

A Room-Temperature Reactive-Template Route to Mesoporous ZnGa_2O_4 with Improved Photocatalytic Activity in Reduction of CO_2 **

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Mesoporous materials are of scientific and technological interest due to their potential applications in various areas.^[1] Over the past two decades, significant effort has been devoted to the synthesis of mesoporous materials. For instance, mesoporous silica and phosphate metal oxides have been synthesized and applied widely in many industrial processes.^[2] However, little progress has been made in the synthesis of mesoporous metal oxides containing more than one type of metal. To date, a limited number of routes including evaporation-induced self-assembly (EISA) and nonaqueous solvent methods have been developed to synthesize multimetallic mesoporous materials such as $\text{Pb}_3\text{Nb}_4\text{O}_{13}$,^[3] $\text{Bi}_{20}\text{TiO}_{32}$,^[4] SrTiO_3 , MgTa_2O_6 , $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-x}$,^[5] and $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$.^[6] In these routes, introducing surfactant molecules or a template is a general method used to construct the mesostructures. Challenges in using the template method to synthesize multimetallic mesoporous materials are uncontrolled phase separation in the multicomponent reactions and poor thermal and chemical stability of the resulting mesoporous structure.^[7] Maintaining the complete mesostructure during removal of the template by heating or chemical treatment is a key process for obtaining the expected mesostructures, and increases the uncertainty in a given synthetic route. In addition, to obtain a crystalline mesoporous material, high-temperature heat treatment is usually required for crystallization of the product. However, this process probably induces collapse of mesostructures.

Recently, we developed a synthetic route to mesoporous multimetal oxides that uses the inorganic starting reactants directly as pore makers which aid in building the mesoporous structures of multimetal oxides and improve the thermal stability of the resulting mesostructure.^[8]

However, in these reported synthetic routes, postcrystallization and introducing or removing an exotemplate are usually needed. In recent years, a route that does not require template removal, which was named “reactive hard templating”, was developed to synthesize porous TiN/carbon composite materials.^[9] In this route, the template consists of nanostructures of porous graphitic C_3N_4 , which thermally decomposes completely during formation of porous TiN. This route provides a means to overcome the problems associated with synthesizing multimetal mesoporous materials. A simplified soft-chemistry route based on a reactive template is expected to allow synthesis to proceed at room temperature without requiring the introduction or removal of a template. Here we report a novel direct method for preparing mesoporous ZnGa_2O_4 with a wormhole framework by an ion-exchange reaction at room temperature involving a mesoporous NaGaO_2 colloid precursor. The method does not require any additional processes and can be extended to prepare other porous materials, such as CoGa_2O_4 and NiGa_2O_4 .

The X-ray diffraction (XRD) pattern of NaGaO_2 powder, which can be indexed as the orthorhombic phase (JCPDS 76-2151), is presented in Figure 1. Scanning electron microscopy (SEM) revealed that the powder particles are irregular in shape with little agglomeration, and most of the particles are larger than 500 nm in diameter (see Supporting Information). The as-prepared NaGaO_2 powder can be dispersed in water to form a suspension. When the NaGaO_2 suspension is illuminated with a 532 nm laser, a Tyndall effect is observed, that is, the suspension behaves as a colloid (see Supporting Information). Multimodal measurements of particle size distribution by dynamic light scattering show that the NaGaO_2 colloidal particles exhibit two peak distributions: 20% of the particles have an average size of 70 nm, and 80% an average size of 335 nm. Most particulate or macroscopic materials in contact with a liquid acquire an electric charge on their surfaces. The zeta potential is an important and useful indicator of this charge that can be used to predict the stability of colloidal suspensions. The zeta potential of NaGaO_2 colloidal particles is -21.57 mV (pH 6). This is lower than the critical zeta potential of ± 30 mV for maintaining colloid stability in an aqueous system,^[10] that is, the colloidal particles are slightly

