Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Highly crystalline PtCu nanotubes with three dimensional molecular accessible and restructured surface for efficient catalysis

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EXPERIMENTAL SECTION

Materials.

$CuCl_2 \cdot 2H_2O$, glucose, toluene, dimethyl sulfoxide (DMSO) , isopropanol, hexane, methanol, perchloric acid, sulfuric acid were all from Shanghai Chemical Reagent Co. Ltd; platinum (II) chloride was from J&K Chemical Ltd; hexadecylamine (HDA) and Nafion were from Sigma–Aldrich. All chemical reagents were used without any further purification. Double-distilled deionized water (DIW, 18.2 MΩ) was used for the synthesis.

Synthesis of Cu NWs.

Cu NWs were prepared through a hydrothermal method reported previously. Briefly, with 85.5 mg $CuCl_2 \cdot 2H_2O$ and 99 mg glucose dissolved in 40 mL deionized water (DIW), 0.54 g HDA was added under vigorous stirring for 5h to form a blue-sky emulsion. After that, the emulsion was transferred into a 100 mL polytetrafluoroethylene-linked stainless batch tank reactor and reacted in an oven at 120 °C for 24 h. The products were centrifuged and washed with DIW three times to separate the surfactant and by-products. Finally, Cu NWs were collected by hexane and stored in the fridge for future use.

Synthesis of PtCu NTs.

In a typical synthesis, 60 μmol Cu NWs were dispersed in a mixed DMSO and toluene solution (volume ratio 1:1) followed by 10 min ultrasonication. After sufficient bubbling with N_2, the dispersion was refluxed in a 100 mL three-necked flask at 120 °C for 10 min. Then 30 μmol $PtCl_2$ were added into the system under 800 rpm magnetic stirring and reacted for 2h. We named the product as Pt_1Cu_1 NTs. And, 10, 20 and 40 μmol $PtCl_2$ precursors were added to obtain Pt_1Cu_5, Pt_1Cu_2 and Pt_2Cu_1 NTs catalysts, respectively.

Morphological, structural and elemental characterizations.

SEM was performed with a field-emission scanning electron microanalyzer (Zeiss Supra 40). TEM and HRTEM images were obtained on JEOL-2100F TEM instrument. HAADF-STEM, EDS and elemental mapping images were obtained on JEM-ARM 200F. XRD patterns were obtained with a Philips X'Pert Pro Super X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ=1.54178 Å). XPS were determined on an X-ray photoelectron spectrometer (ESCALab MKII) with an excitation source of Mg Kα radiation (1253.6 eV). Inductively coupled plasma (ICP) data was obtained by using an Optima 7300 DV instrument. Electrochemical measurements were carried out with a three electrode system on an electrochemical workstation (Autolab, Swiss).

Electrochemical measurements.

Electrochemical measurements were carried out with a three electrode system on an electrochemical workstation (Autolab, Swiss). We used platinum foil, Ag/AgCl (3.5 M) and glassy carbon rotating disk electrode (RDE) (PINE, 5 mm diameter, 0.196 cm2) as the counter, reference and working electrodes, respectively. All of the electrode potentials were recorded with Ag/AgCl electrode and calibrated to a reversible hydrogen electrode (RHE). First of all, the catalysts were suspended in 25 mL acetic acid at 60 °C for 11h with magnetic stirring. Then, after washing with water and isopropanol, the catalysts were dispersed in a mixture of isopropanol and 0.5% v/v Nafion solution. The PtCu NTs were dropped on a rotation disk electrode (RDE) with a polished glassy carbon surface (PINE, 5 mm in diameter) with the Pt loading of 3 µg. Surface cleaning and activating was executed by CV scanning in a N_2-saturated 0.1 M $HClO_4$ solution at room temperature with a sweep rate of 250 mV s^{-1}. The electrochemical surface area (ECSA) was measured by integrating the hydrogen-adsorption charge. Methanol oxidation reaction (MOR) was studied in a N_2-saturated 0.5 M H_2SO_4 and 1 M methanol mixed solution at room temperature with a sweep rate of 50 mV s^{-1}. The stability was tested by chronoamperometry at 0.7 V vs RHE.

