Fabrication of bismuth-rich $Bi_3O_4Br_xI_{1-x}$ solid solutions for improved photocatalytic N_2 fixation in pure water

Amanj Kheradmand, Yuxiang Zhu, Yijiao Jiang*

School of Engineering, Macquarie University, Sydney, NSW 2109, Australia

Background and Motivation

To date, ammonia (NH_3) has been chiefly synthesized by the Haber–Bosch process in the industry. This reaction consumes 1-3 % of global energy annually, releasing a massive volume of greenhouse gas emissions of carbon dioxide [1]. Considering the fossil fuels crisis and environmental concerns, developing a more sustainable process for NH_3 synthesis under mild conditions is crucial. Among different ways for fixing nitrogen (N_2) under ambient conditions, photocatalytic NH_3 generation has piqued researchers' interest due to its use of renewable solar energy as the driving force, low cost of materials, environmental friendliness, ease of operation, and low energy consumption [2]. However, the photocatalytic activity for NH_3 generation is still insufficient. This reaction involves the multiple-electron transfer and thus may be more kinetically challenging, requiring a significant amount of energy to overcome the kinetic limitations [3]. Another limitation is the cleavage of a highly stable N-N triple bond to activate dinitrogen [4]. Therefore, the development of novel photocatalysts with high efficiency for N_2 fixation is a significant challenge facing the scientific community. In this work, the bismuth-rich $Bi_3O_4Br_xI_{1-x}$ solid solutions were synthesized for improved photocatalytic NH_3 production.

Photocatalytic activity

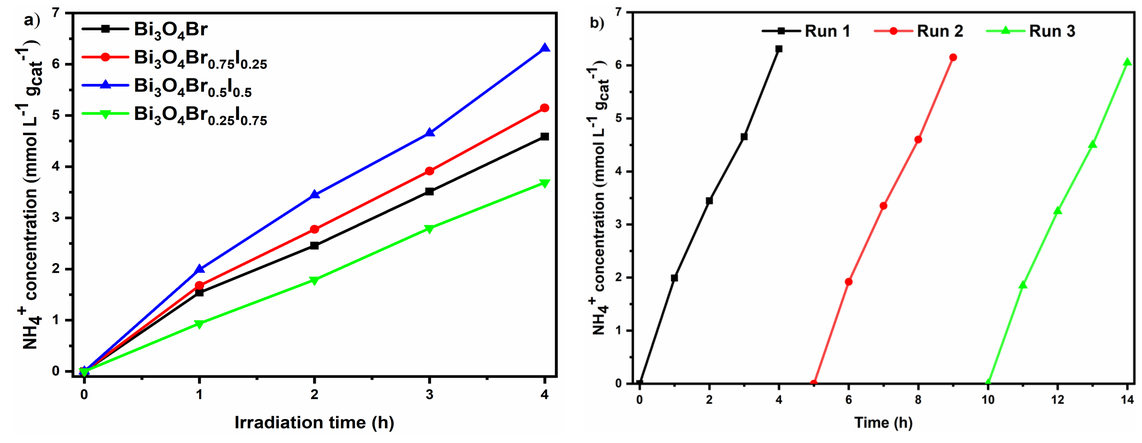

Figure 1. a) NH_3 generation over various $Bi_3O_4Br_xI_{1-x}$ photocatalysts. Reaction conditions: 40 mg of catalyst in 40 mL of DI water under visible light radiation (≥420 nm), b) Cycling runs for NH_3 generation over $Bi_3O_4Br_{0.5}I_{0.5}$

- $Bi_3O_4Br_{0.5}I_{0.5}$ exhibits the best photocatalytic rate of 6.308 mmol/L.g.
- $Bi_3O_4Br_{0.5}I_{0.5}$ reveals exceptional photocatalytic stability with almost no obvious reduction in activity.

