Supporting information

Monodispersed Sub-5.0 nm PtCu Nanoalloy as Enhanced Bifunctional Electrocatalyst for Oxygen Reduction Reaction and Ethanol Oxidation Reaction

Taiyang Liu,[a] Kai Wang,[b] Qiang Yuan,*[a] Zebin Shen,[c] Ye wang,[c] Qinghong Zhang,[c] and Xun Wang*[b]

a Department of Chemistry, College of Chemistry and Chemical Engineering, Guizhou University, Guiyang, Guizhou province 550025, P. R. China,

b Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.

c State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, P. R. China
*E-mail: qyuan@gzu.edu.cn; wangxun@mail.tsinghua.edu.cn

Experimental section:

Chemicals: Platinum(II) acetylacetonate ($Pt(acac)_2$, 97%), copper(II) acetylacetonate ($Cu(acac)_2$, 97%) were purchased from Sigma-Aldrich. Polyvinyl Pyrrolidone (PVP-8000), Hydroxylamine hydrochloride (99%), Sodium iodide (NaI, 99.5%) and N,N-Dimethylformamide (DMF, 99.8%) were purchased from Aladdin. Pt/C catalyst was purchased from Johnson Matthey. Chemicals were used as received without further purification. The super pure water (18.25MΩ cm) was used as solvent.

Synthesis of 5nm $Pt_{68}Cu_{32}$ nanoparticles

In a typical synthesis nanoparticles: 12 mg of $Pt(acac)_2$, 15.8 mg of $Cu(acac)_2$, 99.2 mg of NaI and 30 mg of Polyvinyl Pyrrolidone (PVP-8000) were added into 8 mL DMF solution and stirred for 15 minutes. Then added 70 mg of Hydroxylamine hydrochloride into the mixed solution and stirred for 5 minutes. The resulting homogeneous mixture was transferred to a 15 mL Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 130°C for 8 hours before it was cooled to room temperature. The products were separated three times by centrifugation and washing cycles at 10,000 rpm for 30 minutes with ethanol. The collected product was redispersed in ethanol. By adjusting the ratio of Pt ($Pt(acac)_2$, 12 mg) and Cu ($Cu(acac)_2$, 7.9 mg) precursors, the other $Pt_{85}Cu_{15}$ nanocrystals can be obtained.

Characterizations: The size and morphology of the nanocrystals were determined by a HITACHI H-7700 transmission electron microscope (TEM) at 100 kV, and a FEI Tecnai G2 F20 S-Twin high- resolution transmission electron microscope (HRTEM) equipped with energy dispersive spectrometer (EDS) analyses at 200 kV. The high-angle annular dark-field scanning TEM (HAADF-STEM) was determined by a FEI Tecnai G2 F20 S-Twin HRTEM operating at 200 kV. The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ=1.5418 Å) with graphite monochromator (40 KV, 40 mA). X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI

Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, USA), using Al K_α X-ray radiation (1486.6 eV) for excitation. Binding energies were corrected from charge effects by reference to the C1s peak of carbon at 284.6 eV. The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of samples was performed on IRIS Intrepid II XSP (ThermoFisher).

Characterization of electrocatalytic activity:

Electrochemical experiments were carried out in a standard three-electrode cell at room temperature controlled by CHI 760E electrochemical analyzer (CHI Instruments, Shanghai, Chenghua Co., Ltd.). The super pure water (18.25 MΩ cm) purified through a Milli-Q Lab system (Nihon Millipore Ltd.) was used as solvent. The working electrode is a glassy carbon (GC, Φ=5 mm) electrode embedded into a Teflon holder. Prior to the electrochemical test, the GC electrode was mechanically polished using successively alumina powder of size 1.5, 1.0 and 0.05 μm. It was then cleaned in an ultrasonic bath. Then took a certain amount of PtCu and Pt/C catalyst powder and dispersed with super pure water under ultrasonic bath (The concentration of the $Pt_{85}Cu_{15}$, $Pt_{68}Cu_{32}$ and Pt/C is 0.6 μg/μl, 0.4 μg/μl and 1.0μg/μl Pt, respectively.). The suspension of nanocrystals was spread on the GC electrode (the loading mass of the $Pt_{85}Cu_{15}$, $Pt_{68}Cu_{32}$ and Pt/C is 6.6μg, 6.2μg and 4.0μg Pt, respectively.). As soon as the electrode was dried under infrared lamp, 4 μL Nafion diluents (1 wt.% Nafion® solution) was coated onto the electrode surface. A Ag/AgCl electrode and a platinum foil were used as the reference and counter electrode, respectively.

