Supporting Information

Bifunctional PtCu Electrocatalysts for N_2 Reduction Reaction under Ambient Conditions and Methanol Oxidation

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Chemicals and materials

Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Tianjin Delan, Pt≥30%), copper chloride ($CuCl_2$, Aladdin, 98%), sodium bicarbonate ($NaHCO_3$, AR, Sinopharm Chemical Reagent Co., Ltd, ≥99.5%), sodium carbonate (Na_2CO_3, AR, Sinopharm Chemical Reagent Co., Ltd, ≥99.8%), salicylic acid ($C_7H_6O_3$, AR, MACKLIN), trisodium citrate dihydrate ($C_6H_5Na_3O_7$ $2H_2O$, AR, Sinopharm Chemical Reagent Co., Ltd, ≥99.0%), anhydrous sodium sulfate (Na_2SO_4, AR, Sinopharm Chemical Reagent Co., Ltd, ≥99.0%), sodium borohydride ($NaBH_4$, SIGMA-ALDKICH, 99%), sodium nitroprusside ($C_5H_4FeN_6Na_2O_3$, MACKLIN, 99.98%), hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$, Aladdin, 99.99%), ammonium chloride (NH_4Cl, MACKLIN, 99.99%), sodium hypochlorite solution (NaClO, AR, MACKLIN, 6~14%), ethyl alcohol (C_2H_6O, Wuxi Yasheng, ≥99.7%), hydrochloric acid (HCl, AR, Sinopharm Chemical Reagent Co., Ltd), isopropyl alcohol (C_3H_8O, Sinopharm Chemical Reagent Co., Ltd, ≥99.7%), nafion ($C_9HF_{17}O_5S$, DU PONT, 5 wt%), 4-(dimethylamino) benzaldehyde ($C_9H_{11}NO$, Accela ChemBio Co., Ltd, 98%), N,N-dimethylmethanamide (DMF) (C_3H_7NO, AR, Aladdin, 99.5%), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd, 95.0%-98.0%), absolute methanol (CH_3OH, Sinopharm Chemical Reagent Co., Ltd) were used without any further treatment.

Characterization

Transmission electron microscopy (TEM) image was obtained using Hitachi HT7700 operating at an accelerating voltage of 120 kV. Scanning electron microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) were operated on Hitachi 8100

scanning electron microscope. Elemental mapping was completed using Oxford.X-ray diffractometer (XRD) patterns come from SMART APEX Ⅱ. The XPS spectra was recorded on Escalab 250Xi. The absorption spectrum was collected on TU 1810. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out using an Optima 300DV (PerkinElmer) to determine the composition of the alloy NCs and mass of the electrocatalysts dropped on the working electrode.

