Enhanced Photoelectrochemical Properties of Cu$_2$O-loaded Short TiO$_2$ Nanotube Array Electrode Prepared by Sonoelectrochemical Deposition

Yanbiao Liu, Haibin Zhou, Jinhua Li, Hongchong Chen, Di Li, Baoxue Zhou* and Weimin Cai

Copper and titanium remain relatively plentiful in earth crust. Therefore, using them in solar energy conversion technologies are of significant interest. In this work, cuprous oxide (Cu$_2$O)-modified short TiO$_2$ nanotube array electrode was prepared based on the following two design ideas: first, the short titania nanotubes obtained from sonoelectrochemical anodization possess excellent charge separation and transportation properties as well as desirable mechanical stability; second, the sonoelectrochemical deposition technique favours the improvement in the combination between Cu$_2$O and TiO$_2$ nanotubes, and favours the dispersion of Cu$_2$O particles. UV-Vis absorption and photo-electrochemical measurements proved that the Cu$_2$O coating extended the visible spectrum absorption and the solar spectrum-induced photocurrent response. Under AM1.5 irradiation, the photocurrent density of the composite electrode (i.e. sonoelectrochemical deposition for 5 min) was more than 4.75 times as high as the pure nanotube electrode. Comparing the photoactivity of the Cu$_2$O/TiO$_2$ electrode obtained using sonoelectrochemical deposition with others that synthesized using plain electrochemical deposition, the photocurrent density of the former electrode was ~2.2 times higher than that of the latter when biased at 1.0 V (vs. Ag/AgCl). The reproducible photocurrent response under intermittent illumination demonstrated the excellent stability of the composite electrode. Such kind of composite electrode material will have many potential applications in solar cell and other fields.

Keywords: Cu$_2$O; Short TiO$_2$ nanotube array; Sonoelectrochemical deposition

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Fujishima and Honda first demonstrated in 1972 that water could be electrolyzed by irradiating an n-type TiO$_2$ photoanode with solar energy and hydrogen could be produced at the photocathode in an electrochemical cell [1]. This fascinating discovery initiated lots of investigations in search of more efficient semiconductor materials for photoelectrochemical applications. Among the available photosensitive semiconductor materials, TiO$_2$ considered as one of the most promising photocatalysts due to its special features, such as low cost, chemical inertness and photostability [2]. However, its wide band gap (3.0~3.2 eV) allows it to absorb only ultraviolet light which accounts for merely ~5% of the solar photons, thereby hampering its wide use. Therefore, considerable attempts aimed at improving the visible light absorption of TiO$_2$ have been taken [3-5]. Among them, sensitization of TiO$_2$ with narrow bandgap semiconductors, including CdS, CdSe, Fe:O$_3$, SnO$_2$, etc, has been reported recently to reveal promising reactivity under visible light illumination [6-8].

Cuprous oxide (Cu$_2$O) is a semiconductor having a direct band gap of 2.0 eV, which has been studied previously for application in solar energy converting devices [9]. A major attraction of Cu$_2$O is that it is an inexpensive, non-toxic and readily available material. However, semiconductor materials with band gap suitable for capturing a significant fraction of incident solar...

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spectrum energy (≈0.8-2.4 eV) typically suffer UV induced photocorrosion [10]. It has been reported that the stability of Cu2O were greatly altered by the material it was coupled with. For instance, Cu2O coupled with ZnO was reported to be unstable [11], while Cu2O/TiO2 junctions are relatively stable [12, 13]. Therefore, the applications of the visible-light- responsive Cu2O/TiO2 composite electrode into photoelectro-chemical fields have become a hot subject [10, 14]. Since the conduction band of Cu2O is ca. ~1.0 eV more negative than that of TiO2, the coupling of the semiconductors should have a beneficial role in improving charge separation and transfer, as given in Fig. 1. Excited electrons from Cu2O can be quickly transported to TiO2, arriving at the electron collectors from external circuit [14]. Factors affecting the photoelectrochemical reactivity of Cu2O/TiO2 electrode include the transfer and recombination of photo-generated charges as well as the incident light absorption, which is further determined by the morphological structure of Cu2O and TiO2 as well as their combination effectiveness. Therefore, two aspects, including TiO2 and Cu2O, can be taken into consideration.

