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Article

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Synthesis of Pt-Rare Earth Metal Nanoalloys

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ABSTRACT: Chemical synthesis of platinum-rare earth metal (Pt-RE) nanoalloys, one of the most active catalysts for the oxygen reduction reaction, has been a formidable challenge, mainly due to the vastly different standard reduction potentials of the two metals and high oxophilicity of the latter. Here we report a universal chemical process to prepare Pt-RE nanoalloys with tunable compositions and particle sizes. Pt and RE metal ions from the most common hydrated metal salts are first atomically embedded into an in-situ formed C-N network, yielding a stable compound insensitive to O₂ and H₂O. The Pt-RE nanoalloys are subsequently obtained by heating the compound under a mild reducing atmosphere (e.g. 3.3% H₂/Ar). The key intermediate step of the process is the formation of RE carbodiimides (RE₂(CN₂)₃) along with Pt particles. This synthesis mechanism suggests an efficient strategy to prepare nanoalloys with highly reactive metals.

INTRODUCTION

The enhanced properties of metallic materials through alloying has led to their broad applications in engineering, electronics, and catalysis.¹⁻⁵ Among them, Pt-Rare earth metal (RE) alloys are particularly interesting for the catalysis of oxygen reduction reaction (ORR) in fuel cells. In the past decade, theoretical and experimental studies have shown that Pt-RE alloys exhibit remarkable ORR activities, among the highest of all ORR catalysts ever reported.⁶⁻⁹ The activity enhancement originates from the formation of a compressively strained Pt overlayer, which, indicated by DFT calculations, lowers the OH binding energy towards the predicted optimum value, i.e. ~ 0.1 eV weaker than on Pt (111).⁶⁻⁹ Furthermore, high stabilities of Pt-RE alloys in fuel cells are anticipated, given the stable alloy structures due to the exceptionally negative alloy formation energies (Figure S1a) and the formation of a protective Pt overlayer in acidic media.^{6,10} From a manufacturing point of view, contrary to what the name implies, several RE metals are actually quite abundant. For example, cerium, yttrium, and lanthanum have similar abundance to that of nickel or copper (Figure S2a), and their current prices (for the oxides) are less than 0.01% of that for the platinum metal (Figure S2b).

Chemical synthesis of Pt-RE alloys in the form of nanoparticles (i.e. the nanoalloys) for practical applications is truly challenging. First of all, Pt and RE metals have vastly different standard reduction potentials, e.g. 1.188 V for Pt²⁺/Pt and -2.279 V for Gd³⁺/Gd (Figure S1b). The low reduction potentials of RE metals are far beyond the stability range of water. As a result, the traditional wet chemical techniques carried out in aqueous or protic solvents¹¹⁻¹⁴ are no longer applicable. In addition, the reduction of RE ions to the pure metallic phases needs super strong reducing agents such as solvated electrons from alkali metals.^{12,15} After the reduction, the metallic RE phases exhibit extremely high oxygen affinity due to the formation

of strong metal-oxygen bonds. Compared to the energy gain by forming alloys with Pt (e.g. -4.0 eV for Pt₃Y), the number is more than doubled for oxide formation (e.g. -9.9 eV for 1/2Y₂O₃) (Figure S1a).^{16,17} Because of this effect, any processes for the synthesis of bulk Pt-RE alloys always need to be carried out in an inert atmosphere free of O₂ or H₂O.¹⁸

Thus far, the superior ORR performance of Pt_xRE nanoalloys has only been realized with the model samples prepared by a physical gas aggregation technique. The basic process of this technique is to use Ar⁺ sputtering to break down a bulk Pt-RE alloy target into atomic vapor, which is then guided by time-of-flight mass filtering to condense back into nanoparticles on a substrate.^{6,9,19} It is a very sophisticated process, ideal for fundamental studies but not suitable for making materials for practical applications. Regarding the scalable synthesis of Pt-RE nanoalloys by a chemical approach, various attempts have been made.²⁰⁻²⁹ Among them, only a few have shown firm evidence of the Pt-RE alloy formation, such as the verification of distinct alloy structures by X-ray diffraction (XRD) or/and the metallic RE phases in the alloys by X-ray photoelectron spectroscopy (XPS).²⁴⁻²⁶ In this regard, Kanady *et al.* prepared Pt₃Y nanoparticles by heating specific metal salts in vacuum using alkali metal triethylborohydrides (MEt₃BH, M = Na, K) as the reducing agent.²⁵ Roy *et al.* prepared Pt₃Y through the heat-treatment of Pt particles with YCl₃ under a highly purified H₂ atmosphere.²⁴ These attempts clearly showed the possibility of preparing the alloys but no success has been achieved in preparing Pt-RE nanoalloys with properly controlled properties such as compositions and particles sizes. The strategy employed by most previous attempts was to use strong reducing agents to reduce the metal salts in a controlled environment free of O₂ or H₂O. To achieve that, multiple steps of purification of the precursor chemicals and the surrounding atmosphere by using e.g. a glove box, ultrahigh vacuum, and/or organic solvents, were

needed, which inevitably increased the complexities and difficulties of the processes. Moreover, the poor dispersion of the metal salts before or during the reduction was another critical issue yet to solve, leaving the alloy particle sizes out of control.^{24, 25} In contrast to Pt alloys with late transition metals such as Co and Ni,³⁰⁻³² due to the lack of an efficient synthesis approach, the properties of Pt-RE nanoalloys have largely been unexplored.

RESULTS AND DISCUSSION

Figure 1. Schematic illustration of Step 1: In-situ formation of the Pt-RE-NC compound. (a) The starting material, which is the solid mixture of a Pt salt, a RE metal salt, a nitrogen-rich compound, and a carbon support. (b) The Pt-RE-NC compound obtained after the heat-treatment of the starting mixture in Ar. It shows the chemical structure of carbon-supported C-N network with atomically dispersed Pt and RE ions.

