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Engineering Bunched Pt-Ni Alloy Nanocages for Efficient Oxygen Reduction in Practical Fuel Cells

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Abstract: Development of efficient and robust electrocatalysts is critical for practical fuel cells. We report one-dimensional bunched Pt-Ni alloy nanocages with a Pt-skin structure for the oxygen reduction reaction, which display high mass activity (3.52 amperes per milligram platinum) and specific activity (5.16 milliamperes per square centimeter), or nearly 17 and 14 times higher as compared with a commercial Pt/C catalyst. The catalyst exhibits high stability with negligible activity decay after 50,000 potential cycles. Both the experimental results and theoretical calculations reveal the existence of fewer strongly-bonded Pt-O sites induced by the strain and ligand effects. Moreover, the fuel cell assembled by this catalyst delivers a current density of 1.5 amperes per square centimeter at 0.6 Volts and could operate steadily for at least 180 hours.

Platinum (Pt) is the most active electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells and metal-air batteries with promising stability (1-3). Nevertheless, the state-of-the-art Pt catalysts still lack activity and stability with respect to the cost and availability for large-scale commercial implementation (4, 5). Engineering the near-surface composition of nanostructured Pt alloys represents one promising approach to enhance the electrocatalytic performance of Pt-based electrocatalysts, in which the exposure of highly active sites with optimum performance can be maximized (6, 7). Adding other transition metals can enhance the catalytic performance via ligand and strain effects through modifying the binding strength of Pt-oxygen intermediates (8-10).

The introduction of open nanostructures, including hollow and porous nanoparticles such as nanocages (NCs) and nanoframes, may help in achieving this goal and also enhance mass transfer (11). Porous metal structures usually exist as nanoparticles and typically do not display long-term stability because they agglomerate or detach from the (usually carbon) support (12, 13). In contrast, one-dimensional (1D) nanostructures and their assemblies can exhibit enhanced stability because of their inherent anisotropic, higher flexibility and higher conductivity (14). The anisotropy of 1D nanostructures can lead to greater surface

contact with the usual carbon support, thus resulting in high stability (15). Recently, 1D Pt-based alloy nanostructures have been explored for their promising ORR activity and stability (16, 17). However, these solid 1D nanostructures contain a substantial proportion of noble metals in the bulk versus at the surface, which limits the noble-metal utilization (18). Moreover, although desirable ORR performance has been established in model studies with, for example rotating disk electrodes (RDEs), relatively few works have studied nanostructured Pt electrocatalysts in a complete cell configuration (19). The limitations in comparing performance at the RDE-level with those at the cell-level are known (20). To this end, it follows that optimum ORR catalysts based on Pt should be designed by having a high Pt utilization efficiency (porous nanostructures), a favorable nanoscale chemical environment for ORR (chemical alloying) with an optimized structure in terms of the exposure of active site and stability derived from both the nanostructure itself as well as its interface with the support.

We demonstrate Pt-Ni bunched nanocages (BNCs) in 1D form that exhibited superior ORR activity and durability compared to conventional Pt electrocatalysts. We first prepared 1D Pt-Ni bunched nanospheres (BNSs) by reducing varying ratios of Pt and Ni precursors in oleylamine by a one-pot solvothermal method. Treatment under acidic conditions selectively removed Ni species to leave 1D Pt-Ni BNCs with ultrathin walls composed of a Pt-skin and a residual Pt-Ni alloy below this skin (Fig. 1A). The nanostructures with a Pt_{1.5}Ni starting composition exhibited the highest mass and specific activities of 3.52 A mgPt⁻¹ and 5.16 mA cm⁻², respectively. These values are more than one order of magnitude higher compared to a commercial Pt/C catalyst (60 wt%, Johnson Matthey, JM), and comparable to those of very recently reported Pt nanostructure catalysts (Supplementary table S1). The catalyst also exhibited superb durability with a negligible activity decay (less than 1.5%) after 50,000 potential cycles. In addition, the Pt-Ni BNCs electrocatalyst showed improved performance in a full cell test compared with commercial Pt/C, both in a hydrogen-air proton exchange membrane fuel cell (PEMFC) and an air-breathing PEMFC setup at room temperature and ambient

pressure. In situ x-ray absorption fine structure (XAFS) and theoretical calculations revealed that the PtNi alloy nanostructures had optimal adsorption energies of oxygen intermediates with respect to Pt.

