Electronic Supplementary Information for :

Scalable synthesis of Cu-based ultrathin nanowire networks and their electrocatalytic properties

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1. Experimental Section

Materials. $CuCl_2$ and concentrated hydrochloric acid (HCl) were obtained from Beijing Chemical Corp (China). Polyvinylpyrrolidone (K•30) (PVP), H_2PtCl_6 and $PdCl_2$ were bought from Shanghai chemical reagent (Co. LTD.). $NaBH_4$ was obtained from Sigma-Aldrich. Commercial Pt black was bought from Alfar-Aesar. All agents used here are of analytical grade and used without further purifications. Before the synthesis, the H_2PdCl_4 (56.4 mol L^{-1}) was prepared by dissolving 1 g $PdCl_2$ into 1 mL of concentrated HCl (12 mol L^{-1}) and diluted to a volume of 100 mL, followed by heating at 60 °C for one hour with a water bath. Then the H_2PdCl_4 solution was cooled and stored at 4 ℃ for the further use.

Instruments. TEM, HRTEM, HAADF-STEM, energy dispersive X-ray spectrum (EDS) elemental mapping measurements (EDS-elemental mapping) were made on a TECNAI G2 high-resolution transmission electron microscope equipped with a EDS collector, voltage operated was 200 kV. For the above measurements, the CuM NNWs samples were deposited on the carbon-coated Mo grid in order to eliminate the interference of copper element. The relatively low resolution TEM images were obtained on a HITACHI H-600 TEM with an accelerating voltage of 75 kV. Scan electron microscope (SEM) results were made on a XL30 ESEM. XRD patterns of the as-synthesized CuM naonowire networks were recorded on a D8 ADVANCE (BRUKER, Germany) diffractometer using Cu−Kα radiation with a Ni filter (λ = 0.154059 nm at 30 kV and 15 mA). The exact compositions of the prepared CuM nanowire networks were determined by ICP-MS (X Series 2, Thermo Scientific USA). XPS and Auger electron spectra measurements were performed on an ESCALAB-MKII spectrometer (VG Co.,United Kingdom) with Al Ka X-Ray radiation as the X-ray source for excitation. Fourier transform infrared spectroscopy (FT-IR) was utilized with BRUKER Vertex 70 FT-IR spectrometer. A CHI 832B electrochemical workstation (Chenhua Instruments Corp, Shanghai, China) was employed to conduct the catalytic tests.

Synthesis of CuPd NNWs. At room temperature, 2 mL of freshly prepared $NaBH_4$ (2 mg mL^{-1}) solution was added into 15 mL of water under stirring, then an aqueous mixture with a volume of 2 mL which containing 200 μL of H_2PdCl_4 (0.0564 mol L^{-1}) and 114 μL of $CuCl_2$ (0.1 mol L^{-1}) was injected into the above solution under vigorous stirring (stirring rate: 500 rpm). Note: the mixture of H_2PdCl_4 and $CuCl_2$ was added into the $NaBH_4$ solution in 15 seconds. After finished the reaction, the precipitates were collected by centrifugation, and washed with water several times.

Synthesis of CuPt NNWs. The process was the same as the synthesis of PdCu NNWs, except by replacing the H_2PdCl_4 as 59 μL of H_2PtCl_6 (0.193 mol L^{-1}).

Synthesis of CuPdPt NNWs. 3 mL of freshly prepared $NaBH_4$ (2 mg mL^{-1}) solution was added into 15 mL of water under stirring, then an aqueous with a volume of 2 mL aqueous solution which containing 200 μL of H_2PdCl_4 (0.0564 mol L^{-1}), 59 μL of H_2PtCl_6 (0.193 mol L^{-1}) and 114 μL of $CuCl_2$ (0.1 mol L^{-1}) was injected into the above solution under vigorous stirring. After finished the reaction, the precipitates were collected by centrifugation, and washed with water several times.

Electrochemical tests. The tests were performed with a three electrode system: a KCl saturated Ag/AgCl electrode was utilized as the reference electrode, while a platinum wire was served as the auxiliary electrode. The working electrode utilized in the tests is a glassy carbon electrode, which was cleaned before the experiment. For GOR measurements, a calculated amount of catalyst suspension was dropped on the working electrode, reaching a metal loading mass of 42.5 μg cm^{-2} (note: $m_{metals}=m_{Pd}+m_{Pt}$) for all the catalysts. After dried by an infrared lamp, 4 μL of Nafion (0.02% wt) ethanol solution was injected onto the electrode and dried again before experiments.

