

CuO_x functionalized silicon photoanodes for efficient photoelectrochemical water splitting devices

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Abstract: Photoelectrochemical (PEC) water splitting using solar light to produce clean fuels (hydrogen) is a promising renewable source to fulfill the raising global energy demands and overcome environmental problems. This technology is attractive because it can provide equal or even more energy at a lower cost than other kinds of solar cells, and it solves the problems of sunlight intermittence and location dependency, as the energy can be stored and transported in the form of chemical bonds. In this field, the development of active, stable and cost-effective photoelectrocatalysts or photoelectrodes is essential to ensure the good function of water splitting cells. Here a highly active CuO_x/Cu protected silicon photoanode has been prepared, with onset potential at 0.51 V vs. SCE in 0.2 M borate buffer (pH 9). The electrode is stable showing a constant current density of 0.8 mA/cm² at 0.59 V vs. SCE for 1 hour under illumination of simulated 1-sun. These findings may have important implications in the advance of this technology, as they provide a cost-effective solution that shows excellent performance.

Introduction

PEC cells use a built-in potential generated at a semiconductor-liquid junction under sunlight illumination, which can drive uphill chemical reactions. One of the most desired chemical reactions to drive using this method is the splitting of water because it produces hydrogen fuel in a clean manner [1]. In such device, a semiconductor electrode is immersed in an aqueous solution and illuminated to split water into hydrogen and oxygen directly at the semiconductor surface, producing

chemical fuels that can be stored and transported [2] (Figure 1). Silicon and III-V semiconductors are excellent light absorbers with high carrier mobilities, allowing the possibility to split water under light [3-4]. Silicon is preferred due to its low price but, unfortunately, silicon is only able to produce modest current densities in the scale of $\mu\text{A}/\text{cm}^2$ that decay very fast (some minutes) due to premature corrosion [5], and the III-V semiconductors are also extremely prone to photoanodic corrosion [6-8].

For these reasons, passivating the silicon surface with a protecting layer of stable material that suppresses photocorrosion has become one of the main challenges of this technology. To date, the cheapest metal based coating with highly active performance has been achieved using nickel based coating. In 2013, M. J. Kenney et al. [9] evaporated a 2 nm Ni layer on the native oxide of a silicon wafer, leading to Ni/SiO₂/nSi photoanodes with extraordinary activity and stability (up to 80 hours in a mixed lithium borate-potassium borate electrolyte). And very recently, Lewis' group reported the NiO_x coated np⁺-Si and n-Si photoanodes able to split water for over 50 days in 1 M KOH (aq) [10]. The NiO_x layer not only protected the silicon from corrosion but also acted as water oxidation catalyst. Another very efficient coating is TiO₂ based coating. Chen et al. [11] and Hu. et al. [4] reported corrosion-resistant and high efficient photoanodes based on silicon or other semiconductors. In these photoanodes, TiO₂ coatings grown by atomic layer deposition (ALD) can prevent corrosion, have electronic defects that promote hole conduction, and are sufficiently transparent to reach the light-limited performance of protected

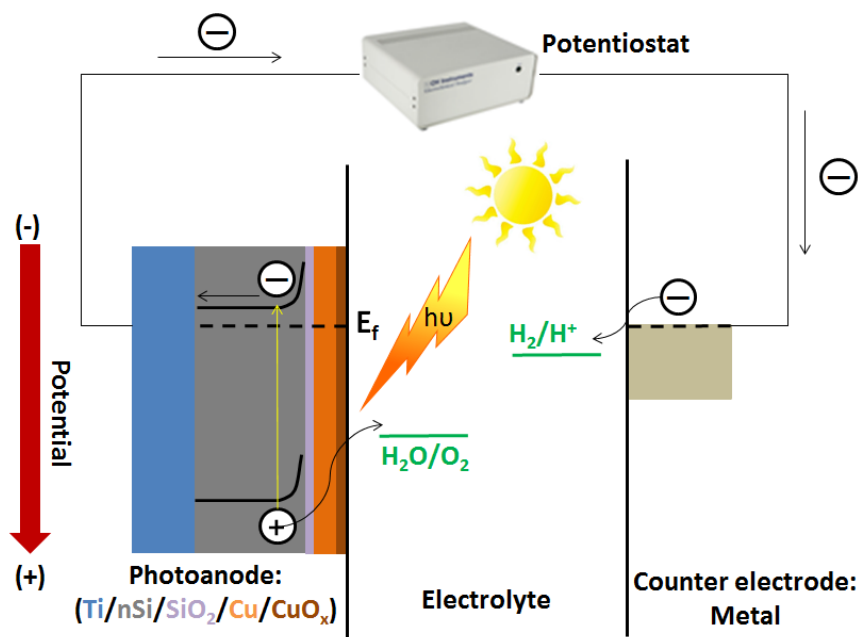


Figure 1. Scheme of the PEC cell developed in this work. The cell is built of a Cu/CuO_x protected n-Si photoanode connected to a metal counter electrode through a potentiostat. When the sunlight illuminates the surface of this photoanode, it induces charge separation. The generated holes migrate to the surface and are used to produce O₂ from water. The electrons in the conduction band move to the counter electrode to reduce water and produce hydrogen.

semiconductors.