Herein, we report a universal synthesis route to Pt-RE nanoalloys with tunable alloy compositions and particle sizes, which follows a fundamentally different strategy. The synthesis process still starts from the commonly available metal salts, even in their hydrated forms (e.g. $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$). Instead of preparing the alloys by directly reducing the metal salts in an H_2O - and O_2 -free environment, we first embedded the metal ions into a C-N network and deposited the structure onto a carbon support, whereby the metal dispersion issue was resolved, the metal ions were stabilized and thus the oxide formation was suppressed. This product is referred to as Pt-RE-NC compound. Secondly, the Pt-RE nanoalloys were obtained by heating the compound in a dilute H_2 atmosphere (e.g. 3.3% H_2/Ar), which was achieved through an unexpected intermediate step and will be discussed later in detail.

Step 1: In-situ formation of the Pt-RE-NC compound.

It has been reported that graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), a compound consisting of an ordered C-N network, has a strong complexing affinity to metal ions and decomposes at temperatures higher than 550 °C.³³⁻³⁷ Based on this idea, a simple in-situ synthesis approach was developed to embed both Pt and RE metal ions into the C-N network, as illustrated in Figure 1a. Different from the conventional way of forming the complex by soaking $\text{g-C}_3\text{N}_4$ into a solution of metal ions,³⁸ the metal salts and a carbon support were directly incorporated into the polymerization process of $\text{g-C}_3\text{N}_4$, whereby much higher contents of metal ions up to 50 wt% were homogeneously embedded into the $\text{g-C}_3\text{N}_4$ structure, as schematically represented in Figure 1b.

Figure 2. Characterization of a Pt-Gd-NC compound. (a) XRD patterns of the used carbon support (a graphitized carbon black), the Pt-Gd-NC compound, and the product obtained by a control synthesis without CN_2H_2 in the starting precursors. The reference patterns are Pt (JCPDS 65-2868) and GdOCl (JCPDS 12-0798). (b-c) Pt 4f and Gd 4d XPS spectra of the Pt-Gd-NC compound (black curves) in comparison to the corresponding metallic phases of a commercial Pt/C and a previously reported PtGd alloy¹⁹ (green curves). (d-g) HAADF-STEM image of the Pt-Gd-NC compound and the corresponding EDS elemental maps of Pt ($\text{L}\alpha_{1,2}$), Gd ($\text{L}\alpha_{1,2}$) and N ($\text{K}\alpha_{1,2}$).

The detailed experimental results of a Pt-Gd-NC compound are shown in Figure 2a-g. It was prepared by heat-treatment of the solid mixture of $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$, GdCl_3 , CN_2H_2 , and carbon support in Ar. At temperatures higher than 550 °C, the formed g- C_3N_4 partially decomposed, resulting in a disordered (or amorphous) C-N network, which still effectively coordinated the Pt and Gd ions. The N content of the compound was as high as 25.4wt% by SEM-EDS or 27.6 at% by XPS (see the detailed elemental contents of the series of samples in Tables S1, S2 and the narrow-scan N 1s XPS spectra in Figure S3). ICP analysis showed contents of 8.7 wt% Pt and 11.1 wt% Gd (Table S1). The XRD pattern of the compound is similar to that of the carbon support, without signs of metal or metal oxide crystals (Figure 2a). This result was further confirmed by STEM (Figure 2d) and TEM images (Figure S4), with no metal or metal oxide particles observed. On the other hand, the high-resolution elemental maps (Figure 2d-g) revealed the uniform distribution of Pt, Gd, and N across the sample. The Pt $4f_{7/2}$ XPS peak shifted positively by 2.7 eV from metallic Pt (71.3 eV) (Figure 2b), similar to Pt complexes such as $\text{K}_2[\text{Pt}(\text{CN})_4]_3 \cdot \text{H}_2\text{O}$.³⁹ The Gd $4d_{5/2}$ peak also shifted positively from metallic Gd (141.3 eV) by 2.3 eV (Figure 2c), indicating that both metals were still in their oxidized forms.

The stabilizing effect of the C-N network on the dispersed metal ions is surprisingly strong. Attempts to reduce even just Pt from the compound without breaking up the C-N network were unsuccessful, despite the use of a very strong reducing agent of solvated electrons (i.e. the solution of Na in liquid NH_3) (Figure S5). We speculate that this effect originates from the strong coordination bonds between metal ions and the N sites with lone pairs of electrons in the C-N network. Besides, the separated metal ions in the C-N network might also create an additional barrier to the formation of metallic particles by e.g. restricting the nucleation. This stabilizing effect is vital for both Pt and RE ions. Without it, the synthesis under the same conditions in the absence of cyanamide (CN_2H_2) resulted in the formation of GdOCl and Pt particles (in the size of 40 and 24 nm respectively, by the Scherrer equation), as revealed by the XRD pattern shown in Figure 2a. Thanks to the stable complexing structure, the Pt-RE-NC compound is

insensitive to H_2O and O_2 and can be handled directly in the ambient environment.

Step 2: Formation of the Pt-RE nanoalloys. For the alloy formation, the metal ions need to be released from the C-N network and reduced. Releasing the metal ions was achieved by heat-treatment of the Pt-RE-NC compound at a temperature above 550 °C for a certain time to completely break up the C-N network. The process is illustrated in Figure 3. With the decomposition of the C-N network, Pt ions were reduced into metallic nanoparticles in H_2 while RE metal ions were transformed into the crystalline phase of RE carbodiimide ($\text{RE}_2(\text{CN}_2)_3$), a crystal with each RE atom bonded with 5 N-C-N groups, as illustrated in Fig 3. The formation of $\text{RE}_2(\text{CN}_2)_3$, also previously synthesized by solid-state reactions between RECl_3 and $\text{Li}_2(\text{CN}_2)$ in a sealed ampule and used as luminescent materials,^{40, 41} is a unique chemistry of the present synthesis process. Under the further reduction in H_2 , the $\text{RE}_2(\text{CN}_2)_3$ phase, well-dispersed over and therefore in good contact with the Pt nanoparticles, is reduced to form the Pt_xRE nanoalloys in Sample iii. The excess $\text{RE}_2(\text{CN}_2)_3$ is slowly oxidized into RE metal oxides (RE_xO) during the heat-treatment, which can be easily removed by acid leaching, yielding the final material of Sample iv.