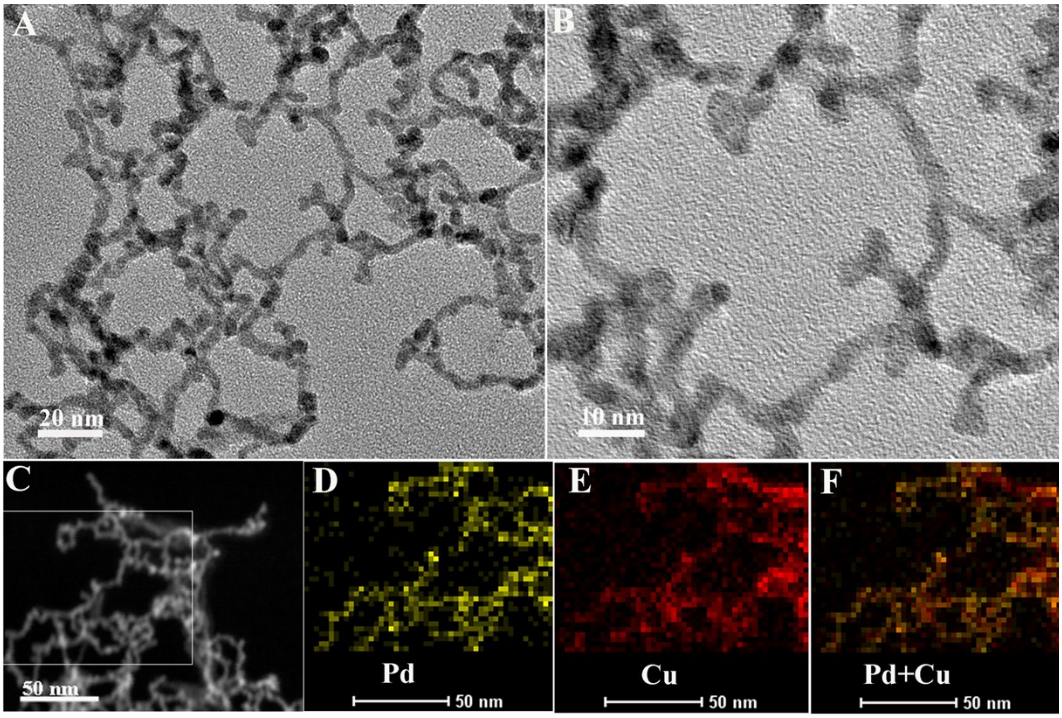

Fig. S1 (A, B) Typical TEM images of CuPd NNWs with different magnifications. HAADF-STEM (C) and the corresponding elemental mapping results (D-F) of the white square marked regions in (C) of CuPd NNWs.

