1/RuO2. The average Pt oxidation numbers in Pt1/RuO2 and Pt1/VXC-72 are estimated to be +2.90 and +1.22, respectively, by integrating the XANES spectra (Supplementary Fig. 5)10,24. The different charge of Pt in RuO2 and VXC-72 is likely a result of the different coordination. As revealed by the k³-weighted extended XAFS (EXAFS) at the Pt L₁-edge, no peak at 2.64 Å from Pt–Pt is observed for either Pt1/RuO2 or Pt1/VXC-72, indicating full atomic dispersion for both catalysts (Fig. 2b), consistent with the HAADF-STEM images. Specifically, the R-space spectrum of Pt in Pt1/RuO2 has a dominant peak at 1.62 Å from Pt–O coordination, in agreement with the PtO2 case (Fig. 2c)22,23. In contrast, the dominant peak of Pt1/VXC-72 shifted to 1.83 Å (Fig. 2b). To determine the coordination of Pt in both catalysts, the main R-space peaks were fitted against corresponding models (see ‘Computational details’) by Fourier transform. For Pt1/RuO2, the coordination number of Pt–O is estimated to be 4 with an average bond length of 1.99 Å (Supplementary Fig. 6 and Supplementary Table 1). For Pt1/VXC-72, the Pt–C bond coordination number is 3, and the average bond length is 1.93 Å (Supplementary Fig. 6 and Supplementary Table 1). Also, the wavelet-transform plots of Pt1/RuO2 and Pt1/VXC-72 show a maximum at ~7.5 Å⁻¹ corresponding to the Pt–O/C bonds (Fig. 2c). No intensity maximum at ~12.5 Å⁻¹ corresponding to the presence of Pt–Pt bonds was observed for either catalyst, consistent with the EXAFS (Fig. 2c).

The RuO2 support contains Ru 4f and X-ray absorption near-edge structure (XANES) spectra of Pt1/RuO2 shows a new peak at 11,568 eV, suggesting that Pt is positively charged in Pt1/RuO2 due to the electron transfer from Pt to the surrounding O atoms in the RuO2 support (Fig. 2a)22,23. The Pt1/VXC-72 catalyst is characterized by a similar Pt-to-VXC-72 electron transfer. However, the white-line peaks suggest that the Pt in Pt1/VXC-72 has a lower charge state than the one observed for Pt1/RuO2. The average Pt oxidation numbers in Pt1/RuO2 and Pt1/VXC-72 are estimated to be +2.90 and +1.22, respectively, by integrating the XANES spectra (Supplementary Fig. 5)10,24. The different charge of Pt in RuO2 and VXC-72 is likely a result of the different coordination. As revealed by the k³-weighted extended XAFS (EXAFS) at the Pt L₁-edge, no peak at 2.64 Å from Pt–Pt is observed for either Pt1/RuO2 or Pt1/VXC-72, indicating full atomic dispersion for both catalysts (Fig. 2b), consistent with the HAADF-STEM images. Specifically, the R-space spectrum of Pt in Pt1/RuO2 has a dominant peak at 1.62 Å from Pt–O coordination, in agreement with the PtO2 case (Fig. 2c)22,23. In contrast, the dominant peak of Pt1/VXC-72 shifted to 1.83 Å (Fig. 2b). To determine the coordination of Pt in both catalysts, the main R-space peaks were fitted against corresponding models (see ‘Computational details’) by Fourier transform. For Pt1/RuO2, the coordination number of Pt–O is estimated to be 4 with an average bond length of 1.99 Å (Supplementary Fig. 6 and Supplementary Table 1). For Pt1/VXC-72, the Pt–C bond coordination number is 3, and the average bond length is 1.93 Å (Supplementary Fig. 6 and Supplementary Table 1). Also, the wavelet-transform plots of Pt1/RuO2 and Pt1/VXC-72 show a maximum at ~7.5 Å⁻¹ corresponding to the Pt–O/C bonds (Fig. 2c). No intensity maximum at ~12.5 Å⁻¹ corresponding to the presence of Pt–Pt bonds was observed for either catalyst, consistent with the EXAFS (Fig. 2c).

The RuO2 support contains Ru 4s with the binding energy at the range of ~70–85 eV (Supplementary Figs. 1b and 7), which is very close to the XPS signature of Pt 4f. Therefore, the Pt1/RuO2 XPS peaks in the ~68–82 eV range were deconvoluted into Ru 4s and Pt 4f, i.e., Pt 4f1/2 and Pt 4f3/2 (Fig. 2d). The binding energies of the Pt 4f were measured to be 73.6 and 76.9 eV for Pt1/RuO2, and 72.9 and 76.2 eV for Pt1/VXC-72. The higher binding energy of Pt1/RuO2 compared to Pt1/VXC-72 implies that Pt in Pt1/RuO2 has a higher oxidation state, in agreement with the XANES results. Moreover, the O 1s spectrum of bare RuO2 was deconvoluted into three characteristic peaks at 529.3, 530.2, and 532.3 eV (Fig. 2e), which can be attributed to M–O, M–OH, and adsorbed oxygen, respectively25. After the incorporation of Pt single atoms into RuO2, the O 1s of Pt1/RuO2 shows a new peak at 531.3 eV. This peak can be attributed to the appearance of oxygen vacancies on the surface resulting from Pt single atoms (Supplementary Fig. 8)22,26. These data support the existence of Pt–O in Pt1/RuO2, in agreement with the XANES characterization. In addition, the O 1s of Pt1/VXC-72 is similar to that of
VXC-72 (Supplementary Fig. 9), indicating that there is no Pt–O interaction in Pt1/VXC-72. In other words, Pt–C coordination is dominant in Pt1/VXC-72.

