Carbon-supported PtCo₂Ni₂ alloy with enhanced activity and stability for oxygen reduction

Ya-Rong Zheng^{1†}, Min-Rui Gao^{1†}, Hui-Hui Li¹, Qiang Gao¹, Muhammad Nadeem Arshad^{2,3}, Hassan A. Albar³, Tariq R. Sobahi³ and Shu-Hong Yu^{1*}

The commercialization of proton exchange membrane fuel cells (PEMFCs) is still restricted by the well-known dilemma, that is, the heavy dependence of using expensive platinum (Pt) catalyst to negotiate the sluggish oxygen reduction reaction (ORR) kinetics in fuel cell cathodes. Here, a carbon-supported PtCo₂Ni₂ alloy catalyst with low Pt usage was synthesized via a simple method, which exhibited exceptional ORR activity with a more positive half-wave potential ($E_{1/2}$) ~57 mV, which was more positive than the state-of-the-art Pt/C catalysts. Moreover, the alloy catalyst performs excellent durability after 10,000 harsh cycles compared with that of Pt/C catalyst in acidic solution, which may be developed as a promising alternative for Pt-based catalysts in fuel cell technology.

Proton exchange membrane fuel cells (PEMFCs) have drawn intensive attention as promising candidates for non-polluting and high-efficiency energy conversion in automotive and portable power [1–3]. However, large-scale commercialization of this technology is greatly hindered by the heavy dependence of using rare Pt as electrocatalysts [4–7]. Considerable efforts have been devoted to developing alternative Pt-free electrocatalysts, while Pt is still the most effective oxygen reduction reaction (ORR) catalyst, especially in acidic environment [8–14]. Therefore, to make PEMFCs economically competitive, an effective way is to develop composition and surface tunable Pt-based alloy catalysts with low cost, high activity and durability [15–20].

Recently, a number of studies demonstrated that Pt-based multimetallic electrocatalysts (alloyed with Ni, Co, Fe, Cu, etc.) with altered surface electronic structure would exhibit high catalytic activity for the ORR [21–34]. Recently, our research on Pt-based binary and ternary electrocatalysts revealed that excellent catalytic activity for ORR, formic acid oxidation, and methanol oxidation could be achieved by alloying Pt with other cheaper transition

elements such as Pd, Ni, and Cu by taking advantages of the altered electronic structure of Pt and the favorable surface composition of the alloy electrocatalyst [18,21,24,35,36]. For instance, a mixed PtPd alloy surface could be obtained by surface atomic redistribution of ternary PtPdCu upon potential cycling in an acidic electrolyte, and the distinctive topmost layer played a key role in the enhancement of catalytic activity [35]. Moreover, we found that mixed-PtPd-shell ternary PtPdCu nanoparticle nanotubes also showed significant enhancement for ORR by using copper nanowires as templates [18]. The core/shell Pd/PtFe catalysts also show improved ORR activity and durability, which is highly associated with the FePt shell thickness [37]. It is believed that the arrangement of composition of the topmost layer, and rationally introducing foreign metals to modify the electronic structure of Pt are critical factors to enhance the electrochemical performance of Pt-based ORR catalysts [38].

On the other hand, carbon support technology has been verified to be an effective way to boost the catalytic activity of Pt-based catalysts and to avoid nanoparticle aggregation, thus effectively reducing Pt usage and lowering the fuel-cell cost [39–41]. Herein, we report a facile method to directly load PtCo₂Ni₂ trimetallic alloy onto Vulcan carbon and its fabrication is simple, economic, and easily scaled up. The atomic ratio of Pt, Co, and Ni in the catalysts can be tuned through a thermal treatment way and highly active CoNi/Pt core/shell structure was achieved at the annealing temperature of 600°C, which exhibited exceptional ORR activity with onset potential of 0.98 V and a 57 mV positive shift of $E_{1/2}$ as compared with commercial Pt/C catalyst. The alloy catalyst performs excellent durability after 10,000 ORR potential cycles.

The process of depositing PtCo₂Ni₂ ternary alloy nanoparticles (NPs) onto Vulcan XC-72R were illustrated in

¹ Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Science at Microscale, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

² Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

³ Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

[†] These authors contributed equally to this work.

