Examination of the Photocatalytic Activity of Differently Shaped Bismuth Tungstate Microcrystals

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Abstract

In this study, Bi_2WO_6 photocatalysts with different morphologies were obtained by a one-step hydrothermal method. The resulted 3D structures (e.g. "flowers") (d ≈ 2 μm) consisted from individual nanoplates. The synthesis procedure involved acetic acid, a surfactant (Triton X-100) and a shaping agent, such as urea, thiourea and glycine. The effect of these compounds were also investigated in-detail. The crystallization was performed using the well-known hydrothermal method. The above mentioned morphological changes significantly influenced the photocatalytic activity, which was evaluated successfully by the degradation of Rhodamine B (RhB) under UV irradiation.

Introduction

Nowadays semiconductor photocatalysis is an intensively studied research field due to its potential in solar energy conversion and degradation of organic pollutants. The most studied semiconductor in photocatalysis is titanium dioxide, because it is photostable, biologically inert, and it can be produced cheaply [1]. Besides, the industry already uses titania in several applications. Its major drawback is that UV light is required for excitation. An emerging alternative is bismuth tungstate, which is active under visible light (λ > 400nm) [2]. This property can be an advantage, because the major component (38 – 40 %) of the sunlight's emission spectrum is in the visible range, while the UV light is just 3-5 % of the full spectrum [3]. The activity of the photocatalysts can be maximized by shape-tailoring with appropriate chemical reagents, such as in case of titanium dioxide, where F^- ions are applied for the stabilization of reactiva crystallographic planes [4]. Therefore, if the shape is changing, then the physical and chemical properties of the chosen material is also changing. This means that the photocatalytic activity is also influenced. In our preliminary experiments octyl phenol ethoxylate (Triton X-100), was used, while the influence of the hydrothermal treatment time was investigated. It was found that the hydrothermal treatment time significantly influenced the morphology of the Bi_2WO_6, together with the observed photocatalytic activity [5].

Experimental

Controllable synthesis of Bi_2WO_6 microflowers

$Bi_2(NO_3)_3 \cdot 5\ H_2O$ (5 mmol) was dissolved in 43 mL 36 % acetic acid (transparent solution, A). After that, $Na_2WO_4 \cdot 2\ H_2O$ (2.5 mmol), Triton X-100 (1.25 mmol) and thiourea (1.25 mmol) were dissolved in 68.8 mL distilled water (transparent solution, B). The solution B was added dropwise into solution A, under continuous stirring. The solution containing the amorphous precipitate was transferred into a Teflon-lined stainless steel autoclave. The temperature was adjusted and maintained at 180 °C for 15 h, and cooled down to room temperature without the usage of a supplementary cooling agent. The gained powder was collected and washed five times with ethanol and deionized water. After that, the catalysts were dried at 40 °C for 12 h [5]. The synthesis strategy is listed in Table 1, where the different shape-directing agents were listed.

Sample name	Used materials	
TU	thiourea	triton X-100
TU-TRX	thiourea	✕
U	urea	triton X-100
U-TRX	urea	✕
G	glicine	triton X-100
G-TRX	glicine	✕
TRX	✕	triton X-100

Table 1. Used ashaping agents and the samples' nomenclature

Characterization

The obtained microcrystals were analyzed using scanning electron microscopy (SEM), and X-Ray diffraction (XRD), while the optical features were followed by diffuse reflection spectrometry (DRS).

Photocatalytic activity tests

The photocatalytic activity tests of the samples were carried out by the photodegradation of a Rhodamine B (RhB) at 25 °C. 6 × 6 W fluorescent UV lamps were used as a light source (λ_{max} = 365 nm). The experiments of RhB degradation were performed as follows: 0.1 g Bi_2WO_6 was added to 100 mL RhB solution (initial concentration: $5 \cdot 10^{-5}$ M). Before the UV illumination, the suspension was stirred for 30 minutes in the dark. After the lamp was switched on, in every 30 minutes, 2 mL suspension was collected and centrifuged. The concentration of Rhodamine B were determined by UV-Vis spectroscopy (detection wavelength = 553 nm).

