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# Germanium-substituted $Zn_2TiO_4$ solid solution photocatalyst for conversion of $CO_2$ into fuels



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# ABSTRACT

Photocatalytic CO<sub>2</sub> reduction conjugated with H<sub>2</sub>O oxidation is regarded as a promising artificial photosynthesis system because it can simultaneously solve energy and environment problems. Here, a novel solid solution,  $Zn_2Ti_{1-x}Ge_xO_4$  ( $0 \le x \le 0.15$ ), with high photocatalytic activity for the reaction was successfully synthesized via a facile molten salts route. The Zn-based solid solutions with size about 200 nm have a homogeneous inverted cubic spinel structure (*Fd3m*) and a continuously modulated band gap with the Ge content. For the CO<sub>2</sub> reduction reaction with H<sub>2</sub>O under simulated solar irradiation, the  $Zn_2Ti_{1-x}Ge_xO_4$  solid solutions display not only high activity for the conversion of CO<sub>2</sub> into CH<sub>4</sub> and CO fuels, but also long-term stability (>60 h of catalytic reaction). Experimental results and theoretical calculations indicated that the conduction and the valence bands of the cubic spinel  $Zn_2TiO_4$  are positively shifted by introducing  $Zn_2GeO_4$  with a pseudocubic inverse spinel structure, but the band gaps of solid solutions are simultaneously modulated with the introduction of germanium. Nevertheless, the  $Zn_2TiO_4$  affords a light-carrier effective mass and strong electron delocalization by forming a solid solution with  $Zn_2GeO_4$ , which is beneficial to improving migration of photogenerated electrons and holes. As a synergistic result of band gap narrowing and high carrier diffusion, good conversion efficiencies for production of solar fuels through the reactions of CO<sub>2</sub> reduction with H<sub>2</sub>O are achieved.

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#### 1. Introduction

The conversion of CO<sub>2</sub> and water into fuels and chemicals over semiconductor-based photocatalysts has been attracting extensive research interest as one of the best prospective routes to transform solar energy into chemical energy [1,2]. Various photocatalysts for the reaction, including single-metal oxides (e.g., TiO<sub>2</sub>, WO<sub>3</sub>) [3–7], metal sulfides or phosphides (e.g., ZnS, CdS, p-GaP) [8–11], binarymetal oxides (e.g., Bi<sub>2</sub>WO<sub>6</sub>, ZnGa<sub>2</sub>O<sub>4</sub>, Zn<sub>2</sub>SnO<sub>4</sub>, Zn<sub>2</sub>GeO<sub>4</sub>) [12–17], and semiconductor-based composites (e.g., CdS/graphene, Zn<sub>1.7</sub>-GeN<sub>1.8</sub>O/graphenes, Fe<sub>2</sub>V<sub>4</sub>O<sub>13</sub>/rGO/CdS) [18–22], have been developed. However, most of them can be used only under UV light and suffer from low conversion efficiency and poor photostability during the photocatalytic reaction, which has greatly hindered commercial applications in this field. So highly efficient and stable photocatalysts still are a huge challenge facing research on CO<sub>2</sub> photoreduction to fuel.

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In the design and development strategies for various photocatalytic materials, constructing solid solutions has been experimentally demonstrated to be quite suitable for CO<sub>2</sub> reduction with H<sub>2</sub>O [13]. On one hand, the photoabsorption range of a solid solution can be optimized by controlling foreign atoms to simultaneously meet the requirements of the half-reaction of CO<sub>2</sub> reduction and the half-reaction of water oxidation [5]. On the other hand, the additional energy states associated with optimized foreign atoms can be highly delocalized, which is favorable for improving charge mobility and enhancing photocatalytic performance [23]. Many studies have demonstrated that the mixing of orbitals in  $d^{10}$  oxides' hybridized s and p orbitals confers a large dispersion in k-space on the band and thereby a high mobility of photogenerated electrons [24–31]. High mobility of photoexcited electrons enhances the photocatalytic activity of a given semiconductor photocatalyst. For instance, ternary metal oxides (e.g., zinc germanate/zinc stannate) in which the  $Zn^{2+}$  ion is in a  $d^{10}$  electronic configuration have exhibited a competitive advantage in the photoreduction of  $CO_2$  into solar fuels [15,16]. Among these metal oxides with  $d^{10}$  electronic configuration, zinc titanate generally exists in three different crystalline phases, including the



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ZnTiO<sub>3</sub> (hexagonal), Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub> (cubic), and Zn<sub>2</sub>TiO<sub>4</sub> (cubic). As compared with ZnTiO<sub>3</sub> and Zn<sub>2</sub>Ti<sub>3</sub>O<sub>8</sub>, cubic spinel Zn<sub>2</sub>TiO<sub>4</sub> with  $d^{10}$  electronic configuration has been found to have not only important electrical and photochemical properties (e.g., catalytic properties) [32–34], but also high chemical stability and a band gap comparable to that of TiO<sub>2</sub> [35,36]. Meanwhile, the refractory spinel oxide typically forms extended series of solid solutions, which is extremely tolerant of different cationic replacements (e.g., Sn<sup>4+</sup>, Fe<sup>3+</sup>, and Zr<sup>4+</sup>) [37–39]. Thus, to design and construct Zn<sub>2</sub>TiO<sub>4</sub>-based solid solutions by introducing foreign atoms in a particular way can be a feasible and effective route to achieving series of novel and high-performance photocatalytic materials for the photocatalytic reduction of CO<sub>2</sub>.

