

Electronic Supplementary Information

An anion-controlled crystal growth route to Zn₂GeO₄ nanorod for efficient photocatalytic conversion of CO₂ into CH₄**

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SI-1 Characterization of Na_2GeO_3

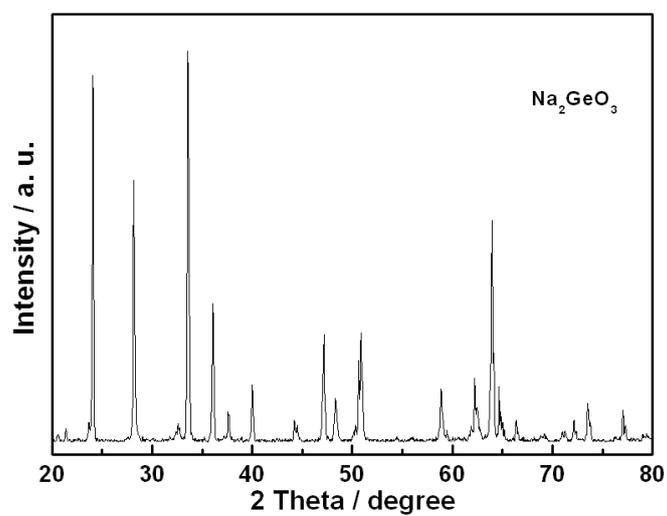


Figure S1. XRD pattern of Na_2GeO_3 powders obtained by heating the stoichiometric mixture of Na_2CO_3 and GeO_2 at $900\text{ }^\circ\text{C}$ for 12 h. The XRD pattern is in good agreement with JCPDS 70-0754.



Figure S2 The Tyndall effect observation for Na_2GeO_3 colloidal solution by 532 nm laser illuminating

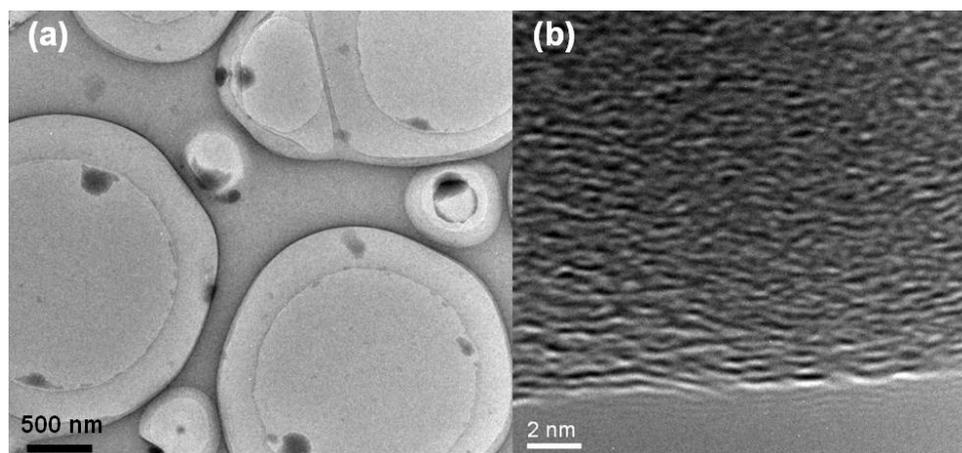


Figure S3 SEM image (a) and HRTEM of the crystal lattice for Na_2GeO_3 colloidal particles.

