Microwave Synthesis of Bismuth-Rich Oxyiodide for Photooxidation of Arsenite (As(III))

Thanchanok Charoensuk, Jirapinya Kanmuntha, Chuchai Sronsri, Sulawan Kaowphong

Department of Chemistry, Faculty of Science, Chiang Mai University

Abstract

Semiconductor-mediated photocatalysis is a promising technology for addressing water contamination caused by pollutants. Bismuth oxyiodide (BiOI) is a notable photocatalytic material due to its unique layered crystal structure and visible light responsiveness, providing excellent physicochemical and photocatalytic properties. However, the photocatalytic efficiency of BiOI is limited by the high recombination rate of photogenerated electron-hole pairs, resulting from its narrow energy band gap (1.77 eV), which reduces its utilization efficiency. Additionally, the low reduction ability of electrons in the conduction band (CB) and low oxidation ability of hole in the valence band (VB) restrict its broader photocatalytic applications. Bismuth-rich oxyiodide ($Bi_xO_yI_z$) exhibits tunable elemental ratios and adjustable electronic band level. Increasing the Bi content leads to more negative CB and more positive VB potentials. In this research, $Bi_xO_yI_z$ (BiOI, $Bi_7O_9I_3$, and Bi_5O_7I) were successfully synthesized using a cyclic microwave irradiation method (640 W, 5 cycles). The effect of NaOH contents on the formation of material was investigated. The results demonstrated that the NaOH content influenced the ratios of x, y and z in $Bi_xO_yI_z$. BiOI was obtained when 0, 2, and 4 mmol NaOH were added to the reaction. In contrast, $Bi_7O_9I_3$ and Bi_5O_7I were formed when 6 and 8 mmol NaOH were used, respectively. Among the studied photocatalysts, Bi_5O_7I exhibited the highest photooxidation efficiency for the highly toxic arsenite (As(III)), converting it into environmentally safer arsenate (As(VI)). Within 360 min under visible light, Bi_5O_7I and $Bi_7O_9I_3$ oxidized 98.80% and 77.90% of As(III) (20 ppm), respectively, while BiOI oxidized only 3.20%. The enhanced photocatalytic performance of Bi_5O_7I and $Bi_7O_9I_3$ compared to BiOI was attributed to the efficient separation and migration of photogenerated charge carriers as well as the favorable electronic band positions. These factors improved the redox ability of the charge carriers, leading to an increasing the generation of active species.

Introduction

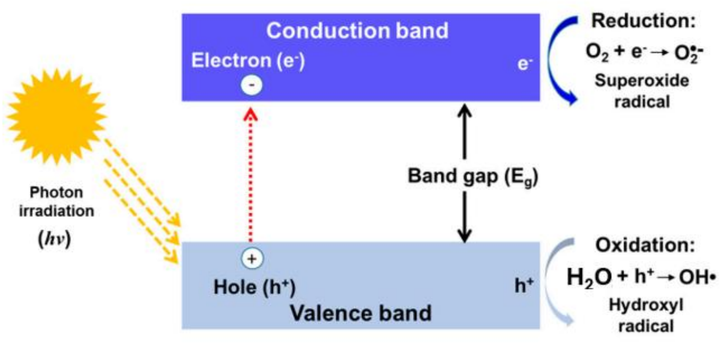

Fig. 1 The fundamental process of generating chare carriers.

- **Photoexcitation**
- **Generation of electron/hole pair and migration to the photocatalyst's surface**
- **Reduction reaction : conduction band (CB)**

