Supporting Information

Pt-Bi co-deposit shell on Au nanoparticle core: high performance and long durability for formic acid oxidation

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Supporting figures:

A. TEM images and particle size distributions of Pt-Bi/Au NPs and Pt/Pt-Bi/Au NPs

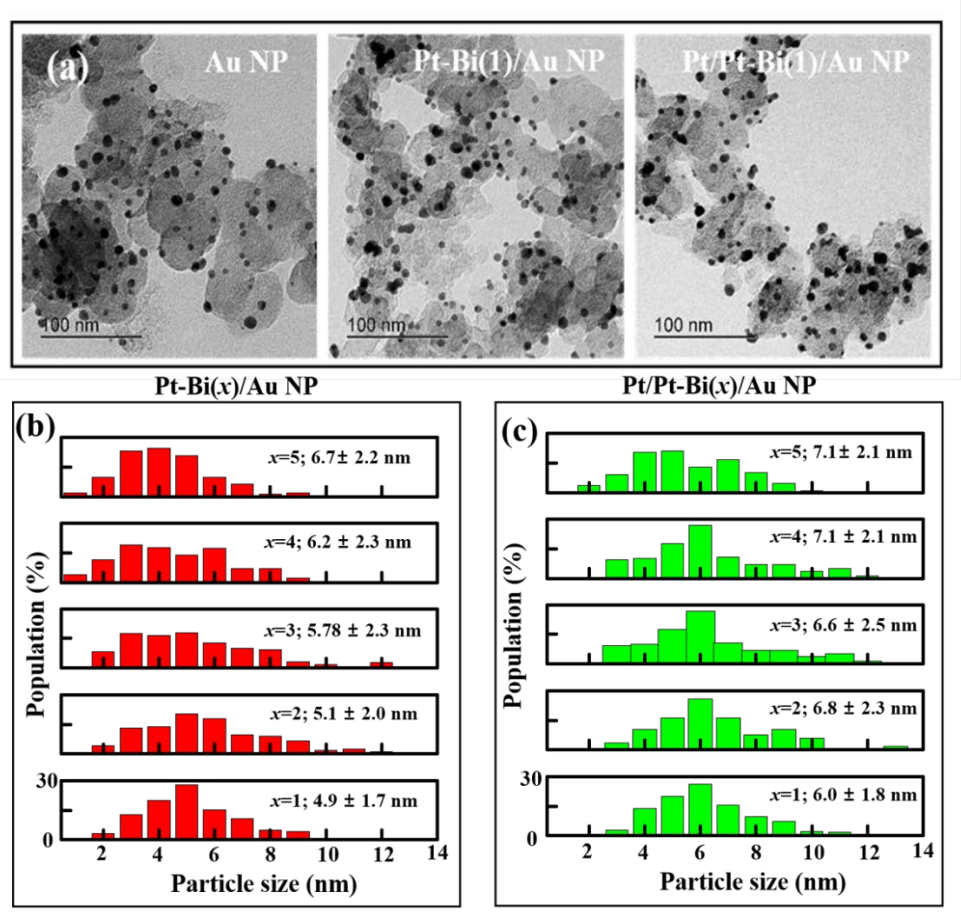


Figure S1. Size distributions of Pt-Bi(*x*)/Au NPs and Pt/ Pt-Bi(*x*)/Au NPs. **(a)** Typical TEM images of Au NP, Pt-Bi(1)/Au NP and Pt/Pt-Bi(1)/Au NP. Particle size distributions of **(b)** Pt-Bi(*x*)/Au NPs and **(c)** Pt/Pt-Bi(*x*)/Au NPs estimated by measuring more than 100 particles in TEM. In **(b)** and **(c)**, *x* is the number of co-deposition cycles of Pt and Bi.

