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ARTICLE

Tailoring Ruthenium Exposure to Enhance the Performance of *fcc* Platinum@Ruthenium Core-Shell Electrocatalysts in the Oxygen Evolution Reaction

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The catalytic properties of noble metal nanocrystals are a function of their size, structure, and surface composition. In particular, achieving high activity without sacrificing stability is essential for designing commercially viable catalysts. A major challenge in designing state-of-the-art Ru-based catalysts for the oxygen evolution reaction (OER), which is a key step in water splitting, is the poor stability and surface tailorability of these catalysts. In this study, we designed rapidly synthesizable size-controlled, morphology-selective, and surface-tailored platinum-ruthenium core-shell (Pt@Ru) and alloy (PtRu) nanocatalysts in a scalable continuous-flow reactor. These core-shell nanoparticles with atomically precise shells were produced in a single synthetic step with carbon monoxide as the reducing agent. By varying the metal precursor concentration, a dendritic or layer-by-layer ruthenium shell can be grown. The catalytic activities of the synthesized Pt@Ru and PtRu nanoparticles exhibit noticeably higher electrocatalytic activity in the OER compared to that of pure Pt and Ru nanoparticles. Promisingly, Pt@Ru nanocrystals with a ~2-3 atomic layer Ru cuboctahedral shell surpass conventional Ru nanoparticles in terms of both durability and activity.

1. Introduction

Water splitting has received considerable attention from researchers because it can provide a renewable route for the production of hydrogen, which is the cleanest form of combustible energy. However, the oxygen evolution half-reaction (OER) ($2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ in acid solutions) is currently a major bottleneck in the water splitting scheme because it requires high energy for its initiation and induces rapid degradation in the currently available catalytic materials.¹⁻⁵ Metallic ruthenium (Ru) and/or ruthenium oxide (RuO₂) nanoparticles are the state-of-the-art catalysts that exhibit the lowest overpotentials for this reaction. This low overpotential is due to their weaker interaction with the

oxygenated species under the OER electrochemical conditions.⁶⁻⁹ However, these optimal nanoparticles still exhibit low stability during the electrooxidation of water.^{7, 9, 10}

One method for tailoring the stability and catalytic activity of nanoparticle catalysts involves controlling their size and shape with particular facets that exhibit increased stability and activity. Another method that is commonly used for the same purpose involves alloying or shelling the active nanoparticle material with another metal, which may result in improved catalytic performance over the single metal nanoparticles due to catalytic synergy between the combined metals.¹¹⁻¹³ For example, by alloying Ru with Pt, lower overpotentials and a higher activity was achieved for different electrochemical reactions, such as the OER, methanol oxidation reaction (MOR) and the hydrogen oxidation reaction (HOR).¹⁴⁻²⁰ Recent research has demonstrated that further increases in the catalytic activity can be achieved by controlling the morphology of the nanoparticles to form Pt@Ru core-shell nanomaterials. This improvement is due to the introduction of an uncommon phase and new active sites (i.e., the interfacial sites).^{21, 22} However, there is still a limited understanding of the stability of these nanoparticle species and how to tailor the surface and shell thickness to form catalysts with a high stability and high catalytic activity.

For commercial viability, these catalysts must be not only highly active and stable but also readily reproducible on a large scale. Unfortunately, the previously reported syntheses for making platinum-ruthenium core-shell nanocrystals with different sizes and shapes were carried out in batch

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preparations, and most of these processes required multiple steps.^{18, 19, 23} As a result, these nanoparticle systems are inherently difficult to scale-up because of the sensitivity of their growth kinetics towards changes in the experimental parameters including the method of introducing the starting materials and temperature as well as chemical gradients across the system due to increased reaction volumes.²⁴ Recently, the use of continuous-flow synthesis has shown great promise in overcoming these previously mentioned challenges for metal, bimetallic and quantum dot nanomaterials.²⁵⁻²⁹

In this study, we designed rapidly synthesizable, size-controlled, morphology-selective, and surface-tailored platinum-ruthenium core-shell (Pt@Ru) and alloy (PtRu) nanocatalysts in a scalable continuous-flow reactor. We demonstrate that the particle size and shape can be intricately controlled by the temperature, total metal concentration, and gaseous reducing agent (carbon monoxide). In addition, we demonstrate the ability to tailor the growth of the ruthenium shell to form dendritic or layer-by-layer (~2-3 layers) shells on platinum seeds by varying the total metal concentration. By controlling the Ru shell surrounding the Pt core, the stability and activity of the nanoparticles were enhanced in an acidic solution for OER electrocatalysis. Promisingly, the Pt@Ru nanocrystals with cuboctahedral shells (~2-3 layers) were highly active and extremely stable compared to the alloy and conventional Ru nanocrystals.

