

A Cobalt–Platinum–Ruthenium System for Acidic Methanol Oxidation

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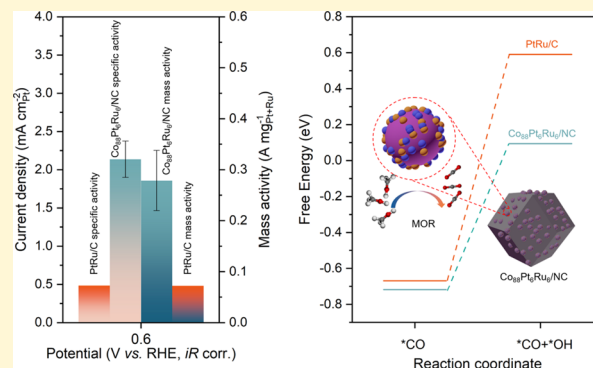


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ABSTRACT: The electrochemical oxidation of methanol is a crucial catalytic reaction in direct methanol fuel cells (DMFCs). Platinum (Pt) or Pt-alloy electrocatalysts have dominated the space, especially in acidic conditions, and different design strategies are needed to achieve both high specific and mass activities. Herein, we comprehensively developed a system of cobalt–platinum–ruthenium nanoparticles within three-dimensional nitrogen-doped porous carbon (Co–Pt–Ru/NC) as an efficient methanol oxidation reaction (MOR) catalyst and investigated different factors such as Pt loading and acid treatment. We found that the intermediate Pt loading displayed MOR activity as low as 0.3 V_{RHE} (versus the reversible hydrogen electrode) and exhibited the highest specific activity ($2.1 \pm 0.2 \text{ mA cm}_{\text{Pt}}^{-2}$) and mass activity ($0.28 \pm 0.06 \text{ A mg}_{\text{Pt+Ru}}^{-1}$) at 0.6 V_{RHE}, which is 4.4 times and 3.9 times higher than the commercial PtRu/C catalysts, respectively. Furthermore, the catalytic activity remains nearly unchanged in acid-treated catalysts after cobalt is partially dissolved in acidic conditions. Through density functional theory calculations of the MOR on our catalyst surface, the enhanced activity was found to originate from cobalt weakening CO adsorption on Pt sites, while simultaneously facilitating OH formation on Ru sites, effectively lowering the energy barrier for the rate-determining step in the MOR and showing promising potential for DMFCs.



INTRODUCTION

Methanol (CH₃OH) is a valuable chemical both in industrial synthesis and as a fuel. In recent years, significant work has been dedicated to improving the efficiency of methanol production by CO₂ reduction and achieving the goal of net-zero emission.^{1–4} As more methanol becomes available, a natural question arises, owing to its high energy density and liquid state, the design of efficient direct methanol fuel cells (DMFCs), in which methanol is a medium for storing and converting electrical energy from chemical energy.^{5,6} The volumetric energy density of methanol is around 15.6 MJ L⁻¹, which is three times higher compared to that of liquid H₂ (4.7 MJ L⁻¹),⁷ making these devices particularly suited for portable applications where size can be a major limitation. Nevertheless, the development of DMFCs has been slow since the early studies of this device in the 1950s,⁸ primarily due to the 6 e⁻ required for the methanol oxidation reaction (MOR, theoretical potential of 0.02 V), CH₃OH + H₂O ⇌ CO₂ + 6(H⁺ + e⁻), leading to sluggish kinetics at the anode.^{9,10}

Tremendous efforts have been dedicated to designing active electrocatalysts for the methanol oxidation reaction (MOR). Platinum (Pt) and Pt-based catalysts have dominated electrocatalyst design for this reaction,^{11–13} especially within DMFC devices,^{14–16} due to their high acid resistance and relatively

lower overpotential compared to other transition metal catalysts.^{17,18} However, in contrast to the nearly negligible overpotential of the hydrogen oxidation reaction that occurs at the anode in a hydrogen fuel cell,^{19–22} the overpotential for MOR on Pt surfaces (>0.45 V with state-of-the-art catalysts^{23–25}) still greatly limits the efficiency of DMFCs. As such, considerable efforts have been made toward engineering Pt surfaces and nanoparticles to increase the MOR activity. For example, Lee et al. have reported the significant role of surface steps on Pt nanoparticles for catalyzing the MOR, resulting in ~200% enhanced activity with increasing surface steps on ~2 nm Pt nanoparticles.²⁶ Also, Suntivich et al. have shown that the catalytic activity of Au_{0.5}Pt_{0.5}/C nanoparticles could be tuned by controlling the surface Pt to Au ratio, where a ~30 to 70 Pt to Au ratio showed 2 orders of magnitude higher MOR activity compared to pure Pt/C.²⁷ Moreover, the high cost and the scarcity of Pt still hinder the practical application of

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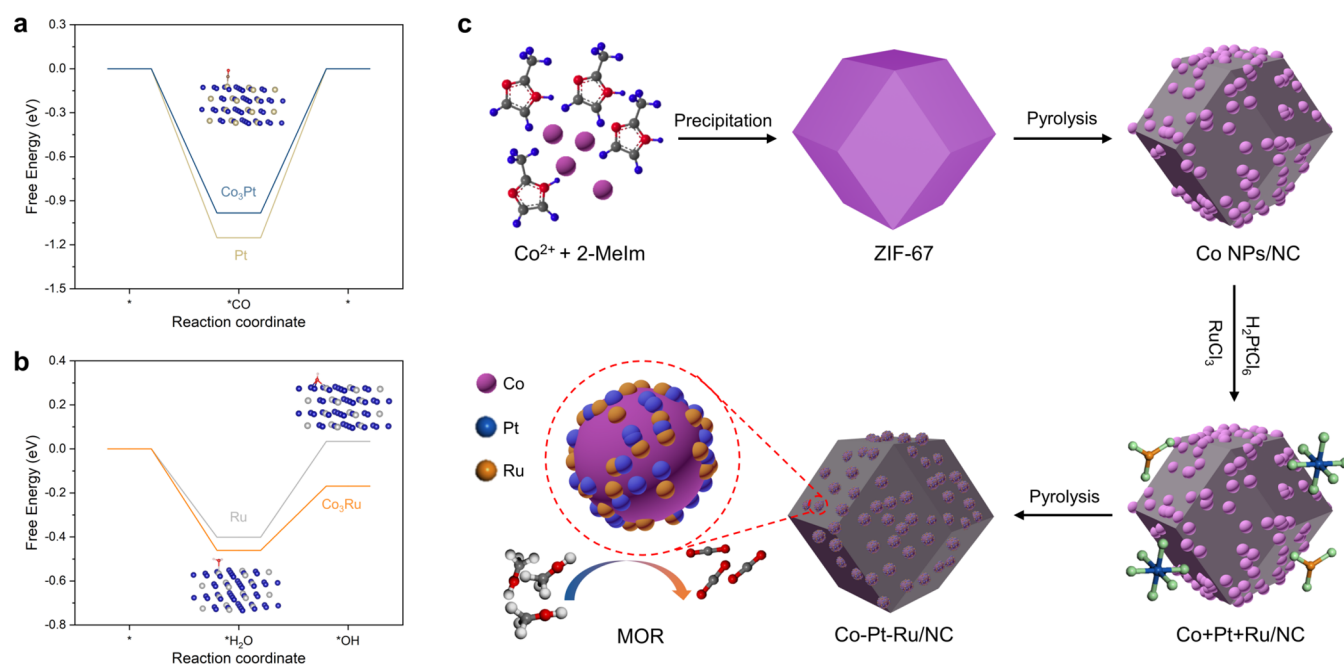


Figure 1. Free energy diagrams of (a) Pt and Co₃Pt for CO adsorption, and (b) Ru and Co₃Ru for H₂O and OH adsorptions. The free energy values are referenced to 1 bar H₂ and H₂O(l). (c) Schematic of the Co–Pt–Ru/NC synthesis.

DMFCs. Therefore, a deeper understanding of MOR electrocatalysts is required for the rational design of low Pt loading or Pt-free electrocatalysts for DMFC use.

