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Short communication

Photocatalytic degradation of methyl orange by $BiOI/Bi_4O_5I_2$ microspheres under visible light irradiation

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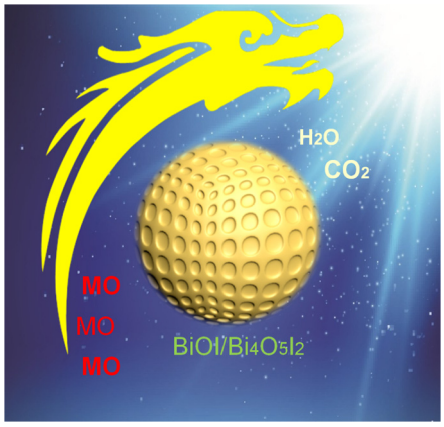
GRAPHICAL ABSTRACT



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ABSTRACT

$BiOI/Bi_4O_5I_2$ composites were synthesized by calcinations with BiOI microspheres at 400 °C. The $BiOI/Bi_4O_5I_2$ composites demonstrate 5 times higher photocatalytic activity than the pristine BiOI for methyl orange (MO) degradation under the irradiation of visible light. Moreover, the $BiOI/Bi_4O_5I_2$ composites have superior cycling stability. Such enhanced photoactivity is due to the significantly enhanced separation efficiency of photo-generated.

Photocatalysis has been used to remove the organic contaminants in wastewater [1–3]. Among the visible light active Bi-based photocatalysts, BiOI has the smallest band gap (1.6–1.9 eV) and unique structure (layered crystal structure consisting of $[Bi_2O_2]^{2+}$ layers sandwiched between two slabs of halogen ions) [4]. This structure can effectively generate more photocatalytic electrons and holes, which is benefited to the photocatalytic performances for degradation of the RhB and methyl orange (MO). However, low efficiency of photogenerated charge carriers limits its practical application [5,6].

Heterojunction, doping, and defect construction have been

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performed to improve the photocatalytic performance of BiOI [7–9]. Formation of heterojunctions could significantly enhance the separation of photogenerated charge carriers and the composites are photocatalytically more active than the individual components [10], such as Pd/BiOI/MnOx [11], $Bi_2S_3/Bi_2O_3/Bi_2O_2CO_3$ [12], $BiOI@Bi_{12}O_{17}Cl_2$ [13]. However, using one photocatalyst as a substrate and loading another photocatalyst onto the surface of the former will make the solid-solid contact interface unstable. This shortcoming leads to the difficulties of photoelectrons transport between two catalysts. Therefore, it is urgent to find a simple method to consolidate the interface inside the catalysts.

Calcination is extensively applied for constructing two phase contact interface. This will consolidate the interface, improving the photocatalytic performance [14,15]. For example, Cai et al. calcined $Bi_2O_2CO_3$ to form $Bi_2O_2CO_3/Bi_2O_3$ p-n heterojunction and they found that $Bi_2O_3/Bi_2O_2CO_3$ photocatalyst displayed much higher photocatalytic performance for the degradation of methylene blue than pure $Bi_2O_2CO_3$ and Bi_2O_3 under visible light [14]. These features inspired us to improve the photoactivity of BiOI by calcining BiOI to form BiOI/$Bi_4O_5I_2$ composites. The BiOI/$Bi_4O_5I_2$ composites demonstrate 5 times higher photocatalytic activity than the pristine BiOI for MO degradation under the irradiation of visible light. Moreover, the BiOI/$Bi_4O_5I_2$ composites have superior cycling stability. Such enhanced photoactivity is due to the significantly enhanced separation efficiency of photogenerated.

The BiOI/$Bi_4O_5I_2$ composites were obtained by annealing the pristine BiOI at 400 °C in air, which is according to the TG result (Fig. S1). As displayed in Fig. 1, BiOI and BiOI/$Bi_4O_5I_2$ composites consist of many microspheres self- assembled by nanosheets. SEM results reveal that morphology of microsphere has no change after thermal treatment. The detailed structure information of BiOI/$Bi_4O_5I_2$ composites is further studied by transmission electron microscopy (TEM). The images demonstrate that BiOI/$Bi_4O_5I_2$ composites appearance with microsphere-like (1.5 μm) and the microsphere composed of nanosheets. High-resolution TEM image of BiOI/$Bi_4O_5I_2$ displays that some interplanar distance of 0.30 nm and 0.317 nm appearance, which are corresponding to (102) plane of BiOI and (111) plane of $Bi_4O_5I_2$, respectively [16]. This result suggests that BiOI/$Bi_4O_5I_2$ composite is obtained after annealing BiOI at 400 °C in air.

