**Supporting Information**

# Co-sputtered CuPt/Ag alloy nanoparticles and comparative catalytic performance of mono-, bi-, and tri-metallic nanoparticles in oxygen reduction reaction

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M KOH: (a, d) CV curves, (b, e) LSV curves, and (c, f) K-L plots.

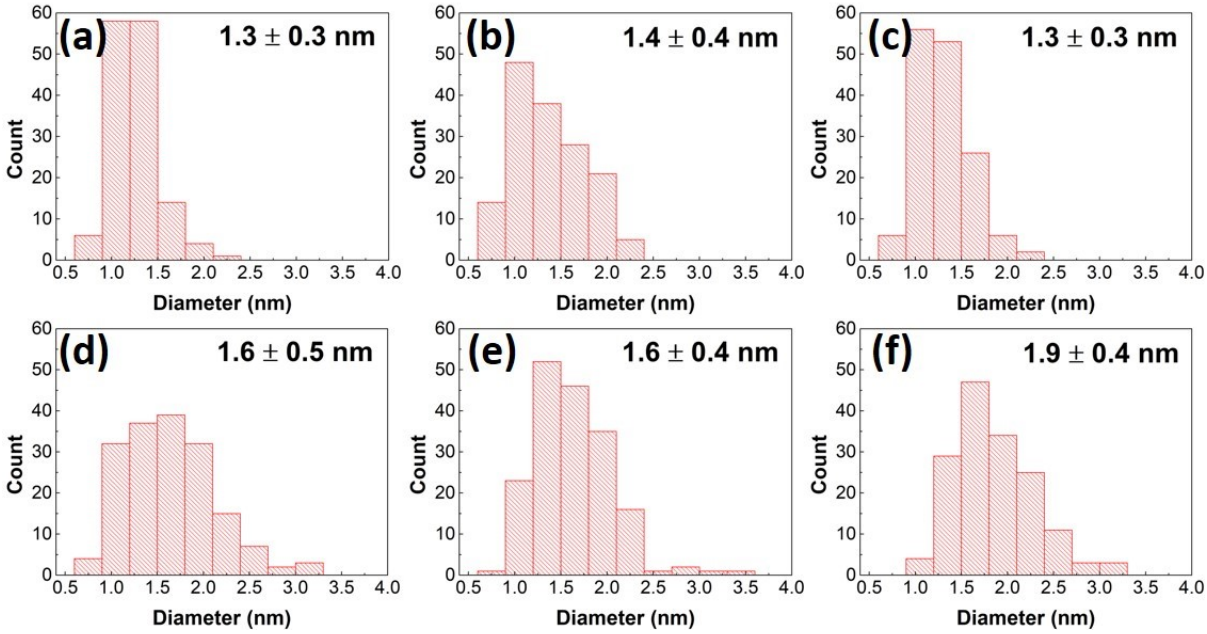


**Fig. S1.** Size distributions and (inset) average sizes of Ag/Cu/Pt NPs sputtered onto PEG for 30 min: (a) (CuPt)50Ag0, 1.3 ± 0.3 nm; (b) (CuPt)50Ag10, 1.4 ± 0.4 nm; (c) (CuPt)50Ag20, 1.3 ± 0.3 nm; (d) (CuPt)50Ag30, 1.6 ± 0.5 nm; (e) (CuPt)50Ag40, 1.6 ± 0.4 nm; and (f) (CuPt)50Ag50, 1.9 ± 0.4 nm.

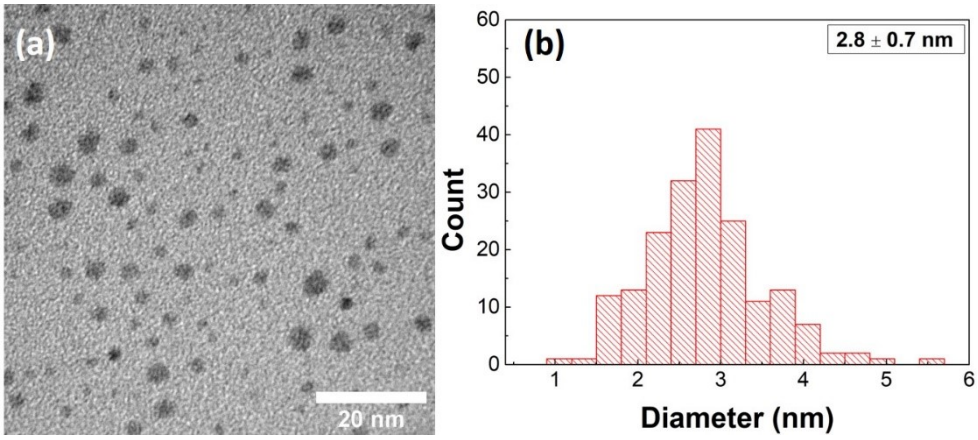


**Fig. S2.** (a) TEM image and (b) size distribution of sample (CuPt)0Ag50 sputtered onto PEG. The average size of this sample is 2.8 ± 0.7 nm.

