



# In-situ self-sacrificial fabrication of lanthanide hydroxycarbonates/graphitic carbon nitride heterojunctions: nitrogen photofixation under simulated solar light irradiation



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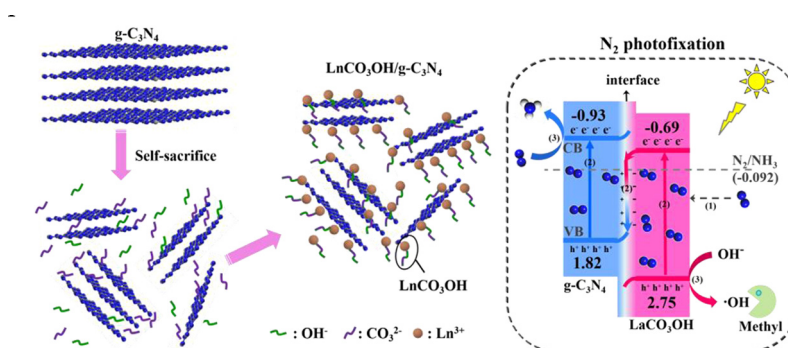
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## HIGHLIGHTS

- $\text{LnCO}_3\text{OH}/\text{g-C}_3\text{N}_4$  was synthesized by using the decomposition products of  $\text{g-C}_3\text{N}_4$ .
- $\text{LnCO}_3\text{OH}/\text{g-C}_3\text{N}_4$  exhibited well-combined interface though Ln–N bonds.
- $\text{LnCO}_3\text{OH}/\text{g-C}_3\text{N}_4$  showed high chemisorption to  $\text{N}_2$ , activating more  $\text{N}_2$ .
- The charges separation was accelerated in  $\text{LnCO}_3\text{OH}/\text{g-C}_3\text{N}_4$  Z-scheme heterojunction.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

$\text{LnCO}_3\text{OH}/\text{g-C}_3\text{N}_4$  (named Ln–CN, Ln=La, Pr) heterojunction was synthesized with a facile in-situ hydrothermal method by self-sacrificing a part of  $\text{g-C}_3\text{N}_4$  as anion source. The photocatalytic activity of Ln–CN heterojunction was evaluated by nitrogen photofixation under simulated solar light irradiation. The result displayed that Ln–CN exhibited considerable improvement in nitrogen photofixation compared to  $\text{g-C}_3\text{N}_4$  and  $\text{LnCO}_3\text{OH}$ . Strong nitrogen adsorption energy offered by chemical adsorption ensure that more nitrogen was adsorbed and activated on the surface of Ln–CN. Moreover, in Ln–CN Z-scheme heterojunction, the electron at CB of  $\text{LnCO}_3\text{OH}$  transferred to VB of  $\text{g-C}_3\text{N}_4$  through the Ln–N interface channel. The recombination rate of charges carriers was reduced, leaving more electron at CB of  $\text{g-C}_3\text{N}_4$  to reduce the adsorbed nitrogen. Results from time-resolved PL, photocurrent, and EIS characteristics further proved Ln–CN showed low recombination rate of photogenerated charges carriers. Finally, the stability of Ln–CN was certified to be excellent, which is significant for practical application. This study presents a simple self-sacrificial method to synthesize  $\text{LnCO}_3\text{OH}/\text{g-C}_3\text{N}_4$  heterojunction, which can be extended to the fabrication of other  $\text{g-C}_3\text{N}_4$ -based heterojunction.

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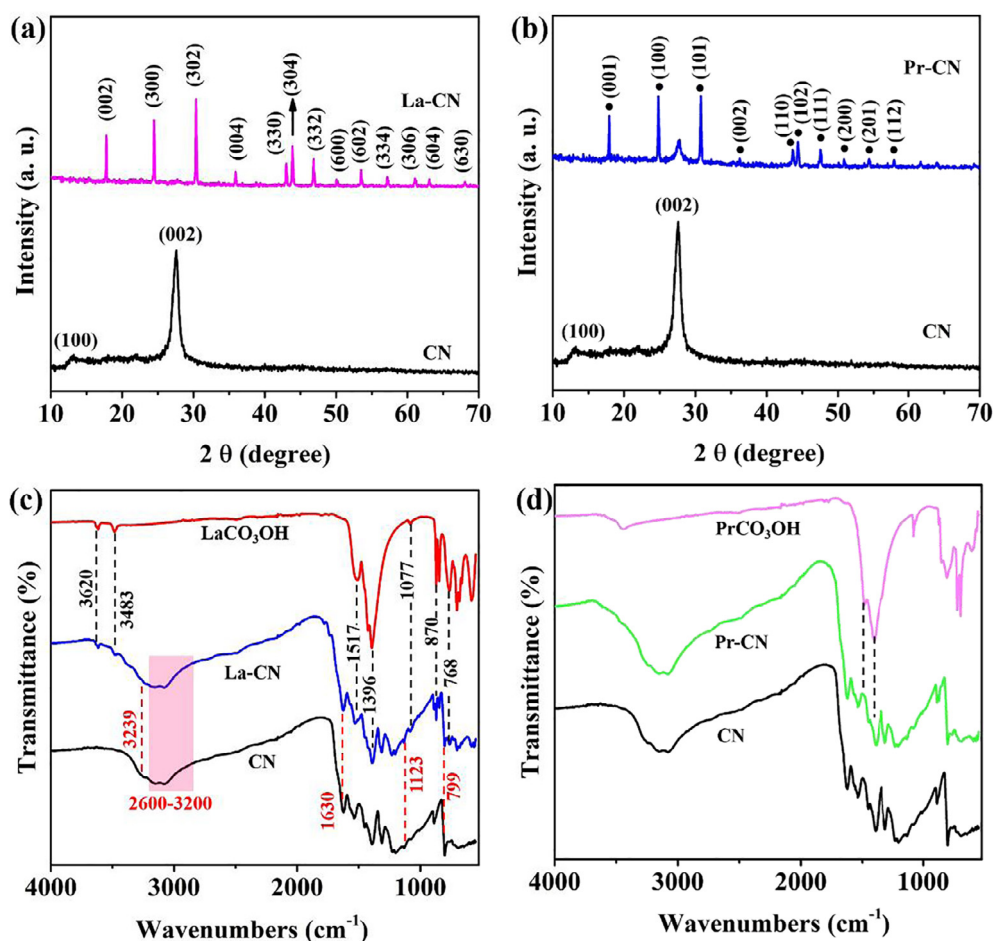


