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Noble-Metal-Free Colloidal-Copper Based Low Overpotential Water Oxidation Electrocatalyst

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Abstract: Water oxidation catalysis is gaining more attention in recent times owing to its potential for solar and chemical energy conversion and for green fuel generation. The overwhelming hurdle in this quest is to develop a noble-metal-free, efficient, low overpotential water oxidation electrocatalyst exhibiting tremendous stability and to be obtained from earth-abundant materials. We show here unique copper-based water oxidation electrocatalyst derived from thin film Cu-colloidal nanoparticles and is highly efficient, robust for water oxidation. The catalyst advantageously exhibits nanobeads and nanorods type mixed morphological features with narrow size distribution. The onset for oxygen evolution reaction occurs at a small potential of 1.45 V_{RHE} (η =220 mV) which is the lowest observed relative to other copper-based materials. The catalyst also maintains remarkable stability during long-term water electrolysis experiments. Moreover, the catalyst shown to exhibit a high electroactive area with a Tafel slope of 52 mV dec⁻¹, high TOF of 0.81 s⁻¹ and mass activity of 87 mA mg⁻¹. Copper is an interesting material because it can also serve as CO₂ reduction catalysts at the cathode side. The straightforwardly prepared, handy, and inexpensive Cu-based electrocatalytic system is a flexible catalyst for electrooxidation of water and for chemical energy conversion and is an attractive alternative to Pt, Ir, and Ru based electrocatalysts obtained from expensive resources and tedious methods.

Introduction

Electrochemical splitting of water into molecular hydrogen and oxygen ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2$) is one of the most promising schemes for the sustainable production of clean and renewable fuel such as hydrogen.^[1,2] It is highly desirable to use renewable energy sources to split water into its elemental constituents which can also be lined in with CO₂ capture and conversion (a major environmental pollutant) into storable carbon-neutral

fuels.^[3,4] Water splitting is two-step reaction including oxidation and reduction. The water oxidation ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$) is essential half reaction it provides reductive equivalents for conversion of H₂O to free protons (H⁺) that can be combined with CO₂ reduction scheme to produce methanol, formic acid, and other liquid fuels.^[5,6] However, the oxygen evolution reaction (OER) in water oxidation is kinetically sluggish during overall water splitting thus limiting and rendering the entire process for practical applications.^[7,8] To overcome this, an efficient water-oxidation electrocatalyst is required that operate at low electrochemical potential along with high activity in the employed condition.^[9,10] Furthermore, for industrial implications, the imperishable catalytic system should be inexpensive, earth-abundant, easily approachable and highly stable under the vigorous oxidative conditions.

Traditional low overpotential water-splitting electrocatalysts include Pt/C for the hydrogen evolution reaction (HER) and RuO₂ and IrO₂ the for the OER. However, their scarcity, high acquisition costs, and poor performance for long-term water oxidation tests in alkaline solution hamper their suitability for widespread practical applications of these materials.^[11-13] Recent advances in water oxidation catalysis are mainly focused on lowering the energy cost or overpotential for kinetically sluggish oxygen evolution reaction engaging effective and modest catalytic system that are cheap and widely accessible.^[14,15] On the other hand, the search is on to find the best electrocatalysts that comprise a noble-metal-free system for efficient water electrolysis.^[16,17] Both single metal-oxides and mixed-oxides systems have been tested for water oxidation under alkaline conditions.^[18-20] Recently, metal-carbide,^[21] metal-phosphide,^[22,23] metal-selenide,^[24] metal-vanadate,^[25] and other noble-metal-free electrocatalysts^[26-29] are also engaged for OER studies. But most of these electrocatalysts initiate oxygen evolution at higher overpotentials, and the best electrode/electrocatalytic system is required to operate at much lower overpotential relative to standard 1.23 V (vs RHE). They should also be producing high current density, low or modest Tafel slope value in aqueous solution at neutral or near-neutral pH conditions.^[30]

Various synthesis methods,^[31,32] fine structural modifications,^[33,34] heteroatom doping^[35,36] have been used to accelerate water oxidation catalysis but finding a robust material having low onset overpotential and high current density for OER remains a big challenge in this field.^[37] Noble-metal-free single metal-oxide electrocatalysts are simple and interesting materials but most oxides of Ni, Co, Mn, Fe, prepared by tedious synthesis methods, undergo degradation during OER and not stable for long-term application.^[38-40] Copper is an interesting and emerging material for water oxidation catalysis due to its low cost and abundance and is an attractive alternative to Pt, Ir, Ru, based electrocatalysts that are obtained from expensive sources.^[41-43] Copper-based materials can also serve as CO₂ reduction catalysts at the cathode side that can be combined