PtRu is the current benchmark electrocatalyst for the MOR.^{28,29} Previous studies on the surfaces of well-defined Pt_xRu_{1-x} alloys have shown that the addition of Ru to Pt enhances the MOR activity by ~30 times by decreasing the coverage of poisoning CO species, leading to an optimal in MOR activity when there is a specific balance between the Pt and Ru ratios that optimizes the rate of methanol dehydrogenation on Pt sites and rate of formation of surface oxygenated species on Ru sites, strongly supporting the bifunctional effects of Pt and Ru for promoting the MOR.²⁹ Density functional theory (DFT) calculations have further supported the proposed bifunctional effect, as the presence of Ru in PtRu has been calculated to facilitate water dissociation to form surface-bound OH (*OH), further accelerating the oxidation of coadsorbed *CO in the final reaction step *CO + *OH ⇌ CO₂ + H⁺ + e⁻.^{30,31} Leveraging the bifunctional effect, other alloys have also been developed for the MOR, such as PtSn,^{32–34} which shows nearly comparable activity to PtRu. However, a significant amount of MOR catalyst development has centered on different synthesis strategies to increase the activity of PtRu for the MOR. For example, Chen et al. have synthesized Ru₁Pt_n alloys with Ru atomically dispersed in Pt nanocrystals.³⁵ However, the activity of Ru₁Pt_n is similar to that of Pt/C catalyst at 0.5 V_{RHE}, as Pt is the main component in Ru₁Pt_n. Conversely, Poerwoprajitno et al. created single Pt-atom-on-Ru catalysts by spreading Pt islands on Ru branches.³⁶ Although this catalyst shows a lower onset potential than that of Ru₁Pt_n, the mass activity is comparable to that of commercial PtRu/C when normalized by the noble metal mass. In either case, there is always an abundance of underutilized Pt or Ru sites. Thus, the atomic dispersal strategy, where an electroactive component of the alloy is used as the host may be extreme as it can lead to the underutilization of Pt or Ru. To achieve both high specific

activity and mass activity for the MOR, suitable support for both Pt and Ru, as well as proper loading of Pt and Ru, should be explored in order to maximize the utilization of both metals. As such, ternary metal composites are a reasonable system, as Pt and Ru loadings can be effectively varied. There are several reports on ternary metal composites for the MOR; however, the onset potential for the MOR of these catalysts is still higher than 0.6 V_{RHE} due to the absence of Ru or the heterogeneous distribution of Ru.^{37,38} Moreover, when transition metals are employed in acids, one unavoidable problem is that the catalyst will gradually transform under acidic conditions through processes such as rearrangement and partial dissolution.^{39–42} Thus, finding a suitable substrate, regulating the loading of Pt, and investigating the change of catalyst under acidic conditions are of significance for the rational design of MOR catalysts.

D-band theory has been demonstrated to provide guidance for the experimental results and the explanation of surface-adsorbate interaction strengths.⁴³ Previous DFT calculations have shown that the surface Pt d-band shifts to lower energy compared to that of pure Pt(111) when cobalt (Co) serves as a subsurface,⁴⁴ which indicates that the strong adsorption of *CO on Pt sites could be alleviated to enhance the CO resilience of catalysts.⁴⁵ On the other hand, ΔE_O can be regulated by a downshift of about 0.51 eV by replacing Ru with Co on a Ru surface on the top of a Co substrate.⁴⁶ Therefore, based on scaling relations,⁴⁷ *OH adsorption might also be stronger on Ru sites with Co substitution, which could further facilitate CO removal on the catalyst surface. As such, Co appears to be a promising candidate to serve as a host substrate for Pt and Ru to increase the MOR activity. Herein, we synthesize a ternary system composed of cobalt–platinum–ruthenium nanoparticles within three-dimensional nitrogen-doped porous carbon (Co–Pt–Ru/NC) for the MOR. The system allows for easy adjustment of the Pt loading, with optimal performance observed at intermediate loading levels. Benefiting from the optimized binding energy of the intermediates, Co₈₈Pt₆Ru₆/NC demonstrates MOR activity

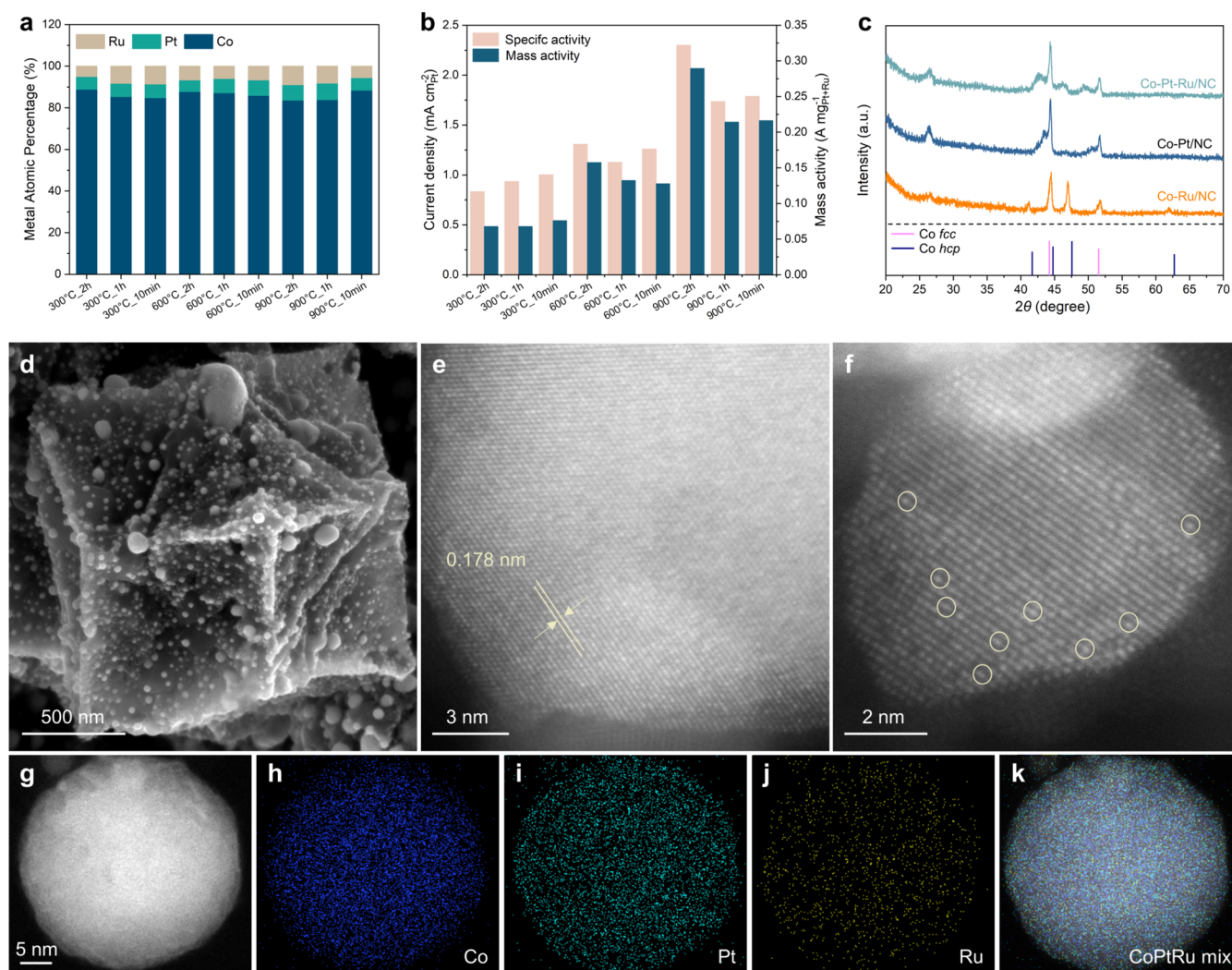


Figure 2. Optimization of synthesis and structural characterization of Co–Pt–Ru/NC. (a) Metal atomic percentages measured using ICP-OES of Co, Pt, and Ru in Co–Pt–Ru/NC synthesized under different conditions. (b) Specific and mass activities at 0.6 V vs RHE of Co–Pt–Ru/NC synthesized under different conditions. (c) XRD patterns of Co–Ru/NC, Co–Pt/NC, and Co–Pt–Ru/NC catalysts. SEM image (d), HAADF-STEM images (e and f, circled atoms are Pt and Ru), and corresponding EDX mapping (g–k) of Co–Pt–Ru/NC. The normalized atomic metal compositions were Co: 71.2%, Pt: 14.1%, and Ru: 14.7%.

as low as 0.3 V_{RHE} , while commercial PtRu/C displays no activity at this voltage. The most active catalyst achieves $2.1 \pm 0.2 \text{ mA cm}_{\text{Pt}}^{-2}$ and $0.28 \pm 0.06 \text{ A mg}_{\text{Pt+Ru}}^{-1}$ at 0.6 V_{RHE} , which are 4.4 and 3.9 times higher than the respective metrics of PtRu/C. Acid treatment results reveal that the material maintains superior activity compared to PtRu/C, even after soaking in 0.1 M HClO_4 for 200 h. Moreover, DMFCs constructed with optimized $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ as the anode catalyst also deliver a higher peak power density than when PtRu/C is used, even when the anode catalyst loading is decreased to 30% of the loading of the commercial benchmark.