On the other hand, the use of water oxidation catalyst (WOC) on the surface of the semiconductor can improve the performance of the photoanodes because they help the charge separation and speed up the oxygen evolution reaction that takes place on the surface. Most of the reported examples use noble metals such as palladium [12] platinum [13], iridium [11] or ruthenium [3, 14] oxides but also other earth-abundant metallic oxides like NiO_x [9-10]. Molecular copper as well as copper oxides have recently been shown to be active in the electrocatalytic water oxidation reaction but their uses are still at their early stage [15-17]. Yu et. al. [18] reported a facile oxidative electrodeposition method to prepare highly active and stable (over 10 hours in 0.2 M borate buffer pH 9) copper oxide catalyst by electrodeposition of Cu²⁺ from borate buffer solution under near neutral conditions. More recently, Du et al. [19] reported that formation of a compact film of CuO_x on Cu surface can prevent anodic corrosion and result in sustained catalytic water oxidation. A rapid method for the preparation of highly

photoactive CuO thin films on conductive glass was reported [20], based on very simple reductive electrodeposition and post annealing steps, however, in this case the copper oxide was not used as water oxidation catalyst, but as a photocathode. Compared to other metals based oxides, copper is especially interesting due to its earth-abundance and low cost. With these precedents, the aim of this work is to explore the use of active CuO_x films on n-Si based photoanodes and study its photoelectrochemical performance. And also, trying to enhance the performance of nickel based silicon photoanodes [9] using CuO_x films.

First of all, the activity of the CuO_x will be optimized under electrocatalytic conditions by depositing the films on conductive substrates using three methodologies including electrodeposition techniques as described in the literature [18, 20-22] as well as physical vapor deposition (PVD) techniques. In a second step, the optimum film depositing conditions will be used to modify the n-Si semiconducting material. Finally, the new produced photoelectrodes will be tested for the

overall water splitting reaction in a PEC configuration according to Figure 1. In this configuration, when the sunlight illuminates the surface of the CuO_x/Cu based silicon photoanode, it induces charge separation. The generated holes migrate to the interface and are used to produce O_2 from water. And the electrons in the conduction band move to the counter electrode to reduce water and produce hydrogen.

Experimental section

General considerations

All reagents were purchased from Aldrich unless otherwise stated.

The Fluorine doped Tin Oxide (FTO)-coated glass was purchased from Xop Fisica (thickness, 2.3-3.0 mm; visible transmittance, 80-81.5%; resistance, 6-9 Ω/cm^2). Before the deposition and characterization tests, the FTO-coated glass was ultrasonically cleaned in deionized water, propanol, deionized water, acetone and then ethanol for 10 min each.

Phosphorous-doped [100] n-type silicon wafers (0.3-0.5 $\text{ohm}\cdot\text{cm}$) were purchased from ProLog. Ohmic contact of 20 nm titanium was deposited to the backside of the wafers by e-beam evaporation (PVD75 Kurt J. Lesker). Before any deposition, the Si wafers were washed with acetone, ethanol, deionized water in ultrasonic bath, each for 10 minutes.

Electrochemical experiments for the preparation of the CuO_x films were performed in a standard three-electrode configuration cell with Ag/AgCl or SCE (saturated KCl) reference electrode and Pt wire as the counter electrode at ambient temperature controlled by a CHI 660D potentiostat (CH Instruments, Inc.).

UV-Vis characterization was performed on Cary 50 (Varian) UV-Vis spectrophotometer in air condition. Before all the analysis, the FTO electrodes were cleaned.

Transmission electron microscopy (TEM) characterization was performed using a JEOL TEM (model 1011).

For the photocatalytic reactions, the illumination was provided by a 150 W Xe Arc Lamp (LS-150, ABET technology), equipped with a UV-light filter ($\lambda < 400$ nm) and calibrated to 1 sun ($100 \text{ mW}/\text{cm}^2$)

using a calibrated silicon photodiode at 25 °C.

The 0.2 M borate buffer solution (pH 9) was obtained by mixing a 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ solution and a 0.2 M H_3BO_3 solution in a ratio of 8:2 (v/v). All pH values were measured with a HI 4222 pH-meter (Hanna Instruments) using a calibrated Crison 5029 electrode (Crison Instruments). The electrode of the pH-meter was calibrated in three kind of standard solutions (pH 4.01, 7.00, 9.21) subsequently before the measurements.