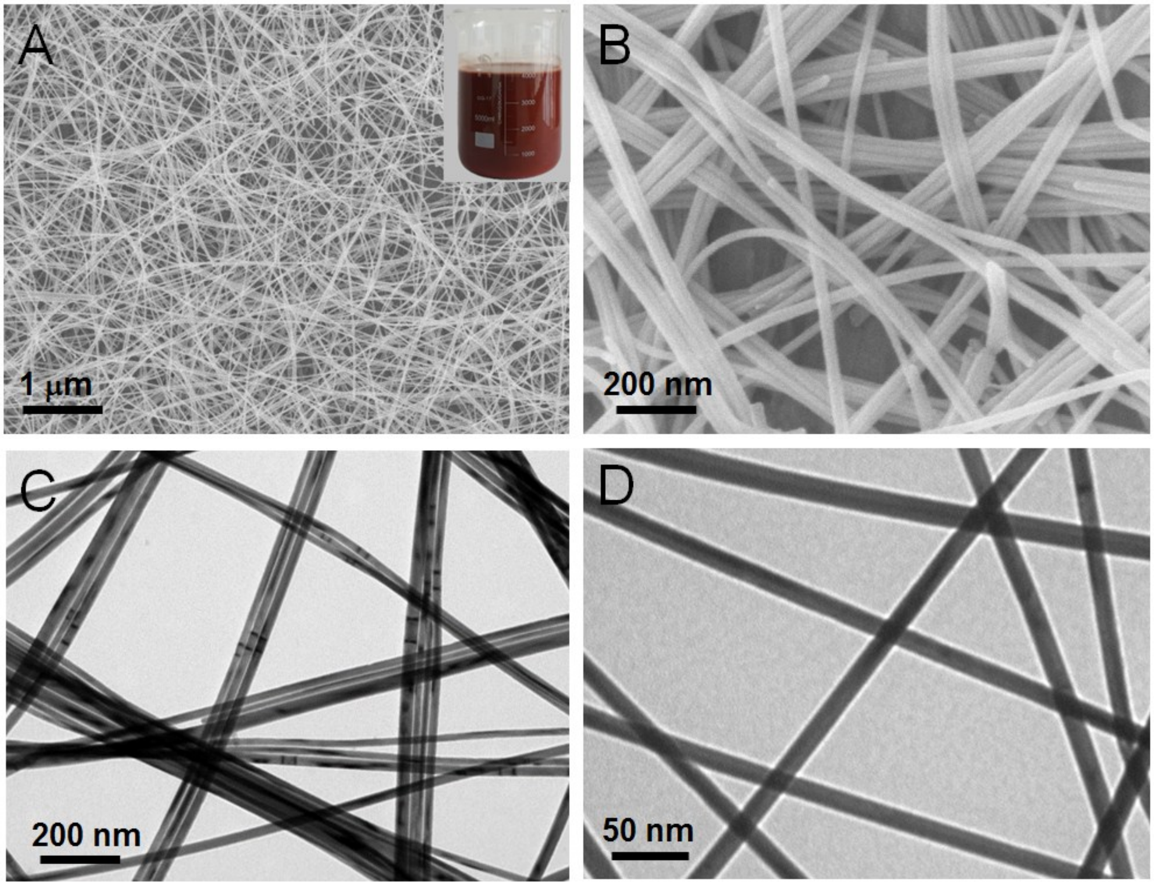

Fig. S1. (A, B) SEM images of the Cu NWs. The inset in (A) show the picture of the Cu NWs dispersion which can be stored for more than one year. (C, D) TEM images of the Cu NWs with uniform diameter.

Fig. S2. The pictures of HDA-capped Cu NWs dispersion. The left is in toluene and right in DMSO.

