

Electronic Supplementary Information (ESI)

Novel Nickel-Palladium Catalysts Encased in a Platinum Nanocage

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A. Electronic State of the Metals in Ni-Pd-Pt NPs

Photoelectrons were excited by monochromated Al K α radiation. Detection was performed with a delay-line detector and a concentric hemispherical analyzer. The X-ray tube was operated at 150 W. The pass energy of the concentric hemispherical analyzer was 20 eV for narrow-scan spectra. The analyzed area on the specimen surface was 300–700 mm² and was located in the center of the irradiated region. For the sample preparation, the precipitated NPs were deposited on carbon tape and dried in air. The instrument was operated at a vacuum level of 1×10^{-8} torr. Pd3d and Pt4f areas show that Pd and Pt are present in the zero valent metallic state in the Ni-Pt/Pd alloy NPs. The Pd3d and Pt4f XPS analytical results are shown below for Ni-Pd-Pt NPs:

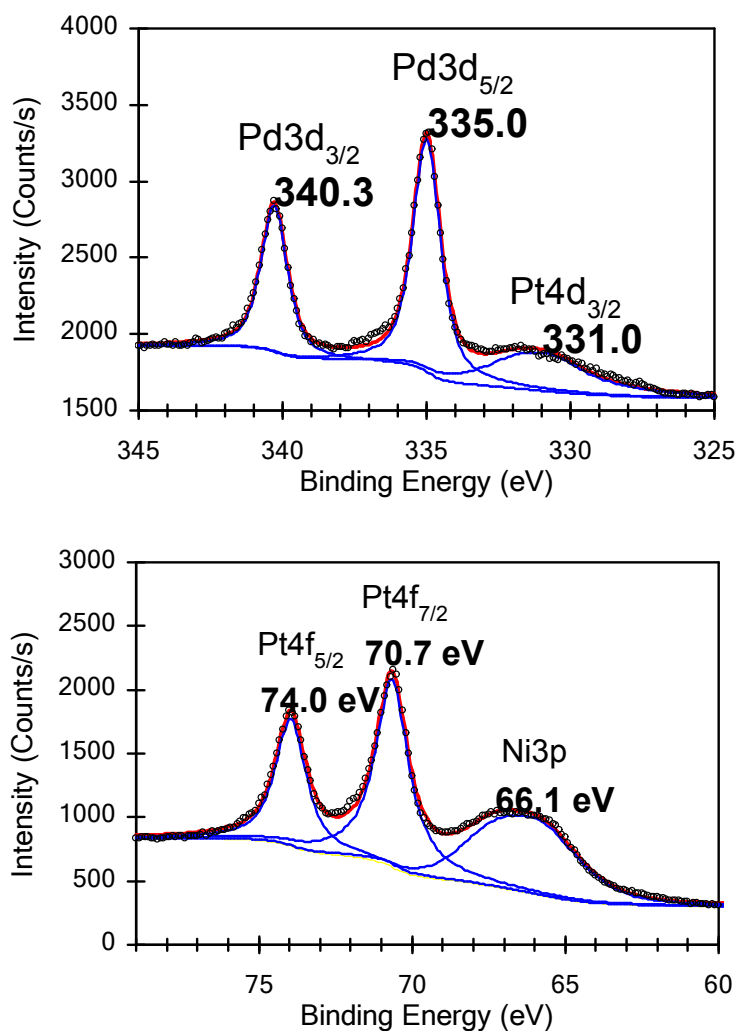


Fig. S1. XPS spectra taken for Ni-Pd-Pt NPs in the Pd3d and Pt4f areas. Pd3d and Pt4f areas show that Pd and Pt are present in the zero valent metallic state in the Ni-Pd-Pt alloy NPs.

B. Elemental Distribution in Ni-Pt NPs.

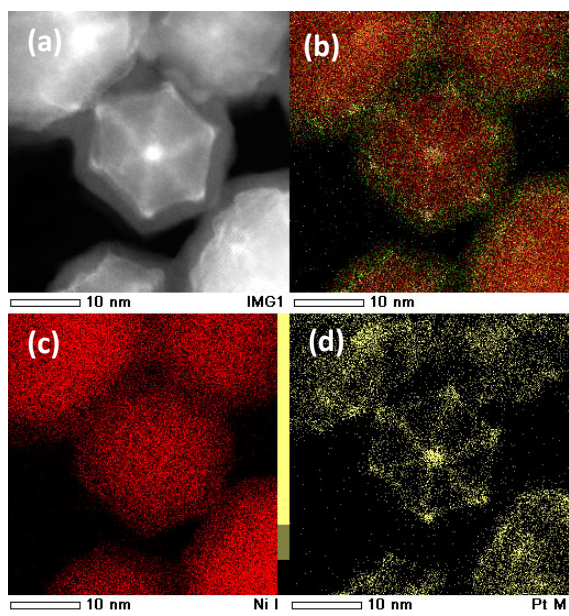


Fig. S2. EDS Mapping results of Ni-Pt NPS. (a) STEM-HAADF image and (b-d) EDS elemental mapping images of the Ni-Pt NPs. (b) overview of the mapping results, (c) Ni K edge, and (d) Pt M edge.