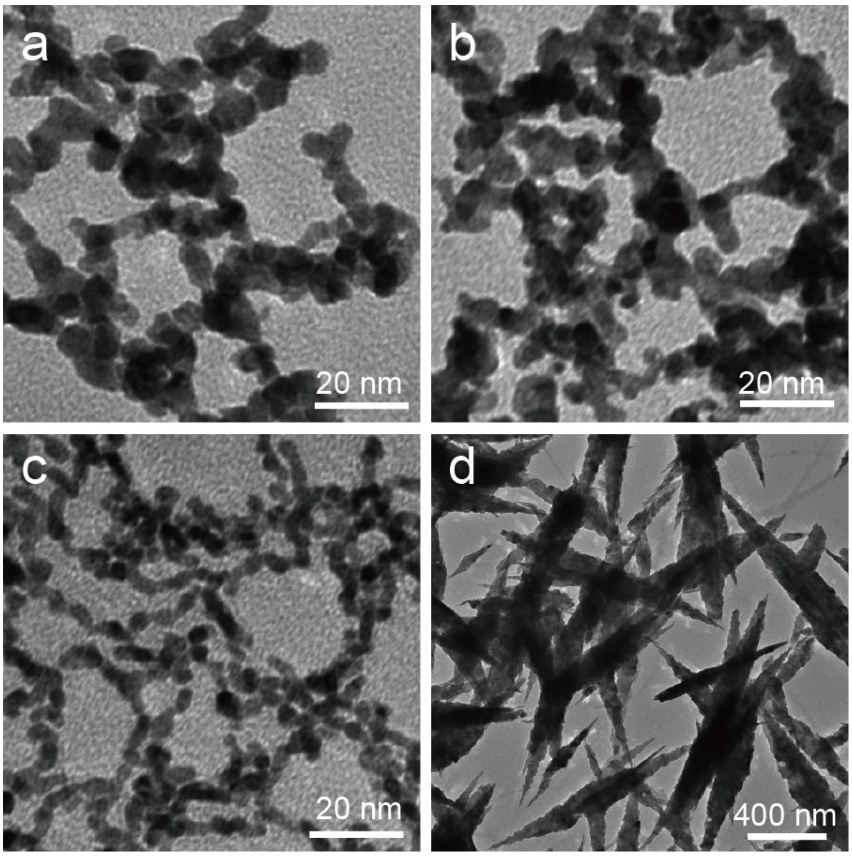

Fig. S1 TEM images of $Pt_{15}Cu_2$ (a), Pt_5Cu (b), pure Pt (c), and pure Cu (d), respectively.

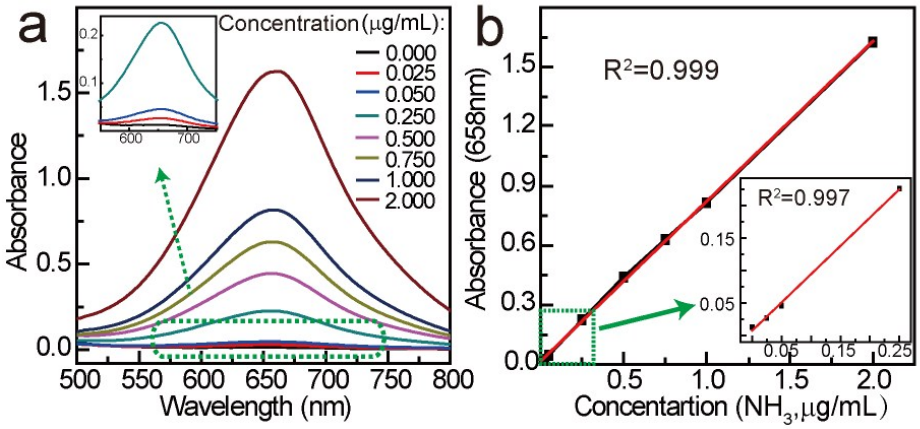

Fig. S2 (a,b) Absorption curves and the corresponding calibration line of the indophenol assays with the existence of the various concentration of NH_4Cl after incubated for 2 h at room temperature.

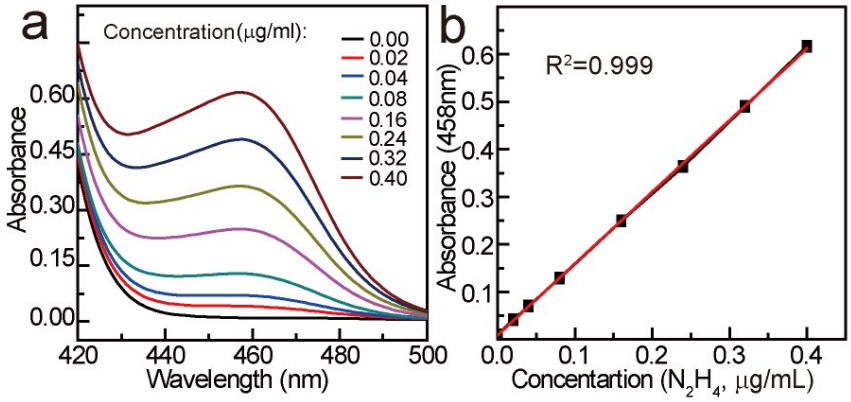

Fig. S3 (a,b) Absorption spectrum and the calibration curves using the Watt and Chrisp method to determine the concentration of N_2H_4. $N_2H_4 \cdot H_2SO_4$ with varying concentration was incubated 15min before each test at room temperature.