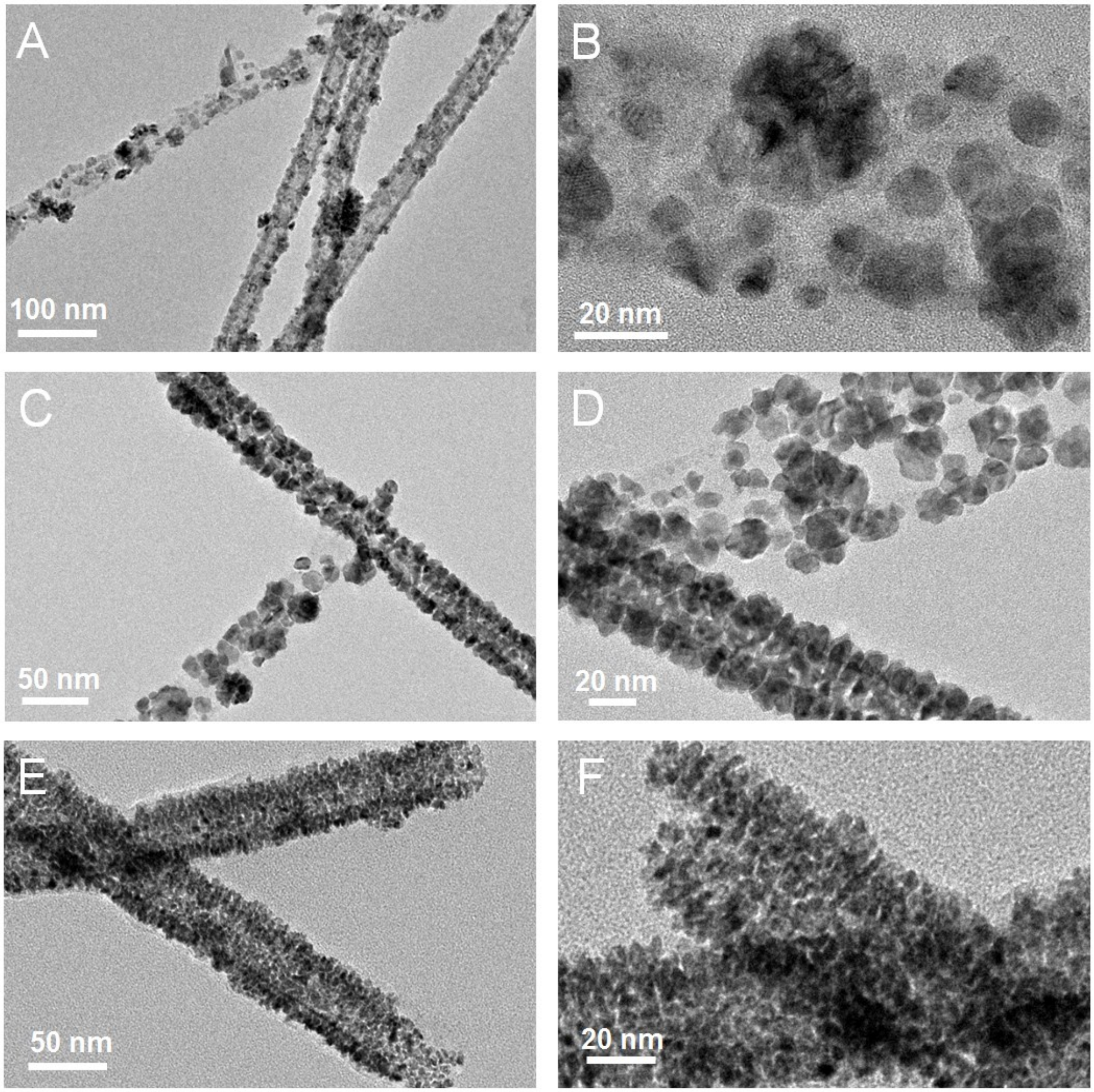

Fig. S3. (A, B) pure toluene, (C, D) mixture of toluene and DMSO (7:2) and (E, F) mixture of toluene and DMSO (2:7).

Table S1. The bulk composition of Pt_2Cu_1 NTs , Pt_1Cu_1 NTs , Pt_1Cu_2 NTs and Pt_1Cu_5 NTs before AA etching and after AA etching. The surface composition of the NTs after AA etching.

Sample	Pt (at%, bulk) before AA etching	Pt (at%, bulk) after AA etching	Pt (at%, surface) after AA etching
Pt_2Cu_1	27.3	39.2	44.3
Pt_1Cu_1	27.2	39.0	42.6
Pt_1Cu_2	25.3	38.2	43.6
Pt_1Cu_5	11.6	33.2	42.6

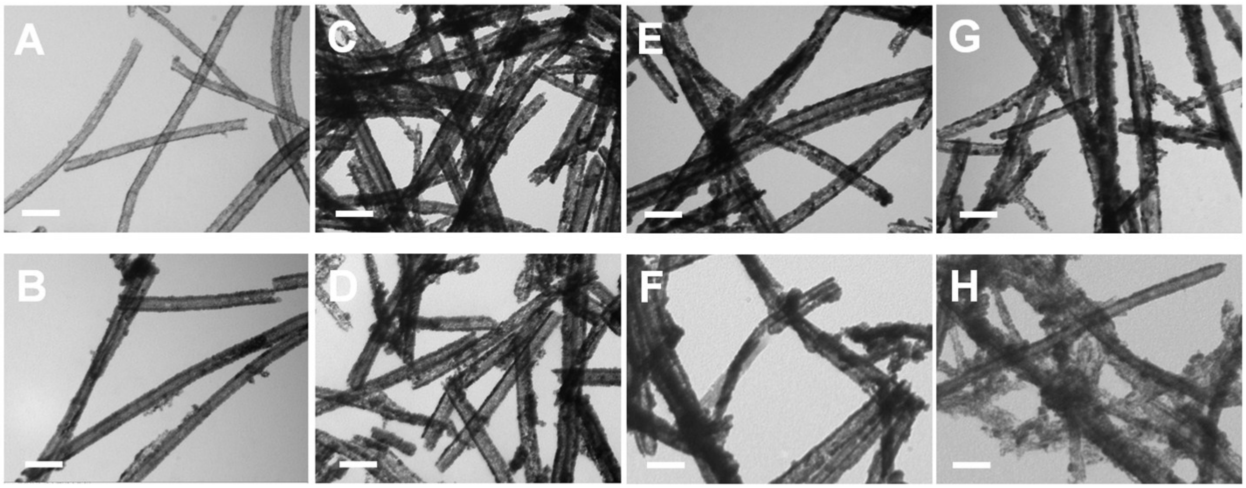

Fig. S4. TEM images of (A) Pt_2Cu_1 NTs, (C) Pt_1Cu_1 NTs, (E) Pt_1Cu_2 NTs and (G) Pt_1Cu_5 NTs before AA etching. TEM images of (B) Pt_2Cu_1 NTs, (D) Pt_1Cu_1 NTs, (F) Pt_1Cu_2 NTs and (H) Pt_1Cu_5 NTs after AA etching. The scale bar is 100 nm.