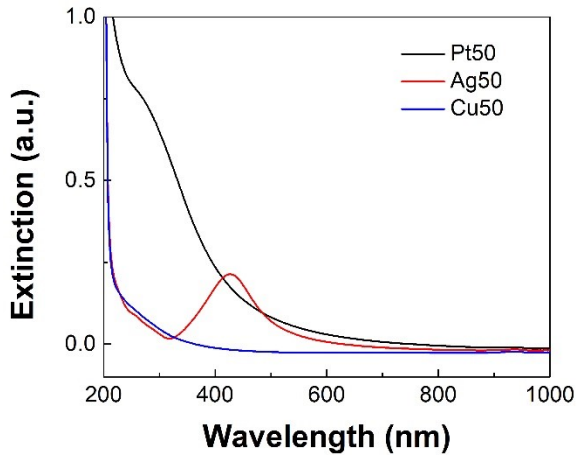


**Fig. S3.** UV-Vis spectra of pure Pt, Ag and Cu NPs sputtered onto PEG with 50 mA sputtering current.

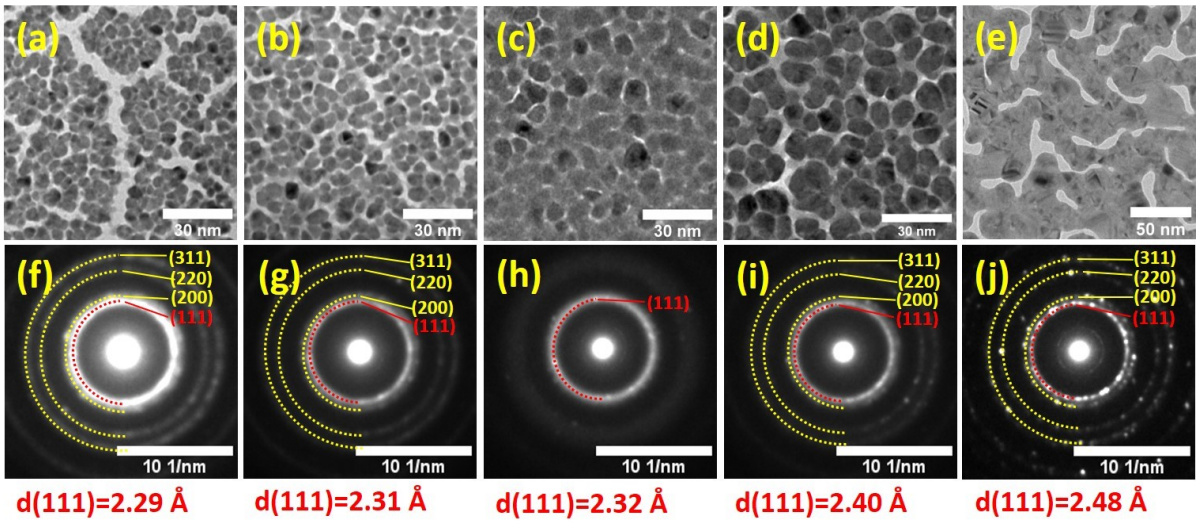


**Fig. S4.** (a-e) TEM images and (f-j) SAED results of the samples co-sputtered on the TEM grids for 10 min: (a,f) (CuPt)50Ag0, (b,g) (CuPt)50Ag10, (c,h) (CuPt)50Ag30, (d,i) (CuPt)50Ag50, and (e,j) (CuPt)0Ag50. The lattice spacings of (111) planes of the corresponding samples are 2.29 Å, 2.31 Å, 2.32 Å, 2.40 Å, and 2.48 Å, as written below the SAED patterns.

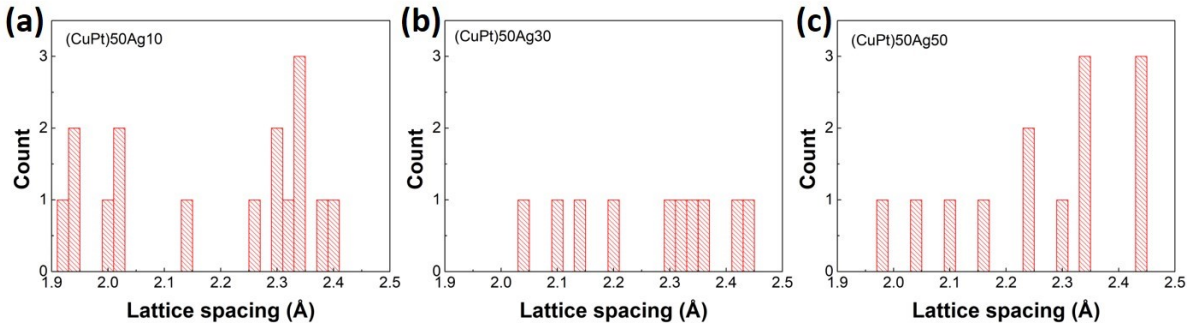


**Fig. S5.** Lattice spacing distributions of the NPs co-sputtered onto PEG: (a) (CuPt)50Ag10, (b) (CuPt)50Ag30, and (c) (CuPt)50Ag50.

