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Structure of Ru/Pt Nanocomposite Films Fabricated by Plasma-Enhanced Atomic Layer Depositions

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A nanoparticle comprising a Ru core covered with a shell of Pt atoms (Ru@Pt core–shell nanoparticle) has attracted considerable attention as a very active catalyst to remove CO from hydrogen feeds through selective oxidation since significant quantities of CO in reforming hydrocarbons poison the current hydrogen fuel-cell devices [1-3]. The particles are chemically prepared by deposition of Pt atoms from a deoxygenated solution of H_2PtCl_6 on the Ru nanoparticles dispersed on XC-72 active carbon [1] or by Pt coating by adding $PtCl_2$ to Ru/glycol colloid [2-5]. Here, we report on the structural analysis of a new Ru and Pt nanocomposite film (Ru/Pt film), which was prepared by successive plasma-enhanced atomic layer depositions (PE-ALDs) of Pt and Ru, by means of analytical electron microscopy.

PE-ALD of Pt films was performed using $MeCpPtMe_3$ [$C_5H_4CH_3Pt(CH_3)_3$] and Ar/O_2 plasma. The Pt films deposited on the Si wafer at 200^{o}C had a low resistivity of 16.2 μΩ cm. Ru films were grown using $Ru(EtCp)_2$ [$Ru(C_2H_5C_5H_4)_2$] precursor. The resistivity of the Ru thin film deposited on a Si wafer at 300^{o}C was as low as 11 μΩ cm. For transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) observations, a Ru/Pt film was prepared on a very thin amorphous carbon film supported on the Cu grid for TEM. The $MeCpPtMe_3$ PE-ALD of 30 cycles was made on the carbon films heated at 300^{o}C, followed by PE-ALD of 100 cycles using EBCHDRu [$C_{14}H_{18}Ru$] as the precursor at the same temperature. The EBCHDRu provided a comparable growth rate of Ru film with the $Ru(EtCp)_2$. Analytical electron microscopy was performed with an atomic scale high-resolution (HR) JEOL ARM200FC microscope equipped with a cold field-emission gun and aberration correctors as well as a 60 mm^2 silicon drift detector for energy dispersive X-ray spectroscopy (EDS), and with a JEM-2800 microscope with an objective lens of *C*s of 0.7 mm attached with a JEOL 100 mm^2 SDD for EDS.

Analytical electron microscopy shown in Figures 1 and 2 and HRTEM revealed that the 30-cycle PE-ALD of Pt forms Pt ribbons 2~3 nm wide as a result of island growth on the C substrate. The following 100-cycle PE-ALD of Ru forms pure Ru ribbons 2~3 nm wide between the Pt ribbons, and changes the Pt ribbons to PtRu (7:3) alloy ribbons with the fcc A1 structure. The pure Ru ribbons are composed of Ru crystallites with the hcp A3 structure but poor in quality exhibiting ill-defined lattice fringes in HR-BF and HAADF STEM images. Hence the Ru/Pt film is a nanocomposite film comprising pure Ru ribbons and PtRu alloy ribbons with 2~3 nm in their widths, which resembles the Ru@Pt core–shell nanoparticles with the fcc A1 structure of PtRu and poor crystalline hcp A3 structure of Ru [3]. The structure of Ru/Pt film or the sizes of Pt and Ru particles are controllable by changing the PE-ALD condition such as the number of deposition cycles, deposition temperature and post-deposition heat treatments. The PE-ALD would be one of potential techniques to produce a fuel cell catalyst such as Ru@Pt core–shell nanoparticles.