2. Experimental

2.1 Chemicals

Platinum(II) acetylacetonate (98%) and ruthenium(III) acetylacetonate (99%) were purchased from STREM. Oleylamine (technical grade, 70%) was purchased from Acros. Toluene and tungsten carbonyl (97%) were purchased from Sigma Aldrich. All of the chemicals were used as received without further purification.

2.2 Pt-Ru Nanocrystal Synthesis

2.2.1 Pt@Ru_{Dendritic}: A flow reactor device obtained from Uniqsis Ltd. (FlowSyn Multi X) was fitted with a 20 mL Teflon-coated stainless steel coil reactor and a 30 bar inert back pressure regulator. This flow reactor device has two pumps (*i.e.*, A and B). Pump "A" streamed a solution containing the platinum and ruthenium precursors (3 mM for each metal) dissolved in oleylamine (73% by solution volume) and toluene (27% by solution volume) in a sonicator. Pump "B" was set to drive another stream of 28 mM W(CO)₆ in toluene. It is important to note that carbon monoxide is generated by the thermal decomposition of W(CO)₆.^{26, 30} Both pumps were set to a flow rate of 2.0 mL/min. Once the pressure stabilized, the pumps were started. The two streams entered a mixing zone and then continued through the pre-heated and pressurized coil reactor at 300 °C and 30 bar. A black solution indicated that the reaction occurred, and this solution flowed to the collection zone. The product was precipitated with ethanol and centrifuged at 13,200 RPM for 15 minutes. The supernatant was discarded, and the particles were washed with ethanol

three times. After the product was purified, it was redispersed in toluene. The particles were cleaned prior to further characterization.

2.2.2 Pt@Ru_{Cuboctahedral}: A concentration of 11 mM for each metal precursor was prepared in the same way as for Pt@Ru_{Dendritic}. To dissolve the higher concentrations of the precursor, the solution was heated to 70 °C and stirred on a hot plate until the metal precursors completely dissolved.³¹ The other steps were carried out as described above.

2.2.3 PtRu_{Alloy}: The starting solution for making the Pt@Ru_{Dendritic} nanoparticles was used. However, W(CO)₆ was not used, and only toluene was allowed to flow through pump "B". The rest of the synthesis was carried out as described above.

2.3 Characterization techniques

2.3.1 Transmission Electron Microscopy. The TEM characterization was carried out on a transmission electron microscope (from FEI Company of Model Titan 80-300 ST) equipped with an extra-brightness field emission gun (x-FEG). Moreover, TEM was carried out by operating the scope at an accelerating voltage of 300 kV and in BF-TEM and HRTEM modes. The nanoparticle size distributions were measured by considering over 500 particles. It is important to note that for the TEM measurements, the samples were drop-cast on a 400 square mesh copper grid that was pre-coated with a thin carbon film. The elemental composition and map ratios were obtained via energy dispersive X-ray spectroscopy (EDS) from EDAX, Inc. Before EDS acquisition, the stage was tilted to an optimized position of +14 degrees. Then, the diameter of the nanoparticles was determined from the TEM images (Table S1 and Fig. S1 D-F), and the composition was determined by energy dispersive X-ray spectroscopy (EDS) using the Pt-L peak (9.44 keV energy) and Ru-K peak (19.23 keV energy) (Fig. S1 A-C).

High-resolution high-angle annular dark field STEM (HAADF-STEM) analysis of the samples was performed on a Titan 80-300 ST operating at 300 kV and equipped with a spherical aberration corrector (C_s-Corrector) for the probe. The C_s-corrector was aligned each time such that its third-order spherical aberration coefficient (C₃) was less than a micron. The core-shell formation and alloy formation in the Pt@Ru samples were investigated using the STEM-EDS spectrum imaging (SI) technique. SI datasets were acquired using a pixel size of 0.4 nm and a dwell time of 1 second. Finally, the Pt and Ru maps were generated using the Pt-L peak (9.44 keV energy) and Ru-L peak (2.56 keV energy) in the SI datasets.

2.3.2 X-Ray Diffraction (XRD). A powder XRD Bruker D8 Advance instrument using Cu K α radiation (1.5409 Å) as the X-ray source was utilized to perform all the XRD measurements. The nanoparticles were drop-cast onto zero background silicon plates. The diameter of these particles was determined from the XRD profiles using Scherrer's formula³² (Table S1).