C. Identification of Oleylamine Adsorbed on the Surface of Ni-Pd-Pt Particles

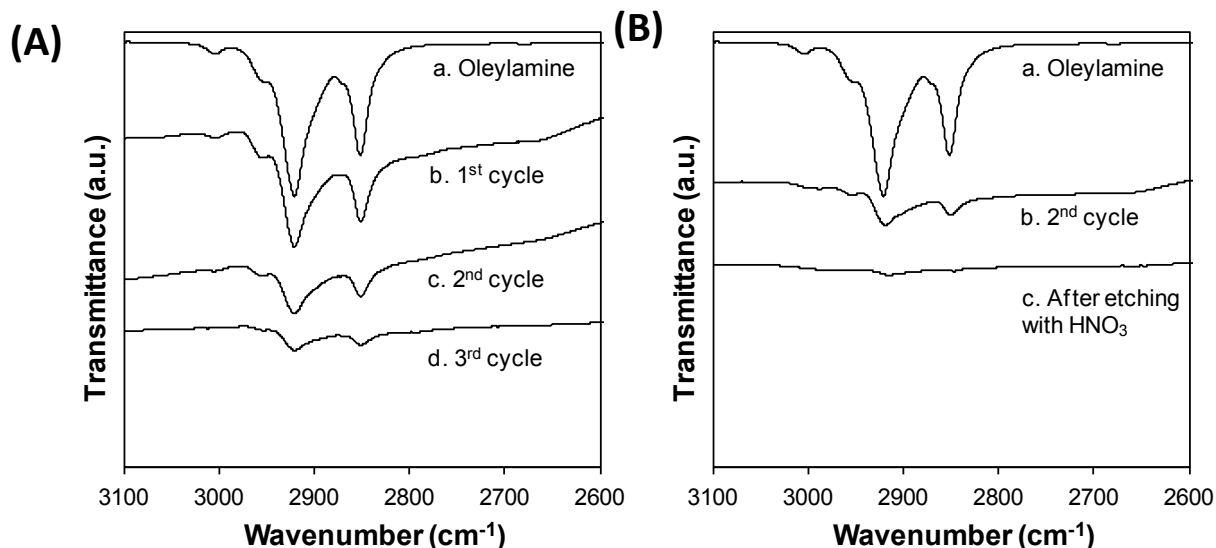


Fig. S3. FTIR spectra of Ni-Pd-Pt samples. The figures (A) and (B) shows the results of FTIR analysis used to examine the presence/absence of oleylamine. The results in Fig. (A) are that of samples washed with the mixture of toluene and methanol for different number of times. On the other hand, the results for the samples etched with nitric acid after washing with the mixture of toluene and methanol is shown in Fig. (B). For convenience, the analysis was made in the range from 2600 to 3100 cm^{-1} . The symmetric and asymmetric vibration of alkyl chain at 2850 and 2918 cm^{-1} , the stretching vibration mode of CH_3 at 2952 cm^{-1} and the corresponding peak C-H stretching mode of C–H adjacent to the C=C bond at 3005 cm^{-1} are observed in 70 % pure oleylamine (curve (a) in figures (A) and (B)). The spectra show progressive reduction in the intensities of the peaks corresponding to oleylamine with the increase in the number of washing cycles. On the other hand, the removal of oleylamine was confirmed when the sample was etched with nitric acid (curve (c) in Fig. (B)).

D. Estimation of Oleylamine Adsorbed on the Surface of Ni-Pd-Pt Particles

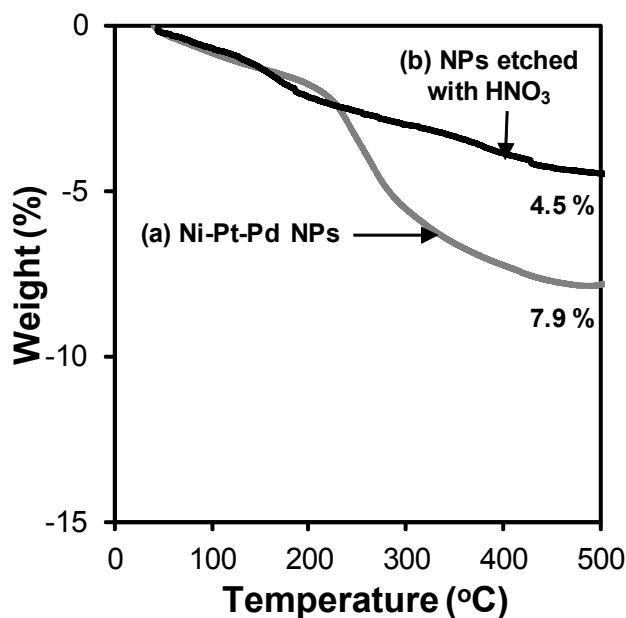


Fig. S4 Thermogravimetric analysis of (a) as-synthesized and (b) acid etched Ni-Pd-Pt particles in N₂ gas atmosphere. The weight loss corresponding to the region below 200 °C, could be ascribed to the desorption of solvents such as toluene and methanol used to wash the particles. At temperatures above 200 °C, a weight loss of 5.8 % and 2.3 %, which could be ascribed mainly to oleylamine were observed for samples washed with (a) mixture of toluene and methanol and (b) nitric acid, respectively. If we assume that the 20 nm cubic Ni-Pd-Pt particles are covered with monolayer of oleylamine, the weight fraction will be around 7.5 % (assuming the cross-section of oleylamine molecule to be 20 Å²). Thus the surfactant coverage in particles used for the measurement of catalytic activity is estimated to be less than 30 %.