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with a water oxidation module.^[44] However, copper-based electrocatalytic systems have not been explored widely for water oxidation catalysis. They show relatively large overpotential for water oxidation and are not stable in oxidative condition.^[45] Recently in-situ produced Cu-oxide nanoleaves ($\text{CuO}_x\text{-NLs}$) type water oxidation electrocatalyst obtained by simple controlled-current anodization were able to initiate oxygen evolution at relatively low potential of 1.55 V_{RHE} in metal ion free electrolyte solution relative to other Cu-based materials.^[46] Nevertheless, new and simple preparation methods are required to investigate that can be easily implanted on a bigger scale.^[47] Furthermore, the nanoscale morphological features are needed to achieve exploiting candid methods and accessible materials which can facilitate mass transport and charge transfer during the catalytic reaction.^[48,49]

We show here colloidal-copper based electrocatalytic system for water oxidation that is favorably nanotextured and can be obtained from facile Cu-colloidal nanoparticles (Cu-CNPs). They are prepared by adding copper ions solution into a carbonate/bicarbonate buffer leading to the colloidal formation (Scheme 1). Surface deposited thin films of Cu-CNPs show remarkable activity and stability during long-term water electrolysis experiments. Relative to other non-noble metals water oxidation catalysts, the Cu-CNPs based electrocatalyst displays initiation of oxygen evolution reaction at an overpotential of $\eta=220$ mV, which is the lowest observed for copper-based material.^[50] This is a simple route to make efficient electrocatalysts for water oxidation.

Scheme 1. A simple illustration of the synthesis process of colloidal-copper NPs and fabrication process for the electrode/electrocatalyst material employed as water oxidation electrocatalyst.

Results and Discussion

The synthesis of colloidal-copper NPs and fabrication of thin-film electrode/electrocatalyst system for water oxidation is outlined in Scheme 1. Copper colloidal ($\text{Cu}(\text{OH})_x/\text{CuO}_x$) based nanoparticles are prepared by mixing Cu^{2+} ions solution and carbonate/bicarbonate anionic electrolytes (pH=8.5). Once formed, the Cu-colloidal nanoparticles are coated on FTO (Fluorinated tin oxide) substrates by simple drop casting to get thin-film electrode coated with Cu-CNPs. They are then annealed at 250 °C and 500 °C to be tested for water oxidation catalysis. The average particle size of the Cu-CNPs is in the range of 100 nm to 140 nm showing good homogeneity (Figure 1a). Cu-CNPs presents the zeta potential of 33 mV showing

good stability of the colloidal system in the carbonate buffer system (Figure 1b). The stability of colloids is highly depending on the electrostatic interaction between the negatively capped nanoparticles and can be controlled by carefully directing the concentration, pH, and volume of electrolyte solution.^[51]

Figure 1. (a) Particle size distribution; (b) zeta potential; (c) scanning electron micrograph image and (d) XRD spectrum for Cu-based colloidal nanoparticles developed in carbonate/bicarbonate based anionic electrolytes (pH=8.5).

Scanning electron microscopic (SEM) image also demonstrates the size of nanoparticles to be in the range of 50 to 150 nm. The nanoparticles are spherical and pseudo-spherical in shape and are agglomerated with each other in form of clumps. However, the individual particles can be seen easily as shown in SEM image (Figure 1c). The phase of the Cu based colloidal NPs is explored via X-ray diffraction pattern (XRD) analysis. The XRD spectrum for Cu based CNPs in the Figure 1d signifies that the position and relative intensity of the 2 θ peaks represented at (16.43°, 23°, 33.20°, 35.80°, 37.80°) match well with standard XRD data of $\text{Cu}(\text{OH})_x$ as reported earlier.^[52] This data suggest that copper-based CNPs are very stable and mainly comprises of Cu-hydroxide type materials.

Annealing of Cu-CNPs thin films at 250 °C (Cu-CNPs/FTO₂₅₀) and 500 °C (Cu-CNPs/FTO₅₀₀) also generate nanoparticulate type morphology (Figure 2a, 2b). However, Cu-CNPs/FTO₅₀₀ film exhibits a spongy nanoparticulate type texture representing much enhanced surface area of thin film (Figures S1 and S2). For water oxidation studies, the cyclic voltammetry experiments are conducted in 0.1 M KOH solution. CV profile of simple Cu-CNPs/FTO shows the appearance of oxidative current at about 1.1 V_{RHE} . The onset of oxygen evolution reaction originates at about 1.62 V_{RHE} and OER onset overpotential is $\eta=390$ mV (Figure 2c). The CV curve for Cu-CNPs/FTO₂₅₀ indicates the Cu oxidative pre-features at about 1.0 V_{RHE} that is followed by a large catalytic peak at 1.57 V_{RHE} along with the onset of oxygen evolution (Figure 2d). A current density of >10 mA/cm^2 is achieved just under the potential of 1.83 V_{RHE} . The OER onset overpotential is $\eta=340$ mV. For Cu-CNPs/FTO₅₀₀

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sample, the water oxidation reaction initiated at much lower potential of 1.45 V_{RHE} with an overpotential of 220 mV in 0.1 M aq. KOH system.

