ENHANCED PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS USING HIGH-ASPECT-RATIO SI/ITO/WO_3 MICROPOST PHOTOELECTRODES

X. Jiang, M. Liu, D. Zheng, X. Zhao, W. Wang and G. Sun
Institute of Robotics and Automatic Information System & Tianjin Key Laboratory of Intelligent Robotics, Nankai University, Tianjin, CHINA

ABSTRACT

This paper reports an enhanced photocatalysis system for organic pollutants degradation, using high-aspect-ratio (HAR) Si/ITO/WO_3 micropost photoelectrodes, fabricated by deep reactive ion etching (DRIE) and sputtering. Compared with traditional Titanium Dioxide (TiO_2) photoelectrodes, Tungsten trioxide (WO_3) coupled with Si can absorb visible light. Besides, an optimized HAR electrode configuration can dramatically increase the surface-to-volume ratio, not only increasing the total incident light intensity, but also facilitating the oxidation-reduction reaction in the semiconductor-liquid interface. The preliminary Methylene Blue (MB) ($C_{16}H_{18}ClN_3S$) degradation test showed that about 83.4% of MB can be degraded within 30 min.

INTRODUCTION

Photoelectrode systems have been of great interest for light-driven water splitting and photocatalysis [1]. So far, a wide range of semiconductor materials have been studied as photoelectrodes [2-4]. However, most of these materials with superior photocatalytic properties only response to UV spectrum, which seriously limits the practical application of semiconductor-based photocatalysis. Alternatively, a tandem photoelectrode system combining silicon photocathodes with a metal oxide that operates as a photoanode has been recently proposed [5-8]. This strategy can enhance the photoactivity and prevent Si from being oxidized. For example, electrical and photoelectrochemcial properties of WO_3/Si photoelectrodes have been investigated in detail [9]. The band gap (2.7 eV) of WO_3 allows for absorption of visible light.

Although material properties are critical to a photoelectrochemcial system, topology also plays an important role [10-14]. Traditionally, photoelectrodes have been mostly designed to a two-dimensional (2-D) planar configuration due to simplicity and easy fabrication. However, the limited reaction surface area makes the photocatalytic performance relatively low. One way to improve the performance is to use an electrode with a larger footprint size. However, one cannot infinitely increase the footprint. Instead, we propose a three-dimensional (3-D) design scheme by introducing HAR micropost photoelectrodes. Unlike a 2-D planar design, 3-D HAR design can provide much larger inner surface area while maintaining the footprint size unchanged.

Furthermore, in order to verify the photocatalytic performance enhancement of 3-D electrodes, we have developed a tandem Si/ITO/WO_3 micropost photoelectrode system for photocatalytic degradation test. Methylene Blue was chosen as the degradable material for the photocatalytic testing. Two different kinds of photoelectrodes, either in a planar sheet (2-D) or a regular array of microposts (3-D), have been fabricated and tested, respectively. The degradation performance of such photoelectrodes was studied and it has been found that by creating micropost array, the photocatalytic degradation of MB is enhanced either in reaction rate and efficiency.

EXPERIMENTAL

Figure 1 shows the schematic illustration of both 2-D and 3-D photoelectrodes. In common, a “sandwich-like” triple layer structure of Si/ITO/WO_3 was used to form the electrode.

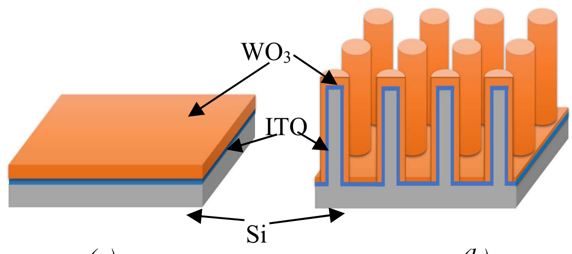
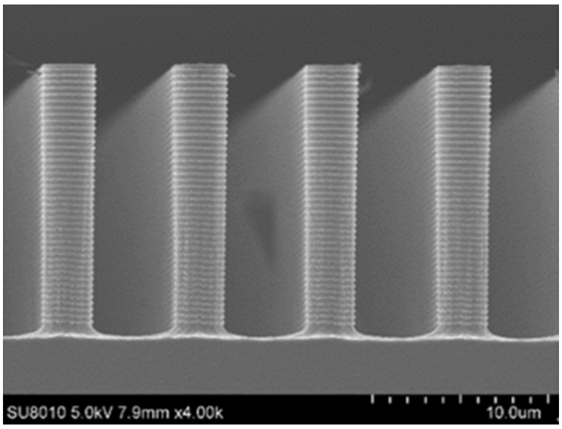


Figure 1: Schematic illustration of Si/ITO/WO_3 electrode configuration for photocatalysis. (a) Two-dimensional (2-D) design. (b) Three-dimensional (3-D) design.

