

COMMUNICATION

Compositional dependence of structures and hydrogen evolution reaction activity of platinum-group-metal quinary RuRhPdIrPt alloy nanoparticles

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Platinum-group-metal quinary RuRhPdIrPt alloy nanoparticles were synthesised with compositions slightly away from equimolar, and their crystal and electronic structures were investigated. Their lattice constant changed linearly with composition, while the *d*-band centre changed nonlinearly. Their catalytic activities for the hydrogen evolution reaction were not correlated with their *d*-band centre.

Multi-element solid-solution alloys including high-entropy alloy defined as a solid solution composed of five or more elements have been studied as structural materials.¹ These solid-solution alloys are found to have unique natures such as the cocktail effect, lattice distortion and sluggish diffusion.² Recently, multi-element alloy nanoparticles (NPs) have also attracted much attention as a new class of catalysts because they show unexpected high activities for many kinds of reactions.^{3–6} Also, it has been confirmed that multi-element alloy NPs show higher thermal and chemical stabilities because of their large configurational entropy in the Gibbs free energy ($G = H - TS$).^{3,4} Therefore, it is important to study multi-element alloy NPs as new materials. To design properties of conventional solid-solution NPs such as binary alloy NPs, their compositional dependence has been investigated.^{7–11} For example, it is known that the lattice constant of binary alloy NPs generally obeys Vegard's law, which is a proportional relationship between their lattice constant and composition.⁷ In addition, the catalytic

activity of binary alloy NPs can be estimated by their *d*-band centre, which is continuously changed with their composition.^{10,12} For multi-element alloy NPs, high-throughput screening can be used to find an optimum composition because of their complex compositional patterns.¹³ However, the compositional dependence of structures and properties away from equimolar has not been well investigated. To gain insight into their nature, it is also necessary to investigate changes in their crystal and electronic structures and properties with composition experimentally.

Here, we focus on platinum-group-metal (PGM) quinary alloy NPs composed of Ru, Rh, Pd, Ir and Pt. Equimolar PGM quinary alloy NPs were reported to have a face-centred cubic (fcc) structure and a broad and featureless valence band (VB) structure. Moreover, they showed a much higher catalytic activity for hydrogen evolution reaction (HER) than monometallic NPs.¹⁴ In this report, we synthesised PGM quinary alloy NPs with several compositions slightly away from equimolar (approximately 6:1:1:1:1 for each metal) by a one-pot polyol method.¹⁴ The crystal structures of the obtained NPs were characterised by scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDX) and synchrotron powder X-ray diffraction (PXRD). The relationship between the crystal structure of the obtained NPs and their composition was investigated. In addition, their VB electronic structures were clarified by hard X-ray photoelectron spectroscopy (HAXPES). HER was selected as the target reaction, and the relationship between electronic structure and HER activity was also studied.

PGM quinary alloy NPs were synthesised directly on carbon support at 20 wt% by a modified one-pot polyol method.¹⁴ The five metal precursors (their amounts are summarised in Table S1) were dissolved in 15 mL of 0.1 M HCl (aq). This solution was mixed with 5 mL of an isopropanol solution dispersing 160 mg of carbon (VULCAN XC-72R) as supporting material. The mixture was sprayed into a preheated triethylene glycol (TEG) solution at 220°C. The obtained solution was cooled to room temperature (RT) and washed with ultra-pure water, ethanol, acetone, and ether several times. Finally, the obtained black powder was collected by centrifugation and vacuum-dried at RT.

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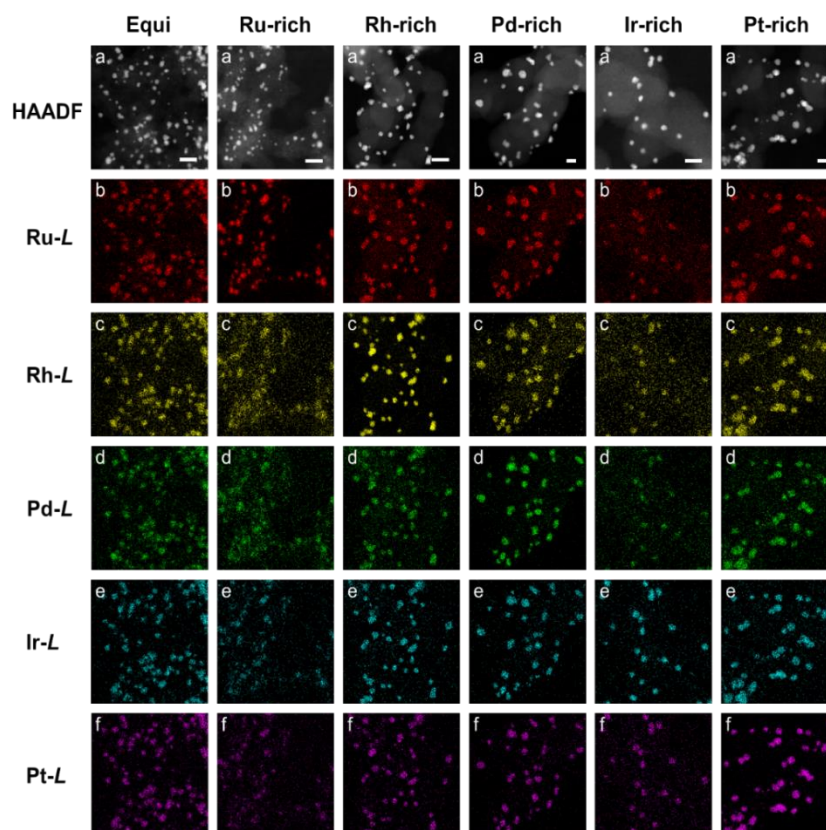


