

Ternary PtIrNi Catalysts for Efficient Electrochemical Ammonia Oxidation

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ABSTRACT: Ammonia (NH₃) has proved to be an effective alternative to hydrogen in low-temperature fuel cells *via* its direct ammonia oxidation reaction (AOR). However, the kinetically sluggish AOR has prohibitively hindered the attractive direct ammonia fuel cell (DAFC) applications. Here, we report an efficient AOR catalyst, in which ternary PtIrNi alloy nanoparticles well dispersed on a binary composite support consisting of porous silicon dioxide (SiO₂) and carboxyl-functionalized carbon nanotube (PtIrNi/SiO₂-CNT-COOH) through a sonochemical-assisted synthesis method. The PtIrNi alloy nanoparticles, with the aid of abundant OH_{ad} provided by porous SiO₂ and the improved electrical conductivity by CNTs, exhibit remarkable catalytic activity for the AOR in alkaline media. It is evidenced by a lower



onset potential (~0.40 V vs reversible hydrogen electrode (RHE)) at room temperature than that of commercial PtIr/C (ca. 0.43 V vs RHE). Increasing NH₃ concentrations and operation temperatures can significantly enhance AOR activity of this PtIrNi nanoparticle catalyst. Specifically, the catalyst at the temperature of 80 °C exhibits a much lower onset potential (~0.32 V vs RHE) and a higher peak current density, indicating that DAFCs operated at a higher temperature are favorable for increased performance. Constant-potential density functional theory (DFT) calculations showed that the Pt–Ir ensembles on {100}-terminated surfaces serve as the active site. The introduction of Ni raises the center energy of the density of states projected onto the group d-orbitals of surface sites and thus lowers the theoretical onset potential for *NH₂ dehydrogenation to *NH compared to Pt and Pt₃Ir alloy. KEYWORDS: electrocatalysis, ammonia oxidation reaction, PtIrNi ternary alloy, DFT calculations, direct ammonia fuel cells

1. INTRODUCTION

Although petroleum-derived fuels often have high energy density, easy transport, and scalability, they are not sustainable and contribute to substantial CO_2 emissions during the energy utilization.¹ Hydrogen is an attractive alternative fuel that has high energy density per weight and produces only water when consumed in a fuel cell.²⁻⁴ However, grand challenges associated with hydrogen production, storage, and transportation still prevent its universal implementation into energy markets. Recently, ammonia (NH_3) , a carbon-neutral fuel, has been found to possess the advantages of low cost, high energy density, and mature transport and storage infrastructure, and has proven to be a cost-effective hydrogen carrier for energy applications.⁵⁻⁷ In addition to a century-old Haber-Bosch process to produce NH₃, recently, electrochemical synthesis through the nitrogen reduction reaction (NRR) has attracted substantial attention by using renewable energy-generated electricity.^{8–12} Apart from being a carrier for hydrogen storage application, ammonia can be directly utilized in a direct ammonia fuel cell (DAFC), where it is electrochemically oxidized at the anode.¹³ Nevertheless, the viable application of DAFCs has not yet been realized largely due to insufficient performance of the key components (*e.g.*, membrane and catalysts). The ammonia oxidation reaction (AOR) is generally kinetically sluggish requiring high overpotentials. The strongly adsorbed reaction intermediates (*e.g.*, *N and *NO) during the AOR usually rapidly deactivate catalysts due to poisoning effects.^{14,15} To overcome the sluggish AOR, rationally designed and synthesized active AOR catalysts for DAFCs are highly demanded.

To date, a variety of transition metals (Pt, Pd, Rh, Ru, Au, Ag, Cu, and Ir) have been investigated for AOR catalysis. Density functional theory (DFT) has predicted that the strength of the *M-N bond on Pt and Ir is between Cu, Ag, and Au on the low end and between Ru and Rh on the high

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Figure 1. Schematic illustration for the synthesis of SiO₂ and CNT-COOH-supported PtIrNi ternary alloys.

end.¹⁵ According to the principle proposed by Sabatier, a lower binding energy (e.g., Cu, Ag, and Au) would not bind NH₃ strongly enough to carry out the reaction, while a higher binding energy (e.g., Ru and Rh) would enable the reaction to occur at lower overpotential but would induce strong bonds with reaction intermediates, poisoning the active sites and slowing down the N-N bond formation. Consequently, metals with optimal binding energy (e.g., Pt and Ir) would be expected to show a high AOR activity.^{16,17} Pt is the most studied and promising metal catalyst for the AOR, capable of generating high current density at relatively high overpotentials.^{15,1} Meanwhile, Ir is well known for its ability to reduce the overpotential of the AOR, but results in relatively low current density.¹⁹⁻²¹ These observations have been theoretically and experimentally studied, and are rationalized by the binding strength of *N,^{15,19,22} which is a poisoning species itself or a precursor to the poisoning species *NO at the catalyst surface.^{14,23} Therefore, the combination of Pt and Ir to simultaneously increase the reaction rate (current density) and reduce the overpotential (onset potential) would be highly desirable for the AOR. To this end, the development of Pt-Ir alloy catalysts has attracted greater research interest compared to other alloys (e.g., Pt-Ni, Pt-Rh, and Pt-Cu).^{16,17,19,24-26} The enhanced AOR activity of the Pt-Ir alloys has been previously reported,^{17,22,27} which has been regarded as the baseline for AOR studies.²²

However, in the case of the Pt–Ir alloy, there exist several different types of Pt–Ir species, including fully alloyed Pt–Ir, partially alloyed Pt–Ir, and nanocomposites ranging from Ir adatom-modified Pt to nonalloyed Pt–Ir oxide. Therefore, the effective modification of the *Pt–N bond strength after alloying with Ir *via* the surface electronic effect and atomic arrangement or coordination is still very challenging.^{28,29} DFT calculations by Estejab and Botte asserted that the AOR mechanism on a Pt cluster involves N₂H₄ formation followed by N₂H₄ dehydrogenation, while on an Ir cluster, NH₃ undergoes successive dehydrogenation to N₂.^{30,31} The addition of Ir to Pt could modify the electronic effect of the catalyst and allow NH₃ oxidation to occur at a reduced overpotential. Therefore, bimetallic Pt–Ir catalysts are able to reduce the

activation barrier and enhance the catalytic activity during the AOR.