RESULTS AND DISCUSSION

Design and Characterization of Co–Pt–Ru/NC. To choose a suitable support for Pt and Ru, DFT calculations were performed to evaluate the binding energy of the key intermediates $^*\text{CO}$ and $^*\text{OH}$. Calculations of ternary and higher mixtures of metals are not convenient due to their complexity and computational cost. For a simple and quick insight, we compared the binding energies of $^*\text{CO}$ on Pt and Co_3Pt (Figure S1). As shown in Figure 1a, $^*\text{CO}$ shows weaker

adsorption on the Co_3Pt surface (-0.98 eV) than on Pt (-1.15 eV). Furthermore, the OH formation processes on Ru and Co_3Ru were also evaluated (Figure S2). First, H_2O is more easily adsorbed on the Ru sites of Co_3Ru , as indicated by the more negative binding energies. The energy barrier for the formation of $^*\text{OH}$ is lower on the Co_3Ru (0.29 eV) surface than on pure Ru (0.43 eV) (Figure 1b). These results imply that Co not only weakens the adsorption of CO on Pt sites but also strengthens the formation of OH on Ru sites, which makes Co an ideal support for Pt and Ru. Co–Pt–Ru/NC catalysts were synthesized via a two-step pyrolysis method, as illustrated in Figure 1c. First, after obtaining ZIF-67 (Figure S3), Co nanoparticles within nitrogen-doped carbon (Co NPs/NC, Figure S4) were prepared by pyrolysis of ZIF-67 at 1000 °C under Ar atmosphere for 2 h followed by cooling naturally, which allowed the adsorption of Pt^{4+} (from $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) and Ru^{3+} (from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) ions. The Pt^{4+} and Ru^{3+} adsorbed Co nanoparticle precursors (Co + Pt + Ru/NC, Figure S5) were then annealed at 900 °C for 2 h under an Ar atmosphere and cooled naturally to form the final product Co–Pt–Ru/NC.

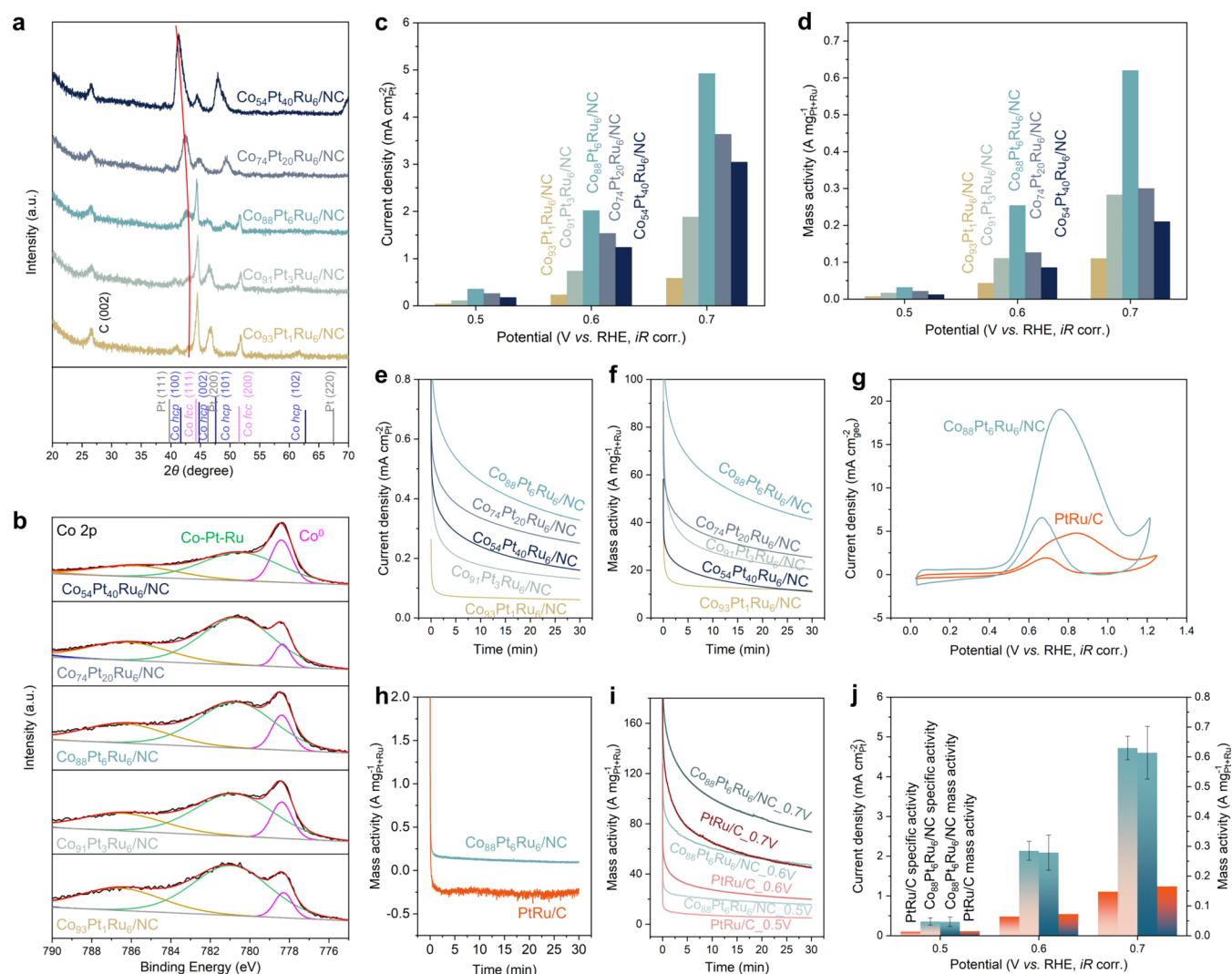


Figure 3. MOR performance and characterization of different Pt-loaded catalysts. (a) XRD patterns of different Pt-loaded catalysts. (b) XPS spectra of Co 2p for different Pt-loaded catalysts. (c–f) Electrochemical performances of different Pt-loaded catalysts. The specific activity (c) and mass activity (d) of the CV at potentials of 0.5, 0.6, and 0.7 V_{RHE}. The specific activity (e) and mass activity (f) of the CA at 0.6 V_{RHE}. (g–j) MOR performance of the optimized $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ compared with that of a commercial PtRu/C catalyst. CV curves were recorded at 0.1 M HClO_4 with 1 M CH_3OH (g). CA results at 0.3 V vs. RHE (h), the mass activity (i) of CA at 0.5–0.7 V_{RHE}. Specific activity and mass activity of the CV at potentials of 0.5, 0.6, and 0.7 V_{RHE} (j).