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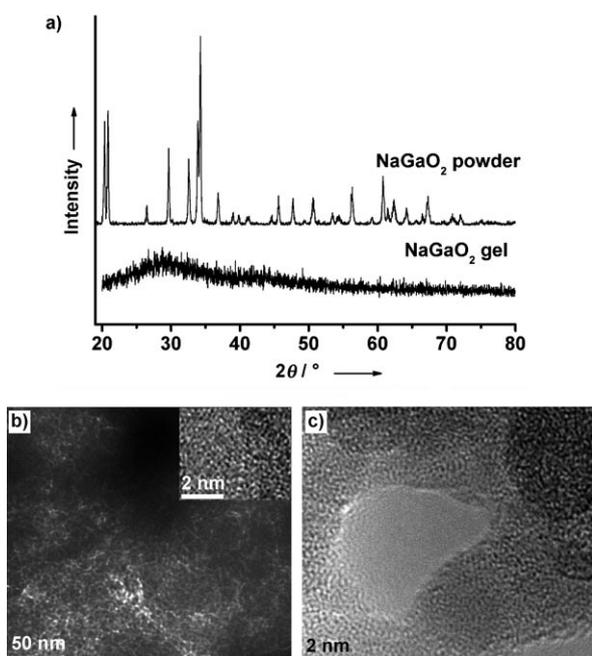


Figure 1. a) XRD patterns of the NaGaO₂ powder and gel. b) TEM and HRTEM (inset) images of NaGaO₂ colloidal particles. c) High-magnification TEM image of a typical mesopore in the NaGaO₂ colloidal particles.

stable and can aggregate easily due to the weak repulsion between them. Upon changing the pH of the NaGaO₂ colloidal suspension, the zeta potential became +42.36 mV at pH 3 and -32.68 mV at pH 11, that is, the stability of NaGaO₂ colloid was improved under both acidic and basic conditions. A gel can be obtained by freeze-drying the NaGaO₂ colloidal suspension. An XRD analysis (Figure 1 a) indicated that the gel is amorphous, and energy-dispersive X-ray (EDX) analysis showed that the Na/Ga atomic ratio in the gel is close to 0.8:1 (see Supporting Information), probably due to elution of sodium ions from the surface of NaGaO₂ colloidal particles. The transmission electron microscopy (TEM) image in Figure 1 b shows that the NaGaO₂ colloidal particles have a typical mesostructure with a wormhole framework. A high-resolution TEM (HRTEM) image of the mesostructure did not reveal the presence of a crystal lattice (inset of Figure 1 b). This implies that the NaGaO₂ colloidal particles are amorphous, consistent with the XRD analysis. The mesopores in the colloidal particles can be observed at high magnification (Figure 1 c).

To understand the ion exchange between NaGaO₂ colloidal suspension and an aqueous solution of Zn(CH₃COO)₂, in situ observations were performed with an optical microscope. When the NaGaO₂ colloidal suspension was left undisturbed under ambient conditions for an extended period, a mesh of aggregated colloidal particles formed on the micrometer scale due to the low stability of the colloid (see Supporting Information). An in situ ion-exchange reaction on the amorphous NaGaO₂ framework could be observed when Zn²⁺ ions were introduced into the reaction system. As illustrated in Figure 2 a, the XRD pattern of the product from the ion-exchange reaction can be indexed as

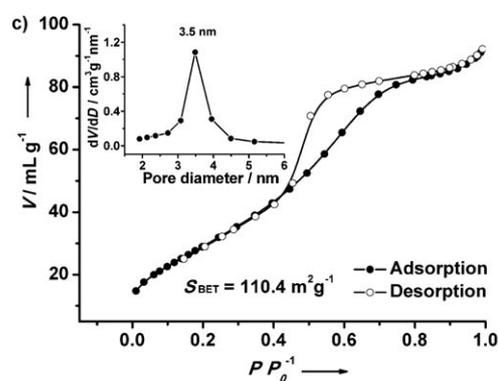
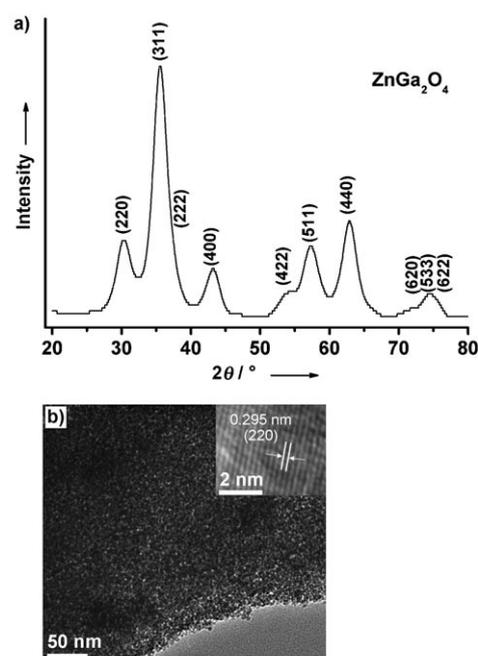