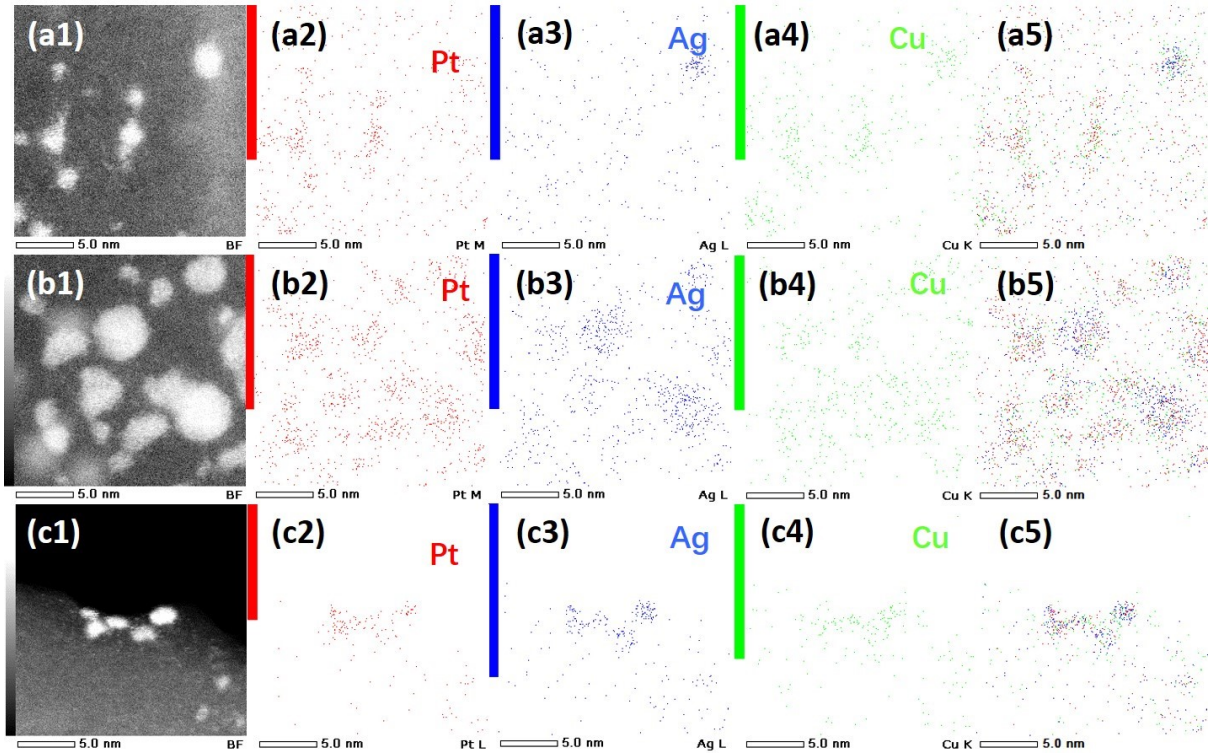


**Fig. S6.** STEM-EDS mapping of (a1-a5) (CuPt)50Ag10, (b1-b5) (CuPt)50Ag30, and (c1-c5) (CuPt)50Ag50. Pt M for (a2) and (b2), Pt L for (c2), Ag L and Cu K. (a5, b5, c5) are overlapping images of Cu, Pt and Ag.

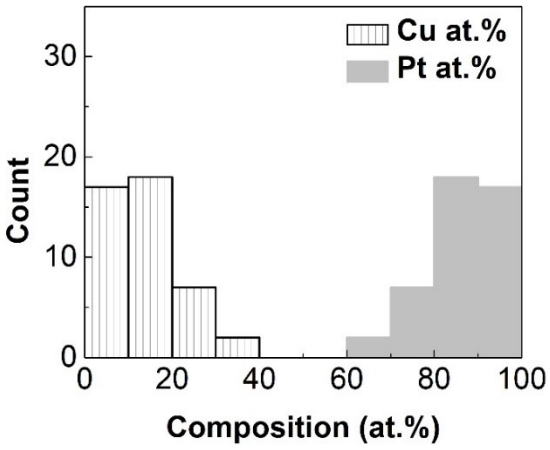


**Fig. S7.** Composition distribution of sample (CuPt)50 sputtered onto PEG using Cu/Pt alloy target. The average compositions of Pt and Cu in the single particles of this sample are 87.2 ± 9.4 and 13.7 ± 9.1, respectively.