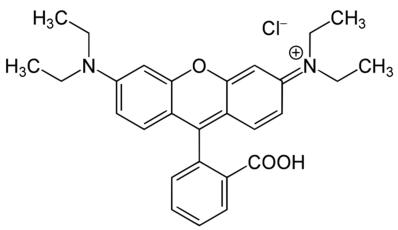

Figure 1. The structure of Rhodamine B

Results and discussion

The results show, that the used shaping agents (Triton X-100, urea, thiourea and glycine) influenced the microcrystals' shapes. As shown in the Figure 2, if the thiourea was changed to urea or glycine, completely different microstructures were formed (not "flower-like" structure). But all samples' shapes were spherical, with a diameter about 2-3 µm. The TU sample has a flower-like structure, while the U sample is similar to a rose, and the G sample does not show any specific shape. Nevertheless, the G sample has the best photocatalytic degradation capacity. Furthermore, if the Triton X-100 was not involved the synthesis, the "flower-like" shape remained. This leads to the conclusion that the main shape controlling reagents are the thiourea and glycine. Nevertheless, all the samples had a secondary structure which consisted from thin sheets.

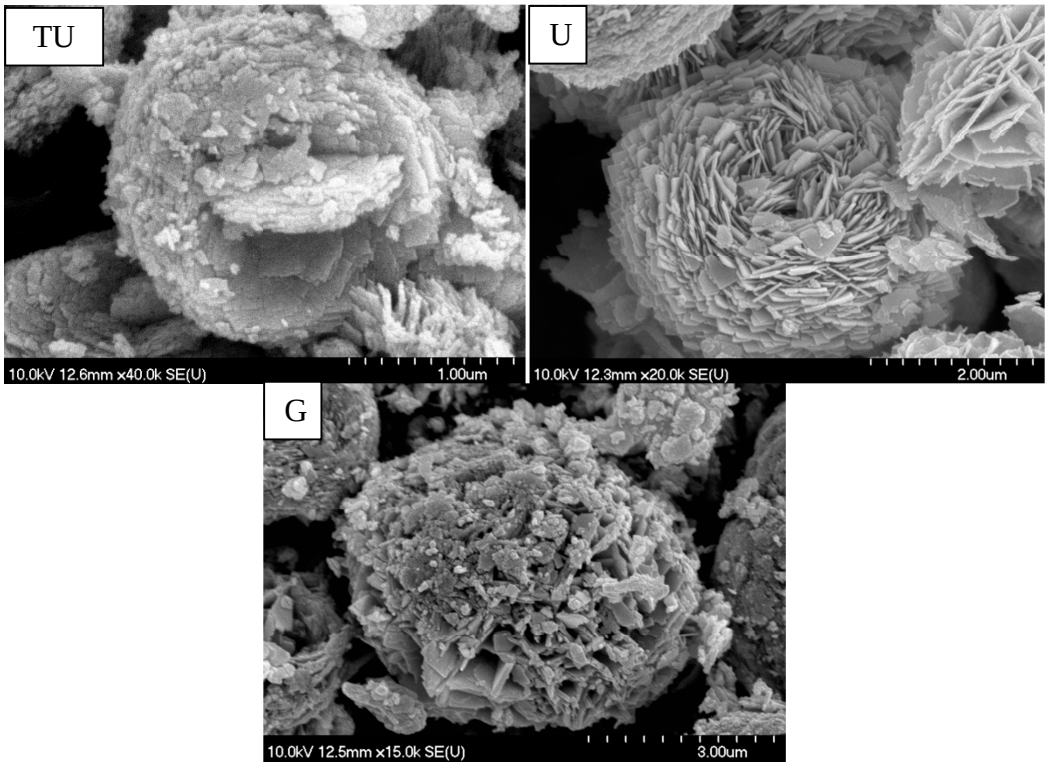

Figure 2. SEM micrographs

The main diffraction peaks the samples can be identified as an orthorhombic crystal structure. The G and G-TRX samples contain a small amount of WO_3 (Figure 3/a.). Furthermore, on the diffuse reflectance spectra is clearly visible, that the G and the G-TRX samples show an additional electron transition band (530 nm), besides the one observed at 410 nm.(Figure 3/b)