The cyclic voltammograms (CVs) were obtained in nitrogen-saturated 0.1M $HClO_4$ solution, and the potential was scanned from −0.25 to 0.9 V (Ag/AgCl) at a scan rate of 50 mV s^{-1}. The scan was repeated several times to ensure that a stable cyclic voltammetry (CV) was obtained.

Voltammogram measurements for ethanol oxidation were carried out in nitrogen-saturated 0.5 M KOH+0.5 M ethanol solution, and the potential was scanned from -0.9 to 0.4 V (Ag/AgCl) at a scan rate of 50 mV s^{-1}.

Electrochemical experiments of ORR were performed using a glassy carbon rotating disk electrode (RDE) (PINE, USA). The ORR measurements were conducted at room temperature in 0.1 M KOH solutions after a flow of O_2 an half hour until saturated, then using a glassy carbon rotating disk electrode (RDE) at a rotation rate of 1600 rpm, and the potential was scanned from 0.15 to 1.05 V (vs. RHE) at a scan rate of 10 mV s^{-1} and were corrected for capacitive currents in N_2 saturation. The kinetic current (i_k) can be derived from the experimental data using the well-known Koutecky-Levich equation: ($1/i = 1/i_k + 1/i_L$) at 0.90 V, where i_L and i are the diffusion limiting current and measured current (0.90V) at kinetic-diffusion control region, respectively.

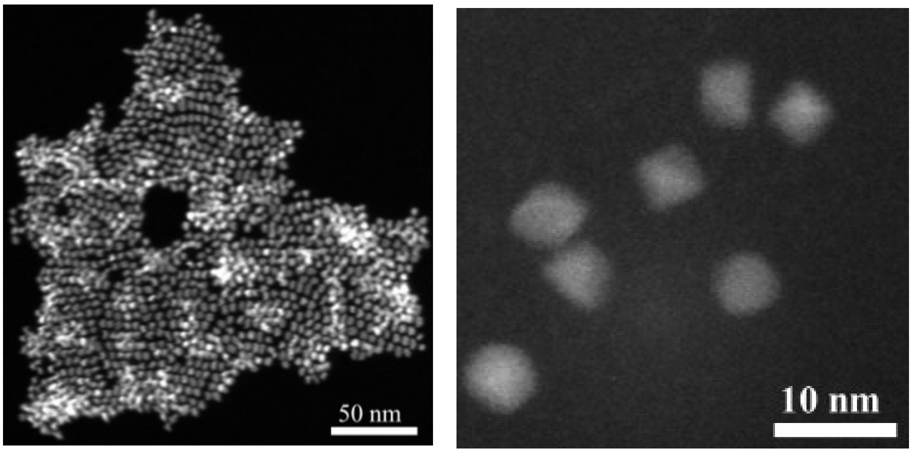

Fig. S1 HAADF-STEM images of the as-synthesized $Pt_{68}Cu_{32}$ nanoalloys.