Figure 2. Characterization of meso-ZnGa₂O₄. a) XRD pattern. b) TEM image (inset: HRTEM image of the crystal lattice). c) Nitrogen adsorption-desorption isotherms and pore size distribution (inset).

cubic spinel ZnGa₂O₄ (denoted meso-ZnGa₂O₄) with a cell parameter of $a = 8.335 \text{ \AA}$, which is in good agreement with JCPDS 38-1240. The composition of the as-prepared ZnGa₂O₄ was further confirmed by EDX analysis (see Supporting Information). The diffraction peaks in the XRD pattern of meso-ZnGa₂O₄ are clearly broadened. From the XRD data, the grain size was estimated by the Scherrer formula to be about 5 nm. Usually, soft-chemical routes performed at room-temperature, such as co-precipitation, produce amorphous ZnGa₂O₄.^[11] In this case, the ion-exchange process occurs by a unique reaction between a weakly acidic Zn(CH₃COO)₂ (pH 6) solution and an alkaline NaGaO₂ (pH 8) colloidal suspension. Aggregation of ZnGa₂O₄ depends strongly on the Zn-containing precursor. In this reaction, the strong electrolyte Zn(NO₃)₂ instead of the weak electrolyte Zn(CH₃COO)₂ will produce amorphous ZnGa₂O₄. This is probably due to the faster reaction rate between Zn(NO₃)₂ and NaGaO₂ than between Zn(CH₃COO)₂ and NaGaO₂. This fact may support the argu-

ment that the reaction rate between $\text{Zn}(\text{CH}_3\text{COO})_2$ and NaGaO_2 is appropriate for nucleating and growing crystalline ZnGa_2O_4 . The TEM images show that meso- ZnGa_2O_4 also has a wormhole framework like the NaGaO_2 colloidal particles (Figure 2b). Apparently, the mesostructure of ZnGa_2O_4 resulted from agglomeration of nanoparticles. An HRTEM analysis indicates that the lattice spacing is 0.295 nm for the (220) plane, which provides further evidence that the product is crystalline ZnGa_2O_4 . Nitrogen adsorption–desorption studies on as-prepared meso- ZnGa_2O_4 showed a type IV isotherm, typical of mesoporous materials (Figure 2c). The pore diameter calculated from the nitrogen adsorption isotherm by the Barrett–Joyner–Halenda (BJH) method is 3.5 nm, and the specific surface area calculated from the linear region of the Brunauer–Emmett–Teller (BET) plot ranging from $P/P_0 = 0.05$ to $P/P_0 = 0.15$ is $110.4 \text{ m}^2 \text{ g}^{-1}$.

It is interesting to discover a formation mechanism of mesopores that does not require introducing a template or surfactant molecules. As illustrated in Figure 3, it seems reasonable to speculate that the NaGaO_2 powder dispersed in

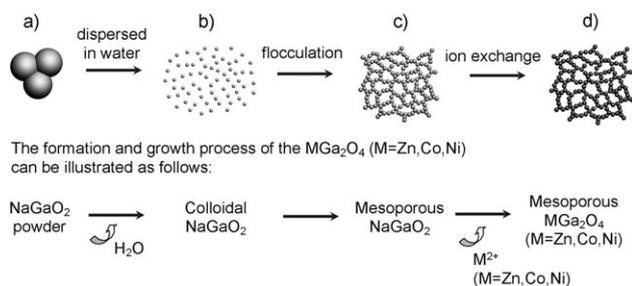


Figure 3. Illustration of the formation of a mesoporous colloidal template and an ion-exchange reaction based on the colloidal template. a) NaGaO_2 solid powder particles. b) NaGaO_2 colloidal particles obtained by dispersing the NaGaO_2 powders in deionized water. c) Formation of a mesoporous NaGaO_2 colloidal template by flocculation. d) Formation of mesoporous ZnGa_2O_4 by ion-exchange reaction on the NaGaO_2 colloidal template.

