A novel Cu$_2$O/Cu grid for photoelectrochemical water splitting

Xing Wang$^1$, Jun Chen$^1$, Xiaoling Wu$^1$, Guoan Cheng$^1$ and Ruiting Zheng$^{1,2}$

$^1$Key Laboratory of Radiation Beam Technology and Materials Modification of Ministry of Education, College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, P. R. China
$^2$Corresponding author, rtzheng@bnu.edu.cn

Abstract. In this study, we reported a novel metal-semiconductor junction grid, which is made of Cu and Cu$_2$O. The Cu$_2$O film is deposited on the surface of a Cu grids by a simple electrochemical deposition method. Cu grids with 200 mesh has larger specific surface area than that of Cu sheet and will enhance the water splitting performance of photo-electrodes. Different Cu-Cu$_2$O grid samples were prepared by changing the electrodeposition time and current. The best deposition parameters for Cu$_2$O films on Cu grids were 3 hours of deposition time and 0.4 mA/cm$^2$ of deposition current density. Under the best condition, the highest photocurrent density was -3.83 mA/cm$^2$ which was higher than -2.36 mA/cm$^2$ of Cu$_2$O films on Cu sheet.

1. Introduction

Since the late 1970s, the increased consumption of fossil fuels led to terrible environmental issues, such as greenhouse gases and air pollution [1]. It is essential to find environmentally-friendly alternative energy sources. Researchers made great efforts to develop next-generation energy conversion and storage technologies [2-8]. Among all these methods, photoelectrochemical (PEC) water splitting is the most environmentally-friendly, clean and simple way to achieve the hydrogen production through photo-chemical conversion[9-12]. Owing to the advantages of easy fabrication and low cost, metal oxide semiconductors are of great potential in solar water splitting [13]. Among all those materials, Cu$_2$O is considered as one of the ideal photocathode materials for water splitting because of its perfect energy band structure. Its conduction band lies 0.7 V negative to the hydrogen evolution potential [14-18]. Taking the fact that Cu$_2$O has a direct band gap of 2-2.2 eV into consideration, theoretically, it can reach a photocurrent of -14.7 mA cm$^{-2}$[19-22]. Luo have demonstrated a photocathode with nanostructured Cu$_2$O/ Ga$_2$O$_3$/TiO$_2$ /RuO$_x$ multilayer structure, the current density of which reaches 10 mA/cm$^2$ at 0 V versus RHE. However, the complicated and expensive synthetic process prevents this photocathode from massive application.

In this study, the Cu$_2$O film was directly deposited on the surface of Cu grids by a simple electrochemical deposition method. Because Cu grids has larger specific surface area than that of flat sheets, it could enhance the performance of photo-electrodes. To explore the influence of synthetic process on PEC performances of grid photocathode, we prepared different Cu- Cu$_2$O mesh samples by changing the deposition time and current. We also deposited Cu$_2$O film on Cu sheet under the same condition for comparison. After photoelectrochemical measurements, we found that the best PEC performance was obtained on the grid sample prepared by 3 hours of deposition time and 0.4 mA/cm$^2$ of deposition current. The highest photocurrent density is -3.83mA/cm$^2$ at 0V vs. RHE, which is much higher than -2.36 mA/cm$^2$ of the flat sheet sample under the same condition. To our knowledge, this is a rather high photocurrent density for bare Cu$_2$O films [23-26]. The reason for the improvement is detailed discussed. These results implied that it is possible to achieve high performance electrode in a low-cost technology.
2. Experimental

2.1 Electrodeposition of Cu$_2$O

The Cu$_2$O thin films were deposited on 200-mesh copper grids. The electrolyte was prepared by 0.2 M Copper(II) sulfate pentahydrate (CuSO$_4$.5H$_2$O, 99%) and 3 M lactic acid (C$_3$H$_6$O$_3$, 85.5%) with 0.5 M potassium monohydrogen phosphate (K$_2$HPO$_4$.3H$_2$O, 99%) buffer. We used the 2 M potassium hydrate (KOH, 85%) solution to adjust the pH of mixed solution to 12. All those chemicals were purchased from Xilong Chemical Co. The temperature of the bath was maintained at 25°C in a constant room temperature. The Cu$_2$O thin films were deposited at a constant current density (Galvanostatic mode) using an electrochemical workstation (CHI660E) in a two electrode configuration (a Pt sheet served as counter electrode). The deposition current density varied from 0.1 to 0.6 mA/cm$^2$ and the deposition time changed from 2 hours to 10 hours.