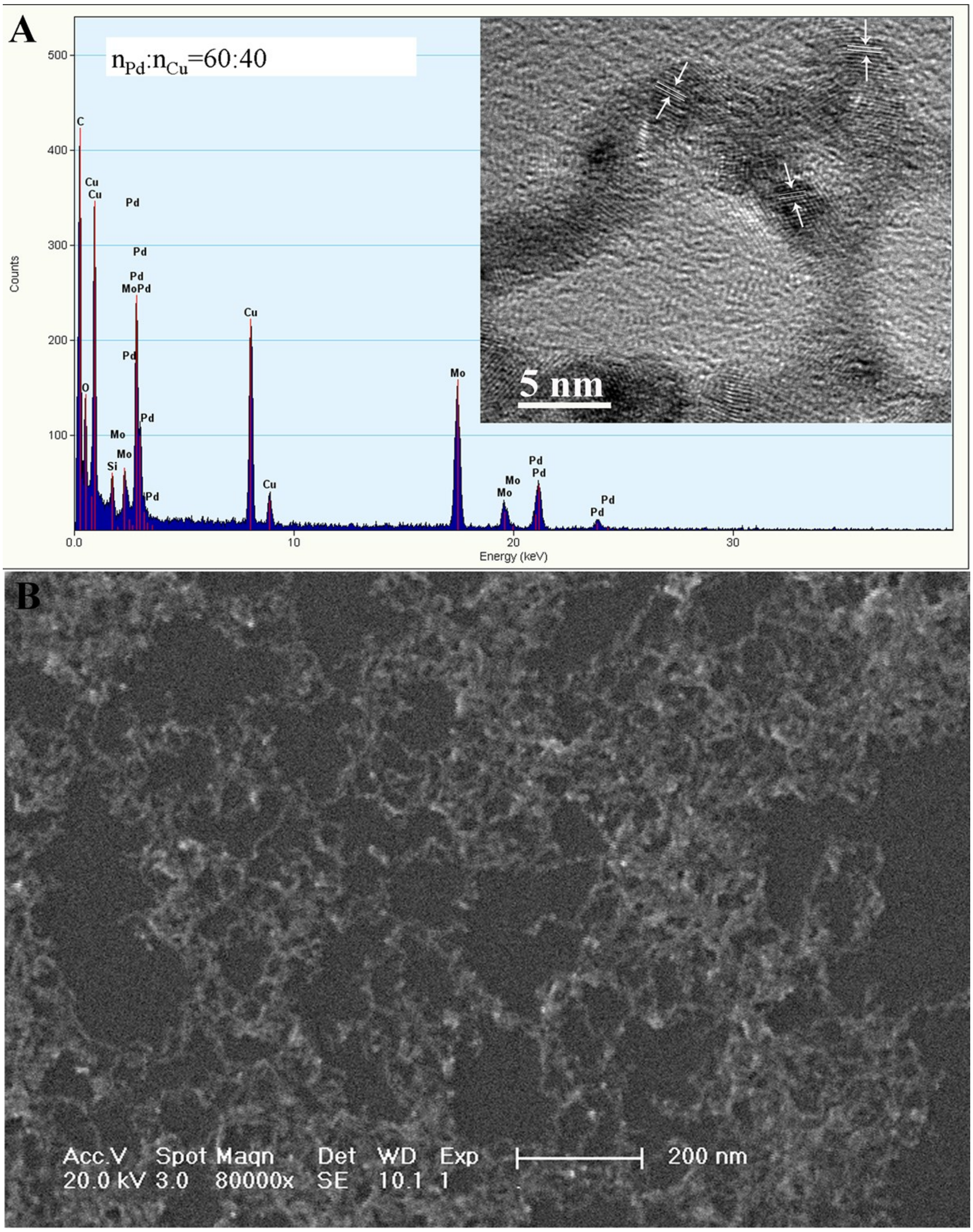

Fig. S2 (A) EDS of the as-prepared CuPd NNWs, the sample was dropped onto a carbon coated Mo grid for the examination, hence the peaks of Mo and C element in the figure are come from the Mo grid substrate, EDS results show the mole ratio of Pd/Cu is 60:40; the inset figure is the HRTEM image of the CuPd NNWs, the white arrows marked lattice space is measured to be 0.22 nm. (B) Typical SEM image of the prepared CuPd NNWs (deposited on Si substrate).

Table S1 The metallic Cu (0 valence) content of the Cu element determined using XPS integral area.

Materials	CuPd NNWs	CuPt NNWs	CuPdPt NNWs
The metallic Cu (0) content	75 %	78 %	82 %

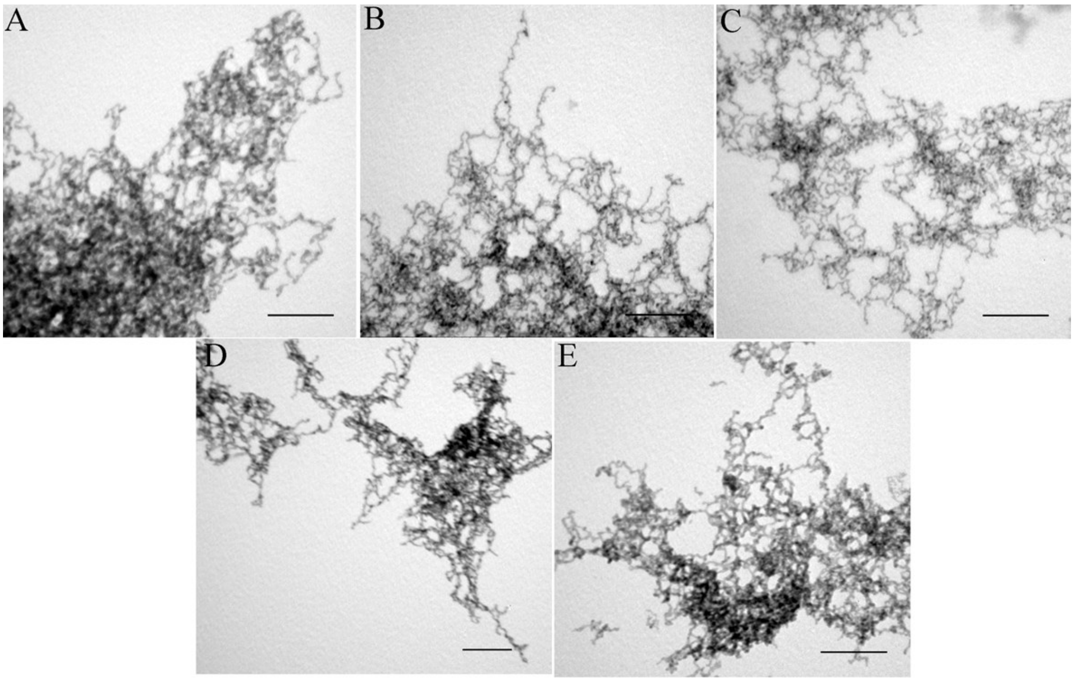

Fig. S3 (A) TEM image of the product by injecting the PdCu precursors into the $NaBH_4$ solution in one second without any stirring. Note: immediately after injecting the PdCu mixture, the solution was shook with hand for 5 five times to mix the solution homogeneously, and after that the solution was settled without any disturbances. (B) TEM image of the product generated at a stirring rate of 280 rpm. (C) TEM image of the product generated at a stirring rate of 900 rpm. (D) TEM image of the product generated by injecting the PdCu precursors into $NaBH_4$ solution in 1 min. (E) TEM image of the product generated by injecting the PdCu precursors into $NaBH_4$ solution in 2 min. All the other synthetic conditions in these controlling experiments are identical to the standard synthetic process of “Synthesis of PdCu NNWs” presented in the experimental section. The scale bar in the images represents 100 nm.