water can form amorphous colloidal particles, which tend to form the mesoporous NaGaO_2 colloid by flocculation due to the weak repulsion between the colloidal particles. The ion-exchange process between Zn^{2+} and Na^+ is expected to be due to the NaGaO_2 mesoporous framework, because ZnGa_2O_4 crystal particles could nucleate and grow there. The mesoporous structure of the NaGaO_2 colloid is maintained in the generated ZnGa_2O_4 after ion exchange, probably because the reaction rate is moderate. For the ZnGa_2O_4 particles suspended in water, a high zeta potential of +52.66 mV was measured. The opposite sign of the charge of zeta potential for the ZnGa_2O_4 particles and NaGaO_2 colloidal particles suggests that the particles attract each other. This would be beneficial for maintaining the NaGaO_2 mesoporous framework during the ion-exchange reaction. Moreover, changes to the pores in NaGaO_2 may take place during phase transformation due to a change in crystal structure. However, the porous structure of NaGaO_2 colloid can compensate for the volume change by tuning the pore size. This may promote the mesostructure of NaGaO_2 being inherited by ZnGa_2O_4 .

The route reported here is applicable to preparation of other mesoporous spinel AB_2O_4 -type oxides. Mesoporous CoGa_2O_4 and NiGa_2O_4 were synthesized by this method. Unlike ZnGa_2O_4 , the MGA_2O_4 ($\text{M}=\text{Co, Ni}$) samples obtained by ion exchange at room temperature are amorphous. The specific surface areas of amorphous NiGa_2O_4 and CoGa_2O_4 are 363.3 and $202.3 \text{ m}^2 \text{ g}^{-1}$, respectively. The samples exhibited a uniform pore size distribution. TEM observations (see Supporting Information) showed that the wormholes in these amorphous products are similar to those in the NaGaO_2 colloid due to the amorphous phase transformation with slight particle growth. By hydrothermal treatment of these amorphous samples at 180°C for 5 h, crystalline mesoporous CoGa_2O_4 and NiGa_2O_4 can be obtained. Compared with the amorphous products, the specific surface areas of crystalline CoGa_2O_4 and NiGa_2O_4 decreased to 82.7 and $87.1 \text{ m}^2 \text{ g}^{-1}$, respectively. The pore sizes of crystalline mesoporous CoGa_2O_4 and NiGa_2O_4 exhibit bimodal distributions (Figure 4), and the average values of the pore diameter were 2.5 and 8 nm, respectively. The grain size of crystalline CoGa_2O_4 and NiGa_2O_4 is about 10 nm (see Supporting Information). Therefore, the results of these experiments indicate that amorphous MGA_2O_4 ($\text{M}=\text{Co, Ni}$) can form rapidly at room temperature, and that subsequent hydrothermal treatment induces crystallization and growth of the amorphous particles. The mesopores in CoGa_2O_4 and NiGa_2O_4 are formed by agglomeration of nanoparticles, similar to meso- ZnGa_2O_4 . Compared with amorphous CoGa_2O_4 and NiGa_2O_4 , the bimodal pore size distribution and low BET surface area of crystalline CoGa_2O_4 and NiGa_2O_4 can be attributed to grain growth during hydrothermal treatment.

AB_2O_4 -type oxides with spinel structure have potential applications in many fields such as catalysis, gas sensors, and photoelectronics. In particular, ZnGa_2O_4 is a transparent and conductive material which should be useful for UV photoelectronic devices.^[12] ZnGa_2O_4 also shows potential as a photocatalyst for wastewater treatment and hydrogen production by water splitting.^[13,14] Here meso- ZnGa_2O_4 was used as a photocatalyst to convert CO_2 into methane (CH_4) under irradiation of UV light.

Carbon dioxide, which is released mainly by burning of fossil fuels, is the primary cause of global warming. Converting CO_2 into valuable hydrocarbons by means of solar energy is one of the best solutions to both global warming and energy shortage. Generally, CO_2 can be photoreduced to CH_4 in the presence of water vapor by using a wide band gap semiconductor such as TiO_2 as photocatalyst. The photogenerated holes in the valence band oxidize water to generate hydrogen ions by the reaction $\text{H}_2\text{O} \rightarrow 1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ ($E_{\text{redox}}^\circ = 0.82 \text{ V vs. NHE}$). The photogenerated electrons in the conduction band reduce CO_2 to CH_4 by the reaction $\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ($E_{\text{redox}}^\circ = -0.24 \text{ V vs. NHE}$).^[15] The electronic structure of ZnGa_2O_4 has been calculated by using plane-wave-based density functional theory.^[14] The valence band was mainly composed of the O 2p orbitals, whereas the conduction band was formed by hybridization of Ga 4s4p and Zn 4s4p orbitals. The band gap of the as-prepared ZnGa_2O_4 was determined from the UV/Vis