2.3.3 X-ray Photoelectron Spectroscopy (XPS). The XPS experiments were carried out using a PHI VersaProbe II instrument equipped with a monochromatic Al K α source. The instrument base pressure was approximately 8×10^{-10} Torr. The X-ray power was 25 W at 15 kV for all the

experiments with a 100-micron beam size at an X-ray incidence and take off angles of 45°. The instrument work function was calibrated to yield a binding energy (BE) of 84.0 eV for the Au 4f_{7/2} line for metallic gold, and the spectrometer dispersion was adjusted to yield binding energies of 284.8 eV, 932.7 eV and of 368.3 eV for the C 1s line of the adventitious (aliphatic) carbon on the non-sputtered samples as well as the Cu 2p_{3/2} and Ag 3d_{5/2} photoemission lines, respectively. A PHI dual charge compensation system was used on all the samples. The ultimate VersaProbe II instrumental resolution was determined to be better than 0.125 eV using the Fermi edge of the valence band for metallic silver. All the XPS spectra were recorded using PHI software SMARTSoft VP v2.3 and processed using PHI MultiPack v9.3 and/or CasaXPS v.2.3.14. The Shirley background was subtracted for the signal above the background measurement. The samples were prepared by drop-casting suspensions of nanoparticles on a Si substrate. Five or six locations on the mounted sample were examined.

2.4 Electrochemical Measurements

The electrodes were prepared using 30 μL of a toluene solution containing 1 mg/ml of the nanoparticles, which was dropped onto a conductive fluorine-doped tin oxide (FTO) glass (1 cm X 2 cm). Then, catalyst-loaded FTO was annealed at 400 °C in air for 30 minutes to remove organic ligands. The ruthenium shell is expected to be oxidized during annealing, as reported previously.^{9, 33} Prior to use, the conductive FTO glass, which were obtained from Sigma Aldrich, were sonicated and washed with water, methanol, isopropanol and acetone (each for 15 min) and then dried in air. The exposed electrode area was 1 cm². The voltammetric measurements were carried out using a Reference 3000 Potentiostat obtained from Gamry Instruments. A custom-made glassy electrochemical cell was assembled with a Ag/AgCl (in 3 M KCl, aq.) reference electrode and a Pt coil counter electrode. The prepared PtRu/FTO electrode was used as the working electrode. 0.1 M HClO₄ and H₂SO₄ solutions were bubbled with nitrogen (N₂) for 5 minutes before each measurement and protected with a nitrogen atmosphere during the entire experimental procedure. All the electrochemical measurements were carried out at room temperature. All the electrode potentials in the current study were referenced to the normal hydrogen electrode (NHE). Note that the obtained potentials were also converted from vs. NHE to vs. reversible hydrogen electrode (RHE) and provided in Table S3. Cyclic voltammograms (CV) were recorded at a scan rate of 50 mV/s from -0.05 V to 1.45 V (vs. NHE) with a 10 mV step size. Each CV corresponds to the fifth scan of five successive cyclic scans. For the stability test, only a 0.1 M HClO₄ solution was used, and the CV was recorded at a scan rate of 100 mV/s from 0.8 V to 1.45 V (vs. NHE) with a 25 mV step size. For these tests, we compare the current density of all the nanoparticles at 1.45 V (vs. NHE). To avoid the high noise due to oxygen bubble accumulation on the electrode surface and to obtain clean CVs, we limited the CV experiments to 1.45 V (vs. NHE, pH=1). Also, to study the stability, the chronoamperometric measurement was performed for Pt@Ru_{Cuboctahedral} nanoparticles in 0.1 M HClO₄

solution at 10 mA cm⁻². Note that ohmic-drop (iR drop) was not calibrated in CVs and the chronoamperogram (CA).

3. Results and discussion

The syntheses of the Pt@Ru core-shell and PtRu alloy nanoparticles were carried out continuously in a single reaction step in a flow reactor. We were able to scale-up the production to nearly 0.6 g of Pt@Ru nanoparticles (*i.e.*, rate of production was 10 mg/min) (Fig. S2). The reaction was run at 300 °C to facilitate the reduction of the ruthenium precursor and at a pressure of 30 bar, keeping the toluene as a liquid and the generated carbon monoxide gas in solution. Toluene was used for to increase the solubility of the metal salts in the solvents and reduce the viscosity of the initial solution to allow it to flow easily in the reactor. Fig. 1 A-C shows the monodispersed nanoparticles of Pt@Ru with a cuboctahedral shell (Pt@Ru_{Cuboctahedral}), dendritic shell (Pt@Ru_{Dendritic}) and PtRu alloy (PtRu_{Alloy}), respectively. The average size of Pt@Ru_{Cuboctahedral} ($\sim\text{Pt}_{61}\text{Ru}_{39}$) was 5.7 ± 0.6 nm (Fig. 1 A), the average size of Pt@Ru_{Dendritic} ($\sim\text{Pt}_{63}\text{Ru}_{37}$) was 6.1 ± 0.6 nm (Fig. 1 B), and the average size of PtRu_{Alloy} ($\sim\text{Pt}_{62}\text{Ru}_{38}$) was 4.2 ± 0.4 nm (Fig. 1 C). The average shell thicknesses obtained from multiple particles and parts of the cuboctahedral and dendritic