Figure 2. Scanning electron micrograph image for (a) Cu-CNP/FTO₂₅₀; (b) Cu-CNP/FTO₅₀₀; (c) Forward potential sweeps for Cu-CNP/FTO, Cu-CNP/FTO₂₅₀ and for Cu-CNP/FTO₅₀₀ at 2 mV s⁻¹; (d) Short-term, time vs. current density curves for bare FTO, Cu-CNP/FTO at 1.77 V_{RHE}, Cu-CNP/FTO₂₅₀ at 1.67 V_{RHE} and for Cu-CNP/FTO₅₀₀ at 1.56 V_{RHE} in 0.1 M KOH electrolyte solution.

From comparative CV analysis, it is obvious that the onset potential for water oxidation reaction is shifting towards the more negative potential by applying the annealing and by increasing the annealing temperature up to 500 °C (Figure 2c). This might be due to the formation of more intense nanoscale catalytic structures by applying and increasing annealing temperature as obvious by SEM measurements (Figures S1, S2). Also, annealing at 500 °C has produced highly porous catalytic film thus presenting a comparatively larger number of active sites for efficient OER. Nanoscale porous materials are considered more efficient catalysts due to having a high surface area which facilitates catalytic performance. Furthermore, adjacent nanoparticles on catalyst surface favored O-O bond formation and evolution of molecular oxygen at a lower energy cost. Further supporting evidence for high efficiency of Cu-CNPs/FTO₅₀₀ sample comes from the study of charge transfer resistance at the electrode-electrolyte interface double layer via electrochemical impedance spectroscopy. The impedance data shows a lower charge transfer resistance for Cu-CNPs/FTO₅₀₀ facilitating high electron transfer at the interface which may also be attributed to the fine nanoscale surface structure of the copper derive electrocatalyst (Figure S3). Further annealing appeared not to produce a profound reduction in the OER onset potential, and 500 °C treatment is ascribed to be the optimal heating for thin-film Cu-CNPs to make efficient water oxidation electrocatalyst.

From short-term chronoamperometry analysis, it is cleared that the Cu-CNPs/FTO type electrocatalyst derived from Cu-CNPs deposited on FTO without applying post-annealing

operations are not very stable (Figure 2d). The catalyst undergoing 40 % degradation under the harsh oxidative environment for electrooxidation of water. Although the Cu-CNPs/FTO₂₅₀ type catalytic film coated on conductor surface and the following annealing at 250 °C shows comparatively higher stability of the electrocatalyst for oxygen evolution reaction with 20% degradation over time (Figure 2d). The degradation of the catalyst may be attributed to the crumbling of catalytic materials from FTO surface due to the vigorous oxygen evolution.^[53] The disintegrating of catalyst from FTO during short-term (controlled potential electrolysis) CPE experiment was also observed from the naked eye during the course of analysis. However, the time vs. current density curve for Cu-CNPs/FTO₅₀₀ electrocatalyst presented remarkable stability with no observable degradation (Figure 2d). The high stability of the catalyst may be attributed to the formation of more-fine nanoparticulate type CuO_x structured on the FTO surface by annealing at 500 °C as revealed by SEM microscopy and X-ray photoelectron spectroscopy (XPS) studies (discussed in the later section).

Further analyses for Cu-CNPs/FTO₅₀₀ based electrocatalyst and simple FTO electrode are conducted to get more insight into the catalytic system. High-resolution SEM images for Cu-CNPs/FTO₅₀₀ sample reveals well pronounced nano-rods type morphological features (Figure S4a-b). The enlarged view of nano-beads type structures grown on FTO surface presented narrow size distribution of nanoparticulate type features. Whereas, these structural modifications were not observed for simple FTO substrate (Figure S4c). The bulk compositional analysis as carried out via energy dispersive X-ray spectroscopy (EDS) showing the presence of 14 % C, 33.66 % O and 46 % Cu in the catalytic film (Figure S4d). The carbon assimilation in the metal oxide is thought to increase the electroactive sites of electrocatalyst while facilitating the good electron transfer and enhance stability.^[6,54]

To understand more about the surface composition and copper status for Cu-CNPs/FTO₅₀₀ electrocatalytic film, the XPS analysis is undertaken. The survey data reveals that catalytic deposits contain Cu, O, and C as the main constituent elements in the deposit. In the survey spectrum of the CNPs/FTO₅₀₀ material, the binding energies in between the 930 eV and 960 eV marked the response from Cu 2p_{3/2} and Cu 2p_{1/2} centered at 934.5 eV and 954.2 eV correspondingly (Figure 3a, 3b), and the peak at 530 eV and 283 eV are indexed to O 1s and C 1s, respectively^[55] as presented in Figures 3c,3d.

