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A Robust and Highly Active Copper-Based Electrocatalyst for Hydrogen Production at Low Overpotential in Neutral Water

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 Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Herein we report a noble-metal-free Cu(0)-based catalyst for electrocatalytic hydrogen evolution reaction (HER) in neutral water with an onset overpotential of only 70 mV. This is, to the best of our knowledge, the lowest value among all the reported copper(0)-based catalysts for HER in water.

For the world's future energy supply, hydrogen (H₂), as a clean and renewable energy carrier, is considered as a promising alternative to fossil fuels.¹ In the past few decades, many efforts have been made to pursue sustainable and efficient hydrogen production from water driven by electricity or solar energy.²⁻⁵ The electrocatalytic strategy for hydrogen evolution reaction (HER) is an important method to produce hydrogen, but it usually requires highly active electrocatalysts to obtain high current density at low overpotential.⁶ To date, the most efficient electrocatalysts for HER are mainly based on noble metals, especially Pt, but one concern is that their high costs significantly limit the practical application of such catalysts in a water splitting device.^{4, 7} Thus, seeking efficient and inexpensive HER electrocatalysts still remains a great challenge in the progress towards clean energy production.¹ Another concern is the reaction media and water resources. Although many electrocatalysts based on inexpensive metals have been reported, such as cobalt,⁸⁻¹⁰ nickel,¹¹⁻¹² iron,¹³⁻¹⁵ and molybdenum disulfide,^{6, 16-17} most examples have been reported to perform in acidic solutions (for example, 0.5 M H₂SO₄). When using basic solutions, the activity of Pt is significantly decreased. Neutral water has large availability and abundance and therefore it is beneficial to directly use it as the water resource for H₂ production.

Compared with other inexpensive metals (Ni, Co, Mo, etc.), Cu could be very attractive for HER due to its much lower cost and higher abundance. In previous studies, less attention has been paid to develop active catalysts made of cheap copper (Cu) element, and only a few copper-based HER catalysts have been used to perform H₂

production. Recently, several mon/dinuclear copper complexes have been reported as homogeneous electrocatalysts toward hydrogen production with high catalytic overpotentials more than 200 mV (Table S1).¹⁸⁻²⁰ Copper metal was also reported as an electrocatalyst to evolve hydrogen but still with quite high overpotential (> 250 mV) and most published copper-based catalytic reactions were performed under basic or acidic conditions.²¹⁻²⁵ More recently, our group reported a copper-based material electrodeposited from copper(II) tris(2-pyridylmethyl)amine complexes as a bifunctional electrocatalyst for both HER and oxygen evolution reaction (OER) at nearly neutral pH (pH 9.2).²⁴ However, the Tafel slope of 320 mV/decade of this copper-based bifunctional electrocatalyst for HER and the overpotential of ~440 mV were both too high for efficient hydrogen evolution. To our surprise, no Cu(0)-based material has been studied in neutral water as an active catalyst for water reduction to produce hydrogen with low catalytic overpotential.

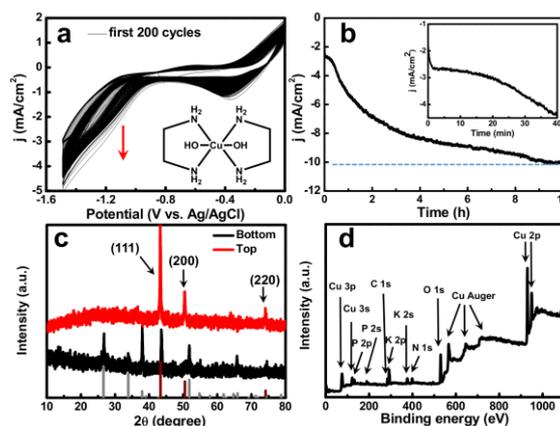


Figure 1. (a) CVs (200 scan cycles) of 3.0 mM Cu-EA in a 0.1 M KPi solution on FTO as the working electrode at pH 7.0. (b) Current density plot for bulk electrolysis at -1.2 V under the same conditions of (a). Inset: a magnified view of the current density plot for bulk electrolysis in the first 40 min. (c) Powder XRD patterns of the catalyst materials scratched from FTO surface (red) and the catalyst/FTO electrodeposited (black). Grey lines: SnO₂ PDF#41-1445; dull red lines: Cu(0) PDF#04-0836. (d) XPS survey spectrum of the electrodeposited Cu(0) material after washing by deaerated ethanol.