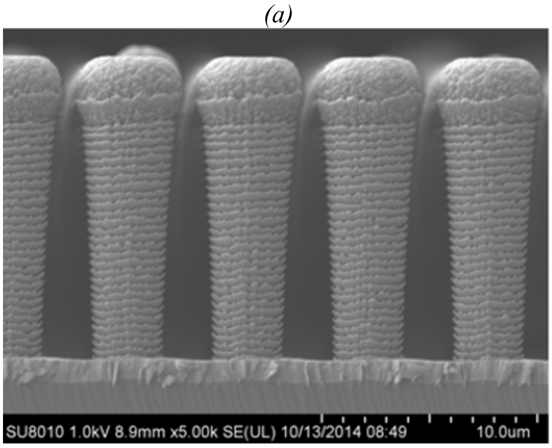
Photoelectrode fabrication

For both 2-D and 3-D photoelectrodes, a very thin layer of Indium Tin Oxides (ITO) was added between Si and WO_3 layers as a buffer layer, in order to improve the electrical connection. Because ITO is a kind of highly doped N-type semiconductor, no bandbending or high potential energy barrier will be introduced in. Moreover, the intrinsic transparency of ITO will not have apparent influence on visible light absorption.

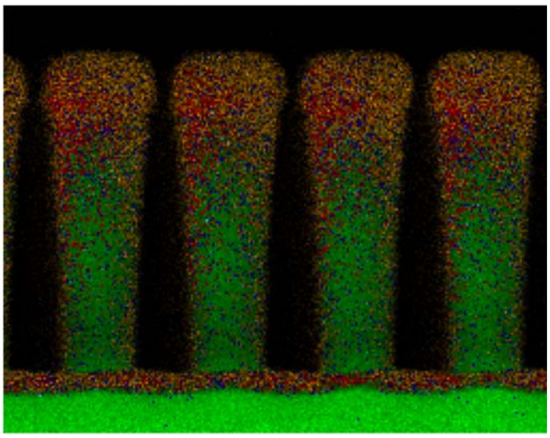
For the 3-D photoelectrode, a regular array of HAR microposts was utilized. Such a structure was chosen for benefits in either an increased effective surface area for incident light or a jam-free path for change carrier transportation. The designed diameter and space are 3.5μm and 7.5μm, respectively. The 3.5μm diameter is less than the diffusion length of charge carrier, minimizing the transportation distance and time of photogenerated carriers from inner bulk material to outer interface. A fairly-doped P-type (100)-oriented Si wafer was used as the fabrication substrate. First, a deep reactive ion etching (DRIE) process was used to form the HAR microposts, with an etching rate of about 3-5µm/min. The final etched height and aspect ratio are about 15µm and 5:1, respectively, as shown in Fig. 2(a).



(a)



(b)



(c)

Figure 2: Fabrication results of high-aspect-ratio (HAR) electrode. (a)SEM image of silicon micro posts after deep reactive ion etching (DRIE). (b)SEM image of Si/ITO/WO_3 photoelectrodes. (c) Element distribution picture of Si/ITO/WO_3 electrode.

As seen from the SEM image shown in Fig. 2(a), the DRIE-etched microposts have nearly vertical sidewall with uniform etching depth. The hundreds of nanometer-scale scallops on the sidewall would not have apparently negative influence in terms of oxidation-reduction reaction at the semiconductor-liquid interface. In fact, the rough sidewall surface can somehow further result in more surface area, which is advantageous to absorbing more incident light.

After DRIE step, the etched Si wafer was thoroughly cleaned in acetone, isopropanol, and HF, followed by deionized (DI) water rinsing, to remove any organic residue and native oxide layer on the surface. Right after the cleaning process, the cleaned Si wafer was promptly loaded into a sputtering chamber for ITO layer growth. The ITO layer was uniformly deposited on the micropost structures by a beam-assisted sputtering at room temperature, with 3sccm Ar flow, 25mA beam current, and 1100eV sputtering energy. The final deposition thickness of ITO layer was dependent on the sputtering time.

Next, a DC reactive magnetron sputtering process was used to deposit WO_3 layer at 500ºC, with 32sccm Ar flow , 8sccm O2 flow, and 100W sputtering energy. Element distribution analysis shown in Fig.2 (c) indicates that the upper part of micropost was fully covered by ITO/WO_3 while the bottom part left partially uncovered, which somehow helps generated electrons diffuse into liquid from Si interface.

For the 2-D photoelectrode fabrication, except for the absence of DRIE process, all other processes, i.e., substrate preparing, cleaning, and ITO and WO_3 growth, were kept consistent with 3-D photoelectrode fabrication.