The preceding results indicate that Pt is atomically dispersed on both RuO2 and VXC-72 but surrounded by distinct coordination environments. Pt–O coordination characterizes in Pt1/RuO2. In contrast, Pt–C coordination is dominant in Pt1/VXC-72.

MOR electrocatalytic activity. Although Pt-based nanoparticles have been the most efficient catalysts for MOR, individual Pt atoms on carbon support are inactive towards that reaction. By replacing the carbon support with RuO2, the coordination of Pt single atoms changes. Herein, we evaluated in the N2-saturated 0.1 mol L\(^{-1}\) KOH and 1 mol L\(^{-1}\) methanol solution the MOR performance of the Pt1/RuO2 SACs. Concomitantly, these materials were compared to Pt1/VXC-72 and commercial Pt/C, see Fig. 3. As revealed by cyclic voltammogram (CV) of Pt1/VXC-72 SACs, no electrocatalytic peak was detected, indicating that Pt1/VXC-72 is inactive towards MOR (Fig. 3a). We also prepared a Pt1/VXC-72 catalyst with a higher Pt loading of 1.48 wt%, i.e., Pt1/VXC-72-1.48, which had a negligible MOR activity.
seasons than that of the commercial 20 wt% Pt/C (441 mA mg⁻¹ \text{Pt}) (reversible hydrogen electrode), which is about 15.3 times higher than that of the reported catalysts to date (Supplementary Table 2). The peak current ratio between the forward (I⁡_f) and backward (I⁡_b) CV scan of the RuO₂ was featureless (Fig. 3c). Further, oxygen vacancies on the RuO₂ surface could not contribute to MOR (Supplementary Fig. 11). These results suggest that its MOR activity was due to having Pt single atoms on RuO₂. The Pt mass activity of Pt₁/RuO₂ was 6766 mA mg⁻¹ \text{Pt} at 0.80 V vs. RHE (reversible hydrogen electrode), which is about 15.3 times higher than that of the commercial 20 wt% Pt/C (441 mA mg⁻¹ \text{Pt} at 0.92 V vs. RHE) (Fig. 3b, d) and significantly larger than the data for the reported catalysts to date (Supplementary Table 2). The peak current ratio between the forward (I⁡₈) and backward (I⁡₇) CV scan can be used to demonstrate the CO₃ads tolerance. The I⁡₈/I⁡₇ of Pt₁/RuO₂ (3.67) is more than twice that of Pt/C (1.81), suggesting an enhanced anti-poisoning ability for Pt₁/RuO₂. Long-term durability is another important criterion to assess the quality of a catalyst. The stability of the Pt₁/RuO₂ SACs and 20 wt% commercial Pt/C was evaluated by chronoamperometry at −0.1 V (vs. Ag/AgCl). After 10 h, the Pt₁/RuO₂ mass activity remained at 6463 mA mg⁻¹ \text{Pt}, a value lower than the 6766 mA mg⁻¹ \text{Pt} of Pt₁/RuO₂ SACs (Fig. 4e). For Pt/RuO₂−700, the oxidation peak at 0.6 and 1.0 V disappeared, showing no MOR activity. The lower MOR performance of these catalysts can be attributed to the Pt aggregation. As is well known, catalytic activity is associated with the number of active sites and single atoms have many more of those compared to clusters or nanoparticles. As expected, due to the presence of Pt clusters or nanoparticles, Pt/RuO₂-0.75 and Pt/RuO₂-1.48, two materials with higher Pt loading than Pt₁/RuO₂ SACs, showed decreased mass activity (Supplementary Fig. 15).

In parallel, an additional sample, denoted as Pt₁/RuO₂-H, was prepared by reducing the Pt₁/RuO₂ SACs in H₂ at 80 °C. In that sample, the RuO₂ support was reduced to metallic Ru with a little Pt surrounding Pt single atoms (thanks to RuO₂, Pt single atoms were aggregated into nanoparticles with a 1–2 nm diameter for Pt₁/RuO₂−500, or even 30 nm diameter for Pt₁/RuO₂−700 (Supplementary Fig. 14 and Fig. 4a, b), respectively. When characterized by CV, Pt/RuO₂−500 showed a mass activity of 2140 mA mg⁻¹ \text{Pt}, a value lower than the 6766 mA mg⁻¹ \text{Pt} of Pt₁/RuO₂ SACs (Fig. 3d). For Pt/RuO₂−700, the oxidation peak between 0.6 and 1.0 V disappeared, showing no MOR activity. The lower MOR performance of these catalysts can be attributed to the Pt aggregation. As is well known, catalytic activity is associated with the number of active sites and single atoms have many more of those compared to clusters or nanoparticles. As expected, due to the presence of Pt clusters or nanoparticles, Pt/RuO₂-0.75 and Pt/RuO₂-1.48, two materials with higher Pt loading than Pt₁/RuO₂ SACs, showed decreased mass activity (Supplementary Fig. 15).

