

**[Supplementary Information]**

**One-Pot Synthesis and Electrocatalytic Activity of Octapodal Au-Pd  
Nanoparticles**

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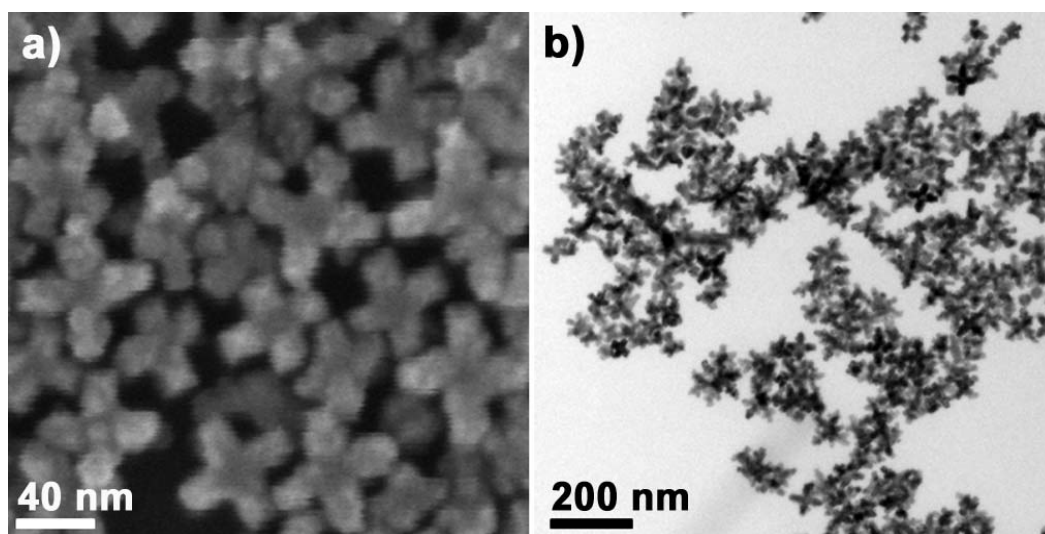
## Experimental

**Chemicals and materials.** NaAuBr<sub>4</sub>·xH<sub>2</sub>O (Aldrich), K<sub>2</sub>PdCl<sub>4</sub> (Aldrich, 98%), HAuCl<sub>4</sub> (Aldrich, 99.99+%), L-ascorbic acid (Dae Jung Chemicals & Metals Co., 99.5%), cetyltrimethylammonium chloride (CTAC, Aldrich, solution in water, 25 wt%), palladium on activated carbon (Pd/C, Aldrich, 10 wt %), and NaBr (Aldrich, ≥ 99%) were all used as received. Other chemicals, unless specified, were reagent grade and high purified water with a resistivity of greater than 18.0 MΩ·cm was used in the preparation of aqueous solutions.