Fig. 1 (a) HAADF-STEM images and EDX maps showing (b) Ru-L, (c) Rh-L, (d) Pd-L, (e) Ir-L and (f) Pt-L of Equi (equimolar), Ru-rich, Rh-rich, Pd-rich, Ir-rich and Pt-rich alloy NPs from the right. The scale bars indicate 10 nm.

Pd-rich (Ru:Rh:Ir:Pt=1:1:6:1:1) NPs were treated by hydrogen at 200°C to remove interstitial carbon.

Transmission electron microscopy (TEM) was used to characterise the obtained NPs. The bright-field TEM images (Fig. S1) show that NPs are well dispersed on carbon. The average particle sizes were 3.6–4.6 nm except for Ir-rich alloy NPs (Ru:Rh:Ir:Pt=1:1:1:6:1) having a slightly smaller particle size (3.0 ± 0.7 nm) than the others. The compositions of the obtained NPs were analysed by X-ray fluorescence (XRF), and the results were consistent with nominal ratios (Fig. S2).

The obtained NPs were characterised by STEM-EDX. Fig. 1 shows high-angle annular dark-field (HAADF) STEM images and corresponding EDX maps of the obtained NPs. The EDX maps show that all the five elements have a homogeneous distribution in the NPs, indicating the formation of the solid solution in all the samples. The element reflecting a brighter colour contrast in EDX maps indicates the main component (approximately 60 at.%) in the obtained NPs. Homogeneous solid-solution structures were also confirmed by line analysis (Fig. S3).

The crystal structures of the obtained NPs were clarified by synchrotron PXRD at the beamline BL02B2 in SPring-8.¹⁵ Fig. 2 shows the XRD patterns of the obtained NPs suggesting a single fcc structure with different peak positions. The lattice constants of the obtained NPs were determined by Rietveld refinement using a single fcc component (Fig. S5). The lattice constant of PGM quinary alloy NPs becomes larger with the same order as the lattice constant of bulk monometals ($a_{Rh} = 3.80$ Å, $a_{Ru} = 3.82$ Å, $a_{Ir} = 3.84$ Å, $a_{Pd} = 3.89$ Å and $a_{Pt} = 3.92$ Å. a_{Ru} were calculated as the ideal fcc lattice constants by $\sqrt{2} \times a_{hcp}$). To determine

whether multi-element alloy NPs have a similar relationship to binary alloy NPs, a weighted mean of lattice constants was calculated using Equation (1):

$$a_{\text{alloy}} = a_{Ru}x_{Ru} + a_{Rh}x_{Rh} + a_{Pd}x_{Pd} + a_{Ir}x_{Ir} + a_{Pt}x_{Pt} \quad (1)$$

where a is the lattice constant of each monometal and x is the atom percentage of each metal from XRF.

The results show that the experimental lattice constants have a linear relationship with the calculated values (Fig. 3). This result suggests that multi-element alloy NPs follow Vegard's law as binary alloy NPs and, even for such complex alloy NPs, that the lattice constant can be estimated when the compositions are obtained.

XPS analysis was performed to investigate the electronic structures of the obtained NPs (Fig. S6). Ru $3d_{5/2}$, Rh $3d_{5/2}$, Pd $3d_{5/2}$, Ir $4f_{7/2}$ and Pt $4f_{7/2}$ peaks were observed and analysed. Each observed peak corresponds to the binding energy of the bulk metal peak.¹⁶ However, the results show that there is a peak shift for each metal from monometallic NPs. The Pd and Pt peaks slightly shifted to the positive direction in all the samples, while the Ir peak slightly shifted to the negative direction by the formation of solid solutions. There were small peak shifts in the Ru and Rh, as shown in Fig. S7. Mg $K\alpha$ was used as the X-ray source energy, and XPS can indicate the surface composition to a thickness of 1 nm. The surface compositions of the obtained NPs were calculated by using their corresponding XPS peaks. The surface compositions obtained by XPS and bulk compositions by XRF were consistent with each other, confirming homogeneous solid-solution structures (Fig. S2).