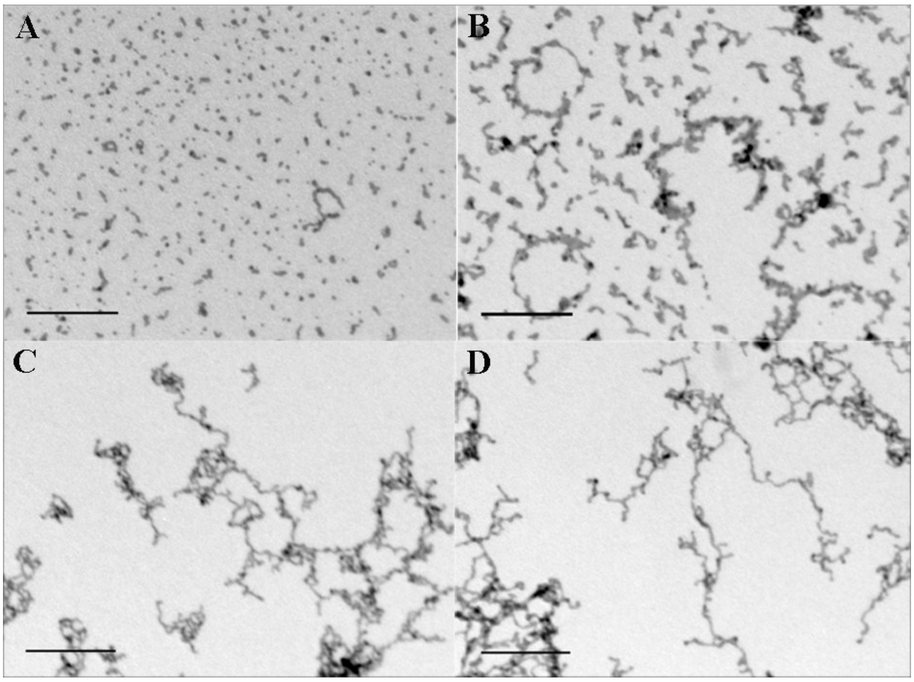

Fig. S4 TEM images of the intermediate products during the synthesis of CuPd NNWs, which collected at (A) 10 s, (B) 1 min, (C) 2 min and (D) 3 min. All the scale bars in the figures represent 100 nm.

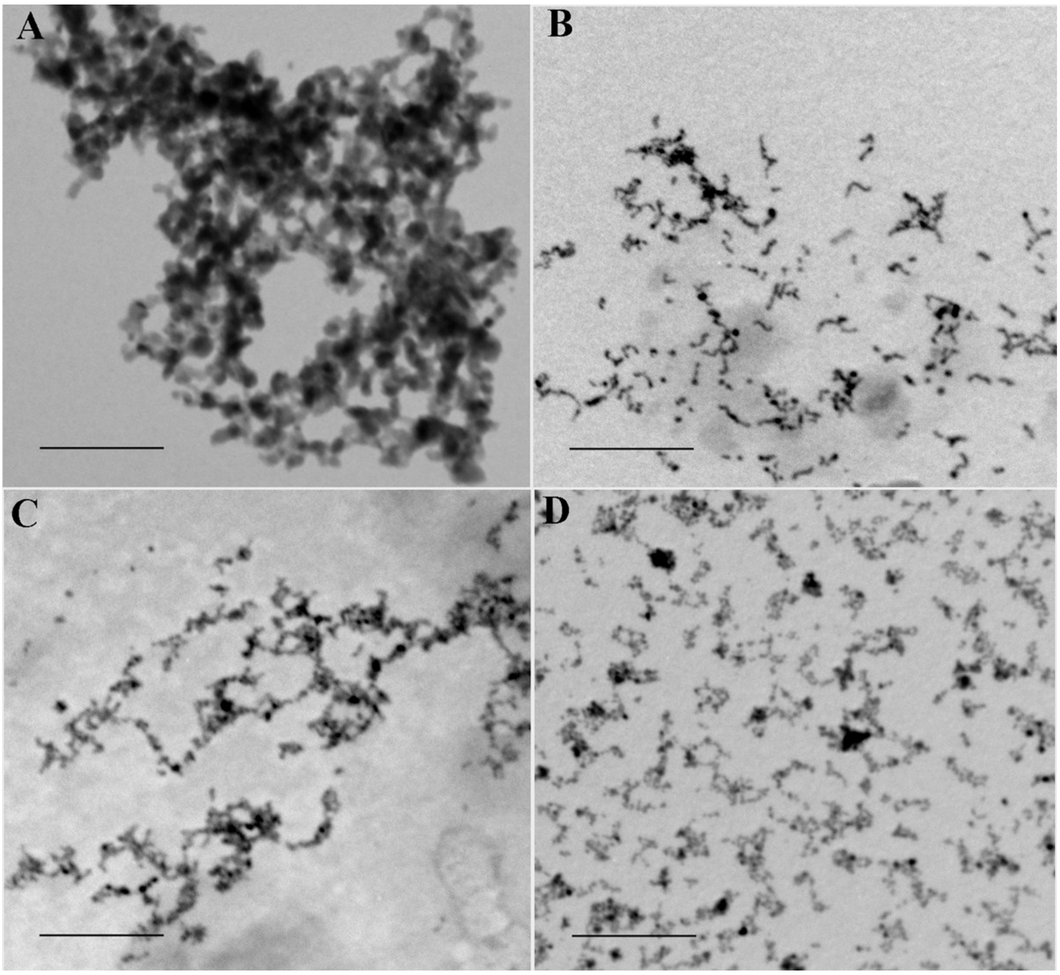

Fig. S5 Representative TEM images of the products prepared with the precursors: (A) $CuCl_2$, other conditions are same to the standard synthesis of CuPd NNWs; (B) H_2PdCl_4, other conditions are same to the standard synthesis of CuPd NNWs; (C) H_2PtCl_6, other conditions are same to the standard synthesis of CuPt NNWs; and (D) H_2PdCl_4 + H_2PtCl_6, other conditions in are same to the standard synthesis of CuPdPt NNWs. All the scale bars represent 100 nm. The results show that without Cu precursor, no nanowire networks structure can be obtained, hence suggesting that Cu precursor played an vital role for the formation of CuM (M=Pd, Pt and PdPt) NNWs.