Fabrication of CuO_x/FTO electrodes:

Oxidative electrodeposition: the CuO_x film was prepared by controlled potential electrolysis of a freshly prepared 0.2 M borate buffer solution (pH 9) containing 1 mM $\text{Cu}(\text{NO}_3)_2$ in a single-compartment three-electrode cell at ambient conditions at 1.1 V vs. Ag/AgCl for 40 min [18]. The resulting film was rinsed with deionized water to remove Cu^{2+} salts and dried with N_2 flow.

Reductive electrodeposition: the CuO_x/FTO electrodes were prepared following a modified procedure from the literature [20]. The FTO electrodes were immersed in a three-electrode, one compartment electrochemical cell filled with 0.025 M $\text{Cu}(\text{NO}_3)_2$ aqueous solution. A controlled potential of -0.5 V vs. SCE was applied for 56 s when the electrodeposition of Cu_2O and Cu^0 took place. Then, the electrodes were taken out, rinsed using deionized water and dried with N_2 flow. Finally, a cyclic voltammetry (CV) was performed from 0 V to 1.6 V vs. SCE in 0.2 M borate buffer solution at pH 9. An irreversible oxidation wave was found, indicating the formation of CuO_x on the surface.

Sputtering: 5 nm or 10 nm Cu^0 film was deposited on FTO coated glass by sputtering (ATC Orion 8-HV. AJA International) at 100 W, with a deposition rate of 1.6 $\text{\AA}/\text{s}$ for 40 s and 80 s, respectively. Then the Cu/FTO electrodes were tested by sweeping to positive potential from 0 to 1.6 V vs. SCE in 0.2 M borate buffer solution (pH 9) to form a layer of CuO_x .

Fabrication of the $\text{Cu}/\text{SiO}_2/\text{nSi}/\text{Ti}$

electrodes:

Sputtering: copper films (5 and 10 nm) were deposited on n-Si wafers by sputtering (ATC Orion 8-HV, AJA International) at a deposition rate of $\sim 1.6 \text{ \AA/s}$. The Cu films on n-Si were deposited at the same time of the Cu/FTO (see above). Copper tape was used to contact the electrodes for electrochemical experiments.

Photoelectrochemical water oxidation catalysis with n-Si based photoanodes:**One compartment cell – teflon box:**

In this configuration, electrodes were analyzed in a one compartment cell with three electrodes. The n-Si based photoanodes were used as working electrodes. A Hg/Hg₂SO₄ (saturated K₂SO₄) reference electrode was used together with a Pt wire as counter electrode. An auto-shutter controlled by the custom made shutter_Ard program was used to hinder the light for the dark or chopped characterization. The PEC properties of the Cu/nSi based electrodes were tested in 0.2 M borate buffer solution (pH 9).

Two compartments cell: In this setup, the n-Si based photoanodes were used as working electrodes. A Ag/AgCl reference electrode and a Pt mesh as counter electrode were used in 0.2 M borate buffer solution (pH 9). An oxygen sensitive OXNP15121 Clark electrode from Unisense was used in air condition to calculate the Faradaic efficiency of the photoanodes.

Results and discussion**Deposition of CuO_x on FTO: electrocatalytic water oxidation**

Many methodologies are available to

deposit materials such as copper on semiconducting or conductive substrates, including PVD, molecular beam epitaxy (MBE), chemical vapor deposition (CVD), and electrodeposition [23]. In this study, we used three different techniques in order to find the best method that can form CuO_x films on n-Si electrodes. We started by studying the deposition of CuO_x by electrodeposition on FTO coated glass substrates, adapting two methods that are described in the literature (methods 1 and 2 in Table 1). In method 1, a positive potential was applied to a 0.2 M borate buffering electrolyte (pH 9) containing 1 mM Cu(NO₃)₂, maintaining the equilibrium between dissolution and precipitation of metal ion to electrodeposit a Cu-B_i film (mainly CuO, where “B_i” stands for borate) on the FTO side of the glass [18]. In contrast, a negative potential was applied in method 2 to produce Cu₂O (not stable) and Cu⁰ from Cu²⁺, after this, positive potentials were applied to introduce an irreversible reaction from Cu₂O and Cu⁰ to CuO.

The third method that we used was a type of PVD technique, that is, sputtering of a Cu target to form a very thin layer of Cu on FTO coated glass. Two different thicknesses of copper (5 and 10 nm) were produced in order to study and compare the catalytic performance of the resulting electrodes. In Figure 2, the surface of analogous 5 nm and 10 nm Cu films, deposited on a copper TEM grid with a thin coating of carbon, can be observed clearly at large (a-b) and small (c-d) scale, respectively. We can observe that the surface of the Cu films is not homogenous and the 5 nm Cu film seems to be rougher than the 10 nm Cu film. The results are reasonable since the thickness is too

Table 1. Summary of methods used in this work to deposit CuO_x films on semiconducting or conductive substrates. All potentials are given vs. the SCE electrode.