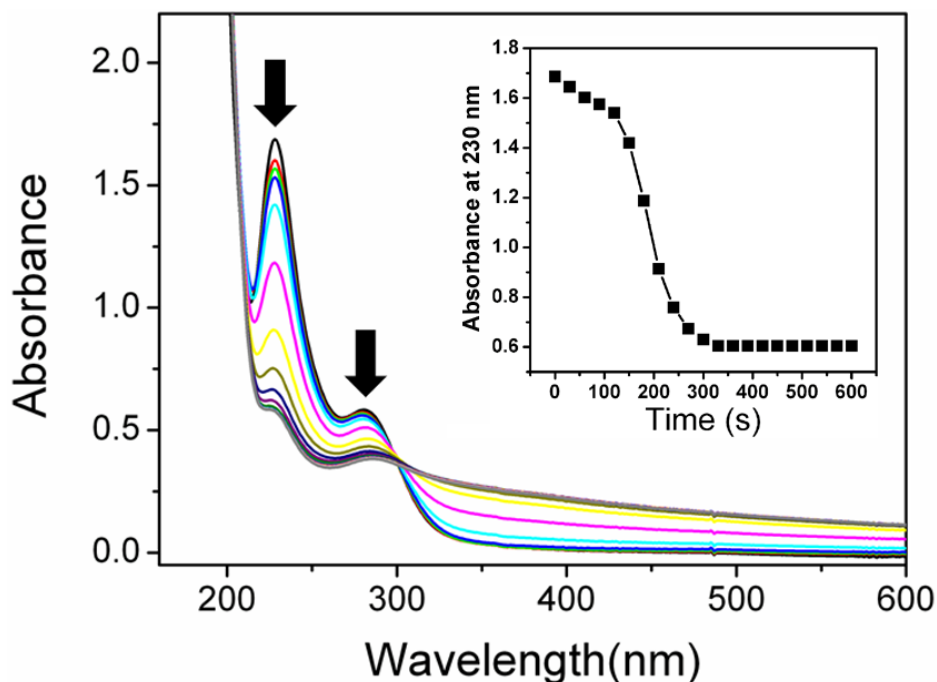
**Preparation of Nanoparticles (NPs).** In a typical synthesis of Au-Pd octapodal NPs, a feeding solution was prepared by adding 10 mL of aqueous solution of CTAC (50 mM) to highly purified water (14.45 mL). An aqueous solution of NaAuBr<sub>4</sub>·xH<sub>2</sub>O/K<sub>2</sub>PdCl<sub>4</sub> mixture in a molar ratio of 1:1 (0.5 mL, 5 mM) was added to this solution, and then an aqueous solution of L-ascorbic acid (0.05 mL, 50mM) was injected with gentle shaking. Next, this solution was heated at 50 °C for about 4 h in a conventional forced-convection drying oven. For comparison, flower-like Au-Pd NPs were also prepared. In a typical synthesis of flower-like Au-Pd NPs, a 1 mL of 30 mM aqueous solution of HAuCl<sub>4</sub>/K<sub>2</sub>PdCl<sub>4</sub> mixtures in molar ratios of 1:1 was added to 47 mL of highly purified water. To this solution, 1 mL of 100 mM L-ascorbic acid was added. After 15 sec, aqueous solution of cetyltrimethylammonium bromide (CTAB, 30 mM) was added drop-wisely with vigorous stirring, and the solution was stirred further for 5 min.

**Characterization of NPs.** The extinction spectra were recorded with a UV-vis absorption spectrometer (Agilent 8453). Scanning electron microscopy (SEM) images of the samples were taken with a field-emission scanning electron microscope (FESEM, Phillips Model XL30 S FEG). High-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) characterizations were performed with a FEI Tecnai G2 F30 Super-Twin transmission electron microscope operating at 300 kV after placing a drop of hydrosol on carbon-coated Cu grids (200 mesh). The effective electron probe size and dwell time used in HAADF-STEM-energy-dispersive X-ray spectroscopy (EDS) mapping experiments

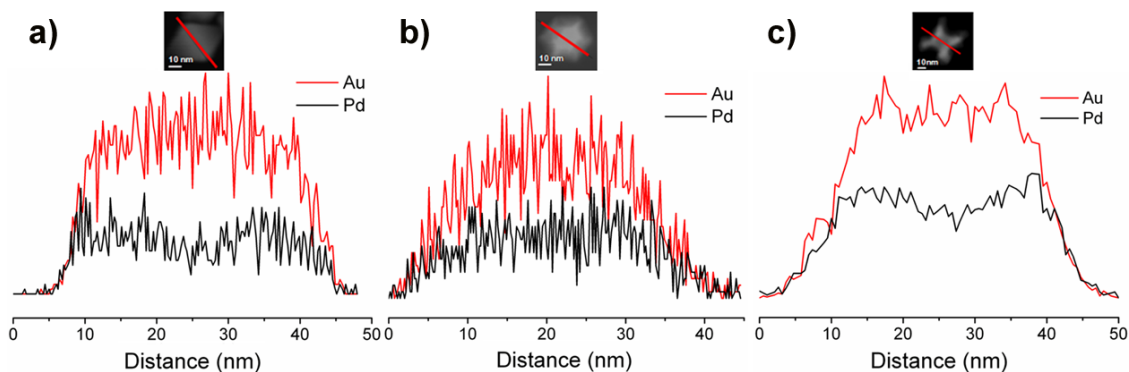
were 1.5 nm and 200 ms per pixel, respectively. The compositions of Au-Pd bimetallic NPs were determined by inductively-coupled plasma-atomic emission spectrometer (ICP-AES, OPTIMA 3300DV). Cyclic voltammetry (CV) measurements were carried out in a three-electrode cell using a CH Instrument Model 600C potentiostat. The drop-casting films of NPs on glassy carbon (GC) electrodes (diameter: 3 mm, geometric area: 0.071 cm<sup>2</sup>) served as working electrodes. Before CV measurements, a 5 μL of aqueous NPs solution which was obtained by centrifugation (0.40 mg<sub>metal</sub>/mL base on ICP-AES) was dropped on GC electrode. For Pd/C catalyst, a 5 μL of aqueous dispersion of Pd/C (0.40 mg<sub>metal</sub>/mL) was transferred onto the GC electrode. The metal loading for each sample was thus 28 μg/cm<sup>2</sup>. After the solution was dried, a 5 μL of Nafion solution (0.05%) was added, and then dried in a dry-keeper. The dried glassy carbon electrode was cleaned again by sequentially washing with ethanol and water to remove stabilizing agents on the surface of NPs. Pt wire and Ag/AgCl (in 3 M KCl) were used as the counter and reference electrodes, respectively. All cyclic voltammograms were obtained at room temperature. The electrolyte solutions were purged with high-purity N<sub>2</sub> gas before use for about 1 h.