Although PtIr alloy catalysts exhibited promising activity, the high cost and scarcity of precious metals are key obstacles for their widespread application. Efforts to reduce the Pt-Ir loading in catalysts with enhanced AOR activity is highly desirable by further alloying with additional earth-abundant metals. However, Pt-based nanoparticles comprising three or more different metals are challenging to synthesize.³ Currently, only ternary PtIrZn catalysts were reported, but with insufficient activity for the AOR.³³ In this work, the knowledge gained from previous reports on Pt-Ni alloys^{24,34} provides a guide for designing novel Pt-Ir-Ni ternary alloys for NH₃ oxidation. Although the AOR on Ni catalysts is hindered by its high energy barrier (1.39 eV) for endothermic hydrazine formation, it still shows promising theoretical onset potential, comparable to that of Pt.^{13,15,35} Therefore, it may be feasible to introduce Ni into Pt-Ir systems to enhance the AOR activity. In addition to metal catalysts themselves, optimal supports often play an equally important role in boosting the catalytic activity due to the unique metal-support interactions and their possible synergistic effects.³⁶⁻⁴⁴ Porous silicon dioxide (SiO₂), possessing strong adsorption ability to complex metal ions, has been recently reported for supporting metal nanoparticle catalysts.^{38,45} The high surface area and porous architecture of SiO₂ would be beneficial for effective metal dispersion. Also, porous SiO₂ could act as a reservoir for OH adsorption, which can facilitate the AOR.^{37,46} Inspired by these understandings, we explored the porous SiO₂ support for deposition of ternary PtIrNi alloy nanoparticles for advanced AOR catalysts. To improve the electrical conductivity and structural integrity, carbon nanotubes (CNTs) were introduced into the catalyst system. Herein, we report a catalyst of PtIrNi alloy nanoparticles supported on a composite support consisting of porous SiO₂ and carboxyl-functionalized carbon nanotube (PtIrNi/SiO₂-CNT-COOH) through a facile sonochemical-assisted synthesis strategy. Compared to commercial PtIr/C catalysts, superior catalytic activity in terms of increased current density and reduced onset potential was achieved on the PtIrNi/SiO₂-CNT-COOH catalyst toward the AOR, making it a good candidate for the anode catalysts in DAFCs.



Figure 2. Morphology, structure, and composition of $PtIr/SiO_2$ -CNT-COOH. (a, b) Transmission electron microscopy (TEM) images; (c–e) HR-TEM images; (f) high-angle annular dark field scanning transmission electron microscopy (HAAD-STEM) image and the corresponding EDS elemental mappings of (g) C, (h) Si, (i) O, (j) Pt, and (k) Ir; and (l) integrated mapping of Pt and Ir.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1. Catalyst Synthesis, Morphology, and Structure. An effective sonochemical-assisted strategy is illuminated in Figure 1, which can prepare PtIrNi ternary alloy nanoparticles deposited on porous SiO₂ and CNT-COOH binary supports. SiO₂ in the composite support has a relatively large surface area (>400 m² g⁻¹) and porous architecture for metal-ion adsorption, while CNT-COOH can improve the electrical conductivity and strengthen the structural integrity. During the synthesis, metal ions of Pt2+, Ir4+, and Ni2+ were reduced by sodium borohydride under ultrasonic environment to form Pt-Ir-Ni ternary nanoparticles. A drastic reaction together with many bubbles can be observed immediately. The sonochemical-assisted reduction method has been previously demonstrated to be effective for the synthesis of bimetallic alloys.^{47,48} The acoustic cavitation can induce extreme but transient local conditions, which can increase the reduction rate giving rise to small and uniform nanoparticles on supports, and also facilitate the formation of ternary PtIrNi alloy.⁴⁷ This effective sonochemical-assisted strategy is easily scalable and can be used to prepare other bimetallic or multimetallic alloy catalysts. It should be noted that the precious-group-metal (PGM, Pt, or Pt-Ir) loadings for all of the prepared catalysts are 10 wt % relative to supports. Molar ratios of Pt/Ir/Ni in the PtIrNi/SiO₂-CNT-COOH catalysts are controlled at 9:1:1,

9:1:3, and 9:1:9, correspondingly. Other samples PtIr/SiO₂-CNT-COOH and PtNi/SiO₂-CNT-COOH with molar ratio of Pt/Ir and Pt/Ni = 9:1, and Pt₅Ir₅/SiO₂-CNT-COOH with molar of Pt/Ir = 1:1 were prepared using an identical procedure and the corresponding metal precursors.