In this study, a series of solid-solution photocatalysts consisting of cubic spinel Zn<sub>2</sub>TiO<sub>4</sub> and pseudocubic inverse spinel Zn<sub>2</sub>GeO<sub>4</sub> were prepared by a facile molten salt route (Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>) at 1273 K for 12 h using stoichiometric mixtures of ZnO, TiO<sub>2</sub>, and GeO<sub>2</sub> as precursors. The as-obtained nanocrystalline Zn<sub>2</sub>Ti<sub>1-x</sub>-Ge<sub>x</sub>O<sub>4</sub> ( $0 \le x \le 0.15$ ) solid solution was shown to exhibit both significantly improved photocatalytic activity and unprecedented photocatalytic stability for conversion of CO<sub>2</sub> to CO and CH<sub>4</sub>. The enhanced performance of Zn<sub>2</sub>Ti<sub>1-x</sub>-Ge<sub>x</sub>O<sub>4</sub> is attributed to two main causes: (i) band-gap narrowing, which is caused by upper shift of the valence band edge from the enhanced *p*-*d* repulsion, and (ii) enhanced mobility and diffusion of photogenerated carriers, which is attributed to the light hole effective mass and strong electron delocalization. These factors enhance the ability of the photocatalyst to convert CO<sub>2</sub> and water into renewable fuels.

#### 2. Experimental

#### 2.1. Material preparation

For synthesis of nanocrystalline  $Zn_2Ti_{1-x}Ge_xO_4$  ( $0 \le x \le 0.15$ ) solid solutions, all regents used were from Sinopharm Chemical Reagent Co. (SCRC) without further purification. In this experiment, Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> served as molten salts media because of their low melting temperature (1104 K). In the typical synthesis of  $Zn_2Ti_{1-x}Ge_xO_4$  solid solutions, dry mixtures of ZnO, GeO<sub>2</sub>, TiO<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub> with molar ratios of 2:0.05:0.95:15:15, 2:0.10:0.90:15:15, and 2:0.15:0.85:15:15 were thoroughly ground in an agate mortar. After 1 h, the starting-mixture compositions were pressed into disks by a mini tablet press machine and put into an alumina crucible, and then the disk-shaped samples were calcined in static air at 1273 K (ramp of 3 K/min) for 12 h. followed by quenching. After cooling to room temperature, the asobtained solid products were collected and washed several times with deionized water by centrifugation to remove Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>. Finally, these precipitates were dried in an oven at 343 K for 12 h. The bulk Zn<sub>2</sub>TiO<sub>4</sub> particles used for comparison were prepared by heating a stoichiometric mixture of TiO<sub>2</sub> and ZnO at 1473 K (ramp of 5 K/min) for 24 h; the product was denoted as Zn<sub>2</sub>TiO<sub>4</sub>-SSR.

## 2.2. Characterization

The crystalline phases of the prepared samples were characterized by powder X-ray diffraction (XRD) by a Bruker D8 Advance X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 0.15406$  nm) operating at 40 kV and 30 mA with a scanning rate of 8°/min from 3° to 85°. The morphologies and sizes of the samples were analyzed by field-emission scanning electron microscopy (FE-SEM, JEOL JSM–6701F). The chemical structure and morphology of the sample were characterized using a JEOL Model JEM 2010 EX microscope at an accelerating voltage of 200 kV. The

morphology and energy-dispersive spectroscopy (EDS) of the samples were observed by transmission electron microscope (TEM; (FEI Tecnai G2 F30 S-Twin, USA). The surface chemical compositions of samples were examined by X-ray photoelectron spectroscopy with an ESCALAB 250 XPS electron spectrometer with a mono-achromatized AlK $\alpha$  X-ray source. The binding energy was referenced to the C1s peak at 284.8 eV. Nitrogen adsorption-desorption studies were performed at liquid nitrogen temperature (77 K) using a Model ASAP 2020 Micromeritics apparatus for the Brunauer-Emmett-Teller (BET) method. CO<sub>2</sub> adsorption-desorption curves were measured at 273 K. The optical absorption properties of samples were recorded by ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) on a Varian Cary 500 Scan UV/ Vis system, in which BaSO<sub>4</sub> was used as the background. The elemental composition of the sample was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 725).