The detailed experimental results for the synthesis of a $\text{Pt}_x\text{Gd/C}$ material were shown in Figure 4a-p, where the naming of the four samples is the same as in Figure 3. **Sample i** is the same Pt-Gd-NC compound discussed in Step 1. **Sample ii** is carbon-supported Pt and $\text{Gd}_2(\text{CN}_2)_3$, obtained by heat-treating Sample i in 3.3% H_2/Ar at 700 °C for 10 min. After this treatment, the C-N network collapsed, resulting in a significant loss of N from 27.2 at% on Sample i to 4.5 at% on Sample ii (Table S2 and Figure S3). The XRD pattern shows the formation of the two crystalline phases, i.e. metallic Pt and $\text{Gd}_2(\text{CN}_2)_3$ (Figure 4a). Revealed by the STEM image and the corresponding elemental maps (Figure 4c-f), the $\text{Gd}_2(\text{CN}_2)_3$ crystals were not in the form of particles but rather a porous phase surrounding the Pt particles. The reduction of Pt ions in Sample i to the metallic phase in Sample ii was also observed from the XPS spectra, which showed the shifted Pt_{4f} peaks towards the metallic phase (Figure 4b). The Gd_{4d} peaks remained at the same positions as for Sample i, reasonably due to the similar Gd-N coordination in both Sample i and the $\text{Gd}_2(\text{CN}_2)_3$ crystal.

Figure 3. Schematic illustration of Step 2: Formation of the Pt-RE nanoalloys. The sequentially depicted chemical structures are: (i) the Pt-RE-NC compound; (ii) the intermediate product of carbon-supported Pt and $\text{RE}_2(\text{CN}_2)_3$ crystals; (iii) the synthesis product of carbon-supported Pt_xRE nanoalloys alongside unreacted $\text{RE}_2(\text{CN}_2)_3$ or RE_xO , and (iv) the final material of carbon-supported Pt_xRE nanoalloys after removing the byproducts by acid leaching. The key alloy formation step from Sample ii to Sample iii is highlighted by a frame.

Figure 4. Experimental results for the synthesis of $\text{Pt}_x\text{Gd}/\text{C}$. The specific samples corresponding to the chemical structures shown in Figure 3 are denoted as **i**, **ii**, **iii**, and **iv**, respectively. **(a)** XRD patterns of the four samples. The reference patterns are Pt_2Gd (JCPDS 65-1745), Pt_3Gd (ICSD 104122), $\text{Gd}_2(\text{CN}_2)_3$,⁴⁰ and Pt (JCPDS 65-2868). **(b)** Pt 4f and Gd 4d XPS spectra of the four samples, in comparison to the corresponding metallic phases of a commercial Pt/C and a previously reported PtGd alloy¹⁹ (green curves). To better compare the peak positions, each Gd 4d spectrum has been normalized by its highest peak. **(c-f)** HAADF-STEM image of **Sample ii** and the corresponding EDS elemental maps of Pt ($\text{L}\alpha_1$), Gd ($\text{L}\alpha_1$) and N ($\text{K}\alpha_{1,2}$). **(g-l)** HAADF-STEM image of **Sample iii** and the corresponding EDS elemental maps of Pt ($\text{L}\alpha_1$), Gd ($\text{L}\alpha_1$), O ($\text{K}\alpha_{1,2}$), the proposed structure model, and the high-resolution TEM image of a Pt_2Gd particle. **(m-p)** TEM image of **Sample iv** and HAADF-STEM image of a Pt_xGd particle, the corresponding EDS line profiles, and EDS elemental maps of Pt ($\text{L}\alpha_1$) and Gd ($\text{L}\alpha_1$).

Figure 5. STEM images of the dealloyed Pt_2Gd particles in Sample iv obtained after acid leaching, which showed the formation of nanoporous structure.

Further heat-treatment of Sample ii in 3.3% H_2 at 700 °C for 30 min resulted in the formation of Pt_xGd nanoalloys in **Sample iii**. The XRD pattern shows that the main alloy phase is Pt_2Gd , alongside a small portion of Pt_3Gd (Figure 4a). The high-resolution TEM image of an alloy particle shows the interplanar distances of 2.65 Å and 2.32 Å with the intersectional angle of 64.6°, characteristic of the (220) and (3 $\bar{1}$ $\bar{1}$) planes of the Pt_2Gd crystal (Figure 4l). During the heat-treatment, the excess $\text{Gd}_2(\text{CN}_2)_3$ was slowly oxidized, forming Gd_xO . The presence of oxides was revealed by the elemental maps showing the distinct distributions of Pt, Gd and O in Sample iii (Figure 4g-j), based on which a structure model is proposed in Figure 4k. Note that oxidation of $\text{Gd}_2(\text{CN}_2)_3$ can be avoided by e.g.

increasing the H_2 concentration to 7%, as shown in the syntheses of Pt-Y and Pt-Ce alloys (Figure S6).

