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Fabrication of metal-free two dimensional/two dimensional homojunction photocatalyst using various carbon nitride nanosheets as building blocks

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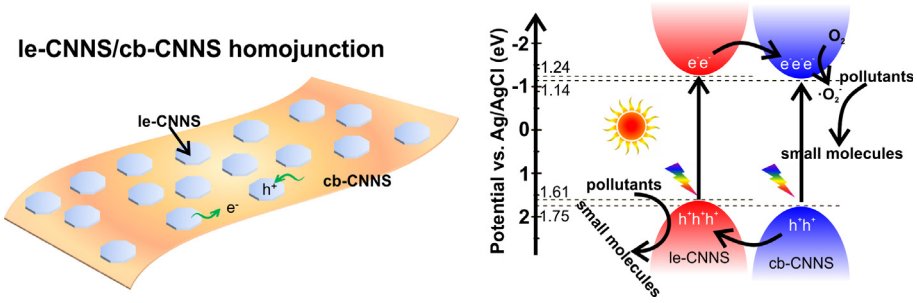
GRAPHICAL ABSTRACT



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ABSTRACT

Semiconductor photocatalysis currently suffered three main problems, low solar energy utilization, high photo-generated charge recombination rate and the heavy metal ions release by the photo-corrosion. Herein, we developed a visible-light-driven homojunction photocatalyst with the metal-free two-dimensional (2D) graphitic carbon nitride nanosheets (CNNS). By employing liquid exfoliation and chemical blowing approaches, we obtained two kinds of CNNS materials (le-CNNS and cb-CNNS) with different band structures, and subsequently fabricated the homojunction photocatalyst. This 2D/2D nanocomposited homojunction photocatalyst exhibited enhanced photocatalytic performance compared to these individual 2D nanosheets materials. Moreover, its well universality and reusability were also demonstrated by photo-degradation of various organic pollutants and five successive runs. By studying the optical properties and the electrochemical behavior, the band alignment of this homojunction was illustrated and the possible mechanism was proposed, where the transmitted electrons on the conduction band (CB) of le-CNNS would transport to the CB of cb-CNNS, and the holes on the valence band (VB) of cb-CNNS transferred to the VB of le-CNNS, therefore promoting the photo-induced carrier separation. Additionally, the photoluminescence, electrochemical impendence and photocurrent measurements further demonstrated that the recombination of photo-excited electron-hole pairs had been efficiently suppressed in the homojunction and were respectively collected on different CNNS components.

1. Introduction

With the rapid development of industry, the environmental issues have been increasingly more serious. Semiconductor photocatalysis technology as a kind of new technique has attracted tremendous attention due to the advantages of strong oxidation

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ability, high stability and mild reaction conditions [1–4]. However, the most used photocatalyst, TiO_2, only works with ultraviolet light, which accounts for less than 5% of sunlight [5,6]. Some typical narrow gap semiconductor photocatalysts, such as CdS [7], Cu_2O [8], PbS [9], will undergo the photo-corrosion in the process of photocatalysis, therefore resulting in the secondary pollution from the release of heavy metal ions. Thus, exploring environment-friendly metal-free photocatalysts is currently urgent for the practical applications of semiconductor photocatalysis. Recently, a CN based polymeric semiconductor, graphitic carbon nitride (g-C_3N_4), has received extensive attention because of its metal-free nature, low-cost and wide raw materials, high stability, narrow band gap (~2.7 eV) and the suitable edge potential of conduction band (CB)/valence band (VB) [10–12]. Nevertheless, the photocatalytic performance of g-C_3N_4 is limited by the fast recombination of photo-generated electron-hole pairs [13].

The construction of heterojunctions by two semiconductors with suitable band alignment is an effective approach to suppress the charge recombination and subsequently promote the separate accumulation of electrons and holes on the two sides of heterojunctions [14–16]. Besides the band alignment of two semiconductors, the creation of heterojunctions is also dependent on other properties of semiconductor, such as electron affinity and work function [15]. Several kinds of g-C_3N_4 based heterojunctions have been fabricated and therefore applied in photocatalysis [17–19]. Semiconductor p-n junctions have widely used in electronics, photovoltaic energy converter and photocatalysis [20]. Recently, coupling of n-type g-C_3N_4 with p-type semiconductors has been employed to form g-C_3N_4 based p-n heterojunctions, for instance Ag_2O/g-C_3N_4 [21] and Cu_2O/g-C_3N_4 [22]. Additionally, the isotype heterojunctions between n-type g-C_3N_4 and other n-type semiconductors have also been developed, such as CdS/g-C_3N_4 [18] and TiO_2/g-C_3N_4 [23]. Compared to raw g-C_3N_4, evident enhancement of photocatalytic activity has been achieved by g-C_3N_4 based heterojunctions, however most of these heterogeneous semiconductors are transitional metal oxides, sulfides and oxometallates, where the risk of heavy metal ions release is inevitable.