$$e^- + O_2 \longrightarrow O_2^{\bullet-}$$

- **Oxidation reaction : valence band (VB)**

$$h^+ + H_2O \longrightarrow OH\bullet + H^+$$

Experimental procedure

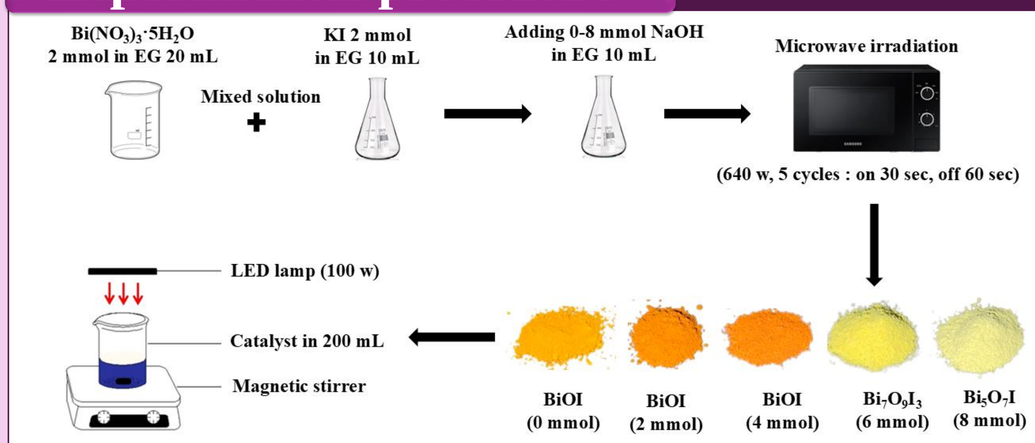

Fig. 2 Experimental step for the photocatalytic oxidation of As(III).

Results and Discussion

PXRD : Purity and crystalline phase identification

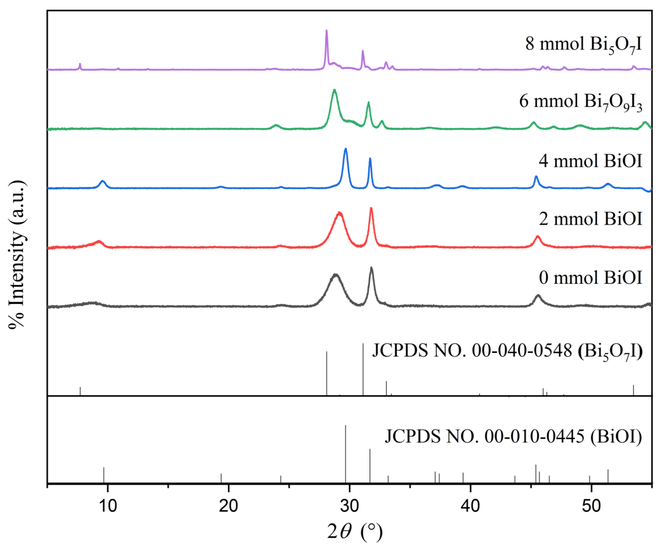

Fig. 3 XRD patterns of BiOI, $Bi_7O_9I_3$ and Bi_5O_7I.

SEM : Morphology

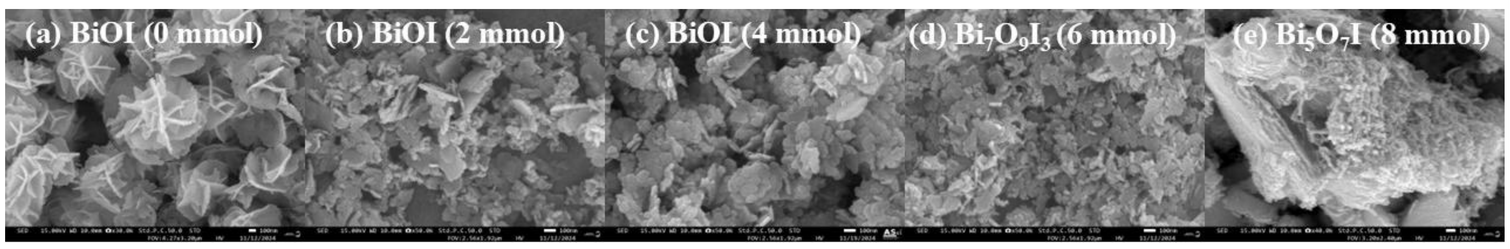

Fig. 4 SEM images of BiOI, $Bi_7O_9I_3$ and Bi_5O_7I.