After the removal of the oxides or by acid leaching, the metallic Gd became the dominant phase in **Sample iv**, exhibiting the same binding energies as a previously reported Pt_xGd alloy (Figure 4b).¹⁹ Elemental mapping (Figure 4o,p) confirmed the presence of Pt and Gd in the alloy particles. The EDS intensity line profiles (Figure 4n) indicated that Gd was mainly contained in the core of the particle, while the surface part was rich in Pt. Besides the removal of oxides, the acid-leaching process also dealloyed the particles. Determined by ICP and XPS, the Pt/Gd atomic ratio was around 5:1 in Sample iv (Tables S1,S2), signifying the loss of Gd from the Pt_2Gd crystals during the acid leaching. Furthermore, HR-STEM images of the dealloyed particles (Figure 5a) exhibited periodic bright and dark regions, a signature feature for the so-called “nanoporous” or “spongy” particles.^{42, 43} This result explained the broadened XRD peaks of the alloys after acid leaching. Due to this effect, the mean particle size of Sample iv determined from the XRD pattern (i.e. 4.2 nm) is much smaller than that directly measured from the TEM images (i.e. 8.5 nm). Thus, throughout this study, the particle sizes were always determined by analyzing TEM images. Besides, the result that literally all the alloy particles had formed the nanoporous structure after acid leaching (Figure 5b) indicated they were encapsulated in carbon phase, which was further confirmed by the

Figure 6. Characterization of a series of Pt-RE nanoalloys. (a) XRD patterns of Pt₃Y/C, Pt₅La/C, Pt₅Ce/C, Pt₂Sm/C, Pt₂Gd/C, and Pt₃Tb/C. The reference patterns are Pt₃Y (JCPDS 65-5161), Pt₅La (JCPDS 65-9345), Pt₅Ce (JCPDS 65-8221), Pt₂Sm (JCPDS 65-8177), Pt₂Gd (JCPDS 65-1745) and Pt₃Tb (JCPDS 65-9540). The broad bump peaks at around 24.5° originate from the carbon support. The two diamond symbols represent the peaks corresponding to a trace of Pt₃Gd phase in the Pt₂Gd/C sample. Note that the sample names represent the crystal structures rather than the actual alloy compositions, which might deviate due to the acid leaching. **(b-g)** TEM images of the series of samples.

Figure 7. ORR performance of a series of Pt₅Ce/C samples with the mean particle size of 3.5 nm, 5.7 nm, and 8.8 nm, respectively. (a) XRD patterns of the series of Pt₅Ce/C samples. The reference pattern is Pt₅Ce (JCPDS 65-8221). **(b)** CO stripping peaks of the series of Pt₅Ce/C samples in 0.1 M HClO₄, in comparison to a Pt/C catalyst (from Johnson Matthey) with the mean particle size of 3.0 nm. **(c)** ORR-Tafel plots, i.e. specific activity as a function of the electrode potential, of the Pt₅Ce/C samples and the reference Pt/C. **(d)** Specific activities and mass activities of the Pt₅Ce/C samples and the reference Pt/C at 0.9 V (vs. RHE) in 0.1 M HClO₄, before and after the AST (i.e. 10,000 potential cycles in Ar-saturated 0.1 M HClO₄ from 0.6 to 1.0 V at the scan rate of 100 mV s⁻¹). The data after the AST is represented by the light color area of the column. The error bars show the standard deviation of the data points from at least three independent measurements. During CO stripping and ORR tests, the catalyst loading (in terms of Pt mass) was the same for each sample, which was 15 μg_{Pt} cm⁻² on the RDE (0.196 cm²).

reasonable ECSA of the samples discussed in the following sessions.

The overall synthesis process is very robust. As tested, the H_2 concentration of the atmosphere can be as low as 3.3%, and the industrial gases containing about 3 ppm O_2 and H_2O can be directly used without further purification. Along the synthesis route, formation of the $\text{RE}_2(\text{CN}_2)_3$ phase together with the Pt nanoparticles from the collapse of the C-N network is clearly the key step. In the atmosphere of 3.3% H_2/Ar with traces of O_2 and H_2O , it is very surprising that the alloy formation reactions between the two phases could proceed. One driving force is surely the exceptionally negative alloy formation energies of Pt-RE alloys, as a control experiment showed that Gd could not be reduced alone from $\text{Gd}_2(\text{CN}_2)_3$ under the same conditions (Figure S7). The other driving force should originate from the unique chemical structure of $\text{RE}_2(\text{CN}_2)_3$. For comparison, it was reported that under the more rigid conditions of 1 bar highly purified H_2 and 800 °C, the alloy formation from the reactions between Pt particles and YCl_3 could only be partially achieved after 3 h of heat-treatment.²⁴ Thus, the alloy formation becomes much more favorable by using $\text{RE}_2(\text{CN}_2)_3$ instead of RECl_3 , either due to the more favorable thermodynamic (e.g. through the likely higher standard Gibbs free energy of $\text{RE}_2(\text{CN}_2)_3$ than RECl_3) or/and improved kinetics (e.g. the better contact with Pt particles). Either way, this synthesis route clearly shows that alloys consisting of highly reactive metals like the RE metals can be obtained under very accessible conditions through the development of a suitable chemical pathway.

Versatility and upscaling. Thus far, a long list of Pt-RE nanoalloys with nearly pure alloy phases has been obtained following this synthesis route, exemplified by Pt_3Y , Pt_5La , Pt_5Ce , Pt_2Gd , Pt_2Sm , and Pt_3Tb , with the Pt loading of about 30wt% on the carbon support. The corresponding XRD patterns, TEM images, and particle size distribution histogram are shown in Figure 6a-g and Figure S8. The synthesis mechanism discussed above has been verified with other RE metals such as Y and Ce, which shows the formation of the same key intermediate phases, including the Pt-RE-NC compound and $\text{RE}_2(\text{CN}_2)_3$ crystals (Figure S6). Beyond the Pt-RE alloy system, this synthesis route was also applicable to the preparation of various alloys, exemplified by Au-Cu, Au-Ni, Pt-Pd, Pd-Ni, Pd-Cu, Pt-Ni and Pt-Cu (Figure S9). Note that these alloys may not necessarily follow the same synthesis mechanism as the Pt-RE nanoalloys. Regarding the synthesis of Pt-RE nanoalloys on a large scale, it's important to point out that the synthesis process can either be conducted step-by-step as shown above, or it can be combined into one continuous heat-treatment step to obtain only the final alloys. Thanks to the facile experimental conditions, the synthesis process is very robust, highly reproducible, and easy to scale up. Thus far, the synthesis scale of 5-10 g per batch has been demonstrated for specific samples, as shown with a $\text{Pt}_5\text{La}/\text{C}$ sample in Figure S10a-c.