* Corresponding author (email: shyu@ustc.edu.cn)

Fig. 1. A typical transmission electron microscopy (TEM) image shows that the particles are fairly well dispersed on the carbon support and have an average size of ~ 5.2 nm (Fig. 2a and inset), but some agglomerates of particles are sporadically observed possibly due to the relative low surface area of Vulcan XC-72R [42]. High resolution TEM (HRTEM) image of PtCo_2Ni_2 NPs reveals that the resolved lattice fringes of (111) planes with a spacing of $2.21 \text{ \AA}$ (Fig. 2b), as well as (220) plane with a spacing of $1.35 \text{ \AA}$. The selected-area electron diffraction (SAED) pattern (inset in Fig. 2b) shows concentric rings that are indexed to the (200), and (311) planes of PtCo_2Ni_2 NPs. The X-ray diffraction (XRD) pattern (Fig. 2c) shows that three diffraction peaks are corresponding to (111), (200), and (220) facets of a face-centered-cubic (fcc) structure. It should be noted that the broad diffraction peak around $2\theta = 25^\circ$ is indexed to the (002) plane of the carbon support. Compared with

Figure 1 Illustration of the synthetic process for carbon-supported PtCo_2Ni_2 ternary alloy nanoparticles

the standard diffraction patterns of pure Pt, all the diffraction peaks shift to higher angles owing to the replacement of smaller Co and Ni metal atoms. There is no observation of any impurity peaks of pure Pt, pure Co, or pure Ni, indicating only single PtCo_2Ni_2 phase in the sample.

The formation of PtCo_2Ni_2 /carbon ternary alloy was further confirmed by scanning TEM energy dispersive X-ray spectroscopy (STEM-EDS) elemental mapping (Fig. 2d). The corresponding elemental maps of Co, Ni, Pt and their overlap indicate that all the three elements are evenly distributed in the nanostructure. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) results suggest that the bulk atomic ratio of Pt, Co, and Ni are 22:39:39, and the composition of Pt, Co, and Ni can be tuned by changing the molar ratio of corresponding precursors during the reactions (Fig. S1).

The as-prepared $\text{PtCo}_2\text{Ni}_2/\text{C}$ was annealed under 5% H_2 balanced Ar atmosphere at 400, 600 and 800°C (denoted as C400, C600, and C800, respectively. Fig. S2) to remove the surface organic molecular and modify the surface atomic structure of PtCo_2Ni_2 alloy [43]. X-ray photoelectron spectroscopy (XPS) was employed to ascertain the modification of surface atomic structure of C400, C600, and C800. As shown in Fig. 3a, doublet peaks at ~ 71.5 and 75 eV are clearly observed, which are attributed to $\text{Pt}4f_{7/2}$ and $\text{Pt}4f_{5/2}$, respectively. The upshift of binding energy (BE) for Pt after

Figure 2 (a, b) TEM and HRTEM images of $\text{PtCo}_2\text{Ni}_2/\text{C}$. The insets of (a, b) show the particle size histogram and the SAED pattern, respectively. (c) XRD pattern of the as-prepared $\text{PtCo}_2\text{Ni}_2/\text{C}$ catalysts. (d) STEM-EDS elemental mapping of the as-prepared $\text{PtCo}_2\text{Ni}_2/\text{C}$ overlap, Co (red), Ni (green) and Pt (yellow), respectively.

Figure 3 (a) XPS spectra of the Pt4f signals for the as-prepared PtCo₂Ni₂/C, C400, C600 and C800, respectively. (b) The Pt, Co, and Ni atomic fraction in the surface region as increasing the annealing temperature measured by XPS. (c, d) EDX line-scan profiles of C600 along the red line.

thermal treatment relative to the as-prepared catalyst derives from the modification of the electronic structure and the downshift of d-band center position [44–46]. The similar trends are also found for other compositions, such as Pt-CoNi/C and Pt₂CoNi/C (Fig. S3). The high-resolution O1s XPS spectrum for the as-prepared PtCo₂Ni₂/C indicates the fitting peak at 531.5 eV associated with oxygen in –OH groups and the peak at 532.1 eV attributed to the physisorbed water at the surface (Fig. S4) [47,48]. The high-resolution XPS spectra of Ni2p of Pt₂CoNi show BE values at 852.0 and 869.4 eV, which correspond to metallic Ni. However, due to the inner migration of Co atoms, we obtained the modest peaks of Co2p spectra (Fig. S5). The atomic fraction of Pt, Co, and Ni in the near-surface region is measured by XPS as shown in Fig. 3b, revealing that more Pt atoms migrate to the outer surface (except C800 sample due to the sintering and coalescence of the NPs at such high temperature) due to the Kirkendall mass-transport effect and the different diffusion rates of migration of each metal in a diffusion couple [45,49]. The energy-dispersive X-ray (EDX) line-scan analysis along the cross-section of PtCo₂Ni₂ (treated at 600°C) further confirms the formation of the Pt-enriched surface structure (Figs 3c and d). The same results were also observed in our previous work that thermal-treated CuPt tubes showed quite weak Cu redox peaks and led to the increase of the Pt atomic fraction in

the surface region [24].