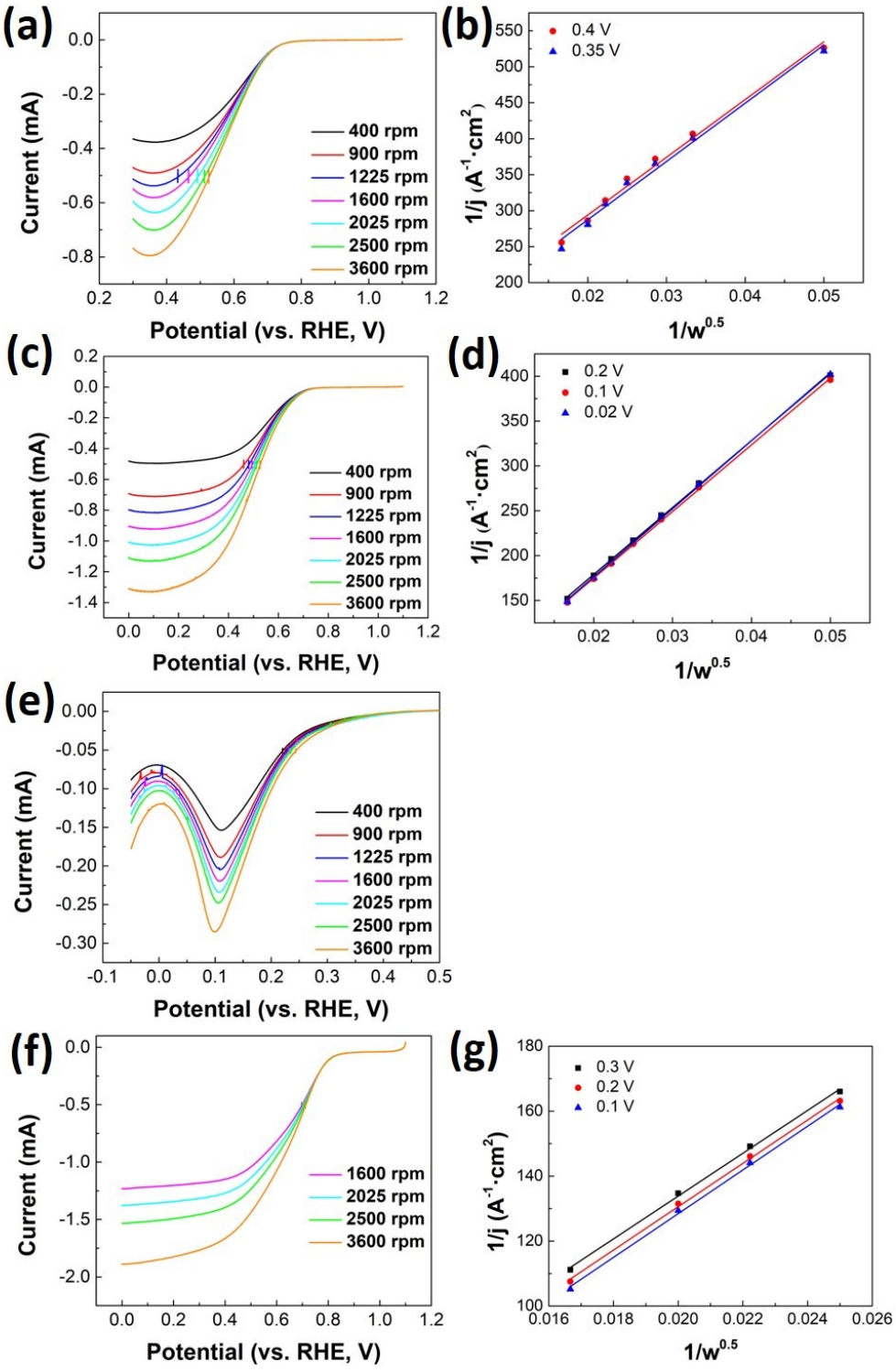


**Fig. S8.** LSV curves at different rotation speeds for ORR and K-L plots of: (a,b) Ag50Pt50/C, (c,d) Pt50/C, (e) (CuPt)50/C, and (f,g) Pt/C reference catalysts.