ORR activity and stability. Concerning the ORR performance, the dealloyed Pt_2Gd particles of Sample iv exhibited a relatively high specific activity of $2.9 \text{ mA cm}_{\text{Pt}}^{-2}$ (Figure S11a-c), 3.9 times as high as the reference Pt/C with the mean particle size of 3.0 nm (Figure S12a,b). The

stability of this catalyst, however, was poor. After the accelerated stress testing (AST) of 10,000 potential cycles, it lost 38% of the mass activity, much higher than that for the reference Pt/C (i.e. 9 %, Figure S11c). It was not a surprising result since nanoporous alloy particles commonly have poorer stabilities than solid core-shell particles with a Pt overlayer.⁴⁴ Previous studies on dealloying processes have shown that alloy particles with high Pt contents (e.g. > 50 at%) and small particle sizes (e.g. < 10 nm) tend to form a core-shell structure after a dealloying process, and those with lower Pt contents and bigger particle sizes tend to form the nanoporous structure.^{43,45,46} To avoid the formation of such nanoporous particles, efforts have been made to synthesize alloy phases with lower RE contents such as Pt_5RE , the bulk phase of which had been reported to show excellent ORR performance.⁶

One of the Pt_5RE alloys we have obtained, i.e. Pt_5Ce , has been investigated for the ORR. Ce is also one of the most abundant and cheapest RE metals (Figure S2). By tuning the synthesis parameters, including carbon supports (with varied surface areas) and metal loadings, three $\text{Pt}_5\text{Ce}/\text{C}$ samples were prepared with the mean particle size of 3.5 nm, 5.7 nm, and 8.8 nm, respectively, as determined from the TEM images (Figures 6d and S13a-c). XRD patterns of these samples showed the presence of pure phase Pt_5Ce alloy (Figure 7a). The high-resolution STEM image (Figure S13d) and EDS line scans (Figure S14) of the particles of different sizes confirmed the formation of Pt-Ce alloys and that they did not form the nanoporous structure after the acid leaching. Note that the different carbon supports used for these three samples are assumed to have no significant effect on the catalyst performance, which should be a valid assumption for RDE tests but might not be true for fuel cell tests.

The CO stripping peaks of these samples in 0.1 M HClO_4 are shown in Figure 7b. With increasing the mean particle size from 3.5 nm to 8.8 nm, the CO oxidation peaks shifted from the similar positions as the Pt/C to much lower potentials, signifying the weakened CO binding on the alloy surfaces. As expected, the electrochemically active surface areas (ECSA) of the samples decreased with increasing the particle size (Figure S15). The ORR Tafel plots are shown in Figure 7c, whereby the specific activities of the samples at 0.9 V vs. RHE were determined, as depicted in Figure 7d. By increasing the particle size from 3.5 nm to 8.8 nm, the activity increased substantially from $1.16 \text{ mA cm}_{\text{Pt}}^{-2}$ to $2.29 \text{ mA cm}_{\text{Pt}}^{-2}$, and further up to $3.95 \text{ mA cm}_{\text{Pt}}^{-2}$, which is 5.3 times higher than the reference Pt/C ($0.75 \text{ mA cm}_{\text{Pt}}^{-2}$) and approaches the reported activities for the bulk Pt_5Ce polycrystalline electrodes (i.e. 6-7 $\text{mA cm}_{\text{Pt}}^{-2}$).^{6,16} This trend of increased specific activity with the particle size is consistent with previous reports, which showed that Pt-RE alloy nanoparticles need to be sufficiently big (at least 5 nm) in order to present the optimum structure with a compressively strained Pt overlayer.^{9,19} Below 5 nm, the Pt-RE alloy particles tend to lose most of the RE atoms during acid leaching, thus diminishing the alloying effect and the ORR performance. As tested, the series of Pt-RE alloys shown in Figure 6a-g with the particle sizes ranging

between 3-5 nm all showed only slightly higher ORR performance than the reference Pt/C (Figure S16a,b).

It is noteworthy that the particle size distribution for the 3.5 nm Pt₅Ce sample is fairly narrow, but the 5.7 nm and 8.8 nm samples have broad size distributions, containing a big amount of small particles below 3 nm and big particles above 10 nm. As a consequence, the mass activities of these two samples are only 1.8 and 1.6 times higher than the Pt/C, respectively (Figure 7d). Regarding the stabilities, the 5.7 nm and 8.8 nm Pt₅Ce/C samples lost similarly 15-16% mass activities after the AST, less than the 3.5 nm Pt₅Ce/C sample (24%) and the dealloyed Pt₂Gd (38%). Further synthesis optimization is needed to improve the ORR performance by tuning the particle size within the optimum range of 5-9 nm and obtaining the more active Pt₅RE alloy phases such as Pt₅Gd and Pt₅Tb.⁶

