Enhanced LED-light-driven photocatalytic antibacterial by g-C₃N₄/BiOI composites

Yeping Li¹ · Qian Wang¹ · Liying Huang² · Xiuquan Xu¹ · Meng Xie¹ · Hao Wang¹ · Shuquan Huang² · Fei Zhang² · Zhengyun Zhao² · Juan Yang³

Received: 5 September 2018 / Accepted: 11 December 2018 / Published online: 17 December 2018
© Springer Science+Business Media, LLC, part of Springer Nature 2018

Abstract

g-C₃N₄/BiOI composites with different ratios were prepared by in-situ generation route at room temperature and applied in antibacterial investigation. Detailed information of the composites was characterized by XRD, TEM, HRTEM, SEM, EDS, BET, XPS, FT-IR, UV-Vis, photocurrent and EIS. The obtained g-C₃N₄/BiOI composites presented excellent antibacterial performance toward *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) under LED track light, with the complete inactivation of bacterial within 30 min. The decomposition of bacterial cells was observed by SEM. The bacterial mechanism was investigated by trapping experiments: holes (h⁺), superoxide anion free radical (O₂^{•-}) and hydrogen peroxide (H₂O₂) were identified as active species for bacterial inactivation, and h⁺ had a main effect in the antibacterial process. The enhanced photocatalytic activities were assigned to an efficient separation and transition of electrons (e⁻) and h⁺ in photocatalytic antibacterial process. This work indicated the g-C₃N₄/BiOI composites are promising photocatalytic antibacterial materials for water disinfection.

1 Introduction

Waterborne bacteria/viruses pose a great threat to human health. Although microorganisms can be inactivated by strategies, such as chlorination [1], ozonization [2], UV irradiation and filtration [3]. However, these technologies also showed some drawbacks, such as high cost, harmful by-products, and low efficiency. It is an urgent need to establish an efficient and environment-friendly approach. Photocatalytic technology based on semiconductor materials can be deemed as a low-cost, environment-friendly advanced oxidation technology and a green way that can inactivate all kinds of microorganisms efficiently [4–7]. For the traditional photocatalytic materials, such as TiO₂ and ZnO [8–10], there are low efficiency of quantum conversion, poor visible light response and low utilization of solar energy, it is difficult to

satisfy the needs of practical applications. Therefore, fabricating novel photocatalytic material with high quantum efficiency, wide spectral response and friendly environment is an interesting work in the field of photocatalytic antibacterial research [11, 12].

Among many visible light-responsive photocatalytic materials, carbon nitride (g-C₃N₄), a polymer semiconductor graphite phase carbonitride, attracts much attention due to its metal-free composition, low cost, structural stability and unique structure of electron band [13–15]. For the monomer g-C₃N₄, because of rapid combination of the photogenerated e⁻ and h⁺, the h⁺ on the valence band (VB) of g-C₃N₄ are not sufficient for the degrading pollutions and inactivating the microorganisms in the environment efficiently. Therefore, nanostructured g-C₃N₄ with large surface area has been designed to improve the performance of g-C₃N₄ under visible light [16–21]. Furthermore, the composites based on g-C₃N₄ have been investigated in photocatalyst antibacterial field, for example, Ag-ZnO/g-C₃N₄ [22], Ag/g-C₃N₄ [23, 24], RGO/g-C₃N₄ [25], TiO₂/g-C₃N₄ [26] etc. By combining materials (Ag, RGO) with good electric ability or semiconductor (ZnO, TiO₂), the composites showed enhanced photocatalytic performance due to the efficient separation of e⁻ and h⁺.

✉ Yeping Li
ypeli@ujs.edu.cn

¹ School of Pharmacy, Jiangsu University, Zhenjiang 212013, People's Republic of China

² School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China

³ School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China

With a narrow band gap (1.77 eV), BiOI have been regarded as one of the most promising material to decontaminate water [27–30]. At present, there have been a lot of investigation on BiOI photocatalytic antibacterial materials, such as BiOI–AgI [31], Ag@AgI/Bi–BiOI [32], Ag/BiOI [33], Ti/BiOI [34] etc. By constructing heterostructures, the activity of these composite catalysts can be enhanced due to the efficient separation of e^- and h^+ . Recently, BiOI and $g-C_3N_4$ were coupled to construct $g-C_3N_4$ /BiOI composites [35–40], which were applied to resolve environmental problems, such as the degradation of MO [35], MB [35, 36], RhB [35, 40] etc. However, the investigation of $g-C_3N_4$ /BiOI composites were mainly focused on the degradation of pollution, there is only one work in the field of photocatalytic antibiosis [41]. In their work, the xenon was selected as the light source and the antibacterial process lasted 7 h against *E. coli*. In view of excellent performance of $g-C_3N_4$ /BiOI composites in degradation of pollution and the preliminary exploration on antibacterial, the obtained $g-C_3N_4$ /BiOI composites are anticipated to show high photocatalytic performance towards photocatalytic antibacterial field.

In this study, $g-C_3N_4$ /BiOI composites were synthesized based on in-situ generation method at room temperature. Results showed that $g-C_3N_4$ /BiOI composites presented high photocatalytic performance towards the destroying of *E. coli* and *S. aureus*. Meanwhile, all the antibacterial experiments were carried out under LED track light irradiation (In this work, it was noted as LED light, the emission wavelength: 450 ± 10 nm), which is stable, low energy-consuming and environmentally-friendly. Compared with previous reported literature [41], our work broadened the scope of antibacterial research, shortened the antibacterial time and improved the antibacterial performance: the obtained $g-C_3N_4$ /BiOI composites could kill *E. coli* and *S. aureus* within 30 min under LED light. Moreover, the $g-C_3N_4$ /BiOI composites were characterized by various tests, and the mechanism of the photocatalytic antibacterial process was investigated by trapping experiments.