## 2.3. Photocatalytic activity measurement

The photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O vapor was carried out in a quartz glass reactor under atmospheric pressure at room temperature. In a typical experiment, 50 mg of the as-prepared photocatalyst was loaded into a 25-mL quartz glass reactor whose top was sealed with a silicone rubber septum. Subsequently, the whole system was subjected to vacuum degassing and then backfilling with high-purity CO<sub>2</sub> gas (99.995%, Changzhou Jinghua Industrial Gas Co.). This evacuation-filling process was repeated several times, and after the last cycle the reactor was backfilled with CO<sub>2</sub> (1 bar). Finally, 20 µL of liquid deionized water was introduced into the reactor from the silicone rubber septum with a microsyringe, and liquid deionized water was gasified by heating with a hair dryer. Prior to illumination irradiation, magnetic stirring (600 rpm) in the dark for 1 h established adsorption/desorption equilibrium. A 300-W Xe arc lamp was used as a light source. The photocatalytic reaction was carried out while the reactor was evacuated after each 10 h and refilled with CO<sub>2</sub> and deionized water. Finally, 0.5 mL of gas was taken from the glass reactor for subsequent gas concentration analysis using a gas chromatograph (GC-7890A, Shimadzu) equipped with a flame ionization detector (FID) and a capillary column (GC-GASPRO,  $30 \text{ m} \times 0.320 \text{ mm}$ ). The generated O<sub>2</sub> was detected by HP 7890 gas chromatography (Ar carrier) equipped with a TCD detector and 5A molecular sieve packed column (10 m  $\times$  mm). Product gases were calibrated with a standard gas mixture and their identity was determined using the retention time and analyzed quantitatively by an external standard method (Fig. S1 in the Supplementary Material).

#### 2.4. Photoelectrochemical measurements

Photoelectrochemical measurements were carried out with a BAS Epsilon workstation using a standard three-electrode electrochemical cell with a working electrode, a platinum foil as the counter electrode, and a saturated Ag/AgCl electrode as the reference. A sodium sulfate solution (0.2 M) was used as the electrolyte, and a 300-W LightningCure Model LC8 spotlight was introduced as the light source. At 365 nm, the output power was 4500 mW cm<sup>-2</sup>. The working electrode was prepared by SnO<sub>2</sub> doped with F (FTO) glass pieces, and was cleaned by sonication in cleanout fluid, acetone, and ethanol in sequence. The photocatalyst was dispersed in ethanol under sonication to form a suspension. A photocatalyst film was fabricated by spreading the suspension onto the conductive surface of the FTO glass.



**Fig. 1.** (a) XRD patterns of  $Zn_2Ti_{1-x}Ge_xO_4$  ( $0 \le x \le 0.15$ ) solid solutions. (b) The enlarged part of the corresponding  $Zn_2Ti_{1-x}Ge_xO_4$  solid solutions' XRD patterns ranging from  $2\theta = 34.0^{\circ}$  to  $36.0^{\circ}$ . (c) Lattice constants and (d) lattice parameters of  $Zn_2Ti_{1-x}Ge_xO_4$  ( $0 \le x \le 0.15$ ) solid solutions.

### 2.5. Models and computational methods

Density functional theory (DFT) calculations were carried out with the CASTEP package from Accelrys [40]. The generalized gradient approximation (GGA) plus the Perdew–Burke–Ernzerhof functional (GGA-PBE) [41,42] was set as the exchange-correlation functional. Brillouin zone sampling was chosen according to the Monkhorst–Pack [43] scheme with a grid spacing of 0.04 Å<sup>-1</sup>, and the *k*-point mesh was  $5 \times 5 \times 5$ ,  $5 \times 5 \times 1$  for  $Zn_2TiO_4$  and  $Zn_2-Ti_{0.9}Ge_{0.1}O_4$ , respectively.

## 3. Results and discussion

The XRD patterns of the Zn<sub>2</sub>Ti<sub>1-x</sub>Ge<sub>x</sub>O<sub>4</sub> ( $0 \le x \le 0.15$ ) samples are shown in Fig. 1a. All samples have the same crystal structure as Zn<sub>2</sub>TiO<sub>4</sub> (JCPDS 25-1164), and the enlarged image indicates a gradual shift of the (3 1 1) diffraction peaks toward higher angles with increasing Ge content (Fig. 1b), suggesting formation of a cubic-spinel-structured Zn<sub>2</sub>Ti<sub>1-x</sub>Ge<sub>x</sub>O<sub>4</sub> ( $0 \le x \le 0.15$ ) solid solution by incorporation of Ge<sup>4+</sup> into the lattice structure of Zn<sub>2</sub>TiO<sub>4</sub>. Additionally, the lattice parameters of the Zn<sub>2</sub>Ti<sub>1-x</sub>Ge<sub>x</sub>O<sub>4</sub> solid solution



Fig. 2. (a) Wide scan XPS survey spectra of the Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution, Zn<sub>2</sub>TiO<sub>4</sub>, and Zn<sub>2</sub>GeO<sub>4</sub>. High-resolution XPS spectra of the Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution, Zn<sub>2</sub>TiO<sub>4</sub>, and Zn<sub>2</sub>GeO<sub>4</sub>: (b) Ti2*p*, (c) Zn2*p*, (d) Ge2*p*, and (e) O1*s*.