Method	Copper Precursor	Description	Ref.
1	Cu(NO ₃) ₂	Oxidative electrodeposition (1.055 V vs. SCE, 40 min)	[18]
2	Cu(NO ₃) ₂	a) Reductive electrodeposition (-0.5 V vs. SCE, 56 seconds) b) CV from 0 V to 1.6 V vs. SCE	[20]
3	Metallic copper	a) Sputtering b) CV from 0 V to 1.6 V vs. SCE	this work

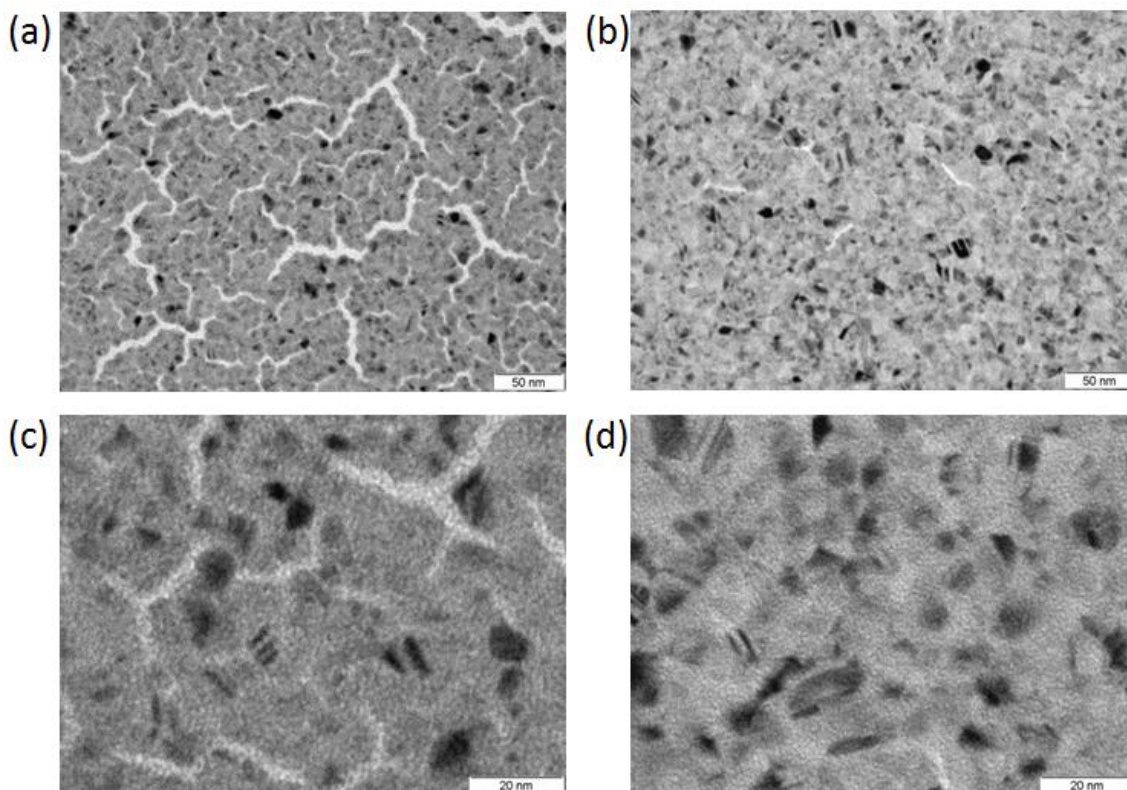


Figure 2. Morphology of the Cu films prepared using method 3 (sputtering) on copper grids suitable for TEM analysis. TEM images of 5 nm (a and c) and 10 nm (b and d) Cu films at large (a-b) and small (c-d) scale. The scale bars are 50 nm for (a-b), and 20 nm for (c-d).

thin, however, rougher surface may provide larger area for the catalytic process. The resulting Cu/FTO electrodes were immersed in a 0.2 M borate buffer solution (pH 9) and a positive potential was applied to form a layer of CuO_x on the surface of the electrode (Method 3 in Table 1).

As shown in Figure 3(a), the onset potential for the water oxidation reaction of the CuO_x /FTO electrodes obtained with the three different methods is very similar and has a shift of ~ 200 mV compared to the bare FTO. In terms of current density, methods 1 and 3 are better than method 2 (compare blue and red traces with green traces in Figure 2a).

The stability of the CuO_x /FTO electrodes was assessed by means of successive CV experiments as well as controlled potential electrolysis. The electrodeposited CuO_x /FTO (methods 1 and 2) decays slightly after each CV scan until it reaches a constant level. On the other hand, the CuO_x /Cu/FTO made from sputtering is stable from the beginning.

Figure 3(b) shows the results of controlled potential electrolysis using CuO_x /FTO electrodes in 0.2M borate buffer (pH 9) at 1.1 V vs. SCE (641 mV overpotential). The current density traces, associated with the water oxidation catalysis, are very stable for all the samples, but the current density of the 10 nm CuO_x /Cu/FTO is much higher than both the electrodeposited CuO_x /FTO at a similar potential. In summary, the results in Figure 3 prove that the CuO_x /Cu/FTO electrodes produced by the sputtering method show the best electrochemical performance.