**Table S1.** Electron transfer number (n) estimated at certain potential from LSV in Fig. S6

| Sample | (CuPt)50Ag30/C | | Ag50Pt50/C | | Pt50/C | | | Pt/C reference | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Potential (V) | 0.2 | 0.1 | 0.4 | 0.35 | 0.2 | 0.1 | 0.02 | 0.3 | 0.2 | 0.1 |
| n | 2.8 | 2.9 | 3.3 | 3.3 | 3.6 | 3.6 | 3.5 | 4.0 | 4.0 | 3.9 |
| Average | 2.9 | | 3.3 | | 3.6 | | | 4.0 | | |

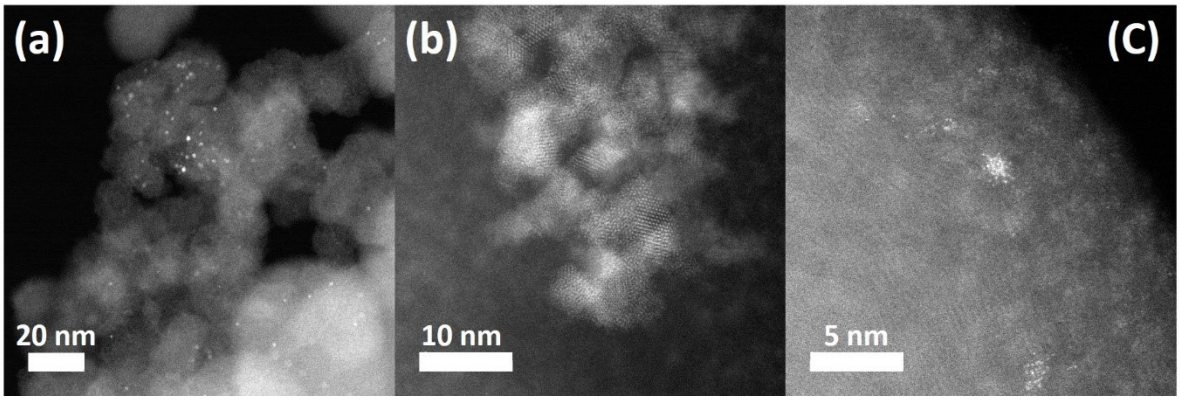


**Fig. S9.** STEM-HAADF images of (a) (CuPt)50Ag0/C before electrochemical test and (b,c) (CuPt)50Ag0/C after electrochemical test.

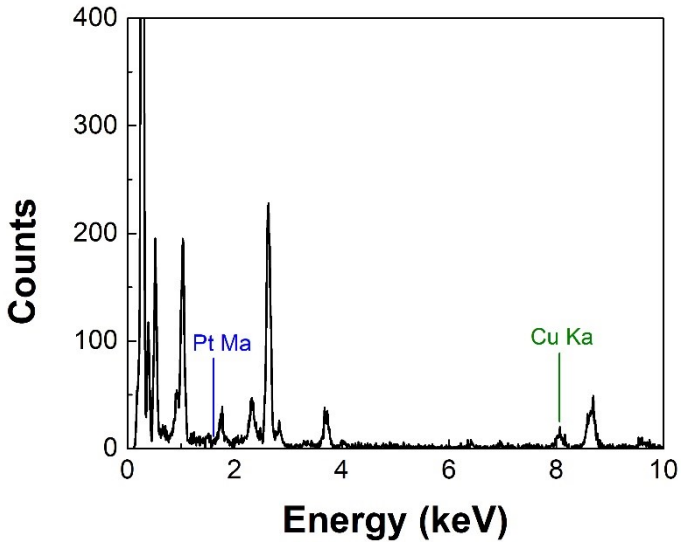


**Fig. S10.** STEM-EDS area analysis spectrum of sample (CuPt)50Ag0, measured after electrochemical test. There is small amount of Cu remained, but Pt was not detected.