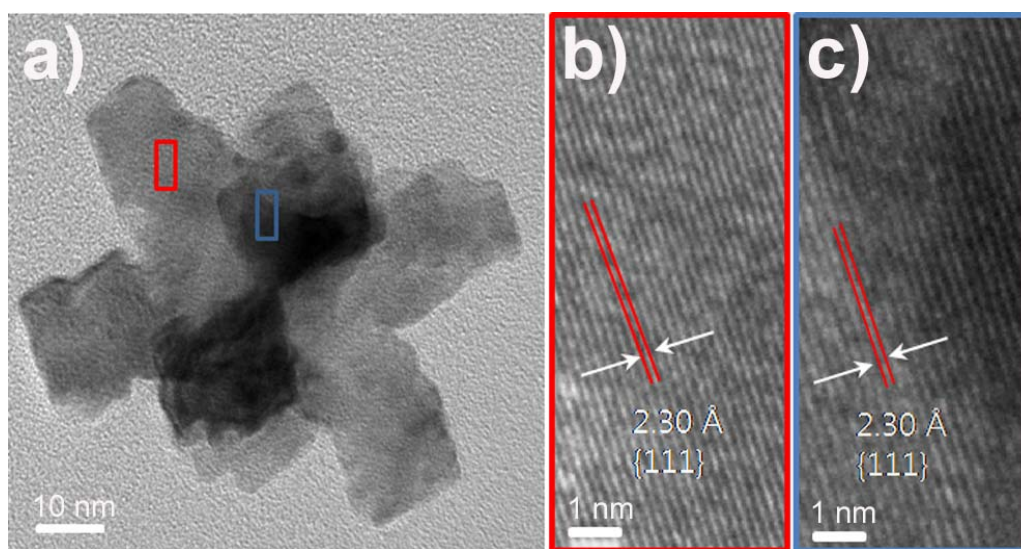
**Fig. S1.** (a) SEM and (b) TEM images of the Au-Pd octapodal NPs.



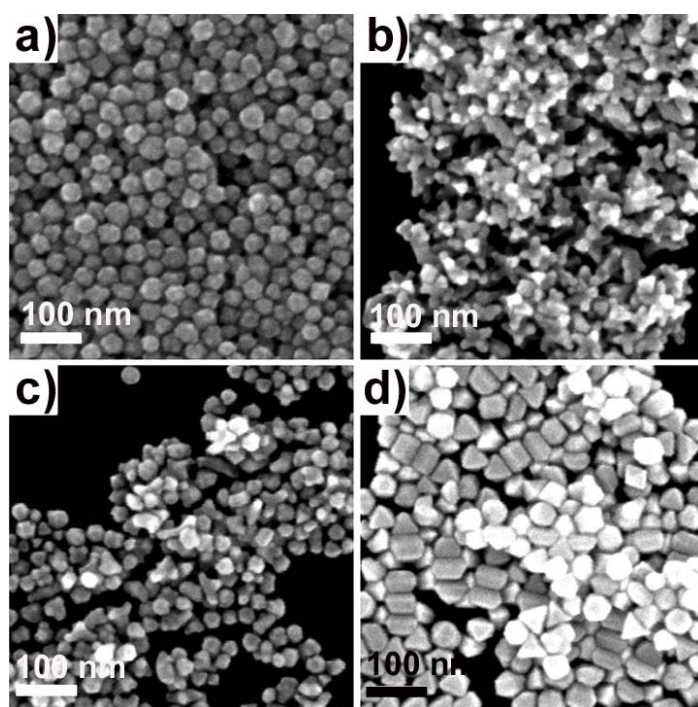
**Fig. S2.** Successive UV-vis absorption spectra of the reaction mixture (30 s interval). The inset shows the plot indicating the variation of absorbance at 230 nm vs. time. In the spectra, the surface plasmon band of Au could not be identified. This might be attributed to the fact that dipolar plasmon oscillation of Au has been strongly damped out when Pd is mixed with Au in the preparation of NPs because Pd has significantly lower conductivity at optical frequency than that of Au. This has been frequently observed in the previous works on the bimetallic Au-Pd NPs (refs.: M.-L. Wu, D.-H. Chen, T.-C. Huang, *Langmuir*, 2001, **17**, 3877; Y. W. Lee, N. H. Kim, K. Y. Lee, K. Kwon, M. Kim, S. W. Han, *J. Phys. Chem. C*, 2008, **112**, 6717). Moreover, relatively larger amount of Pd is present at the outer part of the Au-Pd octapodal NPs than at the inner part of NPs, resulting in the effective damping of Au surface plasmon band.