SI-2 Characterization of Zn_2GeO_4 nanorods

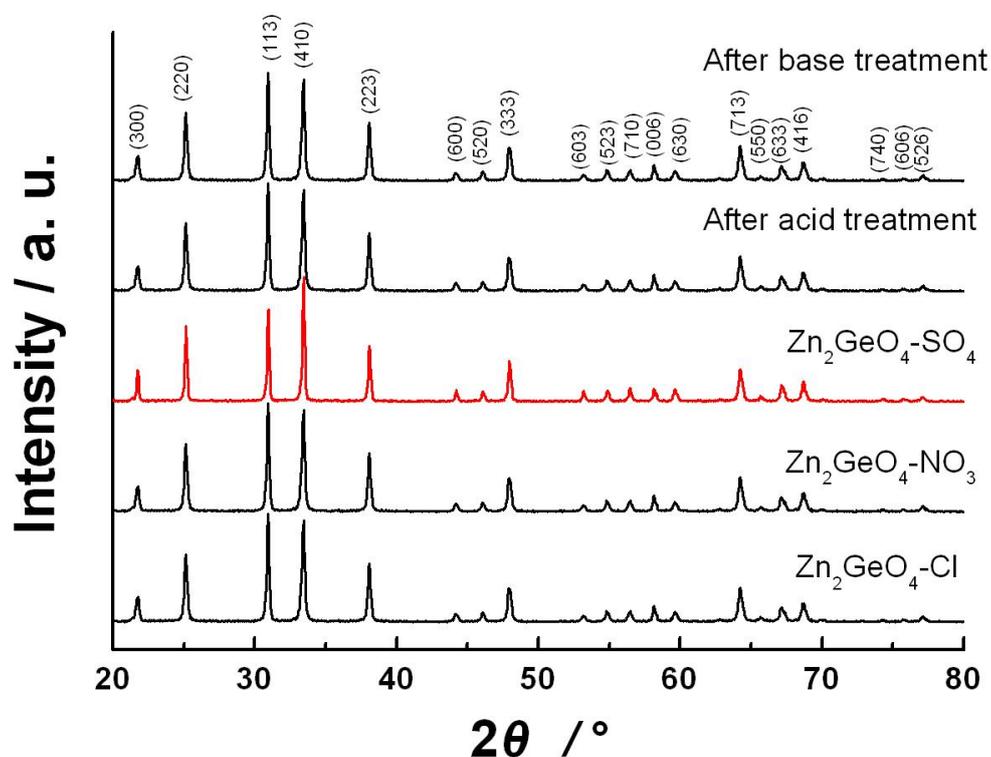


Figure S4. XRD patterns for Zn_2GeO_4 nanorods obtained by hydrothermal reaction at 200°C for 5h using the ZnCl_2 (denoted as $\text{Zn}_2\text{GeO}_4\text{-Cl}$), $\text{Zn}(\text{NO}_3)_2$ (denoted as $\text{Zn}_2\text{GeO}_4\text{-NO}_3$) and ZnSO_4 (denoted as $\text{Zn}_2\text{GeO}_4\text{-SO}_4$) as precursor. The XRD patterns for the as-prepared Zn_2GeO_4 nanorods after hydrothermal treatment at 200°C for 2h in NaOH solution ($\text{pH}=14$) or H_2SO_4 solution ($\text{pH}=0$) were also given here.

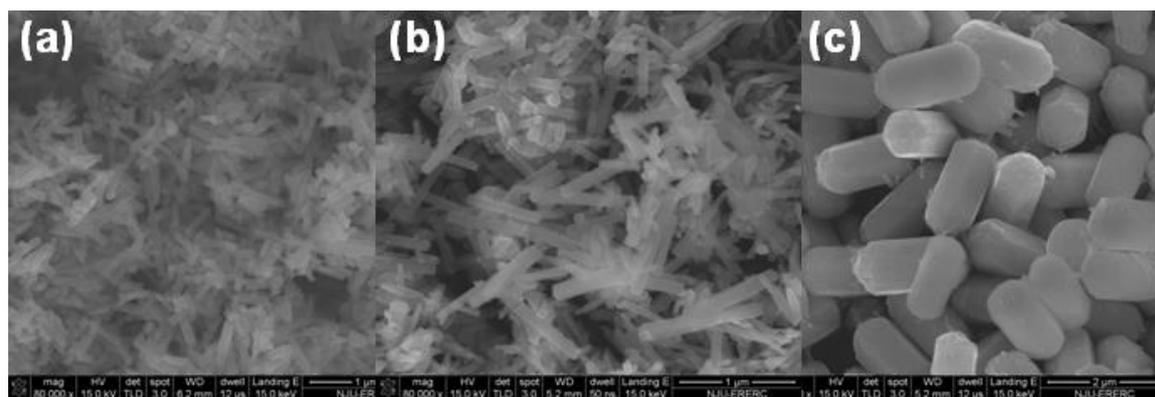


Figure S5. Low-magnification SEM images of Zn₂GeO₄ nanorods prepared by using different zinc salts. (a) ZnCl₂, (b) Zn(NO₃)₂ and (c) ZnSO₄.

