Development of a novel Bi^0-rGO composite with enhanced capture of iodine gas

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1. Introduction

Reprocessing of used nuclear fuel (UNF) assumes a significant role in lessening the generation of high level waste (HLW) but dealing with the highly radioactive spent fuel has always been a challenge.[1] Environmental concern is mainly for volatile iodine, ^{129}I due to its high toxicity and very long half-life of 1.57×10^7 years as well as negative effects on human health, and high environmental mobility.[2,3] For this reason, the capture and storage of iodine is an essential research area to prevent its harmful leakage in order to meet environmental regulations.

To our knowledge, the capture of radioactive iodine species by graphene-based materials is not fully explored. Not long ago, H. Zou et al. reported a novel composite named Bi_2S_3-RGO composite. The composite exhibited a very high iodine uptake capacity of about 1042.8 mg/g and could be successfully solidified in the glass composite material (GCM) in the forms of BiOI and Bi_5O_7I. [4] Another group of researchers [5] has developed bismuth-functionalized graphene oxide (GO) for the removal of both iodide and iodate from radioactive wastewater. Bi-GO showed removal efficiencies (≥95%) for both iodide and iodate which are significantly higher than those of silver-impregnated zeolites. BiOI and $Bi(IO_3)_3$ were the dominant iodine species on the material's surface upon iodide and iodate removal, respectively.

Recently, there has been a growing interest in using bismuth-based absorbents as an alternative to silver-based adsorbents for gaseous iodine capture by scholars at home and abroad due to its unique properties and low cost. Coupled with the excellent properties of bismuth and the high specific surface area of graphene, it is expected that the Bi^0-rGO composite will enable improvements in the maximum sorption capacity and rapid kinetics of iodine adsorption utilizing a chemical affinity for iodine as opposed to physical adsorption of iodine. Additionally, our previous studies and other works [6,7] revealed that metallic (Bi^0) exhibited better iodine adsorption performance than bismuth compounds (Bi_2O_3 & Bi_2S_3).

In this study, we synthesized and investigated a novel sorbent based on Bi^0 and reduced graphene oxide (rGO) with increased iodine capture efficiency. The obtained samples are then investigated using an x-ray diffractometer (XRD).

2. Methods and Results

In this section, Bi^0-rGO composite was prepared by a solvothermal route using Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) as bismuth source and L-Ascorbic acid ($C_6H_8O_6$) as reductant. The synthesis method and iodine adsorption experimental conditions are discussed below.

2.1 Synthesis of Bi^0-rGO composite

$Bi(NO_3)_3{\cdot}5H_2O$ (0.970 g), Graphene Oxide(GO) powder (0.2 g), $C_6H_8O_6$ (0.352g) were dispersed in 60 ml ethylene glycol (EG) and stirred vigorously for 1h followed by ultrasonication for 30 min to form a homogeneous dispersion. Then, the mixture was transferred into a 100 ml capacity of Teflon autoclave, sealed airtight, and heated at 180 ℃ for 24 h. After cooling down to room temperature naturally, the sample was then washed and centrifuged several times using ethanol. Finally, the sample was dried in a vacuum at 60 ℃ for 12 h to obtain a Bi^0-rGO composite. All reagents and chemicals were purchased from Sigma-Aldrich and used without further purification.

2.2 Iodine capture experiment

The iodine gas capture of Bi^0-rGO was studied in static air with a 700 ml desiccator as reported in the previous literature [6,8], as shown in **Fig.1**. Briefly, 0.2 g of non-radioactive iodine crystals are placed into the bottom of the desiccator. Then, 0.05 g Bi-rGO was placed on the stainless-steel plate above the iodine crystal, covered with a knobbed lid, and reacted at 200℃ for several times under static air, and the iodine capture capacity of Bi-rGO was calculated from Eq. (1) by weighing the mass change of the sample before and after iodine exposure at different time intervals.

$$q_e(mg/g) = \Delta m/m_s \times 1000 \quad (1)$$

where Δm (g) and m_s (g) are the mass gain and the initial mass of sorbent, respectively, and q_e (mg/g) represents the iodine capture capacity of sorbent.

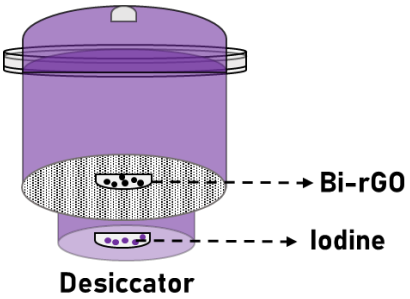

Fig. 1. Gaseous adsorption experimental setup

3. Result and Discussion

Fig. 2. shows a series of XRD analyses of rGO and synthesized Bi-rGO before and after I_2 sorption. Bi^0-rGO composite is comprised of Bi^0 which corresponds to the diffraction pattern of metallic Bi (PDF NO. 01-085-1330). After exposing to the iodine environment, some peaks of Bi^0 still appeared (PDF NO. 01-078-6571) but most of the peaks were attributed to bismuth iodide (BiI_3) (PDF NO. 00-048-1795). [6] Furthermore, the diffraction pattern peak of rGO can be observed with relatively low intensity. [9]

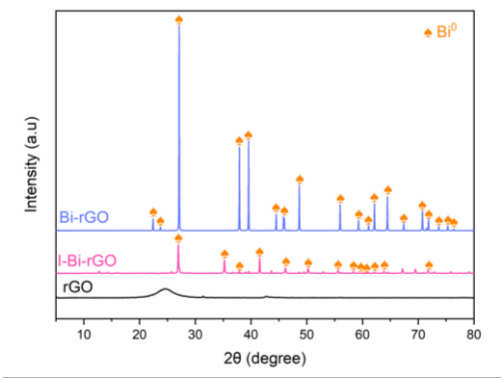

Fig. 2. PXRD patterns of rGO and synthesized Bi-rGO before and after I_2 exposure.