Experimental results

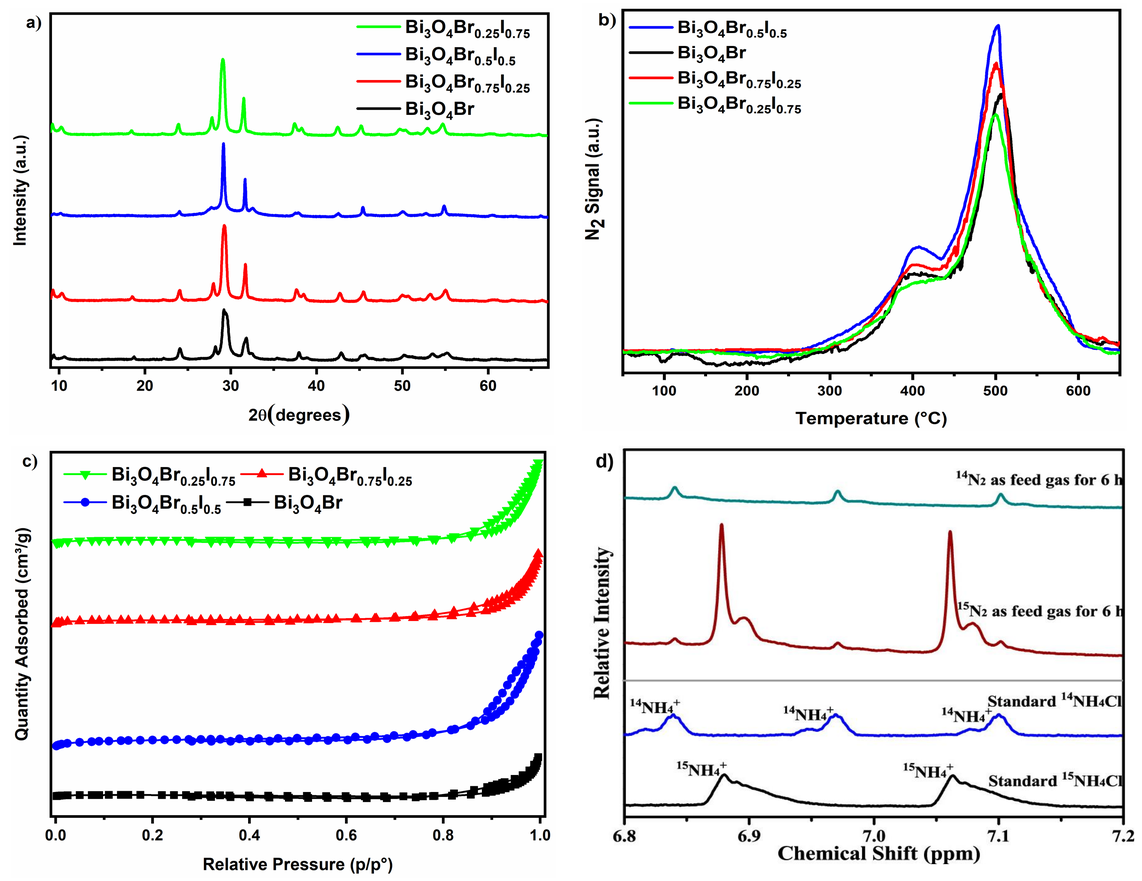

Figure 2. a) XRD patterns, b) N_2-TPD profiles, c) N_2 adsorption-desorption isotherms of the photocatalyst, d) ^1H NMR spectra (400 MHz) of the reaction medium produced from photocatalyst N_2 fixation over $Bi_3O_4Br_{0.5}I_{0.5}$ using $^{14}N_2$ or $^{15}N_2$ as feed and $^{14}NH_4Cl$ and $^{15}NH_4Cl$ samples.

- XRD test confirms the successful fabrication of $Bi_3O_4Br_xI_{1-x}$ solid solution.
- BET and TPD-N_2 analysis display that $Bi_3O_4Br_{0.5}I_{0.5}$ offers not only the higher surface area available for the photocatalytic reaction and but also offers the higher N_2 adsorption capacity and active sites.
- Isotope-labeling ^1H NMR experiments confirm that the generation of NH_3 originates from N_2 reactant.