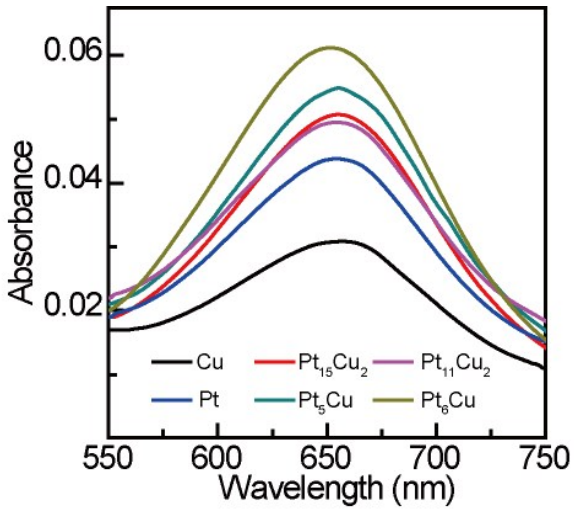

Fig. S4 Absorption spectra of the indophenol assays for the electrolyte after NRR test by employing PtCu alloy with different composition, pure Pt, and pure Cu as the electrocatalysts at −0.2 V versus RHE.

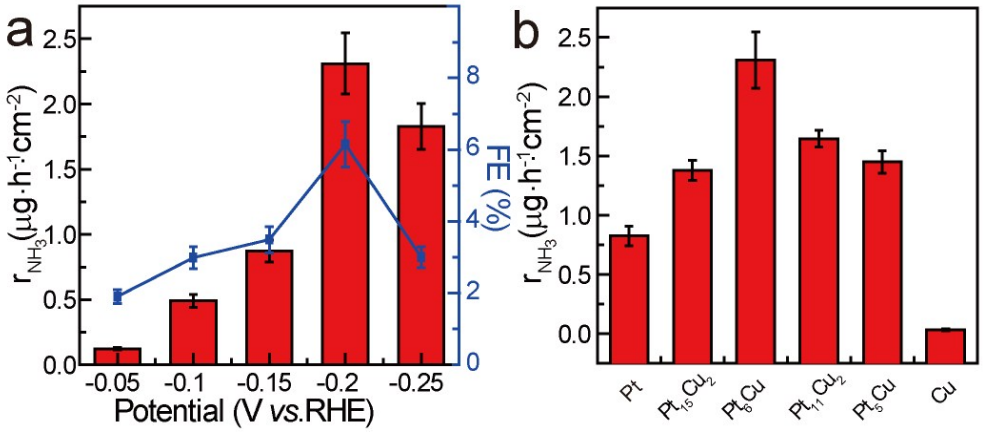

Fig. S5 (a) yield rate of NH_3 and Faradaic Efficiency at selected potentials; (b) yield rates of ammonia formation with different Pt-Cu atomic ratios at −0.2 V versus RHE at room temperature and ambient pressure.

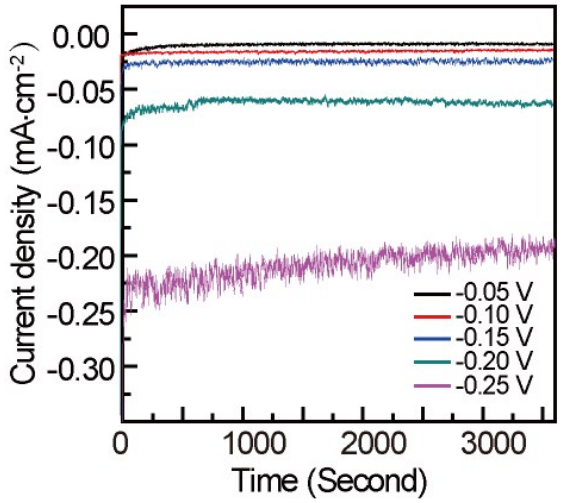

Fig. S6 Chronoamperometric curves of the Pt_6Cu alloy electrocatalysts measured at various applied potentials.

