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$TiO_2/Bi_2(BDC)_3/BiOCl$ nanoparticles decorated ultrathin nanosheets with excellent photocatalytic reaction activity and selectivity

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ABSTRACT

Photocatalysts with excellent photocatalytic reaction activity and ideal selectivity are highly desirable for pollutants clearance and purification of targeted organics from a mixture. Continued efforts toward the goal, we here present a facile hydrothermal route to synthesize TiO_2/Bi-benzenedicarboxylate/BiOCl nanoparticles decorated ultrathin nanosheets with a thickness less than 5 nm on a large scale. The as-synthesized products showed excellent photocatalytic activities for the degradation of various dyes such as rhodamine B, eosin Y and methylene blue in aqueous solution under visible light irradiation. The photocatalytic activities of TiO_2/Bi-benzenedicarboxylate/BiOCl nanocomposites for the degradation of rhodamine B and eosin Y could be adjusted through tuning the content of TiO_2. With increasing the amount of TiO_2, the composites showed declining photocatalytic activities in decomposing of rhodamine B while on the contrary they displayed enhanced photocatalytic activities in decomposing of eosin Y. Interestingly, TiO_2/Bi-benzenedicarboxylate/BiOCl composite nanosheets showed obvious photocatalytic selectivity in a mixed dyes system. The photocatalytic reaction and selectivity mechanisms of the nanocomposites for the degradation of the dyes were discussed on the basis of experimental results. The current study not only develops a new methodology to synthesize ultrathin nanosheets but also provides a novel strategy to design composite photocatalysts with high reaction activity and good selectivity.

1. Introduction

Heterogeneous photocatalysis has been widely considered as a promising approach toward solving increasingly serious environmental and energy-related issues [1–3]. Among various semiconductor photocatalysts, popular TiO_2 and emerging BiOCl photocatalysts have attracted much attention because of their good photocatalytic activities and chemical stability [4–8]. The preparation of TiO_2 and BiOCl with large specific surface area and/or high-energy crystalline facets has been extensively adopted to enhance photocatalytic activities of the materials [9–12]. On the other hand, according to the equation $\tau = r^2/\pi^2 D$, where τ represents the average diffusion time of charge carriers from the bulk to the surface of the grain, r is the grain radius and D is the diffusion coefficient of the carriers, the photogenerated carriers of the photocatalysts with smaller sizes can be more easily transferred to the surfaces of the catalysts [13]. Therefore, in principle, decreasing the sizes of photocatalysts can further enhance their photocatalytic efficiency. However, photocatalysts with smaller sizes are particularly difficult to separate and reuse. Comparatively speaking, two-dimensional nanosheets with thickness in several nanometers and length and width in micron not only can keep the same high photocatalytic activity as nanoscale photocatalysts but also are easily separated by centrifugation. Recently, this kind of two-dimensional nanosheets photocatalysts have stimulated scientists' enormous research interest [14–16]. Up to now, most of nanosheets photocatalysts reported were prepared by exfoliating layered precursors through a soft-chemical process. However, this strategy is only suitable for limited materials. Therefore it is still necessary to develop new methods for synthesizing nanosheets photocatalysts.

On the other hand, photocatalysts with good selectivity are of great significance for the transformation and purification of targeted organics from a mixture system [17–19]. Unfortunately, many photocatalysts are lack of sufficient selectivity because of the presence of nonselective reactive radical species, especially, like $^{\bullet}OH$ [20]. Typically, there are three kinds of approaches to adjust

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the catalytic selectivity of the photocatalysts: (1) purposefully manipulating the photocatalytic reaction route and avoiding the involvement of nonselective reactive species [21]; (2) synthesizing photocatalysts with specifical crystal facets because different crystal facets possess different types of photocatalytic reaction activity [22]; (3) adjusting the adsorption behaviors between the photocatalysts and reagents, including the adsorption ability, site and mode [23]. In contrast, the last method is more popular and efficient because the photocatalytic reaction usually occurs on the surface of the catalyst. Based on this kind of adsorption-induced photocatalytic selectivity, several representative strategies have been reported, such as the fabrication of molecular recognition sites on the vicinity of catalyst [24], textural design of the catalyst with felicitous pore structures [25], and surface modification of the catalyst [26].

It has been widely accepted that the rational fabrication of composite photocatalysts can enhance photocatalytic activity of the materials [27]. However, until now, there are few reports on how to design composite photocatalysts to simultaneously obtain excellent photocatalytic activity and sufficient photocatalytic selectivity derived from adsorption-induced effect.

In this study, we report a novel chemical conversion and deposition-precipitation route to synthesize ternary $TiO_2/Bi_2(BDC)_3/BiOCl$ (BDC = 1,4-benzenedicarboxylate) nanoparticles decorated ultrathin nanosheets, employing $Bi_2(BDC)_3$ nanoplates and $TiCl_3$ as raw materials. The as-synthesized products showed excellent photocatalytic reaction activity in decomposing various dyes such as rhodamine B (RhB), eosin Y (EY) and methylene blue (MB) in water. In addition, the photocatalytic activity of the composite photocatalysts can be tuned through adjusting the amount of TiO_2. Interestingly, the composite photocatalysts showed obvious photocatalytic selectivity in mixed dyes systems. Based on the experimental results, the mechanisms of photocatalytic reaction and selectivity of the composite photocatalysts were proposed as well.