The crystal structures of BiOI and BiOI/$Bi_4O_5I_2$ are analyzed by X-ray diffraction (XRD), which is displayed in Fig. 2a. The peaks of BiOI could be assigned to tetragonal BiOI (PCPDF no.: 10-0445) [17]. While some other peaks appear in the BiOI/$Bi_4O_5I_2$ spectra and could be designated to $Bi_4O_5I_2$ accordingly to the previously reported data [18]. Furthermore, Raman spectra are also carried out to identify the structure of BiOI/$Bi_4O_5I_2$ composites (Fig. 2b). The peaks at 85 cm^{-1} and 147 cm^{-1} are attributed to the Bi—I vibration of BiOI [19]. And the peaks at 300–600 cm^{-1} are due to the change of Bi—O environment. Therefore, the above results also confirm the successful formation of BiOI/$Bi_4O_5I_2$ composites. The electrochemical impedance spectra are performed to study the interface charge separation efficiency under the visible light irradiation and dark (Fig. 2c). The arc radius is smaller, meaning the efficiency of charge transfer is higher [20,21]. Thus, BiOI/$Bi_4O_5I_2$ has the highest charge transfer efficiency among the samples under the visible light irradiation. The fast charge transfer rate of BiOI/$Bi_4O_5I_2$ composites are attributed to the heterojunction, promoting the separation of electrons and holes. Furthermore, as displayed in Fig. S2, The absorption band gap of BiOI/$Bi_4O_5I_2$ shows blue shift compared to the pristine BiOI, revealing that BiOI could utilize more solar light. Undoubtedly, the enhanced photocatalytic activity of BiOI/$Bi_4O_5I_2$ sample cannot be due to the absorbing abilities.

The photocatalytic activity of BiOI and BiOI/$Bi_4O_5I_2$ are evaluated by degradation of MO with irradiation of visible light ($\lambda > 420$ nm). Fig. 3a shows the photocatalytic performance of degradation of MO over BiOI and BiOI/$Bi_4O_5I_2$. The absorption abilities of MO on BiOI and BiOI/$Bi_4O_5I_2$ in darkness are performed before the light on. BiOI sample and TiO_2 show weak photocatalytic performances, and only 40% and 12.2% of MO are degraded within 2 h, respectively. Comparatively, BiOI/$Bi_4O_5I_2$ presents a high photocatalytic activity with a degradation efficiency of 99%. Furthermore, the pseudo-first-order kinetics of BiOI and BiOI/$Bi_4O_5I_2$ are revealed according to Fig. 3a. The apparent rate constant of BiOI/$Bi_4O_5I_2$ (0.044 min^{-1}) is 11 times higher than that of BiOI (0.004 min^{-1}), revealing the excellent photocatalytic activity of BiOI/$Bi_4O_5I_2$ sample. Notably, after 6 successive cycles, the photocatalytic performance only slightly decreased under visible light, confirming the high stability of BiOI/$Bi_4O_5I_2$ (Fig. 3c). Furthermore, the BiOI/$Bi_4O_5I_2$ could also remove other dye pollutants such as RhB, methyl blue (MB), acid orange (AO), phenol and Congo red (CR), which could remove > 95% of these dyes after 120 min (Fig. 3d). All the above results demonstrate that BiOI/$Bi_4O_5I_2$ is a good photocatalyst

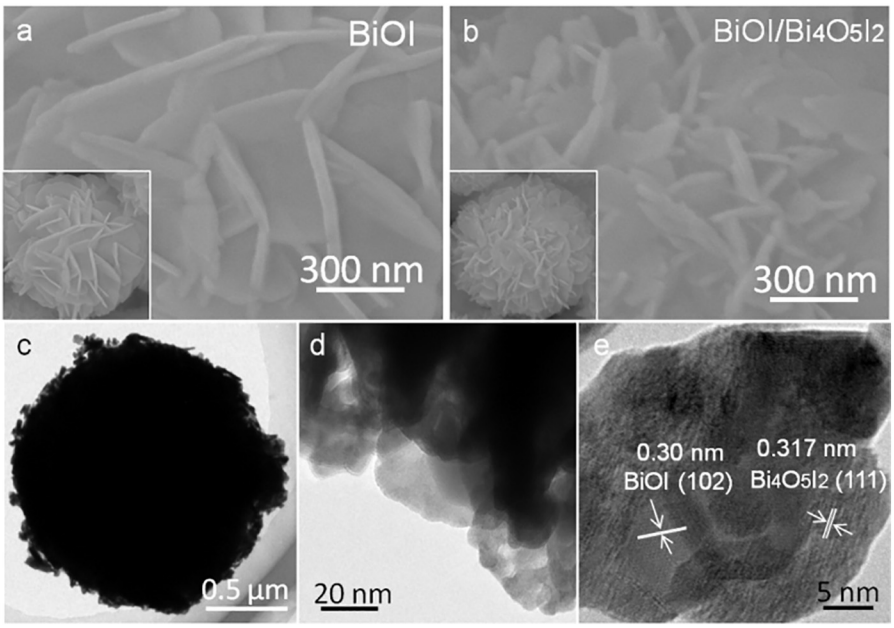

Fig. 1. SEM images of (a) BiOI and (b) BiOI/$Bi_4O_5I_2$. TEM images of BiOI/$Bi_4O_5I_2$ (c, d and e).