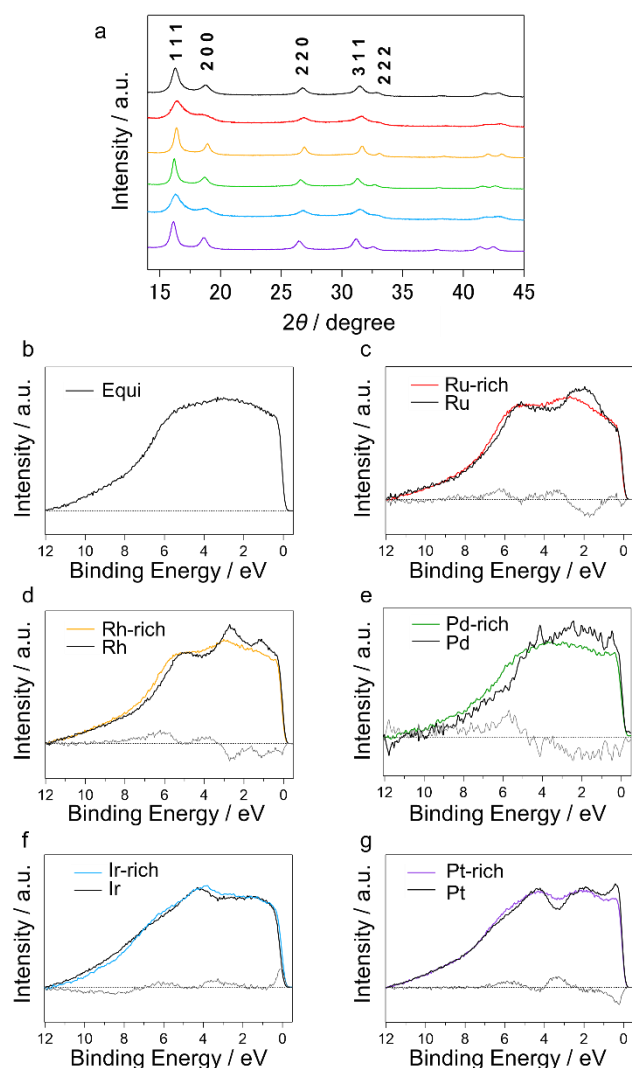


Fig. 2 (a) Synchrotron XRD patterns of Equi (black), Ru-rich (red), Rh-rich (orange), Pd-rich (green), Ir-rich (blue) and Pt-rich (purple) alloy NPs. (b) VB spectrum of equimolar alloy NPs; (b–g) comparison of VB spectrum of each metal-rich alloy NP and its major monometallic NP.

The VB structure was investigated by HAXPES. Fig. 2b–g show that the VB spectra of PGM quinary alloy NPs have fewer features and have broader profiles than those of monometallic NPs. Compared with the VB spectra of equimolar alloy NPs (Fig. 2b), however, the VB spectra of the other alloy NPs slightly reflect the features of the major elements. The *d*-band centre, defined as the centre of gravity of the VB spectra, was calculated and these are summarised in Table S4. For monometallic NPs, *d*-band centres are positioned in the range from -4.294 to -3.443 eV (the deepest centre is Ir, and the shallowest is Pd). For the alloy NPs, the deepest and the shallowest centres are also Ir-rich and Pd-rich, respectively; however, the range of the *d*-band centre was much narrower (-4.142 to -3.922 eV). These *d*-band centres were compared with the values calculated by a linear combination of monometallic *d*-band centres (Fig. 3). Interestingly, the experimental values largely deviated from the estimated values. This large deviation is considered to originate from the hybridisation of the orbitals of the five elements. Different from the crystal structure, we cannot estimate the electronic structure simply by a linear combination using the compositions.

