

Three-Dimensional Hyperbranched PdCu Nanostructures with Highly Electrocatalytic Activity

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Characterization

The scanning electron microscope images (SEM) were obtained with a Hitachi SU-8000 microscope operated at 5 kV. The transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) characterizations were carried out using a JEOL JEM-2100F operated at 200 kV equipped with an energy-dispersive spectrometry analyzer. The samples for TEM and HRTEM characterizations were prepared by depositing a drop of the diluted colloidal suspension on a grid. Wide-angle powder X-ray diffraction (XRD) spectrum was acquired with a Rigaku Rint 2500 diffractometer with monochromated Cu K radiation. Low-angle XRD profiles were obtained by using a NANO VIEWER (Rigaku, Japan) equipped with a Micro Max-007 HF high-intensity micro-focus rotating anode X-ray generator. X-ray photoelectronic spectroscopy (XPS) spectra was carried out at room temperature by using a JPS-9010TR (JEOL) instrument with an Mg K α X-ray source. All the binding energies were calibrated via referencing to C 1s binding energy (284.6 eV).

Electrochemical Characterization

Cyclic voltammograms (CV) and chronoamperometric (CA) experiments were performed using a CHI 842B electrochemical analyzer (CHI Instruments, USA). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) reference electrode, a platinum wire as a counter electrode, and a modified glassy carbon electrode (GCE) as a working electrode. The modified GCE was coated with the as-prepared samples (5.0 μ g) and dried at room temperature. Then, 5.0 μ l of Nafion (0.05 wt%) was coated on the surface of the modified GCE and dried before the electrochemical measurements. Prior to electrochemical measurements, the GCE modified with the as-prepared sample was activated electrochemically by cycling the electrode potential between -0.2 V and +1.2 V (vs Ag/AgCl) in 0.5 M HClO₄. Formic acid electro-oxidation measurements were performed in a solution of 0.5 M HClO₄ containing 0.5 M formic acid at a scan rate of 50 mV s⁻¹. Mass current densities were normalized by the loaded Pd amount, which was determined by inductively coupled plasma mass spectroscopy (ICP-MS).

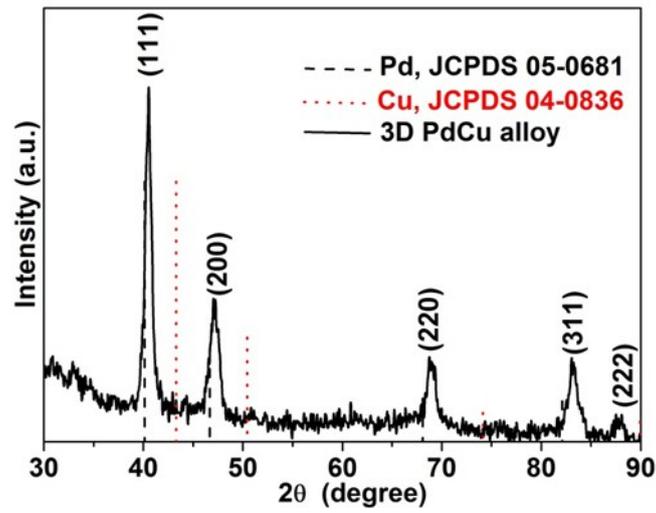


Fig. S1 Wide-angle XRD pattern of the 3D branched PdCu nanostructures.

