Electronic Supplementary Information

Gold nanobipyramid doped with Au/Pd alloyed nanoclusters for high efficiency ethanol electrooxidation

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Supplementary figures

\textbf{Fig. S1} (a) TEM image and (b) corresponding optical spectrum of the AuBPs (Scale bars: 100 nm)
Fig. S2  (a) UV-vis-NIR absorption spectra of AuBPs@Au$_x$Pd$_{1-x}$ nanostructures with varying Au/Pd proportion in the alloy shell. TEM images of the nanostructures obtained under the addition of varying H$_2$PdCl$_4$ of 2mM (b), 1.5mM (c), 1mM (d) and 0.25mM (e) obtained at 65°C with respective addition of 0.2 mL HAuCl$_4$ and 0.2 mL H$_2$PdCl$_4$ (Scale bars: 100 nm).

Fig. S3  Absorption spectra of 4-NP reduced by NaBH$_4$ in the presence of AuBPs@Au$_x$Pd$_{1-x}$. (a) AuBPs@Au$_0$Pd$_1$, (b) AuBPs@Au$_{0.2}$Pd$_{0.8}$, (c) AuBPs@Au$_{0.4}$Pd$_{0.6}$, (d) AuBPs@Au$_{0.6}$Pd$_{0.4}$, (e) AuBPs@Au$_{0.8}$Pd$_{0.2}$. 
Fig. S4  (a) Cyclic voltammograms for the AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts in N\textsubscript{2}-saturated KOH (0.3M) solution at a scan rate of 50 mV s\textsuperscript{-1}. (b) CV curves for the AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts in N\textsubscript{2}-saturated KOH (0.3M) solution containing ethanol (0.5M) at a scan rate of 50 mV s\textsuperscript{-1}. (c) CV curves by the ECSAs. (d) Mass activities (green) and specific activities (orange) of AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts from measurement. Note: AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts were obtained with addition of 0.2 mL HAuCl\textsubscript{4} and 0.2 mL H\textsubscript{2}PdCl\textsubscript{4}. 
**Fig. S5**  (a) specific activity of the AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanostructures obtained at 65°C with addition of HAuCl\textsubscript{4}/H\textsubscript{2}PdCl\textsubscript{4} precursor (0.2 mL and 0.4 mL). (b) Cycling measurement of the AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts obtained at 65°C with addition of HAuCl\textsubscript{4}/H\textsubscript{2}PdCl\textsubscript{4} precursor (0.2 mL and 0.4 mL). (c) specific activity of the AuBPs@Au\textsubscript{0.8}Pd\textsubscript{0.2} nanocatalysts obtained at 65°C with addition of different volume of HAuCl\textsubscript{4}/H\textsubscript{2}PdCl\textsubscript{4} precursor (0.2 mL and 0.4 mL).

**Fig. S6**  (a) Cycling measurement for AuBPs@Au\textsubscript{x}Pd\textsubscript{1-x} nanocatalysts with addition of 0.2 mL HAuCl\textsubscript{4}/H\textsubscript{2}PdCl\textsubscript{4} precursor. (b) Chronoamperometric curves in mixture solution of KOH (0.3M) and ethanol (0.5M) for 1000s at -0.23V versus Ag/AgCl potential.
**Table S1** The AuBPs@Au$_x$Pd$_{1-x}$ with different concentration for Au and Pd precursors

| Sample          | Concentration of H$_2$PdCl$_4$ (mM) | Concentration of HAuCl$_4$ (mM) | Amount of H$_2$PdCl$_4$ (mL) | Amount of HAuCl$_4$ (mL) |
|-----------------|------------------------------------|---------------------------------|------------------------------|--------------------------|
| AuBPs@Au$_{0.8}$Pd$_{0.2}$ | 1                                  | 0.25                            | 0.4                          | 0.4                      |
| AuBPs@Au$_{0.6}$Pd$_{0.4}$ | 1                                  | 1.5                             | 0.4                          | 0.4                      |
| AuBPs@Au$_{0.4}$Pd$_{0.6}$ | 1.5                                | 1                               | 0.4                          | 0.4                      |
| AuBPs@Au$_{0.2}$Pd$_{0.8}$ | 0.5                                | 2                               | 0.4                          | 0.4                      |
| AuBPs@Au$_{0}$Pd$_1$     | 2.5                                | 0                               | 0.4                          | 0.4                      |

**Table S2** Comparison of the AuBPs@Au$_x$Pd$_{1-x}$ with different mole fractions for Au and Pd precursors.

| Sample          | Pd amount of substance concentration (mg/ L) | Pd mass percent | Au/Pd atomic ratio |
|-----------------|----------------------------------------------|-----------------|--------------------|
| AuBPs@Au$_{0.8}$Pd$_{0.2}$ | 0.32                                         | 40.5%           | 44.2:55.8          |
| AuBPs@Au$_{0.6}$Pd$_{0.4}$ | 0.50                                         | 50.0%           | 35.0:65.0          |
| AuBPs@Au$_{0.4}$Pd$_{0.6}$ | 0.96                                         | 65.3%           | 25.5:74.5          |
| AuBPs@Au$_{0.2}$Pd$_{0.8}$ | 1.92                                         | 80.3%           | 11.6:83.4          |
| AuBPs@Au$_{0}$Pd$_1$     | 3.02                                         | 82.9%           | 9.9:90.1           |