Zinc-rich Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ solid solutions with tunable composition prepared from a constant-pH coprecipitation method

Yanling Hu$^{1, *}$, Lihua Wei$^1$, Juan Zuo$^1$, Dongya Sun$^1$, Chunhai Jiang$^1$, Yongsheng Fu$^2$

$^1$School of Materials Science and Engineering, Fujian Provincial Key Laboratory of Functional Materials and Applications, Xiamen University of Technology, Xiamen, 361024, P. R. China
$^2$Key Laboratory for Soft Chemistry and Functional Materials, Nanjing University of Science and Technology, Ministry of Education, Nanjing, 210094, P. R. China
$^*$Corresponding author e-mail: huyanling@xmut.edu.cn

Abstract. Wurtzite Zinc-gallium oxynitrides (Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$) has attracted a great deal of interest these years as photocatalysts capable of overall water splitting and contamination degradation under visible light irradiation. Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ particles were synthesized by nitridation of Zn/Ga/CO$_3$ layered double hydroxides (LDHs) using a coprecipitation method with constant pH of 8. Single-phase Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ with Zn:Ga mole ratios of 2:1, 3:1, 4:1 and 5:1 were obtained, as characterized by X-ray diffraction and scanning electron microscope. Photocatalytic activities of the obtained particles were evaluated under visible-light irradiation against the photodegradation of methylene blue (MB). The oxynitride with a Zn:Ga mole ratio of 2:1 showed the highest photoactivity among all the samples.

1. Introduction
Zinc-gallium oxynitride solid solution (Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$) with a wurtzite structure, also known as GaN:ZnO or ZnGaNO, has attracted a great deal of interest these years as photocatalysts capable of overall water splitting and contamination degradation under visible light irradiation [1-4]. Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ solid solutions have exhibited high quantum efficiency (17.3%) [5], reliable long-term durability [6], and tunable band-gap energy [7].

A number of methods have been employed to synthesize Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ solid solution by nitridation of different starting materials/precursors [8-17]. Most of these precursors require complicated processes and long time of nitridation (5-15 h) at high temperatures (600-850°C) for complete phase transformation. Zn/Ga/CO$_3$ LDHs, however, only need half hour to be transformed into wurtzite structure, which make them as attractive precursors to synthesize Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ photocatalyst. The molecular formula of Zn/Ga/CO$_3$ LDHs can be expressed as $[(Zn^{2+})_{x/2}(Ga^{3+})_{1/2}(OH)_2]^+(CO_3^{2-})_{x/2}$·$yH_2O$, which is a class of intercalation compounds consisted of positively charged brucite-like (Mg(OH)$_2$-type) layers separated by CO$_3^{2-}$ and water molecules.
Typically, LDHs are prepared using coprecipitation methods [18]. Zn/Ga/CO₃ LDHs have been successfully prepared using a coprecipitation method with increasing pHs during the agent mixing process. [13,19]. Our previous work revealed that only a coprecipitation process with a constant pH can obtain single-phase wurtzite Ga₁₋ₓZnₓN₁₋ₓOₓ particles with Zn:Ga of 2:1, while those with decreasing pHs produced a ZnO/Ga₁₋ₓZnₓN₁₋ₓOₓ composite, and those with increasing pHs obtained a porous ZnGaNO/ZnGa₂O₄ structure.[20] In this paper, a coprecipitation method with constant pH was employed to prepare Zn/Ga/CO₃ LDH precursors with different Zn:Ga mole ratios, which would used to synthesize single-phase Ga₁₋ₓZnₓN₁₋ₓOₓ solid solutions with tunable Zn:Ga ratios. The microstructures of the LDHs and Ga₁₋ₓZnₓN₁₋ₓOₓ solid solutions were investigated, and the photocatalytic activities of the Ga₁₋ₓZnₓN₁₋ₓOₓ were evaluated and compared.

2. Experimental

2.1. Preparation of ZnGaNO solid solutions
A series of metallic nitrate solutions (Solution A) were prepared with [Zn²⁺]/[Ga³⁺] mole ratio of 1:1, 2:1, 3:1, 4:1, and 5:1 using a fixed concentration of 0.3 mol/L for Ga(NO₃)₃·9H₂O and increased concentration of Zn(NO₃)₂·6H₂O of 0.3, 0.6, 0.9, 1.2, and 1.5 mol/L. 2 M NaOH and 1 M Na₂CO₃ were mixed to form a base solution (Solution B).