In this present study, we demonstrate that copper(0)-based ethylenediamine (Cu-EA) complex can be used as an excellent

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Electronic Supplementary Information (ESI) available: See
DOI: 10.1039/x0xx00000x

precursor to electrodeposit leaf-like hierarchical Cu(0) material, and this Cu(0) material can highly promote hydrogen production with a catalytic overpotential of only 70 mV in neutral water. In addition, this porous Cu(0) material exhibited excellent robustness for catalytic hydrogen production at a wide range of pH values from 0 to 14. The deposited material was extensively studied by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD).

Leaf-like Cu(0) materials were facily obtained by electrodeposition of the copper(II) ethylenediamine (**Cu-EA**) precursor on conductive fluorine doped tin oxide (FTO) electrodes. Figure 1a shows the cyclic voltammograms (CVs) of **Cu-EA** (3.0 mM) in a 0.1 M potassium phosphate (KPi) solution at pH 7.0 using FTO as the working electrode, an Ag/AgCl (3 M KCl) electrode as the reference electrode, and Pt wire as the counter electrode. In the initial scan between 0 and -1.50 V at a scan rate of 100 mV/s, obvious catalytic potential was observed after -1.0 V vs. Ag/AgCl, accompanied by production of gas bubbles on the electrode. The bubbles were confirmed to be H₂ by gas chromatography (GC). After continuous CV scans for 200 cycles, the catalytic potential for H₂ production had significantly decreased from -1.0 V to -0.80 V. Meanwhile, the current density was highly enhanced, from 3.0 mA/cm² to 5.0 mA/cm² at -1.50 V. The cathodic scan also exhibits a broad feature at $E_{p,c} = -0.38$ V, probably attributed to the oxidation of Cu to Cu²⁺.²³ Moreover, a thin film with dull red was formed during the continuous CV scans.

Bulk electrolysis (BE) of a bare FTO electrode was further performed in the same electrolyte solution at pH 7.0 under an applied potential of -1.20 V (Figure 1b). The catalytic current density was quickly increased and a red thin film was quickly generated in only 3 min. After that, the current density had very slight increase for about 15 min and the red color remained. Interestingly, as the BE process continued, the current density was then significantly enhanced and the color of the deposited materials became dull red. After long-term electrolysis of 10 hours, the catalytic current density reached ~10 mA/cm² and a large amount of gas bubbles were observed on the surface of the electrode (see movie S1 in the supporting information).

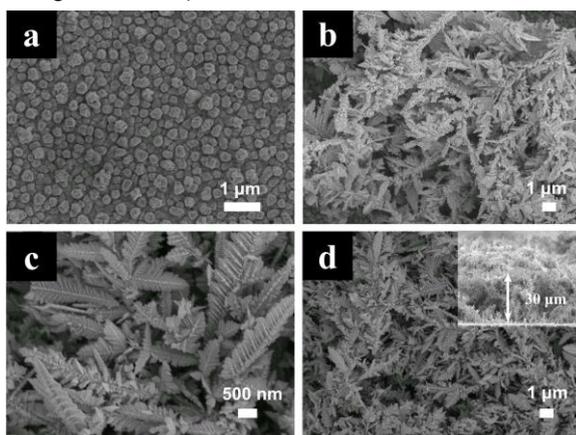


Figure 2. SEM images of the catalyst materials electrodeposited on the FTO surface at -1.2 V in a 0.1 M KPi buffer solution at pH 7.0 containing 3.0 mM **Cu-EA** for 20 min (a), 1 h (b and c), and 10 h (d). Inset: the cross-sectional SEM image of the catalyst materials electrodeposited by bulk electrolysis for 10 h.

