PHOTOCATALYTIC MICROFLUIDIC REACTOR WITH A NOVEL COMPOUND CATALYST FILM USING SOLAR ENERGY

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ABSTRACT

This paper reports a microfluidic reactor (dimensions 10 ×10 × 0.1 mm^3) that utilizes a novel $BiVO_4/TiO_2$ heterojunction film to enhance the photocatalytic performance under solar irradiation. The microreactor inherits many merits from the microfluidics such as fine flow control and large surface-area-to-volume ratio. More importantly, it tackles two fundamental problems of photocatalysis: limited utilization of solar spectrum and severe recombination of photo-excited electrons and holes. These are achieved by using the $BiVO_4$ film to absorb the visible range of solar light and the TiO_2 part to absorb the near UV range, and by using the heterojunction to separate the photo-excited electrons and holes. In experiment, the microreactor using $BiVO_4/TiO_2$ shows a reaction rate about 2 times of that using the commercial P25 TiO_2 film.

KEYWORDS

Microfluidic, photovatalysis, heterojunction, $BiVO_4$, solar energy.

INTRODUCTION

Microfluidics has demonstrates remarkable capabilities in dealing with particles, fluids and light in an integrated platform [1-3] and may bring new opportunities for photocatalysis. For instance, our previous studies [4, 5] have shown that the planar microreactors possess unique advantages for photocatalytic water purification, such as high mass transfer efficiency, large specific interfacial areas and large light receiving area. However, most of the work utilized commercial P25 TiO_2 used as photocatalysts and required UV irradiation, limiting the utilization of the solar spectrum. In addition, the photo-excited electrons and holes experienced severe recombination problem due to the lack of a mechanism to separate them. Recently, great efforts have been put to combine TiO_2 with other narrow-bandgap semiconductors so as to be responsive to a wider light spectrum. These compound photocatalysts often have a heterojunction structure, which brings in an additional benefit to enhance the electron-hole separation and the interfacial charge transfer. It is essential for improving the photocatalytic activity under solar light [6-8].

In this work, we present a planer microreactor for photodegradation of methylene blue under solar light. The microreactor consists of a blank glass cover, a patterned PDMS slab and a $BiVO_4/TiO_2$-immobilized glass substrate. The photocatalytic performance is benefited from both the microfluidic design and the heterojunction film.

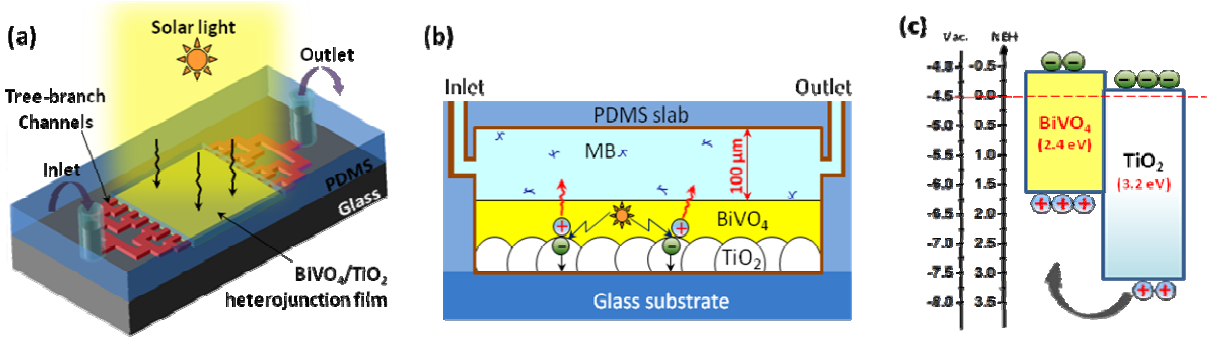

Figure 1: Design and working principle of the microreactor. (a) 3D schematic of the microreactor structure; (b) cross-sectional view of the reaction chamber; and (c) Energy band diagram of $BiVO_4/TiO_2$ heterojunction film.