The morphology, structure, and composition of the prepared PtIr and PtIrNi nanoparticles dispersed on the composite support were studied by high-resolution transmission electron microscopy (HR-TEM). Figures 2a-d and S1 show SiO₂ with amorphous structure integrated with CNTs supporting bimetallic PtIr nanoparticles. The PtIr nanoparticles possess an average size of 6.2 ± 0.2 nm and are mostly located at the edge (Figure 2b-e) of the binary support. Figures 2e and S2 show a typical PtIr alloy particle wrapped by SiO₂ and/or CNTs. A PtIr alloy crystalline lattice spacing of 0.225 nm and a CNT layer spacing of 0.320 nm can be clearly assigned to the face-centered cubic (fcc)-PtIr(111) and C(002) planes, respectively. The formation of the PtIr alloy is evidenced by the interplanar contraction from 0.227 nm of Pt(111) to 0.225nm of PtIr(111).⁴⁹ The elemental distributions of PtIr particles on the SiO₂ and CNT-COOH binary support were characterized by energy-dispersive X-ray spectrometry (EDS) elemental mappings (Figure 2f-i), where the C (blue), Si (yellow), O (cyan), Pt (red), Ir (green), and combined Pt and Ir images further confirm the presence of bimetallic PtIr



Figure 3. Morphology, structure, and composition of $PtIrNi_1/SiO_2$ -CNT-COOH. (a-c) TEM images; (d, e) HR-TEM images; (f) HAAD-STEM image and corresponding EDS elemental mappings of (g) C, (h) Si, (i) Pt, (j) Ir, and (k) Ni; and (l) integrated mapping of Pt, Ir, and Ni.

nanoparticles supported on the SiO_2 and CNT composite support.

Similarly, the PtIrNi nanoparticles deposited on the composite support can be clearly observed from the TEM images (Figures 3a-e and S3). After the introduction of Ni, the PtIrNi ternary alloys have larger particle size (9.3 ± 0.4) nm). Interplanar spacings of 0.320 and 0.220 nm corresponding to (002) of CNT and (111) of fcc-PtIrNi alloy are shown in Figures 3c,e and S4. The obvious reduction of the interplanar spacing from 0.225 nm of PtIr(111) to 0.220 nm of PtIrNi(111) verifies the alloying of Ni into PtIr.¹⁷ Figures 3c and \$5 show that the PtIrNi particles are embedded in the SiO₂ and/or CNTs binary support. Interfaces between SiO₂ and PtIrNi could be clearly identified in these images. The closely interacted SiO₂ and PtIrNi are the key to providing necessary OH⁻ to PtIr sites for the AOR. The EDS elemental mappings, where the C (blue), Si (yellow), Pt (red), Ir (green), Ni (magenta), and integrated Pt, Ir, and Ni images can be clearly observed, indicate that the ternary PtIrNi nanoparticles are well dispersed on the SiO₂ and CNT composite support (Figures 3f-i and S6). While there were a few Ni nanoparticles visible throughout the sample, as shown in the HAAD-STEM mappings (Figure S7), most metals were found in alloy nanoparticles in the catalyst. Note that these isolated Ni species do not contribute to the AOR,³⁴ and only Ni in a PtIrNi alloy is responsible for the improved activity.

The X-ray diffraction (XRD) patterns depicted in Figure 4a indicated that SiO₂ is amorphous,^{50,51} while an obvious C(002) peak at ~26° can be ascribed to CNT-COOH. The characteristic peaks, from left to right, correspond to the (111), (200), (220), (311), and (222) planes, respectively, associated with a Pt fcc structure of Pt for all Pt-based and commercial Pt/C catalysts (Figures 4a,b and S8).⁵² After introducing Ir, Ni, and IrNi, the XRD patterns identify the bimetallic PtIr and PtNi, as well as ternary PtIrNi alloys with a typical fcc structure (Figures 4c,d and S9). Additionally, the peaks of fcc Pt in these alloys shift toward higher angles, suggesting the alloy effect with reduced d space. Such contractions can be explained by the replacement of Pt by the smaller Ir and Ni atoms, leading to decreased lattice spacing. These XRD results are consistent with our HR-TEM and HAAD-STEM mapping results (Figures 2 and 3), further indicating the alloy state of the obtained PtIrNi catalysts.

The N₂ adsorption/desorption isotherms (Figure 5a) show that individual SiO₂ has a large surface area of 445.9 m² g⁻¹, which is crucial for adsorbing metal ions during the synthesis. The deposition of multicomponent metal nanoparticles, *e.g.*, PtIrNi, leads to a significant reduction in the surface area of the PtIrNi₁/SiO₂-CNT-COOH catalyst to 37.0 m² g⁻¹. This is mainly due to the disappearance of microporosity, as evidenced by a decrease in the N₂ uptake at low pressures of the N₂ adsorption/desorption isotherm plots. The optimal



Figure 4. XRD patterns of the synthesized catalysts. (a) Pt/SiO₂, Pt/CNT-COOH, Pt/SiO₂-CNT-COOH, and commercial Pt/C; (b) Pt/CeO₂-CNT-COOH, Pt/TiO₂-CNT-COOH, and Pt/ZrO₂-CNT-COOH; (c) Pt/SiO₂-CNT-COOH, commercial PtIr/C, PtIr/SiO₂-CNT-COOH, PtIrNi₁/SiO₂-CNT-COOH, PtIrNi₁/SiO₂-CNT-COOH, PtIrNi₁/SiO₂-CNT-COOH, PtIrNi₂/SiO₂-CNT-COOH, and PtIrNi₃/SiO₂-CNT-COOH; and (d) the corresponding enlarged region from 65 to 90° for these Pt-based catalysts.

PtIrNi catalyst on the SiO_2 -CNT composite support exhibits mesopore-based architecture (Figure 5b), which would be beneficial for the mass transport and increased number of accessible active sites for the AOR.