The magnified view of C 1s shown a well-pronounced peak at about 283.6 eV which is attributed to the sp² carbon (C-C bond) and a small peak at 286.1 eV is assignable to O-C-O and C-OH groups.^[56] The high-resolution XPS spectrum for Cu 2p revealed a pronounced spin-orbit splitting into Cu 2p_{3/2} and Cu 2p_{1/2} with an energy difference of about 20 eV which is characteristics of CuO type materials as reported previously.^[57] In between these two peaks just next to the Cu 2p_{3/2} XPS signals, there is a satellite peak, positioned at about 941.1 eV which is the characteristics of Cu²⁺ materials with d9 configuration in the ground state as discussed previously.^[46] The obvious shake-up satellite peak is the characteristics of CuO based materials. Cu-CNPs/FTO₅₀₀ sample shows a peak for oxygen at about 530.9 eV which is ascribed to the surface-bound oxide in the catalytic layer.^[57] Consequently, the surface and bulk elemental analysis disclose an active CuO based electrocatalyst exploited here for water oxidation catalysis.

Figure 3. XPS (X-ray photoelectron spectroscopy) spectrum for Cu-CNPs/FTO₅₀₀ sample (a) survey spectrum; (b) enlarged view for Cu 2p; (c) C 1s and (d) O 1s.

XRD spectrum for phase analysis of the Cu-CNPs/FTO₅₀₀ electrocatalyst reveals the presence of CuO and Cu₂O type phases in the catalytic layer (Figure S5). The CuO remains as the dominating phase in the catalytic film.^[58] However, there are some signals representing the contribution of metallic copper in the catalytic layer that might have formed from the reduction of copper oxide. Conclusively, XRD spectrum reveals the very intense diffraction peaks for #Cu₂O and @CuO phases.^[59,60] Further, Raman spectroscopy is also commenced to get more information about the structure of the nanoscale copper oxide-based material. The Raman peaks at 295 cm⁻¹, 332 cm⁻¹, and 614 cm⁻¹ confirm the presence of CuO phase in the catalytic layer (the enlarged view is shown in Figure S6). However, a peak at 440 indicates the presence of Cu₂O phase in the catalytic film.^[61-63] Thus, above conferred analytical justifications confirm that the Cu-CNPs/FTO₅₀₀ electrocatalyst derived from easily made Cu(OH)₂/CuO_x/HCO₃⁻ based CNPs is a mixture of various phases of copper oxides with CuO as the dominating phase. This also supports and validates the finding of XPS and XRD for the chemistry of Cu-CNPs/FTO₅₀₀ electrocatalyst.

Detailed electrochemical characterization of Cu-CNPs/FTO₅₀₀ system is conducted via CV, Tafel measurement, consecutive CVs and incremental multistep CCE analysis (Figure 4). The OER onset potential is E/V = 1.45_{RHE}, with an onset-overpotential η=220 mV (Figure 4a, S7) (enlarged views are shown in inset Figure 4a, S8) which is smallest in the list and better than other Cu-based heterogeneous catalysts reported to date (Table 1). The oxidative prefectures at about 1.0 V_{RHE} (Figure S8) can be ascribed to the surface oxidation of copper to higher oxidation state due to applied anodic potential.^[46] A current density of >15 mA cm⁻² was achieved under 1.63 V_{RHE} and a current density of 10 mA cm⁻² is achieved just under the potential of E_{J=10 mA/cm²} = 1.59 V_{RHE} [η=360 mV]. This shows a substantial electrocatalytic activity of the Cu-CNPs/FTO₅₀₀ sample for the water oxidation reaction. There is a large reduction current also observed that might be originated from

the Cu site reduction along with some O₂ reduction in this potential region. During the catalytic reaction, copper is thought to undergo from +2/+3 oxidation state through OH⁻ adsorption and desorption. This behavior is consistent with other 3d metal oxides as well.^[41,46]

Figure 4. (a) Cyclic voltammetry profile for Cu-CNPs/FTO₅₀₀ sample in 0.1 M KOH electrolyte solution (pH=13) at the scan rate of 2 mV s⁻¹; (b) Tafel plot (overpotential versus log of current density curve) for Cu-CNPs/FTO₅₀₀ electrocatalyst calculated from the polarization curve; (c) 500 consecutive cyclic voltammetry sweeps for the Cu-CNPs/FTO₅₀₀ in 0.1 M KOH electrolyte solution (pH=13). The CV scan rate was 10 mV sec⁻¹; (d) multistep CCE showing potentials profile for consecutive current density increments from 2 mAcm⁻² to 20 mAcm⁻².

