Electronic Supplementary Information

Three-dimensionally grown thorn-like Cu nanowire arrays by fully electrochemical nanoengineering for highly enhanced hydrazine oxidation

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EXPERIMENTAL SECTION

Preparation of CNWAs on foamed Cu. Typically, a piece of Cu foam degreased in acetone and deionized water under ultrasonication for 10 min, respectively, was subject to anodization for different durations under a constant current density of 16 mA/cm² in 3 M freshly prepared NaOH aqueous solution at room temperature. The electrochemical cell was in a two-electrode configuration with a Pt foil counter electrode. The bright orange Cu foam gradually turned light blue during anodization. Subsequently, following thorough rinsing, the anodized Cu foam was again configured as the working electrode. Cathodic current density of 16 mA/cm² was applied for a certain period in 0.5 M Na₂SO₄. During this galvanostatic treatment, the color of the copper foam turned from light blue to dull wine. Upon finishing metallization, the as-obtained samples were rinsed with deionized water and ethanol separately before drying up at room temperature under gentle nitrogen flow.

Preparation of CR-CNWAs on foamed Cu. In a typical chemical reduction route, a piece of anodized Cu foam was dipped in freshly prepared 0.5 M aqueous NaBH₄ solution for 15 min. The sample was then rinsed with deionized water and ethanol separately, and left to dry up at room temperature under gentle nitrogen flow.

Preparation of CNWAs on carbon fabrics. CNWAs on carbon fabrics were prepared similarly to those on Cu foam. First, a layer of Cu was electrodeposited on carbon fabrics by an applying constant potential of -0.4 V on a piece of carbon fabrics for 15 min in 0.6 M aqueous CuSO₄ (pH adjusted to ~2 with H_2SO_4) with Cu wire as reference electrode and Pt wire as counter electrode. Afterwards, the carbon fabrics were anodized in 2 M NaOH at 10 mA/cm² for 15 min and cathodized in 0.5 M Na₂SO₄ for 25 min at 10 mA/cm².

Preparation of CNWAs on coiled wires. CNWAs on a strand of coiled Cu wires were prepared similarly to those on the Cu foam. The electrolyte was 2 M NaOH and anodic current and cathodic current were both 0.5 mA for 4 cm-long wire. The electrochemical reactions were stopped as soon as the potential significantly hiked during alkaline anodization or fell during cathodic metallization, which marked the beginning of oxygen and hydrogen evolution at the working electrode, respectively.

Notes: The current densities in the anodization and cathodization are all described respective to the geometric dimension (area/length) of the substrate. Attention should be paid to the specific substrate used and attempts may be required to adjust the parameters according to specific synthetic scheme when three-dimensional substrate is involved. Generally, in order to prevent favoring side reactions, the current density should not be too low.

Preparation of Pt/C electrode. Commercial 20% Pt/C was stepwise dropped onto Cu foam with mass loading of 10.8 mg/cm². The casting solution was 5 mg/mL Pt/C with 1% Nafion. The electrode

was allowed to dry up in hot air. The mass loading of the Cu nanowires was determined by measuring the mass of loading its hydroxide precursor. A piece of anodized Cu foam was weighed on a microbalance (METTLER TOLEDO) with an accuracy of 10 ug before and after dipping into 1 M HCl to completely remove the Cu(OH)₂ nanowires. The loading mass was calculated to be 16.5 mg/cm². By assuming that all Cu(OH)₂ precursor was transformed into Cu nanostructures, the loading mass of the Cu nanowires was calculated to be 10.8 mg/cm². Note that the amount of (hydr)oxide layer under the Cu(OH)₂ NWAs can also be removed by the HCl, leading to an actually higher weight difference of the sample before and after HCl treatment. Hence, the calculated mass loading of Cu nanowires, and thus that of the loaded Pt/C catalyst, could be higher than the actual loading mass of Cu nanowires.

Characterizations. X-ray diffraction patterns were obtained on an X-ray diffractometer (Rigaku, D/MAX 2550) with Cu Kα radiation generator and a RINT 2000 vertical goniometer. X-ray photoelectron spectroscopy was performed on an X-ray photoelectron spectrograph (VG ESCA 2000) with a Mg Kα as source, and C 1s peak at 248.6 eV was used as an internal standard. Scanning electron microscopy was conducted at 15.0 kV accelerating voltage and 10 uA emission current with a field-emission scanning electron microscope (Hitachi S4800) with an energy dispersive X-ray spectrometer. Transmission electron microscopy images were photographed on a JEOL 2011 microscope, operating at an accelerating voltage of 100 kV and emission current of 100 uA.

Electrochemical Measurements. Electrocatalytic performance was investigated in a three-electrode electrochemical cell linked to an electrochemical workstation (AUTOLAB, PGSTAT302N), employing a Pt mesh counter electrode, a Ag/AgCl (sat. KCl) reference electrode, and working electrodes of interest, respectively. Nonconductive inert epoxy resin was applied on the foam to define the exposed area of the electrodes. Prior to measurements, the electrolyte was purged with high-purity N₂ for 30 min to remove the dissolved O₂. Stirring of the electrolyte solution was absent except for the durability test. Cyclic voltammetry in phosphate buffer solution was performed at 25 mV/s. Linear sweeping voltammetry for polarization data was conducted at 25 mV/s in 3 M NaOH and 1 M hydrazine. Chronoamperometry under a constant applied potential of -0.6 V was carried out to test the durability of the CNWAs. Electrochemical impedance spectroscopy was obtained using AC impedance at an amplitude of 10 mV in a frequency range of 0.1-100k Hz at -0.6 V.

