Supporting information

Detailed experimental procedures

Chemicals and reagents

Sodium hydroxide (NaOH), copper nitrate [$Cu(NO_3)_2$], ethylene diamine (EDA), hydrazine (N_2H_4), ethanol, iso-propanol (IPA), Chloroplatinic acid hexahydrate ($H_2PtCl_6•6H_2O$), and perchloric acid ($HClO_4$) were purchased from Sigma-Aldrich. Nitric acid (HNO_3) was purchased from Fisher Chemical. Nitrogen (N_2, ultra high purity) and oxygen (O_2, ultra high purity) were purchased from Airgas. 5 wt.% Nafion® was purchased from DuPont. All chemicals were utilized as received. All aqueous solutions were prepared by deionized water (DI H_2O, 18.2 MΩ•cm, Millipore).

The preparation of PtCu NTs

PtCu NTs were synthesized by the galvanic replacement reaction using copper nanowires (Cu NWs) as the sacrificial template.

(a) The preparation of Cu NWs

20 mL of concentrated sodium hydroxide solution (15M) in a 500-mL plastic bottle was preheated to 60 °C. Afterwards, 10 mL of $Cu(NO_3)_2$ solution (0.1 M) and 1.6 mL of EDA were sequentially and thoroughly mixed into the preheated solution. The reaction was triggered by adding 250 μL of N_2H_4 solution (35 wt.% dilute from 98 wt.%) and maintained at 60 °C in the water bath for 2 hours. The reddish end product floating on the top of the reaction solution was washed and collected by dispersion-centrifugation (6000

rpm, 10 min, Eppendorf 5810R) in DI H_2O and ethanol for 5 times in each to remove inorganic compound(s) and the residual EDA, N_2H_4, and organic intermediate(s), respectively. The as-prepared Cu NWs were dispersed in ethanol and quantified by quartz crystal microbalance (Maxtek RQCM, Inficon).

(b) The preparation of PtCu NTs

H_2PtCl_6□$6H_2O$ was employed as the Pt precursor in the synthesis of PtCu NTs. Concisely, 120 mL of Cu NWs/ethanol suspension (0.3 mM) was mixed with 60 mL of H_2PtCl_6/ethanol solution (0.3 mM) with a Pt to Cu ratio of 0.5. Both reactants were precooled in a -20 °C refrigerator and the reaction mixture was maintained at -20 °C for 24 hours. The dark brown end product (PtCu NWs) was washed and collected by dispersion-centrifugation (6000 rpm, 10 min) in ethanol for 5 times. Subsequently, acid treatment of the as-prepared PtCu NWs was carried out in 0.5 M nital (HNO_3 in ethanol, diluted from 70%) for 24 hours in a shaker (180 rpm, New Brunswick Scientific) at room temperature. The final product (Pt NTs) was washed and collected by dispersion-centrifugation (6000 rpm, 10 min) in ethanol for 5 times, and dried overnight under vacuum in a vacuum oven (Fisher Scientific).

Characterization

Field emission scanning electron microscopy was conducted on a JEOL 6335F FESEM (10 kV operating voltage) coupled with Noran X-ray microanalysis system. Transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDXS), scanning transmission electron microscopy (STEM), spectrum profile (lines), and spectrum image (maps) were carried out on a Tecnai T12

TEM (120 kV operating voltage) with STEM mode. High-resolution transmission electron microscopy (HRTEM) images were acquired on a JEOL 2010 FasTEM (200 kV operating voltage). The crystal structures of the samples were examined using a Bruker D8 Advance X-ray diffractometer with a Cu-Kα (k = 1.5405 Å) radiation source operating at 40 kV, 40 mA and the scan rate of 5 degree/minute. The XRD patterns were presented after baseline subtraction. X-ray photoelectron spectroscopy (XPS) was conducted in a PHI Multiprobe using an Al-Kα source. The collected spectra were analyzed using the CasaXPS program. All binding energies were calibrated by placing the first C1s line at 284.6 eV.