The Cu-CNPs/FTO₅₀₀ based water oxidation electrocatalyst presented here exhibits a low OER onset potential of E/V = 1.45_{RHE}, η=220 mV relative to other materials (Table 1). Although Cu is not considered good electrocatalyst material as M-OH bond formation is either too strong or too weak thereby hindering its intrinsic catalytic activity. However, Cu-CNPs/FTO₅₀₀ has shown much-improved performance for driving otherwise kinetically sluggish OER. This is attributed to the nanoscale, rough and highly porous surface structure of Cu-CNPs/FTO₅₀₀ enabling a rapid charge transfer as evident by EIS (Figure S3), and enhanced stability due to the insertion of carbon content in the catalytic layer (from carbonate electrolyte) as evidence by EDS and XPS analysis.^[6,32] It was shown previously that catalytic activity of Cu based materials can be enhanced by making defects in structure and carbon incorporation in catalytic layer.^[46] Here, carbon assimilation in the catalytic system is facilitated by employing the simplest colloidal route and inexpensive carbonate electrolyte systems. Correspondingly, we believe that nanostructure, porous spongy morphological attributes of Cu-CNPs/FTO₅₀₀ further reduce kinetic barriers and support O-O bond formation from individual OH entities adsorbed on catalyst surface thus, making the

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system to operate at a much lower energy cost. Porous nanoscale particulates type catalytic film can also provide more active sites and thereby facilitate adsorption/stabilization of reaction intermediate and their conversion for high rate O-O bond formation and subsequent rapid oxygen gas evolution.

Correspondingly, further experiments have been performed to see the effects of different catalyst loading on the FTO surface. Cu-CNPs/FTO₅₀₀ anode obtainable by depositing 10 to 60 μL volume of Cu-CNPs are shown to produce similar catalytic signatures and OER performance during CVs experiments as shown in Figure S9a. However, with 60 μL loading the Cu-CNPs sample shows a broad metal redox peak just prior to water oxidation catalytic wave and current density is also relatively higher as expected for high catalyst loadings (Figure S9b).

The catalytic performance of Cu-CNPs/FTO₅₀₀ is also investigated in various electrolyte solutions with varying pH values from neutral to basic pH range. The results show that catalyst can perform water oxidation reaction under wide pH condition in variety of electrolyte solution such as 0.1 M phosphate buffer (PBS) (pH $\approx$ 6.3), 0.1 M aq. bicarbonate electrolyte solution (pH $\approx$ 8.3) and 0.1 M aq. carbonate electrolyte solution (pH $\approx$ 11) as illustrated in Figure S10. Furthermore, catalyst presents good activity and stability for water oxidation reaction in all aforementioned electrolyte solution during CPE experiment conducted at constant potential (insets Figure S10). Results demonstrate substantial catalytic activity of Cu-CNPs/FTO₅₀₀ catalyst for water oxidation reaction under wide pH range. However, owing to much better catalytic performance in 0.1 M NaOH electrolyte solution, further catalytic studies are performed in basic conditions.

The current vs overpotential measurements for Cu-CNPs/FTO₅₀₀ type electrocatalyst in oxygen evolution regime calculated from the polarization curve reveals the Tafel slope of 63 mV dec⁻¹ as illustrated in Figure 4b. Furthermore, to get a steady state polarization curve and to avoid the current contribution from the capacitance of interphase the Tafel curve is plotted by considering static electroanalytical technique such as chronoamperometry (details are given in experimental section). The resulting Tafel slope of 52 mV dec⁻¹ is corresponding with three electrons transfer during the catalytic process and represent the actual intrinsic catalytic activity of the material (Figures S11, S12). The elementary step involved in OER at anode surface in two-three electron transfer reaction includes oxidation of water/hydroxide to oxyhydroxide.^[46,67]

Table 1. Shows the comparative analysis of different Cu-based electrocatalytic systems for water oxidation reaction and that of Cu-CNPs/FTO₅₀₀ type electrocatalyst.

Catalyst/System ^[a]	Electrolyte	Onset potential [V _{RHE}]	Tafel slope [mV dec ⁻¹]	Ref
Cu-Bi	0.2 M Borate buffer (pH $\approx$ 9)	1.73 V	89	64
Cu-NWs ^[b]	0.2 M Borate buffer (pH $\approx$ 9.2)	1.84 V	-	65
Cu _c -Ni _s NWs ^[c]	0.1 M K-Bi (pH $\approx$ 9.2)	1.69 V	54.5	66
CuO	0.2 M	1.64 V	-	46
Cu-NLs ^[d]	carbonate (pH $\approx$ 11)	1.55 V	-	
Cu-CNPs/FTO ₅₀₀	0.1 M KOH (pH $\approx$ 13)	1.45 V	52	This work

[a] the Cu catalysts are prepared by different methods and are deposited

on various conducting substrates; [b] Cu-NWs = Copper nanowires; [c] Cu-Ni NWs= electroplated nickel onto copper nanowires; [d] Cu-NLs= Copper-oxide nanoleaves.

