Hierarchical porous g-C$_3$N$_4$/Bi$_5$O$_7$I photocatalyst for high gaseous mercury removal

Hui Zhang$^1$, Dao Rao$^2$, Jiang Wu$^*$ and Yu Guan$^1$

$^1$ College of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai 200090, China
$^2$ State Power Investment Corporation Yuanda Environment Protection Co., Ltd. Chongqing 401120, China
$^*$Corresponding author’s e-mail: wjcfd2002@163.com

Abstract. The g-C$_3$N$_4$/Bi$_5$O$_7$I photocatalyst with a hierarchical porous nanostructure (CB-HPN) was successfully synthesized via one-step calcination method. The materials were characterized by XRD, SEM, XPS and PL to investigate the properties of porous nanostructure. The mercury removal efficiency of g-C$_3$N$_4$/Bi$_5$O$_7$I reached up to 80.3%, which was much higher than that of Bi$_5$O$_7$I. It was found that the hierarchical porous nanostructure could modulate the interface charge transfer tracks efficiently and increase the ratio of active factors, thus accelerating photocatalytic oxidation of gaseous mercury (Hg$^0$). Based on the characterization and experiment analysis, a reasonable charge transfer and reaction mechanism for Hg$^0$ oxidation is proposed.

1. Introduction

Gaseous mercury (Hg$^0$) is slowly converted into mercury vapour and can enter the body through the skin at normal temperature, causing neurological disorders, respiratory failure, and even death. It is extremely difficult to convert it into non-toxic substances[1]. The combustion of coal and garbage in thermal power plants is the main cause of mercury pollution. In recent years, the development of photocatalytic technology has given us a new insight for Hg$^0$ removal, and has great development potential in environmental repair[2].

Bismuth oxyhalides (Bi$_5$O$_7$X$_2$, X = Cl, Br and I) have received extensive research attention, because their unique layered structure consist of a layer of [Bi$_5$O$_7$]$^{2-}$ and double layers of X$^-$, such as Bi$_5$O$_7$Cl$_2$ [3, 4], Bi$_5$O$_7$Br [5, 6], and Bi$_5$O$_7$I$_2$ [7, 8]. Among them, Bi$_5$O$_7$I is one of the most promising photocatalysts[5]. However, the photocatalytic property of Bi$_5$O$_7$I is restricted by the carrier separation efficiency and the rapid recombination of light-induced electron-hole pairs (e$^-$-h$^+$). Hence, it is necessary to modify Bi$_5$O$_7$I to meet the requirement of high photocatalytic performance. Graphitic carbon nitride (g-C$_3$N$_4$) is a toxic-free semiconductor with satisfactory visible light response, structure similar to graphene and high chemical stability[9]. Fortunately, the electron structure of g-C$_3$N$_4$ appropriately matches to those of Bi$_5$O$_7$I, so it is expected to compound g-C$_3$N$_4$ with Bi$_5$O$_7$I to improve photocatalytic performance. In this work, we successfully fabricate a g-C$_3$N$_4$/Bi$_5$O$_7$I with hierarchical porous structure via one-step calcination method. The g-C$_3$N$_4$/Bi$_5$O$_7$I heterojunction efficiently modulate the interface electronic structure and provide abundant edge active sites during the photocatalytic process. The photocatalytic removal of Hg$^0$ was used to study the photocatalytic performance of the samples, and a migration path of charges is proposed and discussed.
2. Materials and Methods

Bi(NO$_3$)$_3$·5H$_2$O and KI are unprocessed and analytically pure. g-C$_3$N$_4$ was synthesized as indicated in the previous study conducted by Wu et al.[10]. Detailed synthesis process of g-C$_3$N$_4$/Bi$_5$O$_7$I composites was according to the following steps: Firstly, 5 mmol Bi(NO$_3$)$_3$·5H$_2$O and g-C$_3$N$_4$ (0.5, 1, 2 and 4 mmol) were dissolved in 100 mL deionized water with magnetic stirring for 30 minutes to get suspension A. 5 mmol KI was dissolved in 50 mL deionized water to get solution B. Then solution B was added to the A drop by drop to obtain a suspension. Subsequently, the suspension was stirred for 5 hours continuously. Then the precipitate was washed and dried at 80 °C for 6 hours. Next, the precursor was calcined at 460 °C for 3 hours (3 °C/min heating rate) in a muffle furnace. Finally, the samples were denoted at CB-0.5, CB-1, CB-2, and CB-4 respectively. Bi$_5$O$_7$I without g-C$_3$N$_4$ was prepared using the same method for contrast.

All the samples were tested by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectra (UV–vis DRS) and Photoluminescence spectra (PL) to demonstrate the characterizations clearly.