The elemental compositions of different Pt-based catalysts determined by X-ray photoelectron spectroscopy (XPS) are summarized in Table S1. The atomic metal ratio of Pt/Ir/Ni in the PtIrNi₁/SiO₂-CNT-COOH catalyst is similar to that in their metal precursors used (9:1:1), verifying that all metal precursors are completely reduced in the final catalyst. In contrast to Pt/SiO2-CNT-COOH and PtIr/SiO2-CNT-COOH, an increased Pt content from 1.2 to 2.5 atom % in the PtIrNi catalyst (Table S1) suggests a stronger interaction between binary support and Pt. Also, the low Pt content (0.9 atom %) in the PtIrNi/XC-72 catalyst further confirms the strong adsorption ability of the porous SiO₂ to complex metal ions. Compared to the electronegativities of Ir (2.20), Ni (1.92), and Si (1.98), Pt has a larger electronegativity (2.28). Thus, compared to individual Pt nanoparticles, Pt in alloys should be more metallic with a negative shift of binding energy. To verify these possible shifts, high-resolution Pt 4f for different Pt-based catalysts is summarized in Table S2. First, compared to the Pt/C catalyst, the binding energies of Pt $4f_{5/2}$ and Pt 4f7/2 for the Pt/SiO2-CNT-COOH already show negative shifts of 0.59 and 0.71 eV, respectively. This indicates that there is existing electronic interaction between Si and Pt, thereby changing the charge density of the Pt metal and leading to a shift in the binding energy of Pt.^{50,51} Furthermore, the binding energy shifts of Pt 4f_{5/2} and Pt 4f_{7/2} in PtIr/SiO₂-CNT-COOH (0.57 and 0.63 eV) and PtIrNi₁/SiO₂-CNT-COOH (0.49 and 0.63 eV) are identified. PtIrNi/XC-72 shows the smallest binding energy shifts of 0.45 and 0.51 eV for Pt $4f_{5/2}$ and Pt $4f_{7/2}$, respectively, indicating the weakest interaction between support and IrNi with Pt. Overall, the

binding energy shifts of Pt 4f in PtIr/SiO₂-CNT-COOH and PtIrNi₁/SiO₂-CNT-COOH further confirm the formation of Pt bimetallic and trimetallic alloys (Figure 5c), which confirms the formation of Pt. The possible shifts of binding energies for alloyed Ir (Figures 5d and S10a) and alloyed Ni (Figure S10b), as well as the binary support of SiO₂ (Figure S11a) and CNTs (Figure S11b) in the catalysts are also shown in their corresponding high-resolution XPS data.

2.2. Catalyst Activity for the AOR. The AOR activity of all studied catalysts was evaluated using a rotating disk electrode (RDE) in a 1.0 M KOH + 0.1 M NH₃ electrolyte. A combination of porous SiO₂ with CNT-COOH was used as a composite support for Pt and PtM (M: Ir or/and Ni) nanoparticle deposition. The synergy between SiO₂ and CNT-COOH was demonstrated by a significant AOR activity improvement when using the composite support for individual Pt nanoparticle deposition (Figure 6a). It has been suggested that OH groups near the catalytic surface could participate in the AOR.^{14,37,46,53} In an alkaline media, oxides such as SiO_2 is a reservoir for OH adsorption, thereby enhancing the AOR activity. As a comparison, several commercially available metal oxides (CeO₂, TiO₂, and ZrO₂) were used to replace SiO₂ for Pt nanoparticle deposition and studied for the AOR activity (Figure 6b). The Pt/SiO₂-CNT-COOH catalyst exhibits the highest current density compared to the other metal oxidesupported catalysts, likely due to both the larger OH adsorption capacity and the higher surface area of SiO₂. To further determine the unique benefits of the incorporation of CNT-COOH into the composite support, several popular carbon materials, including graphene oxide (GO), carbon black (XC-72), commercially available CNT-OH, and carboxyl-functionalized CNT (CNT-COOH) were integrated with SiO₂ for Pt nanoparticle deposition as AOR catalysts. The combination of SiO₂ and CNT-COOH displayed the highest



Figure 5. (a) N_2 adsorption/desorption plots and (b) pore size distributions of the pure SiO_2 and $PtIrNi_1/SiO_2$ -CNT-COOH samples. High-resolution Pt 4f (c) and Ir 4f (d) X-ray photoelectron spectroscopy (XPS) data of various Pt-based catalysts.

AOR activity (Figure S12a). This is likely attributed to its smallest charge transfer resistance, as can be demonstrated by the electrochemical impedance spectroscopy (EIS) results (Figure S12b). Optimization of the CNT content was also performed, and it was found that 16.6 wt % CNTs in the support leads to the highest AOR activity (Figure S13). This composition was used for the remaining studies unless otherwise specified. The chronoamperogram (CA) results, *i.e.*, i-t curves (Figure S14), of all of the above-mentioned catalysts, are consistent with their corresponding AOR activity determined by cyclic voltammetry (CV) at a sufficiently low scanning rate. These results clearly demonstrated the advantage of combining porous SiO₂ with CNT-COOH for a composite support in the case of Pt catalysts, exhibiting dramatically enhanced AOR activity relative to Pt/C catalysts (Table S3).

As expected, the onset potentials of AOR on all of these Pt catalysts are very high, around 0.5 V *vs* RHE, according to Figures 6a,b, S12a, and S13, which is insufficient for a DAFC. Previous reports had demonstrated that incorporation of Ir into Pt is a promising strategy for negatively shifting the onset potential of the AOR with reduced overpotentials,^{19,25,26} likely due to the bifunctional mechanism and the electronic effect, as discussed above.^{30,54} For a step-by-step study of the promotional role of Ir and Ni in improving AOR activity, we first introduced secondary metals Ir or Ni at a molar ratio of 9:1 in Pt catalysts. Improved activity of both PtIr/SiO₂-CNT-COOH

and PtNi/SiO₂-CNT-COOH compared to Pt/SiO₂-CNT-COOH and commercial Pt/C was demonstrated (Figure 6c and Table S3). The onset potential (~0.45 V) of the PtIr/ SiO₂-CNT-COOH catalyst shows an obvious negative shift, likely due to the smaller NH₃ adsorption energy of Ir, facilitating the NH₃ adsorption and further oxidation reactions.¹⁵ In contrast, the AOR activity enhancement on the PtNi/SiO₂-CNT-COOH catalyst is insignificant in terms of peak current density (79.2 A g⁻¹), but a decreased onset potential (~0.46 V, Figure 6c and Table S3). Note that pure Ni is nearly inactive of the AOR because electrochemically activated Ni surfaces could be spontaneously oxidized during the reaction, thus reducing the electrocatalytic activity for NH₃ oxidation.³⁴ Alloyed Pt–Ni catalyst seems to generate slightly enhanced AOR activity (Figure 6c), likely due to the improved Pt utilization.^{24,34}