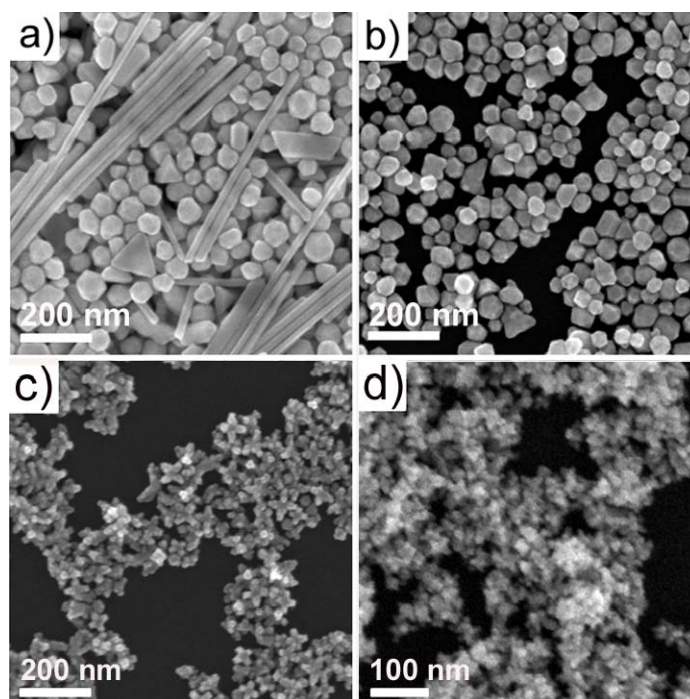
**Fig. S3.** HAADF-STEM images and cross-sectional compositional line profiles of (a) the octahedral Au-Pd NP seed, (b) the truncated Au-Pd nanooctahedron (reaction time: 20 min), and (c) the Au-Pd octapodal NP.



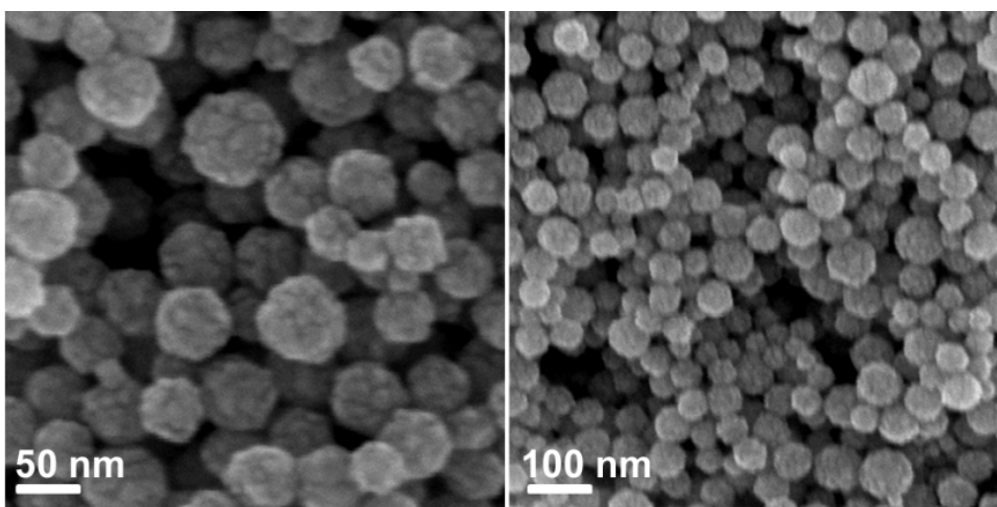
**Fig. S4.** (a) HRTEM image of an Au-Pd octapodal NP. High-magnification HRTEM images of the (b) red and (c) blue square regions in (a).