**Fig. 3.** (a) Large-area and (b) partially enlarged FESEM images of the as-obtained  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution. (c and d) TEM and (e) HRTEM images of the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution. (f) Energy-dispersive X-ray spectroscopy (EDX) spectrum of the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution. (g) Dark-field TEM and corresponding EDX elemental mappings of  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution obtained by TEM. Insert in panel (e) is the corresponding SAED pattern  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution.

are calculated by fitting the XRD data, as shown in Fig. 1c. It is important to note that the lattice constant is increased linearly with decreasing Ge content, obeying the generally known Vegard's law [39]. This may be attributed to isomorphous substitution of lattice Ge<sup>4+</sup> with a smaller radius (0.053 nm) by Ti<sup>4+</sup> with a larger radius (0.0605 nm). Nevertheless, it is further demonstrated in Fig. 1d that the lattice of the solid solution  $Zn_2Ti_{1-x}Ge_xO_4$  ( $0 \le x \le 0.15$ ) evolves with composition from  $Zn_2TiO_4$  to  $Zn_2Ti_{0.85}$ -Ge<sub>0.15</sub>O<sub>4</sub>. However, it should be noticed that when the *x* value is higher than 0.15, the product is a two-phase mixture of the cubic  $Zn_2Ti_{1-x}Ge_xO_4$  (Fig. S2).

X-ray photoelectron spectrum (XPS) measurements were carried out to obtain the chemical state and composition of the  $Zn_2$ - $Ti_{1-x}Ge_xO_4$  solid solution. For comparison, the XPS spectra of  $Zn_2TiO_4$  and  $Zn_2GeO_4$  samples obtained by a similar molten salt route were also determined. As shown in Fig. 2a, in contrast to the chemical compositions of both  $Zn_2TiO_4$  and  $Zn_2GeO_4$  samples, the survey spectrum of the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  sample confirms the simultaneous existence of Zn, Ti, Ge, and O elements in the  $Zn_2Ti_{1-x}Ge_xO_4$  solid solution. To further identify the chemical states of elements in various samples, binding energies of core-level electrons from constituent elements for all samples are illustrated in Fig. 2b–e. Two peaks at 458.66 and 1220.5 eV are clearly observed

for the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  sample, which are assigned to  $Ti2p_{3/2}$  and  $Ge_{2p_{3/2}}$  (Fig. 2b and d), respectively [44]. The two peaks centered at 1022.41 and 530.28 eV are attributed to  $Zn2p_{3/2}$  and O1s (Fig. 2c and e), respectively. However, in contrast to Zn<sub>2</sub>TiO<sub>4</sub>  $(Ti2p_{3/2} \text{ at } 458.85 \text{ eV}, \text{ O1}s \text{ at } 530.33 \text{ eV}, \text{ and } Zn2p_{3/2} \text{ at }$ 1022.15 eV) [45] and  $Zn_2GeO_4$  (Ge2 $p_{3/2}$  at 1220.63 eV, O1s at 530.99 eV, and Zn2p<sub>3/2</sub> at 1022.44 eV) [46], the Ti2p (458.66 eV) and  $Ge2p_{3/2}$  (1220.5 eV) peak positions in the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  samples shift slightly toward lower binding energy, indicating the presence of a new bond (Fig. 2b and d). Compared to the Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>GeO<sub>4</sub> samples, the O1s binding energy is slightly decreased, while Zn2p binding energy is slightly increased for the Zn<sub>2</sub>Ti<sub>0.9</sub>- $Ge_{0,1}O_4$  sample (Fig. 2c and e). The change in binding energies can result from introduction of the Ge atom into the Zn<sub>2</sub>TiO<sub>4</sub>. In addition, the energetic separation ( $\Delta E$ ) between the Zn2p<sub>3/2</sub> and  $Ti2p_{3/2}$  peaks for  $Zn_2TiO_4$  and  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  samples was determined to be ca. 563.3 eV and 563.75 eV, respectively (Fig. 2b and c), much lower than that for the mixture of ZnO and TiO<sub>2</sub> (565.80 eV) [47], confirming the formation of spinel Zn<sub>2</sub>TiO<sub>4</sub>. The result indicates that a more complete phase transformation to cubic spinel structure can occur, as demonstrated by XRD (Fig. 1). On the other hand, we also observed that the  $\Delta E$  value of the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  sample exhibits a certain increase in



**Fig. 4.** (a) UV-visible diffuse reflection spectra of the various samples. (b) The optical band gap energy ( $E_g$ ) of the various corresponding samples. (c) Valence-band XPS spectra of Zn<sub>2</sub>TiO<sub>4</sub>, Zn<sub>2</sub>CeO<sub>4</sub>, and Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution prepared by a molten-salts route. (d) Energy band structure schematic of these materials, calculated from the data in (a), (b), and (c).

comparison with that of  $Zn_2TiO_4$  particles, which further demonstrated the formation of Ge-substituted  $Zn_2TiO_4$  solid solution with a cubic inverse spinel structure.