To provide more insights into the electrodeposited copper-based materials from **Cu-EA** precursor, the catalyst materials were characterized by powder X-ray diffraction (XRD). As the color of the

deposited materials in the initial 20 min was different from that formed in the latter 10 h, the surface layer of the catalyst film was scratched from FTO as the top sample and the residue was used as the bottom sample shown in Figure 1c. The diffraction pattern (red plot) for the top sample can be ascribed to Cu(0) phase with a cubic structure (PDF#04-0836). The bottom sample on the FTO showed the diffraction patterns (black plot) corresponding to both Cu(0) cubic structure and the FTO substrate (PDF#41-1445). The similar crystalline phases of these two catalyst samples suggested nearly the same composition of the deposited materials on the top and the bottom of FTO.

The chemical compositions and the valence states of the catalyst film were examined by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum revealed the deposited materials mainly contain Cu, O, K, P, N, and C elements (Figure 1d) and the C 1s peak (285.0 eV) was used as the reference. The K, P, and N elements were probably either from the electrolyte or from the ethylenediamine ligand, which can be easily removed after washing with water for a few times (Figure S1). Figure S2a and S2b show the high-resolution XPS spectra of Cu 2p and Cu LMM. In the Cu 2p spectra, obvious peaks of Cu 2p_{3/2} and Cu 2p_{1/2} were observed with binding energies located at 932.2 and 951.9 eV, respectively, which suggest that the valence state of copper is zero.²⁶⁻²⁸ The presence of Cu(0) could be further confirmed by the Cu LMM binding energy at 918.6 eV.²⁸ Therefore, the oxygen signal that appeared in the survey spectrum is probably attributed to the absorbed gas molecules.²⁷⁻²⁹

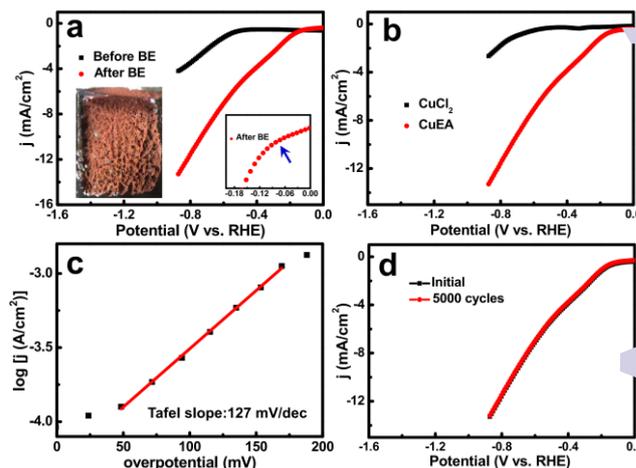


Figure 3. (a) Polarization curves for the FTO electrode before and after bulk electrolysis at -1.2 V for 10 h in a 0.1 M KPi buffer solution at pH 7.0 containing 3.0 mM **Cu-EA**. Inset: magnified LSV data from -0.16-0 V. (b) Polarization curves for catalyst materials deposited from **Cu-EA** (red) and CuCl₂ (black) in a clean 0.1 M KPi solution. (c) Tafel plots for catalyst materials from **Cu-EA** in 0.1 M KPi. (d) Polarization curves for catalyst materials deposited from **Cu-EA** in 0.1 M KPi for the first cycle and 5000 cycles at a scan rate of 100 mV/s between 0 and -1.5 V.

Figure 2 shows SEM images of the electrodeposited Cu(0) materials on FTO after different electrolysis times. A short period of 20 min for electrolysis produces deposited materials with the morphology shown in Figure 2a, displaying well-dispersed nanoparticles with an average diameter of ~200 nm. With increasing electrolysis time, the morphology was significantly changed. After 60 min, the catalyst nanoparticles were fully covered by interlaced leaf-like units, which exhibited well-defined porous frameworks (Figures 2b-2c). The leaf-like morphology of the deposited materials was still the same even after 10 hours of electrolysis but its thickness was increased to ~30 μ m (the inset of Figure 2d). In order to compare **Cu-EA** precursor with a simple

divalent copper salt, the SEM images of the electrodeposited materials from 3.0 mM CuCl₂ in 0.1 M KPi at pH 7.0 are shown in Figure S3. The results show that the morphology of the deposited catalyst from CuCl₂ was quite irregular with aggregated materials on FTO surface, suggesting smaller surface areas and less active sites for catalytic reaction. In addition, their catalytic activities will be discussed in the following studies.