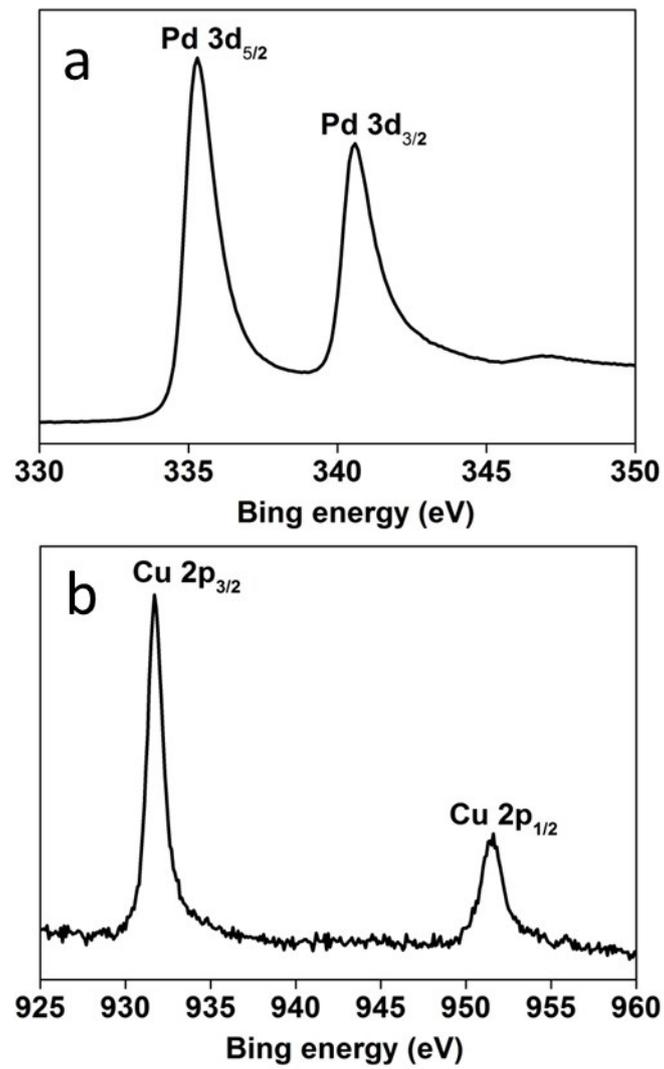


Fig. S2 High resolution XPS spectra for a) Pd 3d, b) Cu 2p of the 3D branched PdCu nanostructures.

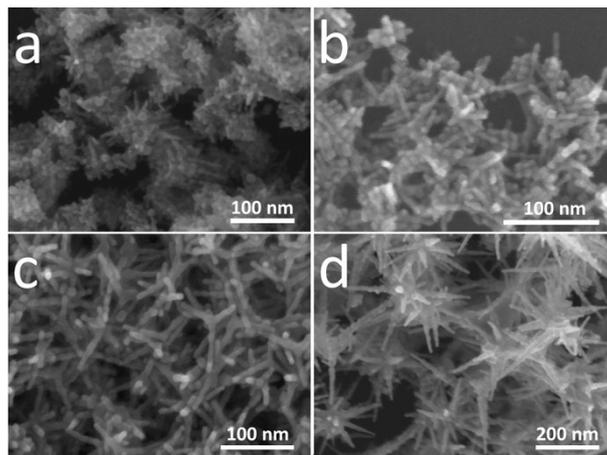


Fig. S3 SEM images of the samples prepared with different amounts of KBr: a) 0 mg, b) 10 mg c) 80 mg, and d) 150 mg.

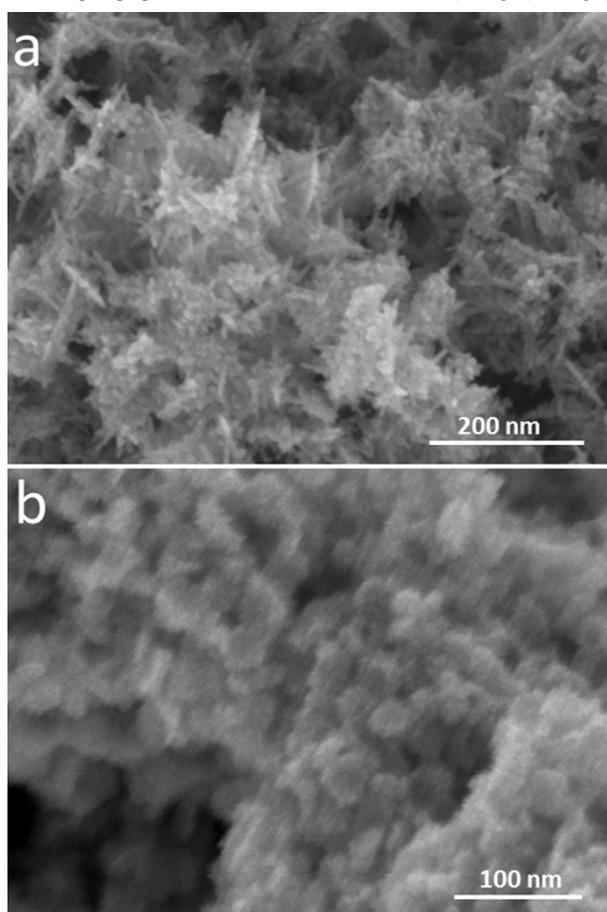


Fig. S4 SEM images of the samples prepared by replacing KBr with a) KCl and b) KI.

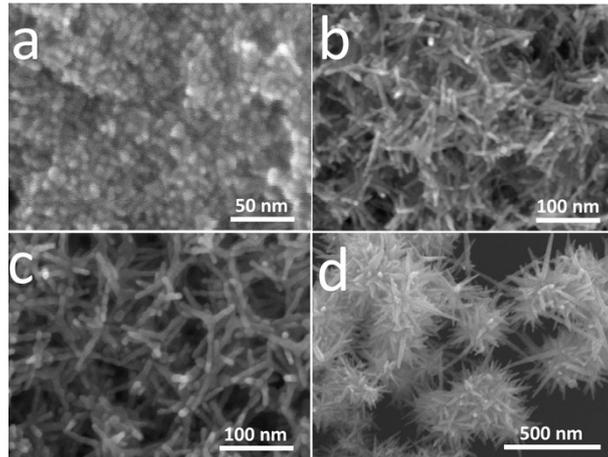


Fig. S5 SEM images of the samples prepared with different amounts of HCl: a) 0 mmol, b) 0.3 mmol c) 0.6 mmol, and d) 1.2 mmol.