EXPERIMENT

Device design and working principle

The planar microreactor is designed as illustrated in Fig. 1(a). A PDMS slab is molded to have tree-branch microchannels and a reaction chamber before it is bonded onto a glass substrate immobilized with the $BiVO_4/TiO_2$ compound photocatalyst. The reaction chamber has the dimension of 10 × 10 × 0.1 mm^3, and the $BiVO_4/TiO_2$ films have the same surface area (10 × 10 mm^2) with the reaction chamber. The enlarged cross-sectional view of the microreactor is shown in Fig.1 (b). The compound film consists of a nanoporous TiO_2 film covered with a dense $BiVO_4$ film. The porous structure improves the surface/volume ratio and is beneficial to the photocatalysis. Under the irradiation of the solar light, the $BiVO_4$ film absorbs the visible part of the solar spectrum and the TiO_2 absorbs the near UV, yielding the utilization of a wide spectrum of the solar light.

Fig. 1 (c) shows the energy band diagram of the $BiVO_4/TiO_2$ heterojunction. $BiVO_4$ is considered an intrinsic semiconductor, the Fermi level in $BiVO_4$ lies in the middle of conduction band and valence band. Typically TiO_2 is a n-type semiconductor. When these two types of semiconductor materials are joined together, the heterojunction

structure is formed [8]. For this reason, the photo-generated electrons and holes would flow to different directions due to the difference of potential levels. This would significantly reduce the recombination of the electrons and holes and would thus enhance the photocatalytic efficiency.

Fabrication and characterization of the compound photocatalyst film

Following the same method in our previous research [4, 5], the nanoporous TiO_2 film was prepared by the sol-gel method. It included two stages: the preparation of the TiO_2 colloid and the creation of porous TiO_2 film on the glass slide. On the first stage, 10% wt. TiO_2 powders (Degussa P25) were slowly dispersed in 120 ml water containing acetylacetone, Triton X-100, PEG20000 to form the TiO_2 colloid. On the second stage, the painting method was used to form a porous TiO_2 film onto a glass slide, which was subsequently annealed at 500 °C for 2h. In the next step, a thin film of bismuth vanadate ($BiVO_4$) was grown on the porous TiO_2 film by the pulse laser deposition (PLD) method. The deposition was carried out in the oxygen atmospehere of 200 mtorr at 500 °C with pulse energy about 300 mJ focused on a $BiVO_4$ ceramic target (10 mm in diameter). The compound film was also characterized by XRD, SEM and UV-vis absorbance spectrum.

Device fabrication and efficiency test

Standard UV lithography was used to fabricate the master mold for the microreactor. First, negative photoresist SU-8 50 was spin coated at 1500 rpm for 60 s onto a silicon wafer substrate and was then baked. Reaction chamber and inlet/outlet were then patterned with a mask. As a result, the SU-8 master was obtained. After cleaning it, a prepolymer solution of PDMS in a 10:1 mixture ratio was poured on the SU-8 master and cured at 80 °C for 1 h. Finally, the cured PMDS slab was peeled off and was ready for bonding with the glass substrate.

The photo of the fabricated microreactor is shown in Fig. 2(a), the overall footprint is 3 cm × 2.5 cm (not including the full lengths of the tubes and the wires). Two steel tubes are used as the inlet and outlet. For easy visualization, the tree-branch microchannels and the reaction chamber are filled with green dye solution.