Electrochemical measurements

(a) Experimental setup

All electrochemical measurements were performed in a customized three-electrode electrochemical cell with a Luggin capillary and a water jacket (Adams & Chittenden Scientific Glass) on a PGSTAT302N potentiostat (Metrohm Autolab). A glassy carbon rotating (ring) disk electrode [R(R)DE, 5 mm diameter, Pine Research Instrumentation], a mercury/mercurous sulfate (Hg/Hg_2SO_4, saturated K_2SO_4, CH Instruments), and a Pt sheet (1 x 1 cm^2) attached to a Pt wire were applied as the working, reference, and counter electrode, respectively. All potentials in the results are based on the reference of reversible hydrogen electrode (RHE). 0.1 M $HClO_4$ (diluted from 70%) was used as the electrolyte through out the electrochemical experiments. All electrochemical experiments were conducted at 25 °C controlled by a circulating water bath (Isotemp 3016D, Fisher Scientific).

(b) The preparation of working electrodes

Before the electrode modification, the R(R)DE was polished with polishing alumina (0.05 μm) on a moistened velvet polishing pad. The polished electrode was rinsed with and sonicated (1 minute) in DI H_2O to obtain a mirror finish. Three different Pt based electrocatalysts, namely PtCu NTs, Pt/C (40 wt.% Pt nanoparticles supported on Vulcan XC72, E-TEK), and Pt black (Sigma-Aldrich) evaluated in this work were dispersed in 20% IPA aqueous solution by ultra-sonication on an ice bath for 30 minutes with an ultrasonic processor (Sonics & Materials).

6 μL of the well-dispersed catalyst ink was pipetted on the surface of R(R)DE and dried with the rotation speed of 700 rpm in air at room temperature for 30 min, resulting in a Pt loading of 21.0, 34.2, and 47.9 μg/cm^2 for PtCu NTs, Pt/C, and Pt black, respectively. Afterwards, 10 μL of 0.05 wt.% Nafion® (diluted from 5 wt.%) was dropped on the electrode and dried with the rotation speed of 700 rpm in air at room temperature for 60 min, yielding a Nafion® film thickness of about 0.1 μm. Subsequently, the modified electrode was further dried under vacuum for 30 min. Finally, the as-prepared working electrode was electrochemically cleaned by running cyclic voltammetry (CV) from 0.03 V to 1.252 V for 40 cycles at the scan rate of 200 mV/s in the N_2 purged electrolyte.

(c) Electrochemical surface area (ECSA)

Prior to the CV measurement, the electrolyte was purged by N_2 for 1 hour. All experiments were performed in N_2 environment. The stabilized cyclic voltammogram scanning from 0.03 V to 1.252 V at the sweep rate of 50 mV/s from the 19th cycle was recorded for the subsequent analysis. The ECSA was analyzed by measuring the charge (Q) associated with the adsorption and desorption of hydrogen after double layer correction in the hydrogen adsorption/desorption region. The ECSA (cm^2/mg) can be calculated by the following equation:

$$ECSA = \frac{0.5 \cdot Q}{m \cdot q_H} = \frac{0.5 \cdot A_H}{m \cdot q_H \cdot s}$$

where m is the loading of Pt (mg/cm^2); q_H is the adsorption charge of a monolayer hydrogen on the Pt surface which as been estimated to be 0.21 mC/cm^2; A_H is the area of the hydrogen adsorption/desorption region after double layer correction on the cyclic voltammogram (mA□V/cm^2); s is the scan rate of the CV (V/s).

(d) Oxygen reduction reaction (ORR)

Prior to the ORR test, the electrolyte was purged by O_2 for 1 hour. All experiments (except the background data) were performed in O_2 environment. In a typical measurement, a positive going linear sweep voltammetry (LSV) with the RDE rotating at 1600 rpm was carried out from 0.11 V to 1.13 V at the scan rate of 10 mV/s to examine the catalytic activity of different Pt based electrocatalysts towards ORR. The background current was recorded at the same experimental condition in N_2 purged electrolyte. The kinetic current (i_k) at 0.9 V was calculated according to the Koutecky-Levich equation:

$$1/i = 1/i_k + 1/i_l$$

and thus,

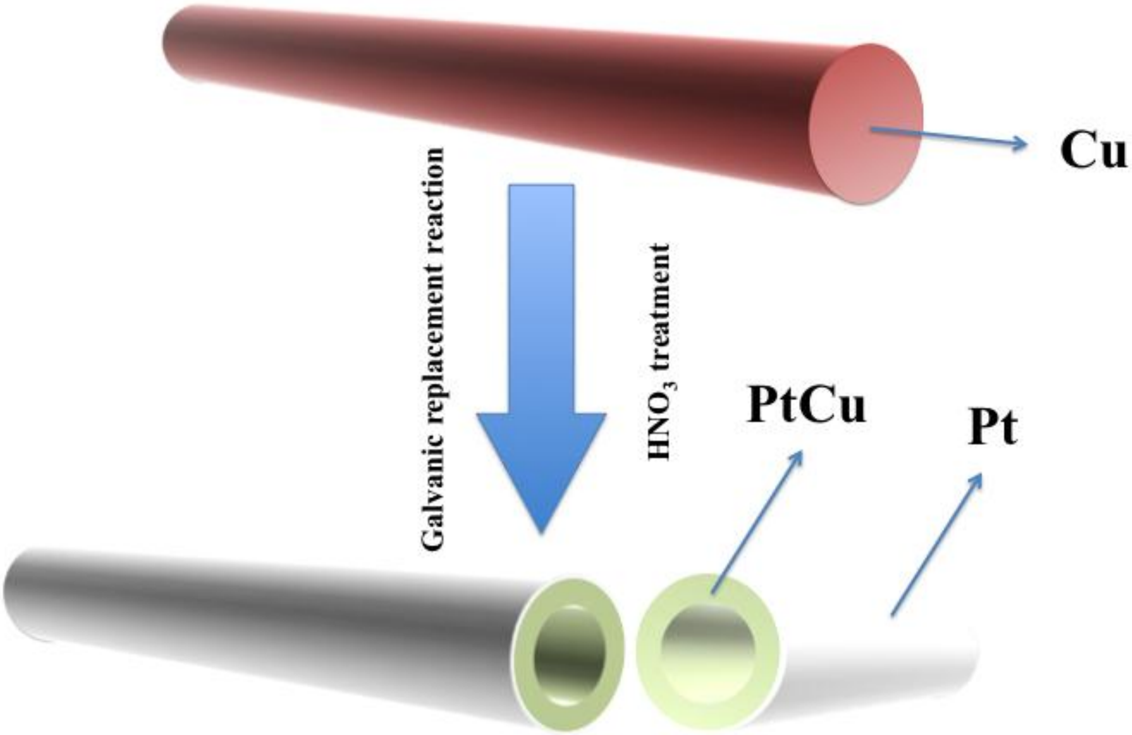
$$i_k = i_l \cdot i/(i_l - i)$$

where i is the measured current at 0.9 V and i_l is the diffusion limiting current. In this work, all i_l were taken at 0.3 V. The reported mass activity and specific activity are i_k normalized by the loading and the ECSA, respectively, of Pt. LSV was also performed at the rotation speed of 400 rpm, 900, rpm, 2500 rpm, and 3600 rpm to investigate the kinetic properties of the catalysts of interest.

The electron transfer number (n) of PtCu NTs-catalyzed ORR was ascertained by RRDE rotating at 1600 rpm with the potential of Pt ring electrode at 1.2 V where the oxidation of hydrogen peroxide (H_2O_2) is under diffusion control. The collection efficiency (N) of the RRDE is 0.25.

(e) Accelerated durability test (ADT)

ADT was conducted by cycling the modified RDE from 0.6 V to 1.1 V at the sweep rate of 50 mV/s in the O_2-saturated electrolyte with a continuous flow of O_2. The ECSA data and the ORR data after a certain number of ADT cycling (0, 500, 1000, 2000, 3000, 4000, 5000, 6000) were determined in fresh 0.1 M $HClO_4$ solution as shown in the previous descriptions.



Scheme 1. The schematic illustration of the galvanic replacement reaction from Cu nanowires to PtCu nanotubes.