A series of iodine sorption experiments were performed on Bi^0-rGO under the conditions of 200 ℃ to assess the effect of contact time and isothermal sorption on their capture performance. As shown in **Fig. 3.**, the main focus was on the desorption experiments conducted on the samples to evaluate the proportion of total sorbed, chemisorbed and physisorbed of iodine. After the sorption experiment, the samples were reacted again at 130 ℃ for 4 h with an iodine-free and unsealed desiccator. The chemisorbed value can be obtained through Eq. (1) and the physiosorbed value can be calculated by subtracting from total sorbed value.

In **Fig.3a**., it is observed that the sorption reaction time increased from 0 to 150 min and then kept constant. The results showed that the sorption capacity reached a record sorption capacity of 1115.7 mg/g which is slightly higher than other reported materials. [4,10] Additionally, the high iodine capture capacity from the composite was mainly attributed to the chemisorbed in the stable form of BiI_3.

Fig.3.b. shows a different amount of iodine concentrations (C_e) tested with a reaction time of 4 h and a maximum sorption capacity of around ~1240 mg/g was achieved. Based on these results, the sorption mechanism of Bi^0-rGO will be further investigated through TGA, SEM, XPS and other analyses.

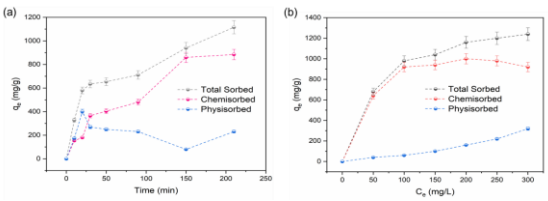

Fig. 3(a) Sorption kinetics (b) Sorption isotherm.

4. Conclusions

In this work, Bi^0-rGO composite was prepared by the solvothermal method and the results demonstrated the novel composite as an exceptional sorbent with a high iodine capture capacity (1115.7 mg/g) within 2 h, of which the chemisorbed amount was about 884.61 mg/g. Furthermore, the composite captured iodine gas mainly in the stable form of BiI_3 and further research is to be performed for the immobilization of the iodine waste forms produced for the stable storage of ^{129}I.

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REFERENCES

[1] S.U. Nandanwar, K. Coldsnow, V. Utgikar, P. Sabharwall, D. Eric Aston, Capture of harmful radioactive contaminants from off-gas stream using porous solid sorbents for clean environment – A review, Chem. Eng. J. 306 (2016) 369–381. https://doi.org/10.1016/j.cej.2016.07.073.

[2] J.H. Yang, Y.J. Cho, J.M. Shin, M.S. Yim, Bismuth-embedded SBA-15 mesoporous silica for radioactive iodine capture and stable storage, J. Nucl. Mater. 465 (2015) 556–564. https://doi.org/10.1016/j.jnucmat.2015.06.043.

[3] J.H. Yang, J.M. Shin, J.J. Park, G. Il Park, M.S. Yim, Novel synthesis of bismuth-based adsorbents for the removal of 129I in off-gas, J. Nucl. Mater. 457 (2015) 1–8.

https://doi.org/10.1016/j.jnucmat.2014.09.057.

[4] H. Zou, J. Guo, M. Song, F. Yi, X. Wang, N. Pan, H. Li, W. Li, L. Bian, Bi2S3-reduced graphene oxide composite for gaseous radioiodine capture and its immobilization within glass composite material, Prog. Nucl. Energy. 135 (2021) 103705. https://doi.org/10.1016/j.pnucene.2021.103705.

[5] S. Han, W. Um, W.S. Kim, Development of bismuth-functionalized graphene oxide to remove radioactive iodine, Dalt. Trans. 48 (2019) 478–485. https://doi.org/10.1039/C8DT03745K.

[6] Z. Tian, T.S. Chee, X. Zhang, L. Lei, C. Xiao, Novel bismuth-based electrospinning materials for highly efficient capture of radioiodine, Chem. Eng. J. 412 (2021) 128687. https://doi.org/10.1016/j.cej.2021.128687.

[7] A. Tesfay Reda, D. Zhang, X. Xu, M. Pan, C. Chang, C. Muhire, X. Liu, S. Jiayi, Bismuth-impregnated aluminum/copper oxide-pillared montmorillonite for efficient vapor iodine sorption, Sep. Purif. Technol. 270 (2021) 118848. https://doi.org/10.1016/J.SEPPUR.2021.118848.

[8] Z. Tian, T.S. Chee, L. Zhu, T. Duan, X. Zhang, L. Lei, C. Xiao, Comprehensive comparison of bismuth and silver functionalized nickel foam composites in capturing radioactive gaseous iodine, J. Hazard. Mater. 417 (2021) 125978. https://doi.org/10.1016/j.jhazmat.2021.125978.

[9] Z. Zhang, C. Zhou, L. Huang, X. Wang, Y. Qu, Y. Lai, J. Li, Synthesis of bismuth sulfide/reduced graphene oxide composites and their electrochemical properties for lithium ion batteries, Electrochim. Acta. 114 (2013) 88–94. https://doi.org/10.1016/j.electacta.2013.09.174.

[10] Q. Xian, L. Chen, W. Fan, Y. Liu, X. He, H. Dan, L. Zhu, Y. Ding, T. Duan, Facile synthesis of novel Bi0-SBA-15 adsorbents by an improved impregnation reduction method for highly efficient capture of iodine gas, J. Hazard. Mater. 424 (2021) 127678. https://doi.org/10.1016/j.jhazmat.2021.127678.