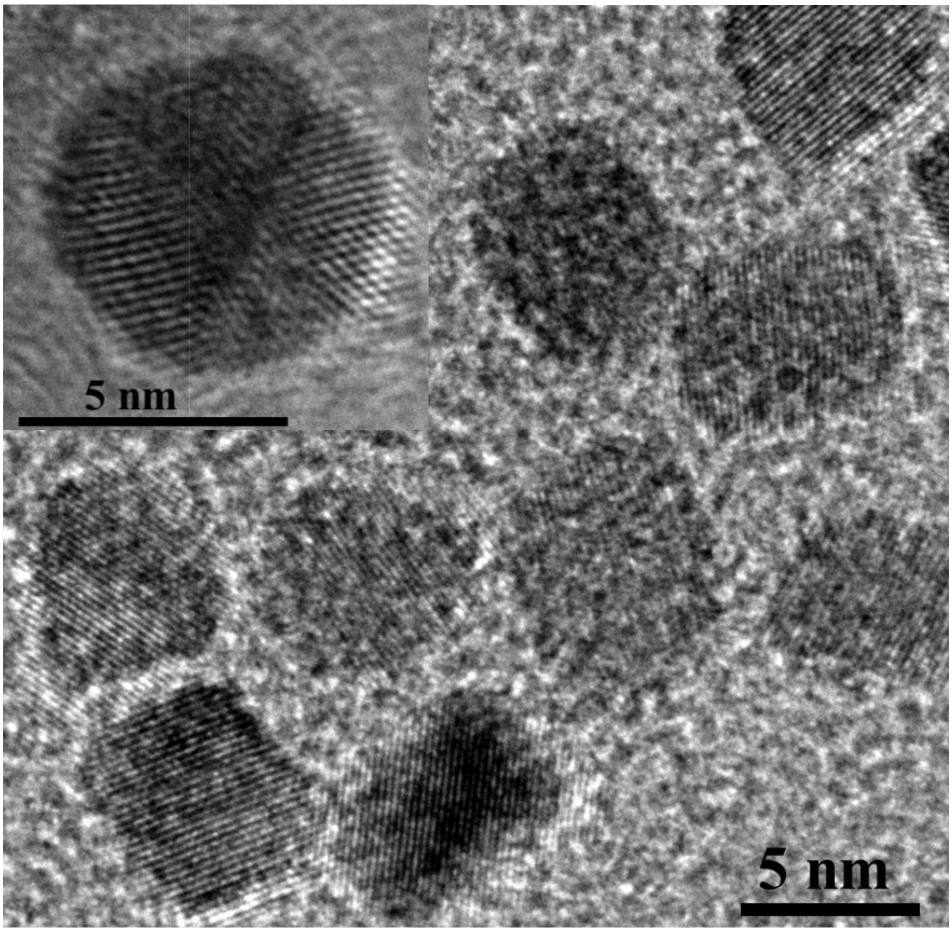

Fig. S2 HRTEM images of the as-synthesized $Pt_{68}Cu_{32}$ nanoalloys.

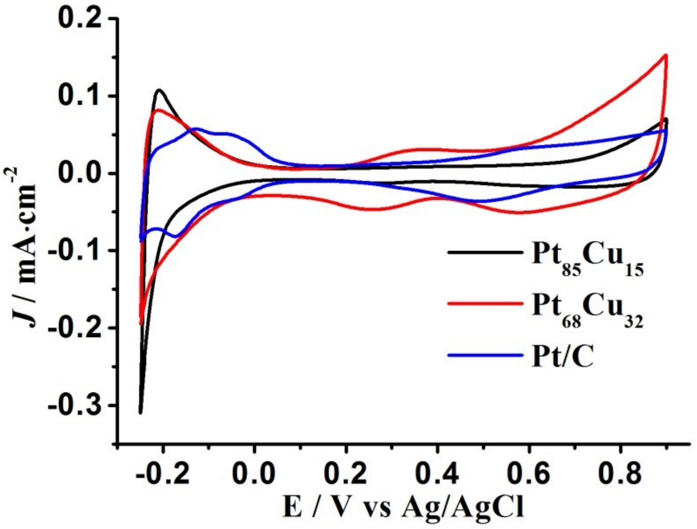

Fig. S3 CVs of the as-synthesized $Pt_{85}Cu_{15}$ nanoalloys, $Pt_{68}Cu_{32}$ nanoalloys and the commercial Pt/C with a scan rate of 50 mV/s in a 0.1 M $HClO_4$ solution at room temperature.

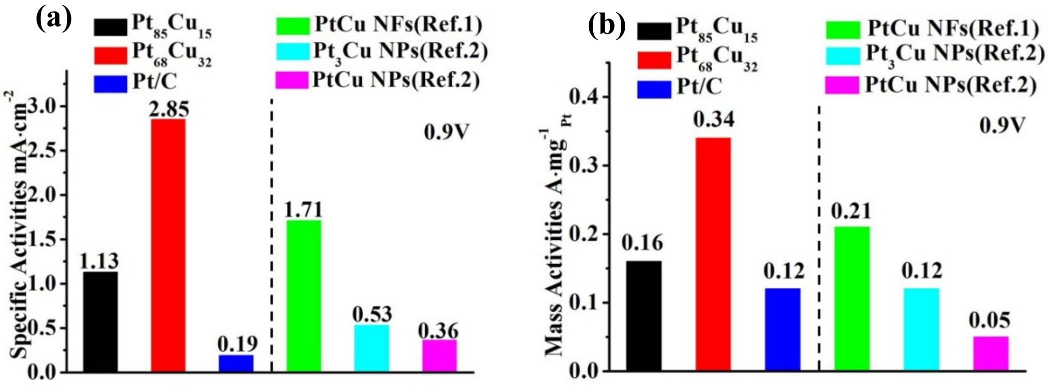

Fig. S4 The comparison of (a) specific activity and (b) mass activity of $Pt_{68}Cu_{32}$ nanoalloy, $Pt_{85}Cu_{15}$ nanoalloy, commercial Pt/C, PtCu nanoframe (NFs)[1], Pt_3Cu nanoparticles (NPs) and PtCu nanoparticles (NFs)[2].