From the viewpoint of TiO2, the highly ordered TiO2 nanotube array (TNA) obtained from the anodization of titanium in HF or [F]-based electrolyte can reduce the scattering of free electrons and enhance electron mobility [15], which offers the potential for improved electron transport leading to higher photocatalytic efficiency. Therefore, the coupled Cu2O/TNA photoanode might facilitate kinetic separation of photogenerated charges and decrease the recombination rate within the electrode materials [16, 17]. However, the structural parameters (i.e. tube length and tube diameter) of the TNA film directly influence the transport resistance of photogenerated electrons and the recombination rate among photogenerated charges as well as the practical engineering application of electrode materials. Literatures [18, 19] have also demonstrated that the increase in length of nanotubes may not contribute positively to the photoelectrochemical performance of electrode materials. Recently, a short TNA (referred as STNA) film electrode prepared via sonoelectrochemical anodization route (anodization under irradiation of ultrasonic wave) was reported by our group [20]. Compared with the long nanotubes synthesized by conventional magnetic agitation technique [15, 21], the STNA electrode shows excellent charge separation and transfer properties and desirable mechanical stability.

As for Cu2O, the combination of Cu2O with nanotube layer and the morphological structure of Cu2O were significantly affected by the Cu2O preparation pathways. To date, Cu2O can be fabricated by many different techniques including thermal, anodic and chemical oxidation as well as reactive sputtering [22]. Among these different synthesis techniques, the electrochemical deposition technique offers the simplest and most controllable way of synthesizing Cu2O/TNA electrodes [23]. However, obtaining a composite electrode with better quality, evenly distributed Cu2O particles and a strong combination of Cu2O and TiO2 nanotubes may be more useful if ultrasonic waves can be integrated into the electrochemical process, since the sonochemical process can help increase the mass transfer throughout the reaction system and accelerate the diffusion of [Cu+] ions onto the nanotubes.

Based on the above design ideas and our previous work [19-21, 24-26], an efficient photoelectrochemical photoanode (Cu2O-decorated STNA) was prepared via sonoelectrochemical anodization and sonoelectrochemical deposition (SED, electrochemical deposition under ultrasonic wave irradiation) methods in this work. To our best knowledge, no study has been reported to date regarding the application of SED technique into fabrica tion of Cu2O/TiO2 composite electrode. In our research, the detailed synthesis process, characterization, and photo- electrochemical property testing for this composite catalyst were also discussed.

Experiments

Materials

Titanium sheets (0.25 mm thick, 99.9% purity) were supplied by Sumitomo Chemical (Japan). Hydrofluoric acid (HF, ≥40 wt%), ethanol, acetone, sodium sulfate, sodium acetate and cupric acetate were purchased from Sinopharm Chemical Rea-
gent Company without further treatment prior to use. All solutions were prepared using high-purity deionized (DI) water.

**Preparation of STNA**

The detailed methodology of the preparation of short, robust and highly-ordered titania nanotube array have been published in our previous work (see Fig. S1 in Supplementary Information) [20]. The anodized samples were then rinsed with DI water and dried in air. Subsequently, the as-prepared STNA samples were crystallized by annealing in air atmosphere for 3 h at 450°C with heating and cooling rate of 1°C/min.

**Cu2O sonoelectrochemical deposition**

The Cu2O/STNA was synthesized by the sonoelectrochemical deposition method (SED) in a solution contained 0.1 M sodium acetate and 0.02 M cupric acetate at -0.25 V for 5 min at room temperature. In all cases, the electrolyte was freshly prepared. After the deposition, the samples were immediately removed from the electrolyte and sequentially rinsed with DI water. The prepared Cu2O/STNA electrodes were then annealed at 200°C for 60 min in nitrogen atmosphere. In order to examine the effect of ultrasonic waves, the Cu2O-decorated STNA were prepared by plain electrochemical deposition (PED) under the same conditions without sonication treatment.

**Characterization**

The surface morphology of the samples was characterized with a field emission scanning electron microscope (PHILIPS, Netherlands, Sirion200) equipped with an energy dispersive X-ray spectroscopy (OXFORD, U.K.). An X-ray diffractometer (BRUKER, AXS-8, and ADVANCE) was used to determine the crystalline structure of the samples. The composition of the samples was analyzed with an X-ray photoelectron spectroscopy (Kratos, Axis Ultra DLD, Al Kα radiation). Light absorption properties of the electrode materials were measured using a UV-Vis diffuse reflectance spectrum (TU-1901, Beijing Purkinje General Instrument Co., Ltd).