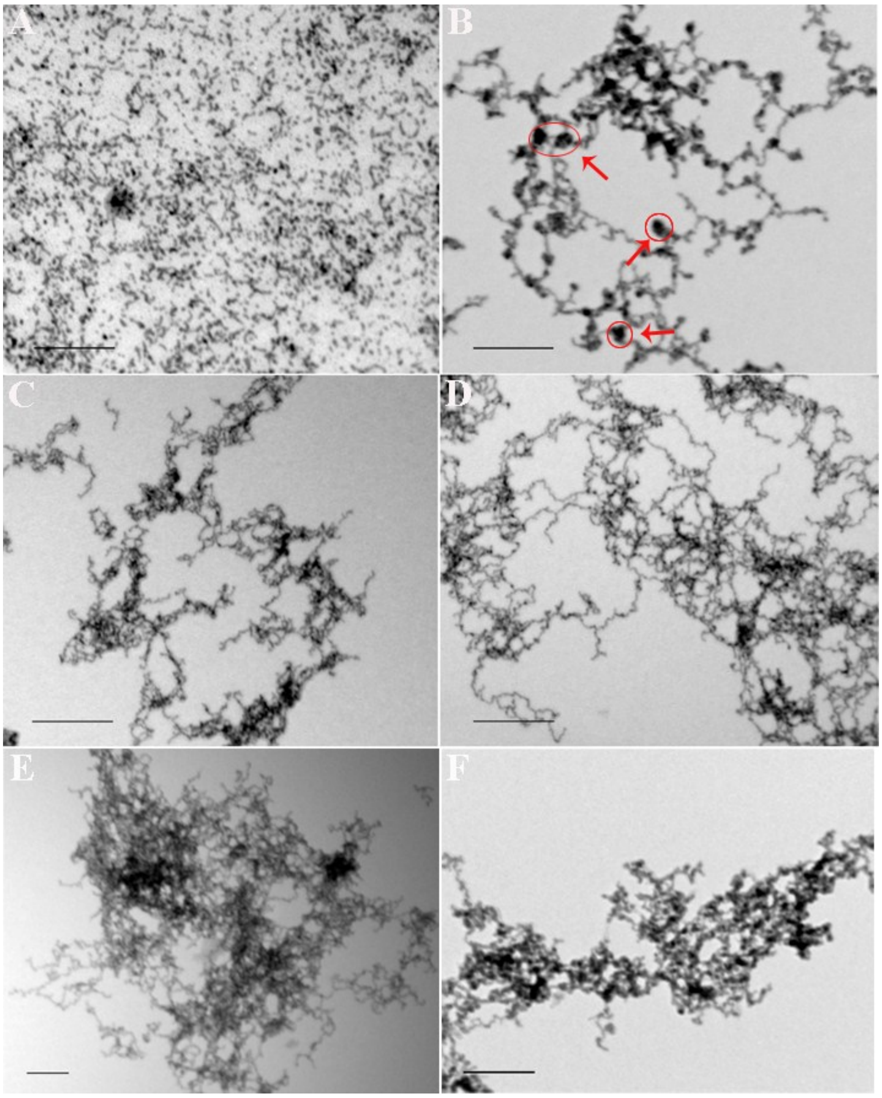

Fig. S6 TEM images of the products synthesized by (A) adding a mixture (2 mL of an aqueous solution) containing 200 μL of H_2PdCl_4 (0.0564 mol L^{-1}) and 114 μL of $CuCl_2$ (0.1 mol L^{-1}) into an aqueous solution containing 15 mL of water, 30 mg of PVP and 2 mL of $NaBH_4$ (2 mg mL^{-1}); (B) adding 2 mL of $NaBH_4$ (2 mg mL^{-1}) into 15 mL of water containing 200 μL of H_2PdCl_4 (0.0564 mol L^{-1}) and 114 μL of $CuCl_2$ (0.1 mol L^{-1}), as marked by the red arrows and circles, some spherical nanoparticles can be generated; (C) by adjusting the volume of $CuCl_2$ to 5 μL; (D) by adjusting the volume of $CuCl_2$ to 57 μL; (E) by adjusting the volume of H_2PdCl_4 to 100 μL, the other conditions in (C-E) are same to the standard synthesis of CuPd NNWs; (F) by increasing the concentration of the reactants, that is, by adding a mixture (2 mL aqueous solution) containing 1 mL of H_2PdCl_4 (0.0564 mol L^{-1}) and 0.575 mL of $CuCl_2$ (0.1 mol L^{-1}) into an aqueous solution containing 7 mL of water and 10 mL of $NaBH_4$ (2 mg mL^{-1}) under stirring. The scale bar represents 100 nm.