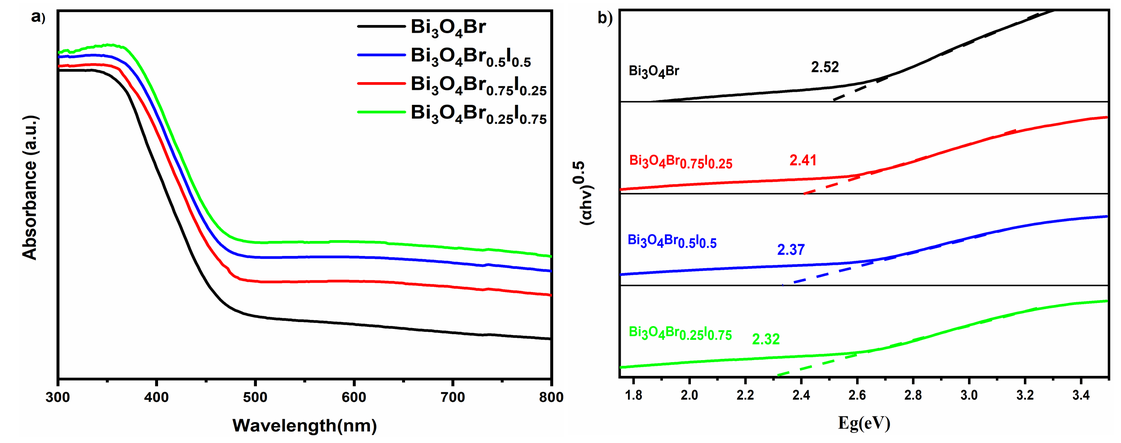

Figure 3. a) UV-Vis spectra for $Bi_3O_4Br_xI_{1-x}$ solid solution samples, b) Tauc plots of the samples.

- The bandgap value would be adjusted in $Bi_3O_4Br_xI_{1-x}$ samples by changing x from 1 to 0.25. The lower the x, the lower the bandgap.

