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 mm3) that utilizes a novel BiVO4/TiO2 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 BiVO4 film to absorb the visible range of solar light and the TiO2 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 BiVO4/TiO2 shows a reaction rate about 2 times of that using the commercial P25 TiO2 film.

KEYWORDS
Microfluidic, photovatalysis, heterojunction, BiVO4, 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 TiO2 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 TiO2 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 planar microreactor for photodegradation of methylene blue under solar light. The microreactor consists of a blank glass cover, a patterned PDMS slab and a BiVO4/TiO2-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 BiVO4/TiO2 heterojunction film.](image)

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 BiVO4/TiO2 compound photocatalyst. The reaction chamber has the dimension of 10 × 10 × 0.1 mm3, and the BiVO4/TiO2 films have the same surface area (10 × 10 mm2) 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 TiO2 film covered with a dense BiVO4 film. The porous structure improves the surface/volume ratio and is beneficial to the photocatalysis. Under the irradiation of the solar light, the BiVO4 film absorbs the visible part of the solar spectrum and the TiO2 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 BiVO4/TiO2 heterojunction. BiVO4 is considered an intrinsic semiconductor, the Fermi level in BiVO4 lies in the middle of conduction band and valence band. Typically TiO2 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 TiO₂ film was prepared by the sol-gel method. It included two stages: the preparation of the TiO₂ colloid and the creation of porous TiO₂ film on the glass slide. On the first stage, 10% wt. TiO₂ powders (Degussa P25) were slowly dispersed in 120 ml water containing acetylacetone, Triton X-100, PEG20000 to form the TiO₂ colloid. On the second stage, the painting method was used to form a porous TiO₂ film onto a glass slide, which was subsequently annealed at 500 °C for 2h. In the next step, a thin film of bismuth vanadate (BiVO₄) was grown on the porous TiO₂ film by the pulse laser deposition (PLD) method. The deposition was carried out in the oxygen atmosphere of 200 mtorr at 500 °C with pulse energy about 300 mJ focused on a BiVO₄ 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.

![Microreactor Image](https://example.com/microreactor.png)

**Figure 2:** (a) Photograph of the microreactor; (b) scanning electron micrograph of the compound BiVO₄/TiO₂ film; and (c) XRD of the BiVO₄ 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 TiO₂ layer is 3 µm thick and the BiVO₄ layer is 40 nm thick. The porous structure of the TiO₂ is well preserved as the PLD-deposition of 40-nm BiVO₄. Fig. 2(c) shows the XRD diffraction patterns of the PLD-deposited BiVO₄ 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 \( \text{Effective residence time} = \frac{\text{Chamber volume}}{\text{Flow rate}} \). 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/cm². For control experiments, microreactors without any catalyst film, with only the porous TiO₂ film and with only a porous (not dense) BiVO₄ 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 TiO₂ film, the degradation increases obviously with the effective residence time. And in the microreactor with the porous BiVO₄ film (1.5 µm thick), the degradation rate is similar. In contrast, the microreactor using the BiVO₄/TiO₂ 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 TiO₂ film and the porous BiVO₄ film. Here we choose the 3-µm porous BiVO₄ film.
rather than the 40-nm dense BiVO₄ film for comparison is because the former represents roughly the best photocatalytic performance that can be achieved using BiVO₄ under the solar light.

Figure 3 (a) The photocatalytic performance of the microreactor using BiVO₄/TiO₂ film as compared to the other control experiments; (b) influence of the BiVO₄ 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 BiVO₄ film for maximum photocatalytic efficiency. Different thicknesses (20 – 100 nm) of BiVO₄ on the porous TiO₂ film are investigated. The results are plotted in Fig.3 (b). The best photocatalytic performance is found to occur at the BiVO₄ film thickness of 40 nm.

CONCLUSIONS
A planar photocatalytic microreactor is demonstrated to achieve enhanced photocatalytic activity under solar irradiation. It adopts a BiVO₄/TiO₂ 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 BiVO₄ film (40 nm thick) combined with the porous P25 TiO₂ film is also explored to maximize the photocatalytic performance.

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REFERENCES

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