Photoelectrochemical Property, Photocatalytic Degradation and Photocatalysts for Hydrogen Production of CUO and WO_3 Loaded TiO_2 Nanotube

X. S. Yang and H. Kim

Abstract—**Titanium dioxide has been considered one of the most promising photocatalytic materials due to its relatively low cost, chemical stability, and photo stability. In this work, CUO and WO_3 were loaded on anodic TiO_2 annotate and the photo electrochemical, photocatalytic and photo catalysts for hydrogen production activity were investigated. TiO_2 annotate was prepared by iodization method. CUO and WO_3 were loaded by wet impregnation method. The annealed samples were soaked in a mixture solution containing tungsten acid and Cu $(NO_3)_2$ and then post-annealed to fabricate Cu-loaded TiO_2 annotate. The obtained samples were characterized by SEM, EDX, XRD and the photo electrochemical property, photocatalytic degradation of MB and photo catalysts for hydrogen production under UV illumination was measured and compared. The photocurrent (potential=1 V) of Cu-WO_3 loaded annotate is 1.41 times higher than that of unloaded annotate and is 1.15 times higher than that of pure WO_3 loaded annotate. The hydrogen generation rate of Cu-WO_3 loaded annotate is 1.42 times higher than that of unloaded annotate. After UV irradiation for 2 h, the degradation efficiency of MB for Cu-WO_3 loaded annotate is 1.12 times higher than that of pure WO_3 loaded sample.**

Index Terms—**Titanium oxide annotate, Hydrogen generation, Photo electrochemical property.**

I. INTRODUCTION

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2 Titanium dioxide occurs in nature as well-known minerals: rutile, anatase and brookite. TiO_2 is a wide band-gap semiconductor ($E_g \approx 3.2$eV), which has attracted significant attention of researchers because of many interesting chemical and physical properties that make it suitable for a variety of applications, such as photocatalytic degradation of pollutants, dye sensitized solar cells, gas sensors and hydrogen generation by water photoelectrolysis [1]. In order to be effective, the Titania needs to be able to both act on a lot of water molecules and be exposed to a large amount of sunlight. Many approaches such as tinplating synthesis, hydrothermal reactions, and anodic oxidization have been developed to prepare TiO_2 annotates. The anodic oxidization is the relatively simple technique that can easily fabricate uniformly highly ordered and vertically oriented self-organized nanotubes [2].

Highly ordered, vertically oriented TiO_2 nanotube arrays fabricated by potentiostatic anodization of titanium constitute a material architecture that offers a large internal surface area without a concomitant decrease in geometric and structural order [2-3]. In the past few years, a lot of work has been down to study the improved photoelectrochemical and photocatalytic activity using modified, doped or decorated of TiO_2 Nanotubes by Ni, Fe, Nb, Zn, Mg, WO_3 [5-7]. The direct photosplitting of water to hydrogen and oxygen has been regarded as the most promising approach ever since Fujishima and Honda reported the photoelectrochemical water splitting at a TiO_2 electrode [8].

Tungsten trioxide has been considered as mixture material with TiO_2 for water splitting because the WO_3 can offer relatively small band gap [9]. Copper oxide as a semiconductor has potential application for its catalytic and photo activity properties.

Park *et al.* founded that tungsten trioxide coatings significantly enhanced the visible spectrum absorption of the titanium dioxide annotate array and hydrogen gas generated efficiency was about 0.87% [7]. Cu particles had been deposited on TiO_2 by incipient-wetness impregnation followed by low-temperature calcinations/reduction, and the metallization process leads to significant enhancement in photocatalytic activity of TiO_2 for H_2 production from aqueous methanol solution [9]. Embedded CuO_x@TiO_2 was prepared by a water-in-oil micro emulsion method, showed higher hydrogen production rates H_2 Production from ethanol and glycerol solutions [10]. TiO_2 photo catalyst with deposited CUO was synthesized by the impregnation method using P25 as support, and exhibited high photocatalytic hydrogen generation activity from methanol/water solution. [11]. Xu *et al.* fabricated efficient Cu incorporated TiO_2 (Cu-TiO_2) photo catalysts for hydrogen generation using four methods: in situ sol-gel, wet impregnation, chemical reduction of Cu salt, and in situ photo-deposition. It was found that all prepared samples had excellent light absorption ability [12].