The synthesis conditions were first explored by changing the heating temperature and time during the second pyrolysis (300, 600, and 900 °C; 10 min, 1, and 2 h). The X-ray diffraction (XRD) patterns showed that the two peaks near 44° become closer and more obvious as the heating temperature increases because high temperatures can improve the Co–Pt–Ru mix better (Figure S6). The morphology of the prepared products was examined using scanning electron microscopy (SEM, Figure S7). The samples treated below 300 °C showed rough surfaces and large chunks because of incomplete carbonization and poor mixing, while the samples treated at higher temperatures and longer pyrolysis times led to uniform nanoparticles. The atomic percentages of Co, Pt, and Ru in the materials under different synthesis conditions were examined using inductively coupled plasma optical emission spectrometry (ICP–OES). There were no significant differences in the metal loadings resulting from the different synthesis conditions (Figures 2a and S8), indicating that the difference in performance was not due to different loadings. The residual

Cl in the samples was examined by ion chromatography (Figure S9), which showed that almost no Cl was present in catalysts synthesized at different temperatures, excluding the effect of Cl on activity. Cyclic voltammetry (CV) polarization curves (Figure S10) of the materials showed that the catalyst synthesized at 900 °C for 2 h had the highest specific and mass activities. Figure 2b compares the specific and mass activities of all samples at 0.6 V_{RHE}, which shows a monotonic increase in the MOR activity with heating temperatures. For the samples heated at lower temperatures (e.g., 300 °C), two superimposed peaks in the forward CV scan (i.e., anodic direction) were observed, most likely indicating poor mixing of the metals, consistent with the XRD results. Chronoamperometry (CA) results also showed poor activity of the materials prepared at 300 °C. The material heat-treated at 600 °C for 2 h exhibited activity similar to that of the materials treated at 900 °C at 0.6 V_{RHE}, but a lower activity at 0.7 V_{RHE} (Figure S11). As the most active synthesis conditions were found to occur when the Co + Pt + Ru/NC precursor was heated at 900 for 2 h, these

synthesis conditions were adopted for future studies. Co–Pt/NC and Co–Ru/NC were prepared to better understand the effects of Pt and Ru doping (Figure 2c). The presence of Pt induces a Co peak shift toward lower 2θ , most likely due to the strain imparted by the larger atomic radius of Pt. As the doping of Ru can lead to a partial phase change of Co from face-centered cubic (*fcc*) to the hexagonal close-packed (*hcp*) polymorph,⁴⁸ the new peak near 46.4° upon heating at higher temperatures can be explained by the local transformation of *fcc*-Co to *hcp*-Co upon Ru substitution.

The morphology of ZIF-67 was polyhedral, and Co–Pt–Ru/NC maintained this shape after pyrolysis (Figure S12). During the first pyrolysis, the carbonization process made the ZIF-67 hollow, and the second pyrolysis made the Pt and Ru dope into Co nanoparticles. The nanoparticles anchored on the hollow carbon skeleton (Figure S13) are Co–Pt–Ru nanoparticles (denoted as $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$, according to the nominal composition, Figure 2d). The atomic structure of the nanoparticles was further explored by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), where the interplanar spacing of $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ was measured to be 0.178 nm (Figure 2e), which matches well with the (200) planar spacing of *fcc*-Co (0.177 nm). The nanoparticles also appear to be covered by an adventitious carbon layer (Figure S14a), which may have acted to prevent aggregation during the second thermal treatment. To obtain a clear view, bright-field (BF) and dark-field (DF) images cross-validated the presence of Pt and Ru within a Co host as a dispersal of higher-intensity atoms (darker atoms in BF and brighter atoms in DF) within the lower-intensity Co matrix can be observed (Figure S14b–e). A proportion of the atoms within a nanoparticle showed a higher intensity than the rest, which, coupled with the similar (200) interplanar spacing between $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ and *fcc*-Co, strongly suggests that Pt and Ru were successfully incorporated into the Co host (Figures 2f and S14f). Energy-dispersive X-ray spectroscopy (EDX) elemental mapping analysis revealed that Co, Pt, and Ru were homogeneously distributed throughout the structure (Figure 2g–k). EDX mapping also confirmed the existence of carbon and nitrogen as conductive supports (Figure S15). The normalized atomic metal compositions of Pt and Ru are higher than those measured from ICP-OES results (Figures S16 and S17), which might be attributed to nonuniform alloying in some nanoparticles measured using EDX, as ICP-OES takes a representative average across the entire synthesized powder. We note that while Co atoms can be observed in pure Co NPs/NC (Figure S18), imaging the interplanar spacing of $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ can be potentially challenging due to scattering from the disordered incorporation of Pt and Ru (Figure S19).

Tuning Pt Loading in Co–Pt–Ru/NC. Considering the price of Pt, the goal of Pt-alloy catalyst design is always to minimize Pt usage, while maximizing activity and durability. Therefore, we aimed to optimize the material for catalyzing the MOR by tuning the Pt loading in Co–Pt–Ru/NC by changing the amount of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ during the adsorption step at ambient conditions, while maintaining the same absolute Ru loading, as confirmed by ICP-OES results (Figure S20). The prepared samples were denoted as $\text{Co}_{93}\text{Pt}_1\text{Ru}_6/\text{NC}$, $\text{Co}_{91}\text{Pt}_3\text{Ru}_6/\text{NC}$, $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$, $\text{Co}_{74}\text{Pt}_{20}\text{Ru}_6/\text{NC}$, and $\text{Co}_{54}\text{Pt}_{40}\text{Ru}_6/\text{NC}$, according to their nominal metal atomic compositions during synthesis. The XRD patterns (Figure 3a) show that with the addition of a small Pt amount, the

$\text{Co}_{93}\text{Pt}_1\text{Ru}_6/\text{NC}$ has almost the same XRD pattern as Co–Ru/NC, albeit with a small hump (43.1°) at the left of the Co peak, which matches closely with the (111) reflection of Co_3Pt . With higher Pt loading, the intensity of the small hump at 43.1° increased, and another peak related to the Co_3Pt (200) reflection appeared at 49.7° , as can be seen for $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$. Also, all peaks progressively shifted toward the left as Pt loading increased, which suggests that more Pt was doped into the Co owing to the higher interplanar spacing of Pt compared to Co_3Pt (or Co–Ru) for the same planes. However, if excessive Pt precursor was added, the two peaks around 43 and 44° merged into one peak, which also occurred, similar to the other two peaks located at around 50 and 51° . The fact that the two asymmetric peaks at 41.3 and 47.9° for $\text{Co}_{54}\text{Pt}_{40}\text{Ru}_6/\text{NC}$ could be deconvoluted into two peaks also demonstrates this point. In fact, new peaks at around 41.3 , 47.9 , and 70° were observed for $\text{Co}_{54}\text{Pt}_{40}\text{Ru}_6/\text{NC}$, which correspond closely to a Pt-rich phase (interpreted from their close proximity to the (111), (200), and (220) reflections of pure Pt, respectively), most likely indicating that Pt alloyed with Co. In this case, Pt is the main support instead of Co, and thus, the $\text{Co}_{74}\text{Pt}_{20}\text{Ru}_6/\text{NC}$ composition demarcates a transition between the host Pt-poor phase at lower Pt loading and the host Pt-rich phase at high Pt loading. X-ray photoelectron spectroscopy (XPS) was conducted to examine the chemical states of the different elements (Figure S21), which also confirmed the presence of Co, Pt, and Ru. The peak fitting of Co 2p from $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ was composed of three peaks centered at 778.4, 780.8, and 786.6 eV (Figure 3b), which can be attributed to Co^0 in the nanoparticle,⁴⁹ alloyed Co in Co–Pt–Ru,⁵⁰ and a satellite peak, respectively, which are consistent with a previously reported work.⁴⁵ The Co peak of Co–Pt–Ru shifted positively with increasing Pt loading (0.50 eV from $\text{Co}_{93}\text{Pt}_1\text{Ru}_6/\text{NC}$ to $\text{Co}_{54}\text{Pt}_{40}\text{Ru}_6/\text{NC}$) potentially due to the stronger interaction between Co and Pt with more Pt in the system. The Pt 4f peak in these samples can be deconvoluted into two pairs of doublets, including Pt^0 and Pt^{2+} . Similarly, the Ru 3p peak could be fitted by Ru^0 and RuO_2 for both Ru $3p_{3/2}$ and Ru $3p_{1/2}$. However, the Pt and Ru peaks did not display a clear trend, most likely due to the complexity of the system.