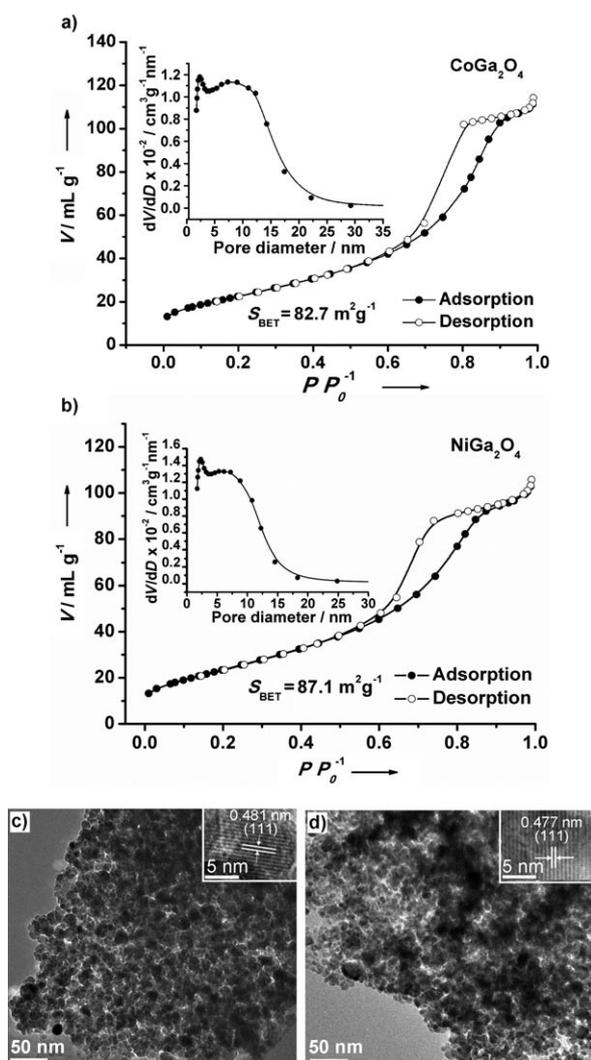


Figure 4. Nitrogen absorption–desorption isotherms, pore size distribution (inset), TEM images, and HRTEM images of the lattice (inset) for a, c) CoGa₂O₄ and b, d) NiGa₂O₄ obtained by hydrothermal treatment of amorphous MGa₂O₄ (M = Co, Ni) samples, prepared by ion exchange at room temperature.

absorption spectrum to be 4.4 eV (see Supporting Information). The position of the conduction and valence bands in as-prepared ZnGa₂O₄ was determined by the following equation: $E_{CB} = X - E_c - 0.5 E_g$, where E_c is the energy of free electrons on the hydrogen scale (4.5 eV), X is the electronegativity of the semiconductor, and E_g is the band-gap energy of the semiconductor. The edge of the valence band E_{VB} of ZnGa₂O₄ was determined to be 3.13 V versus NHE, which is more positive than $E^\circ(\text{H}_2\text{O}/\text{H}^+)$ (0.82 V vs. NHE). The edge of the conduction band was estimated to be -1.27 V versus NHE, which is more negative than $E^\circ(\text{CO}_2/\text{CH}_4)$ (-0.24 V vs. NHE). This indicates that the electrons and holes photogenerated on irradiation of ZnGa₂O₄ can react with adsorbed CO₂ and H₂O to produce CH₄. Figure 5 shows that meso-ZnGa₂O₄ (CH₄: 5.3 ppm h⁻¹) exhibits higher activity than ZnGa₂O₄ (CH₄: trace) obtained by solid-state reaction of ZnO and Ga₂O₃ at 1100 °C for 16 h (denoted ss-ZnGa₂O₄). This is related to strong gas adsorption by the