In this work, CUO and WO_3 were loaded on anodic TiO_2

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annotate using wet-impregnation method and the photo electrochemical property, photocatalytic degradation of MB and photo catalysts for hydrogen production were investigated.

II. EXPERIMENTAL

A. *Sample Preparation*

The TiO_2 annotates were prepared by iodization method, shown in Fig. 1. The titanium foil (0.25 mm thick, 99.7%, Aldrich) was chemically etched by immersing in a mixture of HF and HNO_3 acids (ratio of $HF/HNO_3/H_2O$ 1:1:2 in volume) for 30 s. After rinsed in DI water, the foil was pretreated by rinsing in an ultrasonic bath of methanol, 2-propanol and acetone for 10 min in turn, and then dried. The iodization was carried out using a two-electrode cell with Pt foil (0.1 mm thick, 99.9%, Aldrich) as the cathode, separated from Ti anode with a distance of 1 cm. The electrolyte was glycerol (99%, Showa) and H_2O (1:1 in volume) containing NH_4F (0.5 wt. %). The iodization was done at a constant potential of 15 V (with a voltage ramp of 0.1 V/s) for 3 h at room temperature.

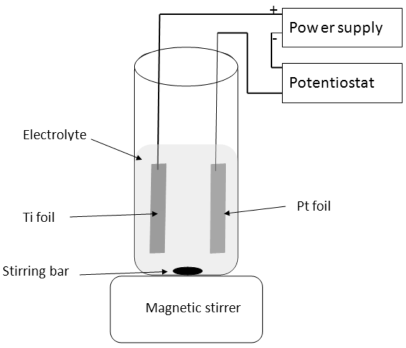


Fig. 1. Fabricate anodic titania nanotube.

The as-anodized samples were rinsed with DI water and dried in air. After annealed at 450 ^{c}o for 2h, the samples were soaked in a mixture solution containing tungsten acid (0.05 mol/L) and $Cu(NO_3)_2$ (Cu/W=10% in atom) for 5 min, dried, and was then post-annealed at 450 °C for 2 h to fabricate the CuO and WO_3 co-loaded TiO_2 annotates. The detailed procedure is shown in Fig. 2.

B. *Micro structural Characterization*

The morphology of the samples was examined using a scanning electron microscope (SEM, Hitachi S-3500N). The crystal phases were studied by X-ray diffraction using the diffract meter (XRD, Expert Analytical).

C. *Performance of Photo electrochemical Property*

The photo electrochemical properties of the annotate arrays were investigated by an electrochemical workstation (Zanier IM6ex) using a three-electrode configuration with the annotate arrays as working electrode, saturated Ag/Agile as reference electrode, Pt foil as counter electrode. The light source is a 300 W UV lamp.

D. *Performance of Hydrogen Generation*

The Photoelectrocatalytic hydrogen generation measurement was performed in a glass cell using a 300 W UV lamp as the light source. The electrolyte solution used was a mixture which contained 5% of methanol in water. Evolved gas was analyzed by gas chromatography and the volume of generated H_2 was measured by the water displacement method.

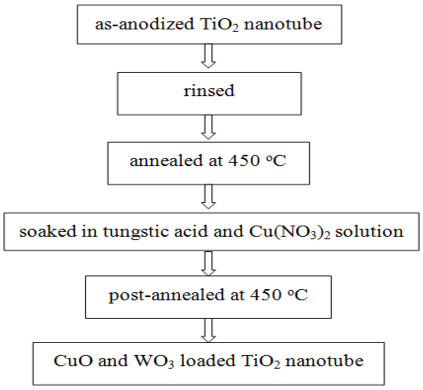


Fig.2. Procedure to prepare CuO and WO3 loaded TiO2 nanotube.

E. *Performance of Photocatalytic Degradation*

For photocatalytic property, samples were immersed in ethylene blue (MB) solution (5 ppm) in a batch reactor and illumination was applied through UV lamp. The evolution of the MB concentration was measured by UV-vis spectrometry (Cary 100, Varian) following its 660 nm characteristic band.

III. RESULTS AND DISCUSSION

A. *Microstructure*

The SEM images of the as-anodized annotate are shown in Fig. 3. The tube diameter is about 140 nm, the wall thickness is about 40 nm and the length is about 4 µm.

