

Electronic Supplementary Information

Preparation of $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$ nanoparticles with enhanced NO_x decomposition activity under visible light irradiation by nitridation of Zn_2GeO_4 nanoparticles designed precisely

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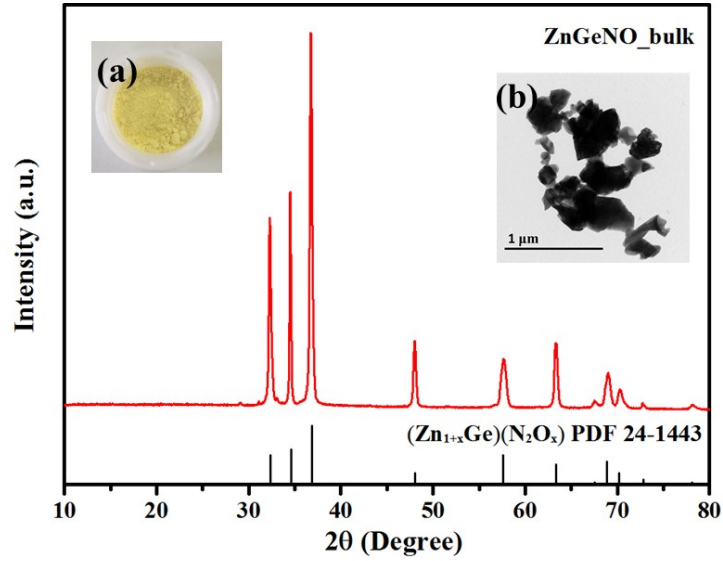


Fig. S1 XRD pattern of $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$ synthesized by nitridation of a mixture containing ZnO and GeO_2 (ZnGeNO_bulk) (insets: (a) appearance and (b) TEM image of ZnGeNO_bulk).

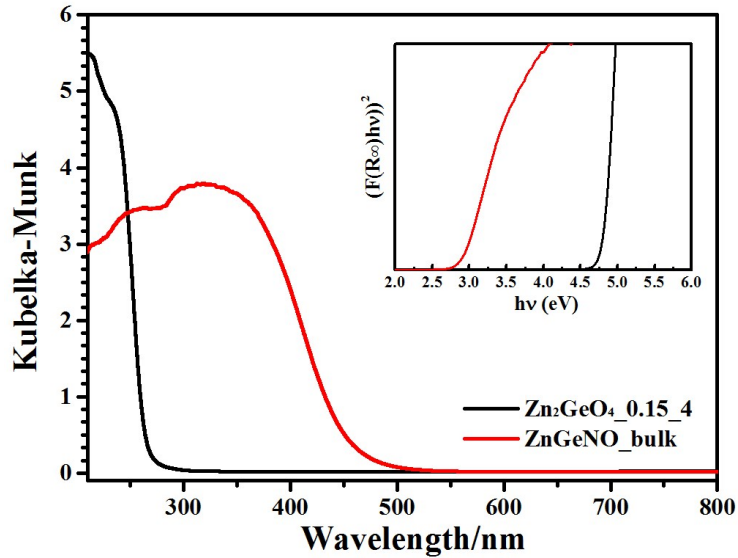


Fig. S2 UV/Vis diffuse reflectance spectra of $\text{Zn}_2\text{GeO}_4_{0.15_4}$ and ZnGeNO_bulk (inset: plots of $(F(R_\infty)hv)^2$ versus (hv) for obtaining the band gaps of above samples).