2. Experimental section

2.1. Materials and reagents

$TiCl_3$ aqueous solution (20%, dissolved in 3% of hydrochloric acid) was purchased from Alfa Aesar. The other reagents including $Bi(NO_3)_3 \cdot 5H_2O$, 1,4-benzenedicarboxylate, NaOH, KCl, ethylene glycol, RhB, EY and MB were analytical grade reagents, purchased from Aladdin and used as received. In all experimental processes, water used was ultrapure water unless otherwise stated.

2.1.1. Preparation of $Bi_2(BDC)_3$ nanoplates

1 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved into 20 mL of ethylene glycol under stirring. The solution was marked as A. 4.25 mmol of NaOH and 2 mmol of 1,4- benzenedicarboxylate were put into 10 mL of ultrapure water. Continuously agitating till the aqueous solution became clear. The solution was labeled as B. Then B was slowly added into A with a rate of two drops per second. After that, the solution was allowed to stand for 4 h.

2.1.2. Preparation of $TiO_2/Bi_2(BDC)_3/BiOCl$ nanosheets

In a typical procedure, 0.2 mmol of the as-synthesized $Bi_2(BDC)_3$ nanoplates and 0.2 mmol of $TiCl_3$ aqueous solution were added into 20 mL of water. After 5 min stirring, the solution was put into a Teflon® lined stainless steel autoclave with 40 mL of capability and heated at 100 °C for 2 h. After the autoclave was cooled to room temperature, the products were separated centrifugally and washed three times with ultrapure water and absolute ethanol. Finally, the products were dried under vacuum at 60 °C for 4 h.

2.2. Characterization

The measurements of C, H, and O elements were performed on a PE 2400II CHNS/O elemental analyzer. Fourier transform infrared (FT-IR) spectra were obtained on a Bruker EQUINOX 55 FT-IR spectrometer ranged from 4000 to 400 cm^{-1}. The thermogravimetric (TG) curves were recorded on a Diamond TG-DTA thermal analysis instrument (PerkinElmer). Powder X-ray diffraction (XRD) patterns were carried out on a Bruker D8 Advanced X-ray diffractometer using CuKα radiation (λ = 0.15418 nm) at a scanning rate of 8° min^{-1} in the 2θ range of 10–70°. Raman spectra were collected on an inVia laser micro-Raman spectrometer using a Nd:YAG laser operating at 532 nm. Field emission scanning electron microscopy (FE-SEM) images were taken on a Nova NanoSEM 200 scanning electron microscope. Atomic force microscope (AFM) images were achieved on a Nanoscope IIIa atomic force microscope with tapping mode. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL 2010 microscope, using an accelerating voltage of 200 kV. The energy dispersed X-ray (EDX) spectra were operated on FE-SEM and HRTEM, respectively. The UV–vis diffuse-reflectance spectra (DRS) were recorded on a UV2450 (Shimadzu) using $BaSO_4$ as reference. The Brunauer–Emmett–Teller (BET) surface area was measured with an ASAP2020.

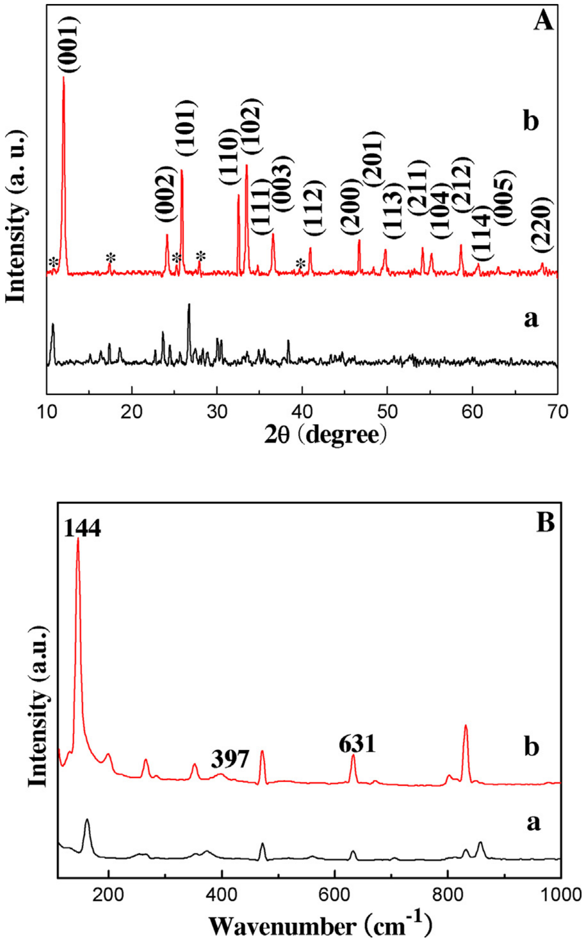

Fig. 1. XRD patterns (A) and Raman spectra (B) for $Bi_2(BDC)_3$ nanoplates (a) and $TiO_2/Bi_2(BDC)_3/BiOCl$ composites (b).