Another important aspect of the CuO_x films if we want to use them for PEC applications is their transparency, because we need the light to go through the CuO_x film in order to reach the semiconductor (Figure 1). In order to know better if the sputtered Cu can be useful for the n-Si photoanodes, we analyzed the CuO_x /Cu/FTO samples by UV-Vis spectroscopy (Figure 4). We did the analysis before and after the controlled

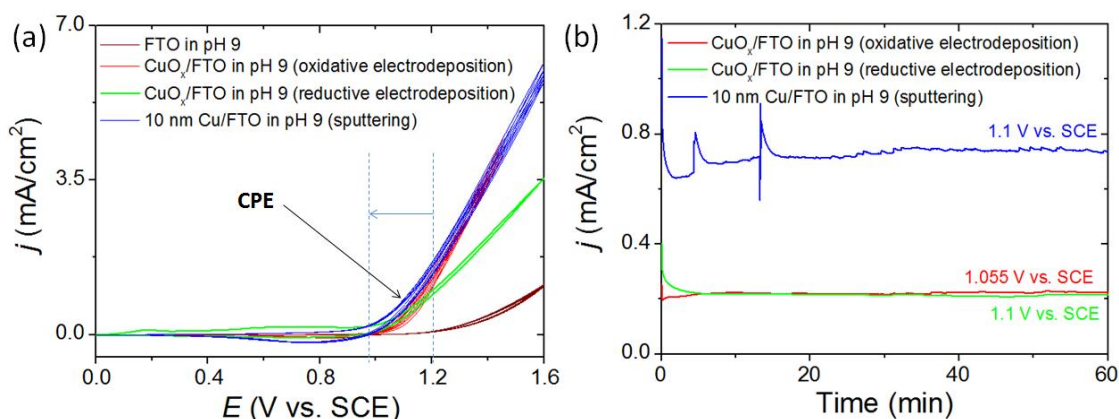


Figure 3. Electrochemical water oxidation performance of CuO_x/FTO electrodes. (a) CVs of bare FTO (brown), oxidative electrodeposited CuO_x/FTO (red), reductive electrodeposited CuO_x/FTO (green) and 10 nm sputtered $\text{CuO}_x/\text{Cu}/\text{FTO}$ (blue) in 0.2 M borate buffer solution (pH 9). All the CV scans were obtained without iR compensation by using an SCE reference electrode, a Pt counter electrode, and at a scan rate of 100 mV/s. (b) Current density traces obtained without iR compensation by controlled-potential electrolysis (CPE) of oxidative electrodeposited CuO_x/FTO (red), reductive electrodeposited CuO_x/FTO (green) and 10 nm Sputtering $\text{CuO}_x/\text{Cu}/\text{FTO}$ (blue) in 0.2 M borate buffer solution (pH 9) at about 1.1 V vs. SCE.

potential electrolysis to see if there was any change. As it can be observed in Figure 4, after the electrochemical experiments the copper films (both 5 nm and 10 nm) are more transparent ($\sim 100\%$) in the visible light range than the initial films (compare solid and dashed curves). Moreover, the transparent $\text{CuO}_x/\text{Cu}/\text{FTO}$ electrodes are still fully active as they show no decay of the electrochemical performance. These results make the sputtering Cu very promising to enhance the performance of n-

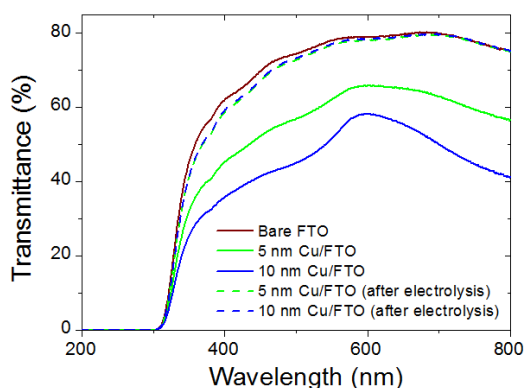


Figure 4. Transparency of the Cu film. UV-Vis analysis of 5 nm (green) and 10 nm (blue) $\text{CuO}_x/\text{Cu}/\text{FTO}$ before (solid curves) and after (dashed curves) the electrochemical tests. The signal of the bare FTO substrate is also shown as reference.

Si based photoanodes.