FIGURES



Fig. S1 Experimental setups of (a) alkaline anodization and (b) cathodic metallization. Typical chronopotentiometric records of (c) alkaline anodization of Cu foam for 30 min and (d) cathodic metallization of the corresponding anodized Cu foam. The cathodization durations generally lasted 1 to 2 times as long as the corresponding anodization durations to ensure complete reduction of the precursor Cu(OH)₂ NWAs, which also can be indicated by evolution gas bubbles (presumably hydrogen) at the working electrode.



Fig. S2 SEM images of Cu foam anodized under different conditions: (a) $j = 16 \text{ mA/cm}^2 \text{ in 3 M NaOH}$, (b) $j = 16 \text{ mA/cm}^2 \text{ in 0.5 M Na}_2\text{SO}_4$ and (c) $j = 2 \text{ mA/cm}^2 \text{ in 3 M NaOH}$; (d)-(f) are the XRD patterns of the samples from (a)-(c), respectively. Scale bars of the insets are all 1 um. The SEM images are false-colored.



Fig. S3 XPS analysis of the as-prepared CNWAs: (a) Cu 2p and (b) O 1s spectra. According to the relative content of Cu2O and CuO are calculated



Fig. S4 (a) TEM, SEAD (inset) and (b) HRTEM images of Cu nanowires. Asterisk stands for diffraction ring of Cu₂O.



Fig. S5 Digital photograph of (a) coiled Cu wires subject to the synthetic procedures and their SEM images (b,c). Digital photograph (d) of a piece of carbon fabrics with CNWAs and its SEM images (e,f).



Fig. S6 CV of (a) CNWAs, (b) CR-CWAs and (c) primitive Cu foam in non-faradic potential window at 10 mV/s.



Fig. S7 SEM images of $Cu(OH)_2$ NWAs produced at different anodization durations: (a) 6, (b) 10, (c) 20, (d) 30, and (e) 50 min. (f) Length of the $Cu(OH)_2$ nanowires as a function of anodization duration. All scale bars are 10 um. For the Cu foam anodized for 6 min, the nanowires were short, sparse and hardly aligned. Upon prolonging anodization time to 10 min, both length and density of nanowires increased and alignment was improved. Yet, incomplete coverage of nanowires was still obvious, which was not observed for the samples that experienced longer anodic durations (\geq 20 min).



Fig. S8 SEM images of Cu nanowires derived from the $Cu(OH)_2$ nanowires produced at different anodization durations: (a) 6, (b) 10, (c) 20, (d) 30, and (e) 50 min. All scale bars are 10 um. (f) Thickness of the resulted Cu NW film as a function of anodization duration. Because of deformation of the Cu nanowires, the thickness of the nanowires arrays film became generally smaller than the length of the corresponding Cu(OH)₂ precursors. Specially, for the 6-min anodized sample, the Cu nanowires were so sparse like their precursor that they barely formed NW film.



Fig. S9 Polarization curves of HzOR for CNWAs prepared with different anodization durations.



Fig. S10 SEM images of CR-CNWAs at low (a) and high (b) magnifications. Aggregates were found at the tips of the NWAs owing to the less controlled manner of the direct wet-chemical route. This cause decreased ESA and dampened electrocatalytic performance, as also supported by the smaller EDLC (Fig. S6).



Fig. S11 Zoomed *J*-t curve of CNWAs showing half of the 2.5% activity loss occurred at the initial 10% test period.

TABLES

Electrocatalyst	Onset Potential (V)	Scan Rate (mV/s)	Electrolyte	Ref.
Carbon Fiber Cloth Supported Co	-1.1 vs Ag/AgCl (KCl	10	$1 \text{ M KOH} + 20 \text{ mM N}_2\text{H}_4$	S1
Ni ₁ Co ₃ Alloy	-0.19 vs reversible hydrogen electrode	20	1 M KOH + 100 mM N ₂ H ₄	5
N-doped Holey Graphene	-0.15 vs. saturated calomel electrode	20	0.1 M PBS + 10 mM N ₂ H ₄	11
Polypyrrole-derived N and O Co- doped Mesoporous Carbon	-0.36 vs saturated calomel electrode	10	0.1 M PBS + 50 mM N ₂ H ₄	13
Ag ₂ O Nanowire Arrays	-0.85 vs saturated calomel electrode	50	0.1 M NaOH + 4 mM N ₂ H ₄	S2
Polyaniline/Pt Nanoparticle	0.15 vs saturated calomel electrode	50	1 M H ₂ SO ₄ + 100 mM N ₂ H ₄	6
Ti-supported NanoAg/Ti Eectrode	-0.6 vs saturated calomel electrode	100	1 M NaOH + 70 mM N ₂ H ₄	S3
Carbon Supported Pd Nanoparticles	-0.05 vs saturated calomel electrode	20	0.05 M H ₂ SO ₄ + 10 mM N ₂ H ₄	7
Cu Nanocubes-graphene Paper	-0.10 vs saturated calomel electrode	100	0.1 M KOH +10 mM N ₂ H ₄	12
Sandwich-type Reduce Grahpene Oxide/Cu Composite	-0.15 vs saturated calomel electrode	100	0.1 M KOH + 10 mM N ₂ H ₄	14
CNWAs	-0.82 vs Ag/AgCl (KCl saturated)	25	$3 \text{ M KOH} + 1 \text{ M N}_2\text{H}_4$	This work

Tab. S1 Comparison of HzOR performance in terms of onset potential.*

*Because the electrolyte, scan rate of voltammetry, mass loading of the catalysts, types of conducting substrate vary in different works, the comparison is elementary and is merely based on the onset potentials.

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