Fig. 1 Bright-field TEM micrographs of **A)** Pt@Ru_{Cuboctahedral}, **B)** Pt@Ru_{Dendritic} and **C)** PtRu_{Alloy}. **D-F)** HAADF-STEM images of **A-C**, respectively, using a 16 color filter in ImageJ to show the Z-contrast intensity variations (ESI Fig. S1). The facets were indexed based on Fig. S3.

shells were 0.7 ± 0.2 nm and 1.8 ± 0.3 nm, respectively, as shown in Fig. 1 D and E. The final composition was approximately identical for all the platinum-ruthenium nanoparticles and was slightly rich in platinum compared to the starting ratios.

To illustrate the formation of facets and elemental segregation, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) analysis was conducted, and the results are shown in Fig. 1 D-F. The HAADF-STEM micrographs were colored using the 16-color palette to enhance the Z-contrast of the images. Pt@Ru_{Cuboctahedral} exhibited an intense core of red and white colored atoms with 2-3 layers that are a lighter blue color, which is not expected to be due to thickness variations (Fig. 1 D). The core of the Pt@Ru_{Dendritic} nanoparticle is red, indicating a much higher Z-contrast. Therefore, the core is predicted to be rich in platinum (Fig. 1 E), and the light blue shell is rich in ruthenium (Fig. 1 E). The alloy shows an intensity variation that is similar to what would be expected for thickness variations across a cuboctahedral nanoparticle (Fig. 1 F). The Pt@Ru_{Cuboctahedral} and PtRu_{Alloy} nanoparticles were enclosed by the low index {111} and {100} facets (purple lines in Fig. 1 D and F), and the Pt@Ru_{Dendritic} possessed a high density of edge and step sites in its shell, indicating that it has a high-energy surface structure (Fig. 1 E). All of the nanoparticles were viewed down the [110] zone axis of the fcc crystal structure.

Fig. 2 HAADF-STEM images of **A)** Pt@Ru_{Cuboctahedral}, **B)** Pt@Ru_{Dendritic} and **C)** PtRu_{Alloy}. **D-O)** EDS mapping of elemental distributions of each corresponding Pt-Ru single particle.

To determine whether the nanoparticle intensity variations corresponded to elemental variations, STEM-EDS spectrum imaging was carried out. Fig. 2 A-C shows the HAADF-STEM images of the nanoparticles used for the STEM-EDS mapping of the Pt@Ru and PtRu nanoparticles. For both Pt@Ru nanostructures, the EDS Pt L-edge is shown in red, and the EDS Ru L-edge is shown in green (Fig. 2 E-F and I-J). The overlap of the two spectra indicates a core-shell structure (Fig. 2 G and K). For the alloy, the Pt and Ru signals overlapped completely (Fig. 2 M-O), which is in good agreement with the HAADF-STEM images.

As a complementary technique, XPS was utilized to confirm all the nanostructures. The XPS depth profiling measurements were in a good agreement with the HAADF-STEM and STEM-EDS spectrum imaging results for the three nanostructures shown in Fig. 3. The profiling of the platinum ruthenium nanoparticles supported on a Si substrate was performed by subjecting the sample to Ar⁺ sputtering and monitoring the Pt 4f, Ru 3p_{3/2} and C 1s core level peaks as a function of time. During the initial stages of depth profiling for the Pt@Ru_{Dendritic} nanoparticles, a rapid decrease in the "C" signal intensity was observed, and the intensity of the peaks corresponding to Pt and Ru increased sharply. This rapid decrease in the C signal was due to the removal of the capping agent. During the later stages (after approximately 1 min of profiling), the intensity of the Ru signal reached its maximum followed by a steady decrease, and the Pt signal continued to increase to its

Fig. 3 XPS depth profiling of the Pt-Ru nanostructures. Purple and pink lines show the maximum composition peak for Pt and Ru.

maximum after 30 seconds (Fig. 3). These results are indicative of the core-shell structure of nanoparticles comprised of a Ru shell and Pt core. A similar trend was observed for the Pt@Ru_{Cuboctahedral} nanoparticles (Fig. 3) even though the effect was less pronounced due to the small size of the Ru shell. The signal intensity of Pt and Ru for the Pt@Ru_{Alloy} nanoparticles reached a maximum at nearly the same time, suggesting that the nanoparticles are alloys (Fig. 3).