B. What happens during rinse step of mixed ionic layer of Pt and Bi on Au

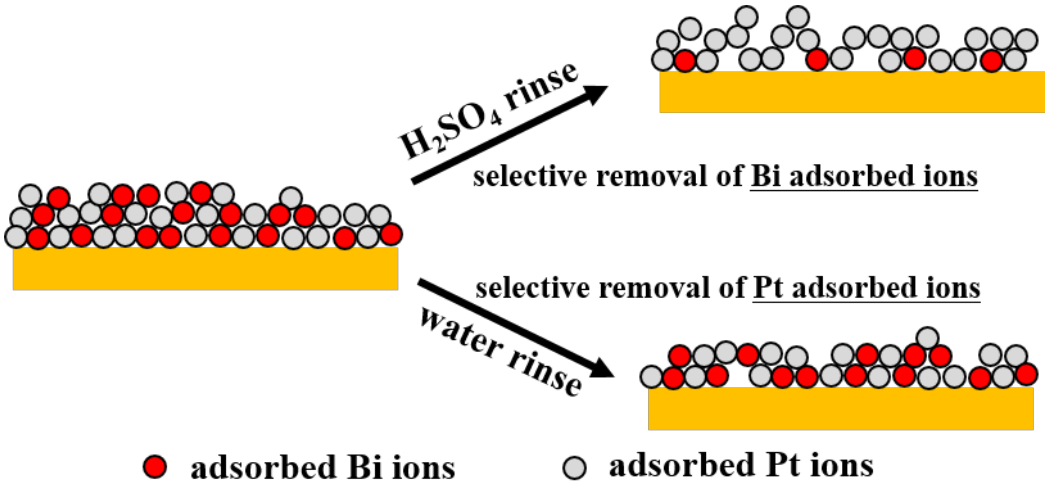


Figure S2. Illustration of the effects of rinsing mediums in the rinsing step after co-adsorption of Pt and Bi on Au NP. The numbers of Bi and Pt ions in this figure do not represent the quantitative results in the main text.

Figure S2 illustrates the effects of rinsing mediums in the rinsing step after co-adsorption of Pt and Bi on Au NP. As stated in the main text, H_2SO_4 rinse removes Bi ions selectively, while water rinse eliminates Pt ions moderately. A high solubility of Bi_2O_3 in a H_2SO_4 solution would be a reason for the selective removal of Bi ions from the mixed ionic layer during H_2SO_4 rinse. In fact, as the concentration of H_2SO_4 in H_2SO_4 rinse solution increased, the Bi/Au ratio of Pt-Bi/Au NPs decreased. Likewise, a low solubility of Bi_2O_3 in water results in the stability of Bi ions in the mixed ionic layer during water rinse.

