

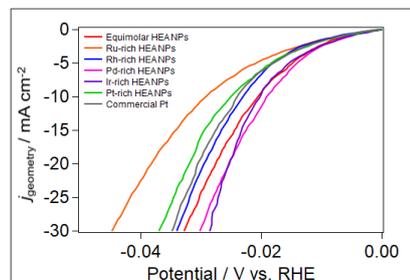
Composition Dependence of Catalytic Activity of Platinum-Group-Metal High-Entropy Alloy Nanoparticles for Hydrogen Evolution Reaction

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Recently, high-entropy-alloy (HEA) has attracted much attention as catalysts. For example, equimolar platinum-group-metal high-entropy-alloy nanoparticles (PGM-HEA NPs) show an extremely high catalytic activity for hydrogen evolution reaction (HER)¹. In spite of the very high compositional designability, the composition dependence of their crystal and electronic structures, and properties have not been well investigated.

Here, we first synthesized PGM-HEA NPs with several compositions (about 6:1:1:1:1 for each metal) directly on carbon support to investigate the composition dependence of PGM-HEA NPs' properties. The obtained NPs were characterized by a scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDX), and powder X-ray diffraction (PXRD). The EDX maps showed that each metal has a homogeneous distribution in the NPs, indicating the formation of the solid solution. The lattice constant was calculated by Rietveld refinement of the XRD patterns and it was found that the lattice constant of HEA NPs follows Vegard's law as with binary solid solutions. X-ray fluorescence (XRF) analysis shows that the compositions are about 6:1:1:1:1 for each metal. These results showed that PGM-HEA NPs were successfully synthesized with several compositions. X-ray photoelectron spectroscopy (XPS) was performed to investigate their electronic structures. In addition, their valence band (VB) electronic structure was revealed by hard X-ray photoelectron spectroscopy. It was found that PGM-HEA NPs showed featureless broader VB compared to those of monometallic NPs. The catalytic activity of HER was investigated by a three-electrode electrochemical measurement (Figure a). Although it is well known that HER activity of monometals has a volcano-shape relationship toward their *d*-band center, we found that PGM-HEA catalysts do not show this relationship. This result suggests that HEA NPs have different mechanism to catalyze HER from conventional catalysts.



Figure(a) HER polarization curve

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