**Apparatus and methods**

The photoelectrochemical experiments were performed in a rectangular shaped quartz reactor (20×40×50 mm) using a three-electrode system with a platinum foil counter electrode, a saturated Ag/AgCl reference electrode and a TiO2 work electrode. The supply bias and work current were controlled using a CHI electrochemical analyzer (CHI 660C, CH Instruments, Inc., USA). The photocurrent was measured at a scan rate of 20 mV·s⁻¹ with 0.1 M Na2SO4 solution as the electrolyte. A 350 w Xe lamp (Shanghai Lansheng Electronic Co., Ltd) was used as the simulated solar light. For the visible light irradiation, the white light was passed through an optical filter (Nantong Zhenhua co., Ltd), which cut off wavelength below 400 nm.

**Results and discussion**

Figure 2(a) presents a typical field emission scanning electron microscope (FE-SEM) image of the titania nanotube array obtained by sonoelectrochemical anodization of titanium in HF-H2O electrolyte, which reveals a regularly arranged pore structure of the film. These pores possess a uniform distribution ~65 nm in diameter and ~280 nm in length. Details on the formation mechanism of the nanotubes synthesized by sonoelectrochemical anodization were described elsewhere [20]. A light green colored deposit is observed on the nanotube surface within 1 min and only a few octahedral Cu2O particles are deposited (see Fig. 2(b)). As the deposition time increases, the size of Cu2O particles and their surface coverage increases and the color of the surface also changes from light green to reddish-violet. After 5 min, the nanotube surface becomes extensively coated with a relatively uniform layer of octahedral Cu2O deposits having side length of ~400 nm and some particles are inserted into the tubular structures (see Fig. 2(c)). For further deposition, the Cu2O layer clearly covers nearly the entire nanotubular surface (see Fig. 2(d)). Figure 2(e) presents the FE-SEM image of typical Cu2O-loaded STNA fabricated by plain electrochemical deposition (PED) method for 5 min. Compared with the samples prepared with SED for 5 min (see Fig. 2(c)), the Cu2O deposits with different size are unevenly distributed throughout the nanotube surface when applying the PED method. This indicates that the SED technique is helpful in obtaining a more uniform distribution of Cu2O particles on the STNA surface. The success of the preparation of Cu2O-loaded STNA is further confirmed by the elemental dispersive X-ray (EDX) spectrum. The characteristic peaks in the spectrum are associated with Ti, O, and Cu, and the atomic ratio of Cu element is ~5.21% for the Cu2O/STNA sample with Cu2O SED for 5 min (see Fig. 2(f)).
Figure 3(a) compares the X-ray diffraction (XRD) patterns of a typical as-annealed STNA sample taken before and after Cu$_2$O SED process at -0.25 V for 5 min. As can be seen that the STNA sample without Cu$_2$O deposition exhibits strong characteristic peaks of titanium substrate and weak characteristic peak of anatase TiO$_2$ (this can be attributed to the short tube length of the nanotube layer, ~280 nm). While the Cu$_2$O-loaded sample shows clearly the crystalline phase of Cu$_2$O. Furthermore, the characteristic peaks of Cu and CuO are not found, which also testifies to the superiority of this method with regard to electrode purity. The UV-Vis absorption spectra of plain TiO$_2$ nanotubes and sonoelectrochemically prepared Cu$_2$O/STNA electrode (deposition time of Cu$_2$O is 5 min) are given in Fig. 3(b). It is evident that the pure STNA electrode has no obvious absorption of visible light. However, the spectrum of Cu$_2$O/STNA shows evident absorption in both the UV and visible region, indicating the Cu$_2$O deposits can be used to sensitize the TiO$_2$ nanotubes for longer wavelength region of sunlight and the enhanced ability of the Cu$_2$O/STNA electrode to absorb visible light makes it a promising photocatalyst for solar-driven applications.