The CV curves of methanol oxidation of the materials with different Pt loadings were normalized by the Pt electrochemically active surface area estimated through the hydrogen underpotential deposition region (Figure S22) to give the specific activity and by the Pt + Ru mass loading to give the mass activity. Both specific (Figures 3c and S23a) and mass activity (Figures 3d and S23b) showed a volcano trend as a function of Pt loading, giving an optimal composition of $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$, which exhibited the highest MOR activity at 0.5, 0.6, and $0.7 V_{\text{RHE}}$. CA measurements were also carried out on these materials at different potentials from 0.4 to $0.7 V_{\text{RHE}}$ in 0.1 V increments (Figures 3e,f and S24 and S25), where the trend of Pt-loading-dependent activity is in agreement with the CV results. For example, both the specific and mass current in the CA measurements at $0.6 V_{\text{RHE}}$ first increased with increasing Pt loading, reaching a maximum with $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ before decreasing with further increased Pt loading. The volcano trend in the MOR activity as a function of Pt loading can be explained by considering that a low concentration of Pt will lead to a small proportion of surface Pt atoms adjacent to the surface Ru atoms, limiting the ability to promote CO oxidation compared to pure Pt. When the Pt loading is increased, statistically, there will be more exposed surface Pt

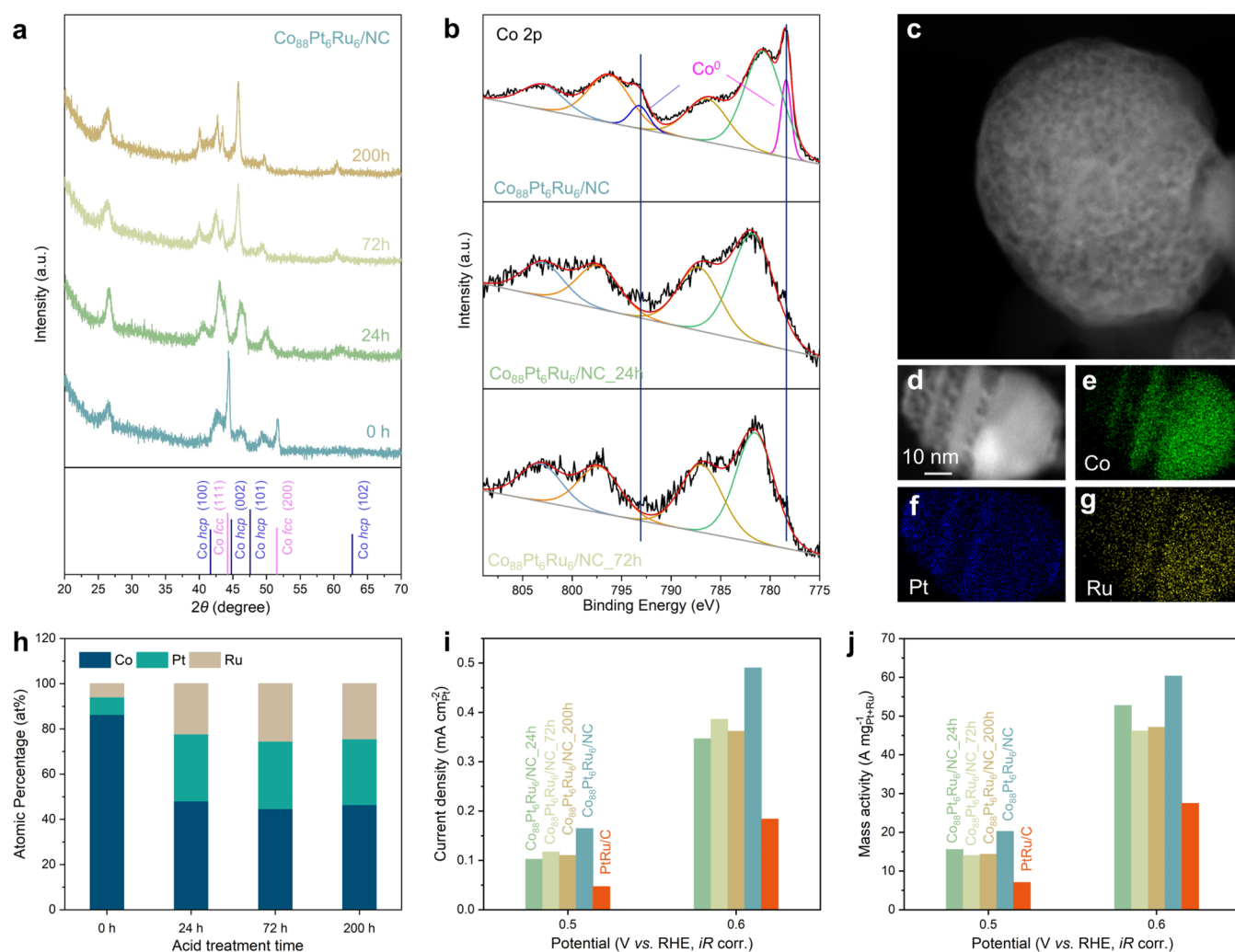


Figure 4. Characterization and electrocatalytic activity of Co₈₈Pt₆Ru₆/NC after acid treatment. (a–h) Characterization of Co₈₈Pt₆Ru₆/NC after acid treatment. XRD patterns (a) and Co 2p XPS spectra (b). HAADF-STEM image of Co₈₈Pt₆Ru₆/NC_{24h} (c) and EDX mapping of Co₈₈Pt₆Ru₆/NC_{24h} during transition (d–g). Metal atomic percentages obtained from ICP-OES (h). (i–j) CA results at 10 min under 0.5 and 0.6 V_{RHE}. The specific (i) and mass activities (j).

atoms adjacent to Ru atoms, which can synergistically enhance CO oxidation and, therefore, the MOR rate. Upon further increasing Pt, the proportion of Pt atoms adjacent to Ru atoms decreased, losing the synergistic effects of both metals and decreasing activity. Furthermore, one of the obvious problems with excessive Pt is that the mass activity decreases since many Pt atoms in the nanoparticles are underutilized. Also, a fixed Ru loading may cause surplus Pt atoms to aggregate, reducing dispersion and making the nanoparticles more susceptible to CO poisoning, as observed for Co₅₄Pt₄₀Ru₆/NC. ICP-OES indicated that the atomic ratio of Pt and Ru in Co₈₈Pt₆Ru₆/NC is close to 1:1, which also explains its excellent activity.

To benchmark the MOR activity of Co₈₈Pt₆Ru₆/NC, commercial PtRu/C (Pt/Ru ~ 1:1, 78 wt % on carbon, Tanaka Kikinzo) was employed as a reference. Co₈₈Pt₆Ru₆/NC has a large geometric current density of 15.96 mA cm⁻² at 0.7 V_{RHE}, which is 4.7 times greater than that of PtRu/C at the same potential (3.38 mA cm⁻²) (Figures 3g and S26). After normalization, the specific (Figure S27) and mass activities of Co₈₈Pt₆Ru₆/NC were both still about 4 times higher than those of PtRu/C (Figure S28). Utilizing CA measurements is a more rational approach for assessing catalyst activity at steady-

state conditions, especially for DMFC applications. In contrast to commercial PtRu/C, which does not show MOR activity until 0.4 V_{RHE}, Co₈₈Pt₆Ru₆/NC showed oxidative current as low as 0.3 V_{RHE} (Figure 3h). The CA results of specific and mass activity under other potentials from 0.4–0.7 V_{RHE} were also compared, as shown in Figures 3i and S29, where Co₈₈Pt₆Ru₆/NC exhibited higher activity under all applied potentials. The specific and mass activities at 0.5, 0.6, and 0.7 V_{RHE} were averaged with the standard deviation taken as error bars across three independent measurements (Figure S30), which were all several times higher than those of the commercial PtRu/C catalyst. Particularly, the high specific activity (2.1 ± 0.2 mA cm_{Pt}⁻²) and mass activity (0.28 ± 0.06 A mg_{Pt+Ru}⁻¹) of Co₈₈Pt₆Ru₆/NC at 0.6 V_{RHE} is 4.4 and 3.9 times higher compared to those of commercial PtRu/C (0.48 mA cm_{Pt}⁻² and 0.072 A mg_{Pt+Ru}⁻¹), respectively (Figure 3j and Table S1).