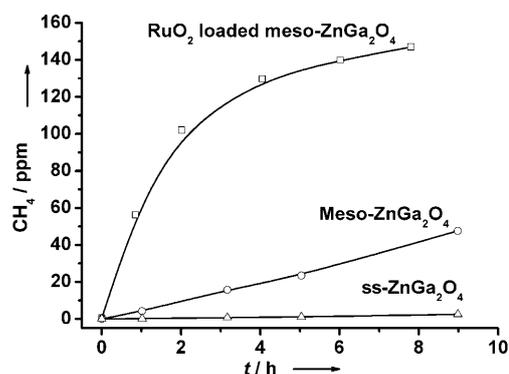


Figure 5. CH₄ generation over various ZnGa₂O₄ samples as a function of irradiation time.

mesostructure and more reaction sites arising from high specific surface area ($S_{\text{BET}} = 110.4 \text{ m}^2 \text{ g}^{-1}$ for meso-ZnGa₂O₄ and $4.6 \text{ m}^2 \text{ g}^{-1}$ for ss-ZnGa₂O₄). The generation rate of CH₄ over meso-ZnGa₂O₄ could be significantly enhanced by loading 1 wt % RuO₂ as co-catalyst to improve separation of the photogenerated electron–hole pairs (CH₄: 50.4 ppm h⁻¹), as demonstrated in photocatalytic water splitting.^[14]

In summary, a reactive templating route to preparing mesoporous ZnGa₂O₄ at room temperature has been reported. The reaction pathway involves an ion-exchange process with a porous NaGaO₂ colloidal template as the precursor. The route is effective for synthesizing porous AB₂O₄-type materials by a simple method. By using RuO₂ as co-catalyst, the as-prepared mesoporous ZnGa₂O₄ shows high photocatalytic activity for converting CO₂ into CH₄ under light irradiation, because of strong gas adsorption and large specific surface area of the mesoporous photocatalyst. Mesoporous ZnGa₂O₄ is potentially an effective photocatalyst for the photoreduction of CO₂.

Experimental Section

NaGaO₂ solid powders were prepared by heating a stoichiometric mixture of Na₂CO₃ and Ga₂O₃ at 850 °C for 12 h. Mesoporous ZnGa₂O₄ was prepared as follows: NaGaO₂ colloidal suspension (0.2 mol L⁻¹, 10 mL) was added to an aqueous solution of Zn(CH₃COO)₂ (0.05 mol L⁻¹, 20 mL) and the mixture stirred for 3 h at room temperature to form mesoporous ZnGa₂O₄. The sediment was separated by centrifugation and dried at 60 °C for 2 h.

Mesoporous CoGa₂O₄ and NiGa₂O₄ were synthesized by a similar procedure. NaGaO₂ colloidal suspension (0.2 mol L⁻¹, 10 mL) was added to an aqueous solution of CoSO₄ or Ni(CH₃COO)₂ (0.05 mol L⁻¹, 20 mL) and the mixture stirred for 1 h. The mixture was then heated in a Teflon-lined hydrothermal autoclave at 180 °C for 5 h to form mesoporous crystalline CoGa₂O₄ or NiGa₂O₄.

The crystalline phases of these as-prepared products were determined by powder XRD (Rigaku Ultima III, CuKα radiation). The size, size distribution, and zeta potential of NaGaO₂ colloidal particles were determined by a zeta potential analyzer (Zeta PALS, Brookhaven Instruments Co., USA). The specific surface area of the samples was measured by nitrogen sorption at 77 K on a surface area and porosity analyzer (Micromeritics TriStar 3000, USA) and calculated by the BET method. The morphology of the samples was observed by TEM (FEI Tecnai G2 F30 S-Twin, USA).

In the photocatalytic reduction of CO₂, ZnGa₂O₄ powder (0.1 g) was uniformly dispersed on a glass reactor with an area of 4.2 cm². A

300 W Xenon arc lamp was used as the light source for the photocatalytic reaction. The volume of the reaction system was about 230 mL. The reaction setup was vacuum-treated several times, and then high-purity CO₂ gas was introduced into the reaction to achieve ambient pressure. Deionized water (0.4 mL) was injected into the reaction system as reducing agent. During the irradiation, about 1 mL of gas was taken from the reaction cell at given intervals for subsequent CH₄ concentration analysis with a gas chromatograph (GC-14B, Shimadzu Corp., Japan).

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