Fig. 1. XRD diffraction patterns of Ln-CN and CN (a-b). IR spectra of CN, LnCO<sub>3</sub>OH, and Ln-CN samples (c-d).

## 1. Introduction

Ammonia, as a kind of fertilizer and one of the most promising indirect hydrogen storage materials, has attracted considerable attention in recent years [1–3]. Using solar light to drive the photocatalytic reduction of nitrogen to ammonia is of particular interests because it mimics photosynthesis and converts solar energy into chemical energy [4–7]. And it is a low energy consumption process than the traditional Haber-Bosch nitrogen fixation process [8]. A lot of photocatalysts have been reported to be applied in nitrogen photofixation [9–14]. However, the catalysts for nitrogen photofixation still face several challenging issues such as low N<sub>2</sub> adsorption and activation energy and high photogenerated charges recombination rate.

Melon-based g-C<sub>3</sub>N<sub>4</sub>, as a novel semiconductor with  $\pi$ -conjugated structure, is a promising photocatalyst [15–18]. It is cheap, highly stable, and non-toxic. Furthermore, the suitable band gap ( $E_g = 2.7$  eV) enables the visible-light absorption [19,20]. Unfortunately, bulk g-C<sub>3</sub>N<sub>4</sub> also suffers from the fast recombination and short lifetime of photogenerated electron-hole pairs, limiting the photocatalytic activity. Complexing with other materials, such as metal, metal oxide, metal sulfide, reduced graphene oxide (rGO), and metal-organic framework (MOF), has been recognized as a relatively simple method to overcome this disadvantage [21–27]. Photogenerated charges can transfer easily between g-C<sub>3</sub>N<sub>4</sub> and the load material. Thus, it can prevent the recombination of the photogenerated electrons and holes. In recent years, lanthanide compounds have attracted the attention of researchers [28–31]. Lanthanide hydroxycarbonates (LnCO<sub>3</sub>OH), as a promising photocatalyst, have been studied extensively in the photocatalytic application recently. Pan et al. [32] reported LaCO<sub>3</sub>OH had the ability of

photocatalytic hydrogen evolution from methanol aqueous solution under UV light irradiation. Recently, LaCO<sub>3</sub>OH/Ag<sub>3</sub>PO<sub>4</sub> was reported for degrading organic dyes under visible light irradiation [33,34]. Therefore, LnCO<sub>3</sub>OH/g-C<sub>3</sub>N<sub>4</sub> photocatalyst with a heterojunction as an electron transfer channel was expected to have a high charges separation efficiency. Besides, the factors affecting the nitrogen photofixation include not only the electron transport rate but also the adsorption and activation of nitrogen. Considering the nitrogen atoms have a positive electron affinity, antibonding  $\pi$ -orbitals of nitrogen will bond to metal cations sites [35,36]. Thus, the formed metal–N bonds are able to activate N≡N bond, making the nitrogen photofixation easier [37]. For LnCO<sub>3</sub>OH/g-C<sub>3</sub>N<sub>4</sub>, Ln<sup>3+</sup> was expected to bond with nitrogen and activate it. Therefore, LnCO<sub>3</sub>OH/g-C<sub>3</sub>N<sub>4</sub> would have a good nitrogen activation property and be able to be applied in nitrogen photofixation.

Currently, the synthesis methods for heterojunction catalysts include in situ synthesis, ion exchange, post-modification and so on [38–40]. Self-sacrificial method, using a kind of material as a sacrificial agent to convert into another material, is a new method to synthesis heterojunction [41]. There was a well-combined interface in the heterojunction prepared by this method. However, the sacrificial material was removed finally in most reports, which was a serious waste. Herein, a cost-effective method, in-situ self-sacrificing method, was used in the fabrication of LnCO<sub>3</sub>OH/g-C<sub>3</sub>N<sub>4</sub> (Ln-CN) heterojunction photocatalysts. As a sacrificial agent, a part of g-C<sub>3</sub>N<sub>4</sub> was used to produce CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup> for LnCO<sub>3</sub>OH formation. The residual g-C<sub>3</sub>N<sub>4</sub> was not wasted and been used as a part of the heterojunction. Then the obtained Ln-CN heterojunctions were applied in nitrogen photofixation. The result showed Ln-CN had considerably higher photocatalytic activity than bulk g-C<sub>3</sub>N<sub>4</sub> and LnCO<sub>3</sub>OH on nitrogen fixation under simulated

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