Acid Treatment of Co₈₈Pt₆Ru₆/NC. The acid stability of Co₈₈Pt₆Ru₆/NC was investigated, as many catalysts can be gradually transformed in an acidic electrolyte or under electrochemical conditions.⁵¹ Co₈₈Pt₆Ru₆/NC after MOR measurements were reserved (approximately 5 h of testing

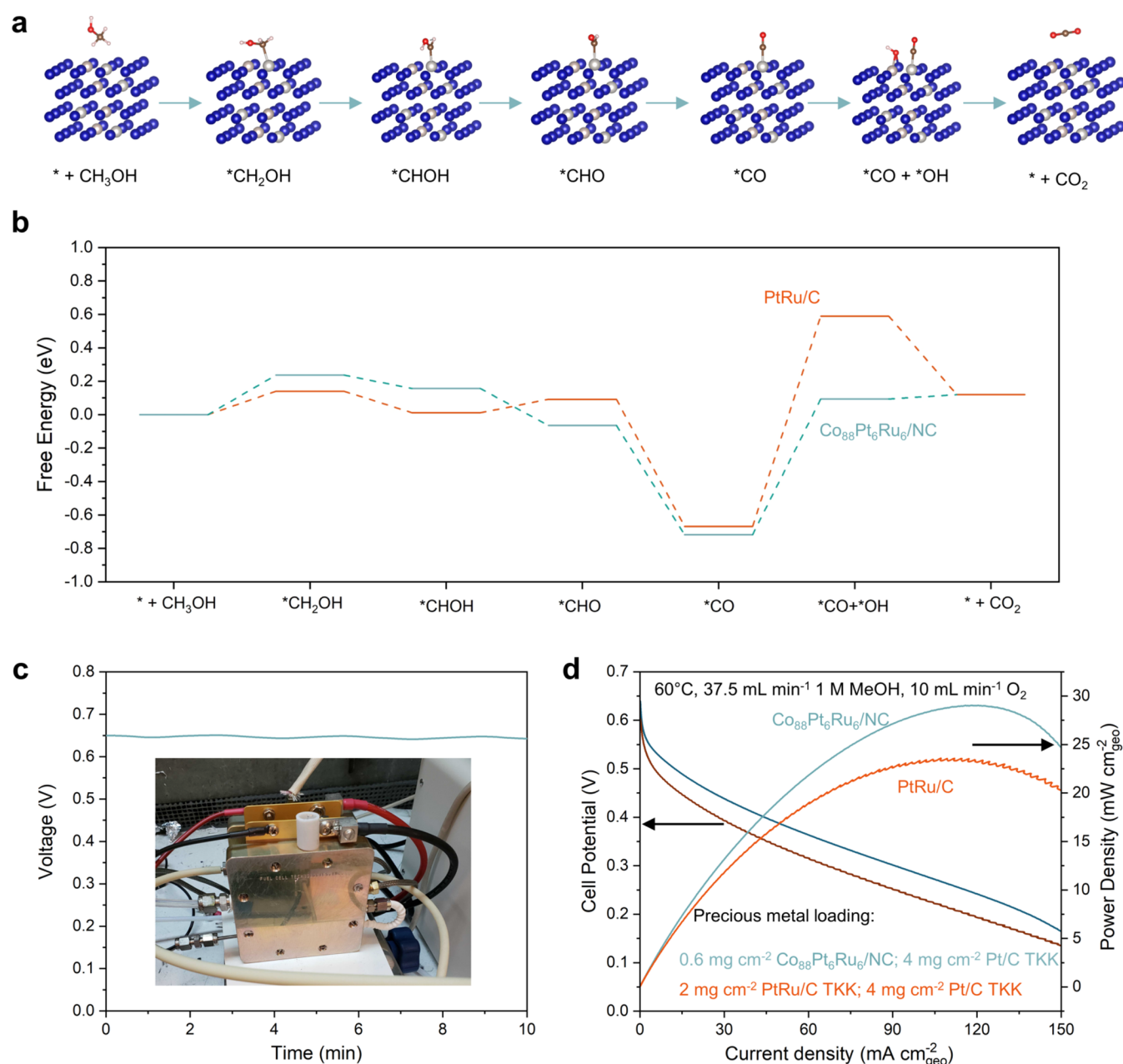


Figure 5. DFT calculations and DMFCs. (a) Reaction pathway for the MOR of Co–Pt–Ru. (b) Free energy diagram of the MOR for Co₈₈Pt₆Ru₆/NC and PtRu/C at 0 V. (c) OCV curve for Co₈₈Pt₆Ru₆/NC; inset is a digital photo for DMFCs. (d) Comparison of DMFC performance of Co₈₈Pt₆Ru₆/NC and PtRu/C catalysts at the anode with 1 M methanol at 60 °C.

time) and then investigated by STEM. The solid nanoparticles appeared to have been etched by acid to form a porous network structure. EDX mapping revealed that Co remained in the structure and all elements continued to be homogeneously distributed (Figure S31).

To understand the acid stability of Co₈₈Pt₆Ru₆/NC, acid treatment was carried out by immersing the pristine material in 0.1 M HClO₄ for 24, 72, and 200 h. From the XRD results (Figure 4a), most of the *fcc*-Co structures were dissolved, as the peak at 44.2° exhibited a notable reduction in intensity while the *hcp*-Co structure peak positions were almost unchanged. The predominant peak around 44° was split into two peaks corresponding to *fcc*-Co and *hcp*-Co. The XPS peaks in the Co 2p energy range of the catalysts after acid treatment could be deconvoluted into only two peaks instead

of the three peaks found in the pristine material (Figure 4b). The peaks around 778 and 793 eV, corresponding to Co⁰, disappeared while the peak around 781 eV (similar to that reported for a PtCo alloy⁵²) remained, suggesting that while Co was dissolved, the Co alloyed with Pt and/or Ru was more stable.⁵³ No significant change of the XPS spectra for the Pt 4f region (Figure S32a) was observed, whereas the peak for Ru 3p_{3/2} was shifted to higher binding energies (Figure S32b), which might be explained by Co⁰ providing charge transfer to Ru or Ru–O formed during acid treatment.⁵⁴ Using STEM, the microporous structure was clearly observed after 24 h of acid treatment (Figure 4c). One nanoparticle in an intermediate state of dissolution was imaged (Figure 4d), where some of the Co was dissolved to form a porous structure and some remained solid. The mapping results showed that the

porous part was Pt-rich, while the solid part was Co-rich (Figure 4e–g). Pt showed stronger intensity after Co was dissolved, indicating that the previously Pt-poor phase lost Co and became porous while the Pt-rich phase almost retained full density, which further supports that the alloying effect of Ru and Pt can make Co more stable in acidic conditions. EDX mapping also revealed homogeneous distributions of Co, Pt, and Ru in the nanoparticles after they were fully etched (Figure S33). The ICP-OES results showed that the relative atomic percentage of Co in the nanoparticles decreased while those of Pt and Ru increased after 24 h of acid treatment (Figures 4h and S34). The metal atomic percentages of $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}_{24\text{h}}$ are 48.1% for Co, 29.6% for Pt, and 22.3% for Ru, which are close to the EDX results for $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ after MOR measurements and acid treatment. However, a longer acid treatment did not alter the ratio among these three elements ($\text{Co}_{44.7}\text{Pt}_{29.9}\text{Ru}_{25.4}$ for 72 h and $\text{Co}_{46.5}\text{Pt}_{29.1}\text{Ru}_{24.4}$ for 200 h), indicating the adoption of a, at least, seemingly metastable structure after partial dissolution in the acid electrolyte.

The MOR activities of the acid-soaked samples were measured to assess the effects of dissolution on electrochemical activity, as shown in Figure S35. The CV curves exhibited similarity across geometric, specific, and mass activities, which is reasonable considering that the metal compositions of the nanoparticles are almost the same. Although the activity is lower than that of pristine $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$, the activities of all acid-treated materials are still higher than that of commercial PtRu/C catalysts and most reported catalysts (Table S1). From the CA measurements (Figures S36 and S37), the specific activity and mass activity of acid-treated samples are slightly lower than those of the samples before acid treatment but much higher than those of the commercial PtRu/C. The currents of the acid-treated samples at 10 min under 0.5 and 0.6 V_{RHE} were selected for comparison, as displayed in Figures 4i and 5j. The specific activities of $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$, $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}_{24\text{h}}$, $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}_{72\text{h}}$, $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}_{200\text{h}}$ were measured to be 20.3, 15.6, 14.1, 14.4, and 7.0 $\text{mA cm}_{\text{Pt}}^{-2}$ at 0.5 V_{RHE} , respectively, and were all at least twice higher compared to PtRu/C, demonstrating the excellent activity and suitability for DMFCs application. The slight decay in the performance might be ascribed to the dissolution of Co in the nanoparticles in the acidic environment, which probably serves as an auxiliary component that regulates the electronic structure of the active sites without being catalytically active.