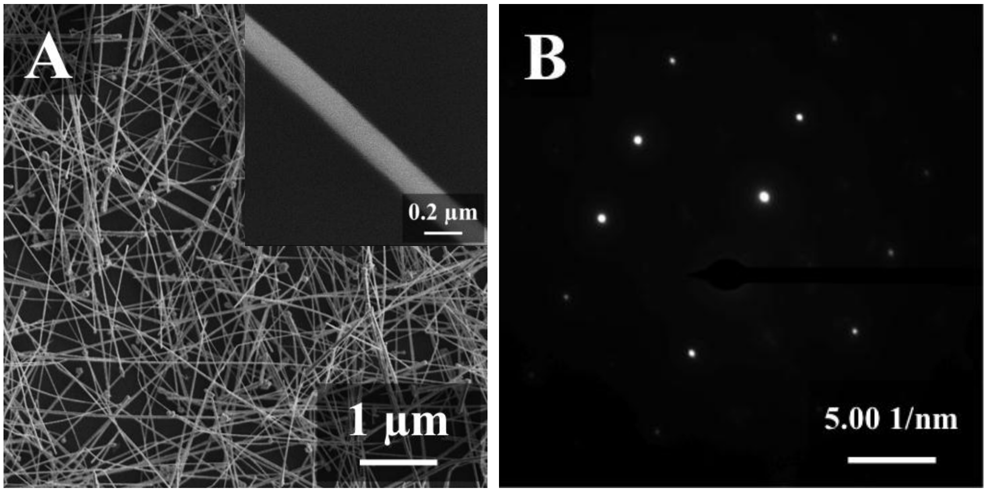


Figure S1. (A) FESEM of Cu NWs with a higher magnification image in the inset. (B) SAED pattern of Cu NWs from TEM.

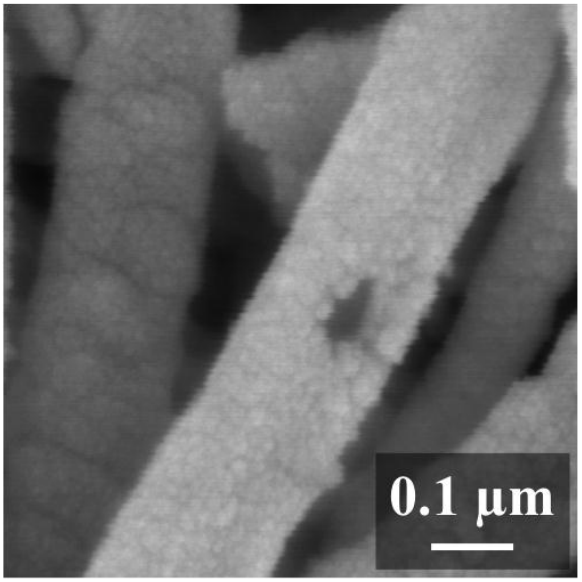


Figure S2. FESEM of PtCu NT with a small pinhole at higher magnification.

