Ion-exchange synthesis of a micro/mesoporous Zn$_2$GeO$_4$ photocatalyst at room temperature for photoreduction of CO$_2$†

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Micro/mesoporous Zn$_2$GeO$_4$ with crystalline pore-walls was successfully synthesized via a simple ion exchange method at room temperature. This structure showed enhanced activity in photoreduction of CO$_2$ in comparison with Zn$_2$GeO$_4$ prepared by a solid state reaction.

Mesoporous materials have attracted much attention due to their outstanding structural characteristics such as high surface area and strong adsorption, which are widely applied in the fields of photocatalysis, separation, sensors, battery materials, pharmaceutical carriers, and magnetic materials. Over the past decades, many mesoporous materials including metal, alloy, nonmetal elementary substance, metal oxides, and phosphate metal oxides have been successfully synthesized. As for the synthesis of multimetallic oxide materials which contain more than two types of metal elements, nevertheless, little progress has been made. Generally, an evaporation-induced self-assembly (EISA) route is an efficient way for synthesizing some mesoporous multimetallic oxide materials including MgTa$_2$O$_6$, Pb$_3$Nb$_4$O$_{13}$, Bi$_2$0TiO$_32$, and SrTiO$_3$. However, the micro/mesoporous structure of the Zn$_2$GeO$_4$ photocatalyst has not been synthesized yet. Herein, we have developed an environment-friendly room temperature (RT) route to prepare micro/mesoporous Zn$_2$GeO$_4$ by cation exchange between Zn$^{2+}$ and non-mesoporous colloid particles of Na$_2$GeO$_3$ hydrates. It is worth noting that the micro/mesoporous photocatalyst possessed a crystalline pore-wall, which would benefit the stability of the porous structure and migration of photo-excited electrons and holes. The micro/mesoporous Zn$_2$GeO$_4$ shows enhanced activity in photoreduction of CO$_2$ in comparison with Zn$_2$GeO$_4$ prepared by solid state reaction.

Scheme 1 shows the designed schematic route for synthesizing micro/mesoporous Zn$_2$GeO$_4$. Firstly, colloidal suspensions of Na$_2$GeO$_3$ hydrates are formed by hydrolyzing the Na$_2$GeO$_3$ powder in water. Secondly, the colloidal suspensions of Na$_2$GeO$_3$ hydrates are dropped into the Zn(CH$_3$COO)$_2$ solution and the ion exchange between Na$_2$GeO$_3$ hydrate suspensions and Zn$^{2+}$ results in the formation of amorphous micro/mesoporous Zn$_2$GeO$_4$. Finally, crystalline micro/mesoporous Zn$_2$GeO$_4$ is obtained by the Ostwald ripening of the amorphous Zn$_2$GeO$_4$ in the reaction solution. More experimental details are introduced in ESI.

The X-ray diffraction (XRD) pattern of the as-prepared Na$_2$GeO$_3$ is shown in Fig. 1a. All peaks are indexed to a orthorhombic phase Na$_2$GeO$_3$ and consistent with JCPDS additional templates. However, the mesoporous multimetallic oxides with a crystalline pore-wall synthesized without introducing or removing extra-templates are still seldom reported.

As an important wide-band-gap photocatalyst, Zn$_2$GeO$_4$ showed good activities for water splitting, degradation of pollutants, and photoreduction of CO$_2$. Up to now, Zn$_2$GeO$_4$ with special morphologies such as nanorods and nanobelts achieved enhanced photocatalytic activities. However, the micro/mesoporous structure of the Zn$_2$GeO$_4$ photocatalyst has not been synthesized yet. Herein, we have developed an environment-friendly room temperature (RT) route to prepare micro/mesoporous Zn$_2$GeO$_4$ by cation exchange between Zn$^{2+}$ and non-mesoporous colloid particles of Na$_2$GeO$_3$ hydrates. It is worth noting that the micro/mesoporous photocatalyst possessed a crystalline pore-wall, which would benefit the stability of the porous structure and migration of photo-excited electrons and holes. The micro/mesoporous Zn$_2$GeO$_4$ shows enhanced activity in photoreduction of CO$_2$ in comparison with Zn$_2$GeO$_4$ prepared by solid state reaction.