Fig. 4 shows the XRD pattern of all the nanocrystals, indicating the *fcc* crystal structure. The (111) peak for all the nanoparticle systems was shifted toward higher 2θ values compared with that of pure Pt. The shift to higher 2θ values was due to alloying of PtRu_{Alloy} as well as the compressive strain from the ruthenium shell on the platinum core.³⁴ The XRD patterns also reveal information regarding the average crystallite size, which was calculated using Scherrer's equation. The average crystal sizes were calculated to be 4.6, 6.2 and 3.2 nm for Pt@Ru_{Cuboctahedral}, Pt@Ru_{Dendritic} and PtRu_{Alloy}, respectively (Table S1). No characteristic *hcp* peaks for pure Ru were detected in the pattern (Fig. 4). In addition, only one phase was observed for PtRu_{Alloy} and Pt@Ru_{Cuboctahedral}. For the Pt@Ru_{Dendritic} nanoparticles, an asymmetry in the peaks towards higher 2θ values was observed and fit²⁶ to a 2.3 nm shell, which is in good agreement with the shell values measured from the STEM images. The cuboctahedral shell of the Pt@Ru nanoparticles was not detected, which is expected for a shell size less than 1 nm.³⁵

The difference in the formation of the Pt@Ru_{Cuboctahedral} and Pt@Ru_{Dendritic} nanoparticles was due to the concentration variation of the metal precursors. The other major parameter that affected the growth was the carbon monoxide gas. To investigate the distinct growth patterns, the pure elements were studied to understand the effect of each component during the synthesis. For pure Pt synthesized at high concentrations with carbon monoxide, monodisperse cuboctahedral Pt nanoparticles were observed (Fig. 5 A). For lower concentrations, the particles were polydispersed in both

size and shape with irregular growth (Fig. 5 B). Without carbon monoxide, the Pt nanoparticles were polyhedral (Fig. 5 C). The HR-TEM images indicate the formation of smaller and low index faceted particles when a higher concentration of the metal precursors was used. However, larger irregularly shaped Pt nanoparticles were formed when a lower metal concentration was used (Fig. S4 A-B). In the absence of CO, the Pt nanoparticles have a mixture of cuboctahedral and spherical morphologies (Fig. S4 C). For the Ru nanoparticles, Fig. 5 D-E shows the formation of branched Ru in the presence of CO at high and low metal concentrations, respectively. In the absence of CO and at low metal concentrations, Ru forms small nanoparticles, as shown in Fig. 5 F. It is important to note that for ruthenium, the reduction required more than 2.5 minutes to form nanoparticles but nanoparticles were observed by 30 seconds for platinum.

The reactions for the Pt@Ru systems were performed at different residence times to study their formation (Fig. S4). The core-shell nature of the nanoparticles had begun to develop within 30 seconds (Fig. S5 A and E), and the particles reached a high degree of uniformity by 2.5 minutes (Fig. S5 C and G). The dendritic system had a slower addition of Ru compared with the cuboctahedral system. For the alloys, Ru began to be incorporated after 1 minute, and then, it was alloyed into the structure by 1 minute (Fig. S5 J-L and Table S2). The carbon

Fig. 4 XRD patterns of the Pt-Ru nanoparticles. The blue and black dashed lines correspond to the *fcc* Pt(111) and Ru(111) peak, respectively.

Fig. 5 Pt and Ru nanoparticles prepared under the standard conditions with two different concentrations in the presence of CO **A&D**) 11 mM and **B&E**) 3 mM, respectively. **C&F**) are the Pt and Ru nanoparticles in the absence of CO with a 3 mM concentration.

monoxide appears to restrict the ability of the nanoparticle to alloy and facilitate the reduction of Ru more rapidly on the surface of the Pt core.

Based on the results for the ruthenium alone, small discrete nanoparticles were formed in the absence of carbon monoxide, and larger aggregated or branched structures were formed in the presence of carbon monoxide. Therefore, carbon monoxide may destabilize ruthenium and facilitate the formation of high-energy surfaces. For platinum, the carbon monoxide also facilitated the growth of larger particles as well as irregularly shaped particles at lower concentrations. The concentration of the initial metals in the solution affected the formation of the platinum seeds as well as the formation of the Ru shell, which is similar to previous results with core-shell nanoparticles where the seeds control the shell structure.^{31, 36} The formation of larger Pt seeds with no shape control resulted in fewer seeds in solution, and therefore, thicker Ru shells grew on the irregularly shaped Pt nanoparticles. For the smaller cuboctahedral seeds, the growth occurred via a layer-by-layer growth mechanism with close matching of the ruthenium in its less common fcc crystal structure.^{37–38} The appearance of the fcc crystal structure of ruthenium may be due to Ru templating onto the fcc Pt core in both core shell systems.²² As the ruthenium shell becomes thicker, the higher-energy surfaces that are favored by the ruthenium synthesized in the presence of carbon monoxide would control the core-shell surface structure.