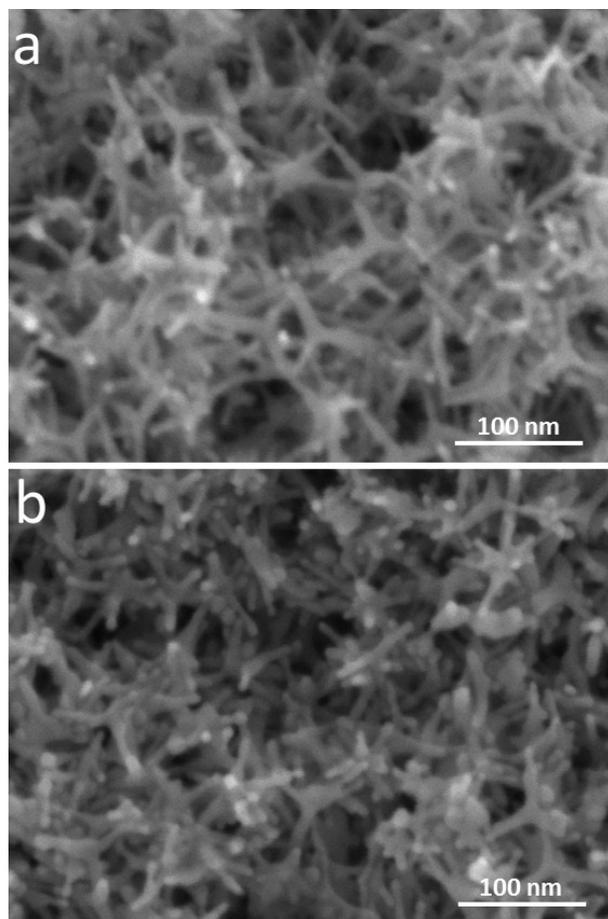


Fig. S6 SEM images of the samples prepared by replacing HCl with a) HNO_3 and b) H_2SO_4 .

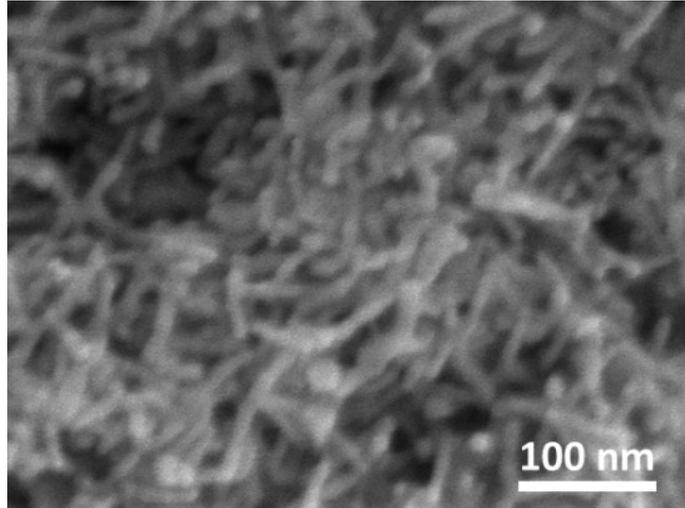


Fig. S7 SEM image of the sample after electrocatalyzing formic acid oxidation for 1000 s.

Table S1. Comparison of the surface area and the activity of 3D branched PdCu nanostructure with previous reported Pd-based catalysts.

Sample name	Surface area (m ² g ⁻¹)	Condition	Scan rate (mV s ⁻¹)	Mass activity (A mg ⁻¹ Pd)	Reference
3D branched PdCu alloy	76.9	0.5 M HClO ₄ ⁺ 0.5 M HCOOH	50	1.84	Present work
Mesoporous Pd film	--	0.5 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.93	[S1]
Pd/Graphite Oxide	41.8	0.5 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.90	[S2]
Single crystalline Pd tripods	20	0.5 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.49	[S3]
Branched Pd tertrapods	--	0.5 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.37	[S4]
Pd-P nanoparticle networks	18.9	0.5 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.61	[S5]
Nanobranched porous Pd-Sn	18.6	0.5 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.98	[S6]
Nanowire	98.2	0.5 M H ₂ SO ₄ ⁺	50	0.94	[S7]
PdNi/Graphite Oxide		0.5 M HCOOH			
PdCo nanoassemblies	--	0.5 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.28	[S8]
Mono-dispersed PdCu nanoparticle	--	0.1 M H ₂ SO ₄ ⁺ 0.5 M HCOOH	50	0.35	[9]
Ideal Pd nanowires with 10 nm in diameter	33	--	--	--	[10]

Reference

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- [S10] Assuming cylindrical Pd nanowires (with 10 nm in diameter) with smooth surface, we theoretically calculated the surface area.