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the Zn(CH$_3$COO)$_2$ solution, a white precipitate was produced from Na$_2$GeO$_3$ dispersed in water, a dry gel was obtained by drying. In addition, the Na$_2$GeO$_3$ powder can be well dispersed in water and the Tyndall scattering effect was observed when the suspension was illuminated with a 635 nm laser beam, which revealed a colloidal characteristic of the suspension (see Fig. S2, ESI†). To find out the composition after Na$_2$GeO$_3$ dispersed in water, a dry gel was obtained by drying the colloidal suspension under vacuum at room temperature. The XRD pattern (Fig. 1b) of the gel exhibits that the Na$_2$GeO$_3$ sample has transformed into Na$_2$GeO$_3$-based hydrates (such as Na$_2$GeO$_3$·7H$_2$O, Na$_2$H$_2$GeO$_4$(H$_2$O)$_6$, Na$_3$HGeO$_4$·5H$_2$O, and Na$_2$Ge$_2$O$_6$·5H$_2$O). The SEM image shows that the dry gel is composed of aggregated particles with sizes from 100 nm to 1 μm (see Fig. S1a, ESI†). The nitrogen adsorption–desorption isotherms of the dry gel indicate that no mesoporous structure existed and the BET surface area is about 3.6 m$^2$/g (see Fig. S1c, ESI†). The nitrogen adsorption–desorption isotherms (Fig. 2b) are identified as type IV, revealing the mesoporous characteristic of this material. The BET surface area calculated from the linear region of the plot is 90.5 m$^2$/g.

distribution of pore sizes (inset of Fig. 2b) calculated through the Barrett–Joyner–Halenda (BJH) method shows existence of micropores (1.2–2 nm) and mesopores (2–12 nm). The micropores and mesopores occupy about 18.1% and 81.9%, respectively. The structure is corroborated by transmission electron microscopy (TEM) observations. Fig. 2c shows the TEM image of the as-prepared Zn$_2$GeO$_4$, exhibiting a wormhole-like structure, and existence of micropores and mesopores. A representative high-resolution TEM (HRTEM) image (Fig. 2d) shows that the micro/mesoporous Zn$_2$GeO$_4$ is crystallized with a lattice space measured as 0.29 nm, which corresponds to a (120) plane of the hexagonal phase Zn$_2$GeO$_4$. It should be noted that the crystalline pore-wall structure in the micro/mesoporous Zn$_2$GeO$_4$ is clearly observed.

Fig. 1 XRD patterns of (a) Na$_2$GeO$_3$ prepared by SSR, (b) dry gel of Na$_2$GeO$_3$ hydrates, and (c) Zn$_2$GeO$_4$ prepared at a reaction time of 12 h.

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The formation process from colloidal suspensions of Na$_2$GeO$_3$ hydrates to micro/mesoporous Zn$_2$GeO$_4$ was investigated. The pH value for the colloidal suspensions of Na$_2$GeO$_3$ hydrates was about 14 because Na$_2$GeO$_3$ hydrolyzed in water. The zeta potential for the colloidal suspensions of Na$_2$GeO$_3$ hydrates was about −25 mV, which indicated that the colloidal suspension was slightly unstable because the boundaries between stable and unstable colloidal suspensions were generally taken at either +30 or −30 mV. The ion exchange between Na$^+$, H$^+$ and Zn$^{2+}$ has caused the diffusion of Na$^+$ and H$^+$ in Na$_2$GeO$_3$ hydrate colloidal particles, which formed many vacancies and gaps. These vacancies and gaps were evolved into amorphous microporous and mesoporous structures during the substitution of Zn$^{2+}$ and formation of Zn$_2$GeO$_4$. It was demonstrated in the TEM observations that an erosion-like amorphous micro/mesoporous structure was formed for the Zn$_2$GeO$_4$ product obtained at a reaction time of 3 h (see Fig. S4a and b, ESI†). After ion exchange, the pH value of the Zn$_2$GeO$_4$ colloidal suspension decreased to 7 and the zeta potential was about −1 mV, which indicated that the Zn$_2$GeO$_4$ suspension was quite unstable and easily aggregated. With prolonging the reaction time, the amorphous micro/mesoporous structure crystallized as extra templates.
were not needed to support the pores, the Zn$_2$GeO$_4$ sample exhibited crystalline pore-walls. In order to confirm this process, the products obtained at different reaction times such as 3, 6, 12, and 20 h were investigated. With prolonging the reaction time from 3 h to 20 h, the amorphous phase Zn$_2$GeO$_4$ was gradually transformed into well crystallized Zn$_2$GeO$_4$ (see Fig. S5, ESI†). The BET surface areas decreased with prolonging the reaction time, which was 162.7, 131.8, 90.5, and 54.3 m$^2$ g$^{-1}$ with the stirring times of 3, 6, 12, and 20 h, respectively. The decrease in BET surface areas could be realized as the grain growth resulted from Ostwald ripening.