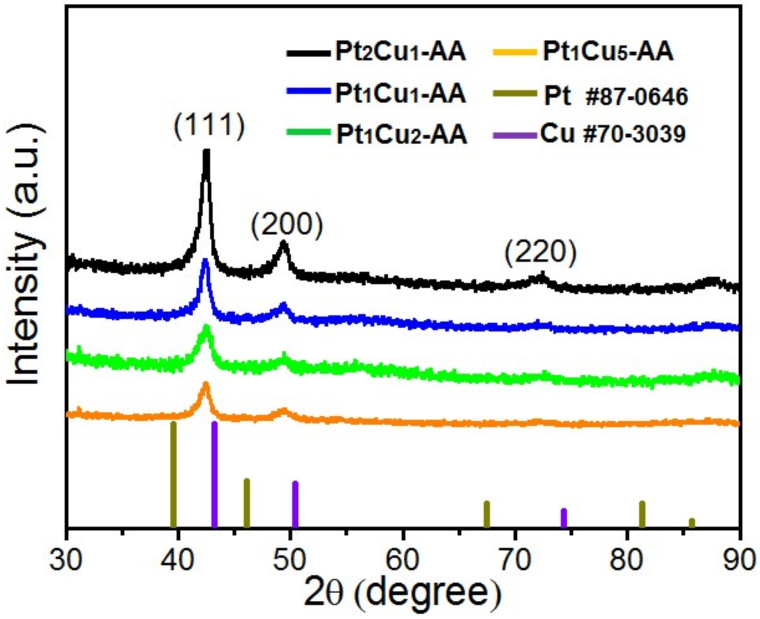

Fig. S5. The XRD pattern of Pt_2Cu_1-AA, Pt_1Cu_1-AA, Pt_1Cu_2-AA and Pt_1Cu_5-AA NTs.

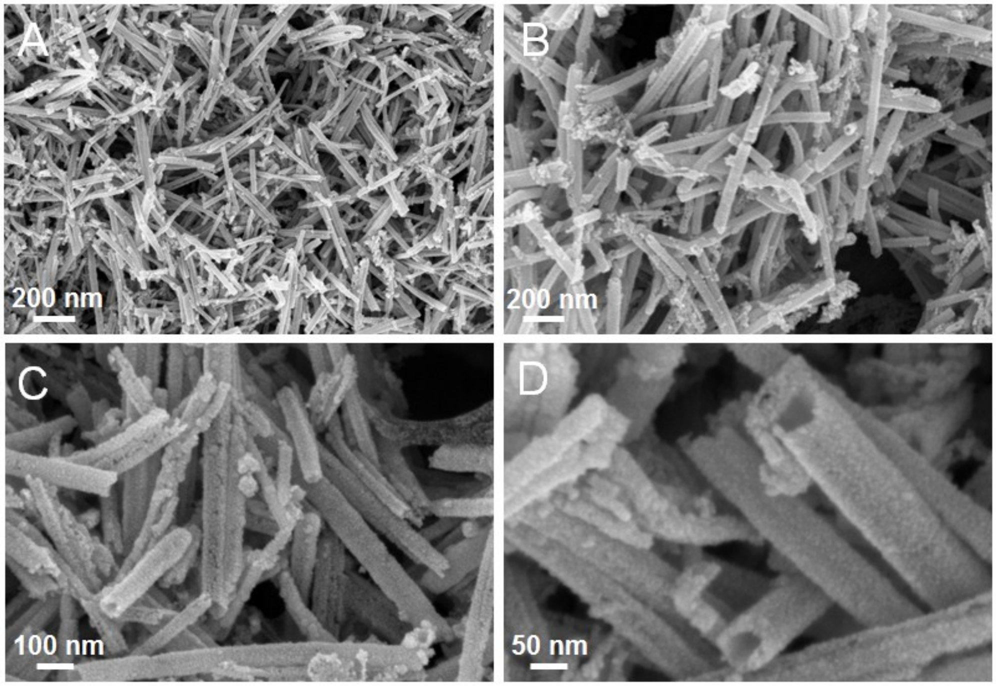

Fig. S6. SEM images of the Pt_1Cu_1-AA NTs.

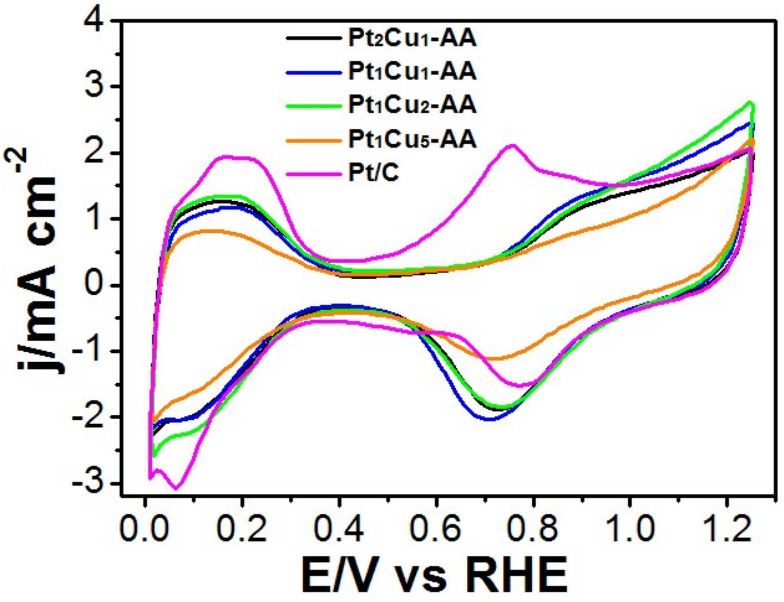

Fig. S7. CV profiles of the catalysts recorded in Ar-saturated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV/s.