Bunched nanospheres. The Pt-Ni BNSs were synthesized in nearly 100% yield from platinum (II) acetylacetonate ($\text{Pt}(\text{acac})_2$), nickel (II) acetylacetonate ($\text{Ni}(\text{acac})_2$), cetyltrimethylammonium bromide, and oleylamine mixtures that were ultrasonicated and then heated to 180 °C for several hours (see supplementary materials and fig. S1). Compositions studies varied from Pt_3Ni , Pt_2Ni , $\text{Pt}_{1.5}\text{Ni}$, Pt_1Ni_1 and PtNi_2 samples, and the transmission electron microscopy-energy dispersive spectroscopy (TEM-EDS) profiles together with inductively couple plasma-optical emission spectrometer (ICP-OES) results suggest a complete reduction of the precursors because the Ni/Pt ratios of the final products were nearly the same as the ratios used in the synthesis mixture (fig. S2). We further studied the effect of the concentration of the various reagents, the Pt/Ni ratio in the synthesis solution on the formation of the structures (figs. S3 to S6). The X-ray diffraction (XRD) patterns of Pt-Ni BNSs with varying Pt-Ni composition (Pt_xNi_y -BNSs) confirmed the efficient alloy formation (fig. S5), indicating that the composition can be adjusted by judicious choice of the amount of Pt and Ni precursors (21). Only when no Ni was present during the synthesis, Pt nanowires (NWs) with a smooth surface were obtained. The surfaces became rougher with the increasing Ni/Pt feeding ratio (fig. S6). We used TEM-EDS to monitor time-dependent reaction progress, which revealed the formation of Pt NWs prior to Ni inclusion. This sequence is expected given the higher redox potential of Pt (figs. S7 and S8). Finally, stable PtNi alloys are formed under solvothermal conditions (22).

Representative scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images emphasize the uniform 1D morphology of the as-synthesized samples for the $\text{Pt}_{1.5}\text{Ni}$ composition (labeled as PtNi-BNSs and this one after etching leads to the best ORR activity) with a length of hundreds of nanometers consisting of bunched nanospheres (Fig. 1, B and C). High-resolution TEM images reveal lattice fringes of 0.227 nm at the nodes and 0.216 nm at the shells (Fig. 1D), corresponding to (111) planes of Pt and

Pt-Ni alloys (23), respectively, suggesting that the alloyed Pt-Ni nanospheres would be connected by Pt-rich NWs. Scanning transmission electron microscopy (STEM)-energy dispersive x-ray spectroscopy (EDS) line-scanning of the nodes of different regions showed the existence of Ni in the nodes and an average Pt/Ni ratio is roughly 5/1 (fig. S9). It seems that the nanospheres were Ni-rich compared with the nodes, because the scans may not reveal the overall compositions, while Pt-rich alloys can be confirmed at the nodes. Atomic-resolution TEM images depict the uneven surface of the PtNi-BNSs (i.e., Pt_{1.5}Ni composition) and the occurrence of high-index (211) and (311) facets (Fig. 1, E and F). The presence of abundant high-index facets is favorable for ORR, because they exhibit distinct binding energies with oxygen-containing surface intermediates in the ORR mechanism (24). The presence of alloyed features is verified by STEM-EDS elemental mapping analysis, emphasizing the homogeneous distribution of Pt and Ni across the analyzed zone, which contains a Ni-rich core (Fig. 1G). The line-scan analysis of PtNi-BNSs demonstrates that both Pt and Ni elements are dispersed uniformly across the whole sphere, with an atomic Pt/Ni ratio according to TEM-EDS profile near 60/40 (Fig. 1H). This result is consistent with the bulk elemental ICP-OES analysis that informed a Pt/Ni ratio of 62/38.

Bunched nanocages. We obtained Pt-enriched bunched nanocages by selectively removing the more reactive Ni species through a simple acid-etching method. TEM images of the PtNi-BNCs (note: this sample is from the PtNi-BNSs after the etching) showed that the samples were still highly dispersed without structural collapse after the etching treatment (Fig. 2A). The presence of internal voids was deduced from the observation of the darker walls of the nanocages (Fig. 2B). The average wall thickness was ~2.2 nm (Fig. 2C), roughly corresponding to 11 atomic layers. The lattice fringe of 0.221 nm was consistent with the (111) plane of a Pt-Ni alloy (23), and was slightly larger than that of PtNi-BNSs because of the decreased Ni content after etching. In addition, the high density of steps and ledges was well preserved during the etching step (Fig. 2D). STEM-EDS elemental mapping indicated that skin structure of the wall in the Pt-Ni nanocages was Pt-rich (Fig. 2E).