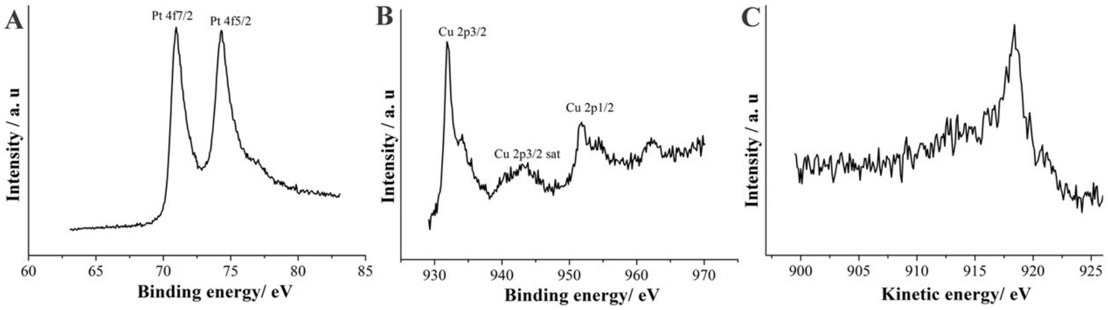

Fig. S7 XPS spectra of as-prepared CuPt NNWs: (A) Pt 4f; (B) Cu 2p and (C) Auger electron spectrum of Cu 3LMM. From the figure, we can know that Pt is mainly existed in metallic 0 valence state, since there are no obvious shoulder peaks in Pt 4f XPS spectra. For Cu, however, the peak marked with Cu 2p3/2 sat indicates the presences of Cu (with +2 valence), which may be originated from the adsorbed Cu^{2+} species or the oxidation of metallic Cu (with 0 valence) on the catalyst surface. Because of the peak intensity of Cu 2p3/2 (corresponding to the Cu with 0 or +1 valence) is much stronger than that of Cu 2p3/2 sat (corresponding to the Cu with +2 valence), most of the Cu elemental are existed in 0 or +1 valence. Supplemented by Auger electron spectrum of Cu 3LMM, we can exclude the presence of Cu species with +1 valence, because the peak at kinetic energy of 918.6 eV signifying the Cu (0 valence) is dominantly existed in the product. (Note: $E_{\text{Kinetic energy}} = hn - E_{\text{Binding energy}}$, when used Al Ka X-Ray radiation as the X-ray source for excitation, hn =1486.6 eV).

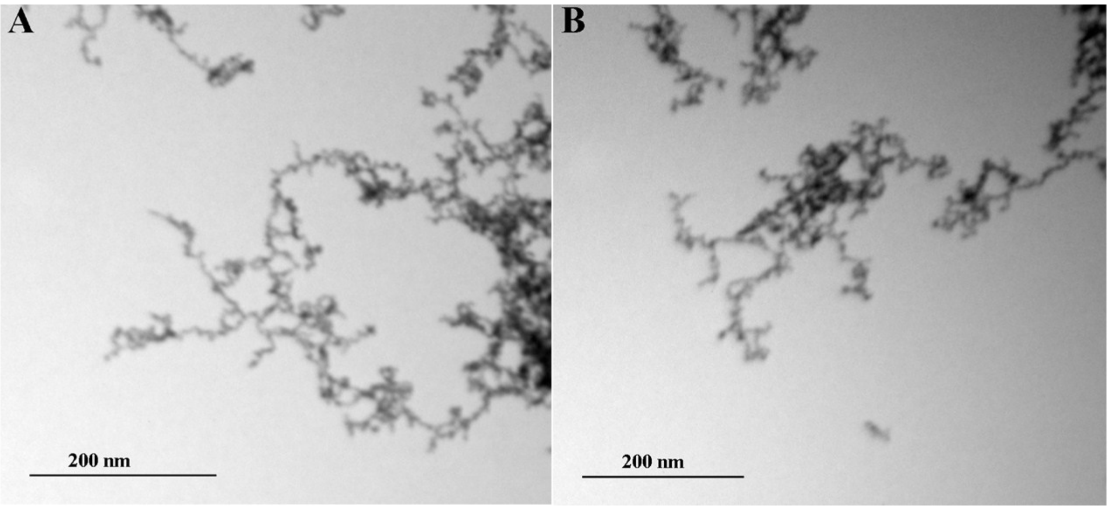

Fig. S8 Typical TEM images of (A) $Pd_2Pt_2Cu_1$ NNWs; (B) $Pd_1Pt_2Cu_2$ NNWs.