To reveal the origin of MOR activity, several control samples were used, see Fig. 4. In the first set of samples denoted as Pt₁/RuO₂−500 and Pt₁/RuO₂−700, Pt₁/RuO₂ was annealed in air at 500 and 700 °C, respectively. After heat treatment, Pt single atoms on RuO₂ were aggregated into nanoparticles with a 1–2 nm diameter for Pt₁/RuO₂−500, or even 30 nm diameter for Pt₁/RuO₂−700 (Supplementary Fig. 14 and Fig. 4a, b), respectively. When characterized by CV, Pt/RuO₂−500 showed a mass activity of 2140 mA mg⁻¹ \text{Pt}, a value lower than the 6766 mA mg⁻¹ \text{Pt} of Pt₁/RuO₂ SACs (Fig. 4e). For Pt/RuO₂−700, the oxidation peak between 0.6 and 1.0 V disappeared, showing no MOR activity. The lower MOR performance of these catalysts can be attributed to the Pt aggregation. As is well known, catalytic activity is associated with the number of active sites and single atoms have many more of those compared to clusters or nanoparticles. As expected, due to the presence of Pt clusters or nanoparticles, Pt/RuO₂-0.75 and Pt/RuO₂-1.48, two materials with higher Pt loading than Pt₁/RuO₂ SACs, showed decreased mass activity (Supplementary Fig. 15).

In parallel, an additional sample, denoted as Pt₁/RuO₂-H, was prepared by reducing the Pt₁/RuO₂ SACs in H₂ at 80 °C. In that sample, the RuO₂ support was reduced to metallic Ru with a little RuO₂ left as confirmed by XRD (Supplementary Fig. 16). The different structure led to a changed coordination environment for Pt single atoms. The HAADF-STEM of Pt₁/RuO₂-H shows that the Pt atoms are isolated on the support (Fig. 4c). Compared to that of Pt₁/RuO₂, the EXAFS spectra of Pt₁/RuO₂-H show a prominent peak at 2.49 Å due to Pt-Ru bond (coordination number n = 9), and the 1.62 Å peak of Pt-O is negligible (Fig. 4d, Supplementary Fig. 17, and Supplementary Table 1). These results suggest that the Pt atoms have distinct coordination in Pt₁/RuO₂ and Pt₁/RuO₂-H, i.e., Pt-O coordination for Pt₁/RuO₂ and Pt-Ru for Pt₁/RuO₂-H. Accordingly, the Pt₁/RuO₂-H shows no MOR activity (Fig. 4e). Instead, Pt₁/RuO₂-H shows enhanced capacitive current and polarization current starting from −0.9 V in the forward scan, resulting from higher relative Ru content in Pt₁/RuO₂-H than Pt₁/RuO₂. In consideration of the coordination of Pt-O in Pt₁/RuO₂ and Pt-C in Pt₁/VXC-72, it can be concluded that the coordination of Pt single atoms governs MOR activity. On the basis of the preceding results, the origin of MOR activity in Pt₁/RuO₂ SACs can be attributed to: (i) the existence of large numbers of atomic Pt sites; and (ii) the environment surrounding Pt single atoms (thanks to RuO₂, Pt single atoms turned into MOR-active catalysts).
The CO resistibility of the catalysts was evaluated by CO stripping tests\textsuperscript{6,9}, see Fig. 5. For commercial Pt/C, a main peak appeared in the first forward scan with onset and peak potentials at 0.448 and 0.711 V (Fig. 5a), respectively, where the latter value has been previously attributed to CO electrooxidation taking place on Pt nanoparticles\textsuperscript{5}. Downsizing the Pt nanoparticles to the atomic scale in Pt\textsubscript{1}/VXC-72 reduces the onset potential of CO electrooxidation to \sim 0.276 V (Fig. 5b), a value much lower than that of commercial Pt/C (0.448 V). This reduction indicates that Pt single atoms trigger CO electrooxidation, consistent with the literature, where Pt single atoms have been shown to weaken CO adsorption, thereby facilitating the oxidation of CO at a lower potential\textsuperscript{9}. Compared to Pt\textsubscript{1}/VXC-72 and commercial Pt/C, Pt\textsubscript{1}/RuO\textsubscript{2} SACs triggered CO electrooxidation at a lower onset potential of 0.152 V with a minute peak around 0.673 V (Fig. 5c), suggesting an enhanced anti-poisoning capability for Pt\textsubscript{1}/RuO\textsubscript{2}. Such a change indicates that introducing RuO\textsubscript{2} as a support favors CO electrooxidation. As is well known, oxophilic RuO\textsubscript{2}...
boots water dissociation, which, in turn, facilitates the formation of adsorbed OH and the oxidative removal of CO$_{ads}$ on Pt sites, which, in turn, facilitates their regeneration$^{36}$. As shown in Fig. 5d, RuO$_2$ alone electrooxidized CO at an low potential of 0.076 V. Hence, both single atomic Pt and RuO$_2$ favor the electrooxidative removal of CO, leading to the superior stability of Pt$_1$/RuO$_2$.