Ir and Ni were then simultaneously introduced into the Pt catalyst to prepare a ternary catalyst. The PtIrNi₁/SiO₂-CNT-COOH (molar ratio of Pt/Ir/Ni = 9:1:1) demonstrated a significantly enhanced AOR activity (Figure 6c and Table S3) in terms of both the peak current density (124.0 A g⁻¹) and reduced onset potential (~0.40 V) compared to the binary PtIr/SiO₂-CNT-COOH (peak current density: 90.6 A g⁻¹, onset potential: ~0.45 V) and commercial PtIr/C (peak current density: 25.1 A g⁻¹, onset potential: ~0.43 V). The onset potentials of PtIrNi₂/SiO₂-CNT-COOH (molar ratio of Pt/Ir/Ni = 9:1:3) and PtIrNi₃/SiO₂-CNT-COOH (molar ratio of Pt/Ir/Ni = 9:1:3)



Figure 6. CV curves for different catalysts in Ar-saturated 1.0 M KOH + 0.1 M NH₃ at 5 mV s⁻¹ and 900 rpm under ambient conditions: (a) comparison between CNT-COOH, commercial Pt/C, Pt/SiO₂, Pt/CNT-COOH, and Pt/SiO₂-CNT-COOHJ; (b) comparison between Pt deposited on CNT-COOH combined with SiO₂, CeO₂, TiO₂, and ZrO₂; and (c) comparison between Pt, PtIr, PtNi, PtIrNi₁, PtIrNi₂, PtIrNi₃ deposited on SiO₂-CNT-COOH, and commercial PtIr/C. (d) AOR activity comparison for the catalysts in (c) at 0.5 V *vs* reversible hydrogen electrode (RHE). (e) CV curves of the PtIrNi₁/SiO₂-CNT-COOH catalyst in the presence and absence of NH₃. (f) CA of the commercial Pt/C, Pt/SiO₂-CNT-COOH, commercial PtIr/C, PtIr/SiO₂-CNT-COOH, and PtIrNi₁/SiO₂-CNT-COOH in Ar-saturated 1.0 M KOH with 0.1 M NH₃ at 900 rpm at 0.65 V *vs* RHE under ambient conditions.

ratio of Pt/Ir/Ni = 9:1:9) also show negative shifts of onset potential compared to the PtIr/SiO₂-CNT-COOH catalyst; however, the peak current densities are decreased. The currents normalized to PGM mass at 0.5 V vs RHE are selected for a comparison of AOR activities of different catalysts.²² The improved activity of the ternary catalyst further suggests the synergy of alloying Pt with IrNi (Figure 6d). Considering both the peak current density and onset potential (Table S3), PtIrNi₁/SiO₂-CNT-COOH (molar ratio of Pt/Ir/ Ni = 9:1:1) was regarded as the optimal ternary PtIrNi AOR catalyst, which was further studied in next sections.

The effect of mass ratios between SiO₂ and CNT-COOH in the optimal PtIrNi catalyst was investigated (Figure S15). A mass ratio of 5:1 between SiO₂ and CNT-COOH resulted in the best AOR activity, compared to other mass ratios of 1:1 and 1:5. The interfaces of SiO2 and PtIrNi in these three PtIrNi catalysts that are supported on different mass ratios of SiO₂ and CNT-COOH are correlated with increased activity, as can be demonstrated by the HR-TEM characterizations (Figures 3c, S5, S16, and S17). When there are more interfaces of SiO₂ and PtIrNi in the catalyst, a better AOR activity can be obtained $(SiO_2/CNT-COOH = 5:1)$, whereas when such interfaces are reduced, it will result in poorer AOR activity $(SiO_2/CNT-COOH = 1:1 \text{ and } 1:5)$. These results further confirm the critical role of SiO₂ in the ternary PtIrNi catalyst. Therefore, the interfaces between SiO2 and PtIrNi nanoparticles are believed as the key source of reaction sites for the AOR due to the supplies of OH groups from SiO₂, while the interfaces between PtIrNi and CNTs mainly contributed to electron transfer (Figure S15). Figure 6e shows a typical CV curve for the optimal PtIrNi catalyst in 0.1 M KOH in the

presence and absence of NH₃, showing an NH₃ oxidation peak in the potential range of 0.3–0.9 V *vs* RHE. The deactivation at higher potentials (0.68–0.9 V *vs* RHE) is attributed to strongly adsorbed reaction intermediates (*e.g.*, *N and *NO) that block the active Pt surface.^{20,22,23,55} Therefore, the AOR is limited to a narrow potential window and cannot be driven by applying a high overpotential based on Tafel plots. CA characterization (Figures 6f and S18) further demonstrates that the optimal PtIrNi had the highest current density (*e.g.*, 17.6 A g⁻¹ after 500 s) at 0.65 V *vs* RHE, superior to commercial Pt/C (3.9 A g⁻¹) and commercial PtIr/C (2.15 A g⁻¹, Pt/Ir = 1:1) catalysts. The optimal PtIrNi₁ catalyst supported on SiO₂-CNT-COOH binary support shows the highest activity relative to other supports, including XC-72 or CeO₂-CNT-COOH (Figure S19 and Table S4), further verifying the critical role of using porous SiO₂ in the catalyst.