The band gap energy (E_g) of each sample was estimated based on the theory of optical absorption with following equation (1) proposed by Tauc, Davis, and Mott:

$$(\alpha hv)^{1/n} = A(hv - E_g) \quad (1)$$

where A , h , v and E_g are a proportional constant, the Plank constant, the frequency of vibration($1/\lambda$) and the band gap, respectively. The value of the exponent n is either

1/2 for a direct allowed transition or 2 for an indirect allowed transition. Since both $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$ and Zn_2GeO_4 exhibit direct allowed transitions, and $n = 1/2$ is used for these samples. $F(R_\infty)$ is proportional to the value of the absorption coefficient α , therefore the α in the Tauc equation is substituted by $F(R_\infty)$ with Kubelka-Munk function for estimation of the optical absorption edge energy. So, the above relational expression becomes:

$$(F(R_\infty)hv)^2 = A(hv - E_g) \quad (2)$$

Thus, the curve that plots the value of $(hv - (F(R_\infty)hv)^2)$ on the horizontal axis hv and vertical axis $(F(R_\infty)hv)^2$ is drawn. By the extrapolation of the straight portion of the plot of $(F(R_\infty)hv)^2$ versus (hv) to the $F(R_\infty) = 0$ point, the E_g values of the prepared samples can be estimated. The band gaps of $\text{Zn}_2\text{GeO}_4_{0.15_4}$ and ZnGeNO_bulk are estimated to be 4.8 eV and 2.8 eV, respectively.

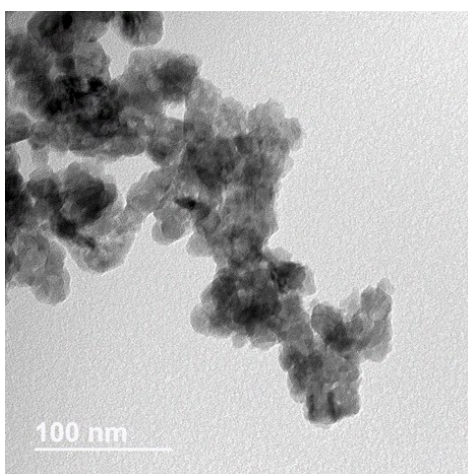


Fig. S3 High magnification TEM image of $\text{ZnGeNO}_4_{0.15_4}$ sample.

Table S1. The abbreviated names of $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$ samples nitrated for 1 h and the corresponding precursors synthesized with different volume of TEA.

Sample (ZnGeNO_X_1) ^a	Precursor ($\text{Zn}_2\text{GeO}_4_A_B$) ^b	Volume of TEA (mL)	Specific surface area (m^2/g)
ZnGeNO_0_1	$\text{Zn}_2\text{GeO}_4_0.15_0$	0	20.1
ZnGeNO_2_1	$\text{Zn}_2\text{GeO}_4_0.15_2$	2	35.5
ZnGeNO_4_1	$\text{Zn}_2\text{GeO}_4_0.15_4$	4	39.7
ZnGeNO_6_1	$\text{Zn}_2\text{GeO}_4_0.15_6$	6	29.4
ZnGeNO_8_1	$\text{Zn}_2\text{GeO}_4_0.15_8$	8	25.7

^a ZnGeON_X_1 : X is the volume of TEA used in the preparation of Zn_2GeO_4 precursors during solvothermal reaction; 1: 1 h nitridation; ^b $\text{Zn}_2\text{GeO}_4_A_B$: A is the molar concentration of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Na_2GeO_3 ; B is the volume of TEA (mL).

