



Facile synthesis of highly efficient nano-structured gallium zinc oxynitride solid solution photocatalyst for visible-light overall water splitting



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ABSTRACT

Gallium-zinc oxynitride (GaZnON) solid solution is a photocatalyst capable of effective overall water splitting under visible light. In order to address the inefficiencies of the synthesis of GaZnON solid solution (e.g., 10+ h at 850 °C under 250 ml min⁻¹ NH₃ flow), a facile technique is proposed. The technique utilizes crystalline Ga³⁺ and Zn²⁺ layered double hydroxides (LDHs) material as an atomic-level uniform precursor, and urea as the nanotemplated source of nitrogen. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis confirm the formation of wurtzite GaZnON in a 12 min process through distribution of the uniform Ga³⁺ and Zn²⁺ LDHs precursor within the nanotemplate formed through urea pyrolysis. The structural, optical, and electrochemical properties of the prepared samples were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy, and photoluminescence (PL) analysis. The newly synthesized photocatalyst consists of nanopores distributed uniformly through the surface and bulk of the solid solution particles; the presence of these nanopores improves the active surface area of the photocatalyst up to seven times, as compared to the one for traditionally prepared solid solution photocatalyst. The proposed technique is capable of controlling the composition of the final photocatalyst in a wide range of ZnO content ([Zn]/[Zn + Ga] up to 0.66). Apparent quantum yield (AQY) up to 2.5% at 420–440 nm was achieved by the photocatalyst with bulk [Zn]/[Zn + Ga] = 0.32, loaded with 1 wt% Rh nanoparticles. The effect of crystal defects and Zn content of the solid solution on the PL emission of the samples revealed that the GaZnON samples prepared with the LDHs precursor contain fewer crystal imperfections, which aids their water-splitting performance. The performance of the newly synthesized photocatalyst is among the highest reported in the open literature for photocatalysts loaded with a single co-catalyst. This photocatalyst has potential for future improvement through enhancement of the crystalline structure and improvement of the charge separation.

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1. Introduction

Providing clean and renewable sources of energy is arguably the most challenging task that humanity faces in the current century. One of the most viable and promising technologies that has attracted the attention of researchers in the last decade involves splitting water to hydrogen and oxygen on the surface of a visible-light-activated semiconductor photocatalyst, using photo-induced charges. Particularly in the last few years, many scientists have focused on metal oxynitride semiconductors as a new class of photocatalysts. These photocatalysts are known to be active for many

electrochemical reactions under visible light irradiation, including overall water splitting.

GaZnON solid solution, also known as (Ga_{1-x}Zn_x)(N_{1-x}O_x), where *x* is the ZnO fraction in solid solution crystalline structure, is one of the few photocatalysts reported to be active for overall water splitting under visible light irradiation. This solid solution photocatalyst yields a promising rate of hydrogen evolution at 420 nm with apparent quantum yield (AQY) of as high as 5.9% [1]. However, the long synthesis time at high temperature and flow of ammonia (10+ h, 850 °C, and 250 mL min⁻¹), is considered to be a serious drawback of the traditional synthesis method for this photocatalyst.

Various temperatures (ranging from 690 °C to 900 °C) and various durations (mostly over hours) have been reported to be effective for fabrication of GaZnON solid solutions with variable properties, and functionalities corresponding to the composition,

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morphologies, and structures of the starting materials [2–10]. The optimal temperature and duration for the synthesis of the nanostructured GaZnON solid solution is a function of various competing factors, which potentially control the morphology, crystallinity, optical properties, and electrochemical performance of the final product. Although a high synthesis temperature (>850 °C) enhances the rate of solid state reaction, it adversely affects the characteristics of the prepared photocatalyst at nanoscale.

At relatively low nitridation temperatures (<700 °C), the chemical transformation from spinel ZnGa₂O₄ to the wurtzite oxynitride GaZnON is slow, due to insufficient energy to overcome the nitridation activation barrier, and the slow diffusion rates of atoms, both within and between the component's structures. It has been reported that spinel phase formation is the key step of the solid-state reaction, while the phase transition from spinel ZnGa₂O₄ to wurtzite GaZnON solid solution can take place in time of the order of minutes at 850 °C [5], or temperatures as low as 650 °C, using ZnO and ZnGa₂O₄ nanocrystals in the precursor [2]. Particularly for a solid-state reaction, the structure and morphology of the precursor are of great importance. It has been suggested that the intimate contact between the starting materials plays a crucial role in controlling the rate of solid-state reaction [10–12]. Due to the importance of solid–gas phase diffusion in the nitridation step, the crystallinity and structure of the starting precursor, as well as its introduction into the active nitrogen source are arguably the most effective parameters. Without a massive contact between the solid–solid starting materials and the gas–solid reactants, the synthesis time increases substantially. Therefore, a uniform nanostructured precursor with high surface area in contact with an effective and sufficient source of nitrogen is essential for GaZnON solid solution synthesis.