2 Experiments

2.1 Materials

All reagents (from Sinopharm Company) were used without being purified. Distilled water was applied to every experiment in this work.

2.2 Synthesis of $g-C_3N_4$ and $g-C_3N_4$ /BiOI

$g-C_3N_4$ was obtained by the traditional calcination route. Firstly, urea was added to alumina crucible. Under air atmosphere, the temperature was raised up to 160 °C with 20 °C/

min heating rate and kept for 1 h in muffle furnace. Then, the temperature was raised to 520 °C with the same heating rate and kept for 2 h. Finally, the product was cooled to 25 °C and then yellow $g-C_3N_4$ was collected.

$g-C_3N_4$ /BiOI composites were prepared by in-situ generation method at room temperature. 0.97 g $Bi(NO_3)_3 \cdot 5H_2O$ and 0.176 g $g-C_3N_4$ were put into in 30 mL ethylene glycol (EG) under ultrasonication for 1 h to form solution A; 0.332 g KI and 0.08 g NaOH were put into in 40 mL distilled water to form solution B; the solution B was added drop by drop into the solution A by stirring for 1 h. Then, the obtained sediments were washed by distilled water and ethyl alcohol several times. Finally, the obtained sample was dried at 60 °C, which was named as 20% $g-C_3N_4$ /BiOI (the mass content of $g-C_3N_4$ in the composite was 20%). Similarly, 10% $g-C_3N_4$ /BiOI and 30% $g-C_3N_4$ /BiOI composite were synthesized by adjusting the content of $g-C_3N_4$.

2.3 Materials characterization

The crystal phase of photocatalyst was tested by X-ray powder diffraction (Shimadzu XRD-6000 X-ray diffractometer) at a scan rate of 7 °C/min. The morphologies were observed by transmission electron microscope (JEOL JEM-2010) and scanning electron microscope (JEOLJSM-7001F), which was equipped with an energy-dispersive spectroscope (EDS). The pore size and pore distribution were conducted by Brunauer–Emmett–Teller (BET) (TriStar II 3020 surface area and porosity analyzer). The surface species of the composite were obtained by X-ray photoelectron spectroscopy (XPS) with a monochromatic Mg $K\alpha$ source. The functional groups of the samples were detected by using a fourier transform infrared spectrometer (FT–IR). The absorption performance of light was analyzed through a UV–Vis diffuse reflection spectroscopy (DRS) (Shimadzu UV-2450 spectrophotometer). The photocurrent and the electrochemical impedance spectroscopy (EIS) were measured by the electrochemical workstation (CHI 760B Chenhua Instrument Company). The antimicrobial performance of $g-C_3N_4$ /BiOI composites was estimated by LED track light (Shenzhen Hanwen Lighting Technology Company).

2.4 Electrochemical experiments

The photocurrent and the electrochemical impedance spectroscopy (EIS) were measured by the electrochemical workstation. The preparation procedures of working electrodes were as follows: First of all, 5 mg sample was dissolved in 1 mL EG to make a slurry. Then, 20 μ L suspensions were coated into indium tin oxide (ITO) glass with 1 cm $\times$ 0.5 cm area. Finally, the electrode was dried at 60 °C for 2 h. Besides, platinum plate and saturated calomel electrode (SCE) as the counter electrode and the reference electrode,

respectively. 0.1 M Na_2SO_4 and 0.1 M KCl solution containing 5 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ were used as the electrolyte in the photocurrent and EIS, respectively.

2.5 Antibacterial activity

The antimicrobial performance of $\text{g-C}_3\text{N}_4/\text{BiOI}$ composites was estimated by using *E. coli* and *S. aureus* as the model of bacteria, 35 W LED light as the light source. All the glasswares and nutrient agar related in the experiment were sterilized at 121 °C for 30 min. The bacteria grew in the nutrient broth at 37 °C for 16 h under agitating at 180 rpm. The received bacteria suspensions was centrifuged at 10000 rpm for 6 min and washed with sterilized saline solution (0.85% NaCl) several times to exclude the impact of the fluid medium. Then the bacterial particles were suspended in a sterilized salt solution. The bacteria level for antibacterial process was 10^7 colony forming units (CFU)/mL, which was modulated by gradient dilution using sterilized saline (0.85% NaCl).

The sample was added to a saline solution containing bacteria (concentration of sample was 0.2 mg/mL). Under aseptic conditions, the LED light was turned out, and the mixed solution with catalyst and bacteria were sucked out at 0 min, 5 min, 10 min, 20 min, and 30 min, respectively. Then, at the end of reaction, the 100 μL mixed solution with catalyst and bacteria were coated evenly on the culture medium, and then the culture mediums were placed in the incubator at 37 °C for 18 h. All the experiments were parallel to three times, and the data shown in this paper were the average of three times.

