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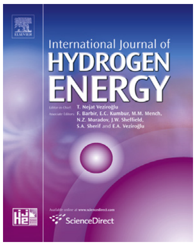

ZnCr LDH nanosheets modified graphitic carbon nitride for enhanced photocatalytic hydrogen production

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ZnCr layered double hydroxides (ZnCr LDH) nanosheets modified graphitic carbon nitride ($g-C_3N_4$) nanohybrids were fabricated via a self-assembly procedure through electrostatic interaction between these two components. Such 2D-2D inorganic-organic hybrid material was employed for photocatalytic hydrogen production under visible light for the first time. The physical and photophysical properties of the hybrid nanocomposites were investigated to reveal the effect of ZnCr LDH nanosheets on the photocatalytic activities of $g-C_3N_4$. It was found that 1 wt% ZnCr LDH nanosheets modified $g-C_3N_4$ was optimal for the formation of intimate interfacial contact. The visible light photocatalytic H_2 production activity over $g-C_3N_4$ was enhanced about 2.8 times after ZnCr LDH nanosheets modification. The significant enhancement in photocatalytic performance for ZnCr LDH/$g-C_3N_4$ heterojunction should be attributed to the promoted charge transfer and separation efficiency, resulting from the intimate interfacial contact and Type II band alignment between ZnCr LDH and $g-C_3N_4$.

Introduction

Driven by decreasing fossil fuel consumption, increasing energy demand and environmental pollution, the search for clean and sustainable energy is attracting massive research interest. During last few decades, photocatalytic hydrogen production from water, perceived as one of most promising technologies to convert solar energy to H_2, has attracted much attention [1–3]. Up to now, numerous semiconductor materials have been explored for this application, such as oxides [4,5], sulfides [6,7] and nitrides [8,9]. However, the photocatalytic efficiency generally suffers from limited light absorption, poor charge transport properties or sluggish interfacial kinetics toward water splitting [10]. Therefore, the design of efficient and stable photocatalysts is always an important issue. Semiconductors hybridization has been shown to be an effective method to enhance photocatalytic activity through a heterojunction structure formed by different components [1,11]. It will result in a spatial separation of photo-generated electrons and holes, a decrease of their recombination probability, and thus an increase of their lifetime and photocatalytic efficiency. Since most advantages of the hybridization technique originate from the chemical interaction between hybridized components on their interface, nanostructured materials with expanded surface area become promising building blocks for the synthesis of hybrid materials [12,13]. Compared with other nanostructured

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materials, the two-dimension (2D) nanosheets of layered materials are unique because of their unusually high anisotropy in crystal structure and morphology [14–17]. It makes it possible to design and synthesis novel hybrid type materials with versatile and tailorable physicochemical properties. One typical example of 2D nanosheets is the reduced graphene oxide nanosheets prepared by the exfoliation of graphite oxide [18,19]. This material has been extensively explored to construct highly efficient photocatalysts with other semiconductors [20].

In fact, compared with graphene nanosheets, the 2D nanosheets of inorganic solids, due to their adjustable components, have much diversity in crystal structure, chemical composition, surface properties, and so on [21,22]. The most important trait is that the 2D inorganic nanosheets boast a broad spectrum of physicochemical properties, and moreover these properties are tunable by changing the chemical composition of the pristine compound [13]. Despite such unique and intriguing advantages of inorganic nanosheets, there are still only limited numbers of studies regarding the inorganic nanosheet-based hybrid materials.

Layered double hydroxides (LDHs), typical 2D inorganic materials, have received great attention in the field of photocatalytic water splitting [23–28] due to their interesting physicochemical properties such as large surface areas, positively charged brucite-like layers, and compositional flexibilities in both hydroxide layers and interlayer anions [29]. It is noted that the action of formamide on LDHs can induce their exfoliation into nanosheets with a sub-nanometer-level thickness [30,31]. Researchers have used the exfoliated ZnCr LDH as an efficient matrix for electronic coupling with hybridized semiconductor species, leading to the synthesis of new efficient photocatalysts with significant photocatalytic activity enhancement [32–35]. Therefore, it is worth to further explore novel nanohybrid photocatalysts constructed by the exfoliated ZnCr LDH nanosheets.