The photocatalytic properties of the samples were evaluated with an experimental system (Figure 1) resemblance to the previous study conducted[11]. Samples (30 mg) were spread uniformly onto a glass plate in a photocatalytic reactor. The entrance Hg$^+$ concentration ($C_{in}$) was set as 60 µg/m$^3$. The mercury removal efficiency (MRE) under 9W LED irradiation with the filter ($\lambda <$ 400 nm) is calculated according to the following equation (1).

$$\eta(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

$C_{out}$ is the mercury concentration (µg/m$^3$) of the outlet of the reactor system.

3. Results and Discuss

The XRD patterns of the materials are illustrated in Figure 2. The peaks of the Bi$_5$O$_7$I sample are in good consistent with the tetragonal phase of Bi$_5$O$_7$I (JCPDS: 40-0548)[9], and the characteristic peaks located at 7.5°, 27.9°, 30.9°, 33° and 45.9° are indexed to (001), (312), (004), (204) and (604) planes of Bi$_5$O$_7$I respectively, which indicates the samples have good crystallinity. It is noticed that the typical pattern of (002) planes at 27.4° for g-C$_3$N$_4$ could not be found in the XRD patterns of g-C$_3$N$_4$/Bi$_5$O$_7$I composites, which may be because the proportion of g-C$_3$N$_4$ in the nanocomposite is so low that the main peaks of Bi$_5$O$_7$I overlaps with that of g-C$_3$N$_4$ [12]. To determine the spatial distribution of Bi, O, I, C, and N elements, the elemental mapping analysis is adopted. As shown in Figure 3, g-C$_3$N$_4$ is supported on Bi$_5$O$_7$I, and the two samples are closely linked together, creating conditions for forming a heterojunction. The results further prove the samples are g-C$_3$N$_4$/Bi$_5$O$_7$I composites.

Figure 1. Diagram of the experimental system.
Figure 2. XRD patterns.

SEM and TEM analyses reveal the structure and morphological characteristics and microstructure of the samples, respectively. Figure 4a demonstrates that pure Bi$_5$O$_7$I sample is composed of uniform nanosheets. With the insertion of g-C$_3$N$_4$, compared with pure Bi$_5$O$_7$I, nanosheets are destroyed and the porous nanostructure appears as shown in Figure 4b. This is because the doping of g-C$_3$N$_4$ during the calcination process destroys the crystal state of Bi$_5$O$_7$I crystal. Moreover, as we can see (Figure 4c), the porous structure is uniform and neat, and the pore size is about 40 nm. For the further investigation of g-C$_3$N$_4$/Bi$_5$O$_7$I, HRTEM image was conducted and the lattice fringes were clearly shown in Figure 4d. The crystal spacing of the measured area was about 0.834 nm, which was coincide with the (001) plane of the monoclinic Bi$_5$O$_7$I.

![Figure 2: XRD patterns](image)

![Figure 3: Elemental mapping](image)

![Figure 4: (a) SEM images of Bi$_5$O$_7$I, (b) SEM images of CB-1, (c)TEM image, (f) HRTEM image](image)

In the survey XPS spectrum (Figure 5a), the peak intensity of CB-1 is much lower than that of Bi$_5$O$_7$I. And the main elements of CB-1 are Bi, I, O, C and N, which is supported by the elemental mapping results. The low C 1s and N 1s peak is due to the low weight doping ratio of g-C$_3$N$_4$. This is consistent with the reason why the g-C$_3$N$_4$ peak in the XRD pattern is covered. The characteristic peaks of Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ are located at 159.35 eV and 164.60 eV respectively, indicating that Bi ion is +3 valences (Figure 5b). Compared with pure Bi$_5$O$_7$I, the peaks of Bi 4f shift 0.26 eV to the higher binding energy, which is ascribed to the formation of heterojunctions between Bi$_5$O$_7$I and g-C$_3$N$_4$. Figure 5c shows two distinct peaks of the C 1s at 284.8 eV and 288.6 eV. The peak around 284.8eV assigned to sp2 bonded carbon (C=C), which can be used as the correction for specimen, while the peak at 288.6 eV is attributed to the functional groups of sp2 bond carbon in N-containing
aromatic rings (N-C=N) [9]. Figure 5d shows that N 1s XPS spectrum of the composite. The fitting results of N 1s are decomposed into two separate peaks: 398.95 eV and 400.68 eV, which are bound to the C-N=C and C-N-H respectively. The XPS results also confirmed the coexistence of g-C₃N₄ and Bi₂O₃-I in the composite, which is consistent with the observation from TEM and XRD.