3 Results and discussion

3.1 XRD analysis

To determine the crystal structure of BiOI, $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{BiOI}$ composites, X-ray powder diffraction spectra were presented in Fig. 1. For $\text{g-C}_3\text{N}_4$, the diffraction peak at 13.1° corresponded to the (100) crystal face, which was assigned to the structure of the triazine ring; the peak at 27.4° corresponded to the (002) crystal plane, which belonged to the stacking peak of the conjugated aromatic ring [42–44]. For BiOI, the diffraction peaks were assigned to (001), (002), (012), (110), (013), (004), (020), (114), (212) crystal plane, which was consistent with the standard BiOI card (JCPDS10-0445) [45]. For $\text{g-C}_3\text{N}_4/\text{BiOI}$ composites, the diffraction peaks were assigned to BiOI, and there were no obvious diffraction peaks of $\text{g-C}_3\text{N}_4$. The result is probably attributed to low contents of $\text{g-C}_3\text{N}_4$ in the $\text{g-C}_3\text{N}_4/\text{BiOI}$ composites and weak crystalline properties of $\text{g-C}_3\text{N}_4$.

Fig. 1 XRD patterns of the BiOI, $\text{g-C}_3\text{N}_4$ and $\text{g-C}_3\text{N}_4/\text{BiOI}$ composites

3.2 Morphological analysis

The morphology of BiOI, $\text{g-C}_3\text{N}_4$, 20% $\text{g-C}_3\text{N}_4/\text{BiOI}$ composite were investigated by TEM (Fig. 2A–C), HRTEM (Fig. 2D, E) and SEM (Fig. 2F). For BiOI, it could be observed flower like microstructure with plenty of nanosheets (Fig. 2A). In case of $\text{g-C}_3\text{N}_4$, lamellar structure were observed clearly (Fig. 2B). For 20% $\text{g-C}_3\text{N}_4/\text{BiOI}$ composite, BiOI nanosheets (dark area) overlapped with $\text{g-C}_3\text{N}_4$ (gray area) each other (Fig. 2C), indicating the successful formation of heterojunction between BiOI and $\text{g-C}_3\text{N}_4$. As the heterojunction interface could facilitate the separation of e^- and h^+ to improve photocatalytic efficiency, in order to further understand heterojunction interface, the HRTEM images were obtained and shown in Fig. 2D, E. From Fig. 2D, it could be found the BiOI nanosheets (black area) attaching to the surface of $\text{g-C}_3\text{N}_4$ (grey area). The area marked by red box in Fig. 2D was enlarged in Fig. 2E. As can be observed in Fig. 2E, the lattice fringes have a spacing of 0.458 nm, corresponding to interplanar spacing of (002) of BiOI (JCPDF 10–0045). The results are accordance with the XRD results (Fig. 1). Figure 2F, G showed the SEM image and EDS spectrum of 20% $\text{g-C}_3\text{N}_4/\text{BiOI}$ composite, respectively. Clearly, the BiOI nanoflowers were attached on the $\text{g-C}_3\text{N}_4$ nanosheets (Fig. 2F), which displayed a good combination of $\text{g-C}_3\text{N}_4$ and BiOI. EDS indicated the existence of C, N, O, Bi and I element in the 20% $\text{g-C}_3\text{N}_4/\text{BiOI}$ composite. It should be noted that Si element originates from silicon base. Based on the TEM, HRTEM, SEM and EDS analysis, it can be concluded that the heterojunction structure formed in the $\text{g-C}_3\text{N}_4/\text{BiOI}$ composites.

Fig. 2 TEM images of **A** BiOI, **B** g-C₃N₄, **C** 20% g-C₃N₄/BiOI composite; **D** HRTEM of 20% g-C₃N₄/BiOI composite; **E** magnified image of the area noted by red circle in **D**; **F** SEM of 20% g-C₃N₄/BiOI composite; **G** EDS of the area noted by red box in **F**. (Color figure online)

3.3 BET analysis

In order to investigate the surface property changing of the g-C₃N₄/BiOI composites after introducing g-C₃N₄ into BiOI, the S_{BET} dates were obtained. The S_{BET} of 10%

g-C₃N₄/BiOI, 20% g-C₃N₄/BiOI and 30% g-C₃N₄/BiOI composites are 26.50 m² g⁻¹, 29.45 m² g⁻¹ and 44.38 m² g⁻¹, respectively, which are much higher than that of pure BiOI (13.87 m² g⁻¹). In view of the large surface area g-C₃N₄ (96.01 m² g⁻¹), the S_{BET} of g-C₃N₄/BiOI composites

increases with the increasing weight content of g-C₃N₄. This fact implies that the existence of g-C₃N₄ is favorable for the formation of high specific surface areas of g-C₃N₄/BiOI composites.

3.4 XPS analysis

The surface species and chemical states of 20% g-C₃N₄/BiOI composite were investigated by XPS spectra (Fig. 3). The high resolution peaks of Bi 4f XPS spectra of the sample were at about 158.9 and 164.1 eV (Fig. 3A), which were according to the characteristic of Bi 4f_{7/2} and Bi 4f_{5/2} [37,

46]. The O 1s peak was at 529.7 eV (Fig. 3B), which was assigned as the Bi–O bond in [Bi₂O₂] layer of BiOI [37, 46]. For I 3d spectrum, the peaks located at 618.8 and 630.3 eV (Fig. 3C) corresponded to the binding energies of I 3d_{5/2} and I 3d_{3/2} [37, 46]. For C 1s spectrum (Fig. 3D), it can be observed two distinct peaks at 284.7, 288.1 eV and a weak peak at 286.1 eV. The peak at 284.7 was attributed to the adventitious carbon on the surface of g-C₃N₄, and the peak at 288.1 eV was ascribed to a C–N–C coordination [47, 48], while the weak peak at about 286.1 eV may be assigned to the C–NH₂ species [37]. For N 1s spectrum (Fig. 3E), three fitting peaks were present at about 400.1, 399.1 and