The ORR performances of the PtCo₂Ni₂/C catalysts were evaluated in O₂-saturated 0.1 M HClO₄ solution on a glass carbon electrode (GCE) at room temperature (Fig. 4). The hydrogen adsorption/desorption and Pt oxide oxidation/reduction peaks are obviously detected in Fig. 4a. The annealed PtCo₂Ni₂/C catalysts show the broadened peaks in the hydrogen adsorption region between 0–0.4 V compared with Pt/C, which is due to the shift of the d-band center of the surface Pt atoms after alloying with Co and Ni [22,31,50] and thus a weakened interaction between Pt and intermediate oxide species, releasing more active sites for O₂ adsorption [51]. In the case of ORR, the coverage of the adsorbed hydroxyl species (OH_{ad}) on the surface active sites will inhibit the O₂ adsorption and hinder the reaction. Upon the cyclic voltammetry (CV) curves of the catalysts, the Pt oxide oxidation peaks (0.8–1.0 V) have positive shifts relative to the Pt/C catalysts, suggesting that the PtCo₂Ni₂/C catalysts could promote the desorption of OH_{ad} during ORR [52]. C600 catalyst shows the highest electrochemical surface area (ECSA) compared with other samples (Fig. 4b). In contrast, C800 performs lowest ECSA due to the growth and ripening of the alloy NPs. The ORR onset potentials for C400, C600, and C800 catalysts are all more positive than Pt/C in the range of 0.9–1.0 V. Furthermore, the *E*_{1/2} of C400, C600 and C800 catalysts are 0.886,

Figure 4 (a) CV curves of Pt/C, C400, C600 and C800 were recorded with a scan rate of 50 mV s⁻¹ after 250 potential cycles in Ar-saturated 0.1 M HClO₄ solution. (b) Specific ECSAs for Pt/C, C400, C600 and C800. (c) ORR polarization curves of Pt/C, C400, C600 and C800, after 250 potential cycles in O₂-saturated 0.1 M HClO₄ solution with a scan rate of 5 mV s⁻¹ and a rotation rate of 1600 rpm at room temperature. (d) Mass and specific activity at 0.9 V (vs. RHE) for the four catalysts. (e) Loss of ECSAs for these catalysts with number of CV cycles in an O₂-saturated 0.1 M HClO₄ solution (0.6–1.2 V vs. RHE, sweep rate, 50 mV s⁻¹). (f) Polarization curves for C600 and Pt/C before and after 10,000 potential cycles.

0.890 and 0.876 V, respectively, indicating the distinctly enhanced ORR kinetics, and the ORR catalytic activity follows the order of C600 > C400 > C800 > Pt/C (Fig. 4c). The kinetic currents are obtained from the ORR polarization curve at 0.9 V (vs. RHE) and normalized to the loading amount of Pt metal to compare the mass activity (MA, based on Pt) of the catalysts (Fig. 4d). The C600 performs the largest MA of 122.17 A g_{Pt}⁻¹ at 0.9 V, which is 1.1, 1.2, and 3.0 times larger than C400, C800, and the Pt/C catalyst. Due to the larger ECSA of C600, and a similar current density with C400 at 0.9 V, while the specific activity (SA)

of C600 is a bit lower than C400. The SA of C400, C600, and C800 are 2.89, 2.63, and 2.56 mA cm⁻², which are much higher than that of Pt/C catalyst. The enhancement in the activity of the treated PtCo₂Ni₂/C catalysts could be due to the altered surface electronic structure and negative shift of the d-band center position induced by alloying [53]. Furthermore, the electrochemical dealloying induced by rearrangement of the surface Pt atoms of the catalyst would provide highly active sites, which also make a great contribution to improve the catalytic activity (Figs S6 and S7) [31,54]. Noted that compared with PtCo/C, PtNi/C,

PtCoNi/C, and Pt₂CoNi/C in this system, the PtCo₂Ni₂/C catalyst showed a more positive half-wave potential and higher limited current density and thus faster ORR kinetics (Figs S8 and S9). We infer that the enhancement might be due to the electronic effect of the additional metal to bimetallic catalysts, which could further change the d-band center of Pt, thus facilitating the adsorption, activation or desorption of molecular oxygen [55].

