Coposition dependence of sub-nanoparticle catalysts in electrocatalytic reactions

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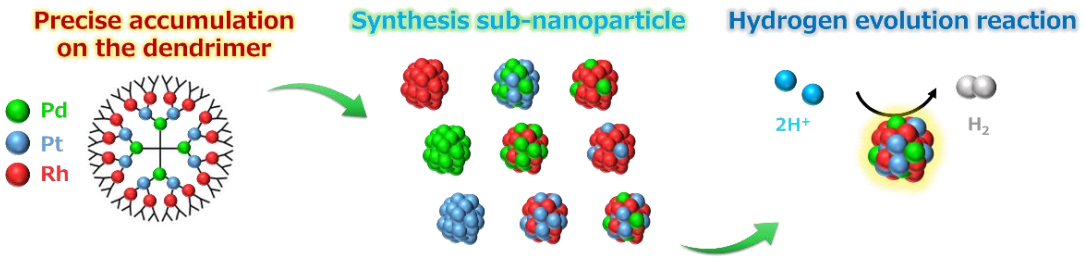
Crystalline bulk and nanoparticles with a grain size larger than 2 nm are crystalline, so their atoms do not mix uniformly and are phase-separated. However, sub-nanoparticles with a particle size of about 1 nm are non-crystalline, so the atoms mix uniformly, and they also exhibit atomic fluidity not seen in nanoparticles or bulk[1,2]. The catalytic activity of sub-nanoparticles can vary greatly by a single atom, and they can perform much better than bulk or nanoparticles[3]. However, synthesis of sub-nanoparticles with a precisely defined number of constituent atoms is extremely difficult, and the relationship between the unique catalytic properties of sub-nanoparticles and their composition and structure has been elucidated only piecemeal, necessitating a systematic evaluation. This study aims to synthesize metal sub-nanoparticles with a precisely defined number of atoms using phenylazomethine dendrimer (DPA-G4) as a template and to systematically evaluate their atomic composition dependence in electrochemical catalytic reactions such as hydrogen generation reactions.

DPA-G4 has a special potential gradient due to the conjugated structure of aromatic rings and imine, which results in different complexation constants for each generation. Therefore, metal salts accumulate in order from the inner layer. Taking advantage of this property, metal salt accumulation in DPA-G4 was carried out by adding 4, 8, and 16 equivalents of palladium, platinum, and rhodium metal salts, respectively, to DPA-G4. The metal salts accumulated on DPA-G4 were then reduced and loaded on a carbon carrier, Ketjen black, and HAADF-STEM observation showed palladium, platinum, and rhodium ternary alloy subnanoparticles with a particle size of about 1 nm, in which atoms were homogeneously intermixed. Hydrogen evolution reaction using the synthesized metal-alloy subnanoparticle catalysts revealed that the catalytic activity was enhanced by alloying in the case of platinum-based subnanoparticles.



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