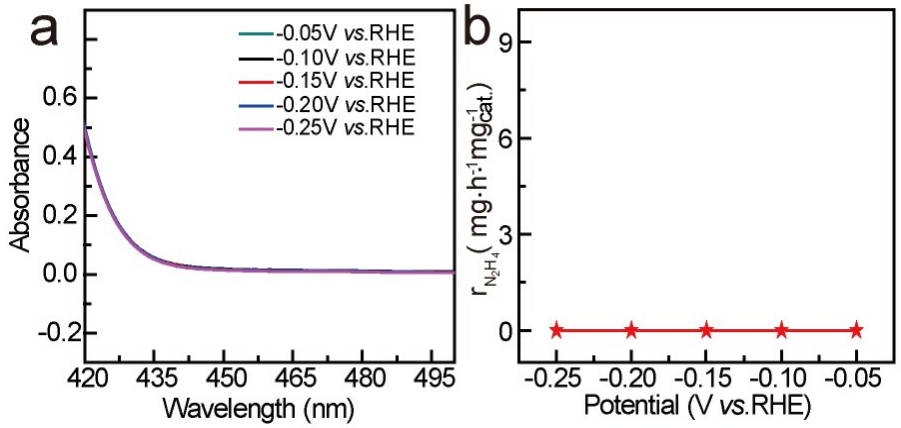

Fig. S7 (a,b) The absorption curves and the corresponding calculated N_2H_4 concentration using Pt_6Cu NCs as electrocatalysts during NRR produce at various applied potentials.

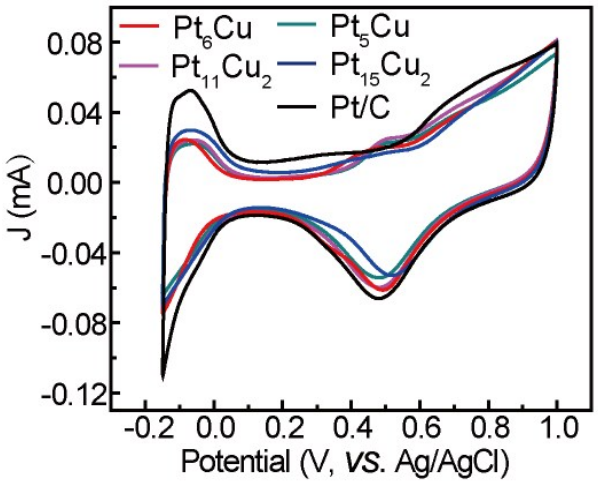

Fig. S8 CV curves for PtCu alloys with different compositions in N_2-saturated H_2SO_4 (0.1 M) solution.

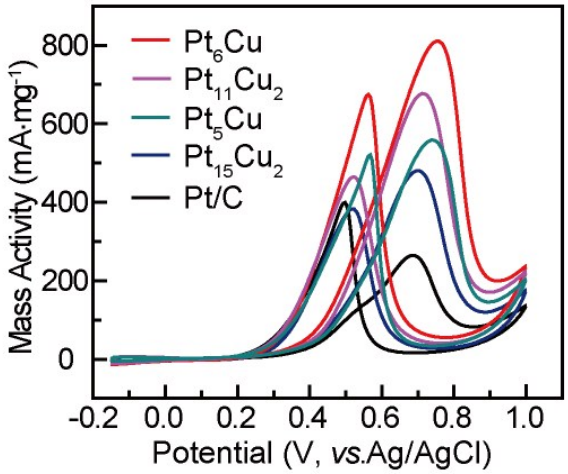

Fig. S9 Mass activity obtained by normalized to Pt mass in the mixture of methanol (1.0 M) and H_2SO_4 (0.1 M) at a scan rate of 50 mV s^{-1}.

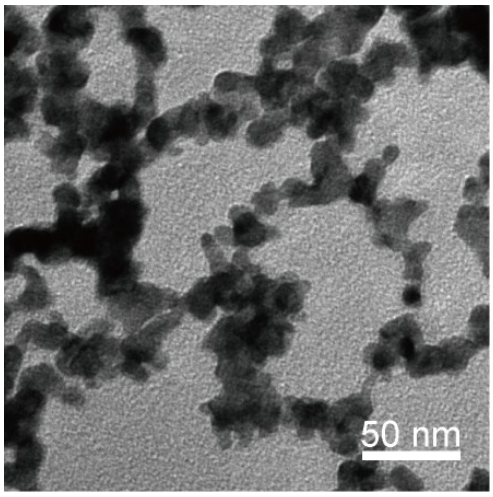

Fig. S10 TEM imaging for the PtCu after the CA measurements.

