

# Cu<sub>2</sub>O/TiO<sub>2</sub> nanotube arrays film with controlled morphology for photoelectrochemical water splitting

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## ABSTRACT

As a promising eco-friendly sensitizer, Cu<sub>2</sub>O particles can be deposited on TiO<sub>2</sub> nanotube arrays (TNTs) in a three-electrode system via electrochemical deposition. The morphology of Cu<sub>2</sub>O is mainly related to the deposition potential, and the size of Cu<sub>2</sub>O nanoparticles can significantly decreased by adding polyvinylpyrrolidone (PVP). The experimental and simulation results indicate that Cu<sub>2</sub>O/TNTs heterojunction has smaller band gap than TNTs, resulting in visible light absorption. The Cu<sub>2</sub>O/TNTs obtained with PVP at -0.3V for 5 min shows better photoelectrochemical properties. Although Cu<sub>2</sub>O can partly be oxidized to CuO in photoelectrochemical measurement, the photocurrent of as-prepared sample remains stable.

## I. INTRODUCTION

Hydrogen can be produced by photoelectrochemical (PEC) water splitting using solar energy [1]. In PEC system, the highly ordered TiO<sub>2</sub> nanotube arrays (TNTs) photoanode has attracted much attention for its large surface areas, excellent controllability and superior electron transport rate. However, the energy conversion efficiency needs to be increased by enhancing the light adsorption as well as the charge separation. The band gap of Cu<sub>2</sub>O is 2.0 eV, which is a promising sensitizer of TiO<sub>2</sub> for the conversion of solar energy [2]. Electrochemical deposition is a commonly used method for preparing Cu<sub>2</sub>O/TiO<sub>2</sub> heterojunction. The current issues are how to control the morphology of Cu<sub>2</sub>O and how to obtain Cu<sub>2</sub>O/TNTs with better properties and stability.

In the present work, Cu<sub>2</sub>O nanoparticles with controlled morphology were deposited on TNTs by adding surfactant polyvinylpyrrolidone (PVP) and changing deposition potential and time. The band alignments were calculated by DFT. And the photoresponse properties, photoelectrochemical performances and stability of the as-prepared Cu<sub>2</sub>O/TNTs were analyzed and discussed.

## II. EXPERIMENTAL AND SIMULATION

**Preparation of Cu<sub>2</sub>O/TNTs.** TNTs were prepared by anodic oxidation method [3]. Cu<sub>2</sub>O/TiO<sub>2</sub> nanotube arrays were prepared in a three-electrode system. TNTs was used as working electrode. Ag/AgCl electrode and Pt mesh were acted as reference electrode and counter electrode, respectively. Electrolytes were 0.4 M CuSO<sub>4</sub>·5H<sub>2</sub>O in 3 M lactic acid solution with or without 0.5 g PVP K30. The pH of electrolyte was further adjusted to 11 with 5 M NaOH solution. The obtained samples were dried at 50 °C for 24 h in vacuum.

**Characterization.** The surface morphology of TNTs and Cu<sub>2</sub>O/TNTs was characterized with a field-emission scanning electron microscope (FESEM; Hitachi, Japan, S4300). The optical absorption spectra was obtained using an UV-Vis spectrophotometer (UV-Vis DRS; Shimadzu, Japan, UV-2450 with IRS-2200) with compressed BaSO<sub>4</sub> powder as standard. The crystal structures of the samples were determined by X-ray diffraction (XRD; D8 Advance Bruker/AXS).

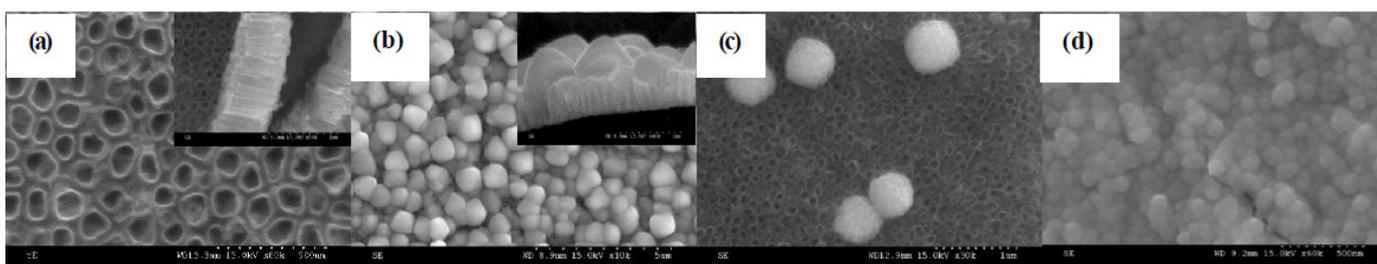
**Photoelectrochemical Activity Measurements.** The PEC experiments were carried out in the three-electrode system with a platinum gauze (30 mm×20 mm) as counter electrode, a saturated Ag/AgCl electrode as reference

electrode and the prepared sample as working electrode in 1 M KOH. A solar simulator (91160, Newport, USA) was used as light source. An AM 1.5 filter was used to obtain one sun light intensity. All the photoelectrical properties were recorded by a CHI electrochemical analyzer (CHI 614C, CH Instruments).