Fig. 2F shows the EDS-line scanning of a single sphere in PtNi-BNCs, further confirming a well-defined Pt-skin structure of the nanocages formed after the Ni etching. The thickness of the outer shell was ~ 0.63 nm, corresponding to roughly two to three atomic Pt layers (25).

On the basis of above analysis, we propose that the wall of nanocages are heterogeneous in composition with Pt-rich skins on both the outer and inner surfaces and Pt-Ni alloy in the inner region of the wall. The precise Pt/Ni atomic ratio of PtNi-BNCs was revealed by the TEM-EDS profile is 80.7/19.3 (fig. S10, A and B), consistent with the ICP-OES result (81:19). The increased Pt/Ni ratio was likely caused by selective Ni leaching. The diffraction peaks of PtNi-BNCs showed a small shift to lower angles compared with PtNi-BNSs (fig. S10C), which is consistent with the lower overall Ni content. X-ray photoelectron spectroscopy (XPS) of Pt 4f revealed a shift of the Pt core levels to lower binding energies compared to Pt/C, likely because of electron donation from Ni to Pt (fig. S10D). The ligand effect would downshift the Pt d-band center, lowering the binding affinity between Pt and oxygen intermediates, and thus enhancing the ORR activity (5).

Electrocatalytic activity. We evaluated PtNi-BNCs as ORR catalysts, and Fig. 3A presents cyclic voltammetry (CV) results of Pt/C (60 wt%, JM), Pt NWs/C, PtNi-BNSs/C and PtNi-BNCs/C in a N_2 -saturated 0.1 M $HClO_4$ solution (fig. S11). The CV curves for carbon-supported PtNi-BNCs was investigated as a function of the Pt/Ni ratio (fig. S12). The electrochemical active surface area (ECSA) measured by hydrogen underpotential deposition (H_{UPD}) of PtNi-BNCs/C was $68.2 \text{ m}^2 \text{ g}_{Pt}^{-1}$, which is substantially higher than that of PtNi-BNSs/C ($43.5 \text{ m}^2 \text{ g}_{Pt}^{-1}$), confirming the advantage of hollow structure created by acid leaching. Moreover, the ECSA values for Pt/C, Pt NWs/C, Pt_3Ni -BNCs/C, Pt_2Ni -BNCs/C, $Pt_{1.5}Ni$ -BNCs/C, Pt_1Ni_1 -BNCs/C and $PtNi_2$ -BNCs/C (note: for convenience, all x and y values in the names of BNCs were labeled the same values as in the starting BNSs) were 56.5, 46.3, 37.4, 59.1, 68.2, 70.7 and $80.3 \text{ m}^2 \text{ g}_{Pt}^{-1}$, respectively, demonstrating the enhanced ECSA of Pt-Ni BNCs with increasing Ni content. TEM images of Pt-Ni BNCs

with varying Ni contents demonstrate the increased porosity with increasing Ni/Pt ratio (fig. S13), in agreement with the larger ECSA values.

We also measure ECSA from the electrooxidation of CO (CO stripping) given the sensitive nature of the Pt alloyed surface, since the ECSA derived from the H_{UPD} method would be lower than that of the real values because of the weakened binding interaction caused by the alloying effects (the ECSA obtained from the CO-stripping should be unaffected, fig. S14). The ECSA values of Pt/C and PtNi-BNCs/C obtained from the CO stripping are 56.7 and 101.5 m² g_{Pt}⁻¹, respectively, thus the $ECSA_{CO}/ECSA_{H_{UPD}}$ ratio measured for Pt/C was equal to 1 but was 1.49 for PtNi-BNCs/C catalyst, verifying the formation of a Pt-skin structure of PtNi-BNCs (4, 26). Fig. 3B and 3C show the linear sweep voltammetry (LSV) curves and Tafel plots, respectively, of Pt NWs/C, PtNi-BNSs/C and PtNi-BNCs/C and the commercial Pt/C reference. The smaller Tafel slope obtained for PtNi-BNCs/C (54 mV decade⁻¹) compared with the other samples demonstrates the enhanced kinetics for the ORR. The mass and specific activities of Pt NWs/C (1.02 A mg_{Pt}⁻¹ and 2.20 mA cm⁻²) and PtNi-BNSs/C (1.89 A mg_{Pt}⁻¹ and 4.34 mA cm⁻²) at 0.9 V were much higher than those of the Pt/C reference (0.21 A mg_{Pt}⁻¹ and 0.36 mA cm⁻²). Furthermore, PtNi-BNCs/C show a mass and specific activities of 3.52 A mg_{Pt}⁻¹ and 5.16 mA cm⁻², which are respectively ~17 and ~14 times higher than those of the Pt/C reference. In general, the catalytic performance was enhanced with increasing Ni/Pt ratio, which can be ascribed to the higher amount of exposed active sites achieved by Ni leaching (fig. S12). The inferior ORR activities of Pt₁Ni₁-BNCs/C and PtNi₂-BNCs/C were ascribed to the structural collapse upon excessive Ni dissolution (fig. S13).