In recent years, metal free polymer like graphitic carbon nitride (g-C_3N_4) is reported to be active for water splitting under visible light, both for hydrogen [36–42] and oxygen [43] production. It should be a good candidate for photocatalytic solar conversion because of low cost, nontoxicity and visible light activity. However, the photocatalytic efficiency of pure g-C_3N_4 was relatively low, mainly due to the fast recombination of photogenerated electron–hole pairs. It has been observed that coupling g-C_3N_4 with layered semiconductors is an effective strategy for improving the photocatalytic properties [28,44]. However, the fabrication of a nanohybrid from g-C_3N_4 with exfoliated ZnCr LDH nanosheets has not been reported yet. According to the research reported, the zeta potential of g-C_3N_4 water suspension is negative, indicating of negatively charged g-C_3N_4 surface [45,46]. In this regard, the derivatives of positively charged ZnCr LDH nanosheets modified negatively charged g-C_3N_4 powder can be prepared by electrostatically derived self-assembly process.

Herein, inspired by above work, we have fabricated a novel kind of nanohybrids by modified the g-C_3N_4 bulk powders with the exfoliated ZnCr LDH nanosheets through electrostatic interaction. These nanocomposites were characterized by the XRD, TEM, UV–vis diffuse reflectance spectra, photoluminescence (PL) spectra, BET surface area, FTIR and XPS etc. Remarkably, the photocatalytic water splitting behavior towards H_2 evolution was significantly enhanced under visible light irradiation in the case of the composites as compared to pure g-C_3N_4 and ZnCr LDH. The enhanced hydrogen production activity should be attributed to the decreased photoinduced charge carriers recombination efficiency, owing to the formation of heterojunction and the Type II band alignment between the two components.

Experimental

Synthesis of photocatalysts

All chemicals in the present study were of analytical grade and used without further purification. ZnCr LDH powder intercalated with NO_3^- was prepared according to the reported procedure [33]. Aqueous solution A of $Zn(NO_3)_2 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ with a molar ratio of 2:1 was dissolved in 40 mL of decarbonated deionized water ($[Zn^{2+}] + [Cr^{3+}] = 1$ M). At the same time, aqueous solution B containing 1 M NaOH was prepared as well. Under the protection of N_2 atmosphere, solutions A (40 mL) and B (80 mL) were simultaneously added into 40 mL of decarbonated deionized water, and the pH of the suspension was maintained at approximately 5.5. The resulting slurry was vigorously stirred for another 2 h and then aged for 24 h under room temperature. The final precipitate was centrifuged with deionized water and dried at 60 °C under vacuum for 24 h. ZnCr LDH nanosheets were prepared by vigorous stirring in formamide (1 g L^{-1}) under N_2 protection to avoid carbonate contamination as reported previously [31,33].

In a typical process for g-C_3N_4 preparation, 5.0 g melamine was added into an alumina crucible and heated to 520 °C by 2 h and kept at this temperature for another 4 h in air. After cooling to room temperature, the yellow block was grinded into powder.

Composites with different mass ratio of ZnCr LDH nanosheets modified g-C_3N_4 (CNLDHs for short) were prepared by dripping exfoliated ZnCr LDH formamide suspension into bulk g-C_3N_4 water suspension under vigorous stirring. The mixture was kept stirring for another 30 min and aged for 24 h at room temperature. Then the composites were washed with deionized water and ethanol and dried under vacuum at 60 °C overnight. 0.1 g g-C_3N_4 was used in each preparation process and the total volume of suspension was kept at 80 mL. In detail, the mass ratio of ZnCr LDH nanosheets was 0%, 0.5%, 1%, 2.5%, 5%, 10% and 100%. And correspondingly, the composites were labeled as CN, CNLDH0.5, CNLDH1, CNLDH2.5, CNLDH5, CNLDH10 and LDH.

Characterization of photocatalysts

Powder X-ray diffraction (XRD) patterns were collected to analyze the crystallographic structure of prepared photocatalyts at room temperature by a PANalytical X'pert MPD Pro diffractometer operated at 40 kV and 40 mA using Ni-filtered Cu-Kα irradiation (Wavelength: 1.5406 Å). A JEOL JSM-7800F scanning electron microscope (SEM) and a FEI Tecnai G2 F30 transmission electron microscope (TEM) at an accelerating voltage of 300 kV were used to characterize the morphology of

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