The growth of TiO_2 annotate is a result of competition between electrochemical oxide formation which can be represented as:

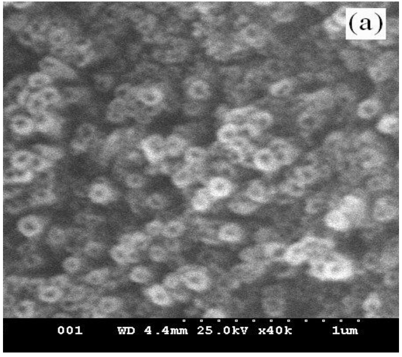
$$Ti + O_2 \rightarrow TiO_2 \qquad (1)$$

And chemical and field-assisted dissolution of oxide which can be represented as:

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \qquad (2)$$

$$Ti^{4+} + 6F^- \rightarrow TiF_6^{2-} \qquad (3)$$

In reaction (1), current decayed with time as the oxide barrier formed. In reaction 2 and 3, current increased due to thinning barrier layer and highly ion activity. To form uniformly highly ordered and vertically oriented self-organized annotate, an equilibrium process between oxide generation and dissolution is needed. In this process, current should keep almost the same value.



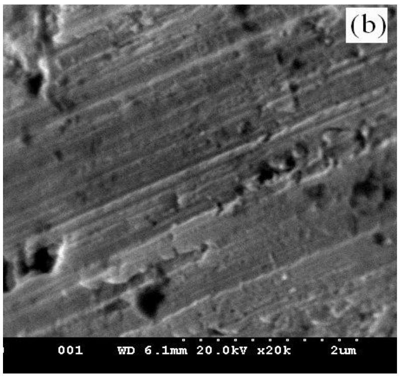


Fig. 3 SEM images of as-anodized TiO2 nanotube arrays; (a) top view, (b) the corresponding cross sectional view.

The morphology of the annotate keeps almost the same feature after annealing the samples at 450 ^{c}o, shown in Fig. 4(a). When soaked in tungsten acid and Cu $(NO_3)_2$ solutions and with post-annealed again at 450 ^{o}C, the samples still keep ordered nanotubular structure with no significant morphology change. Some nanoparticles with diameter of ~20 nm on the surface of the tubes, shown in Fig. 4(b), which were confirmed to be tungsten oxide by EDX analysis.

XRD investigation was carried out for the un-loaded and Coo, WO_3 co-loaded annotate before and after post-annealing. The as-anodized sample is amorphous. When annealed at 450 ^{c}o, anatine phase appears. After loaded and annealed again, additional diffraction peaks corresponding to tungsten trioxide appears, as shown in Fig. 5.

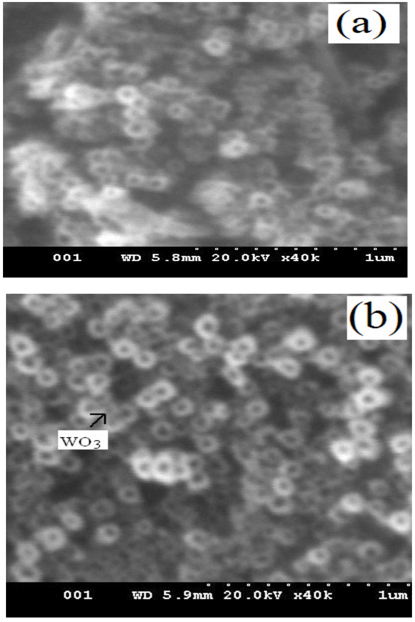


Fig.4. SEM images (top view) of TiO2 annotate arrays (a) annealed at 450 oC, (b) WO3-loaded sample.

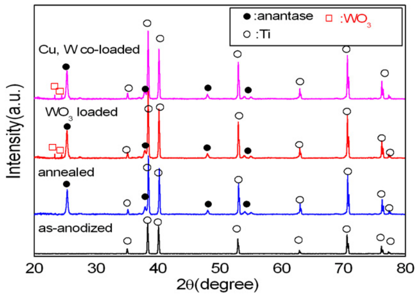


Fig.5. XRD of as-anodized, un-loaded, WO3-loaded and Cu-WO3 co-loaded TiO2 annotate.

B. Photo electrochemical Property

Fig. 6 shows the measured photocurrent density versus potential in 1 M KOH under UV illumination of un-modified TiO_2 annotate. The photocurrent is about 10 times higher than the dark current, which means that the photogene rated charge carrier are much greater that the background electrons. The photocurrent under UV illumination is 0.67 mA/cm^2 (potential=1 V).