To further corroborate the ORR performance obtained at the RDE-level, practical H₂/air and air-breathing PEMFCs tests were conducted (fig. S15) with fuel cells containing PtNi-BNSs/C and PtNi-BNCs/C at a loading of 0.15 mg cm⁻² as a cathode catalyst material. The H₂/air fuel cell of PtNi-BNCs/C delivers a current density of 1.5 A cm⁻² at 0.6 V and achieves a peak power density of 920 mW cm⁻² (Fig. 3E), outperforming the PtNi-BNS/C (1.0 A cm⁻², 770 mW cm⁻²) and Pt/C (0.8 A cm⁻², 600 mW cm⁻²) based systems. Considering

comparable Pt loadings, this performance is among the best reported performance for Pt-based catalysts (table S1). In addition, the air-breathing PEMFC operated at room temperature and ambient pressure exhibited a current density of 170 mA cm^{-2} at 0.6 V, compared with 100 mA cm^{-2} for Pt/C, resulting in an improvement of 70% (fig. S15E). The H_2 /air and air-breathing PEMFCs were stably operated at a constant-working voltage of 0.6 V for at least 180 hours with a negligible decay ($< 3 \%$) of the output current densities (Fig. 3F).

Structural changes under electrochemical operation. To evaluate stability under better defined conditions, Pt/C, PtNi-BNSs/C and PtNi-BNCs/C are subjected to continuous cycling for 20,000 cycles between 0.6 V and 1.1 V in an O_2 -saturated 0.1 M HClO_4 solution. The ORR performance variations recorded every 4000 cycles show that the mass activity and ECSA of Pt/C declined by 61.9% and 59.4%, respectively, and the half-wave potential shift by 54 mV to more negative values compared to the fresh sample (Fig. 4, A and B). In contrast, the high durability of PtNi-BNSs/C was evidenced by the much small loss in mass activity and ECSA by 13.7% and 9.4%, along with a 6-mV negative-shifted half-wave potential (Fig. 4, C and D). The PtNi-BNSs/C sample became hollow and porous after the stability test through electrochemical leaching (dealloying) (fig. S16, A to C), whereas the bunched architecture was destroyed to some degree compared with PtNi-BNCs/C. These results suggest a strong chemical difference between electrochemical dealloying and chemical etching, as structural collapse and Ni leaching caused substantial performance loss of PtNi-BNSs/C (fig. S16D). Comparatively, the performance loss of PtNi-BNCs/C is negligible, even after the prolonged durability test for 50,000 cycles (Fig. 4, E and F). The mass activity and ECSA only dropped by 1.3% and 1.1% after the durability test compared with the fresh one, demonstrating the robustness of PtNi-BNCs/C as an ORR electrocatalyst. The composition and structure of the PtNi-BNCs/C catalysts after the durability test were further investigated. The hollow and core-shell (Pt-rich surface) structures of PtNi-BNCs/C were retained during the durability test (fig. S17), and TEM-EDS revealed that Ni loss was negligible

(fig. S18). The Pt-skin structure may have protected the electrocatalysts against further Ni leaching from the core.