To further assess the durability of the catalyst accelerated degradation experiments are performed in 0.1 M KOH. The successive multi-scan cyclic voltammetry (MSCV) measurements for Cu-CNPs/FTO₅₀₀ electrocatalyst show excellent stability and manifests that the catalyst is highly active and generating similar catalytic signatures after 500 CV cycles for water oxidation catalysis (Figure 4c). In addition, the catalytic performance of the electrocatalyst is investigated by a series of multistep controlled current electrolysis experiments. In the pursuit of the above current is held constant for a minimum of 300 seconds and the resulting potential-time curves are presented in Figure 4d. Upon increasing the current density, the potential of electrode upsurges but soon get stabilized owing to the mechanical sturdiness of the system. This feature proves the stability of the system under anodic environment.

The electrochemically active surface area calculated from the charge under the active reduction peak from OER polarization curve by assuming that each surface Cu atom corresponds to one chemisorbed oxygen atom is found to be 7.5 cm² presenting much enhanced electrocatalytic physiognomies of the system (Figure S13). This method is based on the assumption that all the atoms in electrocatalyst are 100 % electrochemically active (details are given in SI).^[61] Furthermore, turn over frequency and mass activity values are calculated at various applied potential values from 1.45 V_{RHE} to 1.63 V_{RHE} as shown in Figure S14-S15, Table S1. The catalyst favorably shows turn over frequency of 0.8 s⁻¹ and mass activity of 87 mA mg⁻¹ just at 0.35 V (details are given in SI). The choice of η = 0.35 V depends on the well-reported device model, suggesting that 10% efficient solar water splitting device should operate at 10 mA cm⁻² with a maximum overpotential of 0.35 V for oxygen evolution reaction.^[30] The overall electrocatalytic activity has proven that the easily made Cu-CNPs/FTO₅₀₀ type electrocatalyst is a potential, advance, robust, cheap, and efficient electrocatalytic candidate for facilitating the water oxidation reaction.

Figure 5. Extended time electrocatalytic oxygen evolution during controlled potential water electrolysis at Cu-CNPs/FTO₅₀₀ sample at 1.56 V_{RHE} in 0.1 M KOH electrolyte.

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Remarkably lower energy cost for initiating water oxidation catalysis (just 220 mV) at Cu-CNPs/FTO₅₀₀ electrocatalyst compelled us to evaluate the long-term stability of material for water oxidation catalysis under electrochemical conditions. We evaluate the stability of Cu-CNPs/FTO₅₀₀ catalyst under harsh oxidative environment via long-term controlled potential water electrolysis experiment.

Chronoamperometry experiment conducted for Cu-CNPs/FTO₅₀₀ sample presented admirable results and catalyst achieve a current density of >6 mA cm⁻² at the same operating potential of just 1.56 V_{RHE} [η=0.33 V]. The current density remains constant during unremitting 10 hours of electrolysis and the catalyst showed no observable degradation as illustrated in Figure 5. Furthermore, a rich stream of oxygen bubbles could be seen coming out of electrode surface during CPE experiment owing to oxygen evolution reaction. The value of much higher current density and outstanding stability is attributed to the excellent catalytic activity of said catalyst under the employed conditions. An electrochemical investigation such as cyclic voltammetry, Tafel slope analysis, controlled potential electrolysis revealed that the electrocatalyst prepared via exploiting very simple precursors and following low-cost, time effective and straightforward method proved very efficient when being placed in an electrochemical cell for catalyzing water oxidation reaction. The electrochemical activity is even better than observed for other Cu electrocatalyst reported earlier.

Conclusions

Worthwhile capture and subsequent transformation of solar energy into useful gaseous and liquids fuels is getting famous worldwide due to its extreme importance to the expanding global energy demands and environmental apprehensions caused by carbon-based fossil fuels. The development of technologies for the production of chemical fuels or useful compounds with renewable energy (e.g., sunlight, wind, and water) and inexpensive feedstock relies on an abundant supply of protons and electrons to form the reduced products. One of the most suitably abundant sources of these required protons and electrons is water that is plenteous and reachable. Thus making hydrogen from water splitting is very attractive and promising schemes to make clean and renewable fuel. We have made a step forward in this quest and demonstrate a robust and sustained electrocatalytic water oxidation system based on non-noble-metal and eco-friendly copper centered catalytic assemblage. The nanostructured electrocatalytic material exhibiting high stability at much lower overpotential for water oxidation catalysis under the benign conditions can be obtained by exploiting easily accessible, time effective and cost-effective Cu-colloids synthesis that can be easily scaled up. The simplicity and cost-effectiveness of the system and the reaction conditions are appealing and may be of significance in photoelectrochemical and electrochemical water splitting and energy conversion devices.