Fig. 3 XPS spectra of 20% g-C₃N₄/BiOI composite. **A** Bi 4f; **B** O 1s; **C** I 3d; **D** C 1s; **E** N 1s

398.4 eV, respectively. The three peaks could be assigned as the free amino groups (C–N–H), the tertiary nitrogen N–(C)₃ groups and the sp² hybridized nitrogen involved in triazine rings (C–N=C) [49]. In view of the low loading of g-C₃N₄, only weak intensity signals of XPS were observed for C 1 s and N 1 s. These XPS results confirmed the successful synthesis of g-C₃N₄/BiOI composites.

3.5 FT-IR analysis

FT-IR spectra of the BiOI, g-C₃N₄, g-C₃N₄/BiOI composites were shown in Fig. 4. The peak at 808 cm^{−1} was assigned to out-of-plane bending modes of heterocyclic C–N [50]. Several peaks appearing from 1200 to 1650 cm^{−1} belonged to stretching vibration peak of typical aromatic C–N [51–53]. For BiOI, the peak at 478 cm^{−1} was attributed to the stretching vibration of the Bi–O bond [35]. For g-C₃N₄/BiOI composites, the characteristic absorption peaks of BiOI and g-C₃N₄ were all presented, the results confirmed the g-C₃N₄/BiOI composites were prepared successfully.

3.6 DRS analysis

To reflect the optical properties of the composites, the spectra of UV–Vis diffuse reflectance was presented in Fig. 5A. The absorption edge of g-C₃N₄ appeared at 460 nm, which was in accordance with the previous reports on g-C₃N₄ [40]. For BiOI, the absorption edge appeared at 680 nm, which confirmed its excellent visible light absorption performance [54]. In terms of g-C₃N₄/BiOI composites, the absorption edge was at about 670 nm. Compared with g-C₃N₄, the composites showed better visible-light absorbability. The result

indicated g-C₃N₄/BiOI composites could absorb visible light and e[−] could be generated in photocatalytic process.

The E_g of the semiconductor photocatalyst could be obtained through the formula [43, 50, 54–56]:

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (1)$$

where: n depends on the typical transition in the semiconductors (indirect type: n=4; direct type: n=1). For pure g-C₃N₄, n=1; and for pure BiOI, n=4. Therefore, the E_g of BiOI and g-C₃N₄ were calculated as 1.74 eV and 2.84 eV, respectively (Fig. 5B, C). Based on above experimental results, the CB and VB of BiOI and g-C₃N₄ could be measured by the equations as follow [54–56]:

$$E_{VB} = X - E^e + 0.5E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

where: E^e is the energy of free electrons on the hydrogen scale (about 4.5 eV); X is the electronegativity of the semiconductor (the X of BiOI is 5.94 eV [57–59] and the X of g-C₃N₄ is 4.72 eV [48, 56], respectively). So, the VB and CB of the BiOI were figured out as 2.31 eV and 0.57 eV, respectively. The VB and CB of the g-C₃N₄ were 1.64 eV and −1.2 eV, respectively.

3.7 Photocurrent and EIS analysis

Photocurrent and EIS were taken to investigate the separation efficiency of e[−] and h⁺ in the g-C₃N₄/BiOI composites (Fig. 6). The photocurrent-time curves of BiOI, g-C₃N₄ and g-C₃N₄/BiOI composites were shown in Fig. 6A. It could be observed that all the g-C₃N₄/BiOI composites have higher current intensity than g-C₃N₄ and BiOI. At the same time, the current intensity of 20% g-C₃N₄/BiOI composite was about 4 times as that of BiOI and 2 times as that of g-C₃N₄, indicating the e[−]–h⁺ separated efficiency of g-C₃N₄/BiOI composites are higher than g-C₃N₄ and BiOI. In addition, the current intensity almost did not decline after seven times cycles under the LED light, which indicated that the materials were stable. EIS was taken to further investigate the charge carrier transfer properties of the samples (Fig. 6B). For g-C₃N₄/BiOI composites, the spectrum showed a smaller Nyquist radius than g-C₃N₄ and BiOI, indicating the more efficient e[−]–h⁺ separation efficiency in the composite. The result was similar with the literature reported [60]. Based on above results, the hybrid structure existed between g-C₃N₄ and BiOI, promoting an efficient charge separation and leading an improved photocatalytic antibacterial performance.