Electrocatalytic H₂ production using the present Cu(0) materials was further investigated in neutral water (0.1 M KPi). Since the Cu(0) materials deposited for 20 min, 1 h, and 10 h showed different morphologies, LSV data of these materials were measured and shown in Figure S4. From the results, the catalytic current densities were obviously increased for the materials with a longer electrodeposition time and the onset potentials were accordingly decreased. The Cu(0) materials deposited for 10 h exhibited the best performance for H₂ production, which was chosen for further HER study. Figure 3a shows the linear sweep voltammogram (LSV) of the Cu-EA (3.0 mM) solution before and after electrolysis (-1.2 V vs. Ag/AgCl, 10 h) in 0.1 M KPi solution at pH 7.0 under a slow scan rate of 10 mV/s. The LSV data confirmed that the leaf-like Cu(0) material had highly enhanced activity for HER after 10 hours of electrolysis. The Cu-EA solution showed moderate catalytic activity for HER, indicating the formation of active catalyst on FTO is very important to HER. Catalytic current can be only observed at < -500 mV (vs. RHE) for the initial scan in a Cu-EA solution. In contrast, obvious catalytic current can be observed at < -100 mV (vs. RHE) for the Cu(0)/FTO electrode (inset of Figure 3a), which was attributed to the generation of the leaf-like Cu(0) materials. Furthermore, LSV data of the catalyst films electrodeposited from 3.0 mM Cu-EA and CuCl₂ were collected in 0.1 M KPi clean solution at pH 7.0 (Figure 3b). Consistent with the LSV results in Figure 3a, the freshly-prepared leaf-like Cu(0) catalyst exhibited nearly the same catalytic performance for HER in a clean 0.1 M KPi at pH 7.0. Much higher onset potential at ~-600 mV vs. RHE was observed for the catalyst prepared from CuCl₂, which may be attributed to the differences in morphology and porosity in these two catalyst films as discussed above.

Figure 3c shows the Tafel plots, η vs. $\log(j)$ (η is the overpotential and defined as $\eta = V_{\text{app}} - iR - E_{\text{pH}}$, R is the uncompensated resistance, and E_{pH} is the thermodynamic potential for water reduction at a certain pH; i and j are both the stable current density), for the leaf-like Cu(0) catalyst. The Tafel slope of the catalyst is 127 mV/dec ranging from $\eta = 50$ mV to $\eta = 175$ mV. From the plot, it is found that an appreciable catalytic current at 0.2 mA/cm² is observed as low as $\eta = 70$ mV and the current density of 1.0 mA/cm² requires an overpotential of 157 mV. It is noteworthy to mention that when a potential of -70 mV vs. RHE was applied for bulk electrolysis, obvious H₂ gas bubbles can also be observed on the surface of the electrode and the Faradic efficiency is more than 95% (Figure S5), further confirming its low overpotential for HER in the present system. Although such a value of η is higher than the catalytic activity of the Pt/C catalyst reported in the literature,^{9, 30} such a low overpotential of 70 mV makes this leaf-like Cu(0) material the most active electrocatalyst among known copper-based HER catalysts in the neutral aqueous solution.^{21-24, 31} Since copper is a more abundant element than nickel, cobalt, and platinum, the above results indicate it is a promising alternative for HER in practical application.

To probe the catalytic durability of this leaf-like porous Cu(0) material for HER, a long-term potential cycling experiment was performed by continuous CV scans for 5000 cycles at a rate of 100 mV/s. As shown in Figure 3d, the polarization curve after 5000 cycles is nearly identical to the initial curve. The long-term catalytic

performance with negligible loss of anodic catalytic current indicates that the leaf-like Cu(0) material is highly stable for HER in neutral water. The XRD, EDX, and SEM results of the catalyst before and after electrolysis for HER were almost the same, as shown in Figure S6, S7 and S8, which further confirmed the good durability of the catalyst. This excellent durability shows its great promise for possible application of the catalyst.