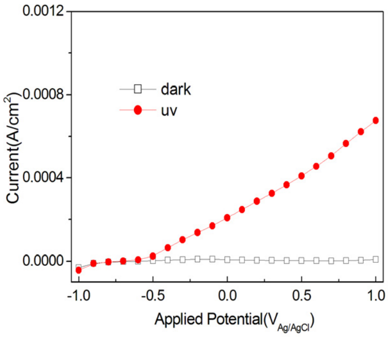


Fig. 6. Photocurrent versus potential for un-loaded TiO2 annotate under dark and UV illumination.

Fig. 7 shows the measured photocurrent density versus potential in 1 M KOH under UV illumination of un-loaded, different amount of WO_3 loaded TiO_2 annotate. WO_3-loaded sample show higher photocurrent compared with un-loaded sample and the photocurrent increases with the WO_3 concentration.

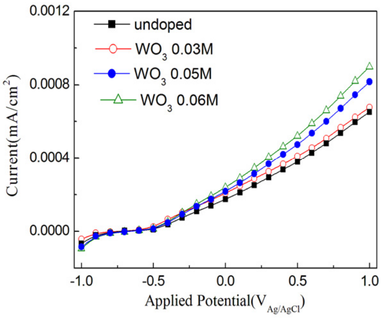


Fig.7. Photocurrent versus potential of undoes and WO3 doped annotate with different tungsten acid concentration in wet impregnation process.

Fig. 8 shows the measured photocurrent density versus potential in 1 M KOH under UV illumination of un-loaded, WO_3-loaded and Cu-WO_3 loaded TiO_2 annotate. After co-loaded with Cu, further improved photocurrent is obtained. The photocurrent (potential=1 V) of Cu-WO_3 loaded annotate is 1.41 times higher than that of unloaded annotate and is 1.15 times higher than that of WO_3 loaded annotate, respectively.

The photo conversion efficiency (η) of light to hydrogen energy in the presence of an external applied potential is calculated as [7]:

η(%) = [(total power output- electrical power output)/light power input]×100=[$j_{pg}(1.23-E_{app})\times 100]/I_0$] (4)

The photocurrent density j_p is in an/cm^2 and the electrical power input is j_pE_{app}. $E_{app}=E_{mea}-E_{aoc}$, where E_{mea} is the electrode potential (versus Ag/AgCl) of the working electrode at which the photocurrent was measured under illumination and E_{aoc} is the electrode potential (versus Ag/AgCl) of the same working electrode at open circuit condition under same illumination and in the same electrolyte.

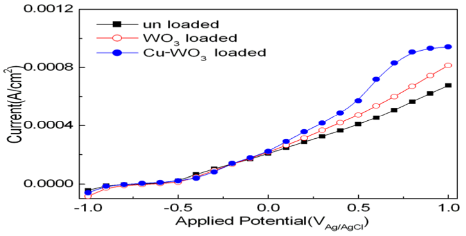


Fig.8. Photocurrent density of un-loaded, WO3-loaded and Cu-WO3 co-loaded TiO2 annotate.

C. Hydrogen Generation

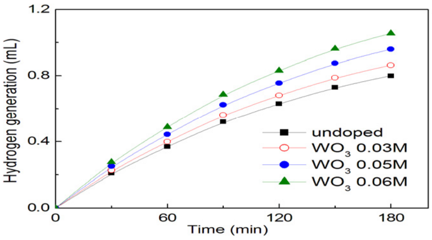


Fig.9. Hydrogen generation of undoped and WO_3 doped nanotube with different tungstic acid concentration in wet impregnation process.

Fig. 9 shows the hydrogen generation properties of un-loaded, different amount of WO_3 loaded TiO_2 annotate. WO_3-loaded samples can generate more hydrogen compared with un-loaded sample and the generated rate increases with the WO_3 concentration.