Overall, the AOR activity of the optimal PtIrNi₁/SiO₂-CNT-COOH catalyst (~0.40 V onset potential, peak current density 124.0 A g⁻¹) is superior or comparable to those of many reported catalysts, such as the CeO₂-modified Pt catalyst (onset potential: ~0.50 V),³⁷ Pt-decorated highly porous flowerlike Ni particles (onset potential: ~0.50 V),²⁴ PtIr/CNT (atomic ratio of Pt/Ir = 4:1, onset potential: ~0.38 V),⁵⁶ PtIr/ N-reduced graphene oxide (rGO) (molar ratio of Pt/Ir = 1:3, onset potential: ~0.37 V),²⁵ PtRh/C (molar ratio of Pt/Rh = 9:1, onset potential: ~0.44 V),²⁵ CuPtRh nanowires (mass ratio of Pt/Ir = 7:1, onset potential: ~0.49 V),⁵⁷ and PtIrZn (mass ratio of Pt/Ir = 8:2, onset potential: ~0.30 V).³³ Detailed comparisons in terms of onset potential and/or peak current density can be found in Table S4. It should be noted that the current ratio of Pt to Ir in commercial PtIr catalysts is



Figure 7. (a, d) CV curves of the PtIrNi₁/SiO₂-CNT-COOH in Ar-saturated 1.0 M KOH with different concentrations of NH₃ under ambient conditions or 1.0 M KOH + 0.1 M NH₃ operating at different temperatures at 5 mV s⁻¹ and 900 rpm. (b, e) AOR activity comparison for PtIrNi₁/SiO₂-CNT-COOH and commercial PtIr/C in the presence of different NH₃ concentrations or temperatures at 0.5 V *vs* RHE. (*c*, *f*) CA of the PtIrNi₁/SiO₂-CNT-COOH in Ar-saturated 1.0 M KOH in the presence of different NH₃ concentrations under ambient conditions or different temperatures at 900 rpm and 0.65 V *vs* RHE.

1:1. Because the current cost of Ir is much higher than that of Pt, it would be desirable to reduce the usage of Ir in catalysts without compromise of the AOR activity. In our experiment, we controlled the molar ratio of Pt/Ir at 9:1. Further enhancement of the AOR activity can be achieved by increasing the Ir content in the PtIr alloy, as evidenced by the Pt₅Ir₅/SiO₂-CNT-COOH catalyst, which shows a further reduced onset potential of ~0.37 V vs RHE (Figure S19), which would be more favorable to yield a higher open-circuit voltage (OCV) in DAFCs.

2.3. Catalyst Deactivation during the AOR. While the initial rapid decline in current density is due to the removal of nonfaradic double-layer currents, the subsequent gradual decay is attributed to the deactivation of Pt alloys, likely due to the formation of poisoning species of NO/NO_x (e.g., generally poison to Pt(100) facet) and *N (e.g., generally poison to Pt(111) facet).^{15,23,58} However, the detailed deactivation mechanism during the AOR is complicated and remains elusive.³⁰ Using the optimal PtIrNi catalyst, deactivation can be identified by the changes of Pt(110) and Pt(111) facet coverages, which were evaluated by using CV curves in a 1.0 M KOH electrolyte (Figure S20). To further evaluate the degradation of the catalysts, RDE tests by cycling the potential of 0.05–0.7 V in Ar-saturated 1.0 M KOH at a scanning rate of 500 mV s^{-1} were conducted, and the catalysts were also measured in 1.0 M KOH and 1.0 M KOH + 0.1 M NH₃ electrolytes before and after the cycling, respectively. The PtIrNi₁/SiO₂-CNT-COOH catalyst exhibited improved AOR stability compared to commercial Pt/C and PtIr/C, as evidenced by a loss of ~48% peak current density after 2000 potential cycles in Ar-saturated 1.0 M KOH (Figure S21a), compared to ~90 and 51% losses for the Pt/C and the PtIr/C catalysts, respectively (Figure S21b,c). These results suggest that the combination of the PtIrNi alloy with the binary

support of SiO₂ and CNT-COOH can improve the catalyst stability. Further improving the AOR stability of the Pt-based catalysts can be realized by increasing the Ir content in the Pt-Ir alloy, as demonstrated by the Pt_5Ir_5/SiO_2 -CNT-COOH in a molar ratio of Pt/Ir = 1:1, which shows a loss of only ~15% (Figure S21d). The AOR activity loss of these catalysts is in good agreement with their losses of the corresponding electrochemically active surface area (ECSA), as demonstrated by the CVs in 1.0 M KOH before and after the 2000 potential cycles (Figure S22).