Experimental Section

Preparation of copper colloids of the type Cu(OH)₂ and Cu(OH)₂/HCO₃⁻: Colloidal NPs comprising of Cu(OH)_x/HCO₃⁻ are

preferably generated exploiting very cost-effective and easily made bicarbonate/carbonate buffer solution. To a 1.0 mL clear solution of 0.1 M Cu(NO₃)₂·3H₂O in water, 0.02 mL of 0.1 M HCO₃⁻ buffer solution is added. The blend was stirred at low speed for a while and allow to stand for few minutes to obtain a cloudy/opaque dispersion of Cu-CNPs. Following that, the so obtained turbid solution is filtered using micro filter syringes to attain homogeneous CNPs. The homogeneity and average size of Cu-CNPs are investigated via particle size analyzer.

Fabrication and characterization of nanoscale copper colloids-based water oxidation electrocatalyst: Furthermore, the thin film electrode or anode material for water catalysis is generated via simple drop casting approach by placing Cu(OH)_x/HCO₃⁻¹ colloids (nanotextured) on FTO surface air dried and then insert in an electrochemical cell as the working electrode for water oxidation catalysis testing. In another experiment, for the sake of structural and morphological modifications in the electrocatalytic film the FTO slides coated with Cu-CNPs is annealed at about 250 °C and 500 °C by keeping inside a furnace for about 1 hour to be tested for lowering energy cost of water oxidation reaction.

Electrochemical measurements: All the electrochemical investigations such as cyclic voltammetry, impedance, controlled potential water electrolysis (chronoamperometry) and controlled-current water electrolysis (chronopotentiometry) are carried out employing a standard three electrode system on a computer-controlled potentiostat (Autolab PG-Stat 10). Fluorine doped tin oxide (FTO) coated glass slides (exposed surface area A=1 cm²) ornate with thin film water oxidation electrocatalyst (exposed surface area A=1 cm²) is served directly as the working electrode. FTO-coated glass slides (Resistivity < 7-10 ohms/sq) are obtained from Aldrich. Prior to used FTO slides are clean carefully by sonicating in methanol, ethanol, ultrapure water and acetone as described earlier^[30]. A spiral-shaped platinum wire (thickness= 1 mm) is used as a counter electrode and is clean by immersing in a 20 % solution of nitric acid for few minutes before placing into the electrochemical system. A saturated silver/silver chloride (Sat.Ag/AgCl) and saturated calomel electrode (Hg/HgO) are used as reference electrodes in mildly alkaline electrolyte solutions. All the electrochemical measurements were performed in the deoxygenated aqueous electrolyte solution at room temperature. Glassware and electrochemical cell were cleaned as described previously.^[68]

Thin film electrocatalyst coated on FTO is directly placed in the electrochemical cell as an anode. The Cyclic voltammograms were conducted in 0.1 M KOH electrolyte solution having pH≈13 by cycling the potential between -0.8 to +1.0 V (vs. Ag/AgCl) [+0.166 to +1.966 V (vs. RHE)]. The cyclic voltammograms were recorded at the scan rate of 20 mVs⁻¹, 10 mVs⁻¹ and 2 mVs⁻¹.

Electrochemical impedance spectroscopy is undertaken to measure solution resistance (R_s) and charge transfer resistance (R_{ct}) of electrode-electrolyte interphase. R_s and R_{ct} were obtained by fitting a simplest Randles circuit using NOVA 1.10 software on Metrohm Autolab, a computer controlled potentiostat.

Calculations of electrochemical constraints: All the potential here is converted into reversible hydrogen electrode (RHE) according to the Nernst equation^[30,65] given below.

$$E_{\text{RHE}} = E_{\text{REF}} + E_{\text{REF}}^0 + 0.059(\text{pH})$$

Here, E_{REF}⁰ for Ag/AgCl is 0.197 V and for SCE is 0.2416 V.

The true polarization potential E_P was calculated from applied potential E_A, measured current (I=Ampere) and uncompensated resistance R_u as following.^[30]

$$E_p = E_A - IR_u$$

Here, uncompensated resistance (R_u) is referred to as solution resistance calculated from EIS.

The overpotential was calculated according to the formula^[30,65]

$$\text{Overpotential } [\eta] = E_{\text{RHE}} - 1.23 \text{ V.}$$

A) Tafel Slope calculation from CV curve: Tafel slope is calculated from CV data taking into account current density and overpotential using the following Tafel equation^[30].

$$\eta = b \log J + a$$

Here, b is Tafel slope.