Fig. 3a and b present typical SEM images of the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$ solid solution. It can be seen clearly that the solid solution sample is composed of a large number of polyhedral nanoparticles, with sizes ranging from 100 to 300 nm (Fig. S3). The morphological characteristics of the sample are also supported by TEM observation (Fig. 3c and d), further disclosing that the as-prepared  $Zn_2Ti_{0.9}$ -Ge<sub>0.1</sub>O<sub>4</sub> solid solution is highly crystalline and the sizes are below 300 nm. Moreover, to make sure of the detailed crystal structure of the polyhedral Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution, HRTEM characterization was also done, as shown in Fig. 3e. Both a uniform lattice fringe and a spot pattern of the selected-area electron diffraction (SAED) (the inset in Fig. 3e) verify that the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution shows apparently single-crystalline characteristics. The distance between the adjacent lattice fringes is 0.485 nm (Fig. 3e), which can be assigned to the interplanar distance of the cubic Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> (1 1 1) plane. The data are almost consistent with the (1 1 1) crystal planes of cubic Zn<sub>2</sub>TiO<sub>4</sub>, according to JCPDS card 25-1164. Furthermore, EDS and TEM mapping are used to establish the composition and distribution of all elements in the solid solution, as shown in Fig. 3f. The Zn, Ti, Ge, and O belonging to the sample are detected, and its composition is very close to the feed ratios. Meanwhile, on the basis of the ICP-OES analysis, the atomic ratio of Zn, Ti, and Ge is ca. 2.05:0.89:0.1, which is nearly

in agreement with the theoretical value. In addition, as shown in Fig. 3g, the elemental mapping images reveal that the  $Zn_2Ti_{0.9}$ -Ge<sub>0.1</sub>O<sub>4</sub> are indeed composed of the elements Zn, Ti, Ge, and O, and all the elements are distributed uniformly over the whole area of the solid solution, suggesting uniformity of  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  without any phase separation. This indicates that the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution can be successfully obtained via the simple molten salt route.

Fig. 4a and b show UV-visible diffuse reflectance spectra (DRS) of samples. The band gap  $(E_g)$  of bare  $Zn_2TiO_4$  prepared by the molten salt route is estimated to be 3.73 eV, corresponding to an optical absorption edge of ca. 332 nm. Zn<sub>2</sub>Ti<sub>0.95</sub>Ge<sub>0.05</sub>O<sub>4</sub>,  $Zn_2Ti_{0.9}Ge_{0.1}O_4$ , and  $Zn_2Ti_{0.85}Ge_{0.15}O_4$  have band gaps of ca. 3.72, 3.70, and 3.71 eV, respectively, corresponding to optical adsorption edges of about 333, 335, and 334 nm. This means that the  $E_g$  of the solid solution is less than the that of  $Zn_2TiO_4$  and of  $Zn_2GeO_4$ (4.5 eV) [31]. According to Fig. S4, the light-absorption edge of the nanostructured Zn<sub>2</sub>TiO<sub>4</sub> sample prepared by the molten salt route exhibit a certain extent of blue shift from those of Zn<sub>2</sub>TiO<sub>4</sub>-SSR prepared by the high-temperature solid state method, which can be explained by size effects [48]. Simultaneously, the band edge position of the conduction band of the cubic spinel Zn<sub>2</sub>TiO<sub>4</sub> can be positively shifted by introducing Zn<sub>2</sub>GeO<sub>4</sub> with a pseudocubic inverse spinel structure. To understand the electronic structure of the Ge-substituted Zn<sub>2</sub>TiO<sub>4</sub> solid solution, valence band XPS (VB XPS) was used for the observation of the valence band electronic



**Fig. 5.** (a) Gas evolution rates under different conditions. (b) Mass spectra of the reaction product from  ${}^{12}\text{CO}_2$  to  ${}^{13}\text{CO}_2$  over  $\text{Zn}_2\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_4$  solid solution in the presence of H<sub>2</sub>O vapor. (c) The photocatalytic performance of P25 TiO<sub>2</sub>, Zn<sub>2</sub>TiO<sub>4</sub>-SSR, and various Zn<sub>2</sub>Ti<sub>1-x</sub>Ge<sub>x</sub>O<sub>4</sub> samples. (d) The photocatalytic stability of the Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution. (e) The CH<sub>4</sub> and (f) CO production rates of various samples.

state of these as-prepared samples (Fig. 4c). We find that the valence band ( $E_{VB}$ ) potentials of Zn<sub>2</sub>TiO<sub>4</sub>, Zn<sub>2</sub>GeO<sub>4</sub>, and Zn<sub>2</sub>Ti<sub>0.9</sub>-Ge<sub>0.1</sub>O<sub>4</sub> solid solution are ca. 2.45, 3.2, and 2.5 V. Accordingly, the conduction band potential ( $E_{CB}$ ) of  $Zn_2TiO_4$ ,  $Zn_2GeO_4$ , and  $Zn_2Ti_{0.9}$ - $Ge_{0.1}O_4$  solid solutions is estimated at about -1.28, -1.20, and -1.20 V, respectively, according to  $E_g = E_{VB} - E_{CB}$  [49]. ( $E_g$ : semiconductor band gap;  $E_{VB}$ : valence band edge potential;  $E_{CB}$ : conduction band edge potential.) This means that the band edge positions of the conduction and valence bands of the cubic spinel Zn<sub>2</sub>TiO<sub>4</sub> can be positively shifted simultaneously by introducing Zn<sub>2</sub>GeO<sub>4</sub> with a pseudocubic inverse spinel structure. However, it is noteworthy that the upshift of the valence band edge potential is much greater than that of the conduction band edge potential. Thus, introducing Zn<sub>2</sub>GeO<sub>4</sub> into Zn<sub>2</sub>TiO<sub>4</sub> can effectively narrow the band gap, as shown in Fig. 4d. The band gap narrowing may promote the photoinduced reaction due to more light absorption. The results of our present work show that Zn<sub>2</sub>GeO<sub>4</sub> plays a dominant role in tuning the energy band structure of Zn<sub>2</sub>TiO<sub>4</sub> with Ge substituting at the Ti site [50].