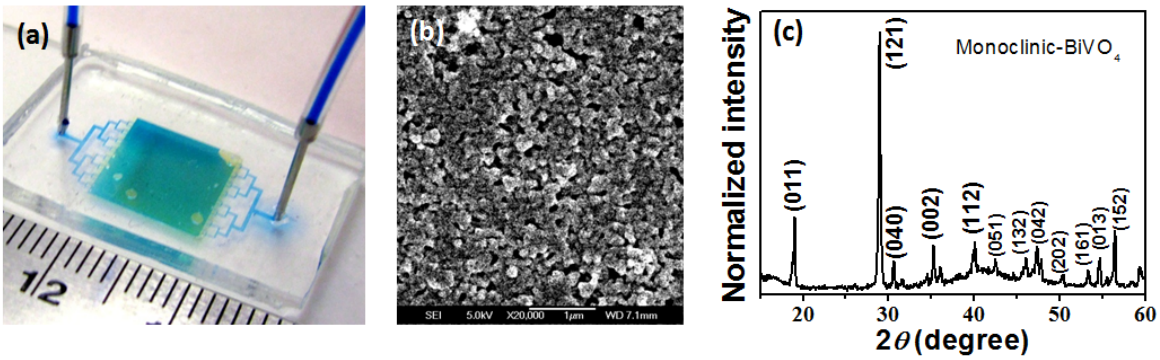

Figure 2: (a) Photograph of the microreactor; (b) scanning electron micrograph of the compound $BiVO_4/TiO_2$ film; and (c) XRD of the $BiVO_4$ deposited by PLD, showing the monoclinic phase.

RESULTS AND DISCUSSION

Characterization of the compound film

Fig. 2(b) shows the SEM image of the compound film. The TiO_2 layer is 3 μm thick and the $BiVO_4$ layer is 40 nm thick. The porous structure of the TiO_2 is well preserved as the PLD-deposition of 40-nm $BiVO_4$. Fig. 2(c) shows the XRD diffraction patterns of the PLD-deposited $BiVO_4$ film. The peaks match well with the monoclinic phase.

Photocatalytic efficiency of the device

In the experiment, photocatalytic reactions were conducted using a Xe lamp. Methylene blue solution (3×10^{-5} M) was used as the model chemical and was driven by a syringe pump. The degraded MB solutions were collected from the outlet and analyzed by a UV-visible spectrophotometer.

In the microreactor system, the flow rate is one of the major factors that affect the photocatalytic reaction efficiency. The flow rate is related to the effective residence time of the MB solution in the reaction chamber by the relationship $Effective\ residence\ time = Chamber\ volume / Flow\ rate$. To investigate the effect of the flow rate, the solutions were pumped at 75, 100, 150, 300 μl/min, respectively. The corresponding effective residence time (i.e., the reaction time) is 8, 6, 4 and 2 s, respectively. The solar light density was tested to be 100 mW/cm^2. For control experiments, microreactors without any catalyst film, with only the porous TiO_2 film and with only a porous (not dense) $BiVO_4$ film were tested under the same conditions. The results are plotted in Fig. 3 (a). It can be seen that the MB solution is scarcely degraded in the microreactor with no photocatalyst film. In the microreactor with the porous TiO_2 film, the degradation increases obviously with the effective residence time. And in the microreactor with the porous $BiVO_4$ film (1.5 μm thick), the degradation rate is similar. In contrast, the microreactor using the $BiVO_4/TiO_2$ film is much faster. The reaction rate constant (represented by the slope of the fitted straight line) is about 2 times of those obtained using the porous TiO_2 film and the porous $BiVO_4$ film. Here we choose the 3-μm porous $BiVO_4$ film

rather than the 40-nm dense $BiVO_4$ film for comparison is because the former represents roughly the best photocatalytic performance that can be achieved using $BiVO_4$ under the solar light.

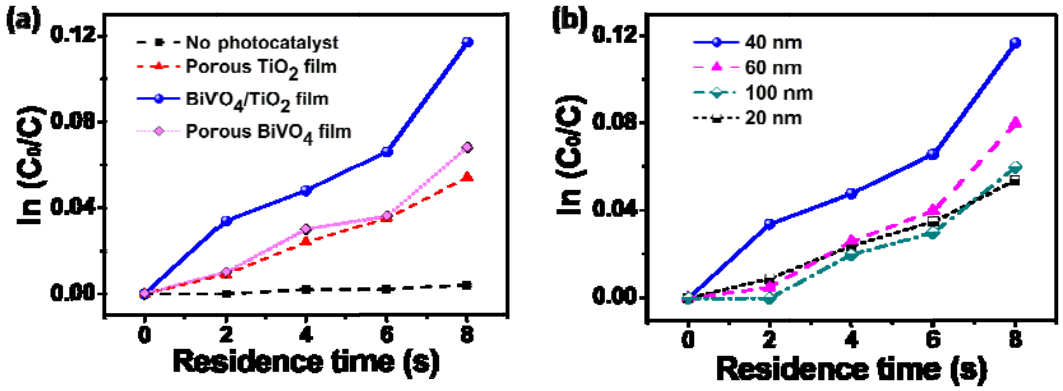

Figure 3 (a) The photocatalytic performance of the microreactor using $BiVO_4/TiO_2$ film as compared to the other control experiments; (b) influence of the $BiVO_4$ film thickness.

