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Photoelectrochemical Response and Semiconductor Characters of $Cu/Cu_2O/CuO/TiO_2$ Nanotube Arrays Photocatalyst

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Abstract. The cocatalysts of various copper morphology modified TiO_2 nanotube arrays (TNTs) were prepared by electrochemical deposition. The morphologies of the samples were investigated by SEM. The reductive and oxidative copper modification strongly reinforce TNTs photocurrent response in UV and visible light region, especially the later one shows higher catalytical activity in visible light from 610nm to 740nm. The reductive copper morphology consists of Cu and Cu_2O, and oxidative one comprises Cu, Cu_2O and CuO by photocurrent analysis. The flat band potentials calculated by Mott-Schottky curves move positive potential direction with the oxidation depth.

1. Introduction

One-dimensional TiO_2 nanotube arrays (TNTs) due to their high aspect ratio and large surface to volume ratio, have displayed excellent charge-transfer and photochemical property in photocatalytical process [1-6]. However, only wavelength below 387 nm, about 5% of solar spectrum energy can be directly utilized due to its large band gap of 3.2 eV. TNTs modification by doping metals such as Au, Pt, Pd, Ag[7-11] or metal oxides such as ZnO, RuO_2, WO_3, CeO_2 [12-15] has been a hot topic of research to improve the solar spectrum absorption efficiency while maintaining its excellent charge-transfer property. The metal ion or metal oxides enhances the photo-catalytic activity by reducing electron–hole pair recombination and/or reducing the band gap.

Cu as a metal of relative abundance and low cost has attracted much attention due to enhancement of the photocatalytic activity [16-23]. It can prevent the recombination of photoexcited electrons and holes as co-catalysts and generate localized surface plasmon resonance(LSPR) effect which promotes the separation of electron-holes [17]. Momeni prepared highly ordered copper doped TiO_2 nanotube arrays thin-film by in situ electrochemical method and the samples exhibited better photo-catalytic activity than the TNTs[19]. The energy band gaps (E_g) of its oxides Cu_2O and CuO are narrower than TiO_2, respectively 2.2 eV and 1.7eV, which can promote visible light absorption [20].Chen et al. have developed a novel core-shell heterostructured Cu/Cu_2O nanowires as efficient visible light photocatalysts [21,22]. Multifunctional CuO nanowire/TiO_2 nanotube arrays photoelectrode has been fabricated applying for photocatalysis [23]. However, very few studies on the photoelectrochemical performance of TNTs co-modification by elemental Cu and its oxides(CuO and Cu_2O) have been reported.

In this work, we prepared $Cu/Cu_2O/CuO/TNTs$ catalysts by electrochemical method successfully, and tested their photo electrochemical response in UV and visible light and semiconductor characters. Moreover, the mechanism of TNTs modification by $Cu/Cu_2O/CuO$ has been analyzed.

2. Experiments

2.1 Preparation of TNTs.

Preparation of TNTs was referred our previous work[15]. The titanium sheets((0.2mm thick, 99.6% purity) were mechanically polished with different abrasive papers and ultrasonically degreased in acetone and ethanol, respectively, finally rinsed with deionized water and dried in air.

All the anodization experiments were carried out in a conventional two-electrode electrochemical cell under magnetic agitation condition at room temperature, with titanium foil as the anode and platinum foil as the cathode. The ethylene glycol solution containing 0.5 wt. % NH_4F and 1.5vol % H_2O was used as electrolyte. The anodization voltage was constant at 20 V with a direct current power supply. The anodization process was performed for 6h to obtain TNTs. After electrochemical anodization, the as-anodized TNTs were immediately rinsed with deionized water and then dried at 100°C. All samples were annealed at 450°C for 1.5 h to transform amorphous TiO_2 to crystalline phase.

2.2 Copper and Oxides Electrochemical Deposition.

The as-prepared TNTs with exposed area 0.2826 cm^2 were inserted in 0.01 M $CuCl_2 \cdot 2H_2O$ alcohol electrolyte for 1 h adsorption. Then, the above TNTs were used as working electrode, a Pt foil as the anode, and a saturated calomel electrode (SCE) as the reference electrode in the electrolyte. A potential E = -6 V was applied in the three electrodes system until a total electricity Q = 0.01 C to reduce Cu^{2+} into elemental Cu deposition on TNTs. This modified sample was named as TNTs-Cu-0.01C. Secondly, the TNTs-Cu sample were oxidized by potentiostat powered by a suitable anodic potential to the sample in supporting electrolyte (0.01 M $CuCl_2$) for total electricity Q = 0.0001C respectively. The oxidized sample was denoted as TiO_2NTs-CuO_x- 0.0001C.