![Figure 5. (a) XPS spectra, (b) Bi 4f, (c) C 1s, (d) N 1s.](image)

In Figure 6a, the absorption efficiency of g-C₃N₄/Bi₂O₃-I, Bi₂O₃-I should be at the same level according to the DRS spectra. So the photocatalytic properties improvement should come from the influence of porous nanostructure. Porous nanostructure helps to improve the separation efficiency of photogenerated carriers. For proving this point, the PL spectra of samples are shown in Figure 6c. Generally, low PL intensity means light-induced e⁻-h⁺ recombination rate is low [13]. Compared with g-C₃N₄ and Bi₂O₃-I, the PL signal intensity for the g-C₃N₄/Bi₂O₃-I with hierarchical porous nanostructure is substantially lower, which clearly shows that the uniform porous structure entirely reduce recombination rate of charges.

The energy band structure of g-C₃N₄/Bi₂O₃-I should be confirmed to the photo-induced e⁻-h⁺ separation mechanism. In the inset (Figure 6a), the band gap energy ($E_g$) of g-C₃N₄ and Bi₂O₃-I determined from the band gap equation are about at 2.70 and 3.05 eV respectively [11]. This is consistent with the previous work[14]. In Figure 6b, Mott–Schottky plots of g-C₃N₄ and Bi₂O₃-I with a frequency of 2000 Hz is showed. According to the Mott-Schottky equation[15], the flat potentials of Bi₂O₃-I and g-C₃N₄ are calculated to be −0.50V and −0.69 V versus the Ag/AgCl electrode, respectively. They are equal to −0.30 V and −0.49 V versus NHE (the normal hydrogen electrode) at the same time [16]. So, the valence band (VB) positions of Bi₂O₃-I and g-C₃N₄ are 2.75 and 2.21 V, respectively ($E_{VB} = E_g - E_{CB}$).

The photocatalytic performances of g-C₃N₄, Bi₂O₃-I and g-C₃N₄/Bi₂O₃-I composites are revealed in Figure 6d. Obviously, mercury removal efficiencies (MREs) of the Bi₂O₃-I and g-C₃N₄ are 56.9% and 31.4%, respectively. Among g-C₃N₄/Bi₂O₃-I, the photocatalytic performance of CB-I is the best and MRE is up to 80.3%, which is consistent with PL emission spectra. The MREs of g-C₃N₄/Bi₂O₃-I are generally higher than that of Bi₂O₃-I. It is due to the electron transfer system formed between g-C₃N₄ and Bi₂O₃-I. Moreover, porous nature leads to an increase in the number of heterogeneous junction interfaces and active centers. It is interpreted that the porous feature plays a vital role in modulating the interface electron band structure and enhancing photocatalytic performance.
Figure 6. (a) UV–vis DRS; (αhν)^1/2 versus (hν) plot (the inset); (b) the Mott–Schottky plots; (c) PL spectra; (d) Removal efficiency.

Based on the above analysis, a reasonable charge transfer mechanism in the photocatalytic process is proposed and displayed in Figure 7a. Obviously, visible light irradiation triggers the formation of e^−h^+ of Bi$_2$O$_3$I and g-C$_3$N$_4$. Since the CB position of Bi$_2$O$_3$I is more positive than that of g-C$_3$N$_4$, the migration of photoelectrons (e^−) from g-C$_3$N$_4$ to Bi$_2$O$_3$I is advantageous. These cumulative e^− located in the CB of Bi$_2$O$_3$I can reduce O$_2$ to •O$_2^−$, because the potential of those e^− (-0.30) is lower than the standard reduction potential of O$_2$/•O$_2^−$ (-0.28 eV). Meanwhile, the remaining holes (h^+) in the VB of Bi$_2$O$_3$I migrate to that of g-C$_3$N$_4$. Holes in the VB of g-C$_3$N$_4$ (2.21 eV) can oxidize OH^− to •OH since the standard reduction potential of •OH/OH^− is 1.99 eV. The photogenerated charges can be efficiently separated and transferred in the g-C$_3$N$_4$/Bi$_2$O$_3$I interface/edge, which enhances their interfacial migration efficiently. Thus, in the photocatalytic process, the efficiency of mercury removal under visible-light irradiation is enhanced, and Hg$^0$ is converted into non-toxic substances by active substances.

Figure 7. Schematic illustration for the charge transfer and separation in system.