For the formation of the alloy, in the absence of carbon monoxide, the ruthenium and platinum readily alloy despite the difference in the reduction speeds. The alloying of platinum and ruthenium, which has been previously reported, is due to diffusion of ruthenium into the originally nucleated platinum seeds.^{39, 40} Carbon monoxide, surface binding adsorbate, has been an important factor in phase segregation in alloy nanocrystals.^{41–44} We hypothesized that the addition of carbon monoxide hinders the formation of the platinum-ruthenium alloy because it binds more strongly to Pt as it is reduced. As a result, a more favorable bond to CO will be formed, promoting the reduction and growth of Ru on the Pt surface. Therefore, the Ru surface growth occurs.

The electrochemical oxygen evolution performance of the Pt@Ru core-shell, PtRu alloy, Pt and Ru nanoparticles were evaluated on anodic FTO-coated glass substrates. Fig. 6 show the cyclic voltammetry (CV) measurements of the Pt@Ru core-shell, PtRu alloy, Pt and Ru nanoparticles in a potential window from -0.05 V to 1.45 V vs. normal hydrogen electrode (NHE). The CVs were performed in two electrolytes (i.e., HClO₄ and H₂SO₄, 0.1 M, pH = 1.00 and 0.96, respectively), as shown in Fig. 6 A-B. For Pt, the commonly voltammetric features, such as the H-deposition between 0.05 and 0.20 V and Pt hydroxide peak at approximately 0.65 V, were observed. The Ru nanoparticles exhibit no characteristic peaks and produced a featureless CV.^{7, 22, 45} The CV of PtRu_{Alloy} contained two voltammetric features between 0.05 and 0.20 V and a bump at 0.6 V, which was shifted by 0.1 V to lower potential compared to that of pure Pt (Fig. 6 A). For Pt@Ru_{Dendritic} and Pt@Ru_{Cuboctahedral}, the CV exhibited broader and smoother

Table 1. OER Onset Potential of the Pt@Ru, PtRu, Ru and Pt Nanocrystals in Two Different Electrolytes DOI: 10.1039/C6CP01401A

Sample	OER onset potential vs. NHE(V) in 0.1M	
	HClO ₄	H ₂ SO ₄
Pt@Ru _{Cuboctahedral}	1.31	1.33
Pt@Ru _{Dendritic}	1.33	1.35
PtRu _{Alloy}	1.33	1.35
Ru	1.35	1.36
Pt	1.39	1.40

Fig. 6 Cyclic voltammetry curves for the Pt@Ru core-shell (cuboctahedral and dendritic), PtRu alloy and pure Pt and Ru nanocrystals in 0.1 M A) HClO₄ and B) H₂SO₄ solutions.

voltammetric features, which are associated with the existence of pure Ru at the surface.

We extrapolate the OER onset potential for the nanoparticles in this study at a point where the anodic current reaches $\approx 0.1 - 0.2$ mA. The studied Ru and Pt nanocrystals exhibited onset of the water oxidation current at approximately 1.35 V (vs. NHE) and 1.39 V (vs. NHE), respectively, as shown in Table 1. In HClO₄, the Ru sample is more efficient compared to the Pt sample with a lower OER onset potential (Fig. 6 A). Pt@Ru_{Dendritic} and PtRu_{Alloy} exhibited better catalytic performance than Ru with a slightly lower potential for the initiation of the water oxidation reaction (Fig. 6 A & Table 1). The Pt@Ru_{Cuboctahedral}-based electrocatalyst outperformed all the other catalytic systems in this study and

exhibited an OER onset at only 1.31 V vs. NHE, as shown in Table 1. The CVs performed in the H_2SO_4 electrolyte also exhibited a similar trend for the OER catalytic activities that increased from the pure metals to the alloy to the core-shell nanostructures ($\text{Pt} \ll \text{Ru} < \text{PtRu}_{\text{Alloy}} < \text{Pt@Ru}_{\text{Dendritic}} < \text{Pt@Ru}_{\text{Cuboctahedral}}$), as shown in Fig. 6 B and Table 1. However, the catalytic currents appeared at higher potentials relative to those observed in the perchlorate system (Table 1). Therefore, for these catalysts, HClO_4 is a better electrolyte system than H_2SO_4 for the OER in acidic environments due to the lower acidity of HClO_4 compared to H_2SO_4 .²⁰