2.2 Structural and Optical Characterization

The microstructure and size of the samples were characterized by scanning electron microscopy (SEM, HITACHI S-4800). The components and chemical structure of the films were determined by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with Cu Ka radiation ($\lambda$=0.1506 nm). The X-ray photoelectron spectroscopy (XPS) data were recorded by an instrument from ESCALAB 250Xi, UK. The UV-vis diffuse reflectance spectra (DRS) were acquired using a Perkin Elmer Lambda 950 UV-vis-NIR spectrophotometer (Perkin-Elmer, USA). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were acquired via a F20 transmission electron microscope.

2.3 Photocurrent measurements

The photocurrent measurements were carried out in a three-electrode configuration under front-side simulated AM 1.5 illumination. The light source used in the water splitting researches was a 300 W xenon lamp with an AM 1.5G filter (MAX-302, Asahi Spectra, USA). The electrolyte was a 0.5 M Na$_2$SO$_4$ solution (pH=6.8). The reference electrode was Ag/AgCl in saturated KCl, and a Pt wire was the counter electrode. The data was obtained by a bipotentiostat (Model AFCBP1, USA).

3. Result and Discussion

Fig. 1 shows the morphologies and microstructures of the samples with different deposition conditions. The deposition time changes from 2 hours to 10 hours and deposition current density is 0.1 mA/cm$^2$. The average thickness of samples is about 2um, and the average diameter of the wire of 200 mesh Cu grids is 75um, as shown in Fig 1(A, B). Fig 1(C) shows the cross section of the Cu$_2$O film on Cu mesh. Fig 1(D) shows the typical XRD pattern of metal Cu and Cu$_2$O film on it. The X-ray diffraction peaks of prepared Cu$_2$O films can be well-indexed to the Cu$_2$O (JCPDS 78-2076). Although the diffraction peak of metal Cu is much higher than that of Cu$_2$O film, it still proves the existence of Cu$_2$O. When Cu$_2$O films are deposited on the surface of Cu mesh, a Schottky junction can be built at the interface of the semiconductor and the metal, as shown in Fig 1(E). When Cu- Cu$_2$O mesh is excited by light illumination, photoinduced electron–hole pairs are generated, the electrons in the conduction band of Cu$_2$O migrate to Cu mesh with the help of the inner electric field, and then transfer to the Pt counter electrode to react with H$^+$ to produce H$_2$. However, the photoinduced holes on the valence band stays on the surface of Cu$_2$O films causing a photocorrosion that is a major issue that researchers have to confront with.
Fig 1. A) Cu$_2$O film deposited on Cu grid. B) Cu mesh. C) cross section of Cu grids with Cu$_2$O. D) XRD pattern of Cu-Cu$_2$O grids. E) Schematic diagram of the charge separation process of the Cu-Cu$_2$O grids under AM 1.5G illumination.

Fig 2(A-D) are SEM images of Cu$_2$O films on the surface of Cu grids at different deposition conditions. Under the same deposition current density, the morphologies change with the increase of deposition time. Fig 2(A) shows the Cu$_2$O film after 2 hours deposition, many round bulges can be observed on the surface of sample. Fig 2(B) exhibits the surface of grid after 3 hours deposition. Many \{100\} faces of Cu$_2$O cube grains can be observed, but some corners of the cube grains are truncated. With the increase of deposition time, some \{110\} faces are presented on the Cu$_2$O grains, as shown in Fig 2(C). At last, we extent the deposition time to 10 hours, the grain stop growing up and some corner of the grain are corroded because of the depletion of Cu$^{2+}$ and decreasing of pH value, as fig 2(D) shows.