Ethanol oxidation reaction (EOR) tests in alkaline medium show an ~5.7-fold higher mass activity of Pt$_1$/RuO$_2$ compared to benchmark Pt/C (2824 vs. 498 mA mg$^{-1}$Pt) (Supplementary Fig. 18). These results suggest that Pt$_1$/RuO$_2$ also has remarkable potential for alcohol oxidation reactions.

**MOR mechanism.** To understand the MOR mechanism, three different models were constructed to simulate the catalytic reaction. The first system had a Pt atom located at the Ru$_{cua}$ (1-fold coordinatively unsaturated Ru) site of the RuO$_2$(110) surface (Pt-RuO$_2$(110)) corresponding to Pt$_1$/RuO$_2$. The second model had a Pt atom bonded to three C atoms on graphene (PtC$_3$) corresponding to Pt$_1$/VXC-72. The final model had a Pt substituting a Ru atom in RuO$_2$ (Pt-RuO$_2$) corresponding to Pt$_1$/RuO$_2$-H, see ‘Methods’ and Supplementary Figs. 19–21. The calculated MOR free energy diagrams of these three samples are shown in Fig. 6.

For the MOR on Pt-RuO$_2$(110), the CH$_3$OH molecule preferentially adsorbs on the site above Ru$_{cua}$ with a reaction free energy of ~0.54 eV (Fig. 6a and Supplementary Fig. 22). Thanks to the highly active O$_{br}$, the scission of O-H bond of the adsorbed CH$_3$OH molecule (CH$_3$OH$^*$ → CH$_3$O$^*$ + H$^*$) proceeds spontaneously (Fig. 6a). For this elementary step, the cleaved H atom bonds to its neighboring O$_{br}$ with a reaction free energy of ~0.26 eV (Supplementary Fig. 22b and Supplementary Table 3). More importantly, the removal of H$^*$ (H$^*$ + OH$^-$ → H$_2$O + e$^-$) to leave the sole adsorbate of CH$_3$O$^*$ is slightly endothermic with a free energy requirement of 0.17 eV at pH = 13 (Supplementary Table 3). Considering that the O-H bond scission is energetically unfavorable, we may propose that the MOR starts with the break of the O-H bond in the methanol molecule and follows the CH$_3$OH$^*$ → CH$_3$O$^*$ → CH$_2$O$^*$ → CHO$^*$ → CO$^*$ pathway$^{32,33}$.

As illustrated in Fig. 6a, the subsequent activations of the C-H bond require energy barriers of 0.39 (CH$_3$O$^*$ → TS$_1$ → CH$_2$O$^*$), 0.49 (CH$_2$O$^*$ → TS$_2$ → CHO$^*$), and 0.29 eV (CHO$^*$ → TS$_3$ → CO$^*$), respectively. The dehydrogenation of CH$_2$O$^*$ has been predicted to be the rate-limiting step for the above-mentioned pathway to CO. This result is consistent with DFT calculations from the Nørskov group showing that MOR on RuO$_2$(110) is limited by the dehydrogenation of CH$_2$O$^*$. Nevertheless, the activation barrier on Pt-RuO$_2$(110) was predicted to be only 0.49 eV, which is lower than the 0.71 eV we computed for pure RuO$_2$. These calculated free energy diagrams for MOR on PtC and Pt-RuO$_2$(101) are shown in Fig. 6b, c for comparison. The adsorption free energy of CH$_3$OH on the PtC3 and Pt-RuO$_2$(101) are ~0.03 and 0.15 eV, respectively. Both values are less negative than that computed for Pt-RuO$_2$(110) (~0.54 eV), implying a weaker interaction between both PtC3 and Pt-RuO$_2$(101) and the methanol molecule in comparison to Pt-RuO$_2$(110). Moreover, the energy barriers needed to cleave the O-H and C-H bonds are significantly higher than those of Pt-RuO$_2$(110) (Fig. 6a–c). The much higher barriers compared to those on Pt-RuO$_2$(110) indicate that the MOR is energetically costly for both PtC3 and Pt-RuO$_2$(101) substrates. These computational results agree with experiments as both suggest that Pt$_1$/VXC-72 and Pt$_1$/RuO$_2$-H are inert towards MOR. As for Pt-RuO$_2$(101), the highest reaction activation barrier (0.79 eV) is much lower than that of both PtC3

**Fig. 6 MOR mechanism.** a–c Calculated reaction free energy and energy barriers for methanol oxidation to CO at: a Pt-RuO$_2$(110), b PtC3, and c Pt-Ru(0001). d Calculated reaction free energy and energy barriers for CO oxidation on Pt-RuO$_2$(110). In (a), the relative energies of CH$_3$O$^*$ and corresponding TS$_2$ computed for RuO$_2$(110) are shown for reference.
(2.06 eV) and Pt-Ru(0001) (1.08 eV) (Supplementary Fig. 24 and Fig. 6b, c), suggesting the enhanced activity of Pt1/RuO2 compared to Pt1/VXC-72 and Pt1/RuO2-H towards MOR.