In water splitting, the oxygen evolution reaction is the most energetically demanding reaction. Although the OER half reaction requires more energy for initiation, most of the activation overpotential originates from this O_2 evolution. To facilitate the kinetic demand of the four-electron oxidation of water, water oxidation catalysts are needed to perform over a narrow potential window to generate high anodic current densities.^{5, 46–48} Therefore, a small current-potential window (the Tafel slope (η vs. $\log j$)) is important for the integration of state-of-the-art electrocatalytic materials with high-efficiency photo-responsive materials.^{49, 50} For the $\text{PtRu}_{\text{Alloy}}$, $\text{Pt@Ru}_{\text{Dendritic}}$, $\text{Pt@Ru}_{\text{Cuboctahedral}}$ and pure Ru nanoparticle-based electrocatalysts, Tafel plots were obtained for the CVs conducted in the 0.1 M HClO_4 electrolyte (Fig. S6). The slopes were calculated for the respective CV current in the 0.1–1.0 mA cm^{-2} region. For $\text{Pt@Ru}_{\text{Cuboctahedral}}$ and $\text{Pt@Ru}_{\text{Dendritic}}$, the observed Tafel slopes were 57 and 66 mV dec^{-1} , respectively (Fig. S6). A Tafel slope of 67 mV dec^{-1} was recorded for the $\text{PtRu}_{\text{Alloy}}$ nanoparticles (Fig. S6). The pure Ru nanoparticle electrocatalyst, which has a relatively higher OER onset potential, produced a Tafel slope of 61 mV dec^{-1} (Fig. S6). Pure Pt typically exhibits a high Tafel slope of 120 mV dec^{-1} .⁵¹ The addition of ruthenium to the platinum nanostructures reduced the values of their Tafel slopes to nearly half of the Tafel slope of pure Pt. To achieve electroneutrality in the reaction during water oxidation, the Tafel slope should be at least 60 mV dec^{-1} , which also indicates a water oxidation mechanism involving the simultaneous addition of one electron and removal of one proton.^{47, 48, 52} A small Tafel slope of 57 mV dec^{-1} for $\text{Pt@Ru}_{\text{Cuboctahedral}}$ nanocrystals indicates that electroneutrality has been achieved and thus these nanoparticles are active towards OER.

It is important to note that the higher activity was due to the ruthenium on the surface, and the Ru in cuboctahedra is more active than that in the Pt-Ru alloy, which does not contain pure Ru on the surface. The high activity of the Pt@Ru nanomaterials may be due to the electronic effect of the electron sharing between the Ru shell and the Pt core.⁵³ We propose that the electronic contribution from the platinum to the ruthenium is optimal when there are ~2-3 layers of ruthenium in the cuboctahedral shell. The alloy behaves more like platinum and has a mixed platinum and ruthenium surface. However, a thicker dendritic shell would have a limited electronic contribution from platinum and behave more like pure ruthenium.

The stability of the platinum-ruthenium nanostructures was examined after 5, 500 and 1000 consecutive cyclic voltammetry scans (Fig. 7 A and Fig. S7 A-E). The working electrode potential was cycled in a range from +0.8 to +1.45 V vs. NHE at a scan rate of 100 mV s^{-1} in N_2 -saturated HClO_4 (0.1 M, pH = 1). The original measurements were allowed to stabilize for five cycles, and no significant decrease in the water oxidation current density was observed for any of nanocatalysts during this time (Fig. 7 A). After holding the electrode for 500 cycles, the water oxidation current density decreased by only 9% for $\text{Pt@Ru}_{\text{Cuboctahedral}}$. The water oxidation current density decreased substantially to 1.13 mA cm^{-2} , 0.53 mA cm^{-2} , 1.03 mA cm^{-2} and 0.29 mA cm^{-2} for the $\text{Pt@Ru}_{\text{Dendritic}}$ (by 42%), $\text{PtRu}_{\text{Alloy}}$ (by 72%), Ru (by 42%) and Pt (by 57%) nanocrystals respectively. (Fig. 7 A). After 1000 cycles over 4 hours, the anodic current density decreased by an additional 6% for $\text{Pt@Ru}_{\text{Cuboctahedral}}$ to 1.61 mA cm^{-2} . Whereas, the oxidation current density of $\text{Pt@Ru}_{\text{Dendritic}}$ and Ru nanocrystals decreased to 0.85 mA cm^{-2} (by 14%) and 0.84 mA cm^{-2} (by 11%) respectively. Finally for $\text{PtRu}_{\text{Alloy}}$ and Pt nanoparticles, the anodic current density was below 0.43 mA cm^{-2} (by 5%) and 0.11 mA cm^{-2} (by 27%) respectively.

Fig. 7 A) Water oxidation current densities and **B)** Ru mass activities for the Pt@Ru core-shell (cuboctahedral and dendritic), PtRu alloy, pure Ru and pure Pt nanocrystals in 0.1 M HClO_4 solution after 5, 500 and 1000 cycles at 1.45 V (vs. NHE).