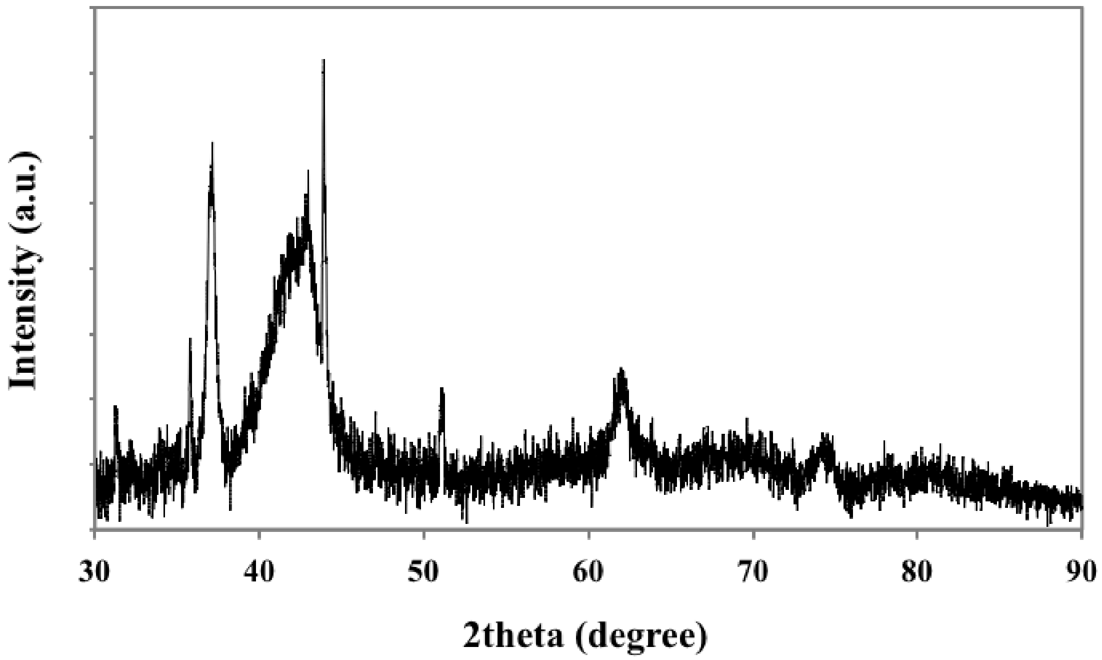


Figure S3. XRD pattern of PtCu before acid treatment.

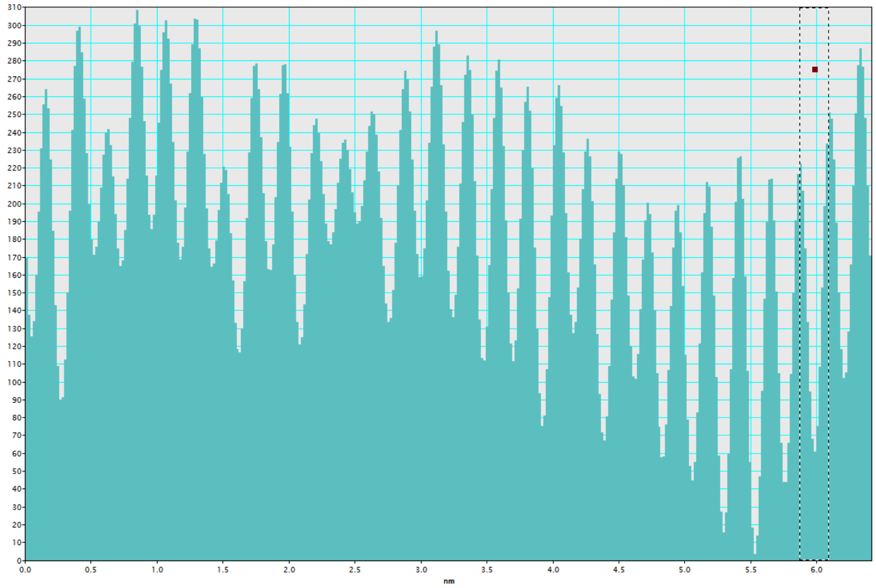
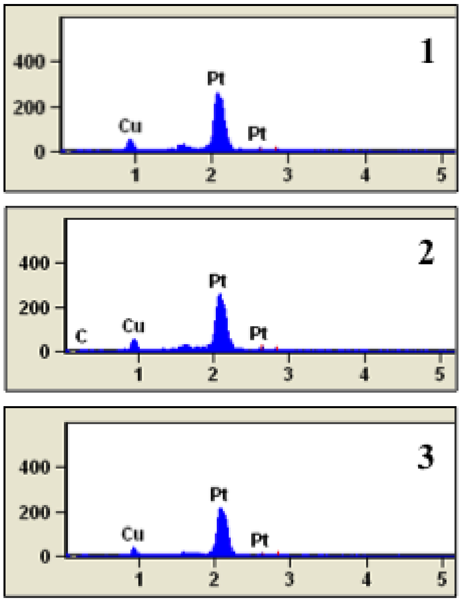
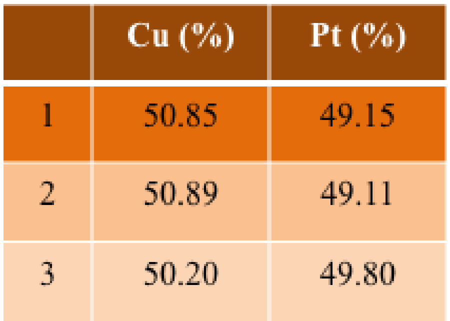


Figure S4. Lattice spacing measured on Gatan Microscopy Suite® for HRTEM.





	Cu (%)	Pt (%)
1	50.85	49.15
2	50.89	49.11
3	50.20	49.80

Figure S5. EDXS spectra of PtCu NTs from three different spots on FESEM.