B) Tafel Slope calculation from Static chronoamperometry technique: Anantharaj et al described that the Tafel slopes obtained from polarization curves such as cyclic voltammogram and linear sweep voltammetry usually recorded at lower scan rate such as 5 mV s^{-1} , 1 mV s^{-1} , and 0.1 mV s^{-1} are actually not steady state as current and overpotential are changing continuously with increasing time. Moreover, the capacitance of interphase can significantly contribute to the total gas evolution current. Because of these demerits, it is more advantageous to have Tafel plots from static electroanalytical techniques such as chronoamperometry and chronopotentiometry where the catalytic interphase is given sufficient time to attain a steady state and Tafel curves are plotted considering overpotential and current densities. The Tafel plots obtained by this method can reflect the intrinsic activity of the catalysts unlike the one derived from voltammogram.^[69]

Current-potential data is collected by performing controlled-potential electrolysis experiment at a variety of applied potential. Typically, the current values are read after 8 to 10 minutes. Prior to data collection, the solution resistance was measured using a blank FTO electrode. The solution resistance of $\approx 30 \Omega$ is used to correct Tafel plot for IR drop.

C) Determination of electrochemically active surface area (ECSA) from charge passed under reduction peak: Electrochemically active surface area for Cu-CNPs/FTO₅₀₀ is determined by measuring the charge ($Q_{\text{Cu, o}}$) from the oxide reduction peak of its CV curve, by assuming that each surface Cu atom corresponds to one chemisorbed oxygen atom. The charge ($Q_{\text{Cu, s}}$) associated with smooth Cu surface is accepted to be $350 \mu\text{C cm}^{-2}$.^[68] Electrochemical surface area is calculated as

$$\text{ECSA} = \frac{Q_{\text{Cu, o}}}{Q_{\text{Cu, s}}}$$

The area under the reduction peak considering redox couple of Cu^{+3} to Cu^{+2} measured directly from CV curve is $5.30 \times 10^{-5} \text{ VA}$.

Hence, charge can be calculated as

$$5.30 \times 10^{-5} \text{ VA} / 0.02 \text{ Vs}^{-1}$$

$$= 0.00265 \text{ As or } 0.00265 \text{ Coulomb.}$$

Finally, the electrochemically active surface area is calculated to be

$$= 7.5 \text{ cm}^2.$$

D) Determination of surface concentration of Cu from CV curve: Charge passed calculated by integrating the area under reduction peak from potential vs. current curve is 0.00265 Coulomb .

$$\text{Then, no of electrons} = (0.00265 \text{ C}) / (1.602 \times 10^{-19} \text{ C})$$

$$= 0.0016583 \times 10^{19} \text{ electrons}$$

The surface concentration of the Cu atom on the electrode is determined by dividing with no of electrons involved in the redox reaction which is 1 for $\text{Cu}^{+2/+3}$, therefore,

$$\text{Surface Conc. of atoms} = 0.0016583 \times 10^{19} / 1$$

$$= 0.0016583 \times 10^{19}$$

E) Determination of TOF from integrated OER CV Curve: We calculated turn over frequency (TOF) at $1.58 \text{ V}_{\text{RHE}}$ ($\eta=0.35 \text{ V}$) as specific potential value. Furthermore, TOF is calculated at various potential value considering the following equation

$$\text{TOF} = \frac{I \times N_A}{A \times n \times F \times \Gamma}$$

Where,

I = current value at a specified potential (Ampere); N_A = Avogadro's constant which is 6.022×10^{23} ; A = Geometrical area of the working electrode which is 1 cm^2 ; n = No of electrons; F = Faraday constant which is 96485 ; Γ = surface concentration of atom on the electrode surface.

$$\text{TOF@ } 1.58 \text{ V} = [(0.0087) \times (6.022 \times 10^{23})] / [(1) \times (4) \times (96485) \times (0.0016583 \times 10^{19})]$$

$$= 0.81 \text{ s}^{-1}$$

Farther details for the TOF calculation at different potentials is given in the supporting information.

F) Mass activity determination: The loading normalized current density or mass activity is calculated according to the following formula.^[30]

$$\text{MA} = \frac{I \text{ @ specific } \eta}{\text{Active mass of catalyst}}$$

Here, J is current density in mA at specific potential value. We choose $1.58 \text{ V}_{\text{RHE}}$ as specific potential value. The corresponding mass activity of 87 mA mg^{-1} is obtained at 0.35 V .

Furthermore, the mass activity is calculated at various applied potential and the resulting mass activity values are presented in Figure S13 and Table S1.

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Keywords: catalysis • electrochemistry • water splitting • copper oxide • low overpotential

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Highly efficient, robust copper centered nano featured electrocatalytic system derived from Cu-colloidal NPs is shown to drive kinetically slothful water oxidation reaction at low potential of 1.45 V_{RHE}. A small Tafel slope of just 52 mV dec⁻¹ was obtained from static chronoamperometry technique (CA) represents well stable kinetic of catalyst for OER. Furthermore, the catalyst presented high stability during long term water electrolysis experiment without undergoing any loss in catalytic activity.

Noor-UI-Ain Babar, Khurram Saleem Joya,* Muhammad Ali Ehsan, Majad Khan and Muhammad Sharif

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Noble-Metal-Free Colloidal-Copper Based Low Overpotential Water Oxidation Electrocatalyst

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