We probe the dynamic changes in oxidation state and local coordination environment at ORR-relevant potentials by in-situ XAFS. Figure 5A shows the potential-dependent Pt-L₃ edge x-ray absorption near-edge spectra (XANES) of PtNi-BNCs/C, emphasizing the metallic state of Pt at applied potentials of 0.54, 0.7 and 0.9 V (vs. RHE). A 5 nm Pt/C (TEC10E50E-HT) reference was used for comparison to reduce the influence of the size effect. For comparison, the Pt-L₃ edge XANES of PtNi-BNSs/C is depicted in fig. S19. The normalized white line intensities (μ_{norm}) at the Pt-L₃ edge increased with increasing applied potentials because of the chemisorption of surface oxygenated species (Fig. 5B) (27, 28). The trends in μ_{norm} with potential differed between the catalysts and were used to understand the mechanistic origins of ORR activity (29). At 0.54 V, both PtNi-BNCs/C and PtNi-BNSs/C showed a higher μ_{norm} than Pt/C, probably because of the chemisorption of *OH and/or *O species in the double layer region (30). With an increase of the potential to 0.7 V, the increase of μ_{norm} (e.g., $\Delta \mu_{\text{norm}} (0.7_0.54) = \mu_{\text{norm}} (0.7 \text{ V}) - \mu_{\text{norm}} (0.54 \text{ V})$) was larger for PtNi-BNSs/C and smaller for PtNi-BNCs/C in comparison to the change for Pt/C. When the potential was increased to 0.9 V, a negligible $\Delta \mu_{\text{norm}} (0.9_0.7)$ was seen for PtNi-BNSs/C and PtNi-BNCs/C relative to Pt/C (Fig. 5C). Together, PtNi-BNSs/C showed an initially higher μ_{norm} at 0.54-0.7 V and subsequently an inhibited μ_{norm} at 0.7-0.9 V relative to Pt/C, similar with previous reports (28, 30). However, PtNi-BNCs/C only showed a higher μ_{norm} at 0.54 V and subsequently the suppressed μ_{norm} over the whole range of 0.54-0.9 V compared with PtNi-BNSs/C and Pt/C. Thus, the in situ XANES characteristic of PtNi-BNCs/C may partly account for its particularly high ORR activity and durability through the inhibition of strong-bounded oxygenated species from 0.54 to 0.9 V relative to Pt/C and PtNi-BNSs/C.

The fitted EXAFS spectra conducted at 0.54 V (Fig. 5D, figs. S19 to S21 and tables S2 to S5), a potential in double layers with the minimum interference from the adsorption of O/OH species, showed bond lengths

of Pt-Pt (BL_{Pt-Pt}) and coordination numbers of Pt-Ni (CN_{Pt-Ni}) in the PtNi-BNCs/C ($BL_{Pt-Pt} = 2.69 \text{ \AA}$, $CN_{Pt-Ni} = 0.6$), PtNi-BNSs/C ($BL_{Pt-Pt}=2.71 \text{ \AA}$, $CN_{Pt-Ni}=1.0$), and Pt/C ($BL_{Pt-Pt} = 2.76 \text{ \AA}$). The evidently shorter BL_{Pt-Pt} for both PtNi-BNCs/C and PtNi-BNSs/C than that for Pt/C could be well ascribed to the smaller-radius Ni than Pt inducing the global stress for PtNi-BNCs and PtNi-BNSs. However, compared to PtNi-BNSs/C, the slightly smaller CN_{Pt-Ni} while a bit shorter BL_{Pt-Pt} for PtNi-BNCs/C indicated an additional source of strain presumably induced by structural defects, as demonstrated in a recent report (7). Additionally, the fitting results of EXAFS at 0.9 V revealed the absence of a definite Pt-O path for both PtNi-BNCs/C and PtNi-BNSs/C (table S3 and table S5), despite a clear electrochemical adsorption of oxygenated species on their surface. This lack of a Pt-O scattering peak in EXAFS for both PtNi-BNCs/C and PtNi-BNSs/C agrees with their XANES results and may be correlated with the surface disorder produced by the defects (steps and grain boundaries, see TEM analysis) and the corresponding disturbance to interfacial water structures (28, 30).