2.3 Photo electrochemical Measurements.

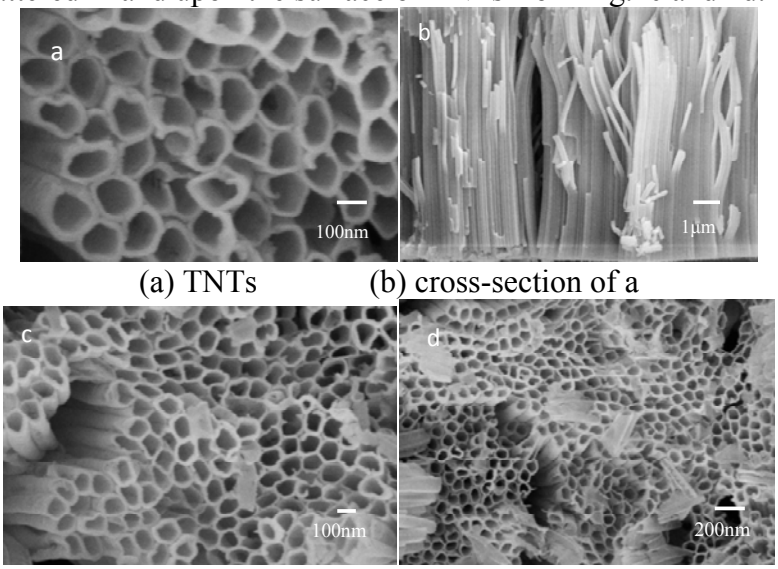
The cyclic voltmmetry curves of TiO_2NTs-Cu-0.01C was performed in 0.1 M Na_2SO_4 solution. The scan potential is from -1V to 1V at a scan rate of 20 mV s^{-1}.

The surface morphology of the prepared samples was characterized with field emission scanning electron microscope (FE-SEM, JSM-7500 F). The photocurrent response were measured in an improved three electrode electrochemical cell with a quartz window and 0.1M Na_2SO_4 as supporting electrolyte. A 450W Xeon lamp, a CT110 monochromator (1/8, Crowntech), and a potentiostat (PARSTAT2273, Princeton Applied Research, Oak Ridge, TN, USA) were also applied for electrochemistry measurements. The Mott-Schottky plots were performed with frequency 1000Hz and applied potential from -1V to 1V.

3. Results and Discussion

3.1 Characterization of Samples

Fig.1 shows the SEM images of the TNTs, TNTs-Cu-0.01C, TNTs-CuO_x-0.0001C. Fig.1a and 1b indicates an average pore size of 60nm and 10μm length. The deposit materials of reductive Cu or oxidative Cu are scattered in and upon the surface of TNTs from Fig.1c and 1d.



(a) TNTs (b) cross-section of a

(c) TiO2NTs-Cu-0.01C (d) TiO2NTs-CuOx-0.0001C

Fig.1 FE-SEM images of the electrodes

3.2 Cyclic voltammetry Curves.

Fig.2 shows that cyclic voltmmetry (CV) curves of TiO_2NTs-Cu-0.01C with good reproducibility for 5 cyclic scans. Two anodic peaks with peak1 and peak2 appear at the potential E=-0.4V and E=0.2V for positive potential sweep, which respectively represent that Cu is oxidized to Cu^+ and Cu^{2+} oxidation peaks. In the reverse scan process, peak3 and peak4 are the Cu^{2+} and Cu^+ reduction peaks.

According to the CV results, the anodic potential E=0.6V was applied to TiO_2NTs-Cu-0.01C oxidation.