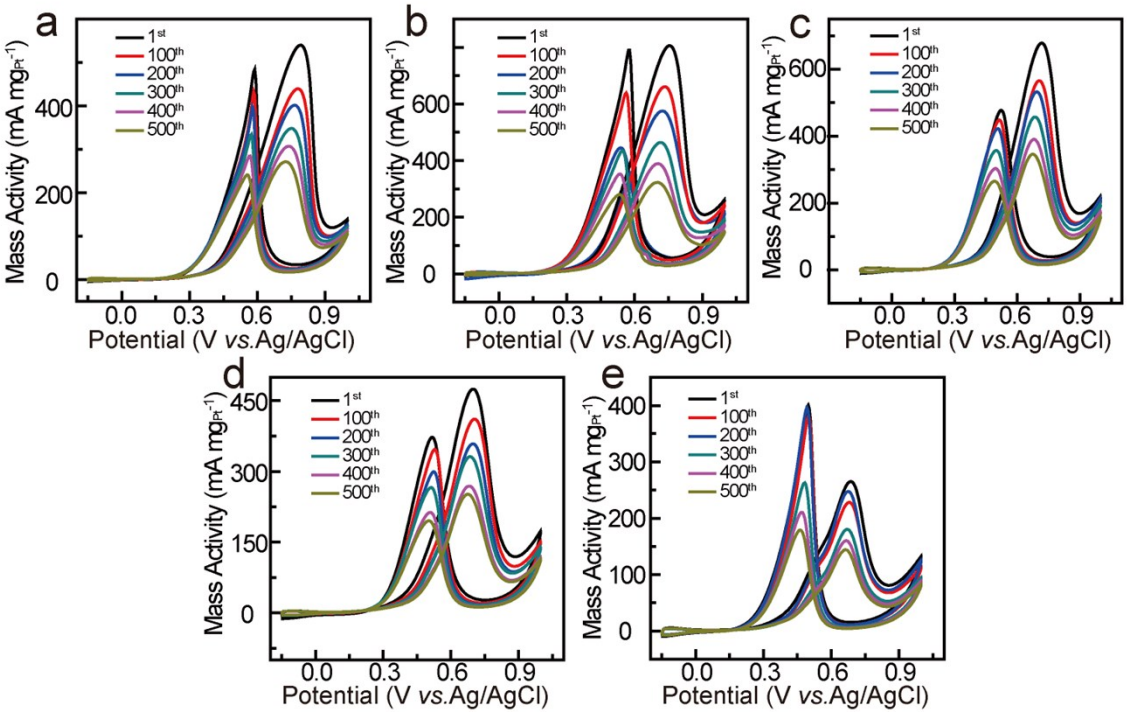

Fig. S11 Representative CV curves measured during cycling measurements at 1st, 100th, 200th, 300th, 400th, and 500th cycle for Pt_5Cu (a), Pt_6Cu (b), $Pt_{11}Cu_2$ (c), $Pt_{15}Cu_2$ (d) and commercial Pt/C (e) electrocatalysts in N_2-saturated H_2SO_4 (0.1 M) solution and CH_3OH (1.0 M).

Table S1. The table of ICP-AES data of PtCu.

PtCu catalyst	Concentration(Pt)	Concentration (Cu)
Pt_5Cu	59.0 μg/mL	11.5 μg/ mL
$Pt_{11}Cu_2$	59.2 μg/mL	11.01 μg/ mL
Pt_6Cu	58.0. μg/mL	9.1 μg/mL
$Pt_{15}Cu_2$	65.0. μg/mL	8.7 μg/mL
Pt	61.0. μg/mL	
Cu		19.1 μg/mL

Table S2. The Pt-based electrocatalysts that are previously reported.

PtCu catalyst	Mass activity	Specific activity	Ref
PtCu NWs	707 mA mg^{-1}		1
PtCu nanocrystals	604.8 mA mg^{-1}	9.4 A m^{-2}	2
PtCu nanowires	390 mA mg^{-1}		3
PtCu nanodendrites	410.4 mA mg^{-1}	14.0 A m^{-2}	4
PtCu Nanoparticles	530 mA mg^{-1}	1.07 mA cm^{-2}	5
PtCu	816 mA mg^{-1}	2.13 A m^{-2}	This work

Reference:

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