The electron structures of  $Zn_2TiO_4$  and  $Zn_2Ti_{1-x}Ge_xO_4$  $(0 \le x \le 0.15)$  solid solution samples can meet requirements for the reduction of CO<sub>2</sub> by H<sub>2</sub>O under simulated sunlight. As displayed in Fig. 5a, a blank experiment reveals that no products are detected in the absence of a photocatalyst or light irradiation. In the absence of H<sub>2</sub>O, it is found that only small amounts of CH<sub>4</sub> and CO were produced over Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub>. Once water was added, as expected, the amounts of the main products (CH<sub>4</sub> and CO) produced by CO<sub>2</sub> photoreduction were significantly increased under light irradiation. This result indicated that CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation might occur simultaneously in the present photosynthesis system to generate CH<sub>4</sub> and CO from direct photocatalytic reaction of CO<sub>2</sub> and H<sub>2</sub>O, while H<sub>2</sub>O can act as an electron donor for photocatalytic CO<sub>2</sub> reduction [49]. To further confirm the origin of the CO and CH<sub>4</sub> products, isotope experiments using <sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub> as substrates were conducted on a GC-MS system (Fig. 5b). As revealed by the peaks at m/z = 17 and 29, <sup>13</sup>CH<sub>4</sub> and <sup>13</sup>CO were the main products of the reaction; this further confirms that the carbon source of the formed reduction products derived



**Fig. 6.** (a) CO<sub>2</sub> adsorption isotherms of Zn<sub>2</sub>TiO<sub>4</sub>, Zn<sub>2</sub>TiO<sub>9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution, and Zn<sub>2</sub>GeO<sub>4</sub> at 273 K. (b) Specific surface areas of the as-prepared Zn<sub>2</sub>Ti<sub>1-x</sub>Ge<sub>x</sub>O<sub>4</sub> samples. (c) Transient photocurrent responses and (d) Nyquist plots for the samples obtained by a molten salts route.

from CO<sub>2</sub>. Moreover, we can observed distinctly from Fig. 5c that each of the prepared  $Zn_2Ti_{1-x}Ge_xO_4~(0\leq x\leq 0.15)$  samples can photocatalytically reduce CO<sub>2</sub> to CO and CH<sub>4</sub> in the presence of H<sub>2</sub>O, and their activities for evolution of gases (CH<sub>4</sub> and CO) were remarkably better than those of the standard photocatalyst P25 TiO<sub>2</sub>. Meanwhile, upon full arc irradiation, CO and CH<sub>4</sub> are generated as the main reduction products of CO<sub>2</sub>, while O<sub>2</sub> is evolved simultaneously as the oxidation product of H<sub>2</sub>O. To the best of our knowledge, this is the first examples of CO<sub>2</sub> photoreduction over  $Zn_2TiO_4$  and  $Zn_2Ti_{1-x}Ge_xO_4$  ( $0 \le x \le 0.15$ ) solid solutions. Furthermore, according to the results in Fig. 5c, for Zn<sub>2</sub>TiO<sub>4</sub> samples, the nanostructured Zn<sub>2</sub>TiO<sub>4</sub> sample obtained by the molten-salt route is superior in activity to the bulk Zn<sub>2</sub>TiO<sub>4</sub>-SSR sample prepared by the solid-state reaction route. In view of Figs. S5 and S7a, it is evident that the difference in photocatalytic activity is related to their particle sizes. Of the  $Zn_2Ti_{1-x}Ge_xO_4$ (0 < x < 0.15) samples, the Ge-substituted Zn<sub>2</sub>TiO<sub>4</sub> solid solutions displayed better activity than the nanostructured Zn<sub>2</sub>TiO<sub>4</sub> sample. It is therefore noteworthy that the amounts of these products increased almost linearly with increasing irradiation time (Fig. 5e and f); especially, the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  sample shows the highest activity, and the maximal evolution rates of CO and CH<sub>4</sub> over the Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution photocatalyst are as high as 11.9 and 0.38  $\mu$ mol h<sup>-1</sup> g<sup>-1</sup>, respectively. The photocatalytic activity decreased in the order  $Zn_2Ti_{0.9}Ge_{0.1}O_4 > Zn_2Ti_{0.95}Ge_{0.05}O_4 > Zn_2$ - $Ti_{0.85}Ge_{0.15}O_4 > Zn_2TiO_4 + Zn_2GeO_4$  (prepared by physical mixing at a molar ratio of  $Zn_2TiO_4/Zn_2GeO_4 = 9:1$  >  $Zn_2TiO_4$  >  $Zn_2TiO_4$ - SSR > P25-TiO<sub>2</sub> (Fig. 5c). At the same time,  $Zn_2TiO_4$  and  $Zn_2Ti_{0.9}$ -Ge<sub>0.1</sub>O<sub>4</sub> solid solution also show higher photocatalytic activity than common semiconductors (Tables S1 and S2 in the Supplementary Material). In addition, Fig. 5d shows that the photocatalytic activity of the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution remains unchanged after 60 h of reaction, and the amount of these products increases almost linearly with increasing irradiation time, indicating good activity and stability of the photocatalyst. From the results of the XRD (Fig. S6), the phase composition of the solid solution photocatalyst is still maintained after 60 h photoreaction. On the basis of analysis of the above results, the germanium-substituted  $Zn_2TiO_4$  solid solutions have the competitive advantages of tunable bandgap (Fig. 4), good photocatalytic activity, and powerful stability. These make it a promising candidate as a new photocatalyst to convert  $CO_2$  into solar fuel in the presence of H<sub>2</sub>O.