We also theoretically studied the stability of Pt-RuO2(110) with respect to CO poisoning, or equivalently, the oxidation CO into CO2. When OH results in the present, CO oxidation proceeds through the CO* + OH* → TS1 → cis-COOH* → TS2 → trans-COOH* → TS3 → trans-COOH* → CO2* pathway35, as shown in Fig. 6d. The rate-limiting step of the overall reaction was predicted to be the cis-COOH* → trans-COOH* step (i.e., the rotation of the H atom in cis-COOH*) with activation barrier of 0.35 eV. This value is even smaller than the barrier computed for the dehydrogenation of formaldehyde on Pt-RuO2 (110), implying that the presence of Pt facilitates the full oxidation of methanol into CO2 on RuO2 (110). We further note that the trans-COOH* → CO2* step (i.e., the desorption of CO2*) has a positive ΔG of 0.33 eV, indicating that the release of CO2 is spontaneous. It is worth mentioning that the adsorption free energies of CO on the PtC3 and Pt-Ru(0001) are ~0.81 and ~0.92 eV (Fig. 6b, c), respectively. Both the values are much more negative compared to that computed for Pt-RuO2 (110) (~0.54 eV), suggesting an increased interaction between CO and the PtC3/Pt-Ru (0001). According to the Brønsted-Evans-Polanyi relationship36,37, higher binding energy correlates to higher activation energies and lower thermodynamic driving force for the reaction. Therefore, we predict that the CO electrooxidation on PtC3 and Pt-Ru (0001) is much more energetically unfavorable with sluggish kinetics in agreement with the experiments above.

In addition to the activation energy barriers, onset potentials were also calculated (Supplementary Fig. 25). The potential-determining step (i.e., the elementary step with the highest onset potential) was found to be, for all three catalysts, the stripping off methanol proton (CH3OH* → CH2OH*). Accordingly, the onset potentials were predicted to be 0.26, 0.92, and 0.33 V for Pt-RuO2(110), PtC3, and Pt-Ru (0001), respectively. Both the lower onset potential and smaller activation barriers suggest that Pt1/RuO2 SACs are more favorable towards the methanol oxidation than Pt1/VXC-72 and Pt1/RuO2-H, in agreement with experimental results.

To unravel the mechanisms underpinning the high MOR activity, we calculated the projected density of states (PDOS) and charge analysis for both Pt and Ru atoms in the Pt-RuO2(110). It is apparent that only the spin-up state of the d2z orbital of Pt is filled while the d2z orbital of Ru, empty (Supplementary Fig. 26). Consistent with the PDOS results, the charge density difference also suggests that more electrons are depleted for the Ru atom than the Pt atom (Supplementary Fig. 27). Specifically, Bader charge analysis suggests that Ru2−3 and Pt on Pt-RuO2 (110) lose 1.61 e and 1.22 e, respectively (Supplementary Table 4). Thanks to the empty anti-bonding d2z orbital, a stronger interaction between the adsorbate (e.g., CH3OH) and Ru,Cu than that of Pt is predicted, in agreement with the calculated adsorption free energies (Supplementary Fig. 22a–c). The orbital interaction between adsorbate, e.g., CH2OH, and the d2z orbital is shown in Supplementary Fig. 28. In the case of RuCu, for which the d2z orbital is empty, the methanol molecule is well stabilized due to the favorable two-center two-electron interaction. Instead, the anti-bonding d2z orbital of Pt is filled with one spin-up electron, resulting in the less-favorable two-center three-electron interaction, thereby destabilizing the adsorbate. Specifically, the filled anti-bonding Pt orbital leads to a weaker adsorption free energy of formaldehyde on Pt-RuO2 (110) (~0.26 eV) compared to that of RuCu(110) (~0.88 eV) (Fig. 6a). The increased energy towards CH2OH* thus lowers the activation barrier (TS2) for the subsequent dehydrogenation (Fig. 6a). We further evaluated the PDOS of the d orbitals with a Pt atom placed on different substrates. Compared to Pt-Ru(0001), the d orbitals of Pt on Pt-RuO2 (110) are characterized by greater delocalization (Supplementary Fig. 29)32 as well as a larger density near the Fermi level. These features facilitate electron transfer and contribute to the enhanced MOR activity of Pt1/RuO2.35 In contrast, the Pt PDOS of PtC3 is small at the Fermi level (Supplementary Fig. 29), suggesting that Pt1/VXC-72 is an ineffective MOR catalyst3. Besides, the additional d electrons in the Pt of PtC3 and Pt-Ru (0001) cause stronger repulsion to the coming ligand, e.g., CH2OH, thus weakening the adsorption of methanol and hindering MOR.

Discussion

We successfully prepared Pt single atoms characterized by distinct coordination environment by leveraging a simple impregnation–adsorption method and tailoring the support. The Pt1/RuO2 SACs not only had a superb mass activity of 6766 mA mgPt−1 but also CO resistibility towards the MOR. Pt1/RuO2 was shown to be a significantly better catalyst compared to the commercial Pt/C benchmark. Theoretical simulations revealed that the Pt-OH RuCu with OBr in Pt1/RuO2 favored dehydrogenation of methanol with a low energy barrier and onset potential compared to that of Pt-C and Pt-Ru bonds. Moreover, CO at Pt1/RuO2 can be removed via electrooxidation at low potentials, leading to enhanced anti-poisoning capability. The discovery of Pt1/RuO2 SACs provides an approach to explore Pt SACs for MOR and related alcohol oxidation reaction.