Interestingly, TEM examinations after ORR measurement showed a nearly hollow but irregular shape for PtNi-BNSs/C while dimensionally uniform hollow structures for PtNi-BNCs/C (figs. S16 and S17). The differences in hollow microstructures between PtNi-BNSs/C and PtNi-BNSs/C were likely caused by the different corrosion methods for the Ni dissolution and the accompanied restructuring, i.e., a moderate acid corrosion for PtNi-BNCs/C vs. an electrochemical corrosion for PtNi-BNSs/C. Expectedly, these microstructural differences induced the distinct density and distribution of defects and correlated microstrain on the surface of catalysts, causing different electrocatalytic in-situ XANES and EXAFS behaviors between PtNi-BNSs/C and PtNi-BNSs/C. Specifically, the irregular hollow structures in PtNi-BNSs/C easily created local overstrained domains that undermined the electrochemical stability of PtNi-BNSs/C to some extent, whereas the dimensionally uniform hollow structures in PtNi-BNCs/C were observed to be stable under the conditions we investigated. Thus, our work suggests that the fine regulation of micro-structures by tailored

synthesis could produce the electrochemically durable hollow-structured ORR catalysts although the hollow structures themselves have high free energy.

Theoretical studies. Based on these experimental data, we performed density functional theory (DFT) calculations to understand the high ORR performance of PtNi-BNCs, using Pt₃Ni-skin and Pt₄Ni-skin models (Fig. 6). It is generally accepted that the atomic O adsorption energy ΔE_{O^*} can be used to evaluate the ORR activity, and the optimal value of ΔE_{O^*} is ~0.2 eV weaker than the one for Pt(111) (5, 31). ΔE_{O^*} is modulated by the d-band center (labeled as ϵ_d) of Pt, while the downshift/upshift of ϵ_d is tuned by surface lattice strain (noted as χ) and coordination environment (coordination number, noted as CN) (32-34). High-index crystal facets such as Pt(211) and Pt(311) exhibit a compressive lattice strain (χ) relative to Pt(111), which brings about a down-shift of ϵ_d of surface Pt atoms and weakening of ΔE_{O^*} . Herein, DFT calculation is focused on investigating the synergistic effect of χ and CN on ϵ_d , and finally on ΔE_{O^*} , and the correlations between them (Fig. 6, A and B) (36), whereas Fig. 6C corroborates that the Pt₄Ni-skin has higher ORR activity than the Pt₃Ni-skin. Both are substantially improved relative to that of Pt(111). ΔE_{O^*} values are, respectively, 0.17 eV and 0.11 eV weaker than on Pt(111), near the optimal value (table S6). Both skins have a 2.5% compressive lattice strain (fig. S22 and table S7). The bridge sites of Pt(211) and (311) have a stronger O binding than those on Pt(111), while the hexagonal close packing sites of them adsorb O slightly weaker. In aqueous solution for ORR at the electrode surface, the bridge sites of high crystal planes are preferentially occupied by water molecules, while the other sites account for the observed high ORR activity (figs. S23 to S26). In addition, the determined potential energy profiles demonstrate that Pt₄Ni-skin has a lower overpotential of ORR than Pt₃Ni-skin and Pt(111) (fig. S27 and table S8). On the basis of above analysis, we propose that the synergistic effects of strain and coordination environment, incorporation of Ni and the appropriate Pt/Ni ratio provide a properly weakened Pt-O binding strength, thus leading to the superior ORR activity of PtNi-BNCs (Fig. 6D). Furthermore, DFT calculations were also conducted to gain insight into the high stability of PtNi-BNCs (fig.

S28). The binding energy of the surface Pt atoms in Pt₄Ni- or Pt₃Ni-skin models is stronger compared to other (Pt(111), Pt(211) and Pt(311)) models, indicating higher stability of the Pt-skin structures under the condition of lattice strain and coordination environment. In addition, it was found that the required activation energy barrier (E_a) for the spillover of surface Pt atoms is substantial, indicating that dissolution of surface Pt atoms is kinetically prohibited for Pt-skin structures, even in the presence of oxygen (O) adsorbates (table S9). The above results convinced well with the observed robust structure of our catalyst during the durability test.

Discussion. We prepared bunched Pt-Ni nanocages and demonstrated that they are efficient and durable ORR electrocatalyst for fuel cells. The as-obtained bunched Pt-Ni alloy nanocages showed high mass activity and specific activity of 3.52 A mg_{Pt}⁻¹ and 5.16 mA cm⁻², respectively, which is 16.8 times and 14.3 times higher than that of a commercial Pt/C catalyst. The catalyst also exhibited robust stability with a negligible activity decay even after 50,000 potential-scanning cycles. The H₂-air fuel cell assembled by this Pt-Ni catalyst achieves a peak power density of 920 mW cm⁻² and delivers a current density of 1.5 A cm⁻² at the voltage of 0.6 V for at least 180 hours, demonstrating the great potential for practical application. In situ XAFS, theoretical calculation and experimental results reveal that such excellent performance could be ascribed to the integration of unique hollow structure and dimensional architecture in the bunched Pt-Ni alloy nanocages. This work provides an effective strategy for the rational design of Pt alloy nanostructures and will revolutionize the future development of catalysts for their practical application in energy conversion technologies and beyond.