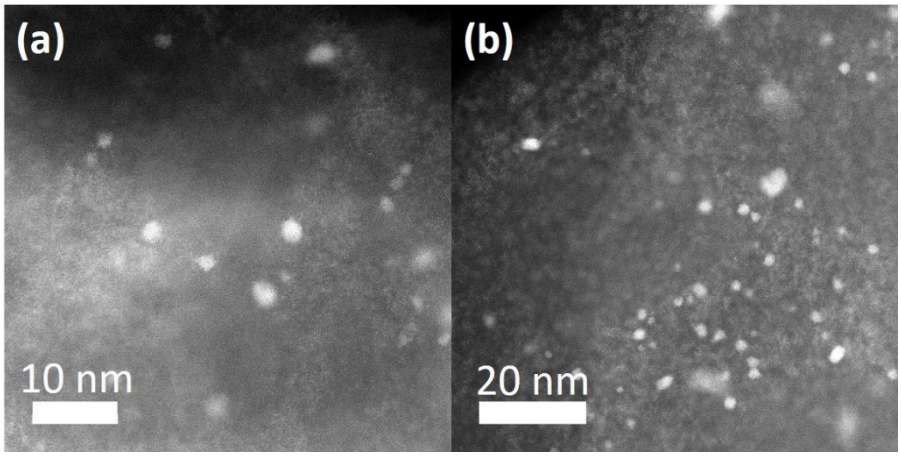


**Fig. S11.** STEM-HAADF images of sample (CuPt)50Ag30/C after electrochemical test.

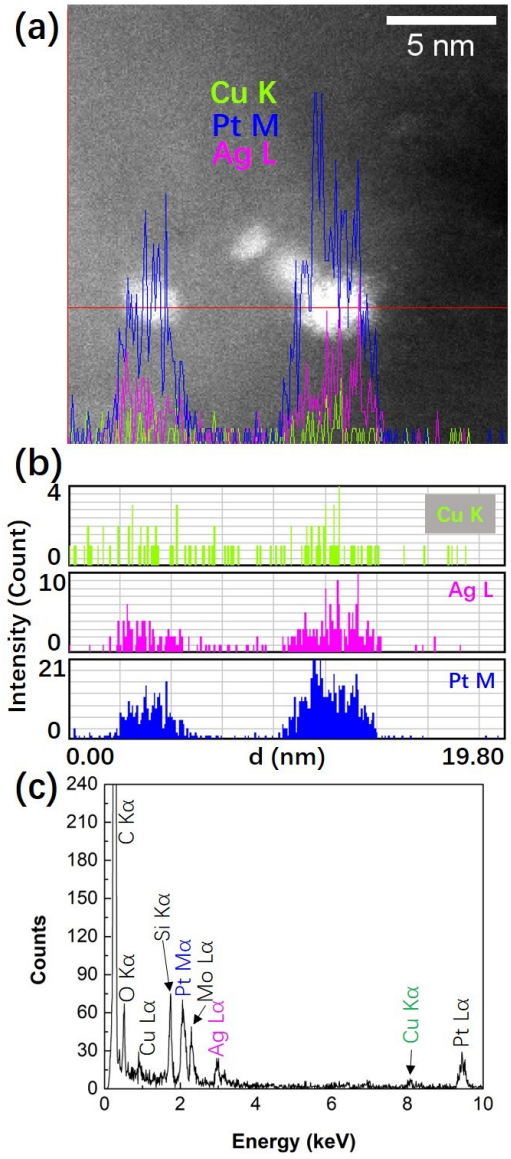


**Fig. S12.** (a,b) EDS elemental line profiles of sample (CuPt)50Ag30/C before electrochemical test at the positions marked by red line crossing the NPs in (a) the HAADF image. (c) EDS spectrum of the line profile shown in (a,b).