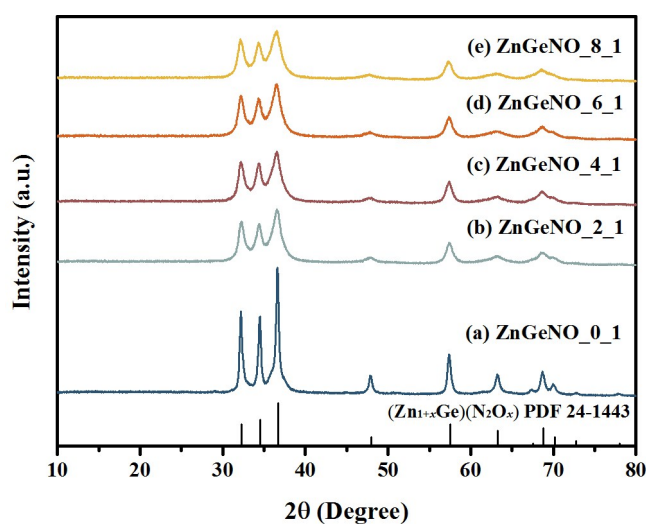


Fig. S4 XRD patterns of $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$ samples nitrated for 1 h with different TEA volume: (a) ZnGeNO_0_1 , (b) ZnGeNO_2_1 , (c) ZnGeNO_4_1 , (c) ZnGeNO_6_1 and (d) ZnGeNO_8_1 .

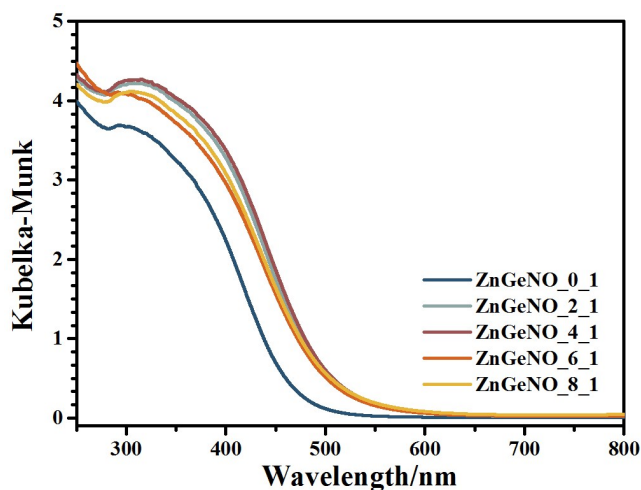


Fig. S5 UV/Vis diffuse reflectance spectra of ZnGeON_X_1 (X: 0, 2, 4, 6 or 8 mL of TEA used in the preparation of Zn₂GeO₄ precursors during solvothermal reaction; 1: 1 h nitridation).

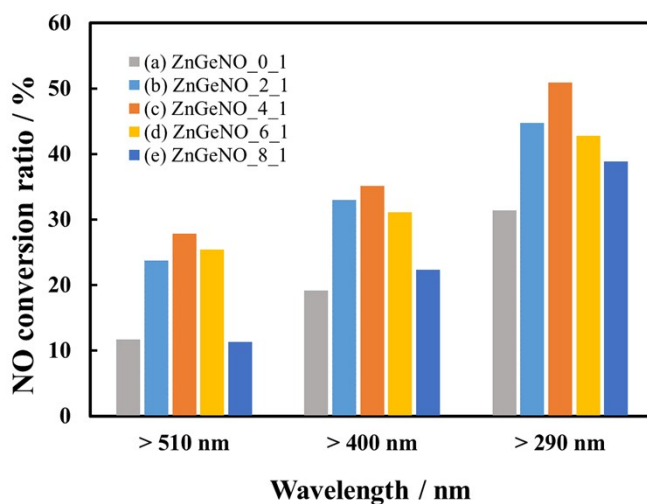


Fig. S6 Conversion ratios of photocatalytic NO_x decomposition activity under irradiation above 510, 400 and 290 nm using different photocatalysts: (a) ZnGeNO_0_1, (b) ZnGeNO_2_1, (c) ZnGeNO_4_1, (d) ZnGeNO_6_1 and (e) ZnGeNO_8_1.