2.4. AOR Reaction Kinetics: NH₃ Concentration and Temperature Effect. To explore the reaction kinetics of AOR on the ternary PtIrNi catalyst, catalytic activity was investigated using the best-performing PtIrNi1/SiO2-CNT-COOH (Figure 7a–c) and a commercial PtIr/C (Pt/Ir 1:1) (Figure S23) catalyst as a function of NH₃ concentration. Both AOR activities are increased with the NH₃ concentration, which is similar to previous reports.⁵⁸ According to the Nernst equation, the thermodynamic potential of the AOR is dependent on the concentration of the reactants, which can be further demonstrated by our results (Figures 7a and S23a). The effect of NH₃ concentration on the catalyst performance can be further demonstrated by the bar chart of current density at 0.5 V vs RHE as a function of NH₃ concentration (Figure 7b). Interestingly, higher NH₃ concentration leads to faster current density attenuation (Figure 7c), suggesting that there is an accumulation of more poisonous species on the PtIrNi alloy surface at higher NH₃ concentration. This is demonstrated by the higher remaining current density (19.3 A g^{-1}) in the electrolyte with 0.5 M NH₃ after 500 s than in the electrolyte with 1.0 M NH₃ (18.6 A g^{-1}). To prove the poisoning effect, we have measured the ECSA changes before and after a constant CA test toward AOR in 1.0 M KOH with different concentrations of NH₃. Three representative NH₃ concen-



Figure 8. (a) Free-energy pathway *via* constant-potential DFT calculations for initial ammonia dehydrogenation steps at 0.3 V vs RHE on Pt(100), Pt₃Ir(100), Pt₃IrNi(100). All surfaces have co-adsorbed *OH (1/4 ML). The geometries for each surface are shown. (b) Group d-orbital density of states projected onto the bridge site of model systems (marked *via* red cross). The vertical red solid lines indicate d-band center.

trations of 0.1, 0.5, and 1.0 M NH₃ were selected to make a comparison (Figure S24). The obvious ECSA loss (12.7% loss) can be observed on the optimal PtIrNi catalyst when the constant CA test was performed in 1.0 M KOH + 1.0 M NH₃ electrolyte, which is larger than those in 0.5 M (6.3% loss) and 0.1 M (3.3% loss) NH₃ solutions. These results confirm that more poisonous adsorbates could be accumulated in an electrolyte with higher NH₃ concentration during a constant CA test for our PtIrNi catalyst, whereas no similar phenomenon is observed on the commercial PtIr/C (1:1) catalyst (Figure S23b).

The temperature-dependent AOR activity of the PtIrNi₁/ SiO₂-CNT-COOH (Figure 7d-f) and commercial PtIr/C (Figure S25) catalysts was studied. Dramatically enhanced AOR activity was achieved at an elevated temperature (up to 80 °C). Specifically, the AOR onset potential of the PtIrNi₁/ SiO₂-CNT-COOH catalyst shifts from ~0.40 V at 25 °C to ~0.32 V at 80 °C. The negative shifts of the peak potential with increased temperatures (Figures 7d and S25a) also indicate that the formation of *N intermediate occurs at less positive potential as temperature increases, allowing higher reaction rate at a lower overpotential. Comparisons shown in Figure 7e between the two catalysts further indicated that, relative to the commercial PtIr/C catalyst, the ternary PtIrNi catalyst is more sensitive to electrolyte temperature, showing about 22-fold increase when the temperature is increased from 25 to 80 °C. Previous studies showed that the DFT barrier for dimerization reactions associated with *NH2 species is high $(\sim 1.0 \text{ eV})$.^{14,15} Nevertheless, these rate-limiting chemical steps for N-N formation become accessible at high operating temperatures.^{22,31} The CA results of the PtIrNi₁/SiO₂-CNT-COOH (Figure 7f) and commercial PtIr/C (Figure S25b) catalysts are congruous with their CV measurement results. The increased current density and reduced onset potential of the AOR indicate that these catalysts are ideally for DAFC

operated at a relatively high temperature with significantly enhanced performance.

According to the data provided in Figure 7e, the standard electrochemical enthalpy of activation for the optimal PtIrNi and commercial PtIr/C catalysts was calculated using the Arrhenius equation (eq 1).⁵⁹

$$(\Delta H_{\rm el})_E = -2.303R \left(\frac{\delta \log J}{\delta(1/T)} \right)_E \tag{1}$$

At 0.5 V vs RHE, the current densities for these two catalysts at different temperatures, expressed as A g⁻¹, are presented in Figure S26. The ΔH_{el} value for the AOR on the optimal PtIrNi catalyst is 50.0 kJ mol⁻¹, comparable to commercial PtIr/C (50.8 kJ mol⁻¹), indicating that a lower Ir content in the ternary catalyst does not increase the activation energy of the AOR.

3. THEORETICAL STUDIES

Figure 8a shows a free-energy diagram calculated via constantpotential DFT for the dehydrogenation of ammonia to adsorbed nitrogen (*N) at 0.3 V vs RHE on three model surfaces. Details regarding the calculations are described in the Supporting Information. The (100) facet has a substantially higher activity for the AOR compared to the (111) facet, and thus model systems were constructed using the (100) facet.^{14,15} Previous studies also showed that the co-adsorbed *OH is relevant in experimental conditions and is crucial for stabilizing *NH species through hydrogen bonding.^{37,46} Three different model systems consisting of Pt(100), $Pt_3Ir(100)$, and Pt₃IrNi(100) were used to investigate how Pt alloys could influence the kinetics of the AOR. It should be noted that the L1₂ structure of the Pt₃Ir bulk structure has two surfaces when cleaved along the (100) direction. One surface consists of 100% Pt atoms, while the second surface consists of 50% Pt

and 50% Ir. The latter surface (shown in Figure 8a) was used to model the Pt_3Ir alloy since Ir bonds more strongly with the NH_x species and thus we expected such a surface to be favored over the Pt skin surface under experimental conditions. To model the PtIrNi, a simple model system was created based on the Pt_3Ir alloy where one surface Pt atom was replaced by one Ni atom.