According to Li and Paracchino’s theory [27], with more \{100\} faces exposed to the electrolyte, the Cu$_2$O film is more active for photocatalysis, which means higher photoelectrochemical performance. Fig 2(E) shows the relationship of photocurrent density at 0 V versus RHE of the as-prepared samples as a function of AM 1.5G illumination time in 0.5 M Na$_2$SO$_4$ solution. The photocurrent density of the sample after 3 hours deposition reaches -1.71mA/cm$^2$, which is the highest of all the samples. The reason may contribute to the more \{100\} faces exposed to the electrolyte. The sample deposited on Cu sheet under same condition has a photocurrent density of -1.1 mA/cm$^2$. 200 mesh Cu grid has larger specific surface area is the reason why the photoelectrochemical performance of Cu$_2$O on Cu grid is much higher than that of Cu$_2$O on Cu sheet. It also can be observed that the photocurrent density of all samples decrease quickly. Even for the best performance sample (3 hour of deposition with the deposition currents of 0.1mA/cm$^2$), the photocurrent was is -0.24mA/cm$^2$ after 200 second of illumination, which is less than 15% of the beginning photocurrent density.
Figure 2. A-D) SEM images of grid surface after deposition different time (2h, 3h, 5h, 10h) of Cu$_2$O, the deposition current densities are all 0.1mA/cm$^2$. E) Photocurrent density of grid electrode as a function of AM 1.5G illumination time in 0.5 M Na$_2$SO$_4$ solution. The Cu$_2$O deposition time of electrodes varied from 2 hours to 10 hours under the same deposition current density (0.1mA/cm$^2$).

From fig 2(E), we can conclude that the perfect deposition time is 3 hours. Furthermore, we fix the deposition time at 3 hour and prepared samples by changing the deposition current densities. Fig 3(A) shows the SEM image of the Cu$_2$O film deposited with current density of 0.2 mA/cm$^2$. The film exposes some incomplete growth Cu$_2$O cubic grains. After 3 hour deposition with 0.4 mA/cm2 of current density, perfect growth Cu$_2$O grains cover the surface of sample,{[100]} faces and the corners of Cu$_2$O cubic are clearly observed, as Fig 3(B) illustrates The average grain size of the cubic crystal is about 1.3um. If the deposition current density increase to 0.6mA/cm$^2$, the cubic morphology of Cu$_2$O grain is still perfect, and the size of the Cu$_2$O cubic grain is about 2 um, much bigger than that in fig 3(B), as shown in fig 3(C). Because the deposition current is too high, some round bulges cover part of the surface on Cu grids, which reduce the area of exposed {[100]} faces, as shown in the inset of fig 3(C). We also deposited Cu$_2$O film on Cu sheet for comparison, as shown in fig 3(D). The deposition time is 3 hours and the deposition current density is 0.4mA/cm2. The general morphologies and size of the grains in fig 3(D) are similar to that in fig 3(B).

Fig 3(E) gives the photoelectrochemical measurement results of four samples. The Cu$_2$O/Cu electrode prepared by the 0.4 mA/cm$^2$ current density has the best photoelectrochemical performance with its photocurrent density reaching -3.83 mA/cm$^2$, which should contribute to the special surface mophonologies and microstructures of the samples. Perfect cubic shape and large area of {[100]} face exposed to the electrolyte means large active reaction area. Under the same synthesis condition, the Cu$_2$O films deposited on Cu sheet has the photocurrent densities of -2.36 mA/cm$^2$ while it is illuminated by AM 1.5 simulated sun light. Comparing to Cu sheet, 200 mesh Cu grid has larger specific surface area, which results in higher photocurrent density. It also can be observed that the photocurrent density of all samples decrease with the extension of illumination time. For the best performance sample(3 hour of deposition with the deposition currents of 0.4mA/cm$^2$), the photocurrent density is -0.85mA/cm$^2$ after 200 seconds of illumination, which is about the 22.2% of the beginning photocurrent density. We can find that the sample with perfect cubic shape still remained the highest photocurrent density after 200 second of illumination of AM 1.5 simulate sun light.

Figure 3. A-C) Cu$_2$O films deposited on Cu mesh with different deposition current densities (0.2,0.4,0.6 mA/cm$^2$) under same deposition time (3 hours). D) Cu$_2$O films deposited on Cu sheet with deposition current density of 0.4 mA/cm$^2$ and deposition time of 3 hours. E) Photocurrent density–time characteristics in 0.5 M Na$_2$SO$_4$ solution, under AM 1.5G light illumination for the electrodes at 0 V versus RHE. The deposition current density varied from 0.2 to 0.6 mA/cm$^2$ under the same deposition time (3 hours).
The HRTEM image of a flat plane on cubic Cu$_2$O grain is presented in Fig 4(A), which is obtained near the surface of the cubic grain. HRTEM image reveals its lattice fringes with the spacing of 0.209 nm, which corresponds to the (200) plane of Cu$_2$O. The lattices with the fringe spacing of 0.246nm, 0.209 nm and 0.298 nm in the round bulges correspond to the (111), (200) and (110) planes of the Cu$_2$O respectively, which indicates the polycrystalline nature of the round surfaces. Compared to sample in fig 4(B), the sample in fig 4(A) only contains a big single crystalline in a grain, that results in less phase boundaries and less defects, which is beneficial for transportation of photo-induced charges and enhancement of photo-corrosion resistance.