Fig. 4 FT-IR spectra of BiOI, g-C₃N₄ and g-C₃N₄/BiOI composites

Fig. 5 **A** The UV–Vis absorption spectra of the BiOI, g-C₃N₄ and g-C₃N₄/BiOI composites; **B** Energy band gap of BiOI; **C** Energy band gap of g-C₃N₄

Fig. 6 **A** Photocurrent of BiOI, g-C₃N₄ and g-C₃N₄/BiOI composites; **B** EIS of BiOI, g-C₃N₄ and g-C₃N₄/BiOI composites

3.8 Antibacterial analysis

The antibacterial performance of obtained composites was estimated by *E. coli* and *S. aureus* under LED light. In the case of g-C₃N₄/BiOI composites without light irradiation, the livability of bacterium did not change after 30 min, indicating that the material itself was not toxic to *E. coli* and

S. aureus [22–26]. Similarly, In direct LED light irradiation and without catalysts, the livability of bacterium did not change after 30 min, indicating the LED light could not inactivate *E. coli* and *S. aureus* directly. When catalysts and light irradiation were both present, the livability of bacterial reduced significantly with the extension of reaction time. For pure BiOI and g-C₃N₄, 74.38% and 86.19% *E. coli* bacterial

cells were inactivated within 30 min, respectively (Fig. 7A, C). Compared with g-C₃N₄ and BiOI, the composites showed efficient photocatalytic antibacterial activity for *E. coli*, among them, the antibacterial rate of 10% g-C₃N₄/BiOI and 30% g-C₃N₄/BiOI could reached 96.56% and 98.31% within 30 min. Remarkably, 20% g-C₃N₄/BiOI composite showed the optimal bactericidal effect and *E. coli* were inactivated completely within 30 min. In the case of *S. aureus* (Fig. 7B, D), the prepared g-C₃N₄/BiOI composites also showed better antibacterial performance than pure g-C₃N₄ and BiOI. All of the composites could kill *S. aureus* within 30 min. Significantly, *S. aureus* was inactivated rapidly by 20% g-C₃N₄/BiOI composite within 20 min, while 77.22% and 84.90% *S. aureus* were inactivated for pure g-C₃N₄ and BiOI within 30 min.

The comparisons of photocatalytic activities of the g-C₃N₄/BiOI composites with various related g-C₃N₄-based and BiOI-based photocatalysts previously reported for the photocatalytic antibacterial of *E. coli* and *S. aureus* were listed in Table. 1. As can be seen, the *E. coli* and *S. aureus* antibacterial ratio of g-C₃N₄/BiOI composite were 100% under 35 W low-energy LED light, which is better than g-C₃N₄-based and BiOI-based photocatalysts (Under Mercury lamp, Xenon lamp, Gallium iodine lamp). This signifies that g-C₃N₄/BiOI composites have great potentials for the antibacterial of microorganisms in water.

To investigate the structure and morphology changes of *E. coli* in the destruction process, SEM was taken to observe the images of bacteria at different photocatalytic time. At the beginning of photocatalytic sterilization, the form of bacterial cells was complete (Fig. 8A). When the sample was irradiated for 5 min, bacteria began to deform (Fig. 8B). After 10 min of irradiation, the bacteria became out of shape and the surface of the bacteria was sunken (Fig. 8C). The cell walls of *E. coli* were destroyed and the morphology of the bacteria changed significantly after 20 min of irradiation (Fig. 8D). Then the membrane of bacteria is seriously damaged, and the bacteria are completely inactivated after 30 min of irradiation (Fig. 8E). These results indicated g-C₃N₄/BiOI composites could destroy the bacteria, and some active species, such as h⁺, e⁻, hydroxyl radical (·OH), H₂O₂, and ·O₂⁻ may be present in the antibacterial process, which may play a certain role on the bacterial cells.

3.9 Disinfection mechanisms

To explore the sterilized mechanism of g-C₃N₄/BiOI composites, trapping experiments were applied in this work to find the major active species during the antibacterial process. The effects of Na₂C₂O₄ (1 mmol L⁻¹), Cr(VI) (0.05 mmol L⁻¹), isopropanol (1 mmol L⁻¹) and catalase (0.05 mmol L⁻¹) were investigated in 20% g-C₃N₄/BiOI

Fig. 7 Bactericidal efficiency against **A** *E. coli* and **B** *S. aureus* with different samples; Photocatalytic antibacterial activities of (a) BiOI, (b) g-C₃N₄ and (c) 20% g-C₃N₄/BiOI composite against **C** *E. coli* and **D** *S. aureus* at different irradiation times under LED light

Table 1 Comparison with other g-C₃N₄-based and BiOI-based photocatalysts in the literature

Photocatalyst	Bacteria model	Catalyst (mg/mL)	BC (CFU/mL)	Time (min)	AR (%)	Light source	References
g-C ₃ N ₄ /BiOI	<i>E. coli</i> and <i>S. aureus</i>	0.2	10 ⁷	30 20	100	LED light (35 W)	This work
Ag–ZnO/g–C ₃ N ₄	<i>E. coli</i>	0.2	10 ⁶	120	NA	ML	[22]
Ag/g–C ₃ N ₄	<i>E. coli</i>	0.1	10 ⁹	90	100	XL (300 W, $\lambda < 420$ nm)	[23]
Ag/g–C ₃ N ₄	<i>E. coli</i> and <i>S. aureus</i>	0.06	10 ⁶	30	95	NA	[24]
RGO/g–C ₃ N ₄	<i>E. coli</i> K-12	NA	2 × 10 ⁶	240	100	XL (300 W, $\lambda < 400$ nm)	[25]
TiO ₂ /g–C ₃ N ₄	<i>E. coli</i>	NA	10 ⁵	180	84	XL (300 W, $\lambda < 420$ nm)	[26]
BiOI–AgI	<i>E. coli</i>	0.1	5 × 10 ⁷	18	100	XL ($\lambda \geq 400$ nm)	[31]
Ag@AgI/Bi–BiOI	<i>E. coli</i> K-12	0.5	10 ^{6.5}	60	100	XL (300 W, $\lambda \geq 420$ nm)	[32]
Ag/BiOI	<i>E. coli</i>	0.5	5 × 10 ⁷	60	100	GIL (400 W, $\lambda > 420$ nm)	[33]
Ti/BiOI	<i>E. coli</i> and <i>S. aureus</i>	0.06	3 × 10 ⁷ 3 × 10 ⁶	24 45	100	XL (300 W, $\lambda > 420$ nm)	[34]