CONCLUSIONS

A series of Pt-RE nanoalloys have been synthesized through a newly developed chemical process. The synthesis starts with the preparation of a Pt-RE-NC compound from the most commonly available hydrated metal salts. The compound shows the chemical structure of carbon-supported C-N network with atomically coordinated Pt and RE metal ions, which as a whole is insensitive to O₂ and H₂O. Upon further heat-treatment at elevated temperatures under a dilute hydrogen atmosphere (e.g. 3.3% H₂/Ar), the C-N network collapses and the metal ions are transformed into RE carbodiimides (RE₂(CN₂)₃) along with Pt particles, which allows the subsequent formation of Pt_xRE nanoalloys under this mild reducing atmosphere. This synthesis mechanism suggests an efficient strategy to prepare nanoalloys with highly reactive metals. A long series of Pt-RE nanoalloys have so far been synthesized, including Pt₃Y, Pt₅La, Pt₅Ce, Pt₂Sm, Pt₂Gd, Pt₃Tb, as well as a number of other bimetallic nanoalloys. The ORR performance of the nanoporous Pt₂Gd particles and the solid Pt₅RE particles of varied sizes have been investigated, which exhibit the expected activity enhancement over pure Pt, with the highest specific activity being 3.9 mA cm_{Pt}⁻², i.e. 5.3 times higher than that of the reference Pt/C. The solid Pt₅Ce particles show better stabilities than the nanoporous Pt₂Gd particles by the AST. Further performance enhancement is expected by optimizing the synthesis parameters to tune the particle sizes and alloy phases.

EXPERIMENTAL SECTION

Catalyst synthesis:

Sample i-iv: To prepare **Sample i** (the Pt-Gd-NC compound), 0.112 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.099 g of GdCl₃ (99.99%, Sigma-Aldrich), 0.9 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.168 g of carbon support (Graphitized carbon, SKU 699624, Sigma-Aldrich, surface area provided by the manufacturer: 50-100 m² g⁻¹) were mixed and ground using an agate mortar and pestle without adding any solvents. It was done directly in the ambient environment. The obtained mixture was then transferred in a quartz boat and put into a tube furnace. Before the heat-treatment, the furnace was evacuated and purged with Ar (≥ 99.999%, H₂O ≤ 3 ppm, O₂ ≤ 3 ppm, Air Liquide) to remove the air. The Ar flow rate was maintained

at 180 mL min⁻¹ throughout the heat-treatment. The furnace was first heated from room temperature to 700 °C at the rate of 10 °C min⁻¹ and then cooled down to room temperature at the rate of ~25 °C min⁻¹, when **Sample i** was collected. **Sample ii** was obtained by heat-treating **Sample i** in 3.3% H₂/Ar (prepared by mixing Ar and H₂ (≥ 99.999%, H₂O ≤ 3 ppm, O₂ ≤ 2 ppm, Air Liquide)) at 700 °C for 10 min and then cooled down to room temperature. The gas flow rate was maintained at 180 mL min⁻¹. **Sample iii** was prepared by heating **Sample ii** in 3.3% H₂/Ar at 700 °C for 30 min and then cooled down to room temperature. The gas flow rate was maintained at the same 180 mL min⁻¹. To remove the possible byproducts (e.g. Gd_xO and Gd₂(CN₂)₃), **Sample iii** (~0.1 g) was leached in 300 mL 1.0 M H₂SO₄ at 70 °C for 2 h under continuous stirring, which was then thoroughly washed with Milli-Q water, and vacuum-dried at 80 °C for 6 h, yielding **Sample iv**.

Pt₅Ce/C (~3.5 nm): 0.5 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.122 g of CeCl₃·7H₂O (99%, Sigma-Aldrich), 2.0 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.439 g of carbon support (Ketjen Black EC300J, BET surface area: 810 m² g⁻¹) were mixed and ground using an agate mortar and pestle. The obtained mixture was then transferred into a tube furnace for heat-treatment. The purging gas was 7% H₂/Ar with the flow rate maintained at 340 mL min⁻¹ throughout the heat-treatment. Note that, given the bigger synthesis scale than that for the mechanism studies, 7% instead of 3.3% H₂/Ar was used to ensure the sufficient H₂ supply. The furnace temperature was first raised from room temperature to 180 °C at the rate of 10 °C min⁻¹ and kept at the temperature for 30 min, then increased to 650 °C at the rate of 10 °C min⁻¹ and kept at the temperature for 2 h, and lastly cooled down to room temperature at the rate of ~25 °C min⁻¹. The obtained product (~0.5 g) was leached in 500 mL 0.5 M H₂SO₄ at 70 °C for 1 h under continuous stirring, which was then thoroughly washed with Milli-Q water, and vacuum-dried at 80 °C for 6 h, yielding the final catalyst. Analyzed by ICP, the sample contained 29.0 wt% Pt and 2.2 wt% Ce. The BET surface area of the catalyst was measured to be 427 m² g⁻¹. After subtracting the surface area related to the alloy particles using the ICP and ECSA data, the specific surface area of the carbon support in the final catalyst was determined to be 593 m² g⁻¹, 73% of the original value.

Pt₅Ce/C (~5.7 nm): 0.5 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.256 g of CeCl₃·7H₂O (99%, Sigma-Aldrich), 2.0 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.439 g of carbon support (Mesoporous carbon, SKU 699632, Sigma-Aldrich, surface area by the manufacturer: 150-250 m² g⁻¹) were mixed and ground using an agate mortar and pestle. The rest of synthesis conditions were the same as those for preparing Pt₅Ce/C (~3.5 nm). Analyzed by ICP, the sample contained 20.0 wt% Pt and 4.5 wt% Ce.

Pt₅Ce/C (~8.8 nm): 0.75 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 1.227 g of CeCl₃·7H₂O (99%, Sigma-Aldrich), 2.4 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.75 g of carbon support (Vulcan 72R, COBAT, BET surface area: 210 m² g⁻¹) were mixed and ground using an agate mortar and pestle. The rest of synthesis conditions were the same as those for preparing Pt₅Ce/C (~3.5 nm). Analyzed by ICP, the sample contained 30.0 wt% Pt and 6.7 wt% Ce.