Deposition of CuO_x on nSi semiconductor: photoelectrocatalytic water oxidation

Silicon is easily oxidized and corroded under electrochemical and PEC conditions in aqueous solution [5-7], so it was not possible to use methods 1 and 2 in Table 1 to form CuO_x on bare Si wafers. Therefore, we tried to use these electrodeposition methods on protected $\text{NiO}_x/\text{Ni}/\text{SiO}_x/\text{nSi}/\text{Ti}$ photoanodes described in the literature [9], which are highly stable in solution. However, the results showed that the CuO_x doesn't help to enhance the performance of the $\text{NiO}_x/\text{Ni}/\text{SiO}_x/\text{nSi}/\text{Ti}$ electrodes. Instead, the photocurrent decreases, likely due to the loss in transmittance of the resulting $\text{CuO}_x/\text{NiO}_x/\text{Ni}/\text{SiO}_x/\text{nSi}/\text{Ti}$ photoanode.

On the other hand, the use of PVD methods like sputtering to deposit the Cu film on n-Si directly are very promising because silicon is stable under PVD conditions. Furthermore, the $\text{CuO}_x/\text{Cu}/\text{FTO}$ electrodes prepared using method 3 in Table 1 show very good electrochemical properties as well as high stability in pH 9 solution, and they are highly transparent in the visible light range after electrochemical tests without any decay of catalytic activity. The Cu film formed by sputtering protects

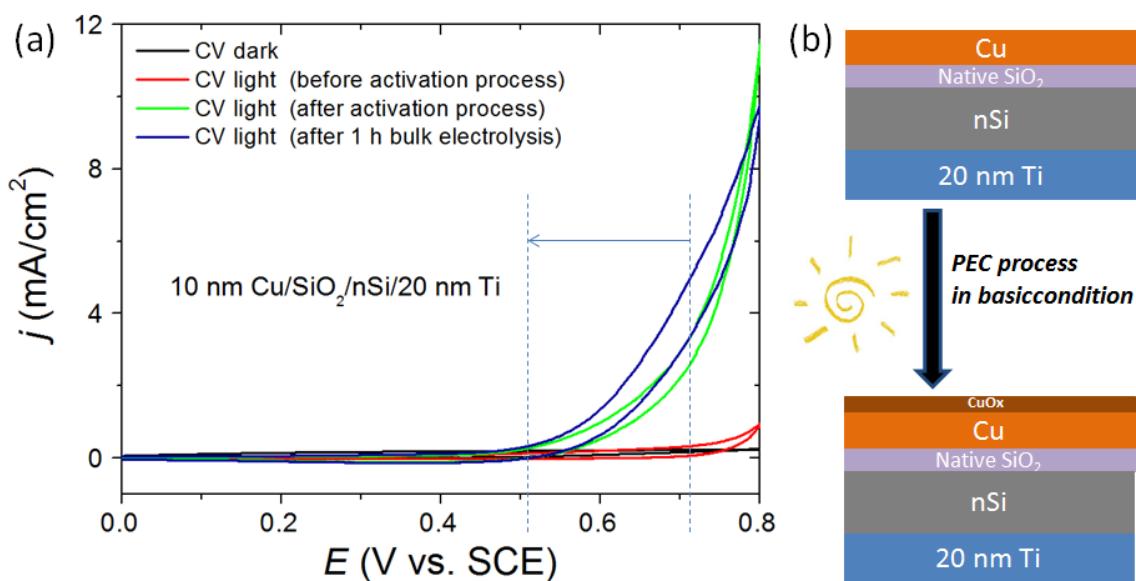


Figure 5. Activation of the Cu/nSi photoanodes. (a) CV scans of 10 nm Cu/SiO₂/nSi/20 nm Ti in the dark or under 1-sun illumination. All the CVs were obtained with iR compensation using a Pt counter electrode, a Hg/Hg₂SO₄ reference electrode at a scan rate of 100 mV/s in 0.2 M borate buffer solution (pH 9). (b) A scheme illustrating the activation of the Cu/SiO₂/nSi/Ti photoanodes by producing a layer of CuO_x at pH 9 under PEC conditions.

the Si electrode from corrosion when immersed in aqueous solution and will act as a catalyst under PEC conditions. Copper-protected photoanodes with the composition Cu/SiO₂/nSi/20 nm Ti with two different copper thicknesses (5 and 10 nm) were obtained following method 3 in Table 1, analogously to the CuO_x/Cu/FTO.

Interestingly, the Cu/SiO₂/nSi/20 nm Ti electrodes are not active at the initial CV scan in 0.2 M borate buffer solution (pH 9). As it can be observed in Figure 5(a), the current density of 10 nm Cu/SiO₂/nSi/20 nm Ti at the first CV scan is very similar between light and dark conditions in pH 9 (compare red and black curves). However, these electrodes are activated after several CV scans at larger potential range and chopped linear sweep voltammetry (LSV). A significant shift of the onset potential for the water oxidation catalysis (from ~0.72 V to ~0.51 V vs. SCE) and obvious increase of the current density can be obtained after this activation process. The activated electrodes are very stable as demonstrated by the CVs before and after 1 hour of bulk electrolysis at 0.8 V vs. SCE (compare green and blue curves in Figure 5). The mechanism of the activation process of this kind of Cu/nSi photoanodes is complex,

involving both soluble and insoluble products and multiple oxidation states with Cu^I, Cu^{II}, Cu^{III}, and/or Cu^{IV} [24-25]. A schematic representation of this activation process is shown in Figure 5(b). Further studies are necessary to fully understand this process.

