

Advantages of C₃N₄ with Layered Double Hydroxides Heterojunctions

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Environmental pollution has been decreased by using photocatalytic technology in conjunction with solar energy. An efficient method to obtain highly efficient photocatalysts is to build heterojunction photocatalysts by combining graphitic carbon nitride (g-C₃N₄) with layered double hydroxides (LDHs).

Keywords: layered double hydroxides ; carbon nitride ; heterojunction

1. Introduction

Environmental pollution has made it extremely difficult for humanity to flourish sustainably ^{[1][2][3][4][5]}. The use of photocatalytic technology to harness clean and reproducible solar energy is widely considered to be the most effective answer to the issues ^{[6][7][8]}. An effective method for reducing pollution is to use photocatalytic technology to degrade organic pollutants by using solar irradiation ^{[9][10]}. In principle, photocatalysis is an oxidation-reduction process. The fundamental components of the photocatalytic process, photocatalysts, are crucial in driving the reaction and harvesting light ^{[11][12][13][14][15]}. Consequently, research into highly effective photocatalysts is crucial for the advancement of photocatalytic technology.

An organic semiconductor having triazine or heptazine as its main constitutional unit and a layer structure resembling graphite is known as graphitic carbon nitride (g-C₃N₄) ^{[7][8][16]}. Since the use of g-C₃N₄ in photocatalytic hydrogen synthesis was initially discovered ^[17], it has garnered considerable interest. Because g-C₃N₄ possesses a smaller band gap (approximately 2.7 eV) than traditional photocatalysts like TiO₂ ^[18], it can be stimulated by visible light. Furthermore, g-C₃N₄ is competitive among other photocatalytic materials due to its excellent chemical stability, high thermostability, affordable raw ingredients, and straightforward production procedure ^{[19][20][21][22]}. However, there are numerous issues with the industrial uses of g-C₃N₄. Only blue and purple lights, with a wavelength of 460 nm, may pass through g-C₃N₄, resulting in a low solar energy utilization rate ^[23]. The redox capacity of g-C₃N₄ is reduced because of the rapid recombination of photocarriers. The specific surface area (SSA) of g-C₃N₄ is relatively tiny because of its bulk characteristics. These flaws prevent g-C₃N₄ from being developed further for photocatalytic uses. To increase the photocatalytic performance of g-C₃N₄, various techniques have been used, including decorating co-catalysts, doping elements (such as F, O, Ni, Fe, etc.), building nanostructures, creating heterojunctions ^{[24][25]}, etc. To boost the separation of charge carriers in g-C₃N₄, creating heterostructures with different semiconductors is the most important technique. Because of the varying Fermi levels between various photocatalysts, when they come into contact with one another, charge carriers can travel across the semiconductors, which ultimately create an internal electric field (IEF) between them. The electric field allows the photoinduced electrons and holes to flow in a certain direction, thereby separating them ^{[26][27]}.

A highly efficient method for improving photocatalytic performance has recently been discovered by creating layered double hydroxides (LDHs)/g-C₃N₄ heterojunctions. Essentially, LDHs are a class of two-dimensional (2D) hydrotalcite-like clay materials made up of exchangeable interlayer anions and positively charged host layers ^{[28][29]}. LDHs and their derivatives have been found useful in a variety of sectors, especially photocatalysis, because of their inexpensive features, excellent chemical stability, customizable composition, homogeneous distribution of cations and anions, and interchangeable interlayer anions. Nevertheless, because of the fast recombination of photocarriers, the photocatalytic activity of single LDHs is unsatisfactory ^[30]. Therefore, by building LDH/g-C₃N₄ heterojunctions with a smart design, it is possible to obtain optimal photocatalysts with top performance while overcoming the drawbacks of g-C₃N₄ and LDHs.

2. Advantages of LDH/g-C₃N₄ Heterojunctions

It has been suggested that one efficient method to enhance the photocatalytic activity of LDH/g-C₃N₄ composites is to build 2D/2D heterojunctions. In addition to providing a large number of surface active sites to create heterojunctions, the 2D structure of LDHs and g-C₃N₄ significantly reduces the distance over which photocarriers must move within the 2D/2D heterojunctions, favoring a photocatalytic reaction [31][32]. LDHs are ideal materials for creating 2D/2D heterojunctions with g-C₃N₄ because of their suitable band structure and variable composition [29]. As is known to all, the band gap of LDHs is about 2.0–3.4 eV, which can be adjusted by changing and regulating the M²⁺ and M³⁺, which is advantageous for the capture of visible light [33]. In addition, the materials' abundance of basic sites makes them useful as heterogeneous photocatalysts for various chemical processes [34]. The active sites of LDH/g-C₃N₄ 2D/2D heterojunctions are also changeable due to the ability to manipulate the cations and anions [35]. Moreover, designing LDHs' interlayer space, number of layers, and functionalization with g-C₃N₄ are all rather simple processes (**Figure 1**). There are several advantages to LDH/g-C₃N₄ heterojunctions as shown below: (i) Owing to the close contact between LDHs and g-C₃N₄, photocarriers can conveniently migrate, which is beneficial for photocarrier separation [36]. (ii) The high surface area in LDH/g-C₃N₄ heterojunctions and their strong light harvesting ability are beneficial for photocatalytic activity [37]. (iii) LDH/g-C₃N₄ heterojunctions exhibit a shorter migration distance than photocarriers, thus reducing the electron-hole recombination [38]. (iv) The band structure can be simply adjusted [39]. All of these advantages ensure them with huge application potential in organic pollutant removal.