Pt₃Y/C, Pt₃La/C, Pt₂Sm/C, Pt₂Gd/C, and Pt₃Tb: Synthesis conditions for these samples were the same as those for **Pt₅Ce/C** (~3.5 nm) except for the different precursor recipes, which were 0.5 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.293 g of YCl₃·6H₂O (99%, Sigma-Aldrich), 2.0 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.439 g of carbon support (Ketjen Black EC300J) for **Pt₃Y/C**, 0.5 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.119 g of LaCl₃·7H₂O (99%, Sigma-Aldrich), 2.0 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.439 g of carbon support (Ketjen Black EC300J) for **Pt₃La/C**, 0.5 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.352 g of SmCl₃·6H₂O (99%, Sigma-Aldrich), 2.0 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.439 g of carbon support (Ketjen Black EC300J) for **Pt₂Sm/C**, 0.5 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.358 g of GdCl₃·6H₂O (99%, Sigma-Aldrich), 2.0 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.439 g of carbon support (Ketjen Black EC300J) for **Pt₂Gd/C**, 0.5 g of H₂PtCl₆·6H₂O (40.87 wt% of Pt, METALOR), 0.256 g of TbCl₃·7H₂O (99%, Sigma-Aldrich), 2.0 g of CN₂H₂ (99%, Sigma-Aldrich) and 0.439 g of carbon support (Ketjen Black EC300J) for **Pt₃Tb/C**.

Physical characterizations: Powder X-ray diffraction (XRD) measurements were performed with a MiniFlex 600 X-ray diffractometer (Rigaku) using a Cu K α (λ = 1.5418 Å) radiation source. The scan speed was 5 degree per min. **Inductively coupled plasma-optical emission spectroscopy (ICP-OES)** analyses were conducted using a Varian Vista-MPX. To prepare the samples for the ICP analyses, the catalyst powders were first heat-treated in the air at 900 °C for 30 min to burn off the carbon support. The metal residues were dissolved in freshly prepared aqua regia from trace metal-grade concentrated hydrochloric and nitric acids. The solution was further diluted with Milli-Q water ($\geq$ 18.2 M Ω ·cm) for the ICP analysis. **Transmission electron microscope (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)** images were obtained at 300 kV with an FEI Titan Analytical 80-300ST TEM equipped with a spherical aberration corrector and an X-Max TLE Energy Dispersive X-Ray Spectroscopy (EDS) detector. To determine the particle size distribution of each sample, more than 400 particles from 3-5 TEM images were counted for the statistics. **The Scanning Electron Microscopy (SEM)-EDS** analyses were conducted using Quanta FEG 200 ESEM. **X-ray photoelectron spectroscopy (XPS)** measurements were carried out on a Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectrometer (XPS) with an Al K α X-ray monochromator. Survey scans were obtained using a pass energy of 200 eV, while narrow scans of specific elements were obtained using a 50 eV pass energy. Data quantification was performed by using the Advantage program. To increase the data accuracy for quantitative comparison, catalyst powders were pressed into dense pellets, on the flat surfaces of which EDS and XPS tests were conducted. The surface areas of the samples were measured using the **Brunauer-Emmett-Teller (BET)** method with the equipment of Micrometrics (Gemini 2375).

Electrochemical measurements: A Biologic VSP multichannel potentiostat was used for the electrochemical tests. The electrolyte was 0.1 M HClO₄ solution, prepared by diluting high-purity 70% HClO₄ (Suprapur®, Merck) with

Milli-Q water. The catalyst inks were prepared by dispersing specific amounts of catalysts (based on the Pt loadings of the catalysts) in a mixture of formic acid ($\geq$ 95%) and Milli-Q water (9:1 v/v), with Nafion (a 5wt% solution) as the binder. The inks were ultrasonicated for about 30 min to yield uniform dispersions. To prepare the thin catalyst film, 10 μ L of the ink was cast onto a rotating disk electrode (RDE, 0.196 cm², Pine Research Instrumentation), yielding the catalyst loading of 15 μ g_{Pt} cm⁻². A standard three-electrode cell was used for the measurements, which included the RDE as the working electrode, a graphite rod (trace metals basis) as the counter electrode and a daily prepared reference hydrogen electrode (RHE) as the reference electrode. The reference electrode and counter electrode were separated from the working electrode compartment respectively using porous glass frits. All glassware was cleaned in Piranha solution and boiled in Milli-Q water at least three times before use. High purity O₂ ($\geq$ 99.999%) and Ar ($\geq$ 99.999%) were used in the measurements. To conduct the ORR tests, the thin-film electrode of the catalyst was first cycled in Ar saturated electrolyte between 0.025 V and 1.025 V at 100 mV s⁻¹ until a stable cyclic voltammogram (CV) was obtained. A CV at the scan rate of 20 mV s⁻¹ was subsequently recorded, which was used later for subtracting the capacitance currents. The electrolyte was then saturated with O₂. The ORR curves were recorded from 0.025 V to 1.025 V at the scan rate of 20 mV s⁻¹. The uncompensated electrolyte (R_u) resistance was measured by electrochemical impedance spectroscopy (EIS), which was recorded at open circuit potential by applying an AC signal with 10 mV amplitude over the frequency range from 100 kHz to 0.1 Hz. After correcting the R_u and the capacitance current, the ORR kinetic current was calculated by further correcting the mass-transfer effect using the Koutecký-Levich equation

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l}$$

, where i_k is the kinetic current, i_l is the diffusion limiting current, and i is the measured current. To determine the electrochemically active surface areas (ECSA), CO stripping tests were conducted. The electrodes were first immersed in CO-saturated 0.1M HClO₄ and hold at 0.05 V for 10 min. Then, the excess CO in the electrolyte was removed by purging Ar for another 15 min. CO stripping curves from 0.025 to 1.05 V were subsequently recorded. The specific activities (j_s) and mass activities (j_m) of the catalysts were calculated from the i_k , ECSA and the applied catalyst loading on the RDE. The ORR Tafel graph was made by plotting the specific activities as a function of the electrode potentials. The catalyst stability was evaluated by the accelerated stress testing (AST), which consisted of 10,000 cycles between 0.6 V and 1.0 V in Ar-saturated 0.1 M HClO₄.⁴⁷