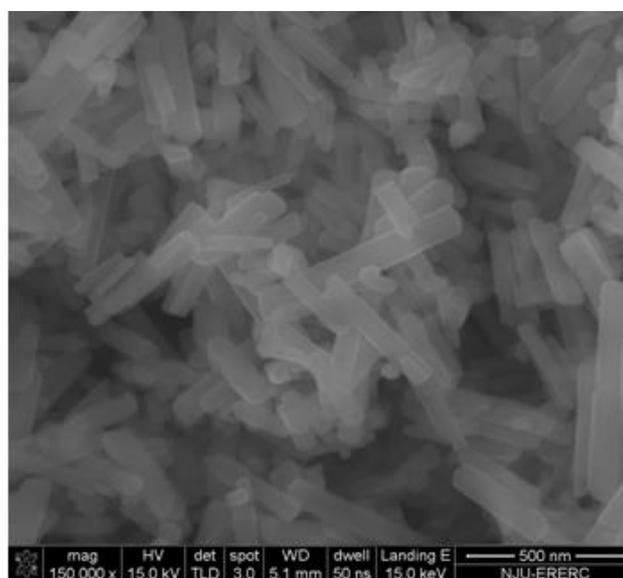


Figure S6. SEM image for Zn₂GeO₄ nanorods, which was prepared by using ZnCl₂ as precursor, after hydrothermal treatment at 200 °C for 5h in NaOH solution (pH=14).

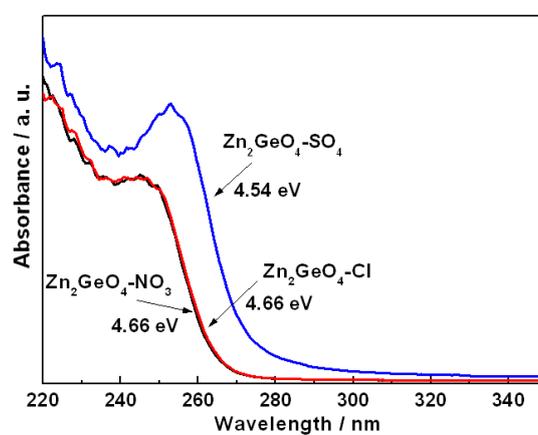


Figure S7 UV-Vis absorption spectra for as-prepared various Zn₂GeO₄ nanorods.

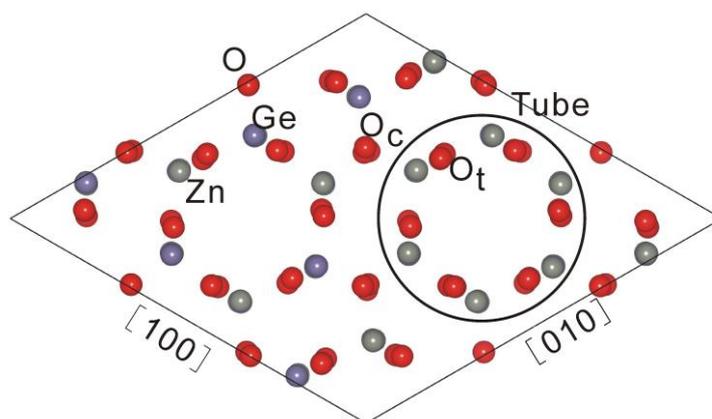


Figure S8. Conventional cell model for bulk Zn_2GeO_4 . The red, grey and purple spheres represent O, Zn and Ge atoms, respectively. Atoms locate in the dark circle is ‘tube’. Oxygen atom in ‘tube’ is designated as O_t , while oxygen atom connecting three ‘tubes’ is O_c .