TEM : Morphology

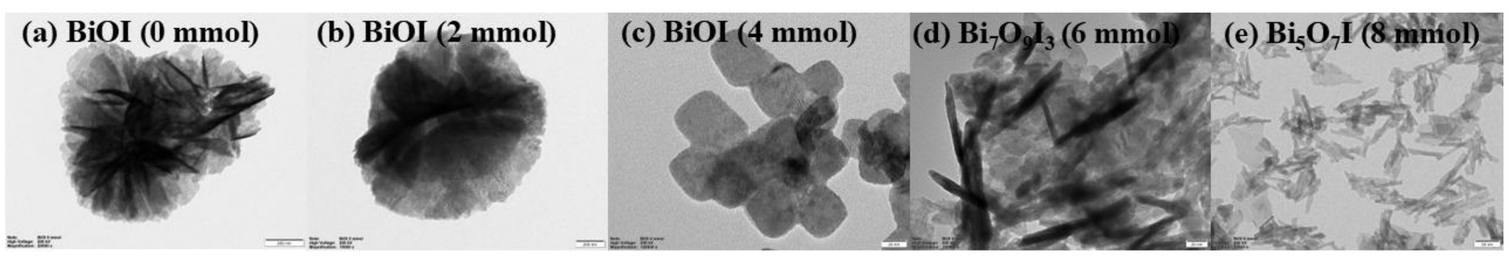

Fig. 5 TEM images of BiOI, $Bi_7O_9I_3$ and Bi_5O_7I.

Photocatalytic activity test :

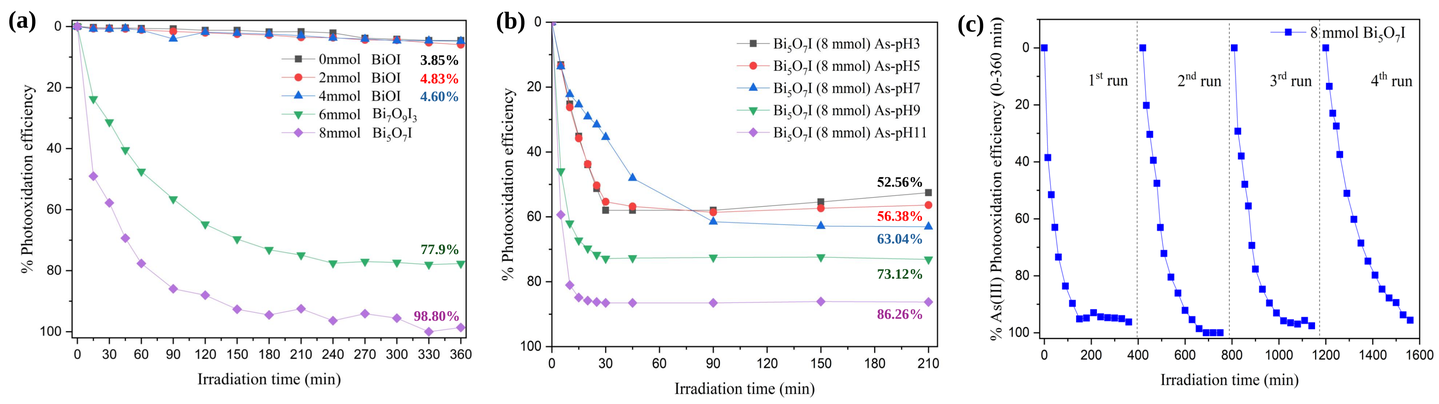

Fig. 6 (a) Photocatalytic oxidation of As(III) by BiOI, $Bi_7O_9I_3$ and Bi_5O_7I. (b) Photocatalytic oxidation of As(III) by Bi_5O_7I under various pH solution. (c) Recycling experiments.

Electrochemical properties and optical property :