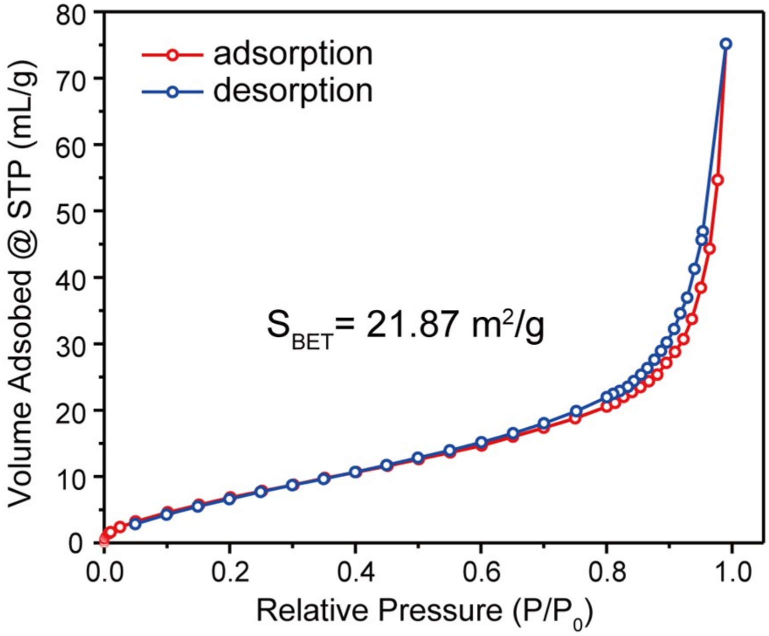

Fig. S8. Nitrogen adsorption-desorption isotherms of PtCu NTs powder prepared without adding carbon support.

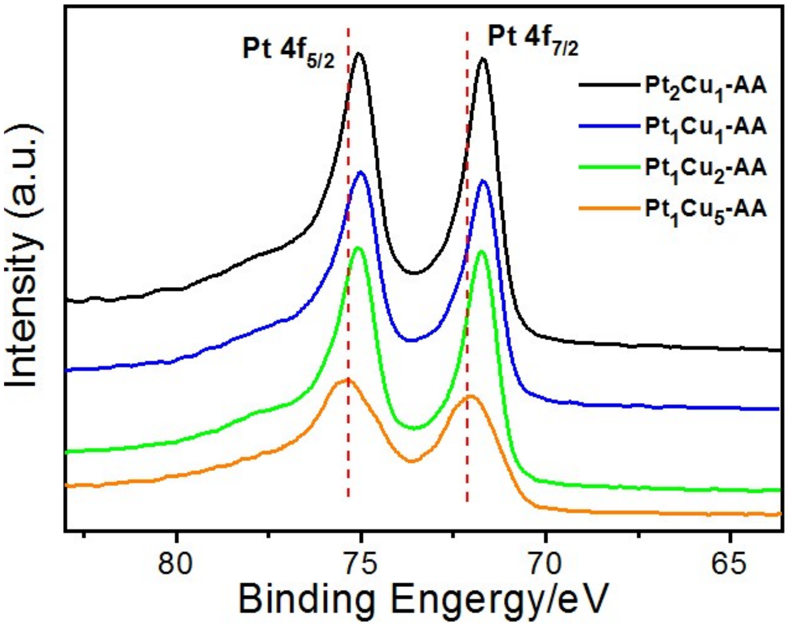

Fig. S9. XPS spectra of Pt 4f core levels of PtCu-AA NTs with different component fractions.

Table S2. Summary of literature catalytic parameters of various Pt-based MOR catalysts.