Figure 6 compares the performance of the CuO_x/Cu/SiO₂/nSi/Ti photoanodes with the CuO_x/Cu/FTO electrodes at pH 9. As a reference, a typical CV scan of the bare FTO electrode in pH 9 is also shown (black curve). The CuO_x/Cu film on FTO shifts the onset potential ~270 mV compared with the bare FTO (from 1.22 V to 0.95 V vs. SCE). Both the FTO and Cu/FTO are not photoactive since these electrodes show the same performance under light and dark conditions in pH 9 solution (not shown). However, when the CuO_x/Cu film is deposited to a good light absorber such as n-Si photoanode, the performance of the resulting electrode shows totally different behavior with and without illumination (solid and dashed brown and blue curves in Figure 6). The CuO_x/Cu/SiO₂/nSi/Ti photoanodes show a shift of about 440 mV of the onset potential compared to that of the CuO_x/Cu/FTO (from 0.95 V to 0.51 V vs. SCE). This 440 mV difference is

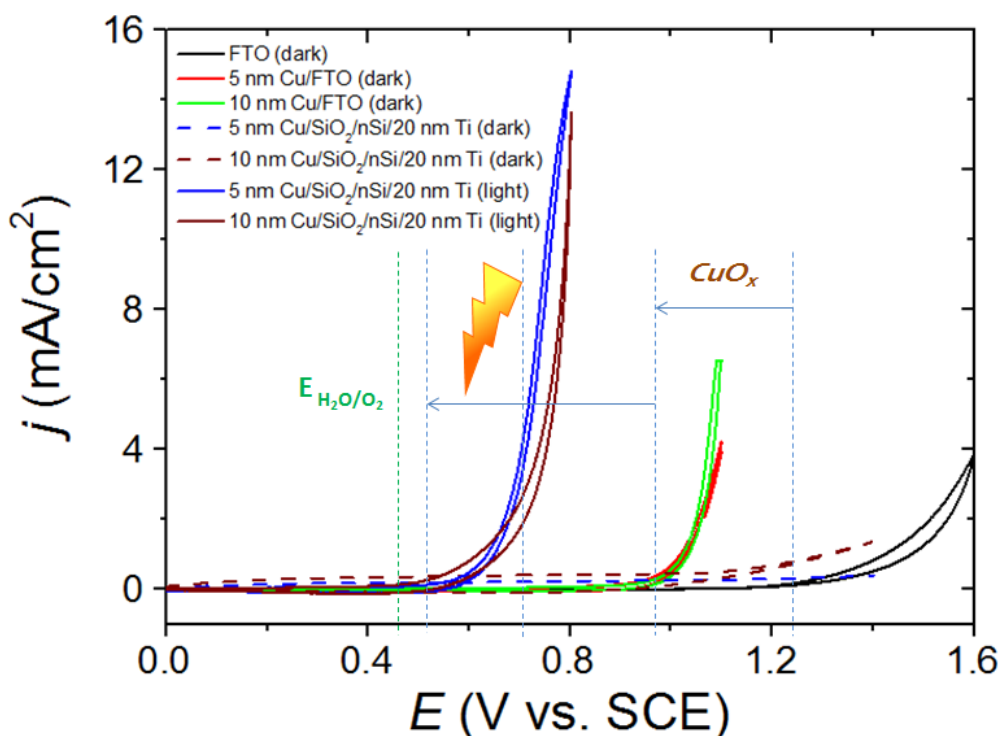


Figure 6. Comparison of the onset potential of the water oxidation reaction of different electrodes prepared in this work. CVs of bare FTO (black), 5 nm (red) and 10 nm Cu/FTO (green) in the dark, 5 nm (blue) and 10 nm (brown) Cu/SiO₂/nSi/20 nm Ti in the dark (dashed curves) and under illumination (solid curves). All the CVs were collected using a Pt mesh as the counter electrode, a SCE or Hg/Hg₂SO₄ reference electrode, with iR compensation at a scan rate of 100 mV/s in 0.2 M borate buffer solution (pH 9).

induced by the illumination of simulated 1-sun, which makes it possible to use sunlight and save energy.