Mechanism Studies and DMFCs. To understand the role of each component within the system, control experiments were conducted to decouple the interactions between the various metal constituents. Co NPs/NC and $\text{Co}_{94}\text{Ru}_6/\text{NC}$ showed no MOR activity below 1.0 V_{RHE} (Figure S38), as expected from the lack of Pt incorporation. $\text{Co}_{94}\text{Pt}_6/\text{NC}$ has a similar onset potential but a higher MOR current density compared to that of commercial Pt/C (TKK, 46 wt %) (Figure S39). We therefore conclude that Pt is the active site for the MOR, and Ru acts to facilitate *CO removal. ZIF-8 was also employed as a precursor to understand the effects of Co. Pure nitrogen-doped carbon was obtained (Figure S40a) because the Zn (boiling point of 907 °C) in ZIF-8 was evaporated during the first pyrolysis process at 1000 °C.⁴⁶ Afterward, the same amount of Pt and Ru precursors were added, which was followed by the second pyrolysis. The XRD results indicate that no Pt or Ru nanoparticles were formed. Furthermore, the

flat cyclic voltammogram of Pt–Ru/NC shows the absence of methanol oxidation. As the ICP-OES results showed only less than 1% Pt and Ru in the composite material, Co also appears to be an important support for loading Pt^{4+} and Ru^{3+} ions on the material prior to the second thermal annealing (Figure S40).

Figure 5a displays the reaction pathway of the MOR on Co–Pt–Ru(001), which was used to simulate the structure of the most active composition, $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$. The * CH_2OH , * CHOH , * CHO , and * CO intermediates were formed as CH_3OH was progressively dehydrogenated on the Pt site. Then, * OH was formed on the Ru site near Pt by water dissociation and reacted with * CO to yield CO_2 . The reaction pathway is the same as that on the PtRu(111) surface (Figure S41). The free energy diagrams for the MOR reaction pathway on the Co–Pt–Ru(001) and PtRu(111) surfaces were calculated to determine the origin of the improved performance at a potential of 0 V_{RHE} (Figure 5b). The elementary step energetics of the first four steps display similar energy changes for both surfaces. For Co–Pt–Ru(001), after the first deprotonation process, the overall formation of * CO is downhill in energy. While the RDS step for both surfaces is * OH formation (from * CO to * $\text{CO} + * \text{OH}$), the activation barrier on Co–Pt–Ru(001) (0.81 eV) is about 0.45 eV lower than that on and PtRu(111) (1.26 eV). As such, it is clear that $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ can effectively lower the energy barrier for CO oxidation and facilitate CO removal, suggesting that the $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ catalyst is resilient to CO poisoning. CO stripping was carried out to further demonstrate this point (Figure S42). $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ exhibited a higher stripping current at 0.5 V_{RHE} , which is consistent with the higher current density during the MOR. Also, $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ had a lower onset potential for CO stripping than commercial PtRu/C, supporting the DFT calculations and explaining why $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ could deliver comparable MOR activity at lower potentials. Commercial PtRu/C displays a prolonged current tail, indicating heightened susceptibility to CO poisoning on the Pt sites. However, the sharp peak of $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ suggests more facile * CO removal on its surface and more available sites for further reactions. Combined with the DFT and CO stripping results, $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ appears to be more resilient to CO poisoning and has a lower energy barrier for the RDS of the MOR, explaining the high MOR activity measured.

Motivated by the impressive MOR performance of the optimized $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$, a direct methanol fuel cell employing $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ catalysts as the anode and commercial Pt/C catalysts as the cathode was constructed to reflect practical applications. The open-circuit voltage of the device was stable at 0.65 V (Figure 5c). Despite a lower loading, the DMFCs driven by $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ could deliver a higher peak power density of $28 \pm 1 \text{ mW cm}^{-2}$ (Figures 5d and S43) compared to DMFCs driven by commercial PtRu/C (23.6 mW cm^{-2}), giving 4.1 times higher power density if normalized by the noble metal loading. Also, its performance was compared with that of other reported DMFCs (Table S2). Although the geometric activity is lower than that of some optimized devices with different loading and operation conditions, the mass activity of our DMFCs ($48.3 \text{ mW mg}_{\text{Pt+Ru}}^{-1}$) is comparable or even higher. Further, the long-term stability of $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ was measured using a three-electrode system (Figure S44) and DMFC (Figure S45). The current decreased by around 70% after 10 h of measurement

and was stabilized for more than 30 h in a three-electrode system, which was mainly due to the accumulation of poisoning species such as CO on the catalyst surface over a long period of time, leading to the inactivation of the active sites and the continuous volatilization of methanol during the test. However, the stability is still better than that of the most reported MOR catalysts as they suffer more than 70% current drop within 1 h. On the other hand, the current only showed a ~35% decrease after 48 h of operation in the DMFC. The better stability in DMFC might be attributed to the fact that flow can remove some of the poisonous species. Although the stability of the MOR has always been a thorny issue, we believe that it can be improved through further engineering adjustments.

CONCLUSIONS

We comprehensively investigate the use of the Co–Pt–Ru system for methanol oxidation. DFT calculations reveal that Co not only weakens *CO adsorption but facilitates the *OH formation as well. The RDS of the MOR is from *CO to *CO + *OH, and Co₈₈Pt₆Ru₆/NC can effectively lower the energy barrier for the RDS. The Pt loading can be tuned by changing the amount of the precursor. At 0.6 V_{RHE}, Co₈₈Pt₆Ru₆/NC has both high specific activity of 2.1 ± 0.2 mA cm_{Pt}⁻² and mass activity of 0.28 ± 0.06 A mg_{Pt+Ru}⁻¹, which are both approximately 4 times higher than the same respective metrics of commercial PtRu/C. Furthermore, the transformation of catalysts in acid conditions revealed that part of the Co can be dissolved in an acidic solution and the solid nanoparticles transform into a (meta)stable porous network structure with a homogeneous distribution of Co, Pt, and Ru. The MOR activity of Co₈₈Pt₆Ru₆/NC after acid treatment was still superior to that of PtRu/C. DMFCs were assembled to fully demonstrate the catalytic performance of Co₈₈Pt₆Ru₆/NC, which can reach a peak power density of 28 ± 1 mW cm⁻², which is 4.1 times that of the commercial PtRu/C catalysts normalized by precious metal loading. For further research, several aspects can be investigated, such as improving the size uniformity of the nanoparticles and finding other transition metals that can regulate the binding energy but are more acid-resistant to support Pt and Ru. Moreover, improving the stability of Co–Pt–Ru/NC and other MOR catalysts is important for practical applications. Our findings demonstrate the clear advantage of using abundant support that, while not necessarily electroactive, changes the electronic structure of electroactive components while simultaneously maximizing their utilization, thereby providing potential new design approaches for the MOR and other electrocatalysts for DMFCs and beyond.

METHODS

Synthesis of Co–Pt–Ru/NC. All chemicals were used as received without further purification. Milli-Q deionized water was used in all experiments. First, ZIF-67 was prepared by a precipitation reaction between Co(NO₃)₂·6H₂O (1.23 g) and 2-methylimidazole (1.46 g) in 50 mL methanol at ambient conditions. After 20 h of reaction, ZIF-67 was obtained by centrifugation and then washed with methanol 3 times, followed by drying in the oven overnight. To prepare Co NPs/NC, an alumina boat crucible loaded with ZIF-67 was placed in a tube furnace, heated to 1000 °C at a rate of 5 °C min⁻¹, and then maintained at that temperature for 2 h under N₂ flow. After that, 100 mg of Co NPs/NC was dispersed in 50 mL H₂O and sonicated for 30 min. 5 mL of H₂PtCl₆·xH₂O (4 mg mL⁻¹) and 5 mL of RuCl₃·xH₂O (4 mg mL⁻¹) were added to the suspension and stirred for 2 h. The

suspension was centrifuged 3 times with water and dried overnight to obtain Co + Pt + Ru/NC. The final product, Co–Pt–Ru/NC, was prepared by the pyrolysis of Co + Pt + Ru/NC at 900 °C at a rate of 5 °C min⁻¹ for 2 h under N₂ flow.

To explore the pyrolysis conditions, the temperature and dwelling time were varied. Co + Pt + Ru/NC was pyrolyzed at 300 °C for 10 min, 1 h, and 2 h, 600 °C for 10 min, 1 h, and 2 h, and 900 °C for 10 min, 1 h, and 2 h. The Pt loading in Co–Pt–Ru/NC was regulated by adding different amounts of the Pt precursor. Typically, the amount of Co NPs/NC and RuCl₃·xH₂O were kept the same, and 1.25, 2.5, 4, 12.5, and 25 mL H₂PtCl₆·xH₂O (4 mg mL⁻¹) were added. The final products were named as Co₉₃Pt₁Ru₆/NC, Co₉₁Pt₃Ru₆/NC, Co₈₈Pt₆Ru₆/NC, Co₇₄Pt₂₀Ru₆/NC, and Co₅₄Pt₄₀Ru₆/NC.

