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Construction of 2D/2D $BiVO_4$/g-C_3N_4 nanosheet heterostructures with improved photocatalytic activity

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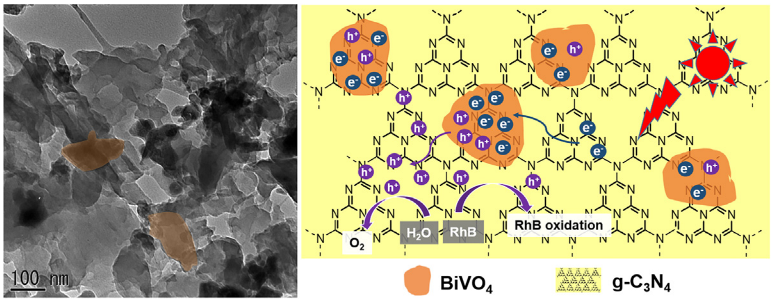
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a two dimensional (2D)/2D $BiVO_4$/g-C_3N_4 heterostructure with strong interfacial interaction was successfully constructed. The as-prepared $BiVO_4$/g-C_3N_4 heterostructures exhibit distinctly enhanced visible light photocatalytic performance toward the degradation of Rodanmin B (RhB) and water splitting to oxygen (O_2) as compared to pristine g-C_3N_4 and $BiVO_4$, which can be attributed to the strong interfacial interaction and abundant 2D coupling interfaces, facilitating efficient charge separation. Among the composites with various ratios, the $BiVO_4$-10/g-C_3N_4 sample achieves the optimum photocatalytic activity for the degradation of RhB, and reached 15.8 and 4.3 times compared to pure g-C_3N_4 and $BiVO_4$. Moreover, the corresponding composite reached a high O_2-production rate of 0.97 μmol h^{-1} under visible light irradiation, which is 12.1 and 2.8 times higher than that of pure g-C_3N_4 and $BiVO_4$, respectively. It was demonstrated that the efficiency of electron-hole separation has certain contribution to the photocatalytic performance over the $BiVO_4$/g-C_3N_4 heterostructure. The present study suggests that the unique 2D/2D $BiVO_4$/g-C_3N_4 hybrid nanosheets should be conducive to improve the photocatalytic performance of organic pollutant degradation and water splitting.

1. Introduction

Semiconductor photocatalyst is a potential material to solve the pollution degradation by utilizing solar energy [1–4]. Therefore, great deals of attention have been received to exploit high efficient photocatalytic semiconductor capable of responding to visible light. Various types' photocatalysts with different morphology

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have been developed to improve the light response range and quantum efficiency [5–7]. Among the geometry of composite material, the 2D/2D heterojunction often shows the excellent separation of electron–hole pairs due to the intimate face-to-face contact as compared to the point-to-face contact in the 0D/2D heterojunction and the line-to-face contact in the 1D/2D heterojunction, which might lead to the enhanced photocatalytic activity [8,9].

Bismuth based semiconductor has received significant interest due to its unique physical properties [10–12]. $BiVO_4$ is one of the most outstanding photocatalysts with an appropriate direct band gap of 2.4 eV for absorbing visible light [13]. However, the high recombination of photo-induced electron and hole is an obstacle to achieve an efficient photocatalytic performance. It is generally believed that coupling two or more semiconductors can reduce the recombination of photo-generated electron-hole pairs [14,15]. Graphitic carbon nitride (g-C_3N_4) is an encouraging candidate material with a suitable bandgap (2.7 eV) and 2D nanosheet structure [15–20]. A series of works have indicated that the appropriate band structure of $BiVO_4$ and g-C_3N_4 can promote the photocatalytic activity due to the efficient photo-induced electron-holes transferring and separation between $BiVO_4$ and g-C_3N_4 [21]. It is known that the synergistic effect between $BiVO_4$ and g-C_3N_4 would be associated with their external morphology, which could significantly influence the photocatalytic performance [22,23]. In particular, 2D/2D multilayered hybrid nanosheets possess a much larger contact area compared to 2D/0D or 2D/1D nanomaterials that are only in point-to-point or line-to-line contact [24,25]. Thus, the larger contact interfaces between 2D/2D composite provide more effective separation of photo-generated electron-hole pairs and outstanding photocatalytic performance. Recently, various morphological types of $BiVO_4$, such as bulk [26–28], nanorods [29], regular polyhedral structures [30,31], leaf-like nanostructures [32], agglomerated particles [33], as well as platelet-like morphologies [34], are used to be hybridized with nanosheet g-C_3N_4. However, to the best of our knowledge, no attempt has been made on construction of 2D/2D heterostructure with ultrathin nanosheet $BiVO_4$ and nanosheet g-C_3N_4, this has motivated us to take up the present study.