Figure 4(a) gives the general scan spectrum of the X-ray photoelectron spectroscopy (XPS) over a large energy range at low resolution of a Cu$_2$O/STNA electrode where the SED time of Cu$_2$O is 5 min, showing the presence of Ti, O, Cu and C. Figure 4(b) shows the Cu 2p core level XPS scans, at higher resolution over smaller energy windows. As can be seen, the Cu 2p core level XPS spectrum has two sharp peaks at 932.3 eV (Cu 2p$_{3/2}$) and 952.2 eV (Cu 2p$_{1/2}$), which is in good agreement with the reported values for Cu$_2$O [14, 27].
The photocurrent density generated by the Cu$_2$O/STNA electrodes and pure STNA electrode in 0.1 M Na$_2$SO$_4$ solution as a function of applied potential under white light illumination are shown in Fig. 5(a). Compared to the plain STNA electrode, the Cu$_2$O-modified STNA electrodes reveal evidently enhanced visible light response. At an applied potential of 1.0 V, the photocurrent density of the composite electrode (i.e. SED time of Cu$_2$O is 5 min) is more than 4.75 times as high as the value of pure STNA electrode. The enhanced photocurrent response of the composite electrode means the electron/hole pair induced by simulated solar light might split and transport more readily within the electrode material. This can be ascribed to the beneficial role of the Cu$_2$O particles on the STNA electrode surface in improving the band structure as well as the charge separation and transfer performance. Moreover, it is not surprising that with the deposition time of Cu$_2$O increased from 1 to 10 min, the atomic ratio of Cu to Ti also increased from 0.015 to 0.27 accordingly (see Fig. S2 in Supplementary Information). However, the photocurrent density of Cu$_2$O/STNA increases as the Cu$_2$O deposition time increases from 1 to 5 min and decreases with a further increase in the deposition time (10 min). This might be due to a very high Cu$_2$O loading, which reduces the reactivity contributed by the TiO$_2$ nanotubes and Cu$_2$O particles inside the tubular structure, ultimately decreasing the overall photoactivity of the nanocomposite electrode material.

In order to examine the effect of ultrasonic waves, Figure 5(b) depicts the variation of photocurrent response in 0.1 M Na$_2$SO$_4$ for Cu$_2$O/STNA electrodes prepared using SED and PED, respectively. The composite electrode obtained by SED obviously shows an obvious enhanced photocurrent density compare to that fabricated by PED. At an applied potential of 1.0 V (vs. Ag/AgCl), the photocurrent density of the former electrode is ~2.2 times as high as that of the latter. The reasons responsible for the enhancement remain unclear at present. This is a subject of current research in our laboratory. We believe that many factors including the Cu$_2$O deposition method as well as the density and the size of loaded Cu$_2$O particles influence the photoelectrochemical performance of the composite electrode material. Further information about the contribution of the UV and visible components of the solar spectrum was calculated by...
doing one experiment under AM 1.5 conditions and one more using an optical filter. The current density obtained under the former condition was attributed to the contribution of both UV and visible part of the solar spectrum, while the current density obtained under the latter condition was only from the contribution of visible light. As can be seen from Fig. 6, ~72.20% of the photoactivity of Cu$_2$O/STNA is contributed by the visible components, whereas for the pure STNA electrode, majority of their reactivity in the UV region contributes to the rest of the photoactivity (98.94%).

![Figure 6. Contribution of UV and visible component of the solar spectrum to the overall reactivity of the Cu$_2$O/STNA electrode and pure STNA electrode.](http://www.nmletters.org)

The stability of the composite electrode was examined by potentiostatic (current vs. time, I-t) measurements. Figure 7 shows the I-t curves obtained from the Cu$_2$O/STNA electrode at two different bias potentials under visible-light illumination. Upon switching off the light, the photocurrent density goes down to zero; whereas the photocurrent increases rapidly to the original value when under illumination again. This indicates that the current observed for this system is mainly due to the photo-reactivity of the catalyst and the charge transfer within the composite electrode is very fast. Moreover, composite electrode exhibits excellent reproducibility of the I-t curves.

**Conclusions**

In conclusion, surface modification of STNA using facile sonochemical technique can successfully fabricate an efficient Cu$_2$O/STNA photoelectrode for photoelectrochemical applications. This electrode material has coupled the advantages of the chemical stability and excellent charge separation and transfer properties of STNA electrode, the photon absorbance spectrum of Cu$_2$O as well as the sonication technology to form n-TiO$_2$/P-Cu$_2$O heterostructure composite electrode. Experimental results have demonstrated that the presence of Cu$_2$O significantly extends the response of TiO$_2$ nanotubes into the visible region. Moreover, the enhanced photoelectrochemical properties and mechanical stability of the composite electrode material make it a highly efficient photoanode material for various potential applications.

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![Figure 7. Photocurrent response of a Cu$_2$O/STNA composite electrode biased at 0.5 V (vs. Ag/AgCl) and 0.8 V (vs. Ag/AgCl) under visible-light illumination.](http://www.nmletters.org)
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