To gain insight into the photocatalytic performance of  $Zn_2Ti_{1-x}Ge_xO_4$  solid solutions, the basic physicochemical properties of these  $Zn_2Ti_{1-x}Ge_xO_4$  solid solutions were characterized. As seen in Fig. S7 and Fig. 6b, the as-prepared  $Zn_2Ti_{1-x}Ge_xO_4$  samples almost have comparable specific surface area and particle size, implying that the texture is not the reason for the difference in the photocatalytic activity (Fig. 5d) of those  $Zn_2Ti_{1-x}Ge_xO_4$  photocatalysts. The CO<sub>2</sub> adsorption on various photocatalysts was evaluated by the BET method at 273 K, as shown in Fig. 6a. The adsorption amount of CO<sub>2</sub> decreased in the order  $Zn_2TiO_4 > Zn_2TiO_9Ge_{0.1}O_4 > Zn_2GeO_4$ , while the photocatalytic activity decreased in the order  $Zn_2TiO_9$ .



**Fig. 7.** (a) Structure of Zn<sub>2</sub>TiO<sub>4</sub>, viewed from the [1 1 0] direction with the unit cell outlined. (b) Constructed model of Zn<sub>2</sub>TiO<sub>4</sub> with the primitive cell, viewed from the [1 0 1] direction. Pink: ZnO<sub>4</sub> tetrahedron, light blue: Zn/TiO<sub>8</sub> octahedron, dark blue: TiO<sub>8</sub> octahedron, green: ZnO<sub>8</sub> octahedron. Calculated band structures and density of states (DOS) of (c) Zn<sub>2</sub>TiO<sub>4</sub> and (d) Zn<sub>2</sub>TiO<sub>9</sub>Ge<sub>0.1</sub>O<sub>4</sub>. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

difference cannot be related to the CO<sub>2</sub> adsorption. Furthermore, the photoelectrochemical characterization of the photocatalyst was performed and is shown in Fig. 6c. As compared with Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>GeO<sub>4</sub>, the Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution electrode gives a significant improvement in transient photocurrents under light illumination. Those transient photocurrent results are in agreement with the photocatalytic activity reported above (Fig. 5). However, we also observed that the photocurrent density for these film electrodes decreased slowly with the on-off illumination cycle increasing, which could be attributed to the establishment of steady diffusion gradients in the system [15]. In order to further reveal the charge transfer process, electrochemical impedance spectroscopy (EIS) was also carried out. The Nyquist plots of the photocatalyst electrodes of Zn2TiO4, Zn2Ti0.9Ge0.1O4 solid solution, and Zn<sub>2</sub>GeO<sub>4</sub> are shown in Fig. 6d. It can be seen that the Zn<sub>2</sub>Ti<sub>0.9</sub>-Ge<sub>0.1</sub>O<sub>4</sub> solid solution shows more decrease in charge-transfer resistance than Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>GeO<sub>4</sub>. The EIS analysis result indicates higher conductivity of the Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution than of the pseudocubic Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>GeO<sub>4</sub>. Therefore, more effective charge transfer was achieved, as well as higher photocatalytic performance.

The band structure of a semiconductor photocatalyst is of vital importance in determining the variation of photocatalytic activity in the  $Zn_2Ti_{1-x}Ge_xO_4$  solid solutions. To understand the electronic structures of cubic  $Zn_2TiO_4$  and  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution, density functional theory (DFT) calculations and generalized gradient approximation (GGA) functional calculation were performed.