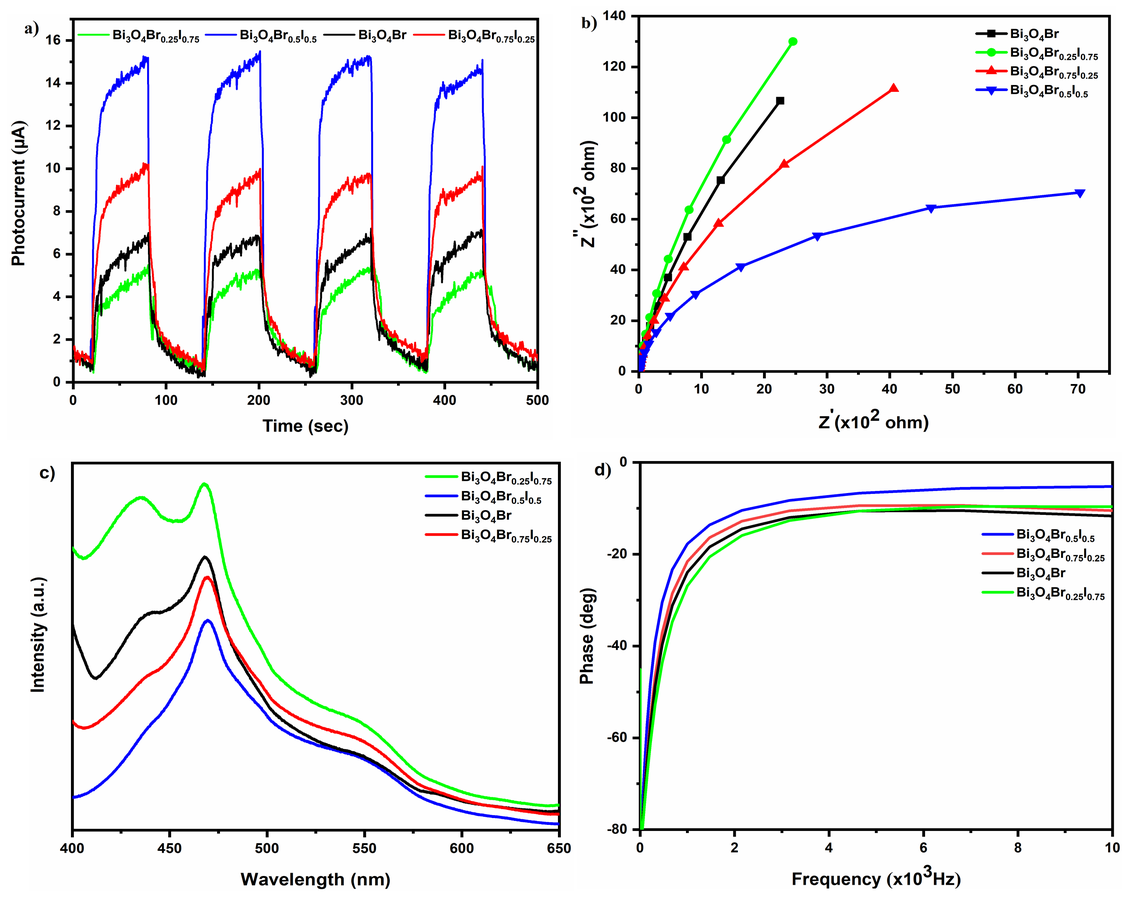

Figure 4. a) Photocurrent results, b) Electrochemical impedance spectroscopy (EIS), c) Photoluminescence (PL) spectra and d) Bode-phase curves of $Bi_3O_4Br_xI_{1-x}$ samples.

- Photocurrent and photoluminescence results demonstrate that $Bi_3O_4Br_{0.5}I_{0.5}$ shows enhancement in the separation of photogenerated electron-hole pairs compared to other samples.
- The EIS results show the resistance for the charge transportation reduced upon alerting Br/I molar ratio.
- Bode-phase indicates that $Bi_3O_4Br_{0.5}I_{0.5}$ has the highest electron's lifetime.

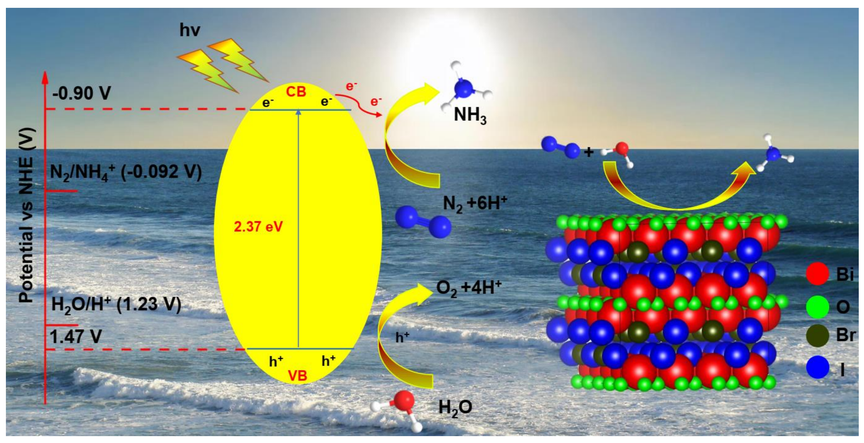

Figure 5. The possible mechanism of the NH_3 synthesis process over $Bi_3O_4Br_xI_{1-x}$ photocatalysts.

Conclusion

- When Br/I molar ratio is 1, the $Bi_3O_4Br_{0.5}I_{0.5}$ exhibits the highest photocatalytic activity in NH_3 generation in pure water without any sacrificial agent.
- Band gaps and band positions could be tunable via the collaborative combination of solid solution and bismuth-rich approaches.
- The improved activity of $Bi_3O_4Br_{0.5}I_{0.5}$ could be attributed to the enhanced photogenerated electrons and holes separation, light-harvesting, redox potential, N_2 chemisorption and declined the recombination rate.

References

1. C. J. M. van der Ham, *Chem. Soc. Rev.* 2014, *43* (15), 5183.
2. Y. Zhu et al., *ACS Appl. Mater. Interfaces.* 2021, *13* (28), 32937.
3. X. Chen et al., *Mater. Horizons.* 2018, *5* (1), 9.
4. M. Cheng et al., *J. Mater. Chem. A.* 2019, *7* (34), 19616.

printed by MegaPrint Inc. www.postersession.com