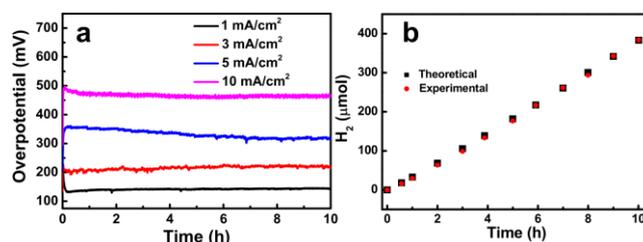


Figure 4. (a) Catalytic overpotential plots for catalyst materials deposited from Cu-EA under various static current densities of 1, 3, 5, and 10 mA/cm² for 10 h in 0.1 M KPi at pH 7.0 with no stirring. (b) Bulk electrolysis and hydrogen production with a deposited Cu(0) catalyst material on FTO electrode in 0.1 M KPi at pH 7.0 at -0.70 V with no stirring.

Furthermore, bulk electrolysis of the catalyst towards practical H₂ production was performed by chronopotentiometry method under different current densities and the results are shown in Figure 4. When a very low overpotential of 150 mV was applied, a stable catalytic current density of 1.0 mA/cm² can be achieved. To achieve higher current densities of 3.0, 5.0, and 10 mA/cm², the required catalytic overpotentials are 220, 325, and 465 mV, respectively. All these applied potentials remain quite stable for long-term electrolysis. The H₂ production and the Faradaic efficiency of the electrodeposited Cu(0) catalyst were measured by gas chromatography (Figure 4b). Bulk electrolysis was performed in a 0.1 M KPi solution at pH 7.0 in a gas-tight electrochemical cell under an inert atmosphere. H₂ bubbles were rapidly generated on the catalyst film, which was proportional to the rising number of the charges passing through the working electrode. The experiment was performed for 10 hours. Comparing the experimental data with the theoretical data, a Faradaic efficiency of >97% for H₂ production was achieved during electrolysis for 10 hours.

The present leaf-like Cu(0) material is not only highly active in neutral water, but also in acidic and basic solutions. Let us first consider an acidic solution. Figure S9a shows the polarization curves of the catalyst in 0.5 M H₂SO₄ at a scan rate of 10 mV/s. The result shows a low onset potential of <-0.2 V for H₂ production, with high current density (10 mA/cm² requires only -260 mV vs. RHE). In addition, the catalytic performance also demonstrated excellent durability and stability, as evidenced by the presence of a curve nearly identical to the initial one with no obvious loss of anodic current after 2000 CV cycles. The Tafel plot of the catalyst obtained from the polarization curve under a much slower scan of 2 mV/min in 0.5 M H₂SO₄ was further studied; it exhibited a smaller slope of 80 mV/dec and low overpotential of 160 mV to achieve 1 mA/cm² (Figure S9b).

Similarly, the Cu(0) material also exhibited high activity under alkaline conditions. Figure S9c shows the polarization curve of the catalyst in 1.0 M KOH. After 2000 cycles of CV scans, the catalyst showed good durability and a low onset potential of <-150 mV vs. RHE. The slope of the Tafel plot is calculated to be 194 mV/dec (Figure S9d). These results for acidic and basic solutions indicate that this present leaf-like Cu(0) material could be utilized as a robust and

highly active catalyst for H₂ production from water over a broad range of pH values from 0-14.

Conclusions

In summary, an artificial leaf-like Cu(0) catalyst was facilely prepared from the Cu-EA precursor in neutral water. The catalyst demonstrated an onset catalytic potential for HER at a very low overpotential of 70 mV, which is the lowest value among the reported copper-based HER catalysts in the neutral aqueous solution. A Faradaic efficiency of >97% during HER performance was achieved during electrolysis for 10 hours. In addition, the Cu(0) catalyst demonstrated excellent chemical durability and low overpotentials for HER from acidic to basic solutions. All of these remarkable features, together with the low cost of the copper, indicate its promising prospect for water reduction to produce H₂.

This work was financially supported by NSFC (21271166, 21473170), the Fundamental Research Funds for the Central Universities (WK3430000001, WK2060140015, WK2060190026), the Program for New Century Excellent Talents in University (NCET), and the Thousand Young Talents Program.

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