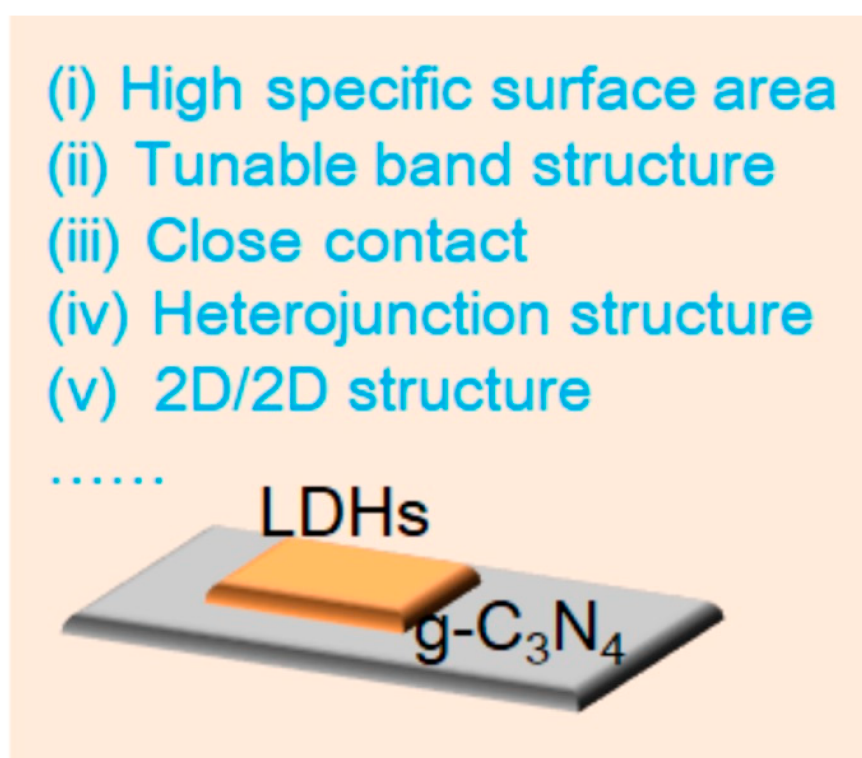


Figure 1. Advantages of LDH/g-C₃N₄ heterojunctions.

Based on the band alignment between the conduction band (CB) and the valence band (VB) of LDHs and g-C₃N₄, the heterojunctions formed between them can be classified into three types: straddling-gap junctions (Type I), staggered-gap junctions (Type II), and broken-gap junctions (Type III). When two semiconductors with staggered band alignment are intimately contacted, and there exists a charge migration between the CB in LDHs and the VB in g-C₃N₄, a Z-scheme system is formed. This Z-scheme system is characterized by an efficient electron-hole separation process, leading to enhanced photocatalytic activity. The charge transfer between the semiconductors results in the formation of a potential difference at the interface, driving the separation of photogenerated charge carriers and reducing their recombination rate. This mechanism significantly improves the overall efficiency and performance of the heterojunction photocatalysts. Therefore, understanding the band alignment and charge transfer processes in heterojunction systems is crucial for the design and optimization of advanced photocatalytic materials with superior performance. Although both the Z-scheme and Type II heterojunctions have the same staggered band alignment, e⁻-h⁺ transfer occurs in opposite directions in these two semiconductors. In contrast to Type II heterojunctions, where photogenerated e⁻ and h⁺ are transferred from high potentials to low potentials, leading to compromised redox capacities, a Z-scheme heterojunction can drive the photogenerated e⁻ in LDHs to migrate and then recombine with the photogenerated h⁺ in g-C₃N₄. This process leaves the high energy h⁺ at the VB of LDHs and the high energy e⁻ at the CB of g-C₃N₄ for photocatalysis [40].

To confirm the existence of the type of heterojunction, band structure analysis is crucial ^[41]. The solid UV-vis absorption and the X-ray photoelectron spectroscopy (XPS) valence band spectrum are common techniques for obtaining the band structure. Through the band structure analysis, researchers can determine what kind of heterojunction it is (Type I, Type II, and Type III). Notably, Type II and Z-scheme heterojunctions share a similar staggered band alignment structure. Nevertheless, their charge transfer pathways are significantly different. In order to determine if the charge transfer route is Z-scheme or type II heterojunctions, it is therefore critically necessary to investigate it in detail using some techniques such as (i) self-confirmation by photocatalytic reactions, products, and radical species, (ii) selective photodeposition of a noble metal, (iii) in situ XPS, (iv) femto-second transient absorption spectra (fs-TAS), (v) photoassisted Kelvin probe force microscopy (photo-KPFM), theoretical calculations, etc. For example, the work function (Φ) plays a crucial role in investigating the energy band alignment and charge transfer of heterojunctions, making it an essential physical parameter ^[42]. Researchers can also determine Φ through theoretical calculations and further determine the charge transfer route.

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