BC bacterial concentration; AR antibacterial ratio; NA not available; ML mercury lamp; XL xenon lamp; GIL gallium iodine lamp

Fig. 8 SEM images of *E. coli* photocatalytically treated with 20% g-C₃N₄/BiOI composite under LED light irradiation for **A** 0 min, **B** 5 min, **C** 10 min, **D** 20 min and **E** 30 min

photocatalytic antibacterial system for the capture of h^+ , e^- , OH and H_2O_2 , respectively. In addition, N_2 was injected into the solution to remove O_2 and then inhibited the formation of $\cdot O_2^-$. The concentration of each capture agent was consistent with the reported concentration to ensure maximum capture and was non-toxic to bacteria [61–64]. As shown in Fig. 9, photocatalytic effects were almost the same in the case of Cr(VI) and isopropanol, all the *E. coli* bacterial cells were inactivated within 30 min. The results indicated that e^- and $\cdot OH$ were not the dominant species in g- C_3N_4 /BiOI photocatalytic system; in the case of passing N_2 and adding the catalase, the photocatalytic effects reduced, there were 82.55% and 74.67% *E. coli* bacterial cells were inactivated within 30 min, respectively. It indicated that $\cdot O_2^-$ and H_2O_2

Fig. 9 Bactericidal efficiency of *E. coli* with different capture agents under LED light

Fig. 10 Photocatalytic antibacterial mechanism diagram of the g- C_3N_4 /BiOI composites under LED light

took effects on the antibacterial. However, when $Na_2C_2O_4$ was applied to consume h^+ , only about 19% *E. coli* bacteria were inactivated after 30 min of irradiation, the sterilized efficiency was reduced significantly. The results showed that the h^+ played a leading role during bacterial inactivation.

Based on the previous discussion and analysis, the dual charge transfer mechanism was produced in this study (Fig. 10). First of all, based on the DRS data, the CB potentials of BiOI, g- C_3N_4 was 0.57 eV, -1.2 eV, respectively. The VB potentials of BiOI, g- C_3N_4 were 2.31 eV, 1.64 eV, respectively. The specific photocatalytic process is as follows: g- C_3N_4 and BiOI were excited by LED light irradiation and e^- and h^+ were generated. The h^+ on the VB of BiOI transferred to the VB of g- C_3N_4 and the e^- on the CB of g- C_3N_4 transferred to the CB of BiOI. Since the potential energy of the VB of g- C_3N_4 is less than the energy of $\cdot OH/H_2O$ ($E^\theta(\cdot OH/H_2O) = 2.27$ eV) [65], h^+ at the VB of g- C_3N_4 could not react with H_2O to produce $\cdot OH$, h^+ would react with the bacteria directly to inactivate the bacteria. In the meantime, the potential energy of the CB of BiOI is higher than the energy of $O_2/\cdot O_2^-$ ($E^\theta(O_2/\cdot O_2^-) = -0.33$ eV) [40], e^- on the CB of g- C_3N_4 could not generate $\cdot O_2^-$. However, there still exists some electrons that did not transfer to the CB of g- C_3N_4 , which could react with O_2 and then generate $\cdot O_2^-$ and H_2O_2 in the system [66, 67]. The two active species $\cdot O_2^-$ and H_2O_2 could play a certain role in inactivating *E. coli* in the process, which was in accordance with the result of trapping experiments. Hence, the dual charge transfer mechanism was confirmed, and similar transfer mechanism was presented in the previous report [31, 32]. Based on above

analysis, h^+ , $\cdot O_2^-$ and H_2O_2 were active species, among them, h^+ played the main role in the antibacterial process.

4 Conclusion

In this paper, efficient photocatalyst g- C_3N_4 /BiOI catalysts were prepared by in-situ generation method at room temperature. The composites showed excellent photocatalytic performance toward *E. coli* and *S. aureus* under LED light irradiation, and the bacterial were completely inactivated within 30 min. The enhanced photocatalytic properties were attributed to efficient separation of e^- and h^+ in the g- C_3N_4 /BiOI composites. Based on trapping experiments, h^+ , $\cdot O_2^-$ and H_2O_2 were active species and dual charge transfer mechanism was confirmed in the photocatalytic sterilization process. As the excellent performance for inactivating *E. coli* and *S. aureus*, g- C_3N_4 /BiOI composites could be applied as a promising material in terms of water disinfection.

Acknowledgements National Nature Science Foundation of China (Grant Nos. 21406094, 21506079 and 51572114), Postdoctoral Foundation of China (Grant No. 2015M571693) and Foundation of Jiangsu University (Grant No. 14JDG184) were genuinely appreciated.