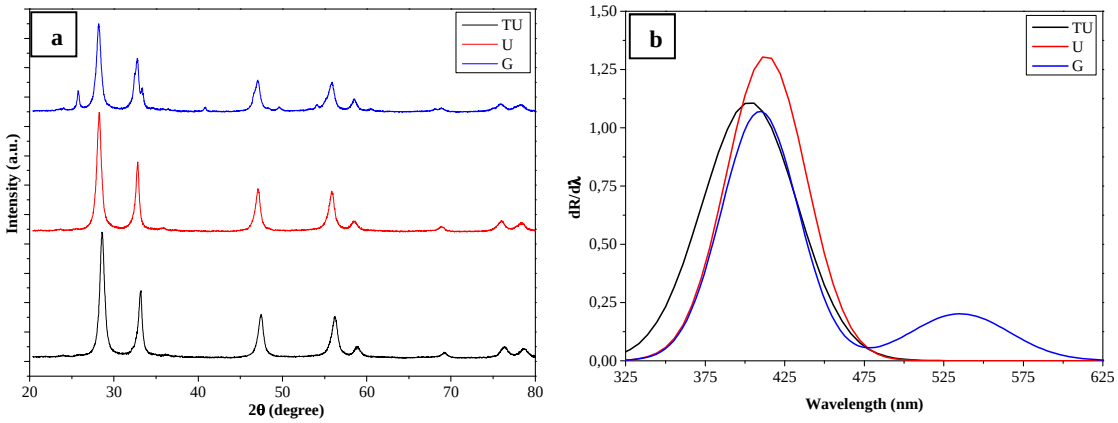

Figure 3. X-ray diffractogram (a) and diffuse reflectance spectra (b)

Finally, the photocatalytic degradation capabilities of the obtained materials were tested for Rhodamie B under UV light irradiation. The decomposition curves are shown in Figure 4.

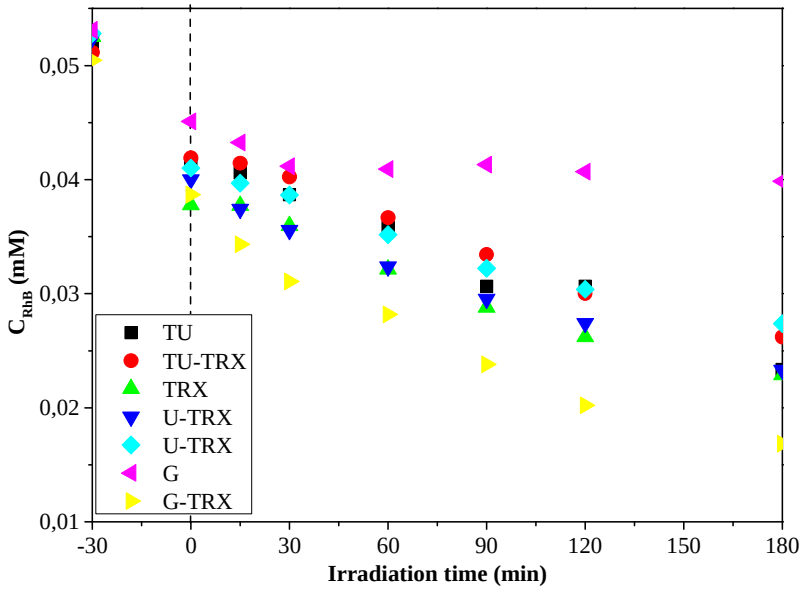

Figure 4. Photocatalytic degradation of RhB

Conclusion

In summary, differently shaped Bi_2WO_6 photocatalysts were successfully synthesized with one-step hydrothermal method. The shaping agents (urea, thiourea and glycine) are the most important in the formation of bismuth tungstate, while the surfactant serves as a size controlling agent. Moreover, the Bi_2WO_6 microflowers showed high photocatalytic activity for Rhodamine B degradation under UV light irradiation.

Acknowledgements

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