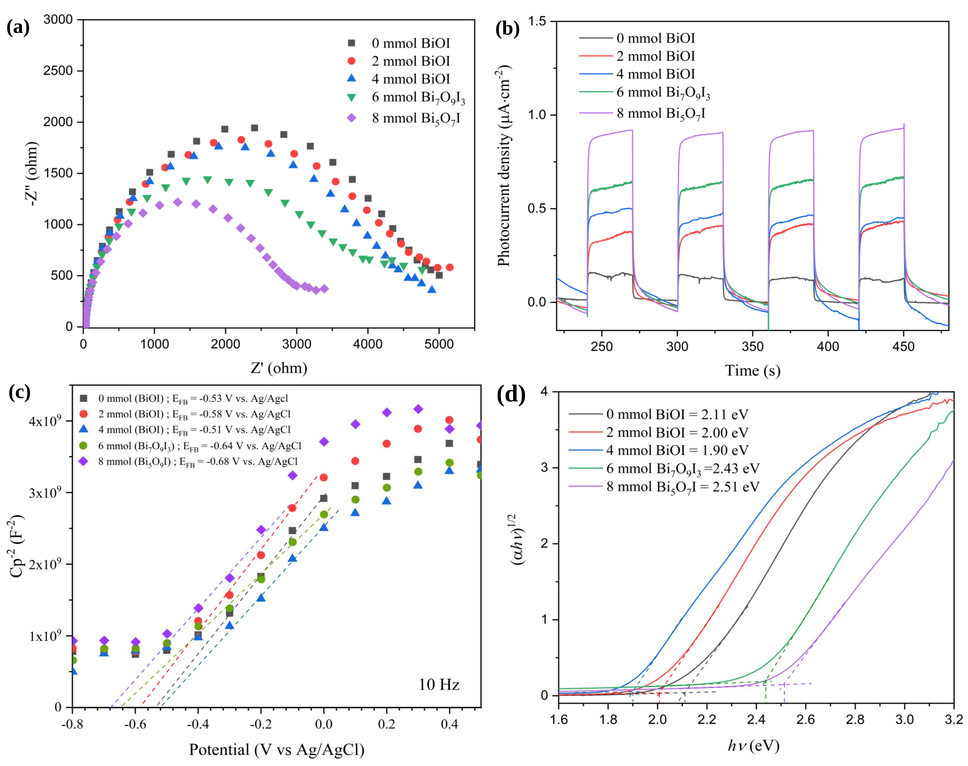

Fig. 8 (a) EIS Nyquist plots, (b) photocurrent responses, (c) Mott Schottky plots and (d) Tauc plots of the $Bi_xO_yI_z$ photocatalysts.

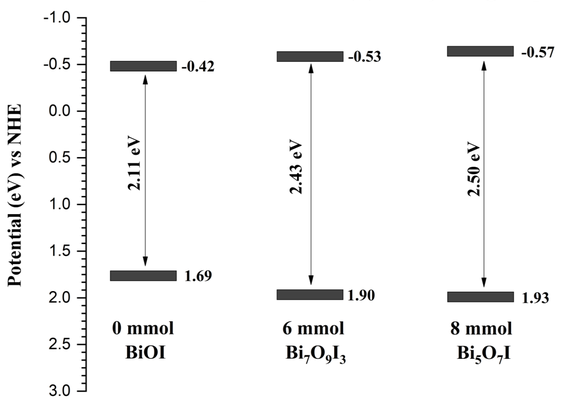

Fig. 9 Band structures of the photocatalysts.

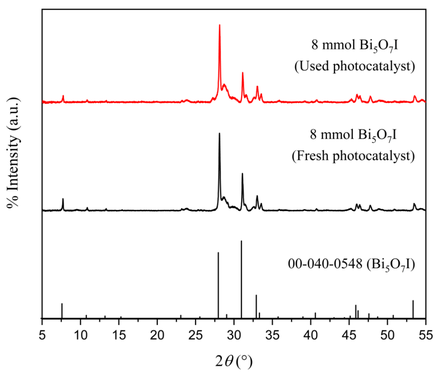

Fig. 7 XRD patterns and photo images of the fresh and used Bi_5O_7I photocatalysts after the 4th run.

Fresh photocatalyst:

Used photocatalyst:

Conclusion

Bismuth-rich oxyiodide (BiOI, $Bi_7O_9I_3$ and Bi_5O_7I) were successfully synthesized with varying NaOH contents. Bi_5O_7I (8 mmol NaOH) catalyst exhibited the greatest photooxidation efficiency; 98.80% of As(III) were converted to As(V). Additionally, the photooxidation efficiency was further improved in the basic solutions. The Nyquist plots revealed that the Bi_5O_7I electrode exhibited the smallest diameter, indicating the lowest charge-transfer resistance compared to the $Bi_7O_9I_3$ and BiOI electrodes. Photocurrent response of the Bi_5O_7I electrode exhibited the highest photocurrent density, reflecting great ability to produce photogenerated of e^-/h^+ under visible light irradiation. Recycling experiments demonstrated the excellent recyclability after four successive reactions for As(III) oxidation. A schematic of the band potentials of the materials illustrated that the bismuth-rich $Bi_xO_yI_z$ showed a higher bandgap energy than BiOI, enhancing oxidation and reduction ability of the photogenerated electrons and holes. Trapping experiments demonstrated that $\bullet O_2^-$ and •OH were the primary reactive species responsible for the photooxidation of As(III).

Acknowledgements

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References

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2. New J. Chem., 2024, 48, 12306-12314.