Encouraged by the high performance of the CuO_x/Cu/nSi photoanode and considering that the stability of the electrodes is critical for real water splitting applications, we performed controlled potential electrolysis for a period of time. Figure 7(a) shows that both the 5 nm and 10 nm CuO_x/Cu/SiO₂/nSi/20 nm Ti photoelectrodes are stable for at least 40 min under controlled potential electrolysis at 0.8 V vs. SCE in pH 9. For the 10 nm Cu/nSi photoanodes, it seems to be more stable (1 hour) than the one with 5 nm Cu. The current density traces of these two electrodes were both obtained without iR compensation, if the resistance of the system is considered, the really applied potentials for collecting 0.8 mA/cm² and 0.6 mA/cm² current densities on 10 nm and 5 nm Cu/nSi photoanodes are 0.59 V and 0.64 V vs. SCE, that accounts for an

overpotential for the water oxidation half reaction of 131 mV and 181 mV at pH 9, respectively.

In order to prove that the current observed in the controlled potential electrolysis is due to the water oxidation reaction, an experiment using an oxygen gas sensor was performed. Figure 7(b) shows the O₂ gas evolution versus time profile produced by a 5 nm Cu/SiO₂/nSi/20 nm Ti photoelectrode in 0.2 M borate buffer solution (pH 9), under simulated 1 sun illumination while operating at a constant potential of 1.16 V vs. SCE for ~1 hour in a two-compartment glass cell. A Faradaic efficiency of 97% was obtained considering a theoretical volume of gas (red dashed line in Figure 7(b)), calculated from the total charge passed, according to the stoichiometry of the water oxidation half reaction $\text{H}_2\text{O} - 4\text{e}^- \rightarrow 2\text{O}_2 + 4\text{H}^+$ and real volume of O₂ gas determined experimentally (red solid line in Figure 7(a)).

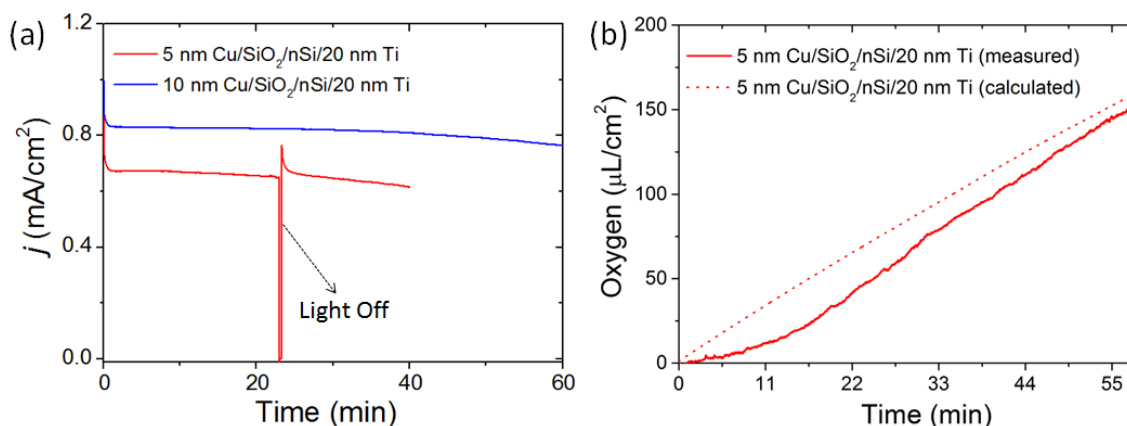


Figure 7. Stability of the $\text{CuO}_x/\text{Cu}/\text{nSi}$ photoanodes. (a) Current density versus time data under constant potential of 0.8 V vs. SCE of a 5 nm (red) and 10 nm (blue) $\text{CuO}_x/\text{Cu}/\text{nSi}$ anode in 0.2 M borate buffer (pH 9) under constant illumination. (b) Oxygen evolution at a $\text{CuO}_x/\text{Cu}/\text{nSi}$ photoanode operated in 0.2 M borate buffer (pH 9) at 1.16 V vs. SCE. Both (a) and (b) were obtained without iR compensation, illuminated by a simulated 1-sun light and using a Pt mesh as counter electrode. A one-compartment teflon box and SCE reference electrode were used for tracing the current density (a) and a two-compartment glass cell and Ag/AgCl reference electrode were used for the oxygen detection experiment (b).

Conclusions

In conclusion, we studied different methods to deposit CuO_x films to protect and activate the n-Si photoanodes for the photoelectrochemical water oxidation reaction. We proved that the PVD processed $\text{Cu}/\text{SiO}_2/\text{nSi}/\text{Ti}$ samples show highly active (onset potential of 0.51 V vs. SCE, with an overpotential of 51 mV) and stable performance under illumination of simulated 1-sun in 0.2 M borate buffer at pH 9 (constant current density of 0.8 mA/cm^2 at 0.59 V vs. SCE for 1 hour, with an overpotential of 131 mV), with faradaic efficiency close to 100%. This methodology helps ~440 mV potentials to be saved by sunlight using a cheap and earth-abundant copper based catalyst in pH 9 solution. This is the first study that uses CuO_x as catalyst in a semiconductor surface to afford highly active and stable photoanodes for the water splitting reaction. This study will be a promising work to provide a solving method for the increasing global energy demand and decreasing fossil fuel reserve.

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