As a key concern for all catalysts, stability determines the practicability. To evaluate this, we performed accelerated durability tests (ADT) by potential cycling between 0.6 and 1.2 V (vs. RHE) for 10,000 potential cycles. As shown in Fig. 4e, the ECSA of C600 and C800 decrease slowly with increasing cycling times and remain more than 90% of the initial value after 5000 CV cycles. After 10,000 cycles, a loss of 13.2% for C800, 19.3% for C600, 25.8% for C400 are observed, comparing with a severe loss of 37.3% for the commercial Pt/C catalyst. Furthermore, the ORR polarization curve of Pt/C has a more negative shift than that of C600 after having been cycled (Fig. 4f). The much better stabilities of the treated alloy catalysts are possibly due to the rearrangement of the near-surface Pt atoms which reduce the surface dangling bonds due to the leaching of Ni and Co [35,56,57].

In summary, we report a one-step route for directly obtain carbon-supported PtCoNi ternary alloy NPs with tunable composition by simply changing the precursor compositions. It has been found that at higher annealed temperature, Pt and Ni atoms in PtCo₂Ni₂/carbon alloy will migrate to the outer surface to form a Pt-enriched surface structure, which exhibits superior ORR activities with the mass and specific activity about 3-fold higher than that of commercial Pt/C catalyst as well as excellent stability after 10,000 cycles. The high ORR performance of this new alloy catalyst is attributed to the favorable surface composition, the altered surface electronic structure, and also the depletion of surface Co, Ni atoms that induce rearrangement of Pt atoms on the near-surface. The present study holds the promise for designing low-Pt ORR catalysts with high performance by multi-alloy strategy. Furthermore, this route is simple, economic, and easily scaled up, which is highly required for the current PEMFC technology.

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- Author contributions** Zheng YR and Gao MR conceived the experiments, analyzed the results and wrote the paper; Yu SH supervised the project, conceived the experiments, analyzed the results and wrote the paper. Li HH, Gao Q, Arshad MN, Albar HA, and Sobahi TR conceived the experiments, collected the data and analyzed the results. All authors contributed to the general discussion.
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Ya-Rong Zheng received his BSc degree in Chemistry at Hefei University of Technology in 2010. He is currently a PhD candidate under the supervision of Prof. Shu-Hong Yu in the Department of Chemistry, University of Science and Technology of China (USTC). His current research interests include design and synthesis of multicomponent alloy catalysts, transition metal chalcogenides, and their applications in fuel cell technology.

Min-Rui Gao received his BSc degree from Hefei University in 2006 and PhD degree in Chemistry from the USTC under the supervision of Prof. Shu-Hong Yu in 2012. He did postdoctoral research at University of Delaware (2012–2014) and Argonne National Laboratory (2015). His main research interests focus on the design and synthesis of cheap and efficient materials for energy storage applications.

Shu-Hong Yu received his BSc degree at Hefei University of Technology and PhD degree from the USTC. He was a postdoctoral fellow with M. Yoshimura (Tokyo Institute of Technology) and a Humboldt Fellow with M. Antonietti and H. Cölfen (MPI of Colloids and Interfaces, Germany). In 2002, he was appointed the Cheung Kong Professor at USTC. Currently, he leads the Division of Nanomaterials & Chemistry at Hefei National Laboratory for Physical Sciences at Microscale, USTC. His current research interests include bio-inspired synthesis and self-assembly of new nanostructured materials and nanocomposites, and their related properties. He serves as editorial advisory board member of journals: *Accounts of Chemical Research*, *Chemical Science*, *Materials Horizons*, *Chemistry of Materials*, *Nano Research*, *CrystEngComm*, *Particle & Particle Systems Characterization*, *Current Nanoscience* and *SCIENCE CHINA Materials*. His recent awards include *Chem. Soc. Rev. Emerging Investigator Award* (2010) and *Roy-Somiya Medal of the International Solvothermal and Hydrothermal Association (ISHA)* (2010).

中文摘要 近年来, 质子交换膜燃料电池由于高成本严重阻碍了其商业化进程, 而目前催化阴极氧气还原反应最高效的催化剂仍然是昂贵的铂催化剂, 因此设计、开发制备少铂、高效、稳定的催化剂是目前此领域研究的热点. 本论文利用一种简便的制备方法得到了碳负载的铂钴镍(摩尔比=1:2:2)三元合金纳米颗粒催化剂, 这种合金催化剂在改变铂电子结构的同时, 大大降低了贵金属铂的用量. 电化学测试结果显示这种多元合金催化剂的半波电势与商业铂碳相比提高了约57 mV, 而且优于同体系制备的二元合金催化剂和其他组分三元合金催化剂. 此外, 在酸性电解质溶液中, 此催化剂表现出更优异的稳定性. 在燃料电池技术领域, 这种多元合金催化剂很可能在将来发展成新电催化剂来替代铂材料.