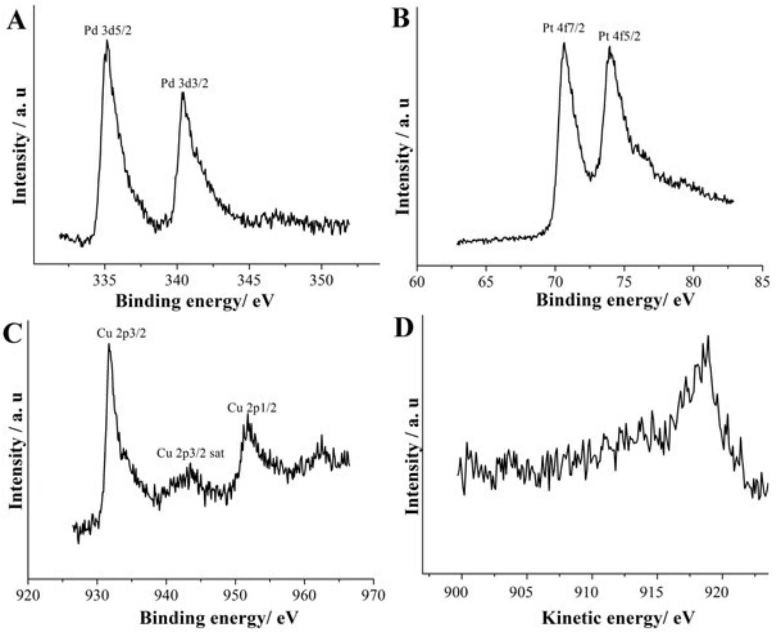

Fig. S9 XPS spectra of as-prepared CuPdPt NNWs: (A) 3d; (B) Pt 4f; (C) Cu 2p and (D) Auger electron spectrum of Cu 3LMM. From the figure, we can know that both Pd and Pt are mainly existed in metallic 0 valence state, since there are no obvious shoulder peaks in Pd3d and Pt 4f XPS spectra. For Cu, however, the peak marked with Cu 2p3/2 sat indicates the presences of Cu (+2 valence), which may be originated from the oxidation of metallic Cu (0 valence) on the catalyst surface. Because of the peak intensity of Cu 2p3/2 (corresponding to the Cu with 0 or +1 valence) is much stronger than that of Cu 2p3/2 sat (corresponding to the Cu with +2 valence), most of the Cu elemental are existed in 0 or +1 valence. From the Auger electron spectrum of Cu 3LMM, we can exclude the presence of Cu species with +1 valence, because the peak at kinetic energy of 918.5 eV signifying the Cu (0 valence) is dominantly existed in the product. (Note: $E_{\text{Kinetic energy}} = hn - E_{\text{Binding energy}}$, when used Al Ka X-Ray radiation as the X-ray source for excitation, hn =1486.6 eV).