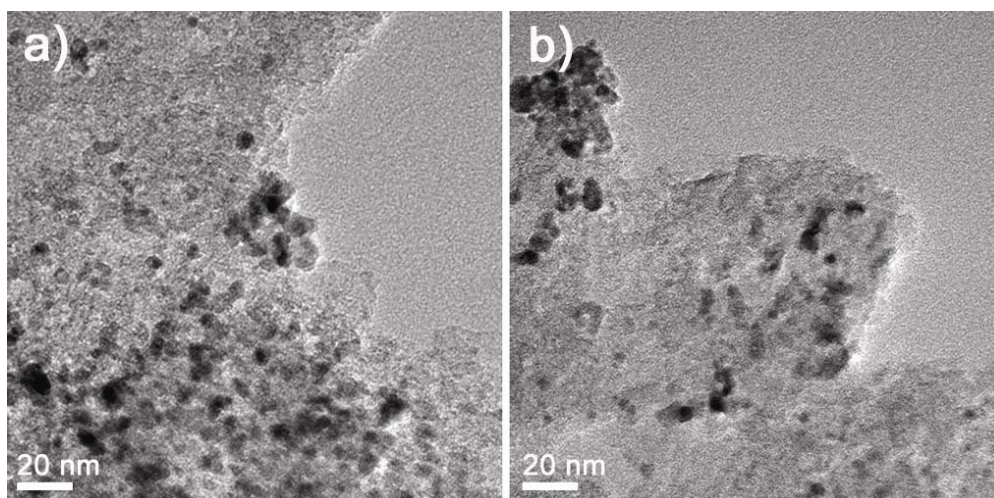
**Fig. S5.** SEM images of the NPs prepared in the presence of different concentrations of NaBr: (a) no NaBr, (b) 0.05 mM, (c) 0.2 mM, and (d) 1 mM.



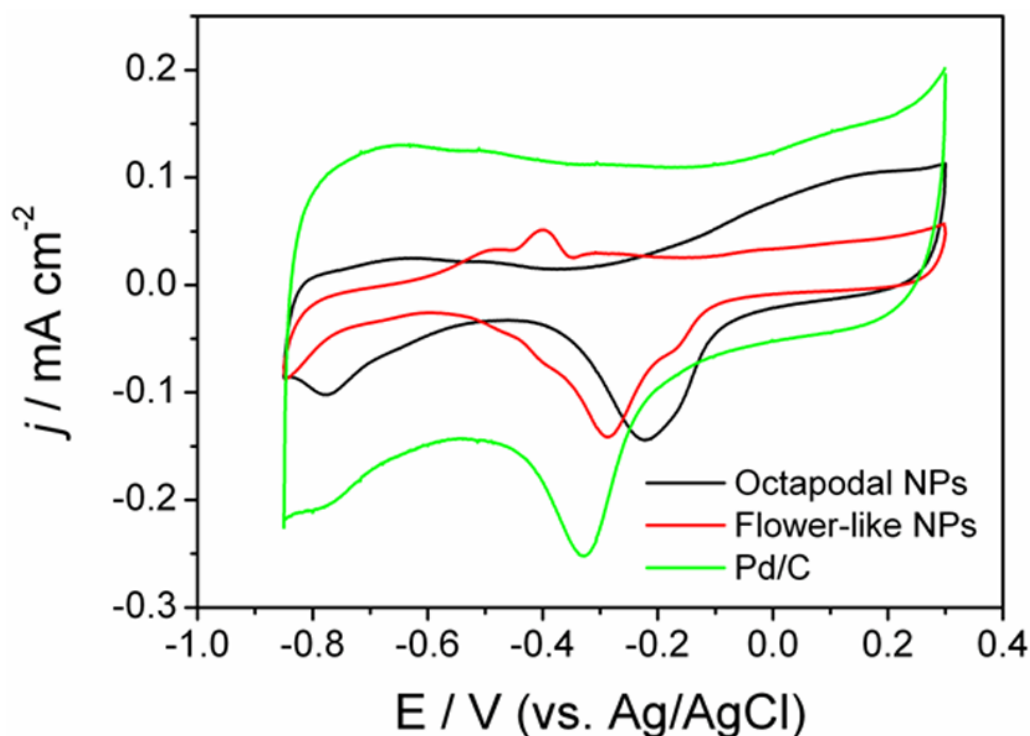
**Fig. S6.** SEM images of the NPs prepared with different concentrations of L-ascorbic acid: (a) 0.04, (b) 0.06, (c) 0.1, and (d) 0.2 mM.