Methods

Materials. H2PtCl6·6H2O, RuO2, and commercial Pt/C (20 wt% Pt) were purchased from Sigma-Aldrich. Carbon black (Vulcan XC-72) was bought from The Cabot Corporation. Methanol and ethanol were purchased from Scharlab.

Synthesis of Pt1/RuO2 and control catalysts. The Pt1/RuO2 catalysts were prepared by an impregnation–adsorption method. Briefly, 50 mg of RuO2 were dispersed in 80 mL of distilled water. Next, 0.25 mL of a H2PtCl6·6H2O solution (2 mg mL−1) was added dropwise: stirring at 70 °C for 5 h followed this. The product was obtained by filtration, repeated washing with water and ethanol, and drying at 70 °C overnight. Pt1/VXC-72 was prepared in a similar manner by using H2PtCl6·6H2O, Pt1/RuO2-H catalyst was obtained by reducing Pt1/RuO2 in H2 at 80 °C. The Pt1/RuO2-500 and Pt1/RuO2-700 catalysts were obtained under the heat treatment of Pt1/RuO2 in the air at 500 and 700 °C, respectively.

Catalyst characterization. The structure and morphology of the catalysts were characterized by XRD (PAAnalytical X’pert Pro, Cu Kα radiation), XPS (Axis Ultra DLD), and TEM (JEOL-JEOL-2010F). The electron paramagnetic resonance (EPR) spectra were recorded at room temperature using JEOL JES-F200. The HAADF-STEM and EDS mapping were carried out using a double Cs-corrected FEI-Thermis microscope operated at 300 kV. The STEM images were obtained with a convergent semi-angle of 25.1 mrad. The HAADF collection angle was 48–200 mrad. The XAFS at the Pt L2,3 edge was obtained on beamline 10C at the Pohang Light Source (PLS) in the Pohang Accelerator Laboratory (PAL), Republic of Korea. The XAFS data were processed and analyzed using ATHENA and ARTEMIS3. The Pt content in the catalyst was measured by ultraviolet visible spectroscopy (UV-vis, Lambda 20, Perkin Elmer). An appropriate amount of a H2PtCl6·6H2O solution (2 mg mL−1) was added to deionized water and diluted to 100 mL. After the adsorption of Pt species by RuO2 in solution, the residual solution was measured by UV-vis, and by the comparison of the absorbance with the working curve, the Pt content in RuO2 was estimated.

Electrochemical characterization. The electrochemical tests were conducted using a CHI 900D work station (CH Instruments). A three-electrode setup was used and all tests were conducted at 25 °C. A graphite rod was used as a counter electrode; (KCl saturated) Ag/AgCl was selected as the reference electrode. To prepare the working electrode, 1 mg of catalyst and 1 mg of VXC-72 were ultrasonically dispersed in a mixture of 200 μL of water, 50 μL of ethanol, and 20 μL of Nafion (Dupont, 5 wt%). Next, 3 μL of the above ink was then placed onto a glassy-carbon electrode (4 mm in diameter) and dried at room temperature. In an N2-purged 0.1 mol L−1 KOH for 10 min at a potential of ~0.95 V vs. Ag/AgCl. CO in the solution was eliminated by bubbling the electrolyte with N2 for 20 min. Stripping tests were carried out from ~0.95 to 0 V at 50 mV s−1 for two consecutive scans.

(2.06 eV) and Pt-Ru(0001) (1.08 eV) (Supplementary Fig. 24 and Fig. 6b, c), suggesting the enhanced activity of Pt1/RuO2 compared to Pt1/VXC-72 and Pt1/RuO2-H towards MOR.
all measured potentials were converted to the RHE using
\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.198 + 0.039 \times \text{pH} \].

**Computational details**

**Models.** The RuO2 substrate was modeled by the \( (x \times 1 \times 1) \) unit cell of RuO2(110) in a six-layer slab with 18 Ru atoms and 36 O atoms. The RuO2(110) surface was chosen because this surface has previously been reported to have the most thermodynamically favorable free energy during most synthesis procedures. Under this framework, the in

pressure (0.035 bar), and

8

( Supplementary Fig. 19b). A 5 × 5 graphene sheet and a one-layered slab of \( (3 \times 3) \) unit cell Ru(0001) were constructed to simulate the VXC-72 and the Ru substrate, respectively. One C atom in the graphene sheet and one top layer Ru atom in the Ru(0001) slab were replaced by the Pt to model the Pt/VXC-72 and Pt/RuO2-H, respectively (Supplementary Figs. 20 and 21). A vacuum space of 15 Å along the c direction was added for all substrates to avoid strong interactions between neighboring substrates.

**DFT calculations.** All the spin-polarized first-principle calculations were performed using the Vienna Ab initio Simulation Package (VASP) with a plane-wave basis set defined by a kinetic energy cutoff 400 eV. The projector augmented wave (PAW) pseudopotentials with valence-electron configurations of \( 2p^62p^62p^61s^2 \), \( 4p^64f^55s^1 \), and \( 5s^2 \) were employed for C, O, H, Ru, and Pt, respectively. The electron exchange-correlation was described using the Perdew-Burk-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) scheme. For all the calculations, a dipole correction along the c direction was also applied. The bottom three layers of the RuO2(110) and the Ru(0001) slabs were fixed during the relaxation, whereas the top three layers were relaxed until the energy and force converged within \( 10^{-7} \text{ eV} \) and \( 0.02 \text{ eV Å}^{-1} \), respectively. The Brillouin zones were sampled using Gamma centered k-points with spacing smaller than \( 2\pi \times 0.04 \text{ Å}^{-1} \).