Acid Treatment of Co₈₈Pt₆Ru₆/NC. To mimic the electrolyte environment, 0.1 M HClO₄ was used for acid treatment of Co₈₈Pt₆Ru₆/NC. Generally, 50 mg of Co₈₈Pt₆Ru₆/NC was dispersed in 50 mL of 0.1 M HClO₄ for 24, 72, and 200 h. After centrifugation 3 times with H₂O and drying overnight, the samples after acid treatment were obtained and named as Co₈₈Pt₆Ru₆/NC_24h, Co₈₈Pt₆Ru₆/NC_72h, and Co₈₈Pt₆Ru₆/NC_200h.

Material Characterization. Powder X-ray diffraction (XRD) was carried out with a Bruker D2 Phaser Gen II X-ray powder diffractometer equipped with a Cu-sealed tube (wavelength λ = 1.5418 Å) at 30 kV and 10 mA. The metal weight and atomic percentages of the samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with an Agilent 5100 DVD inductively coupled plasma optical emission spectrometer. To analyze the morphology of the precursors and products, Zeiss Merlin high-resolution scanning electron microscope (SEM) was used. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was conducted using a probe-aberration-corrected Thermo Fisher Scientific Themis Z G3 60–300 kV S/TEM at 200 kV. Energy-dispersive X-ray (EDX) mapping data were collected using a Thermo Fisher Scientific Super-X detector. The elemental chemical states of the as-prepared products were determined by X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific K-α+ spectrometer using monochromatic Al Kα radiation (1,486.6 eV). The binding energy of the C 1s peak at 284.6 eV was used as the reference.

Electrochemical Measurements. Electrodes were prepared by drop-casting the ink containing the catalyst powder with Nafion on a glassy carbon (GC) disk electrode (Pine Research, 5 mm diameter). Typically, 5 mg of the catalyst was dispersed in a mixture of 980 μL ethanol and 20 μL Nafion (5 wt %) via ultrasonication for 60 min to form the catalyst ink. 10 μL of the catalyst ink was dropped onto the GC with a nominal loading of 250 μg_{catalyst} cm_{geo}⁻² and 46 μg_{Nafion} cm_{geo}⁻². Electrochemical measurements were carried out in a three-electrode setup in a glass electrochemical cell with an Ag/AgCl reference electrode and a carbon rod counter electrode. The Ag/AgCl reference electrode was calibrated in the same electrolyte by measuring hydrogen oxidation/evolution using a platinum working electrode and defining the point of zero current as 0 V vs RHE. The potential was controlled using a Biologic VSP-300 potentiostat. Cyclic voltammetry (CV) was performed in a solution of Ar-saturated 1 M CH₃OH in 0.1 M HClO₄ with a potential range of ~0.05–1.2 V vs RHE at a scan rate of 50 mV/s. The background current was collected from the CV of the catalysts in Ar-saturated 0.1 M HClO₄ before CH₃OH addition. Chronoamperometry (CA) measurements were recorded from 0.3–0.7 V vs RHE with a 0.1 V interval. The ohmic losses were corrected by subtracting the ohmic drop from the measured potential using the electrolyte resistance. The potential after *iR* correction was calculated using $E_{RHE} = 0.263 \text{ V} + E_{\text{tested}} - iR$. More details are provided in the Supporting Information.

CO Stripping Experiments. The CO stripping activities of Co–Pt–Ru/NC and PtRu/C were compared. Typically, after surface cleaning (0.1 M HClO₄), the catalysts were subjected to CO adsorption at 0.05 V vs RHE for 30 min and the solution was then purged with Ar to remove unbound CO. The stripping data were collected using CV at a scan rate of 10 mV/s. The current was corrected using the background current.

DMFC Measurements. The as-synthesized $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ and commercial Pt/C (67%, Tanaka Kikinokuni, "TKK") were used as catalysts at the anode and cathode to fabricate the membrane electrode assembly (MEA), respectively. First, 40 mg of the catalyst powder was dispersed in 2 mL isopropanol alcohol (IPA) with 200 μL Nafion (5 wt %) and sonicated for 1 h. The catalyst was drop-cast onto carbon cloth to reach a loading of 6 mg cm^{-2} for $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ and a precious metal loading of 4 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ for Pt/C as the anode and cathode, respectively. The MEAs were fabricated by sandwiching the Nafion 117 membrane between the anode and cathode, followed by hot pressing at 120 °C under a pressure of 0.2 MPa for 3 min. The assembled DMFC was tested at 60 °C by feeding 1 M CH_3OH at the anode at a flow rate of 37.5 mL min^{-1} and feeding dry oxygen at the cathode at a flow rate of 10 mL min^{-1} . The open-circuit potential was measured first, and linear sweep voltammetry (LSV) was conducted to measure the polarization curves at a scan rate of 10 mV s^{-1} . Commercial PtRu/C (78%, TKK) was used for comparison by replacing $\text{Co}_{88}\text{Pt}_6\text{Ru}_6/\text{NC}$ with PtRu/C with a precious metal loading of 2 $\text{mg}_{\text{PtRu}} \text{cm}^{-2}$.

DFT Calculations. Spin-polarized density functional theory (DFT) calculations were performed with the Vienna ab initio simulation package (VASP) using the projector-augmented plane wave method with a cutoff of 450 eV. The Ru_{pv} pseudopotential was employed for ruthenium, where semicore p states were treated as valence states. Exchange correlation was applied in the Perdew, Burke, and Ernzerhof functional within a generalized gradient approximation (GGA-PBE). The Pt(111) and Ru(0001) surfaces were cleaved from the relaxed bulk material. The Pt(111) and Ru(0001) slabs were constructed as 2 × 2 periodic supercells containing six atomic layers, where the bottom three layers were fixed with vacuum separation >10 Å in the Z-direction and γ -centered k-point sampling of 4 × 4 × 1. The different surface species of methanol electrooxidation (*CH₂OH, *CH₂O, *CHOH, *CHO, *CO, *OH, *H₂O) on the intermetallic structures were placed on one side of the slab. To convert the calculated DFT adsorption energies into Gibbs free energies, the zero point energies and enthalpic and entropic corrections from the vibrational analysis are listed in Table S3. The electronic convergence threshold for the two slabs was 1 × 10⁻⁶ eV with a plane wave energy cutoff of 500 eV. In geometric relaxation, all atoms were relaxed with residual forces smaller than 0.01 eV Å⁻¹. For PtRu(111)²⁵ and cobalt intermetallic Co₃Pt(001), Co₃Ru(001), and CoPtRu(001), a 4-layer slab of 2 × 2 periodic supercells with the bottom two layers was fixed and vacuum-separated >10 Å in the z-direction. The structure converges with 2 × 2 × 1 K-point sampling, an electronic convergence threshold of 1 × 10⁻⁶ eV, a plane wave energy cutoff of 450 eV, and a residual force threshold of 0.01 eV Å⁻¹. For all metallic and intermetallic structures, a Gaussian smearing of 0.1 eV was used. The gas-phase species (H₂, H₂O, CO, and CH₃OH) were computed with a 1 × 1 × 1 k-point sampling, electronic convergence threshold of 1 × 10⁻⁶ eV, plane wave energy cutoff of 500 eV, and residual forces threshold of 0.01 eV Å⁻¹. More details are provided in the Supporting Information.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.4c01008>.

Experimental methods: synthesis; electrochemical methods and protocols; DFT calculations; free energy diagrams and corresponding structures; PXRD patterns; SEM; ICP-OES; HAADF-STEM; EDX; electrochemical characterization; CO stripping; comparison of MEA performance (PDF)

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[#]H.X. and D.Z. contributed equally to this work. J.L., Y.R.-L., and H.X. conceived the original idea. H.X. performed the synthesis, the electrochemical measurements, and data analysis with assistance from D.J.Z. H.X. performed characterization and analysis. J.H.F. and H.X. performed DMFC measurements. J.K. and H.X. performed STEM. H.I. and H.X. conducted DFT calculations. H.X., Y.S.-H., J.L., and Y.R.-L., drafted the manuscript. All authors contributed to the revision of the manuscript.

Notes

The authors declare no competing financial interest.

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