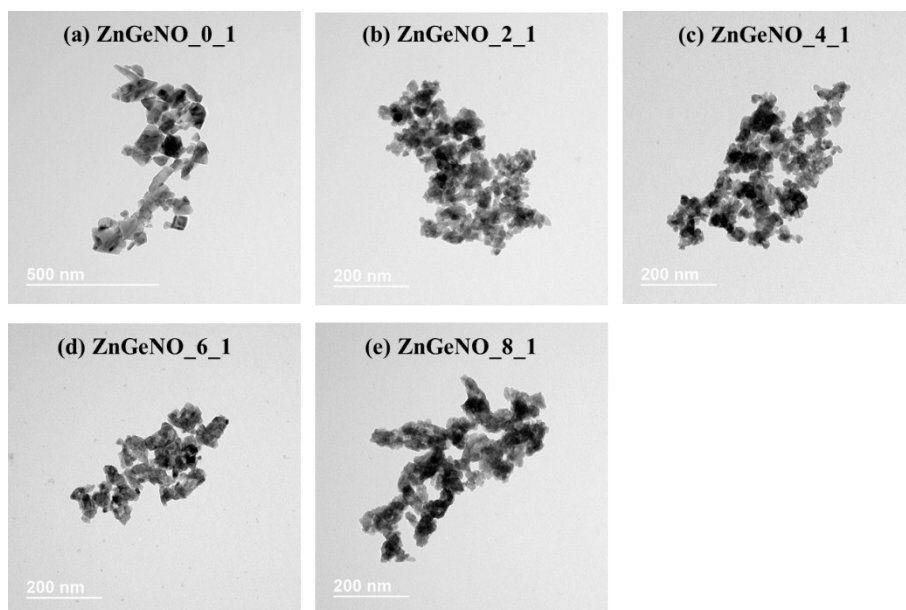


Fig. S7 TEM images of $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$ samples synthesized by nitridation for 1 h of Zn_2GeO_4 synthesized under a presence of different volumes of TEA (0, 2, 4, 6 and 8 mL): (a) ZnGeNO_0_1, (b) ZnGeNO_2_1, (c) ZnGeNO_4_1, (d) ZnGeNO_6_1 and (e) ZnGeNO_8_1.

The photocatalytic NO_x decomposition activity of $(\text{Zn}_{1+x}\text{Ge})(\text{N}_2\text{O}_x)$ obtained by nitridation of different precursors for 1 h are shown in Fig. S6 (referred as ZnGeNO_X_1: X means the volume of TEA (mL) used in solvothermal reaction for the synthesis of Zn_2GeO_4 ; 1 means nitridation of 1 h). The precursors are synthesized with different TEA volume under same hydrothermal conditions (100 °C, 12 h). The photocatalytic activity increased at first and decreased subsequently with increase of TEA additive due to the alteration of particle sizes (Fig. S7). As shown in Fig. 9 and Fig. S6, ZnGeNO_4_1 possessed the best performance on photocatalytic NO_x decomposition activity among all samples. These results indicate that the amount of TEA is critical for morphology control as well as the enhancement of photocatalytic NO_x decomposition activity.