Catalyst type	Test protocol	Mass activity (mA/mg)	Specific activity (mA/cm^2)	ECSA (m^2/g)	Reference
Pt NWs	0.1 M $HClO_4$ + 0.1 M CH_3OH	1312	5.84	21.5	*Nano Res.* **2016**, 9, 2811.
Pt NW/ N-doped low-defect graphene	1.0 M $HClO_4$ +2.0 M CH_3OH	1283.1	--	24.7	*Small* **2016**, 1603013.
Pt-Ni_2P/C	0.5 M $HClO_4$ + 1.0 M CH_3OH	1431.68	4.05	69.34	*Energy Environ. Sci.* **2014**, 7, 1628.
Pt/Mo_2C NTs	0.5 M H_2SO_4 + 0.5 M CH_3OH	--	1.52	31.52	*NPG Asia Mater.* **2015,** 7, e153.
Pt_3Cu icosahedra	0.1M $HClO_4$ + 0.2M CH_3OH	736	2.14	34.4	*Acs Nano* **2015**, 9, 7634.
Dendritic Pt_3Cu nanocubes	0.5 M H_2SO_4 +1.0 M CH_3OH	~930	~1.7	54.3	*Chem. Sci.* **2015**, 6, 7122.
Screw thread-like $PtCu_{2.1}$ NWs	0.1 M $HClO_4$ + 0.2 M CH_3OH	1560	3.31	46.9	*Nano Lett.* **2016**, 16, 5037.
Ultrathin Pt_3Cu wavy NWs	0.5 M H_2SO_4 + 0.5 M CH_3OH	635	2.8	20.3	*Chem. Sci.* **2016**, 7, 5414.
PtNiCu Nanocrystals	0.5 M H_2SO_4 + 2.0 M CH_3OH	--	2.61	--	*Chem. Mater.* **2015**, 27, 6402.
Core/Shell Au/CuPt NPs	0.1 M $HClO_4$ + 0.1 M CH_3OH	411	0.755	--	*J. Am. Chem. Soc.* **2014**, 136, 5745.
Ultrathin PtRuFe NWs	0.1 M $HClO_4$ + 0.5 M CH_3OH	--	2.27	--	*Energy Environ. Sci.* **2015**, 8 , 350.
PtRu/TiWC NPs	0.1M $HClO_4$ + 1.0M CH_3OH	--	~1.8	68±6	*Science* **2016**, 352, 974.
PtCo NWs	0.1M $HClO_4$+ 0.2 M CH_3OH	1020	1.95	52.1	*Nat. Commun.* **2016**, 7, 11850.
PtPb/Pt nanoplate	0.1 M $HClO_4$ +0.1M CH_3OH	1500	~2.6	55	*Science* **2016**, 354, 1410.
High crystalline and open structured PtCu NTs	0.5 M H_2SO_4 + 1.0 M CH_3OH	2252	6.09	38	This work

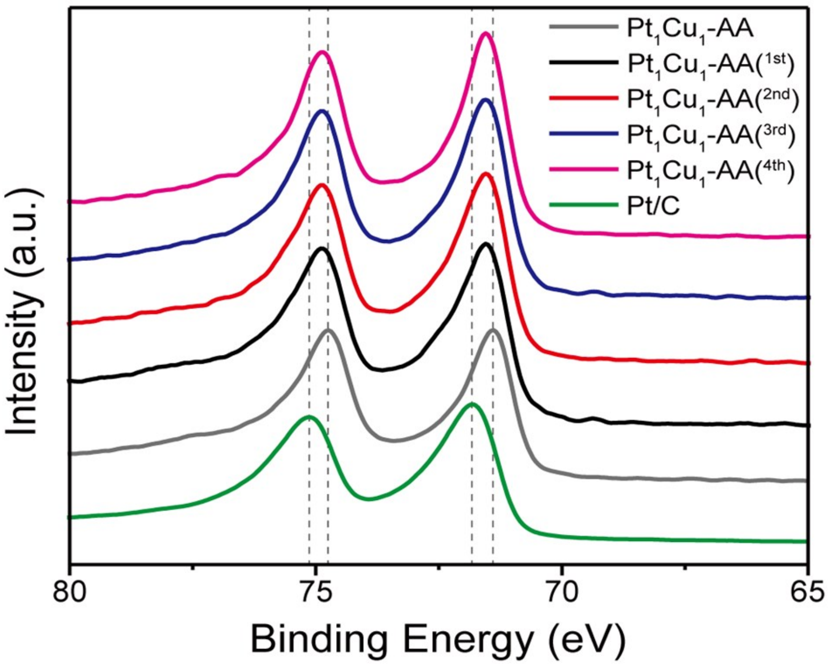

Fig. S10. XPS spectra of Pt 4f core levels of Pt/C catalysts, Pt_1Cu_1-AA NTs and that after per reactivation process.

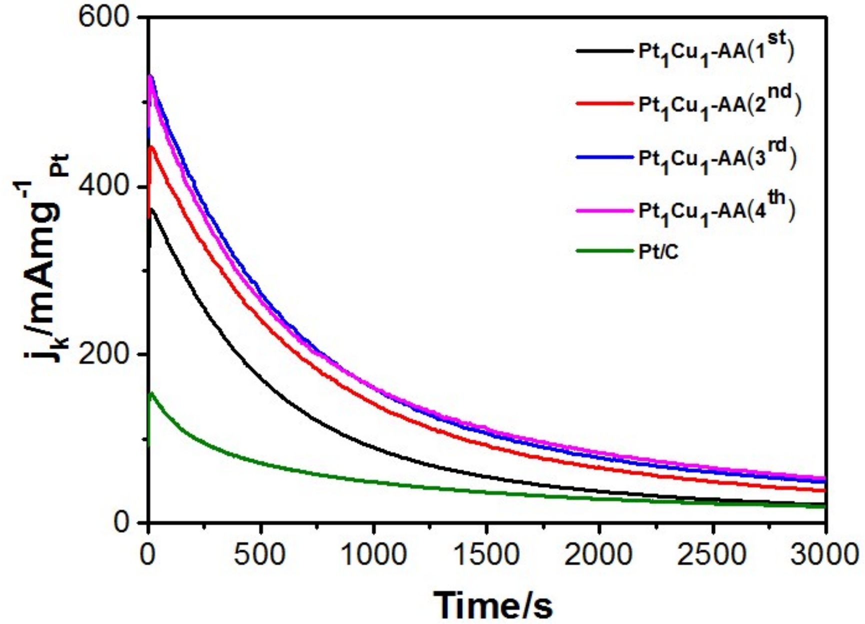

Fig. S11. Chronoamperograms for the MOR at 0.7 V vs. RHE. The tests were performed in 0.5M H_2SO_4 + 1.0 M methanol solution for Pt_1Cu_1-AA NTs and Pt/C catalysts.