Solution A and Solution B were simultaneously added drop-wisely to a vessel containing stirred deionized water (300 mL, the initial pH of the solution was adjusted to 8 by Solution B) at such a rate that the pH of the reaction mixture was maintained at 8. The mixing process was carried out at 40 °C. After complete delivery of the Solution A, the reaction mixture was aged at 80 °C for 12 - 24 h with good stirring. The product suspension was then repeatedly centrifuged and washed with deionized water. After that, the precipitate was dried at 70 °C for 24 h with good stirring. The resulting mixed powder was heated in air at 350°C for 1 h to convert the Ru species to RuO₂.

A 0.1 g sample of the 5 wt.% RuO₂-loaded catalyst powder was dispersed in 100 mL MB aqueous solution. The initial concentration of MB is 15 mg·L⁻¹ with pH of 4.5 (adjusted by H₂SO₄ solution). The mixture was then stirred in the dark for 24 h to attain adsorption equilibrium on the surface of the catalyst. It was then stirred and irradiated under visible light from a 300W Xenon light source (PLS-SXE300C, Perfectlight, China) equipped with a cutoff filter to provide visible light (λ > 400 nm). The average light intensity was 140 mW/cm². The reactant solution was maintained at room temperature by a flow of cooling water during the reaction. About 5 mL of the solution was withdrawn and filtered at given time intervals to be analyzed.

3. Results and Discussions
The XRD patterns for the Zn/Ga/CO₃ LDH precursors and nitridation products with different Zn:Ga mole ratios are shown in Fig. 1(a) and 1(b), respectively. In Fig. 1(a), all five XRD patterns exhibit the major peaks that fit well to a typical LDH structure (JCPDS No. 30-1835, a=3.114 Å, c=22.41 Å). There are minor impurity peaks in the background of 1:1 and 2:1 samples, indicating the presence of a small amount of ZnGa₂O₄ (JCPDS No. 38-1240). And there are increasing amount of additional Zn₃CO₃(OH)₆H₂O (JCPDS No. 11-0287) in the order of 3:1, 4:1 and 5:1 samples. In Fig. 1(b), all five
XRD patterns have major XRD peaks corresponding to a wurtzite structure with lattice parameters close to ZnO (JCPDS No. 36-1451, a=3.249Å, c=5.207Å). 1:1 nitrided sample, however, has additional peaks indicating the presence of ZnGa2O4.

**Figure 1.** XRD patterns of (a) LDH precursors and (b) nitridation products with different Zn:Ga mole ratios in the solutions.

The precise lattice parameters of the wurtzite structure were calculated for each sample using the refinement function of Jade 6.0, and results were drawn in Fig. 2 in comparison with the lattice parameters of ZnO and GaN (JCPDS No. 50-0792, a=3.189Å, c=5.186Å). According to Fig. 2, it is obvious that the lattice parameters of Ga1-xZnxN1-xOx deviations from ideal solid solution behaviour. Lattice parameter c, especially, showed a bowing effect with increasing x in the solid solution. The data are consistent with the results in Ref [15], where the Ga1-xZnxN1-xOx nanoparticles were synthesized from nanocrystalline ZnGa2O4 and ZnO.

**Figure 2.** Lattice parameters a and c of the wurtzite Ga1-xZnxN1-xOx with different Zn:Ga mole ratios

Presented in Fig. 3 are SEM images of the LDH precursors and the corresponding nitridation products. According to Fig. 3 (a), all the precursor particles are platelets with an average diameter of ~300 nm and thickness of less than 100 nm. It is also obvious that 1:1 LDH has a large amount of nanoparticles less than 50 nm in diameter on the surface, which should be ZnGa2O4 according to the XRD results. Fig.3
(a) also show that the amount of ZnGa$_2$O$_4$ nanoparticles decreased in the order of 1:1 LDH, 2:1 LDH, and 3:1 LDH. For the 4:1 and 5:1 LDH, however, cloud-like impurities showed up again, which should correspond to Zn$_4$CO$_3$(OH)$_6$H$_2$O according to Fig. 1(a). After nitridation, 1:1 sample remained the platelet morphology but with ZnGa$_2$O$_4$ nanoparticles appeared inside the oxynitride particles. Figs. 3(b) also showed that all other particles collapsed to form oxynitrides with an average diameter of 200 nm. For the 3:1, 4:1, and 5:1 oxynitrides, it is also noted that uniformity of the particle size decreased with increasing Zn:Ga ratios.