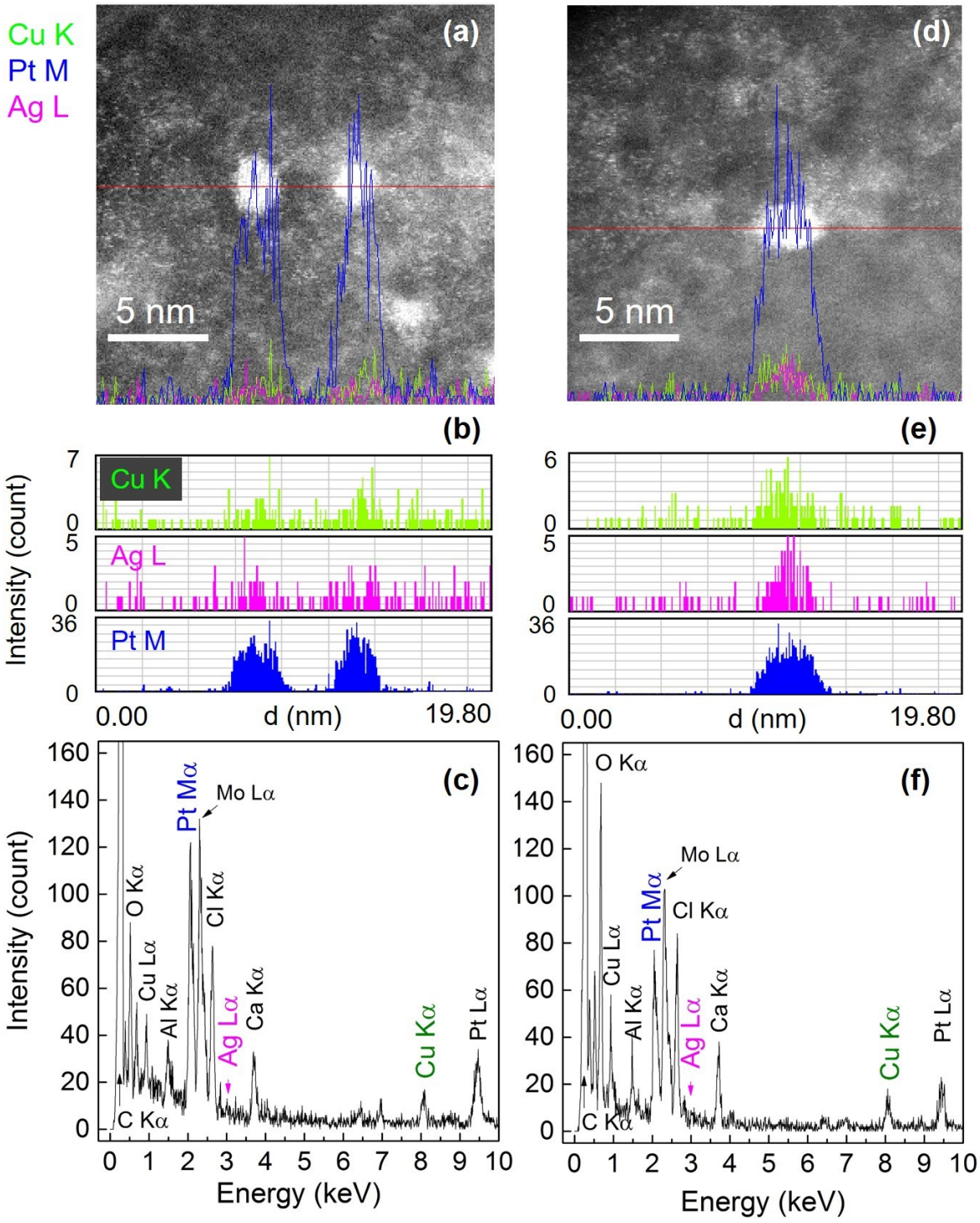


**Fig. S13.** EDS elemental line profiles of sample (CuPt)50Ag30/C after electrochemical test for (a,b) two NPs and (d,e) one NP at the positions marked by red lines crossing the NPs in (a, d) HAADF images. EDS spectra corresponding to the line profile of (c) two NPs shown in (a) and (f) one NP shown in (d).

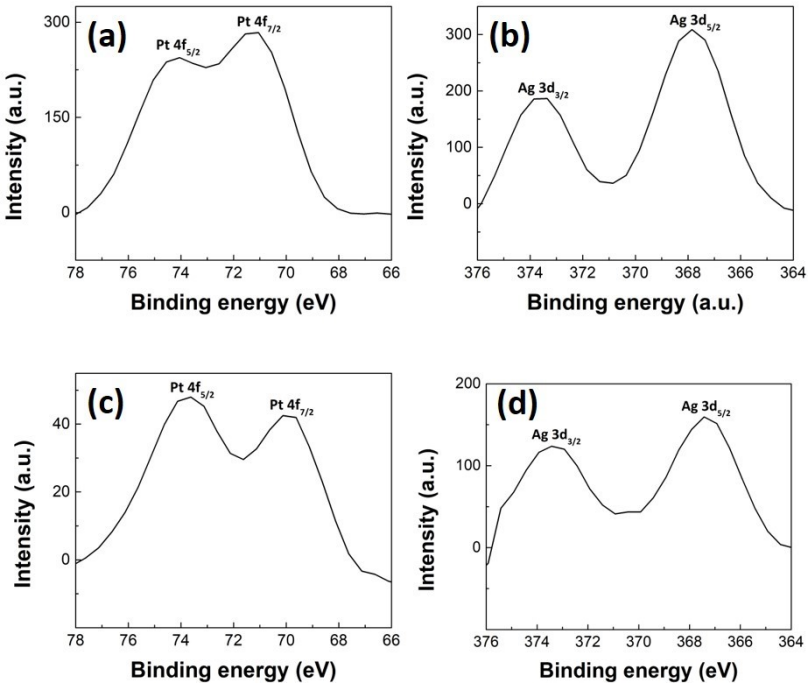


**Fig. S14.** XPS spectra of sample Ag50Pt50/C before (a, b) and after (c, d) electrochemical tests: (a, c) Pt 4f; (b, d) Ag 3d.