C. Voltammograms of various catalysts during durability test

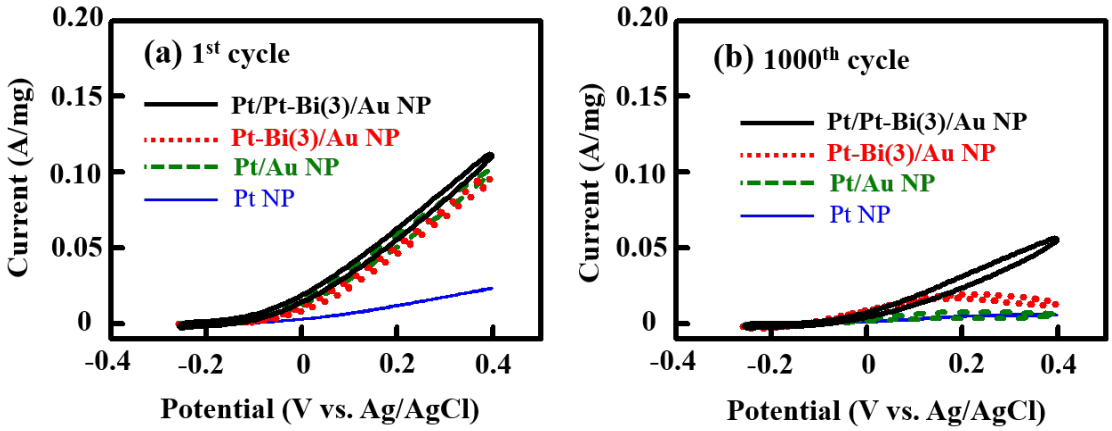


Figure S3. Typical FAO cyclic voltammograms of Pt NP, Pt/Au NP, Pt-Bi(3)/Au NP and Pt/Pt-Bi(3)/Au NP observed for durability tests in 1.0 M HCOOH + 0.1 M H_2SO_4: in **(a)** the 1st cycle, and **(b)** the 1000th cycle. Scan rate: 10 mV/s.

D. FAO current normalization

In this work, the FAO currents observed on various Pt-Bi/Au NPs and Pt/Pt-Bi/Au NPs are compared with that on a commercial Pt NP (the reference catalyst). Because a measured FAO current on a specific catalyst depends on the surface area of Pt, mass of Pt, or total catalysts, an observed current should be converted to a current density referring to a proper physical property to be compared with those on other catalysts. Thus, electrochemically active surface area or mass should be measured in separate experiments.

Surface area of Pt is normally estimated using an electrochemical method. The general method is converting the stripping charge of hydrogen or CO using the conversion factors of 210 or 420 $\mu C/cm^2$, respectively. It should be underlined that the particular conversion factors are based on the adsorption stoichiometry of 1 (i.e. Pt-H $\rightarrow$ Pt + H^+ + e; Pt-CO + H_2O $\rightarrow$ Pt + CO_2 + $2H^+$ + 2e). In other words, it is assumed that one Pt atom adsorbs one hydrogen atom or one CO molecule, which can be confirmed with a H/CO charge ratio of 0.5. When the specific ratio of 0.5 is not sure, Pt surface area measurement using the charges of hydrogen and CO is inappropriate.

Figure S4 shows the H/CO charge ratios of the Pt-base catalysts employed in this work. In the case of Pt NP, the ratio is 0.49±0.02, indicating that the Pt surface area measurement is appropriate. In contrast, the H/CO charge ratios of Pt-Bi/Au NPs and Pt/Pt-Bi/Au NPs depend on the number of depositions. As the number of depositions increases, the H/CO charge ratio increase ~0.25 to ~0.5. One extreme case is Pt-Bi(1)/Au NP, on which the charge of CO was too small to measure precisely, most likely due to a huge background current of the carbon support or quite a low adsorption ability. Therefore, the surface area estimation using electrochemical means is inappropriate especially for the lower number of deposition.

The other alternative is normalization using the total mass of a catalyst spread on GCE or its Pt amount. Estimation of the total mass is simpler than estimation of the Pt amount in the

catalyst. Specifically, an additional information such as Pt-to-Au ratio is needed to calculate a Pt amount. Although the Pt/Au ratios of the investigated catalysts were measured, the additional measured values may increase the uncertainties in the estimated Pt amounts, which increase further the uncertainties in the Pt mass normalized current density especially when they are denominators of small numbers. In this particular regard, the total mass normalization would be more reasonable.

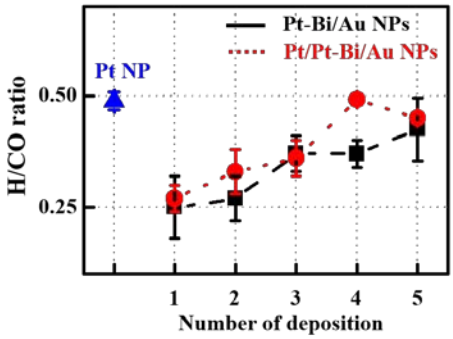


Figure S4. The H/CO ratio of Pt-Bi/Au NPs and Pt/Pt-Bi/Au NPs.