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Authors contributions: B.Y.X. and X.W.L. conceived the idea and designed the experiments. X.T. and L.J.W. carried out the sample synthesis, characterization and measurements. Z.X. provided the in-situ XAFS measurements. Y.Q.S. and E.J.M.H. provided theoretical calculations. X.T. and D.D. performed the fuel cell measurements. BC, HMW and HFL participated the experiment result discussion. X.L.T., X.W.L. and B.Y.X. co-wrote and revised the manuscript. All the authors contributed to the overall scientific interpretation and edited the manuscript. X.T., X.Z. and Y.Q.S. contributed equally to this work. **Competing interests:** The

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SUPPLEMENTARY MATERIALS

Materials and Methods

Figs. S1 to S28

Tables S1 to S9

References (35–54)

Figure Captions

Fig. 1. Structural and compositional characterizations of Pt_{1.5}Ni-BNSs. (A) Schematic illustration of the preparation of PtNi-BNCs. (B and C) TEM images of PtNi-BNSs and (D) the enlarged TEM and the corresponding HRTEM images in the chosen areas (marked by yellow squares). (E, F) Atomic resolution HRTEM images, and (G) HAADF-STEM image and the corresponding EDS elemental mapping of PtNi-BNSs. (H) EDS profile of PtNi-BNSs and STEM-EDS line-scanning profile of a single nanoparticle.

Fig. 2. Structural and compositional characterizations of PtNi-BNCs derived from etching of Pt_{1.5}Ni-BNSs. (A, B) TEM images of PtNi-BNCs, and (C) the enlarged TEM and the corresponding HRTEM images in the chosen areas (marked by yellow squares). (D) Atomic resolution HRTEM image, and (E) HAADF-STEM images. (F) EDS profile of PtNi-BNCs and STEM-EDS line-scanning profile of a single nanocage.

Fig. 3. Electrochemical and fuel cell performance of various Pt based samples. (A) CVs, (B) LSVs, (C) corresponding Tafel plots, and (D) mass and specific activities of Pt/C, Pt NWs/C, PtNi-BNSs/C and PtNi-BNCs/C at 0.9 V (vs. RHE). (E) H₂-air fuel cell polarization plots with Pt/C, PtNi-BNSs/C and PtNi-BNCs/C as the cathode, and (F) stability test of H₂-air and air-breathing fuel cells at 0.6 V.

Fig. 4. Durability performance of various catalysts. (A, C and E) LSV evolutions, and the insets are the CV variations, (B, D and F) mass and specific activity evolutions for Pt/C (A, B), PtNi-BNCs/C (C, D) and PtNi-BNCs/C (E, F) before and after the durability test for various potential-scanning cycles

Fig. 5. In-situ x-ray absorption fine structure (XAFS) and x-ray absorption near edge structure (XANES) analysis. (A) In-situ Pt-L3 edge XANES spectra for PtNi-BNCs, and the enlarged part marked in green square. (B) In-situ potential-dependent white line peak intensities ($\mu(E)$). (C) $\Delta\mu$ -XANES spectra (0.9 V_0.7 V) of PtNi-BNSs and PtNi-BNCs. (D) First shell EXFAS fitting in R space for spectra data at 0.54 V.

Fig. 6. Disentangling the correlation of lattice strain and ligand effects on the d-band center, and the atomic O adsorption energy from DFT calculations. (A) DFT-determined correlation of d-band center and atomic O

adsorption energy with the compressive lattice strain of Pt(111) facet. (B) DFT-determined correlation between d-band center and the generalized coordination number of surface Pt atoms of various Pt(hkl) planes. (C) DFT-determined correlation of atomic O adsorption energy with d-band center of surface sites. Pt(211)-B and Pt(311)-B denote the bridge sites of Pt(211) and Pt(311) planes. (D) Illustration of the synergistic effects derived from both of lattice strain and ligand effects in the catalysts.