**Theoretical Calculations.** The static calculations have been carried out by using the DFT package of Cambridge Serial Total Energy Package (CASTEP) codes. The supercell dimensions of anatase  $\text{TiO}_2$  is  $a = 10.886 \text{ \AA}$ ,  $b = 7.552 \text{ \AA}$  and  $c = 8.623 \text{ \AA}$ . And the interfacial model including  $\text{TiO}_2$  (101) surface and  $\text{Cu}_2\text{O}$  molecule is separated by a 10  $\text{\AA}$  thick vacuum layer. The Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient approximation (GGA) was used as the exchange-correlation function. And all calculations were carried out in reciprocal space.

### III. RESULTS AND DISCUSSION

**The morphology of  $\text{Cu}_2\text{O}/\text{TNTs}$ .** From the Fig.1a of SEM images, the highly ordered  $\text{TiO}_2$  nanotube arrays grown on the titanium substrate have average inner diameter ca. 80 nm and length ca. 780 nm. With the electrochemical deposition at -0.8 V for 15 min, a quantity of  $\text{Cu}_2\text{O}$  nanoparticles was deposited on the top of TNTs, which is octahedron with side length ca. 750 nm (Fig.1b). When the potential is decreased to -0.4V, the nanoparticles turned to be spherical with diameter ca. 600 nm (Fig.1c). In order to further reduce the size of  $\text{Cu}_2\text{O}$ , PVP was added into the electrolyte. The loaded  $\text{Cu}_2\text{O}$  particles with diameter ca. 100 nm are shown in Fig.1d. Therefore, adding PVP into the deposition electrolyte can greatly decrease the size of  $\text{Cu}_2\text{O}$  particle. In the presence of PVP, when depositing for 5 min,  $\text{Cu}_2\text{O}$  nanoparticles with diameter of ca. 100 nm, 35 nm and 30 nm can be prepared at the deposition potential of -0.2 V, -0.3 V, -0.4 V, respectively. It can be concluded that the size of  $\text{Cu}_2\text{O}$  particles decreases with deposition potential increasing. During the electrodeposition with the applied voltage, an electric field between the TNTs and the Pt electrode is formed.  $\text{Cu}^{2+}$  in solution are gathered on the surface of the working electrode and few reduced to  $\text{Cu}^+$ . Then,  $\text{Cu}^+$  further reacted with  $\text{H}_2\text{O}$  molecule and deposited onto the substrate surface. In the process, all the deposition current decreased with time. Moreover, the higher applied potential, the greater deposition current. Therefore, the type of  $\text{Cu}_2\text{O}$  nanoparticles are associated with deposition current, and its formation is controlled by the dynamic process. According to XRD measurements, the characteristic diffraction peak of (111) of  $\text{Cu}_2\text{O}$  is relatively strong, which indicates that  $\text{Cu}_2\text{O}$  can be used as a stable photocatalyst [4].