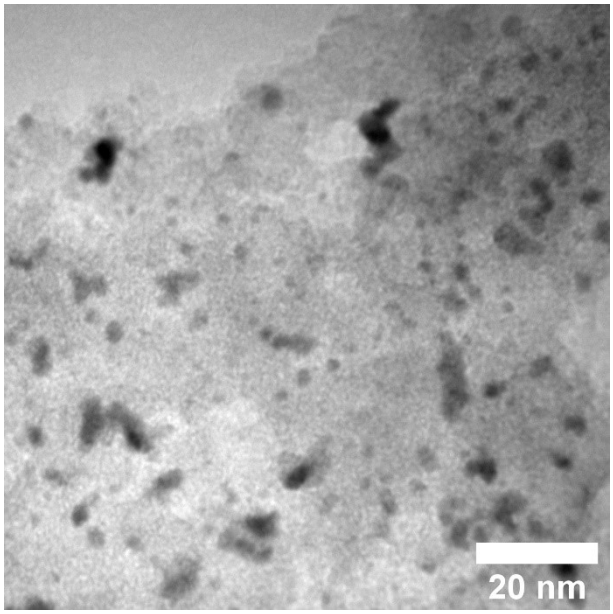


**Fig. S15.** TEM image of commercial Pt/C reference catalyst. The average particle size is 3.5 ± 1.4 nm.

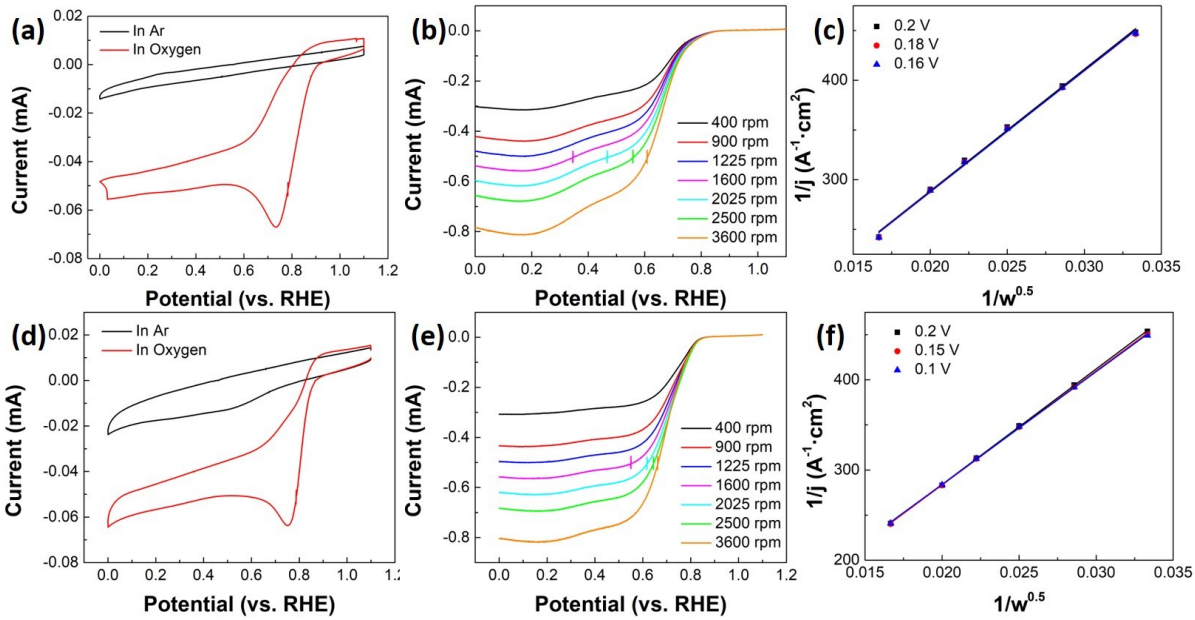


**Fig. S16.** Electrochemical test results of Ag50Pt50/C (a, b, c) and (CuPt)50Ag0 (d, e, f) in 1 M KOH: (a, d) CV curves, (b, e) LSV curves, and (c, f) K-L plots.

**The Koutecký–Levich equation and parameters**

In a rotating disc electrode (RDE) setup, the Koutecký–Levich equation[1] can be expressed as:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B_L \omega^{\frac{1}{2}}}$$

where j is the measured current, $j_k$ is the kinetic current from redox reactions, ω is the rotation speed of the RDE, and $B_L$ is the Levich constant. This form is valid for the diffusion limited region of the linear scan voltammetry (LSV) where kinetic current depends on the applied potential and measured current is only a function of ω.

By plotting 1/j against $1/\omega^{1/2}$, the gradient of the linear plots, $1/B_L$ can be extracted and the electron transfer number can be calculated according to Levich equation.

$$B_L = 0.2nFD_0^{\frac{2}{3}}\upsilon^{-\frac{1}{6}}C_0$$

(B is expressed for ω in rpm)

The parameters used in the calculations were applied by Zhang et al.[2]

F = Faraday constant = 96485 C $mol^{-1}$
D = diffusion coefficient = 1.93e-5 $cm^2$ $s^{-1}$
v = kinematic viscosity = 0.01 $cm^2$ $s^{-1}$
C = concentration of oxygen = 1.26e-3 mol $L^{-1}$

References


1. B. G. Levič, "Physicochemical Hydrodynamics", Prentice-Hall, 1962.
2. L. Zhang, M. Wei, S, Wang, Z. Li, L. Ding, and H. Wang, Highly Stable PtP Alloy Nanotube Arrays Catalyst for Oxygen Reduction Reaction in Acidic Medium. *Chem. Sci.* **2015**, *6,* 3211-3216