ASSOCIATED CONTENT

Supporting Information. Figures S1-S16; Tables S1, S2; References. The additional data that support the findings of this study, are available in the Supplementary Materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Figure 1. Schematic illustration of Step 1: In-situ formation of the Pt-RE-NC compound. (a) The starting material, which is the solid mixture of a Pt salt, a RE metal salt, a nitrogen-rich compound, and a carbon support. (b) The Pt-RE-NC compound obtained after the heat-treatment of the starting mixture in Ar. It shows the chemical structure of carbon-supported C-N network with atomically dispersed Pt and RE ions.

Figure 2. Characterization of a Pt-Gd-NC compound. (a) XRD patterns of the used carbon support (a graphitized carbon black), the Pt-Gd-NC compound, and the product obtained by a control synthesis without CN₂H₂ in the starting precursors. The reference patterns are Pt (JCPDS 65-2868) and GdOCl (JCPDS 12-0798). (b-c) Pt 4f and Gd 4d XPS spectra of the Pt-Gd-NC compound (black curves) in comparison to the corresponding metallic phases of a commercial Pt/C and a previously reported PtGd alloy 19 (green curves). (d-g) HAADF-STEM image of the Pt-Gd-NC compound and the corresponding EDS elemental maps of Pt (La1), Gd (La1) and N (Ka1,2).

Figure 3. Schematic illustration of Step 2: Formation of the Pt-RE nanoalloys. The sequentially depicted chemical structures are: (i) the Pt-RE-NC compound; (ii) the intermediate product of carbon-supported Pt and RE₂(CN₂)₃ crystals; (iii) the synthesis product of carbon-supported PtxRE nanoalloys alongside unreacted RE₂(CN₂)₃ or RE_xO, and (iv) the final material of carbon-supported PtxRE nanoalloys after removing the byproducts by acid leaching. The key alloy formation step from Sample ii to Sample iii is highlighted by a frame.

Figure 4. Experimental results for the synthesis of $\text{Pt}_x\text{Gd}/\text{C}$. The specific samples corresponding to the chemical structures shown in Figure 3 are denoted as i, ii, iii, and iv, respectively. (a) XRD patterns of the four samples. The reference patterns are Pt_2Gd (JCPDS 65-1745), Pt_3Gd (ICSD 104122), $\text{Gd}_2(\text{CN}_2)_3$,⁴⁰ and Pt (JCPDS 65-2868). (b) Pt 4f and Gd 4d XPS spectra of the four samples, in comparison to the corresponding metallic phases of a commercial Pt/C and a previously reported PtGd alloy 19 (green curves). To better compare the peak positions, each Gd 4d spectrum has been normalized by its highest peak. (c-f) HAADF-STEM image of Sample ii and the corresponding EDS elemental maps of Pt (La1), Gd (La1) and N (K α 1,2). (g-l) HAADF-STEM image of Sample iii and the corresponding EDS elemental maps of Pt (La1), Gd (La1), O (K α 1,2), the proposed structure model, and the high-resolution TEM image of a Pt_2Gd particle. (m-p) TEM image of Sample iv and HAADF-STEM image of a Pt_xGd particle, the corresponding EDS line profiles, and EDS elemental maps of Pt (La1) and Gd(La1).

Figure 5. STEM images of the dealloyed Pt₂Gd particles in Sample iv obtained after acid leaching, which showed the formation of nanoporous structure.

Figure 6. Characterization of a series of Pt-RE nanoalloys. (a) XRD patterns of Pt₃Y/C, Pt₅La/C, Pt₅Ce/C, Pt₂Sm/C, Pt₂Gd/C, and Pt₃Tb/C. The reference patterns are Pt₃Y (JCPDS 65-5161), Pt₅La (JCPDS 65-9345), Pt₅Ce (JCPDS 65-8221), Pt₂Sm (JCPDS 65-8177), Pt₂Gd (JCPDS 65-1745) and Pt₃Tb (JCPDS 65-9540). The broad bump peaks at around 24.5° originate from the carbon support. The two diamond symbols represent the peaks corresponding to a trace of Pt₃Gd phase in the Pt₂Gd/C sample. Note that the sample names represent the crystal structures rather than the actual alloy compositions, which might deviate due to the acid leaching. (b-g) TEM images of the series of samples.

Figure 7. ORR performance of a series of Pt₅Ce/C samples with the mean particle size of 3.5 nm, 5.7 nm, and 8.8 nm, respectively. (a) XRD patterns of the series of Pt₅Ce/C samples. The reference pattern is Pt₅Ce (JCPDS 65-8221). (b) CO stripping peaks of the series of Pt₅Ce/C samples in 0.1 M HClO₄, in comparison to a Pt/C catalyst (from Johnson Matthey) with the mean particle size of 3.0 nm. (c) ORR-Tafel plots, i.e. specific activity as a function of the electrode potential, of the Pt₅Ce/C samples and the reference Pt/C. (d) Specific activities and mass activities of the Pt₅Ce/C samples and the reference Pt/C at 0.9 V (vs. RHE) in 0.1 M HClO₄, before and after the AST (i.e. 10,000 potential cycles in Ar-saturated 0.1 M HClO₄ from 0.6 to 1.0 V at the scan rate of 100 mV s⁻¹). The data after the AST is represented by the light color area of the column. The error bars show the standard deviation of the data points from at least three independent measurements. During CO stripping and ORR tests, the catalyst loading (in terms of Pt mass) was the same for each sample, which was 15 μgPt cm⁻² on the RDE (0.196 cm²).