Electronic Supplementary Information

Gold core@silver semishell Janus nanoparticles prepared by interfacial etching

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Figure S1. Fractions of nanoparticles exhibiting a symmetrical and asymmetrical electron density contrast before and after interfacial chemical etching. Data are obtained by statistical analysis of Figure 1.



Figure S2. XPS spectra of (top) Ag3d and (bottom) Au4f electrons of Ag@Au core-shell nanoparticles. The Ag3d doublet is at 368.0 and 374.1 eV, whereas the Au4f at 83.4 and 87.0 eV. These are consistent with metallic Ag and Au, respectively. Based on the integrated peak areas, the Ag:Au atomic ratio was estimated to be 1.61:1.



Figure S3. Representative TEM micrographs of Ag@Au core-shell nanoparticles. Scale bars are (left) 20 nm and (right) 5 nm.



Figure S4. UV-vis spectra of (top) Ag and (bottom) Au nanoparticles at different time intervals after the addition of 20 mM H_2O_2 + NH₃. Insets show the variation of the respective surface plasmon resonance (SPR) intensity with reaction time. One can see that the SPR intensity of the Ag nanoparticles diminished rather quickly, due to effective etching of the Ag nanoparticles by H_2O_2 + NH₃, whereas the SPR intensity of the gold nanoparticles remained largely unchanged, because Au nanoparticles were chemically inert against the H_2O_2 + NH₃ etchants.



Figure S5. RRDE voltammograms of a glassy carbon electrode modified with (top) Ag@Au and (bottom) Au@Ag core-shell nanoparticles in oxygen-saturated 0.1 M NaOH at various rotation rates (specified in figure legends). Catalyst loadings were both 10 μg.



Figure S6. Cyclic voltammograms of a glassy carbon electrode modified with Ag@Au core-shell, Au@Ag core-shell and Au@Ag semishell nanoparticles in 0.05 mM Pb(OAc)₂ + 0.1 M HClO₄ at the sweep rate of 100 mV/s. Catalyst loadings were both 10 μ g. The effective electrochemical surface areas as summarized below were determined by oxygen adsorption on Ag (210 μ C/cm²) and Au (390 μ C/cm²), in which the Ag oxidation peaks and gold oxide reduction peaks were used to obtain the amount of charge.^{1,2}

Samples	Ag@Au core-shell	Au@Ag core-shell	Au@Ag semishell
ECSA (cm ²)	0.70	0.86	1.52

- (1) Trasatti, S.; Petrii, O. A. J Electroanal Chem 1992, 327, 353.
- (2) Motheo, A. J.; Machado, S. A. S.; Vankampen, M. H.; Santos, J. R. J Brazil Chem Soc 1993, 4, 122.