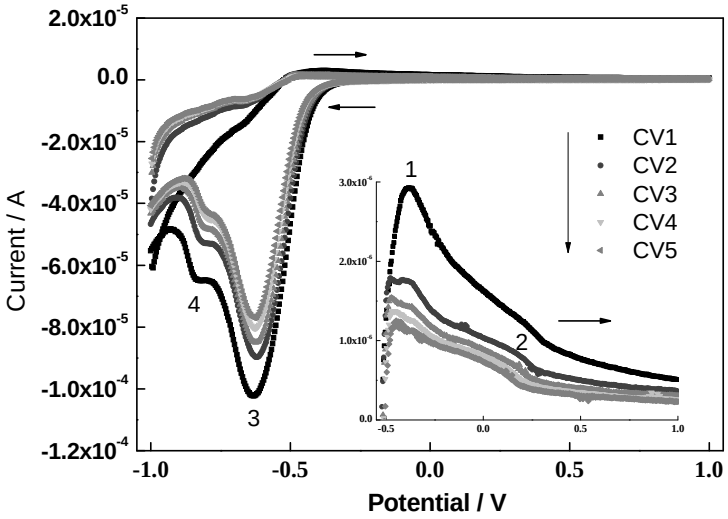


Fig.2 Cyclic voltmmetry curves of TiO2NTs-Cu-0.01C

3.3 Photocurrent Analysis.

The photocurrent spectrums vs. wavelength are showed in Fig.3.The TNTs-Cu-0.01C indicates stronger photocurrent response in visible and UV light region compared to the TNTs. After anode oxidation, oxidative Cu modification strongly reinforces TNTs photocurrent response in visible light region, especially from 610nm to 740nm.

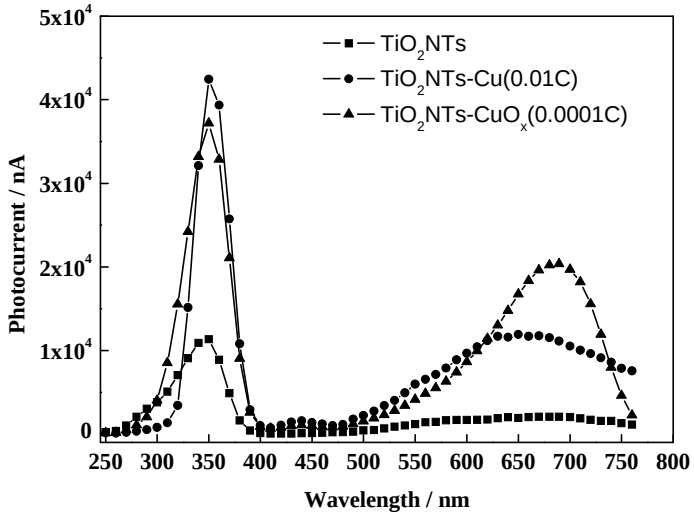


Fig.3 Photocurrent responses plots of TiO_2 nanotubes modified by Cu and its oxide

The relationship between photocurrent I_{ph} and bandgap energy E_g of the amorphous oxide films on alloys can be written in the form[24]:

$$(I_{ph}h\nu / I_0)^{1/n} = A\,(h\nu - E_g) \quad (1)$$

where I_0, $h\nu$, E_g, A and n are fully discussed in [24], and n=2 for the indirect transition of amorphous semiconductors. Fig.4 shows the photocurrent response vs. photon energy plots for TNTs with various Cu deposit from figure 3 transformation. Based on linear fitting, the characteristic E_g of various samples can be derived respectively listed in Table2. TiO_2NTs, TiO_2NTs-Cu-0.01C and TiO_2NTs-CuO_x-0.0001C all obtain the similar E_g1 about 3.1-3.2 eV, which are in accord with Eg of

anatase TiO_2(3.2 eV).The values of E_g2=2.1 eV and 2.14 eV in accord with Eg of Cu_2O (2.2eV) is acquired by TiO_2NTs-Cu-0.01C and TiO_2NTs-CuO_x-0.0001C, and the value of E_g3=1.6 eV in accord with E_g of CuO(1.7 eV) is detected by TiO_2NTs-CuO_x-0.0001C. Simultaneously the electrons on valence band can also transit to the condition band by the elemental Cu as the intermediate level [25]. This promotes the electron-hole pairs separation and enhances the use of visible light.