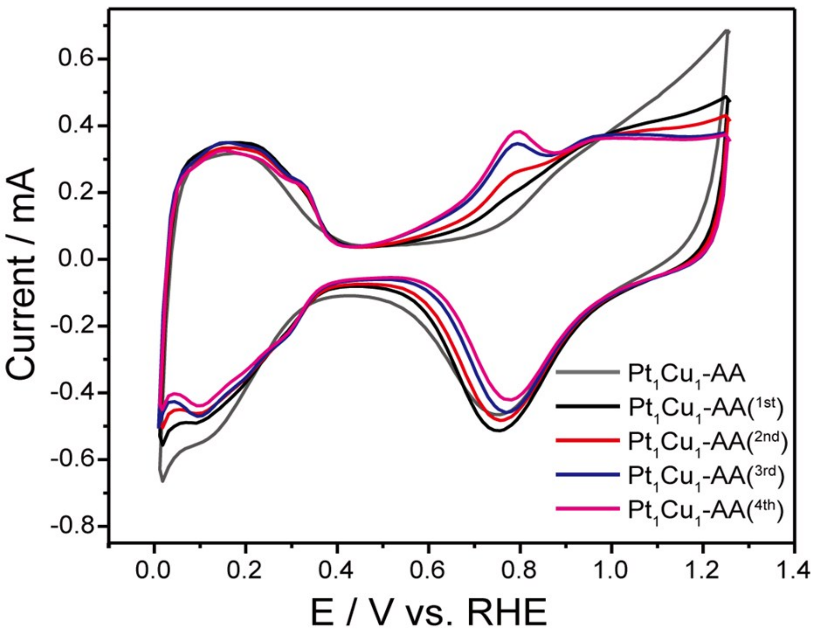

Fig. S12. CV profiles of Pt_1Cu_1-AA NTs and that after per reactivation process recorded in Ar-saturated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV/s.

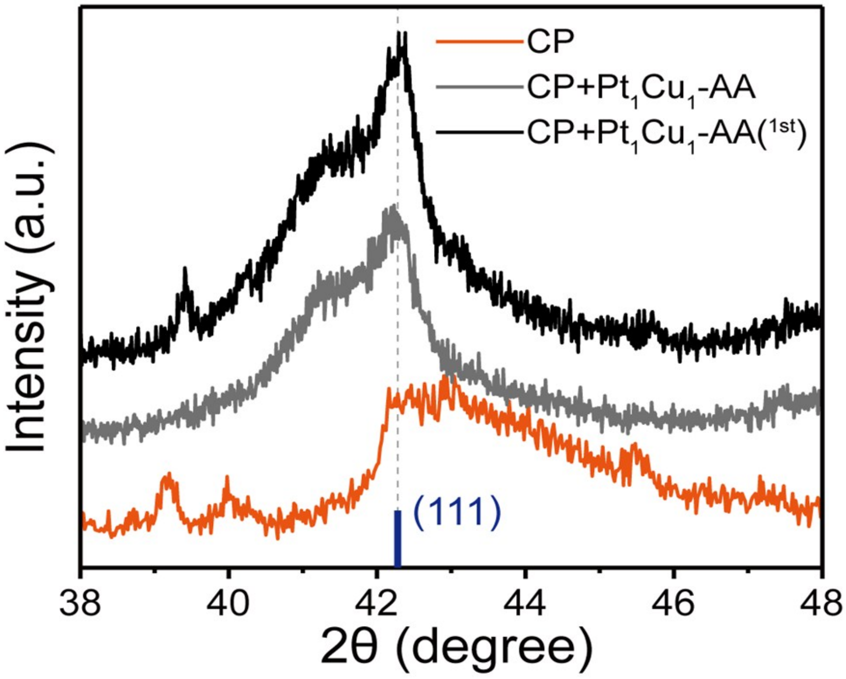

Fig. S13. The XRD pattern of Pt_1Cu_1-AA NTs before and after stability tests supporting on carbon paper (CP). The blue line represent the degree of Pt (111).