In the willemite structure of Zn_2GeO_4 (space group 148, R3H), each of Zn and Ge ion is in a tetrahedral environment of four oxygen atoms. Zn_2GeO_4 consists of one GeO_4 tetrahedron and two ZnO_4 tetrahedra. Every oxygen atom coordinated with one Ge ion and two Zn ions. Meanwhile, Looking from [001] direction, Zn_2GeO_4 can also be considered as the connection of tubes and oxygen atoms (see Figure S8). In the (001) plane, three tubes shared with one oxygen. Upon this consideration, oxygen in tubes is designated as the tube oxygen (O_t), while oxygen atoms connect three tubes were treated as center oxygen (O_c) because this oxygen locates in the center of three neighbored tubes. Then, oxygen vacancies in Zn_2GeO_4 can be classified into oxygen vacancy in tube oxygen (V_{ot}) and in center oxygen (V_{oc}).

Density functional theory (DFT) calculations were used to clarify which kind of oxygen vacancy is relatively easily formed in Zn_2GeO_4 . Formation energies of V_{ot} and V_{oc} were calculated based on the following equation:

$$E_f = E_{\text{Zn}_2\text{GeO}_4 + \text{V}_o} + E_{\text{O}} - E_{\text{Zn}_2\text{GeO}_4}$$

where $E_{\text{Zn}_2\text{GeO}_4 + \text{V}_o}$ and $E_{\text{Zn}_2\text{GeO}_4}$ are the total energies of Zn_2GeO_4 with and without oxygen vacancy, respectively. E_{O} is the total energy per atom of pure oxygen gas. To check the dependence of oxygen vacancy formation energy on cell size, we adopt both primitive cell and conventional cell of Zn_2GeO_4 , which correspond to 43 and 126 atoms, respectively. As a result, concentration of single oxygen vacancy correspond to $x=0.02$ and $x=0.008$ in $\text{Zn}_2\text{GeO}_{4-x}$, and Brillouin zones were sampled using $3 \times 3 \times 3$ and $2 \times 2 \times 3$ meshes for primitive and conventional cell, respectively. All the DFT calculations were performed using the VASP^[1,2] computational package with projected augmented wave (PAW^[3]) method. Generalized gradient approximation (GGA^[4]) in the scheme of Perdew-Bueke-Ernzerhof (PBE^[5]) was used for the exchange correlation functional. The valence configurations of the pseudo-potentials were $2s^2 2p^4$, $3d^{10} 4s^2$ and $3d^{10} 4s^2 4p^2$ for O, Zn and Ge, respectively. The cutoff energy was 500 eV. Geometry relaxation was performed until the residual forces on each ion converged to be smaller than 0.02 eV/Å.

Formation energies of V_{ot} and V_{oc} are listed in Table S1. It is clearly seen that, V_{oc} has smaller

formation energy than V_{ot} . This result is very helpful to understand the discrepancy in activity between Zn_2GeO_4 (110) and (001) surfaces. As can be seen in the atomic structures of Zn_2GeO_4 (110) and (001) surfaces, cutting Zn_2GeO_4 through (110) plane will break all $M-O_c$ bonds ($M=Zn, Ge$), whereas cutting Zn_2GeO_4 through (001) plane will break all $M-O_t$ bonds ($M=Zn, Ge$). Since O_c is easily removed to form oxygen vacancy, Zn_2GeO_4 (110) surface will consist large amount of V_{oc} , leading to the high activity of the Zn_2GeO_4 (110) surface.

Table S1 Formation energies (E_f in eV) of V_{oc} and V_{ot} in Zn_2GeO_4 calculated using both primitive and conventional cell of Zn_2GeO_4 .

Oxygen vacancy	E_f (eV)	
	Primitive cell	Conventional cell
V_{oc}	3.59	3.62
V_{ot}	3.63	3.72