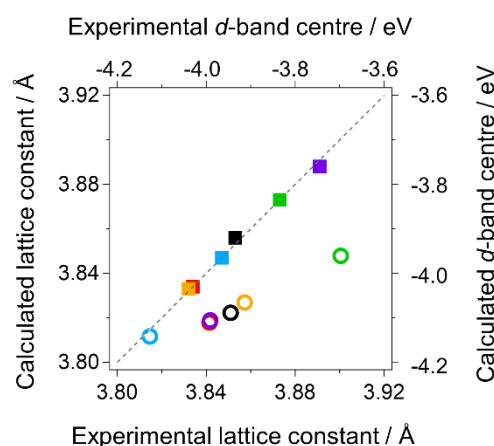


Fig. 3 Relationship between experimental lattice values and calculated values of Equi (black), Ru-rich (red), Rh-rich (orange), Pd-rich (green), Ir-rich (blue) and Pt-rich (purple) alloy NPs. Squares indicate lattice constants and circles *d*-band centres.

HER activity was evaluated in acidic conditions. Commercial Pt was also measured as a standard. 1M HClO_4 (aq) was selected as the electrolyte to avoid unnecessary reactions.¹⁷ The polarization curves of the alloy NPs and commercial Pt were obtained at 5 mV/s (Fig. 4a). The activity of commercial Pt was nearly consistent with the other reports using a similar setup.^{18,19} The current density was normalised by the area of the rotation-disk electrode (0.196 cm^2). Fig. 4b shows overpotentials at 50 mA cm^{-2} . Turnover frequency (TOF) is another value that shows the intrinsic catalytic activity. Based on the Cu underpotential deposition (Fig. S8), the TOF value was calculated (Fig. 4c).¹⁴ These results show that Pt-rich alloy NPs have the highest HER activity and Ru-rich alloy NPs have the lowest activity. Pt-rich alloy NPs exhibited double the activity compared with equimolar alloy NPs.

For the transition monometals, it is known that the *d*-band centre is related to the HER activity because absorption energies are almost linearly correlated to the *d*-band centre.^{10,20} To investigate the tendency of HER activities of multi-element alloy NPs, the relationship between TOF value and *d*-band centre is summarised in Fig. 4d. Although this relationship often shows a volcano-like shape, there is no obvious relationship. Notably, the Pt-rich alloy NP activity was quadruple that of the Ru-rich alloy NPs, but the difference in their *d*-band centre was only 0.005 eV . However, the compositional dependence of the catalytic activity of PGM quinary alloy NPs was not clearly observed because of their complexity. These results indicate that different interpretations of the reaction mechanism such as a combination of multiple factors, for example, composition, local density of state, facet, and size would be needed for multi-element alloy NPs.

In summary, PGM quinary alloy NPs with several compositions (approximately $6:1:1:1:1$ for each metal) were prepared by a one-pot polyol method. We found that the crystal structure of multi-element alloy NPs simply depends on their compositions, while the electronic structure does not. The VB spectrum of the obtained NPs was broad and featureless compared with that of monometallic NPs. The HER activities of PGM quinary NPs were not correlated with their *d*-band centre, indicating that alloy

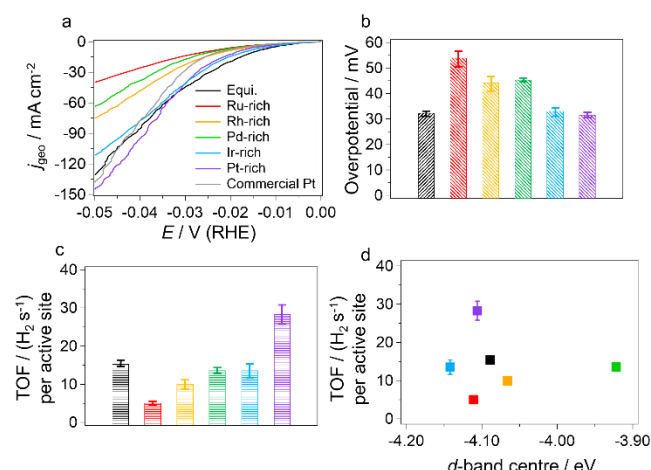


Fig. 4 (a) Polarization curves, (b) overpotentials at a geometric current density 50 mA cm⁻², (c) TOF at 50 mV and (d) relationship between TOF and the d -band centre of Equimolar (black), Ru-rich (red), Rh-rich (orange), Pd-rich (green), Ir-rich (blue) and Pt-rich (purple) alloy NPs and commercial Pt (grey). The error bars were calculated by standard deviation of three measurements.

NPs may have different mechanisms to catalyse HER from conventional catalysts.

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Author Contributions

K. K. and H. K. conceived the idea and designed the research. Y. M. and K. K. performed the synthesis and general characterisation. Y. M. and D. W. performed the electrochemical tests. T. Y., T. T. and S. M. conducted the HAADF-STEM measurements. O. S., S. Y. and O. S. performed the HAXPES experiments. S. K. and Y. K. contributed to the synchrotron XRD measurements. Y. M., K. K. and H. K. discussed the results and wrote the manuscript. All the authors discussed and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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