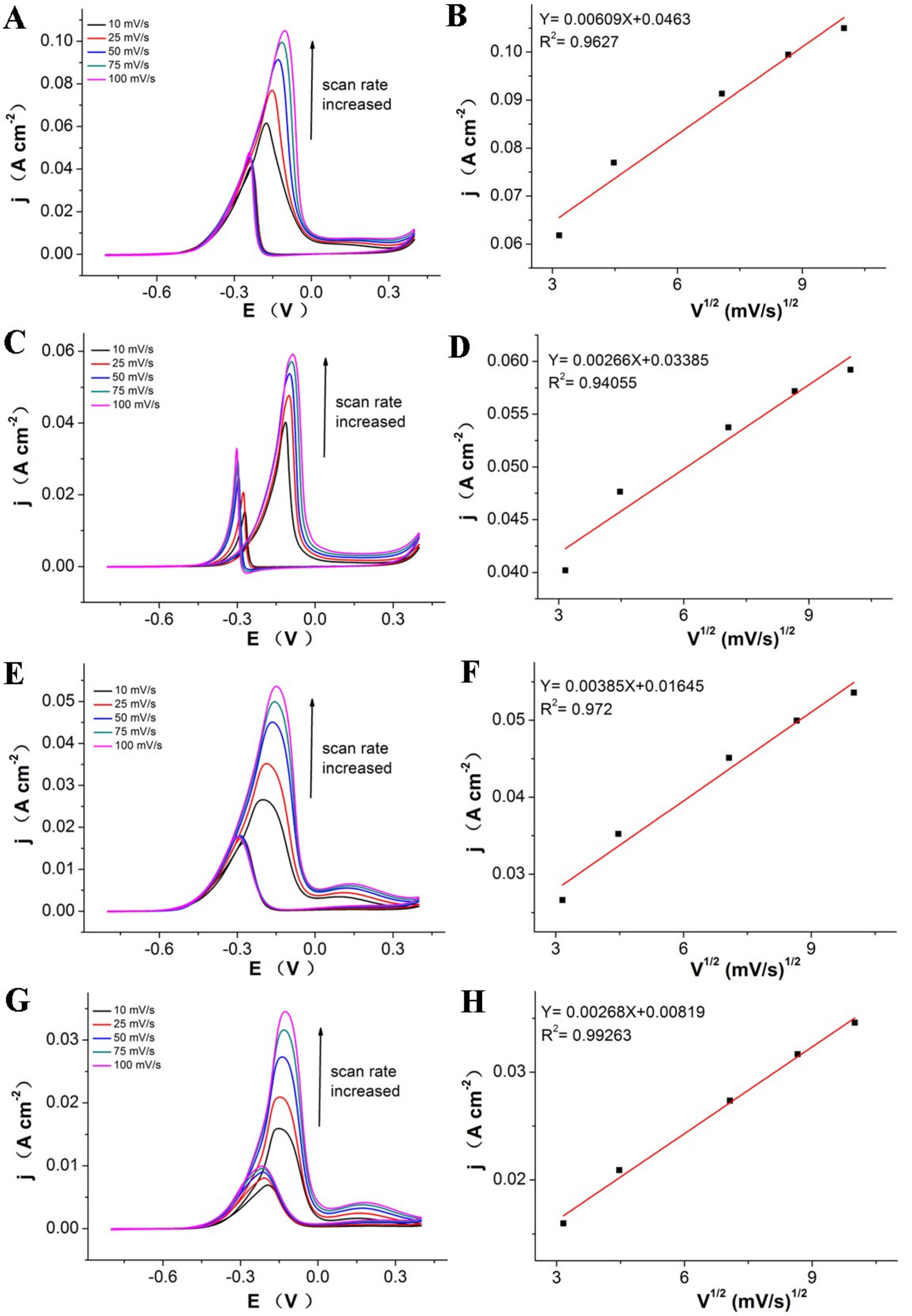

Fig. S10 CV characteristics with different scan rates and the corresponding relationship between the positive-going peak current versus the square root of the scan rate ($V^{1/2}$) on the different materials modified electrodes: (A, B) CuPdPt NNWs; (C, D) CuPd NNWs; (E, F) CuPt NNWs; (G, H) Commercial PBs catalyst. All the potential used in the figures was versus KCl saturated Ag/AgCl electrode.

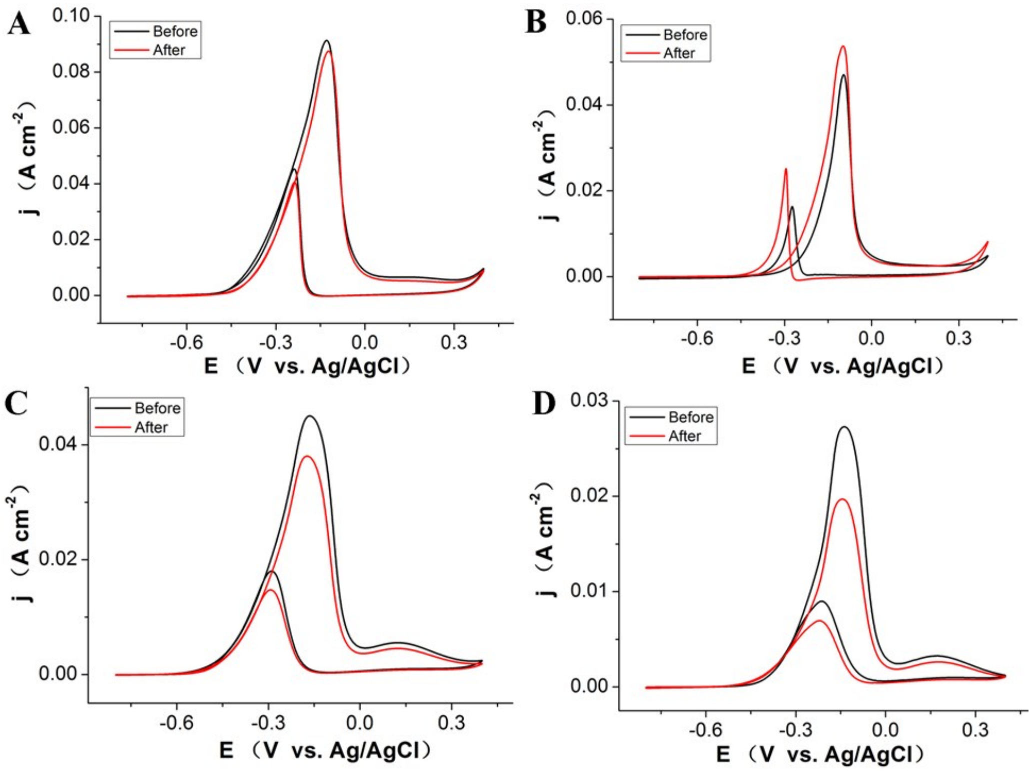

Fig. S11 CV characteristics before and after the j-t test of different materials modified electrodes: (A) CuPdPt NNWs; (B) CuPd NNWs; (C) CuPt NNWs; (D) Commercial Pt catalyst.

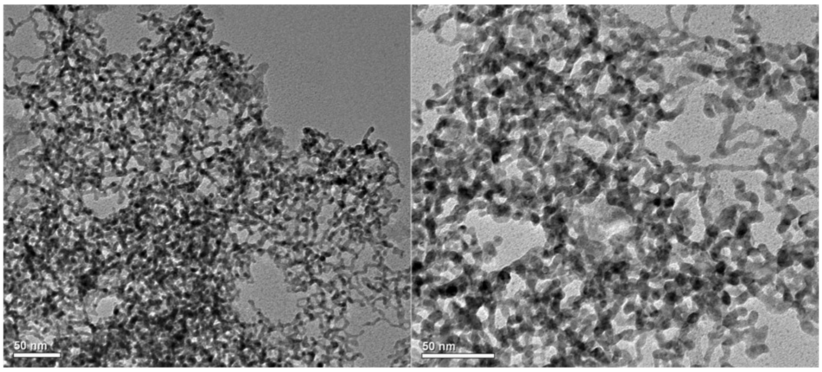

Fig. S12 TEM images of the PdCu NNWs after the electrochemical measurements.