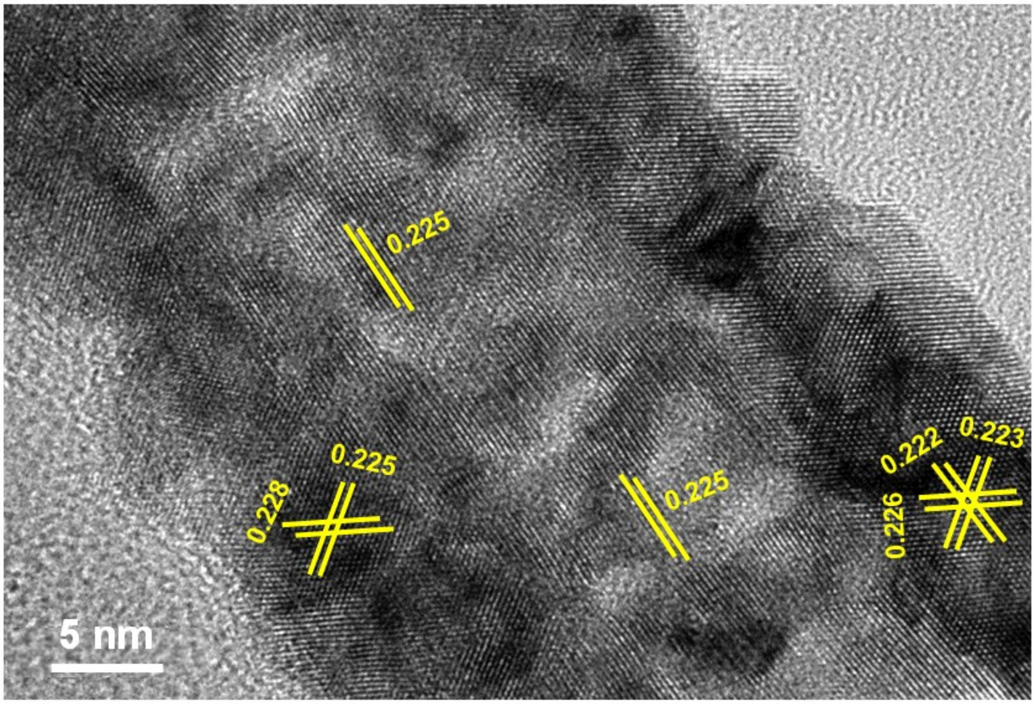

Fig. S14. HRTEM image of Pt_1Cu_1-AA NT after stability tests. To indicate the lattice structure clearly, the magnified HRTEM image of a NT after the stability tests show highly-crystalline nature. Obviously, the individual NPs fused together after stability tests comparing with before that.

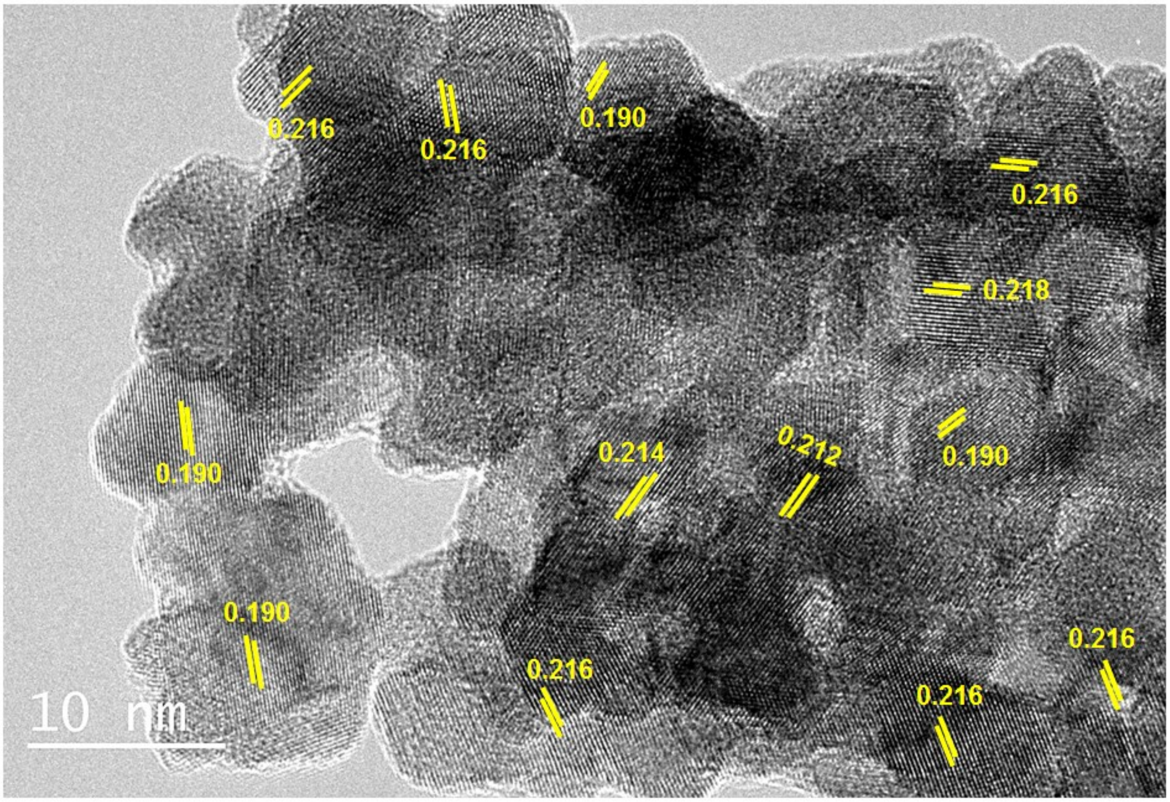

Fig. S15. HRTEM image of Pt_1Cu_1-AA NT before stability tests. To indicate the lattice structure clearly, the individual magnified HRTEM image of the head of a NT composed of inter-connected highly-crystalline NPs was shown.