References

1. S. Richardson, M. Plewa, E. Wagner, R. Schoeny, D. Demarini, *Mutat. Res.* **636**, 178–242 (2007)
2. L.A. Bernal-Martínez, C. Barrera-Díaz, C. Solís-Morelos, R. Natividad, *Chem. Eng. J.* **165**, 71–77 (2010)
3. N. Le-Minh, S.J. Khan, J.E. Drewes, R.M. Stuetz, *Water Res.* **44**, 4295–4323 (2010)
4. M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, *Water Res.* **44**, 2997–3027 (2010)
5. T. Wang, Z. Jiang, T. An, G. Li, H. Zhao, P.K. Wong, *Environ. Sci. Technol.* **52**, 4774–4784 (2018)
6. W. Wang, T. An, G. Li, D. Xia, H. Zhao, J.C. Yu, P.K. Wong, *Appl. Catal. B* **217**, 570–580 (2017)
7. W. Wang, G. Li, D. Xia, T. An, H. Zhao, P.K. Wong, *Environ. Sci.: Nano* **4**, 782–799 (2017)
8. H.A. Foster, I.B. Ditta, S. Varghese, A. Steele, *Appl. Microbiol. Biotechnol.* **90**, 1847–1868 (2011)
9. H. Ma, P.L. Williams, S.A. Diamond, *Environ. Pollut.* **172**, 76–85 (2013)
10. L.K. Adams, D.Y. Lyon, P.J.J. Alvarez, *Water Res.* **40**, 3527–3532 (2006)
11. Q. Li, S. Mahendra, D.Y. Lyon, L. Brunet, M.V. Liga, D. Li, P.J.J. Alvarez, *Water Res.* **42**, 4591–4602 (2008)
12. S.L. Wang, S.H. Lin, D.Q. Zhang, G.S. Li, M.K.H. Leung, *Appl. Catal. B* **215**, 85–92 (2017)
13. Y. Wang, X.C. Wang, M. Antonietti, *Angew. Chem.-Int. Ed.* **51**, 68–89 (2012)
14. A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.O. Muller, R. Schlögl, J.M. Carlsson, *J. Mater. Chem.* **18**, 4893–4908 (2008)
15. S. Cao, J. Low, J. Yu, M. Jaroniec, *Adv. Mater.* **27**, 2150–2176 (2015)
16. J.C. Tong, L. Zhang, F. Li, M.M. Li, S.K. Cao, *Phys. Chem. Chem. Phys.* **17**, 23532–23537 (2015)
17. S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang, P.M. Ajayan, *Adv. Mater.* **25**, 2452–2456 (2013)
18. X. Bai, L. Wang, R. Zong, Y. Zhu, *The J. Phys. Chem. C* **117**, 9952–9961 (2013)
19. M. Mousavi, A. Habibi-Yangjeh, S.R. Pouran, *J. Mater. Sci.: Mater. Electron.* **29**, 1719–1747 (2017)
20. S. Cao, H. Li, T. Tong, H. Chen, A. Yu, J. Yu, H. Chen, *Adv. Funct. Mater.* **28**, 1802169 (2018)
21. S. Cao, Q. Huang, B. Zhu, J. Yu, *J. Power Sources* **351**, 151–159 (2017)
22. S.P. Adhikari, H.R. Pant, J.H. Kim, H.J. Kim, C.H. Park, C.S. Kim, *Colloids Surf. A* **482**, 477–484 (2015)
23. S. Ma, S. Zhan, Y. Jia, Q. Shi, Q. Zhou, *Appl. Catal. B* **186**, 77–87 (2016)
24. W. Bing, Z. Chen, H. Sun, P. Shi, N. Gao, J. Ren, X. Qu, *Nano Res.* **8**, 1648–1658 (2015)
25. W. Wang, J.C. Yu, D. Xia, P.K. Wong, Y. Li, *Environ. Sci. Technol.* **47**, 8724–8732 (2013)
26. J. Xu, Y. Li, X. Zhou, Y. Li, Z.-D. Gao, Y.-Y. Song, P. Schmuki, *Chem.-Eur. J.* **22**, 3947–3951 (2016)
27. H. Cheng, B. Huang, Y. Dai, *Nanoscale* **6**, 2009–2026 (2014)
28. J. Li, Y. Yu, L. Zhang, *Nanoscale* **6**, 8473–8488 (2014)
29. R. Hao, X. Xiao, X. Zuo, J. Nan, W. Zhang, *J. Hazard. Mater.* **209**, 137–145 (2012)
30. L. Ye, J. Chen, L. Tian, J. Liu, T. Peng, K. Deng, L. Zan, *Appl. Catal. B* **130**, 1–7 (2013)
31. J. Liang, C. Shan, X. Zhang, M. Tong, *Chem. Eng. J.* **279**, 277–285 (2015)
32. S. Ning, H. Lin, Y. Tong, X. Zhang, Q. Lin, Y. Zhang, J. Long, X. Wang, *Appl. Catal. B* **204**, 1–10 (2017)
33. L. Zhu, C. He, Y. Huang, Z. Chen, D. Xia, M. Su, Y. Xiong, S. Li, D. Shu, *Sep. Purif. Technol.* **91**, 59–66 (2012)
34. J. Liang, J. Deng, M. Li, T. Xu, M. Tong, *Colloids Surf. B* **147**, 307–314 (2016)
35. J. Di, J. Xia, S. Yin, H. Xu, L. Xu, Y. Xu, M. He, H. Li, *J. Mater. Chem. A* **2**, 5340–5351 (2014)
36. D. Jiang, L. Chen, J. Zhu, M. Chen, W. Shi, J. Xie, *Dalton Trans.* **42**, 15726–15734 (2013)
37. J.C. Wang, H.C. Yao, Z. Y. Fan, L. Zhang, J.S. Wang, S.Q. Zang, Z.J. Li, *ACS Appl. Mater. Interfaces* **8**, 3765–3775 (2016)
38. F. Zhang, L.P. Wang, M. Xiao, F. Liu, X. Xu, E.D. Du, *J. Mater. Res.* **33**, 201–212 (2018)
39. S.R. Wang, W.W. Tu, Z.H. Dai, *Analyst* **143**, 1775–1779 (2018)
40. H. An, B. Lin, C. Xue, X. Yan, Y. Dai, J. Wei, G. Yang, *Chin. J. Catal.* **39**, 654–663 (2018)
41. H. Huang, W. Lin, L. Xie, J. Chen, *Environ. Sci.* **38**, 3979–3986 (2017)
42. M. Xie, W. Wei, Z. Jiang, Y. Xu, J. Xie, *Ceram. Int.* **42**, 4158–4170 (2016)
43. B. Liu, X. Han, Y. Wang, X. Fan, Z. Wang, J. Zhang, H. Shi, *J. Mater. Sci.: Mater. Electron.* **29**, 14300–14310 (2018)
44. S. Vignesh, A.L. Muppudathi, J.K. Sundar, *J. Mater. Sci.: Mater. Electron.* **29**, 10784–10801 (2018)
45. C. Liu, B. Chai, *J. Mater. Sci.: Mater. Electron.* **26**, 2296–2304 (2015)
46. J. Jiang, X. Zhang, P. Sun, L. Zhang, *J. Phys. Chem. C* **115**, 20555–20564 (2011)
47. L. Huang, H. Xu, Y. Li, H. Li, X. Cheng, J. Xia, Y. Xu, G. Cai, *Dalton Trans.* **42**, 8606–8616 (2013)
48. L. Song, Y. Pang, Y. Zheng, L. Ge, *Appl. Phys. A* **123**, 500–510 (2017)
49. K. Li, X. Zeng, S. Gao, L. Ma, Q. Wang, H. Xu, Z. Wang, B. Huang, Y. Dai, J. Lu, *Nano Res.* **9**, 1969–1982 (2016)
50. C. Chang, L. Zhu, S. Wang, X. Chu, L. Yue, *ACS Appl. Mater. Interfaces* **6**, 5083–5093 (2014)
51. S.C. Yan, Z.S. Li, Z.G. Zou, *Langmuir* **25**, 10397–10401 (2009)