The binding energy of one Pt atom with the substrate was evaluated as

\[ E_{\text{b}} = E_{\text{Pt-RuO2}} - (E_{\text{Pt}} + E_{\text{RuO2}}) \],

where \( E_{\text{Pt-RuO2}} \) is the total energy per atom for Pt bulk metal. The transition states (TSs) were located by

\[ E_{\text{TS}} = E_{\text{ adsorbate}} - E_{\text{ substrate}} \],

where \( E_{\text{ adsorbate}} \) is the energy of the isolated adsorbate molecule in the vacuum. The adsorption free energy was further calculated as

\[ \Delta G_{\text{ads}} = \Delta G_{\text{total}} + \Delta G_{\text{TS}} - \Delta G_{\text{IS}} \],

where the adsorption free energy of one water molecule under the saturated vapor pressure (0.035 bar), and \( G(H_2O) \) is the Gibbs free energy of one water molecule under the saturated vapor pressure (0.035 bar), and \( G(H_2O) \) is taken as half of \( G(H_2O) \), i.e., the free energy of \( H_2O \) at standard condition (\( p = 1 \text{ bar}, T = 298 \text{ K} \)).

The computational standard hydrogen electrode was used to calculate the onset potentials. Under this framework, the influence of the applied potential \( U \) was computed by adding \( \Delta G_{\text{ads}} - eU \) to the free energy of a reaction involving the formation of a proton–electron pair. The electrochemical potential pertaining to each elementary step was calculated using \( U = \Delta G/c, \) where \( \Delta G \) is the reaction free energy calculated according to Supplementary Table 5. The overall onset potential was estimated as \( U_{\text{onset}} = \max(\Delta G/e) \).

**Data availability**

All the raw data used in this work are available on reasonable request from the corresponding author.

Received: 7 December 2020 | Accepted: 30 July 2021
Published online: 02 September 2021

**References**

1. Kakati, N. et al. Anode catalysts for direct methanol fuel cells in acidic media: do we have any alternative for Pt or Pt-Ru? Chem. Rev. 114, 12397–12429 (2014).

2. Zhao, X. et al. Recent advances in catalysts for direct methanol fuel cells. Energy Environ. Sci. 4, 2736–2753 (2011).

3. Chen, S. et al. High-performance Pt–Co nanoframes for fuel-cell electrocatalysis. Nano Lett. 20, 1974–1979 (2020).

4. Huang, J. et al. PtCuNi tetrahedra catalysts with tailored surfaces for efficient alcohol oxidation. Nano Lett. 19, 5431–5436 (2019).

5. Huang, W. et al. Highly active and durable methanol oxidation electrocatalyst based on the synergy of platinum–nickel hydroxide–graphene. Nat. Commun. 10, 11053 (2020).

6. Zhang, Z. et al. Efficient ternary synergism of platinum–tin oxide/nitrogen-doped carbon leading to high-performance ethanol oxidation. ACS Catal. 8, 8477–8483 (2018).

7. Wang, X. et al. Bismuth oxohydroxide–Pt inverse interface for enhanced methanol electrooxidation performance. Nano Lett. 20, 7751–7759 (2020).

8. Zhao, D. et al. Atomic site electrocatalysts for water splitting, oxygen reduction and selective oxidation. Chem. Soc. Rev. 49, 2215–2224 (2020).

9. Xiong, Y. et al. Single-atom Rh/N-doped carbon electrocatalyst for formic acid oxidation. Nat. Nanotechnol. 15, 390–397 (2020).

10. Li, Z. et al. Iridium single-atom catalyst on nitrogen-doped carbon for formic acid oxidation synthesized using a general host–guest strategy. Nat. Chem. 12, 764–772 (2020).

11. Zhang, Z. et al. Atomically dispersed materials for rechargeable batteries. Nano Energy 76, 105685 (2020).

12. Wang, Q. et al. Ultrahigh-loading of Ir single atoms on NiO matrix to dramatically enhance oxygen evolution reaction. J. Am. Chem. Soc. 142, 7425–7433 (2020).

13. Quan, R. et al. Single-atom catalysis of CO oxidation using Pt/FeOx. Nat. Chem. 3, 634–641 (2011).

14. Cuesta, A. et al. Three contiguous atoms are necessary for CO formation during methanol electrooxidation on platinum. J. Am. Chem. Soc. 128, 13332–13333 (2006).

15. Kim, Y.-T. et al. Fine size control of platinum on carbon nanotubes: from single atoms to clusters. Angew. Chem. Int. Ed. 45, 407–411 (2006).

16. Qin, R., Liu, K., Wu, Q. & Zheng, N. Surface coordination chemistry of atomically dispersed metal catalysts. Chem. Rev. 120, 11810–11899 (2020).

17. Zhang, J. et al. Tuning the coordination environment in single-atom catalysts to achieve highly efficient oxygen reduction reactions. J. Am. Chem. Soc. 141, 20218–20226 (2019).