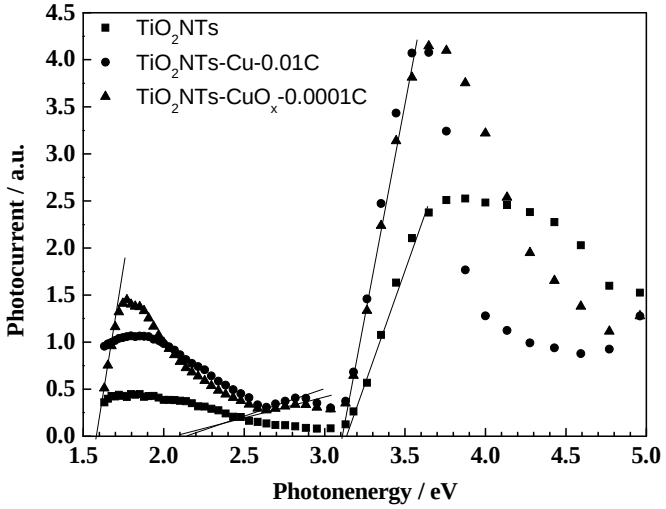


Fig.4 (iphhv/I0)1/2 vs. photon energy of TiO2 nanotubes modified by Cu and its oxide

Through the above results can be known that reductive copper exists in form of Cu_2O and Cu and oxidative copper exists in form of Cu_2O, CuO and Cu. The Eg of Cu_2O or CuO is narrower than that of TiO_2. So they are more benefit to absorb visible light and enhance the photocurrent efficiency of TiO_2NTs.

Table 1. Semiconductor characteristic parameters for TiO_2 nanotube arrays modified by Cu and its oxide (E_g is the energy band gap, E_{fb} is the flat band potential)

	TiO_2NTs	TiO_2NTs-Cu-0.01C	TiO_2NTs-CuO_x-0.0001C
E_{g1}, eV	3.18	3.10	3.10
E_{g2}, eV		2.1	2.14
E_{g3}, eV			1.60
E_{fb}, V	-0.23	-0.09	0.11

3.4 Mott-Schottky Curves.

Fig.5 shows the Mott-Schottky plots for all the samples with flat band potentials (E_{fb}). The intercept of the straight line of Mott-Schottky plot at the potential axis corresponds to E_{fb} list in Table 1. The slopes of three straight lines are positive which illustrates the catalysts before and after modification are n type semiconductor. The E_{fb} of TiO_2NTs-Cu-0.01C(E_{fb}=-0.09V) or TiO_2NTs-CuO_x-0.0001C (E_{fb}=0.11V) moves to positive potential direction compared to TNTs (E_{fb}=-0.23V), which infers the reducibility of electrons transition to conduction band of samples decrease [26].The E_{fb} moves to positive potential direction with the oxidation depth.

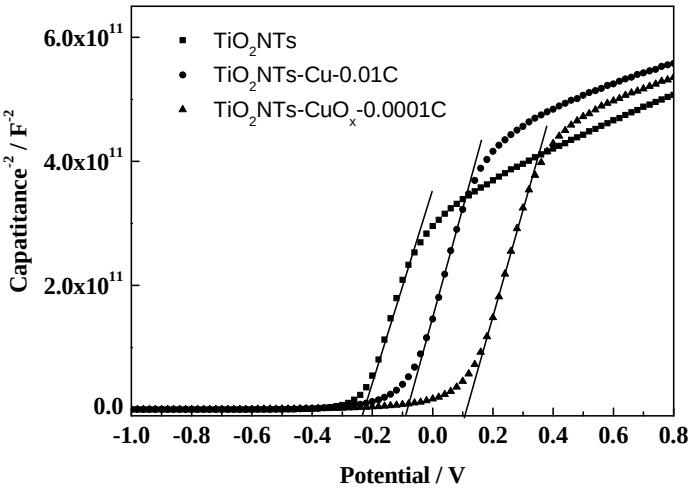


Fig.5 Mott-Schottky curves of TiO2 nanotubearrays modified by Cu and its oxide

4. Conclusion

The modification materials scatter in and upon the surface of TNTs. The reductive copper morphology consists of Cu and Cu_2O by photocurrent analysis, and strongly reinforces TNTs photocurrent response in UV and visible light region. The oxidative one comprises Cu, Cu_2O and CuO by photocurrent analysis, while also promote TNTs photocurrent response in UV and visible light region and especially shows higher catalytical activity in visible from 610nm to 740nm. The flat band potentials become more positive than TNTs after modification.

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