It has been previously shown that, on the Pt(100) facets, the dimerization of *NH2 is kinetically and thermodynamically inhibited, whereas *NH dimerization is more kinetically and thermodynamically favorable.¹⁴ Therefore, the electrochemical dehydrogenation of *NH₂ to *NH is the key step, which determines the formation of N_2 at the (100) surface. Calculations indicated that, at the Pt(100) surface, the dehydrogenation is thermodynamically uphill by 0.15 eV at 0.3 V vs RHE. Previous results showed that the dehydrogenation of *NH₂ to *NH becomes feasible at a potential of 0.5 V vs RHE,¹⁴ which also is in good agreement with the experimentally observed onset potentials shown in Figure 6a. However, for the Pt₃Ir surface, this step is thermoneutral at a potential of 0.3 V vs RHE. Furthermore, with the addition of a Ni atom to the $Pt_3Ir(100)$ surface, the dehydrogenation of *NH₂ to *NH becomes exergonic (energy-releasing) at 0.3 V vs RHE. Accordingly, a lower onset potential of ~0.25 V vs RHE is predicted for the Pt₃IrNi(100) surface. Therefore, from a combination of DFT calculations and experimentally observed improvement, the addition of the Ni is associated with a lower thermodynamic barrier for the dehydrogenation of *NH₂ to *NH.

Electronic structure analysis of active sites was further performed to understand the activity trend. Figure 8b shows the group d-orbital density of states projected onto the bridge site of model systems. The group orbital is a concept introduced by Kelly⁶⁰ to consider the symmetry and ensembles of orbitals interacting with surface species, which can be considered as a linear combination of relevant orbitals of all surface atoms within a cutoff radius. The Supporting Information contains details on how the group d-orbital density of states was calculated. The decrease in the onset potential between Pt(100) and Pt₃Ir(100) (0.5 vs 0.3 V) can be explained within the d-band model.^{30,55} Those Ir atoms at the surface have a higher d-band center relative to Pt atoms at Pt surface (-1.97 vs - 2.25 eV); therefore, less antibonding states are occupied, which leads to stronger adsorption energies, particularly for *NH. With the addition of Ni to the surface, the group d-orbital of density of states shifts up further in energy (-1.97 to -1.87 eV), further strengthening the adsorption of *NH intermediates for enhanced AOR activity. The group orbital model rationalizes the activity trend observed in this work, theoretically supporting the promotional role of Ni into PtIr alloys in facilitating the AOR. An alternative model system is constructed, whereby the nickel atom replaces a subsurface platinum atom. This model system and the accompanying free-energy diagram at 0.3 V vs RHE are shown in Figure S27. The free-energy path is downhill similar to what is shown in Figure 8a, therefore suggesting an overall positive effect of the nickel regardless of whether it is in the surface or subsurface. Table S5 shows that the segregation energy for the nickel atom without the presence of adsorbates is >0.5 eV. It becomes substantially smaller with the presence of adsorbates, e.g., *N. Note that such models have not been validated by in situ experimental characterization that necessitates its further optimization. Nevertheless, theoretical

studies suggested that surface and subsurface nickel atoms could coexist, specifically in the presence of adsorbates.

4. CONCLUSIONS

In summary, we demonstrated two new concepts in this work to design efficient AOR catalysts for potential DAFC applications. The first is the combination of porous SiO₂ with CNT-COOH to prepare a composite support that enables enhanced AOR activity relative to other studied carbon and oxide supports. The second is the rational design of PtIrNi ternary alloys by introducing non-precious-metal Ni into PtIr baseline, which is beneficial for reducing catalyst cost and enhancing the AOR activity in comparison to PtIr alloy catalysts. To this end, we synthesized a catalyst of ternary PtIrNi metallic nanoparticles on the composite support consisting of porous SiO₂ and CNT through a sonochemicalassisted synthesis method. The optimal PtIrNi catalyst at a molar ratio of 9:1:1 shows superior AOR activity and stability in alkaline electrolytes relative to the commercial PtIr/C with a higher Ir content (1:1). Porous SiO₂ with a large surface area strongly adsorbs metal ions during the synthesis and boosts the catalytic activity of the AOR through supplying abundant OH_{ad} to the nearby metallic catalytic sites. The kinetics of AOR are found strongly dependent on the NH₃ concentration and operation temperature. A higher concentration of NH₃ may accelerate the catalyst deactivation, especially for the catalyst with lower Ir content. However, high operation temperature such as 80 °C is favorable for practical application of DAFCs with increased current density and reduced overpotentials. Overall, the superior AOR activity of the optimal PtIrNi catalyst has been demonstrated by the low onset potential of ~0.40 vs RHE and high peak current density (124.0 A g^{-1}) at room temperature, as well as the further reduced onset potential of ~0.32 vs RHE and increased peak current density $(1382.7 \text{ A g}^{-1})$ at 80 °C. The activity enhancement is due to the high intrinsic activity of PtIrNi alloy nanoparticles and the abundant OH provided by SiO₂ along with the improved electrical conductivity contributed by CNTs in supports. DFT calculations further confirmed that the enhancement of the AOR activity of the PtIrNi alloy is due to the lower thermodynamic barrier for the dehydrogenation of *NH₂ to *NH. Electronic structure analysis indicates that the group dorbital of density of states shifts up in energy (-1.97 to -1.87 to -1.87eV) upon the introduction of Ni to the Pt-Ir surface, providing rational understanding on the experimentally measured activity improvements. Therefore, the newly developed PtIrNi₁/SiO₂-CNT-COOH catalyst could be a promising AOR catalyst, which will be further studied in DAFCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.9b04670.

Experimental details; computational details; morphology, structure, and composition; TEM images; HR-TEM images; HAAD-STEM images; elemental mappings; XRD patterns; elemental quantification; binding energy comparison; high-resolution XPS data; CV curves; chronoamperograms; AOR activity comparison; AOR stability tests; catalyst degradation tests; Arrhenius plots; free energy pathway; segregation energy (PDF)

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Notes

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