The optical properties of the as-prepared samples have been investigated by UV-vis diffuse reflection spectra, as shown in Fig 4(C), which describes significant difference of light absorption for Cu$_2$O films when wavelengths are shorter than 550 nm. The sample prepared with 3 hour of deposition time and 0.4mA/cm$^2$ of deposition current density has the best light absorption because the surface of leaning cubic crystal can reflect light several times, enhancing the light absorption and raise the photo-electrochemical performance. For a semiconductor, its band gap can be obtained from the corresponding modified Kubelka–Munk function through the UV-vis diffuse reflectance spectra [28-29]. The band gaps of as-prepared samples can be valued by the classical Tauc plots, as shown in Fig 4(D). The absorption edge energies of different Cu$_2$O/Cu grid electrodes are obtained by the intercept of the tangent to X-axis. The estimated band gap energies of the as-prepared samples are 1.91 eV, 1.93 eV, 1.95eV, respectively. The band gap of the sample prepared by 0.4mA/cm$^2$ of deposition current density is slightly lower than other two, which is in agreement with its stronger light absorption property, as shown in Fig 4(C).

Figure 4. A) HRTEM image of flat plane. B) HRTEM image of round bulges. C) UV-vis diffuse reflectance spectra (DRS) of samples under different deposition conditions. D) corresponding Tauc plots of the samples.
As we can see from the photocurrent-time curves in fig 2 and 4, Cu$_2$O suffered from detrimental photostability issues. According to Toe et. al [30], the photo-generated e$^-$ and h$^+$ can be separated when the Cu$_2$O is irradiated by sun light. The e$^-$ would transfer from conduction band to Pt counter electrode to produce hydrogen. In the meantime, the photo-induced h$^+$ would accumulate on the surface of Cu$_2$O films and oxidize Cu$_2$O. Fig 5(A-C) shows SEM images of the sample with best performance (3 hours of deposition with the deposition currents of 0.4mA/cm$^2$) after 10 seconds, 100 seconds and 3 hours of illumination. It can be observed that the surface of Cu$_2$O become rougher and more porous with the extension of illumination time. In order to study the changes of electrodes surface, XPS are employed to analyse the valence change of Cu$_2$O surface. Fig 5(D-F) shows the results of XPS after 10s, 100s and 3h of illumination. Only the XPS spectrum of the sample after 3 hour illumination reveals identified peaks at binding energies of 934.5 eV and 935.5 eV respectively, which confirms the existence of Cu(OH)$_2$ and CuO. On the other two XPS spectra, we can't find the existence of Cu$^{2+}$. This may due to the CuO and Cu(OH)$_2$ films is too thin to be detected after 10s and 100s of illumination. But the surface oxidation of Cu$_2$O prevent the contact between Cu$_2$O and electrolyte, which can explain why the photocurrent density during first and second light on are so different. In order to further improve the PEC performance of Cu$_2$O electrodes, the sample and cheap method to retard the photocorrosion need to be further studied.

4. Conclusion

To summarise, we provided a novel Cu$_2$O/ Cu grid electrode for photoelectrochemical water splitting and the optimal synthesis parameters for electrodepositing Cu$_2$O films on Cu grid are 3 hours of deposition time and 0.4 mA/cm$^2$ of deposition current density. With this electrode, the highest photocurrent density of -3.83 mA/cm$^2$ is obtained. The reason may contribute to that the surface of Cu$_2$O/ Cu grid electrode prepared by optimal process is covered by compact cubic grains, and the cubic grain with the most exposed {100} faces has the best photoelectrochemical performance. After 200s of illumination, the photocurrent density is -0.85mA/cm$^2$, which is the best among all the samples. These results implies that it is possible to achieve high performance electrode by reducing the phase boundaries and defects in a low-cost electrochemical deposition method.
5. Acknowledgments

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6. References

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