Besides these above heterojunctions, different crystal phases of the same substance have also been used to fabricate heterojunctions, like Degussa P25 TiO_2 [24], rutile/anatase composite [25] and composite of TiO_2 nanoparticles/titania nanosheets [26]. It is of significant importance that the electronic structure of graphitic carbon nitride can be tuned by morphological control [27,28], elemental doping [29,30], and surface modification as well [31]. Thus, it is possible to construct g-C_3N_4 based homojunctions with stagger band alignment and little interface resistance as well by coupling different g-C_3N_4 materials, such as, the S-doped g-C_3N_4/g-C_3N_4 composite [32] and the composite of urea-based g-C_3N_4 and thiourea-based g-C_3N_4 [33].

The enhanced photocatalytic activity of heterojunctions or homojunctions is mainly dependent on the space charge accumulation or depletion at the interfaces of two phases. Consequently, the contacted area between two compositions plays a key role for promoting the separation of photo-excited carriers at the interfaces. Unfortunately, the current g-C_3N_4 homojunctions are usually formed by the as-prepared granular materials, and the contacted area is relatively small because of their low surface area. As a layered material with analogous structure to graphite, tremendous efforts have been devoted to obtained ultrathin two-dimensional (2D) g-C_3N_4 nanosheets (CNNS), as graphene derived from graphite [34]. The synthetic strategies of CNNS are mainly concluded to two categories: top-down routes and bottom-up methods [35,36]. The former includes ultrasonic exfoliation [37,38] and soft-chemical delamination in H_2SO_4 solution [39] or alkali condition [40], and the latter involves the template methods [41] and the chemical blowing approaches [42,43]. As expected, CNNSs attained from various ways have different thickness, lateral size and surface groups, which result in the dissimilar electronic band structures. Therefore, it is possible, in principle, to construct homojunctions using two various CNNSs with suitable band alignment. Herein, we firstly prepared CNNS colloids from the liquid exfoliation of g-C_3N_4 in alkali solution that was denoted as le-CNNS, and employed the chemical blowing route to obtain the bottom-up CNNS marked as cb-CNNS. These two kinds CNNSs were subsequently coupled to form a CNNS-based homojunction photocatalyst without metal composition. We investigated its photocatalytic activity by degradation of organic pollutants under visible light irradiation, and evaluated the stability and reusability, as well as the universality for decomposing other pollutants. Moreover, the possible mechanism of the enhanced photocatalytic behavior was discussed.

2. Experimental section

2.1. Material synthesis

2.1.1. Preparation of le-CNNS

The le-CNNS was prepared by the delamination of the as-synthesized g-C_3N_4 in an alkali solution, as described in our previous report [40]. The g-C_3N_4 sample was obtained by directly heating melamine at 520 °C for 4 h in a muffle furnace. Subsequently, 1 g of the obtained g-C_3N_4 sample was dispersed into a 150 mL NaOH solution (0.2 mol L^{-1}), and the suspension was stirred and heated in 100 °C water bath for 12 h. After decanting the clear supernatant, the sediment was re-dispersed into tubes with 50 mL deionized water. Afterwards, the mixture was centrifuged at 8000 rpm for 4 min to remove precipitation, and finally we obtained le-CNNS colloidal suspension.

2.1.2. Preparation of cb-CNNS

The cb-CNNS was synthesized according to the chemical blowing route using melamine as precursor and NH_4Cl as the chemical blowing agent [43]. Typically, the solid melamine and NH_4Cl with a mass ratio of 1:4 were mixed in agate mortar, and then the mixture was transferred into a crucible. After heating it in the muffle furnace under the same condition to the preparation of g-C_3N_4, the 2D cb-CNNS was obtained.

2.1.3. Fabrication of 2D/2D le-CNNS/cb-CNNS homojunction photocatalyst

Firstly, the solid cb-CNNS was added into the colloidal suspension of le-CNNS with a le-CNNS/cb-CNNS mass ratio of 3:1, and the mixture was stirred for 12 h to obtain a uniform suspension. Then, a certain volume of 1 M HCl was dropwise added to the suspension and subsequently stirred for 1 h at room temperature. The resulting precipitate was collected by filtration, washed thoroughly with deionized water and dried at 60 °C overnight.

2.2. Characterizations

Scanning electron microscopy (SEM) images were obtained with a Quanta 250FEG Field emission scanning electron microscope. Transmission electron microscopy (TEM) observation was performed on a JEOL JEM-2100 electron microscope. The structure of samples was characterized by X-ray diffraction (XRD, DX-2700 diffractometer, Dandong Haoyuan Instrument Co. Ltd., China). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Avatar 370 spectrophotometer using the standard KBr disk method. UV–vis absorption spectra and diffuse reflectance spectra (DRS) were performed on a Shimadzu 2450 UV–vis spectrometer with an integrating sphere using $BaSO_4$ as the reference. X-ray