52. Q. Xiang, J. Yu, M. Jaroniec, *J. Phys. Chem. C* **115**, 7355–7363 (2011)
53. Y. Li, S. Wu, L. Huang, H. Xu, R. Zhang, M. Qu, Q. Gao, H. Li, *J. Phys. Chem. Solids* **76**, 112–119 (2015)
54. H. Huang, X. Han, X. Li, S. Wang, P.K. Chu, Y. Zhang, *ACS Appl. Mater. Interfaces* **7**, 482–492 (2015)
55. L. Yosefi, M. Haghighi, *Appl. Catal. B* **220**, 367–378 (2018)
56. K. Dai, L. Lu, C. Liang, G. Zhu, Q. Liu, L. Geng, J. He, *Dalton Trans.* **44**, 7903–7910 (2015)
57. P. Li, X. Zhao, C.J. Jia, H. Sun, L. Sun, X. Cheng, L. Liu, W. Fan, *J. Mater. Chem. A* **1**, 3421–3429 (2013)
58. L. Chen, D. Jiang, T. He, Z. Wu, M. Chen, *CrystEngComm* **15**, 7556–7563 (2013)
59. A.C. Mera, C.A. Rodriguez, M.F. Melendrez, H. Valdes, *J. Mater. Sci.* **52**, 944–954 (2017)
60. R. Wang, X. Kong, W. Zhang, W. Zhu, L. Huang, J. Wang, X. Zhang, X. Liu, N. Hu, Y. Suo, J. Wang, *Appl. Catal. B* **225**, 228–237 (2018)
61. X. Nie, G. Li, M. Gao, H. Sun, X. Liu, H. Zhao, P.-K. Wong, T. An, *Appl. Catal. B* **147**, 562–570 (2014)
62. W. Wang, Y. Yu, T. An, G. Li, H.Y. Yip, J.C. Yu, P.K. Wong, *Environ. Sci. Technol.* **46**, 4599–4606 (2012)
63. X. Peng, T.W. Ng, G. Huang, W. Wang, T. An, P.K. Wong, *Chemosphere* **166**, 521–527 (2017)
64. G. Li, X. Nie, J. Chen, Q. Jiang, T. An, P.K. Wong, H. Zhang, H. Zhao, H. Yamashita, *Water Res.* **86**, 17–24 (2015)
65. S. Tan, Z. Xing, J. Zhang, Z. Li, X. Wu, J. Cui, J. Kuang, Q. Zhu, W. Zhou, *J. Catal.* **357**, 90–99 (2018)
66. S. Huang, Y. Xu, T. Zhou, M. Xie, Y. Ma, Q. Liu, L. Jing, H. Xu, H. Li, *Appl. Catal. B* **225**, 40–50 (2018)
67. Y. Xu, Q. Liu, C. Liu, Y. Zhai, M. Xie, L. Huang, H. Xu, H. Li, J. Jing, *J. Colloid Interface Sci.* **512**, 555–566 (2018)