**Fig. S7.** SEM images of the flower-like Au-Pd NPs. The Au/Pd ratio was estimated to be 66:34 by using ICP-AES. In the preparation of flower-like NPs, CTAB was used as a surfactant. When CTAB was employed instead of CTAC, a considerable amount of Br<sup>-</sup> ion was present from the beginning of the reaction, causing the formation of flower-like NPs instead of octapodal NPs.

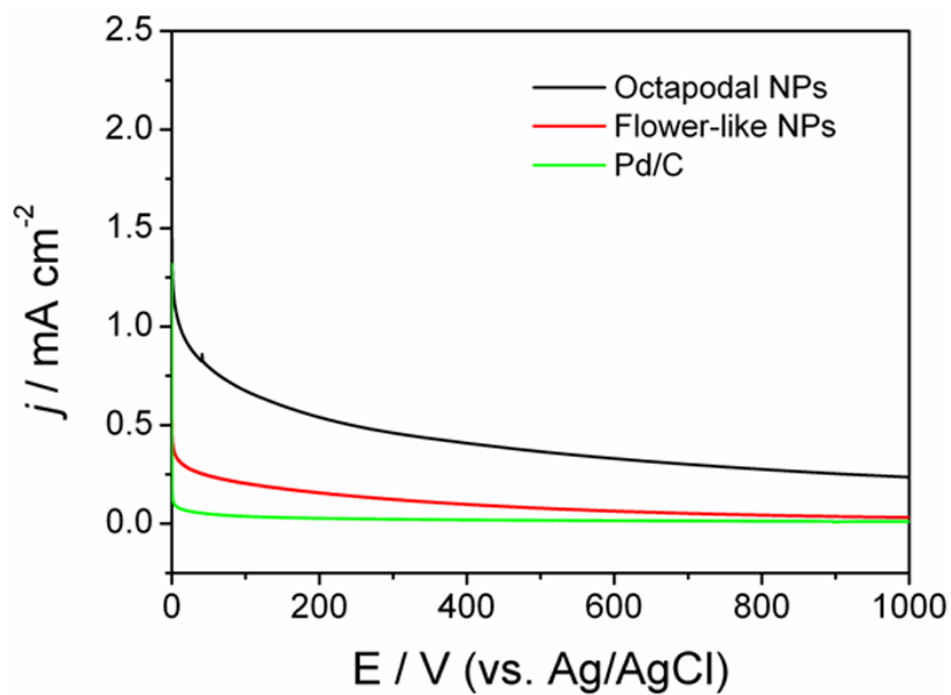


**Fig. S8.** TEM Images of the commercial Pd/C NPs. In the commercial Pd/C sample, roughly spherical NPs with an average size of  $4.74 \pm 0.9$  nm were deposited on the carbon support.



**Fig. S9.** Cyclic voltammograms (CVs) in 1 M KOH of the Au-Pd octapodal NPs, flower-like Au-Pd NPs, and Pd/C on glassy carbon electrodes. Scan rate:  $50 \text{ mV s}^{-1}$ . Current values were normalized with respect to the electrochemically active surface areas (ECSA). ECSA were estimated by the following equation;  $\text{ECSA} = Q_o/q_o$ , where  $Q_o$  is the surface charge that can be obtained from the area under the CV trace of oxygen desorption ( $-0.4 \sim -0.2 \text{ V}$ ) and  $q_o$  is the charge required for desorption of monolayer of oxygen on the Au-Pd surface ( $424 \mu\text{C/cm}^2$ , ref.: Woods, R. In *Electroanalytical Chemistry: A Series of Advances (vol.9)*; Bard, A. J., Ed.; Marcel Dekker: New York, 1974; pp 1-162). Specific ECSA of each catalyst can be estimated to be 43, 45, and  $37 \text{ m}^2/\text{g}_{\text{Pd}}$  for Au-Pd octapodal NPs, flower-like Au-Pd NPs, and Pd/C, respectively.





**Fig. S10.** Chronoamperometric curves for the Au-Pd octapodal NPs, flower-like Au-Pd NPs, and Pd/C on glassy carbon electrodes in 1 M KOH + 0.1 M ethanol at -0.2 V vs. Ag/AgCl. Current values were normalized with respect to the ECSA.