4. Conclusions
In summary, g-C$_3$N$_4$/Bi$_2$O$_3$I heterojunction was fabricated by one step calcination method. The porous properties of the nanomaterials facilitate electron transport and provide abundant edge active sites in the photocatalytic process, greatly improving photocatalytic performance and enhance the efficiency of mercury removal under visible-light irradiation. This paper not only provides new direction for the controllable construction of hierarchical porous structure, but also promotes new ideas for designing photocatalysts to solve environmental pollution.
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References
[1] Zhang, X., Wang, D., Man, X., Wu, J. (2019) Influence of BiOIO3 morphology on the photocatalytic efficiency of Z-scheme BiOIO3/g-C3N4 heterojunctioned composite for Hg(0) removal. J. Colloid Interface Sci., 558: 123-136.
[2] Zhang, H., Tan, S., Wang, D., Wu, J., Xu, W., Zhao, S., Sun, X., Liu, Q., Liu, H., Guan, Y. (2020) Fabrication of bionic flower-like g-C3N4/Bi4O5I2 photocatalyst with enhanced photocatalytic performance. Chem. Phys. Lett., 751.
[3] He, R., Cao, S., Yu, J., Yang, Y. (2016) Microwave-assisted solvothermal synthesis of Bi4O5I2 hierarchical architectures with high photocatalytic performance. Catal. Today, 264: 221-228.
[4] Wang, F., Zhang, J., Jia, D., Ma, Y., Ma, L. (2019) Flower-like structured Fe3O4–MQDs/Bi2WO6/GNs heterojunction with high-efficiently charge transfer for organic contaminants degradation. J. Taiwan Inst. Chem. E., 99: 276-283.
[5] Cheng, H., Wu, J., Liu, Q., Qi, Y. (2019) Morphology-dependent photocatalytic activity of BiSO7I: Different charge separation efficiencies caused by facet synergy and internal electric field. Mater. Lett., 252: 252-255.
[6] Ding, C., Ye, L., Zhao, Q., Zhong, Z. (2016) Synthesis of BixOyIz from molecular precursor and selective photoreduction of CO2 into CO. J. CO2 UTIL., 14: 135-142.
[7] Liu, H., Su, Y., Chen, Z., Jin, Z., Wang, Y. (2014) Bi7O9I3/reduced graphene oxide composite as an efficient visible-light-driven photocatalyst for degradation of organic contaminants. J. Mol. Catal. A-Chem., 391: 175-182.
[8] Xiao, X., Zhang, W.-D. (2011) Hierarchical Bi7O9I3 micro/nano-architecture: facile synthesis, growth mechanism, and high visible light photocatalytic performance. RSC Adv., 1: 1099-1105.
[9] Geng, X., Chen, S., Lv, X., Jiang, W., Wang, T. (2018) Synthesis of g-C3N4/Bi5O7I microspheres with enhanced photocatalytic activity under visible light. Appl. Surf. Sci., 462: 18-28.
[10] Wu, J., Sheng, P., Xu, W., Zhou, X., Lu, C. (2018) Constructing interfacial contact for enhanced photocatalytic activity through BiOIO3/g-C3N4 nanoflake heterostructure. Catal. Commun., 109: 55-59.
[11] Sun, X., Wu, J., Li, Q., Liu, Q. (2017) Fabrication of BiOIO3 with induced oxygen vacancies for efficient separation of the electron-hole pairs. Appl. Catal. B-Environ., 218: 80-90.
[12] Dong, Z., Pan, J., Wang, B., Jiang, Z. (2018) The p-n-type Bi5O7I-modified porous C3N4 nanoheterojunction for enhanced visible light photocatalysis. J. of Alloy Compd., 747: 778-795.
[13] He, Y., Zhang, Y., Huang, H., Tian, N., Luo, Y. (2014) Direct hydrolysis preparation for novel bi-based oxysalts photocatalyst Bi6O5(OH)3(NO3)5·5H2O with high photocatalytic activity. Inorg. Chem. Commun., 40: 55-58.
[14] Cheng, H., Wu, J., Tian, F., Liu, Q. (2019) Visible-light photocatalytic oxidation of gas-phase Hg0 by colored TiO2 nanoparticle-sensitized BiSO7I nanorods: Enhanced interfacial charge transfer based on heterojunction. Chem. Eng. J., 360: 951-963.
[15] Zeng, C., Hu, Y., Guo, Y., Zhang, T. (2016) Achieving tunable photocatalytic activity enhancement by elaborately engineering composition-adjustable polynary heterojunctions photocatalysts. Appl. Catal. B-Environ., 194: 62-73.
[16] Sayama, K., Nomura, A., Arau, T., Sugita, T., Sugihara, H. (2006) Photoelectrochemical Decomposition of Water into H2 and O2 on Porous BiVO4 Thin-Film Electrodes Under Visible Light and Significant Effect of Ag Ion Treatment. J. Phys. Chem. B, 110: 11352-11360.