The photocatalytic process of a photocatalyst is determined by three important parameters: surface area, surface charge carrier transfer rate and electron-hole recombination rate [9]. Increase of the former two and suppression of the last would improve the photocatalytic properties. However, when the speed of surface electron-hole recombination is faster than that of the interfacial charge carrier transfer, the photocatalytic activity would go down. Therefore, there is an optimal thickness of the $BiVO_4$ film for maximum photocatalytic efficiency. Different thicknesses (20 – 100 nm) of $BiVO_4$ on the porous TiO_2 film are investigated. The results are plotted in Fig.3 (b). The best photocatalytic performance is found to occur at the $BiVO_4$ film thickness of 40 nm.

CONCLUTIONS

A planar photocatalytic microreactor is demonstrated to achieve enhanced photocatalytic activity under solar irradiation. It adopts a $BiVO_4/TiO_2$ heterojunction photocatalyst film at the bottom of the reaction chamber to be responsive to both the visible and the UV region of the solar light. The photodegradation performance of the microreactor can be doubled in the reaction time of 10 ~20 s, much shorter than typically several hours in many bulk reactors. And the optimal thickness of $BiVO_4$ film (40 nm thick) combined with the porous P25 TiO_2 film is also explored to maximize the photocatalytic performance.

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REFERENCES

[1] G. M. Whitesides, *The origins and the future of microfluidic*, Nature, pp. 368-373, (2006).
[2] Y. Yang, A. Q. Liu, L. Lei, L. K. Chin, C. D. Ohl, Q. J. Wang, and H. S. Yoon. *A tunable 3D optofluidic waveguide dye laser via two centrifugal Dean flow streams*, Lab Chip, pp. 3182-3187 (2011).
[3] G. V. Casquillas, C. Fu, M. Le Berre, J. Cramer, S. Meance, A. Plecis, D. Baigl, J-J Greffet, Y. Chen, M. Piel and P. T. Tran. *Fast microfluidic temperature control for high resolution live cell imaging,* Lab Chip, pp. 484-489, (2011).
[4] L. Lei, N. Wang, X. M. Zhang, Q. D. Tai, D. P. Tsai, and Helen L.W. Chan. *Optofluidic planar reactors for photocatalytic water treatment using solar energy, Biomicrofluid*, pp. 043004, (2010).
[5] D. Erickson, D. Sinton and D. Psaltis. *Optofluidics for energy applications, Nat. Photon.*, pp. 583-590, (2011).
[6] K. Vinodgopal and P.V. Kamat. *Enhanced Rates of Photocatalytic Degradation of an Azo Dye Using SnO_2/TiO_2 Coupled Semiconductor Thin Films*, Environ. Sci. Technol., pp. 841-845, (1995).
[7] Y. Bessekhouad, D. Robert and J.V. Weber. *Photocatalytic activity of Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ heterojunction, Catal. Today*, pp. 315-321, (2005).
[8] Y. Hu, D. Z. Li, , Y. Zheng, W. Chen, Y. H. He, Y. Shao, X. Z. Fu, and G. C. Xiao, *$BiVO_4/TiO_2$ nanocrystalline heterostructure: A wide spectrum responsive photocatalyst towards the highly efficient decomposition of gaseous benzene*, Appl. Catal. B, pp. 30-36, (2011).
[9] H. P. Li, W. Zhang, B. Li, and W. Pan. *Diameter-dependent photocatalytic activity of electrospun TiO_2 nanofiber,* J. Am. Ceram. Soc., pp. 2503-2506, (2010).

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