Urea, as an abundant, non-toxic organic compound, is suitable for large-scale production, and has been extensively used for nitrides and nitrogen-doped sample preparation [13–26]. At elevated temperatures, urea decomposes via pyrolysis, transforming into nanoscale foam that has been frequently used as a soft template for synthesis of inorganic nanocrystals and porous structures [14,15]. Compared to other template synthesis methods, this soft template method is very convenient and avoids the introduction of impurities [14], and is therefore suitable for synthesis of nanoporous oxynitride semiconductors.

The effectiveness of urea as an active source of nitrogen for the nitridation reaction in reducing the synthesis time of inorganic compounds has previously been reported. Qiu and Gao reported an efficient preparation route of wurtzite GaN powder from gallium-urea complex at lower temperatures (500–600 °C) in 1 h, comparing to the traditional techniques that take place at higher preparation temperatures (>850 °C) for extended periods [19]. Yang et al. reported that the synthesis of GaZnON using urea over a facile microwave technique leads to a remarkable reduction in synthesis time [27]; however, the prepared photocatalyst has not yet been examined for overall water splitting.

The kinetic studies of the pyrolysis reaction, as well as analysis of the evolved gases indicate the dominance of NH₃ gas at elevated temperatures [28,29]. It has been stated that the end products of pyrolysis reactions are highly dependent on the temperature, heating rate, and decomposition environment [28,29]. This is attributed to the corresponding variation in efflux rates of the different reactants, e.g., a higher heating rate leads to a higher gas phase concentration of possible reactants [29].

Layered double hydroxides (LDHs) were discovered in the mid-19th century and have been extensively studied for many applications. Among the numerous applications, mixed-metal oxides prepared by precipitation in the form of LDHs with large specific surface areas (100–300 m² g⁻¹) have been widely studied [30]. LDHs are synthetic anionic materials that can be represented

as [(M²⁺)_{1-x}(M³⁺)_x(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·yH₂O [31]. Their structure contains brucite-like layers in which divalent cations (M²⁺) are replaced by trivalent ions (M³⁺), resulting in a positively charged layered structure. The characteristics of positively charged layers, including the divalent and trivalent cations (M²⁺ and M³⁺, respectively) and the interlayer anion (Aⁿ⁻), as well as their relative composition (x), can be varied over a wide range [31].

The LDHs structure could potentially be identified as a suitable host for a GaZnON precursor for solid-state synthesis of mixed-metal oxynitrides, due to the homogeneity of divalent and trivalent cations at the atomic level, and efficient gas diffusion within the layered structures [11]. Wang et al. utilized LDHs precursor for GaZnON solid solution synthesis through NH₃ nitridation. The synthesized photocatalyst was characterized as well-crystalline wurtzite phase, and its performance was examined for photoreduction of Cr⁶⁺ ions under visible light [10], but not for overall water splitting.

We propose a facile synthesis technique that addresses the difficulties associated with the traditional synthesis route of GaZnON solid solution by utilizing urea as the synthesis nanotemplate nitrogen source, and the Ga³⁺ and Zn²⁺ LDHs as the crystalline precursor that is uniform at the atomic level. This approach potentially reduces the synthesis time, while maintaining the nanoscale structure of the final product. To the authors' knowledge, this is the first study on the synthesis and overall water-splitting performance evaluation of nanoporous GaZnON prepared with LDHs precursor, and the first contribution to a fundamental understanding of its optical, structural, and electrochemical characteristics.

2. Materials and methods

2.1. Precursor preparation

Layered double hydroxides precursor of Ga³⁺ and Zn²⁺ was prepared as described previously [10], with some modifications. Various amount of Ga₂O₃ (99.99+%, Sigma–Aldrich) and ZnO (99+%, Sigma–Aldrich) powder with [Zn]/[Zn + Ga] = 0.06–0.67 was dissolved in 8 M HCl at boiling temperature. The pH of the solution was adjusted to 9 with a mixed aqueous solution of 2 M NaOH and 1 M Na₂CO₃, added drop-wise to the acidic solution under vigorous stirring. The obtained slurry was aged in mother liquor for 18–24 h at 80 °C. The precipitates were collected and washed thoroughly with DI water, and dried overnight in a laboratory oven. The dried powder was mixed with Zn (99+%, Sigma–Aldrich), [Zn]/[Ga] = 0.25, and urea (Sigma–Aldrich) powders in a stainless still ball-mill chamber to obtain a uniform precursor.

2.2. GaZnON alloy synthesis

The prepared LDHs precursor was loaded into a semi-sealed alumina synthesis chamber and placed in a preheated laboratory muffle furnace for solid-state synthesis. The synthesized solid solution samples were calcined in air at 600 °C for 1 h.

For comparison, a mixture of a stoichiometric amount of Ga₂O₃, ZnO, Zn, and urea powders was ball-milled and synthesized in a high temperature muffle furnace. The resulting photocatalyst is denoted as GaZnON-M.

2.3. Co-catalyst nanoparticle photodeposition

The Rh nanoparticle co-catalyst was deposited as the active site for hydrogen evolution through photodeposition, as described previously [32,33] with modifications. Synthesized photocatalyst was stirred in DI water and purged with ultra-pure nitrogen for several hours to obtain an oxygen-free suspension. Oxygen-free

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