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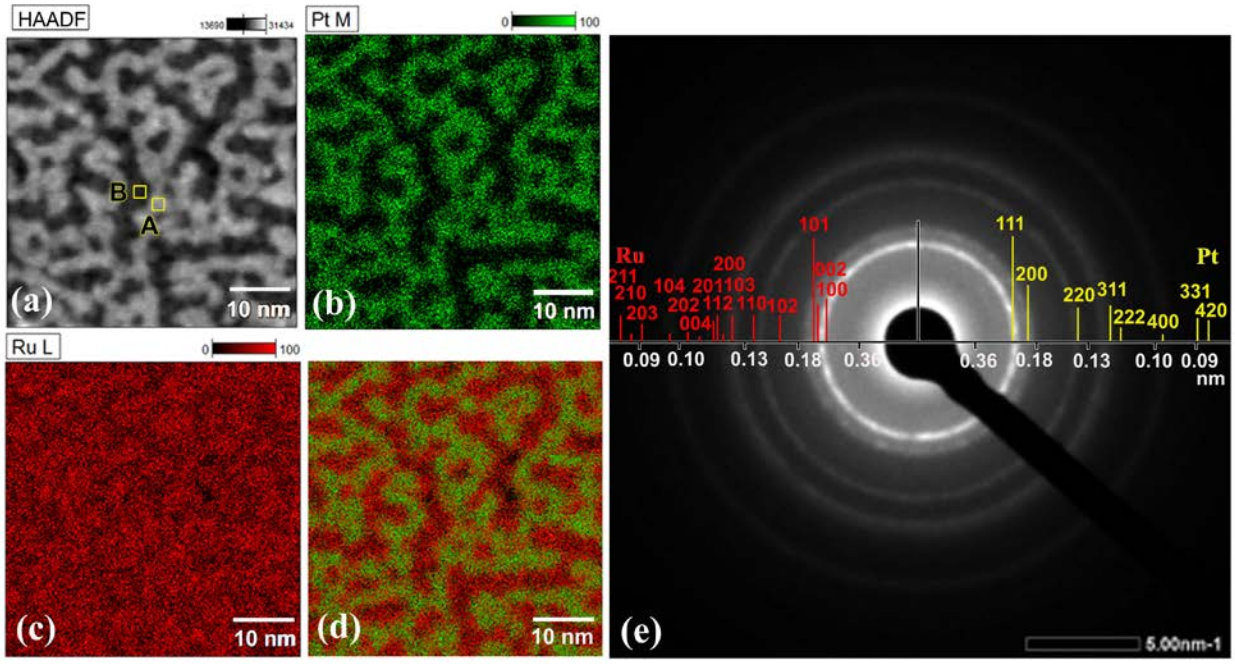

Fig. 1. EDS mapping and electron diffraction of the Ru/Pt nanocomposite film. (a) HAADF-STEM image. (b,c) EDS maps of Pt-M and Ru-L, which were arranged from the original EDS data to display the relative atomic % of Pt and Ru. (d) Composite EDS map corresponding to (b) and (c). (e) Electron diffraction pattern, where the standard powder X-ray diffraction intensities for Pt and Ru crystalline are inset on the right and left, respectively.

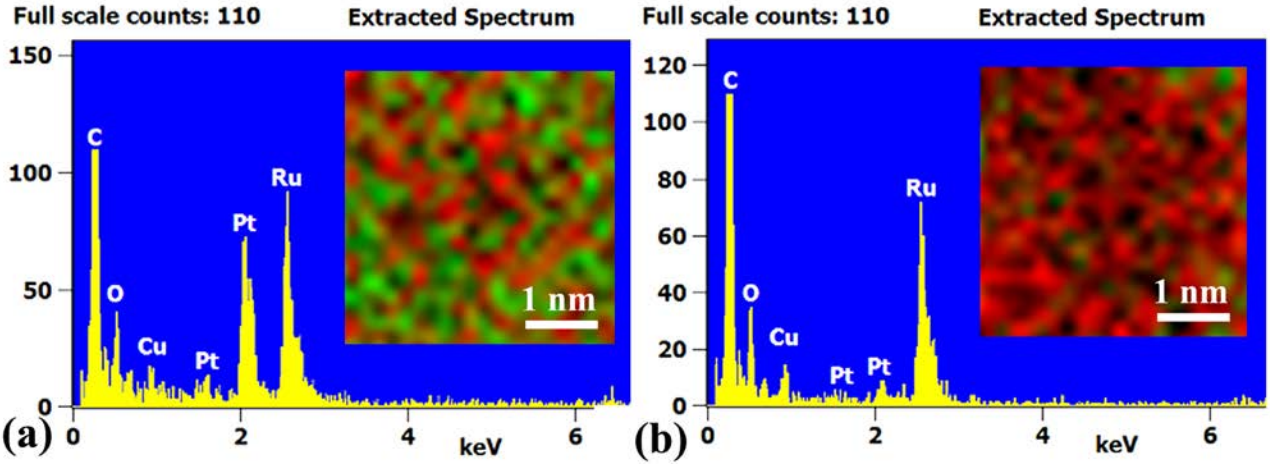

Fig. 2. (a, b) EDS spectra from local areas indicated by squares A and B in Fig. 1(a), respectively. The insets in (a) and (b) show the enlarged images of the corresponding areas to A and B in Fig. 1(d). Assuming the same absorption effect for Pt-M and Ru-L and using Cliff-Lorimer factors of 1.568 for Pt-M and 1.713 for Ru-L, from these spectra we estimated roughly the relative atomic % of Pt to Ru to be 71/29 (=~7:3) for area A and 3/97 (=~0:1) for area B.

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