The catalytic hydrolysis reaction follows first-order kinetics [14]:

$$V_{H_2} = V_{H_2}(\max)(1-e^{-kt}) \qquad (1)$$

In the initial reaction stage, the hydrolysis reaction could be described as a zero-order-like feature:

$$V_{H_2} = V_{H_2}(\max)kt \qquad (2)$$

Then, hydrogen generation rate (HGR) was determined as:

$$\mathrm{HGR} = \mathrm{d}V_{H_2}/\mathrm{d}t \qquad (3)$$

The hydrogen generations properties of un-loaded, WO_3-loaded and Cu-WO_3 co-loaded TiO_2 annotate are shown in Fig. 10. Obviously, CuO-WO_3 co-loaded sample has higher activity of photocatalytic hydrogen generation than that of un-loaded TiO_2 annotate. The hydrogen generation rate of Cu-WO_3 loaded annotate is 0.00802 mL/min, which is 1.42 times higher than that of unloaded nanotube and is 1.16 times higher than that of pure WO_3 loaded annotate, respectively.

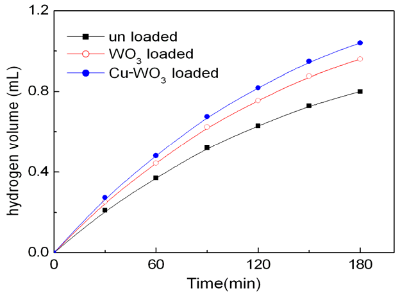


Fig.10. Hydrogen generation of un-loaded, WO3-loaded and Cu, WO3 co-loaded TiO2 annotate.

D. Photocatalytic Degradation

Photocatalytic degradation of MB under UV illumination of of un-loaded, WO_3-loaded and Cu-WO_3 co-loaded TiO_2 annotate is shown in Fig. 11. The photocatalytic degradation reaction follows a pseudo-first-order expression [13]:

$$\ln(c_0/c) = kt \qquad (5)$$

where c_0/c is the normalized MB concentration and k is the apparent reaction rate. The photocatalytic degradation efficiency could be improved by Cu-WO_3 co-loaded method, which can be clearly seen in Fig. 12. After irradiation for 2 h, the degradation efficiency of Cu-WO_3 loaded annotate is 48.7%, which is 1.36 times higher than that of unloaded annotate and is 1.12 times higher than that of pure WO_3 loaded sample, respectively.

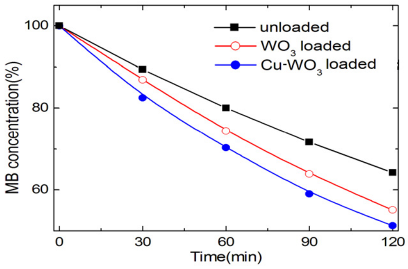


Fig.11. Photocatalytic degradation of MB un-loaded, WO3-loaded and Cu-WO3 co-loaded TiO2 nanotube.

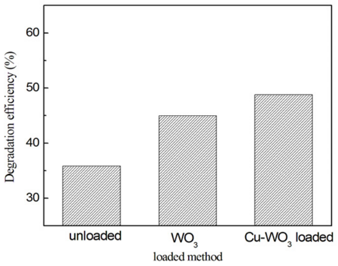


Fig.12. Photocatalytic degradation efficiency (2h UV irradiation) of MB of un-loaded, WO3-loaded and Cu-WO3 co-loaded TiO2 annotate.

IV. CONCLUSION

TiO_2 annotates were prepared by iodization method using glycerol, H_2O and NH_4F as the electrolyte. The annealed samples were soaked in tungsten acid and $Cu(NO_3)_2$ solution and then post-annealed to fabricate CUO, WO_3 co-loaded TiO_2 annotate arrays. The tube diameter of the anodic TiO_2 is about 140 nm, the wall thickness is about 40 nm and the length is about 4 µm. The as-anodized sample was amorphous. The annealed sample was anatase phase. The efficiency of photoelectrocatalytic properties could be improved by Cu-WO_3 co-loaded method for TiO_2 annotates. The photocurrent (potential=1 V) of Cu-WO_3 loaded annotate is 1.41 times higher than that of unloaded annotate and is 1.15 times higher than that of WO_3 loaded nanotube. The hydrogen generation rate of Cu-WO_3 loaded annotate is 0.00802 mL/min, which is 1.42 times higher than that of unloaded annotate and is 1.16 times higher than that of pure WO_3 loaded annotate. After UV irradiation for 2 h, the degradation efficiency of Cu-WO_3 loaded annotate is 48.7%, which is 1.36 times higher than that of unloaded annotate and is 1.12 times higher than that of pure WO_3 loaded sample, respectively.

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