Degradation test setup

To study the organic pollutants degradation performance of the fabricated photoelectrodes, both in 2-D and 3-D configurations, a custom-made experimental setup was built, as shown in Fig. 3. The testing photoelectrode with a footprint size of about 0.5cm x 1cm was mounted on the bottom of a glass beaker. A 15mL MB (10 mg/L) solution was used for as the degradation testing environment. An external condenser was used to maintain the overall volume of organic solution unchanged during the test. A Xenon light source and an irradiatometer S302-C from Thorlabs were used to emulate sunlight and monitor light intensity, separately. The absorption coefficient of MB was analyzed by a spectrophotometer UV-2600 from SHIMADZU. All experiment parameters, e.g., temperature, lighting, and timing, were kept consistent for both 2-D and 3-D photoelectrodes.

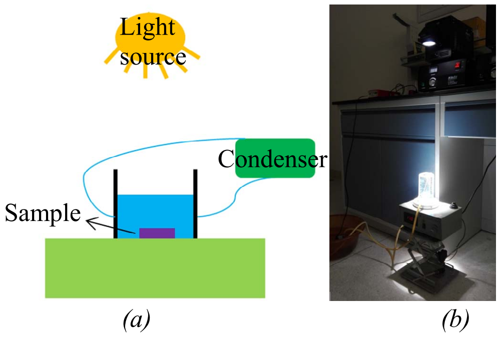
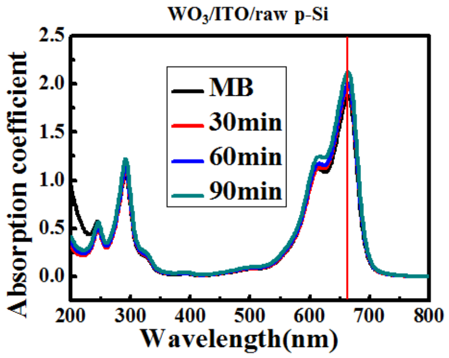


Figure 3: Experiment setup of photocatalysis. (a) Schematic illustration. (b) Photography.

RESULTS AND DISSUSSION

Figures 4 (a) and (b) show the MB degradation results of 2-D and 3-D configuration photoelectrodes, separately. For the planar Si/ITO/WO_3 (2-D) photoelectrode, the concentration of MB has no apparent change after 90 min. Whereas for the processed Si/ITO/WO_3 (3-D) photoelectrodes, the concentration of MB decreased to 16.6 % after about 30 min. The concentration decrease rate of MB was calculated directly by counting the absorption coefficient change corresponding to a wavelength of ~660nm.



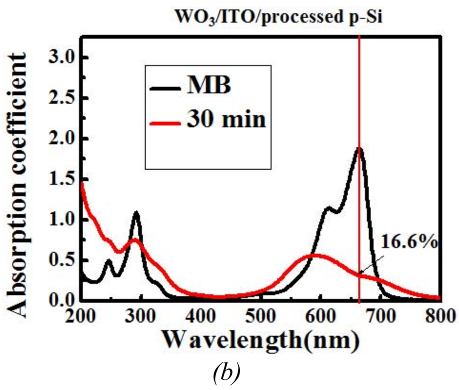


Figure 4: Spectrophotometer analysis results of MB degradation. (a)With unprocessed 2-D electrode. (b)With micromachined 3-D electrode.

The enhanced photocatalytic performance can be attributed to two factors, i.e., more incident visible light and larger oxidation-reduction reaction interface. Figure 5 shows the SEM image of Si/ITO/WO_3 3-D photoelectrodes after 30 min photocatalysis. The inverted umbrella-like structure uniformly over the sidewall indicates a uniform photoelectrochemcial reaction.

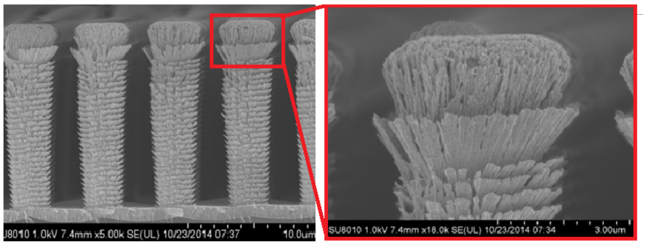


Figure 5: SEM images of Si/ITO/WO_3 photoelectrodes after 30mins photocatalysis experiment.

SUMMARY

Our study demonstrated that photocatalytic performance of a tandem photoelectrode can be significantly enhanced by optimizing the topology structure. High-aspect-ratio micropost photoelectrodes were fabricated and tested using a MB solution. Preliminary degradation testing results showed that the concentration of MB decreases to 16.6 % after about 30 min. In comparison, a 2-D planar sheet photoelectrode did not show apparent degradation at all, under the same experimental condition. Further investigation on the effect of micropost geometry size, such as height, spacing, and aspect-ratio, is underway.

ACKNOWLEDGEMENTS

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CONTACT

*G. Sun, tel: 86-22-23505706; guangyi@nankai.edu.cn
*D. Zheng, 2120140340@mail.nankai.edu.cn