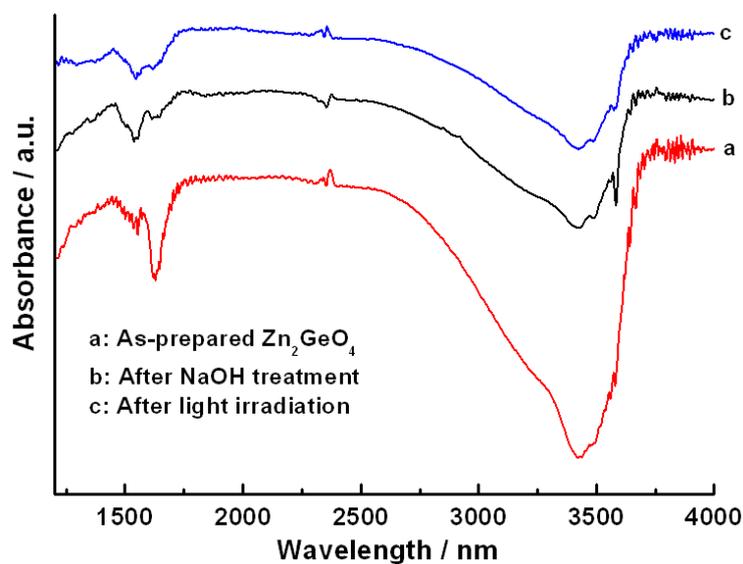


Figure S9. The FT-IR spectra for the as-prepared Zn_2GeO_4 nanorods, the Zn_2GeO_4 nanorods after hydrothermal treatment at $200^\circ C$ for 5h in NaOH solution (pH=14) and the Zn_2GeO_4 nanorods after photoreduction of CO_2 .

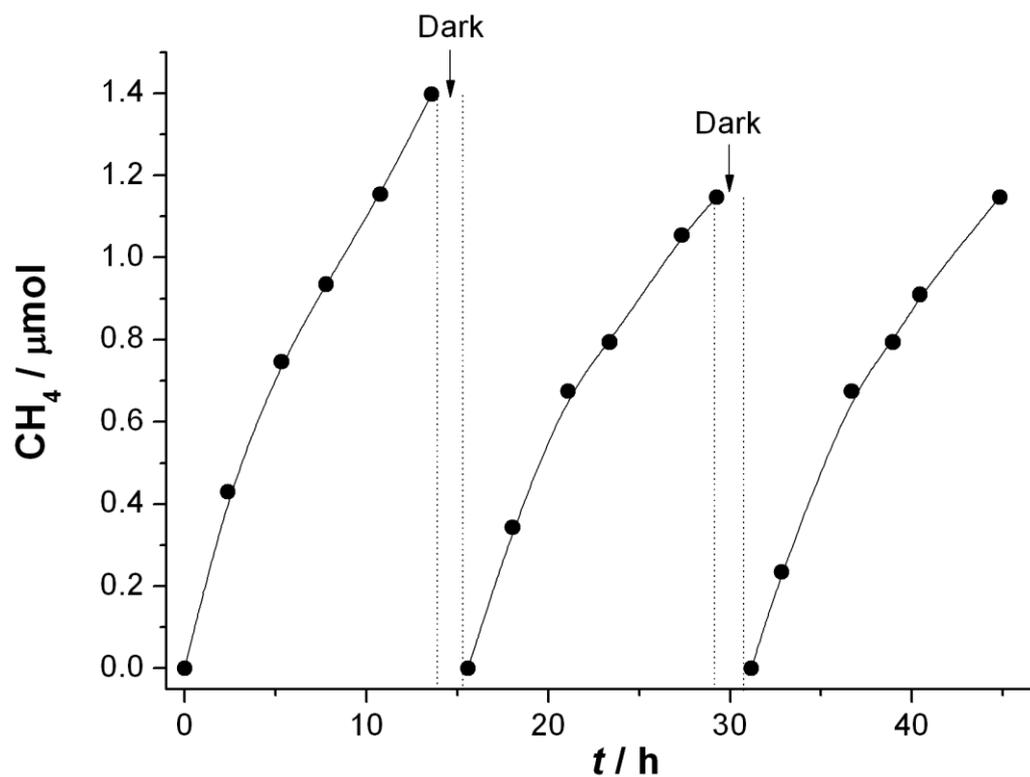


Figure S10. The stability test for the as-prepared $\text{Zn}_2\text{GeO}_4\text{-Cl}$ nanorods. The experiment was repeated three times with an interval of two hours.

Reference

- [1] G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* 1996, **6**, 15.
- [2] G. Kresse, J. hafner, *Phys. Rev. B* 1993, **47**, 558.
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