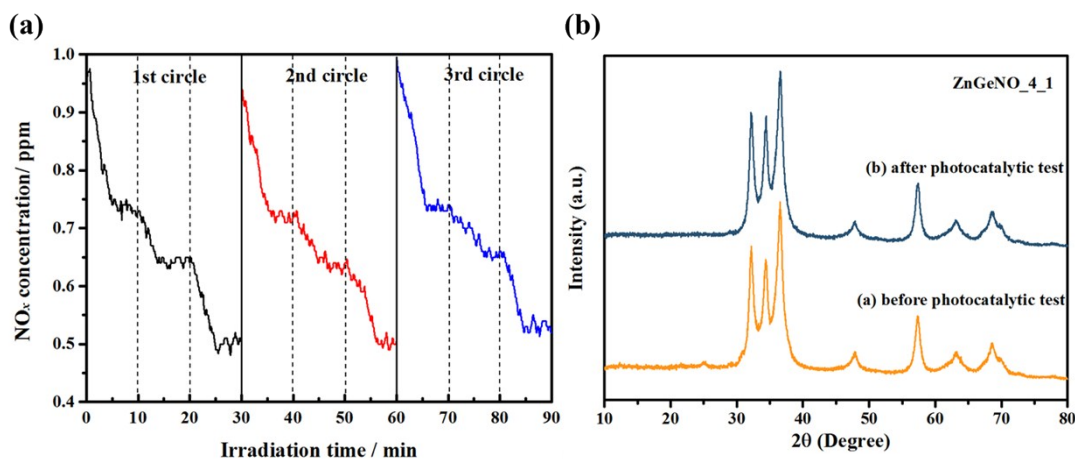


Fig. S8 (a) The three cycles of deNO_x ability of ZnGeNO₄_1 and (b) XRD patterns of ZnGeNO₄_1 sample before and after photocatalytic NO_x decomposition test.

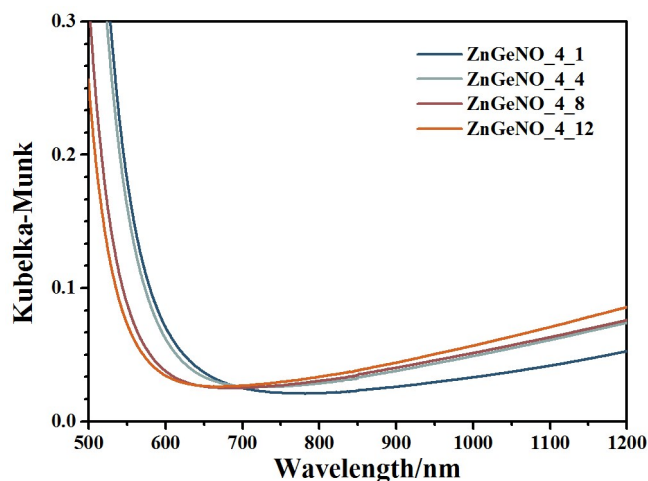


Fig. S9 The magnified UV-vis diffuse reflectance absorption spectra of (Zn_{1+x}Ge)(N₂O_x) samples with different nitridation time.

In the photocatalytic test, the wavelength of Hg lamp was cut by filters, and the samples were irradiated under a range of wavelength. Therefore, the calculated apparent quantum efficiencies are photon conversion between a range of wavelength. In this research, the apparent quantum efficiency (AQE) under irradiation of various light wavelength was calculated according to the following equation according to our previous report¹:

$$AQE(\%) = \frac{F_{NO} \cdot \alpha_{\lambda}}{P_{\lambda} \cdot S} \times 100\%$$

F_{NO} : the flow quantity of NO molecules in the reaction gas ((1 ppm, 200 ml/min, $1.488 \times 10^{-4} \mu\text{mol s}^{-1}$);

α_{λ} : the photocatalytic NO_x decomposition ability;

P_{λ} : the light intensity on the surface of the sample ($\mu\text{mol m}^{-2} \text{s}^{-1}$) and the different light intensity are shown in 2.5 section.

S: the surface area of the samples (20 mm \times 16 mm) (m^2);

Table. S2 The AQE (%) of samples prepared by different conditions in various wavelength ranges.

Sample	AQE (%)		
	290-400 nm	400-510 nm	>510 nm
ZnGeNO_4_1	0.49	0.04	0.05
ZnGeNO_4_4	0.69	0.04	0.02
ZnGeNO_4_8	0.74	0.05	0.004
ZnGeNO_4_12	0.74	0.03	0.007
ZnGeNO_0_1	0.38	0.04	0.02
ZnGeNO_2_1	0.36	0.05	0.04
ZnGeNO_6_1	0.36	0.03	0.04
ZnGeNO_8_1	0.51	0.05	0.02
ZnGeNO_bulk	0.71	0.04	0.005

Reference

1. S. Yin, B. Liu, P. Zhang, T. Morikawa, K.-i. Yamanaka and T. Sato, *J. Phys. Chem. C*, 2008, **112**, 12425-12431.