In this work, 2D nanosheet of $BiVO_4$ with 20–30 nm thickness was synthesized and combined with the 2D nanosheet of g-C_3N_4 to form a heterostructure with 2D/2D morphology. The photodegradation of Rhodamine B (RhB) and water splitting to oxygen (O_2) were examined under visible light irradiation. All of the composite material, except $BiVO_4$-40/g-C_3N_4 exhibits an enhanced performance to pristine g-C_3N_4 and $BiVO_4$. Among them, $BiVO_4$-10/g-C_3N_4 showed the highest photocatalytic activity. Electrochemical Impedance Spectroscopy (EIS) and photocurrent confirmed the efficient electron transfer between $BiVO_4$ and g-C_3N_4, which may due to the large interface region of 2D/2D structure. These current results may provide a new insight to build 2D/2D heterojunction photocatalyst with effective charge separation, which show a great potentiality in the application of water purification and water splitting.

2. Experimental

2.1. Chemicals

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), ammonium metavanadate (NH_4VO_3), sodium dodecyl benzene sulfonate (SDBS), Nitric acid (65–68%), Sodium hydroxide (NaOH), N,N-Dimethylformamide (DMF), urea (H_2NCONH_2), Rhodamine B (RhB) Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), hydrogen peroxide (H_2O_2), silver nitrate ($AgNO_3$), ammonia aqueous solution (25 wt%), sodium sulfate (Na_2SO_4) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and used without further purification. Nafion was provided by Sigma-Aldrich Chemicals Corporation. The water used in this study was deionized and purified through a water purification system (resistivity: $\sim$18 MΩ cm).

2.2. Synthesis of g-C_3N_4 nanosheets

g-C_3N_4 nanosheets was prepared by thermally method under a static atmosphere [16]. 5 g of urea was placed in an alumina crucible with a cover and kept at 550 °C for 2 h with a heating rate of 2 °C min^{-1}. The obtained yellowish resultant was collected and ground into fine powder as the final product.

2.3. Synthesis of $BiVO_4$ nanosheets

The BiVO4 nanosheets were prepared by a hydrothermal method [35]. 1.2250 g of $Bi(NO_3)_3$ $5H_2O$ and 0.2900 g of NH_4VO_3 was dissolved into 5 mL of 4.0 M HNO_3 and 2.0 M NaOH to obtain a pellucid solution, respectively. 0.1250 g of SDBS was then added into both of the above solutions with vigorous stirring for 0.5 h. After that, the two solutions were mixed to give a bisque solution under stirring, followed by an addition of 2.0 M NaOH to adjust the pH value to 7.0. After stirring for another 0.5 h, the mixture was transfered into a Teflon-lined stainless steel autoclave until 80% of the volume of the autoclave was occupied. The autoclave was heated in an oven at 200 °C for 4 h, and allowed to cool down to room temperature. The vivid yellowish precipitate was washed with distilled water and collected by centrifugation, and then dried at 100 °C for 4 h.

2.4. Synthesis of 2D/2D $BiVO_4$/g-C_3N_4 heterostructure

Four samples of g-C_3N_4 hybrid with $BiVO_4$ with different $BiVO_4$/g-C_3N_4 mass ratio were prepared. In a typical process, a certain amount of g-C_3N_4 was dissolved into 20 mL of DMF and held for 15 min under ultrasound. Then, a given amount of $BiVO_4$ was dispersed into the suspension solution under ultrasound for 1 h and stirring for another 12 h. The resultant solution was separated by centrifugation, washed repeatedly with water and ethanol, and dried at 60 °C for 6 h. The final hybrid was signed as $BiVO_4$-z/g-C_3N_4, where z represents the mass percentage of $BiVO_4$.

2.5. Photocatalytic performance

Photodegradation experiments were performed in a quartz bottle (50 mL) at ambient temperature. In a typical experiment, 10 mg of the obtained photocatalyst was suspended in 20 mL 20 mg/L RhB aqueous solution. Before a consistent activity test, the system was kept for 30 min in the darkness under vigorous stirring to achieve an adsorption–desorption equilibrium condition. All the photocatalytic measurements were performed on a 300 W Xenon arc lamp (CEL-PF300-T8, Beijing China Education Au-light Co., Ltd). The light was cut through by a UV cutoff filter (>420 nm) before entering the reactor. The absorbance of RhB was measured by UV spectrometer (JASCO UV-550 spectrophotometer) at 554 nm after centrifugation. The degradation efficiency (%) was calculated by using the following equation:

$$\text{Degradation E}\,(\%) = (C_0 - C)/C_0 \times 100\%$$

where C_0 represents the concentration of RhB before irradiation process, and C represents the time dependent concentration of RhB upon irradiation process.