A UV-visible diffuse reflectance spectrum of the micro/mesoporous Zn$_2$GeO$_4$ shows that the optical absorbance edge is about 270 nm and the band gap for as-prepared Zn$_2$GeO$_4$ micro/mesoporous material is 4.5 eV (see Fig. S6, ESI†). It is reported that a wide-band-gap semiconductor can be used for photoreduction of CO$_2$ to produce CH$_4$ in the presence of H$_2$O. The CO$_2$ is reduced to CH$_4$ by the electrons from the conduction band, CO$_2$ + 8e$^- + 8H^+ \rightarrow CH_4 + 2H_2O$ \[ \text{[1]} \] [22] The photogenerated holes in the valence band were consumed by oxidizing H$_2$O, 2H$_2$O $\rightarrow O_2 + 4H^+ + 4e^- [E^0(O_2/H_2O) = 1.23 V \text{ vs. NHE}]$. In this work, Zn$_2$GeO$_4$ is used for photoreduction of CO$_2$. From the viewpoint of the electronic structure, the valence band of Zn$_2$GeO$_4$ is mainly composed of the O 2s2p orbitals while the conduction band consists of the hybridized Ge 4s4p and Zn 4s orbitals. The edges of the valence band ($E_{VB}$) and conduction band ($E_{CB}$) for Zn$_2$GeO$_4$ are estimated to be 3.88 and $-0.62$ V \textit{via} the Mulliken electronegativity method, respectively. The $E_{VB}$ is more positive than $E^0(O_2/H_2O)$ and $E_{CB}$ is more negative than $E^0(CO_2/CH_4)$, which demonstrates that adsorbed CO$_2$ and H$_2$O can react with the electrons and holes photogenerated from Zn$_2$GeO$_4$ to produce CH$_4$. Fig. 3 shows the CH$_4$ evolution over various Zn$_2$GeO$_4$ samples under full arc Xe lamp irradiation. The Zn$_2$GeO$_4$ obtained by solid-state reaction (SSR-Zn$_2$GeO$_4$) is almost inactive. The micro/mesoporous Zn$_2$GeO$_4$ prepared at a reaction time of 12 h exhibits much higher activity (about 9.5 ppm g$^{-1}$ h$^{-1}$) than SSR-Zn$_2$GeO$_4$ (about 1.4 ppm g$^{-1}$ h$^{-1}$), which is ascribed to strong gas adsorption by the micro/mesoporous structures and more reaction sites arising from high specific surface area (90.5 m$^2$ g$^{-1}$ for micro/mesoporous Zn$_2$GeO$_4$ and 0.6 m$^2$ g$^{-1}$ for SSR-Zn$_2$GeO$_4$). The evolution rate of CH$_4$ over micro/mesoporous Zn$_2$GeO$_4$ could be significantly enhanced by loading Pt as a co-catalyst, since the co-catalyst promotes the multi-electron reaction process which benefits the CO$_2$ photoreduction. The activity of micro/mesoporous Zn$_2$GeO$_4$ loading with different concentrations of Pt (from 0.5 to 2.5 wt%) was investigated (see Fig. S8, ESI†), which showed that the highest activity was achieved when the concentration of Pt was 1 wt% (about 28.9 ppm g$^{-1}$ h$^{-1}$). The apparent quantum yield of CH$_4$ evolution at a wavelength of 251 ± 16 nm was measured to be 0.2%.

In summary, a RT ion-exchange route was developed to synthesize Zn$_2$GeO$_4$ with crystalline pore-walls which achieved enhanced activity in CO$_2$ photoreduction. This synthetic strategy is expected to be utilized in fabrications of unique micro/mesoporous structures of various semiconductor functional materials with advanced properties.

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Notes and references


Fig. 3 CH$_4$ evolution over various Zn$_2$GeO$_4$ samples under full arc Xe lamp irradiation.