[1] Zhicheng Zhang , Zhimin Luo , Bo Chen , Chao Wei , Jian Zhao , Junze Chen , Xiao Zhang , Zhuangchai Lai , Zhanxi Fan , Chaoliang Tan , Meiting Zhao , Qipeng Lu , Bing Li ,Yun Zong , Chengcheng Yan , Guoxiong Wang , Zhichuan J. Xu , and Hua Zhang, One-Pot Synthesis of Highly Anisotropic Five-Fold-Twinned PtCu Nanoframes Used as a Bifunctional Electrocatalyst for Oxygen Reduction and Methanol Oxidation, ***Advanced Materials***, **2016**, 28, 8712-8717.

[2] Mehtap Oezaslan, Frédéric Hasché, and Peter Strasser, $PtCu_3$, PtCu and Pt_3Cu Alloy Nanoparticle Electrocatalysts for Oxygen Reduction Reaction in Alkaline and Acidic Media, ***Journal of The Electrochemical Society***, **2012**, 159**,** B444-B454.

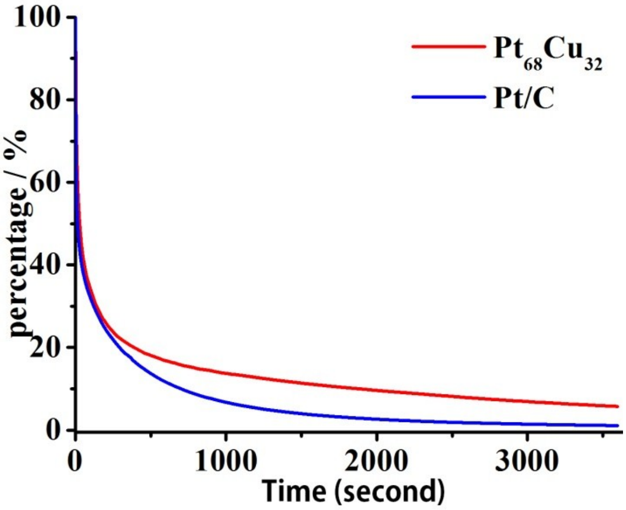

Fig. S5 The comparison of current drop of $Pt_{68}Cu_{32}$ nanoalloys and commercial Pt/C after 3600 s test.

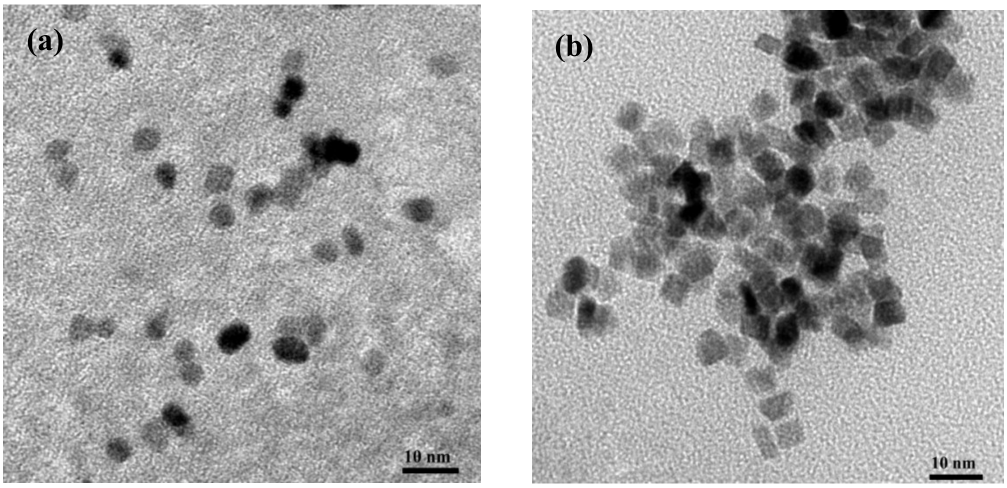

Fig. S6 TEM images of $Pt_{68}Cu_{32}$ nanoalloys. (a) ORR after 1000 cycles ADTs. (b) EOR after current-time test for 3600 s.