![Figure 3. SEM images of (a) LDH precursors and (b) nitridation products with different Zn:Ga mole ratios in the solutions.](image)

EDS/SEM were conducted to identify the atomic composition of metallic elements in the LDHs and oxynitrides, and the mole ratios of Zn:Ga for Solution A, LDHs, and oxynitrides were listed in Table 1 for comparison. It is clear that the Zn:Ga ratios of LDH precursors are very close to those of Solution A. Except for 3:1 oxynitride, Zn:Ga ratios of all nitridation products are slightly higher than those of LDHs, which could stem from reduction of gallium oxide by CH$_4$ and re-deposition of Zn on the surface of particles.

**Table 1. Zn:Ga mole ratio in the solution, LDH precursors, and solid solutions**

| Zn:Ga (Solution A) | Zn:Ga (LDHs) | Zn:Ga (oxynitrides) |
|---------------------|---------------|----------------------|
| 1:1                 | 1.1:1         | 1.3:1                |
| 2:1                 | 2.2:1         | 2.6:1                |
| 3:1                 | 3.1:1         | 2.9:1                |
| 4:1                 | 4.01:1        | 4.2:1                |
| 5:1                 | 4.87:1        | 5.1:1                |

The formation of ZnGa$_2$O$_4$ and Zn$_4$CO$_3$(OH)$_6$H$_2$O in the LDHs can be explained by Fig. 4, which gives the concentrations vs. pHs for Zn and Ga ions and their hydroxylated species in the aqueous solution. For 1:1 and 2:1 samples, there are high level of overlap between [Zn$^{2+}$] and Ga(OH)$_4^{-}$ curves at the pH of 8, leading to the formation of ZnGa$_2$O$_4$ during the aging process of LDHs. When the Zn:Ga ratio is increased, a left shift of all Zn-related curves would occur while Ga-related curves are fixed, resulting in high concentration of ZnO$_2$$^{2-}$ in the aging solution, resulting in an increasing amount of Zn$_4$CO$_3$(OH)$_6$H$_2$O in order of 3:1, 4:1, and 5:1 samples.
Figure 4. Schematic diagram of the distribution of Ga$^{3+}$, Zn$^{2+}$ and their related hydroxylated species as a function of pH. For the curves related to Ga, the data was copied from Ref. [21] with [Ga$^{3+}$] of 2 M. Zinc-related curves were schematically drawn using $K_{sp}$ of 2.09×10$^{-16}$ and [Zn$^{2+}$] of 0.4 M.

Photocatalytic activities of the oxynitride particles with different Zn:Ga mole ratios were evaluated under visible-light irradiation against the photodegradation of MB. The percentage of degraded MB after two hours of visible light irradiation with presence of oxynitrdes are shown in Fig. 5. It’s clear that the oxynitride with a Zn:Ga ratio of 2:1 exhibited the highest photoactivity among all the samples. The reduced photoactivity of 1:1 oxynitride may relate to the inner ZnGa$_2$O$_4$ nanoparticles, which may block the movement of the photogenerated hole-electron pairs, and thereby enhance possibility of recombination. For the 3:1, 4:1, and 5:1 oxynitrides, the decreased photoactivities are likely to be ascribed to improper valence band edge levels where electrons are not able to reduce O$_2$ to O$_2^-$ radicals, which could be the major active species to degrade MB.

Figure 5. MB Photodegradation in the presence of 5 wt.% RuO$_2$-loaded Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ particles with different Zn:Ga mole ratios under visible-light irradiation (λ > 400 nm).

4. Conclusion
Zinc-gallium oxynitrdes were synthesized by nitridation of Zn/Ga/CO$_3$ LDHs using a constant-pH coprecipitation method. Zn/Ga/CO$_3$ LDH platelets with few ZnGa$_2$O$_4$ impurity were obtained for the precursors with Zn:Ga mole ratios of 1:1 and 2:1, and LDH platelets with a small amount of Zn$_3$CO$_2$(OH)$_6$H$_2$O were synthesized for the precursors with Zn:Ga mole ratios of 3:1, 4:1 and 5:1. After nitridation with NH$_3$ and CH$_4$ at high temperature at 800°C for half hour, single-phase wurtizite Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ particles were obtained with Zn:Ga mole ratios of 2:1, 3:1, 4:1, and 5:1, respectively. Nitridation of LDH precursor with Zn:Ga ratio of 1:1, however, leaded to Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ platelets with inner ZnGa$_2$O$_4$ nanoparticles. Photocatalytic activities of the oxynitride particles with different
Zn:Ga mole ratio were evaluated under visible-light irradiation against the photodegradation of MB. Oxynitride particle with a Zn:Ga ratio of 2:1 showed the highest photoactivity among all the samples.

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