18. Tang, C. et al. Coordination tunes selectivity: two-electron oxygen reduction on high-loading molybdenum single-atom catalysts. Angew. Chem. Int. Ed. 59, 9171–9176 (2020).

19. Li, S. et al. Impact of the coordination environment on atomically dispersed Pt catalysts for oxygen reduction reaction. ACS Catal. 10, 907–913 (2020).

20. Gao, Y.-N. et al. Regulating the coordination environment of MOF-templated single-atom nickel electrocatalysts for boosting CO2 reduction. Angew. Chem. Int. Ed. 59, 2705–2709 (2020).

21. Zhang, Z. et al. The simplest construction of single-site catalysts by the synergism of micropore trapping and nitrogen anchoring. Nat. Commun. 10, 1657 (2019).

22. Chen, Y. et al. Engineering the atomic interface with single platinum atoms for enhanced photocatalytic hydrogen production. Angew. Chem. Int. Ed. 59, 1295–1301 (2020).

23. Zhou, K. L. et al. Seamlessly conductive Co(OH2)2 tailored atomically dispersed Pt electrocatalyst with a hierarchical nanostructure for an efficient hydrogen evolution reaction. Energy Environ. Sci. 13, 3082–3092 (2020).

24. Yoshida, H., Nonoyama, S. & Hattori, Y. Y. T. Quantitative determination of platinum oxidation state by XANES analysis. Phys. Sci. T115, 813–815 (2015).

25. Cao, L. et al. Dynamic oxygen adsorption on single-atoms ruthenium catalyst with high performance for acidic oxygen evolution reaction. Nat. Commun. 10, 4849 (2019).

26. Huang, Z.-F. et al. Chemical and structural origin of lattice oxygen oxidation in Co–Zn oxohydroxide oxygen evolution electrocatalysts. Nat. Energy 4, 329–338 (2019).

27. Zhu, C., Fu, S., Shi, Q., Du, D. & Lin, Y. Single-atom electrocatalysts. Angew. Chem. Int. Ed. 56, 13944–13960 (2017).

28. Wang, X. et al. Ultrathin PINiM (M = Rh, Os, and Ir) nanowires as efficient fuel oxidation electrocatalytic materials. Adv. Mater. 31, 1805833 (2019).

29. Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: insights into materials design. Science 355, eaad4998 (2017).

30. Liu, M. et al. Atomically dispersed metal catalysts for the oxygen reduction reaction: synthesis, characterization, reaction mechanisms and electrochemical energy applications. Energy Environ. Sci. 12, 2890–2923 (2019).
31. Zhang, L. et al. Atomic layer deposited Pt–Ru dual-metal dimers and identifying their active sites for hydrogen evolution reaction. Nat. Commun. 10, 4936 (2019).

32. Zhao, L. et al. The oxidation of methanol on PtRu(111): a periodic density functional theory investigation. J. Phys. Chem. C. 119, 20389–20400 (2015).

33. Ferrin, P. & Mavrikakis, M. Structure sensitivity of methanol electrooxidation on transition metals. J. Am. Chem. Soc. 131, 14381–14389 (2009).

34. Latimer, A. A., Abild-Pedersen, F. & Nørskov, J. K. A theoretical study of methanol oxidation on RuO₂(110): bridging the pressure gap. ACS Catal. 7, 4527–4532 (2017).

35. Wang, X. et al. Materializing efficient methanol oxidation via electron delocalization in nickel hydroxide nanoribbon. Nat. Commun. 11, 4647 (2020).

36. Evans, M. G. & Polanyi, M. Further considerations on the thermodynamics of chemical equilibria and reaction rates. Trans. Faraday Soc. 32, 1533–1536 (1936).

37. Bronsted, J. N. Acid and basic catalysis. Chem. Rev. 5, 231–338 (1928).

38. Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12, 537–541 (2005).

39. Wang, T., Jelic, J., Rosenthal, D. & Reuter, K. Exploring pretreatment–morphology relationships: ab initio wulff construction for RuO₂ nanoparticles under oxidising conditions. ChemCatChem 5, 3398–3403 (2013).

40. Wang, H. & Schneider, W. F. Effects of coverage on the structures, energetics, and electronics of oxygen adsorption on RuO₂(110). J. Chem. Phys. 127, 064706 (2007).

41. Over, H. et al. Atomic-scale structure and catalytic reactivity of the RuO₂(110) surface. Science 287, 1474–1476 (2000).

42. Knapp, M. et al. Complex interaction of hydrogen with the RuO₂(110) surface. J. Phys. Chem. C 111, 5363–5373 (2007).

43. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

44. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996).

45. Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).

46. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

47. Henkelman, G. & Jónsson, H. A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. J. Chem. Phys. 111, 7010–7022 (1999).

48. Henkelman, G. & Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. J. Chem. Phys. 113, 9978–9985 (2000).

49. Henkelman, G., Uberuaga, B. P. & Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. 113, 9901–9904 (2000).

50. Norskov, J. K. et al. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J. Phys. Chem. B 108, 17886–17892 (2004).

51. Jiao, Y., Zheng, Y., Jaroniec, M. & Qiao, S. Z. Origin of the electrocatalytic oxygen reduction activity of graphene-based catalysts: a roadmap to achieve the best performance. J. Am. Chem. Soc. 136, 4394–4403 (2014).