Moreover, Ru mass activity for all nanocatalysts was calculated from Fig. 7 A which shows a high current density at 1.45 V vs. NHE with small catalyst loading of only few μg on the electrode surface. Fig. 7 B shows the estimated Ru mass activity for Pt@Ru_{Cuboctahedral}, Pt@Ru_{Dendritic}, PtRu_{Alloy}, and Ru nanoparticles at 1.45 V vs. NHE after 5, 500 and 1000 cycles. We can see clearly that the Ru mass activity of platinum-ruthenium nanoparticles is much higher than that of pure Ru nanoparticles. At the 5th CV, the calculated values of Ru mass activity of Pt@Ru_{Cuboctahedral}, Pt@Ru_{Dendritic}, PtRu_{Alloy}, and Ru nanoparticles are 158 A/g_{Ru}, 162 A/g_{Ru}, 155 A/g_{Ru} and 59 A/g_{Ru} respectively. After 500 CVs, the mass activity decreased dramatically for all catalysts except Pt@Ru_{Cuboctahedral}. The estimated values are 143 A/g_{Ru}, 94 A/g_{Ru}, 44 A/g_{Ru} and 34 A/g_{Ru} for Pt@Ru_{Cuboctahedral}, Pt@Ru_{Dendritic}, PtRu_{Alloy}, and Ru nanoparticles respectively. Lastly, at the 1000th CV, the Ru mass activity was reduced by additional 5% for both Pt@Ru_{Cuboctahedral} and PtRu_{Alloy} with value of 135 A/g_{Ru} and 36 A/g_{Ru}. In comparison at 1000 cycles, the Ru mass activity for Pt@Ru_{Dendritic} and Ru nanoparticles was further decreased by an additional 14% and 11% respectively. Pt@Ru_{Cuboctahedral} showed 4.8 times higher mass activity than pure Ru at 1000 cycles.

To further confirm the high performance and stability of Pt@Ru_{Cuboctahedral} electrocatalysts, we conducted chronoamperometry at 10 mA cm⁻². The chronoamperometry was run for the Pt@Ru_{Cuboctahedral} based catalyst initially produced a 10 mA cm⁻² current density (Fig. 8). In the beginning, there is increased noise due to oxygen bubble formation and accumulation on the electrode surface. The current density reaches 8.4 mA cm⁻² after 10,000 seconds of the oxygen evolution reaction (Fig 8). This indicated that there is a 16% reduction in the current density during the OER measurement. The electrochemical response of Pt@Ru_{Cuboctahedral} nanocatalysts after chronoamperometric operation reproduced the CVs signature well (Fig 7 A) which corroborates the stability of the nanocrystals containing ~2-3 layers of ruthenium in a cuboctahedral shell.

Fig. 8 Chronoamperometric curve for Pt@Ru_{Cuboctahedral} in 0.1 M HClO₄ solution for 10,000 seconds at 10 mA cm⁻².

In acidic media at high anodic potentials, ruthenium has a tendency to oxidize to ruthenium oxide-type species that may modify its morphology and affect the catalytic characteristics.²⁰ We hypothesized that the stability of Pt@Ru_{Cuboctahedral} was due to the highly stable low index facets of the cuboctahedral shell as well as the platinum seed, which added structural integrity and allowed for easy oxidation and reduction without significant rearrangement or segregation of the ruthenium from the platinum core that enhanced the stability. Therefore, the Pt@Ru_{Cuboctahedral} system appears to prevent surface alternation under anodic electrochemical conditions and exhibits ordered surface arrangements with respect to the ruthenium distribution. The high index structure of the dendritic shell may allow for rearrangement and dissolution during the oxidation and reduction cycles due to its higher surface area and less stable facets compared to the low index facets of the cuboctahedral shell.³⁷

4. Conclusions

We designed a rapid and scalable single-step synthesis for shape and surface-composition controlled bimetallic core-shell and alloy platinum-ruthenium nanostructures for the oxygen evolution reaction. The Ru shell layer can be controlled by the total metal precursor concentration in the solution, allowing us to precisely tune the surface roughness and exposed facets. Furthermore, the shape of the initially formed particle seed templates the final shape of the core-shell particle for both Pt@Ru_{Cuboctahedral} and Pt@Ru_{Dendritic}. In addition, the carbon monoxide reducing agent determines whether the final particle is a Pt-Ru alloy or a segregated Pt@Ru. In all the cases, the formed particles have a *fcc* crystal structure and exhibited higher mass activity and greatly enhanced electrocatalytic activity toward the OER compared with that of pure Pt and Ru nanocatalysts. In particular, the nanocrystals of Pt@Ru_{Cuboctahedral} with a ~2-3 layer cuboctahedral ruthenium shell was the best catalyst among all the nanocrystals in terms of both the stability and activity. This result is most likely due to the durability of the Ru shell on the Pt core. Our results suggest that a thin layer of templated material provides ideal electronic synergy between the core and the shell, which results in substantial improvement in the OER catalytic activity in acidic media. This work provides a new direction for the production of commercially viable, stable and active electrocatalysts for use in water splitting.

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Notes

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