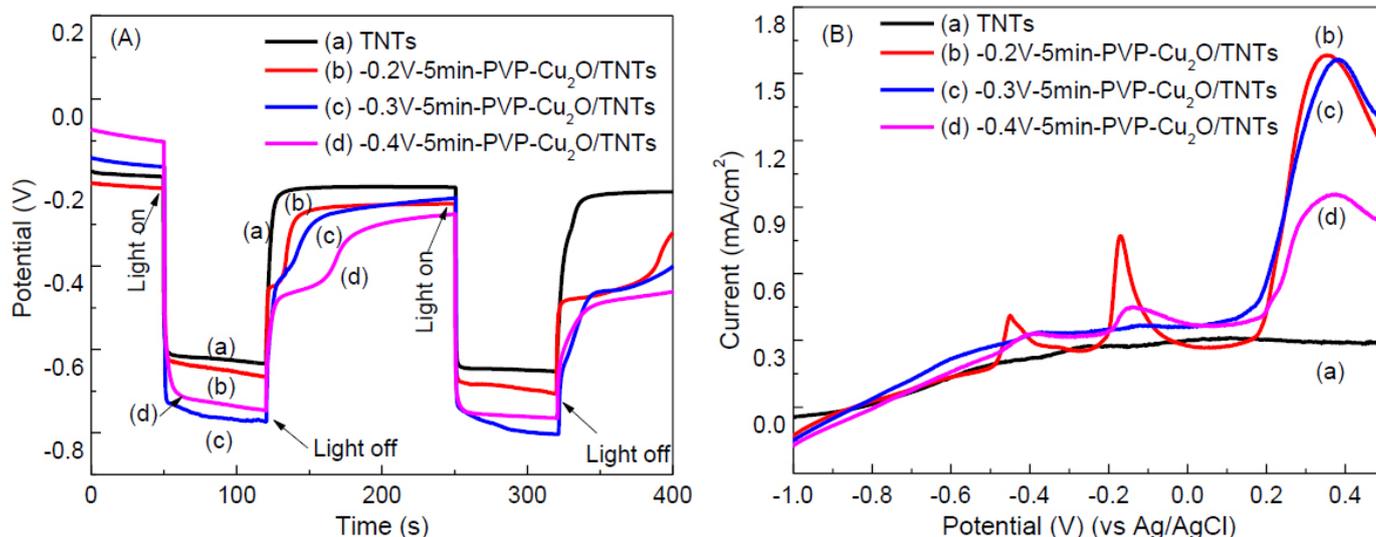


**Figure 1** FESEM images of (a) TNTs, (b) -0.8V-15min without PVP, (c) -0.4V-15min without PVP and (d) -0.4V-15min with PVP.

**Light Absorption Properties.** From the UV-vis DRS, it is found that the as-prepared  $\text{Cu}_2\text{O}/\text{TNTs}$  has the enhanced adsorption in visible light region. Based on the function relationship of  $(\alpha h\nu)^{1/2}$  and  $E_g$ , the band gap of the samples deposited at -0.2 V, -0.3 V and -0.4 V is 2.12 eV, 2.25 eV and 2.46 eV, respectively, which are in good agreement with the experimental results. Moreover, the density of states (DOS) reveal that the electronic structure of  $\text{Cu}_2\text{O}/\text{TiO}_2$  shows the characteristic of conductor, which is different from that of pure  $\text{TiO}_2$ .

**Photoelectrochemical Properties.** Among of samples, -0.3 V-5min-PVP- $\text{Cu}_2\text{O}/\text{TNTs}$  exhibits the relatively better photocurrent. Besides the enhanced light-harvesting property, its morphology of  $\text{Cu}_2\text{O}$  on the surface of TNTs is the key factor. Although the diameter of  $\text{Cu}_2\text{O}$  nanoparticles prepared at -0.4 V have similar to that prepared at -0.3V, but the former densely distributed in the inner and external surface of TNTs, which has a negative influence on the charge transfer and light absorption of TNTs. In the case of the sample obtained at -0.2 V, it shows poor performance due to its large size.

Fig.2A shows the open-circuit potential transient curves ( $U-t$ ) of TNTs and  $\text{Cu}_2\text{O}/\text{TNTs}$ . When the light off, the potential of  $\text{Cu}_2\text{O}/\text{TNTs}$  can't return the initial value, which is related to the stability of  $\text{Cu}_2\text{O}$ . In order to study the stability of  $\text{Cu}_2\text{O}$  thin film, the linear sweep voltammetry (LSV) measurement of  $\text{Cu}_2\text{O}/\text{TNTs}$  was conducted. The anodic peaks in 0.3 ~ 0.4 V (Fig.2B) illustrate that  $\text{Cu}_2\text{O}$  nanoparticles are partly oxidized to  $\text{CuO}$  in the photoelectrochemical measurement [5]. However, the photocurrent of as-prepared samples remains stable in the testing progress.



**Figure 2** Open-circuit potential transient curves ( $U-t$ ) (A) and LSV plots (B) of TNTs and  $\text{Cu}_2\text{O}/\text{TNTs}$  with different deposition potential.

#### IV. SUMMARY

In this paper,  $\text{Cu}_2\text{O}$  nanoparticles were successfully deposited on TNTs by electrochemical deposition method. With the deposition at  $-0.8\text{ V}$  and  $-0.4\text{ V}$  for 15 min, octahedron and spherical  $\text{Cu}_2\text{O}$  nanoparticles were obtained, respectively. The size of  $\text{Cu}_2\text{O}$  can be decreased by adding PVP and increasing potential. The experimental and simulation results indicate that,  $\text{Cu}_2\text{O}/\text{TNTs}$  heterojunctions have narrowed band gap and increased visible light absorption. Among the samples,  $-0.3\text{V-5min-PVP-Cu}_2\text{O}/\text{TNTs}$  exhibits better photoelectrochemical properties. Based on the LSV measurement, it is speculated that few  $\text{Cu}_2\text{O}$  nanoparticles are oxidized to  $\text{CuO}$ , but the photoelectrical system maintains a certain photocurrent.

#### V. REFERENCES

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