 $Zn_2TiO_4$  possesses an inverse spinel-type structure (Fd 3 m, Z = 8)

[51], in which the tetrahedral interstices are occupied by Zn cations (ZnO<sub>4</sub>), while the octahedral interstices are occupied by both Zn and Ti cations (MO<sub>8</sub>, Zn:Ti = 0.5:0.5, Fig. 7a). To further explore the origin of the optical and photocatalytic properties of the Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution, theoretical calculations were performed for the electronic structure of Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>-O<sub>4</sub> solid solution. Considering the fractional occupancies of Ti and Zn atoms, a possible structure replacing two octahedral sites with Ti and the others with Zn was predicted (Fig. 7b). The solid solution was simulated by replacing 1 Ti at the octahedral site with 1 Ge in the  $1 \times 1 \times 5$  supercell of  $Zn_2TiO_4$  (shown in Fig. S8). A primitive cell ( $a_{init} \approx b_{init} \approx c_{init} = 5.989$  Å,  $\alpha = \beta = \gamma = 60^{\circ}$ ), with space group reduced from Fd3mto P1, was constructed. The electronic structure of Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution was researched by DFT calculations. The electronic band structures and densities of states (DOS) near the Fermi levels of Zn<sub>2</sub>TiO<sub>4</sub> and Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>-O<sub>4</sub> are shown in Fig. 7c and d. Zn<sub>2</sub>TiO<sub>4</sub> is an indirect band gap semiconductor with a calculated band gap of about 1.51 eV. This value is much lower than the experimental value of 3.52 eV determined from UV/vis spectra. This can be attributed to the drawbacks of the generalized gradient approximation (GGA) method, which underestimates band gaps [52]. Nevertheless, the calculation offers qualitative comparisons. The conduction band (CB) and valence band (VB) are mainly composed of Ti3d and O2p orbitals. On the other hand, Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> is an indirect band gap semiconductor with a calculated gap of 1.0 eV. Seen from its PDOS, it reveals the presence of an additional VB at the top of the original VB, which is from Ge4s4p orbitals. It has been reported that p-d repulsion in II-VI semiconductors shifts the VB offset [53]. The presence of Zn3d and O2p electrons in the upper valence band provides p-d repulsion for the valence-band maximum. The hybridization of Ge4s4p and O2p in the VB enhances the *p*-*d* repulsion of Zn3*d* and O2*p*, and then shifts the valence band edge upward, resulting in a narrowing of the band gap and the enhancement of band delocalization [12,54,55]. Furthermore, according to our generalized gradient approximation (GGA) functional calculations [56], the average effective masses of photoinduced electrons and holes for the Zn<sub>2</sub>- $Ti_{0.9}Ge_{0.1}O_4$  solid solution are 0.42  $m_0$  and 0.18  $m_0$ , respectively, which is much lower than those of  $Zn_2TiO_4$  (0.5  $m_0$  and 0.53  $m_0$ ). The results indicate that introducing  $Zn_2GeO_4$  into  $Zn_2TiO_4$  is able to decrease the effective mass of photogenerated charge carriers, thus leading to the fast migration of photogenerated electrons and holes in the  $Zn_2Ti_{0.9}Ge_{0.1}O_4$  solid solution. As a result, their synergistic effect on band gap narrowing and high carrier diffusion transfer for Zn<sub>2</sub>Ti<sub>0.9</sub>Ge<sub>0.1</sub>O<sub>4</sub> solid solution leads to a higher photocatalytic activity than that of Zn<sub>2</sub>TiO<sub>4</sub>.

#### 4. Conclusions

In summary, we reported a controllable synthesis strategy for the Ge-substituted Zn<sub>2</sub>TiO<sub>4</sub> solid solution as a highly efficient photocatalyst for the reduction of  $CO_2$  by  $H_2O$  via a molten salts route. By changing the molar ratio of Ti/Ge atoms in  $Zn_2Ti_{1-x}Ge_xO_4$ , a series of  $Zn_2Ti_{1-x}Ge_xO_4$  ( $0 \le x \le 0.15$ ) solid solution photocatalysts were constructed. Introducing Zn<sub>2</sub>GeO<sub>4</sub> into Zn<sub>2</sub>TiO<sub>4</sub> could effectively reduce both the band gap, by elevating the valence band edge from an enhanced *p*-*d* repulsion effect, and the conduction band edge, by introduction of the low-energy orbital of Ge. The Zn<sub>2</sub>Ti<sub>1-x</sub>Ge<sub>x</sub>O<sub>4</sub> solid solution has a low effective hole mass and an enhanced valence band delocalization performance, which are beneficial to improving hole mobility, and thus enhancing the ability of the photocatalyst for water oxidation. As a result, the Gesubstituted Zn<sub>2</sub>TiO<sub>4</sub> solid solution exhibits high activity and continuous stability in converting CO<sub>2</sub> and H<sub>2</sub>O into CH<sub>4</sub>, CO, and O<sub>2</sub>. The synthetic strategy reported here not only is helpful in systematically exploring fabrication of Zn<sub>2</sub>TiO<sub>4</sub>-based solid solutions, but also provides a feasible approach to developing highly light-active photocatalysts for CO<sub>2</sub> conversion into renewable solar fuels.

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#### **Appendix A. Supplementary material**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.01.017.

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