# **Supporting Information**

# Enhanced Photocatalytic Activities of Single-Crystalline ZnGa<sub>2</sub>O<sub>4</sub> Nanoprisms by Coexposed {111} and {110} Facets

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### **S1 Calculation Details:**

## Calculation of the percentages of {111} and {110} facets

Calculation of the percentages of  $\{111\}$  and  $\{110\}$  facets were estimated on the basis of the total surface area of the nanoprism according to the TEM images. Assuming the  $ZnGa_2O_4$  nanoprisms are all hexagonal-shape (pure trigonal-shaped nanoprisms are rare and the calculation results are only slightly deviated), the percentages of  $\{111\}$  facets and  $\{110\}$  facets can be calculated using the following equation:

{111} %=2\*(top {111} surface area)/total surface area of nanoplate\*100 %~75 %

{110} %=6\*(side {100} surface area)/total surface area of nanoplate\*100 % $\approx$ 25 %

### DFT calculation of the surfactant binding energies

Our calculations are performed by the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) implemented in Vienna ab initio simulation package (VASP). The ion–electron interaction is described by projector-augmented wave (PAW) potential and the plane-wave cutoff energy of 500 eV is used. A Monkhorst–Pack k-point mesh with a 8×8×8 *k*-point is used. Both the lattice constant and the positions of all atoms are relaxed until the force is less than 0.02 eV/Å. The criterion for the total energy is set as  $1 \times 10^{-5}$  eV. The bulk crystal structure of the spinel ZnGa<sub>2</sub>O<sub>4</sub> was calculated which yielded the following lattice parameters: a = b = c = 8.462 Å;  $\alpha = \beta = \gamma = 90^{\circ}$ .

The adhesion energies of  $C_{17}H_{33}COO^{-}$  on surfaces of  $ZnGa_2O_4$  (100), (110) and (111) planes were performed to observe the stable geometries and adsorption energies according to equation 1.

$$E_{ads} = E_{slab + C17H33COO} - E_{slab} - E_{C17H33COO}$$
(1)

Where E  $_{slab}$  +  $_{C18H33O2}$  is the total energy of ZnGa<sub>2</sub>O<sub>4</sub> slab and adsorbed C<sub>17</sub>H<sub>33</sub>COO<sup>-</sup> after optimization E  $_{slab}$  is the total energy of ZnGa<sub>2</sub>O<sub>4</sub> slab, E  $_{C17H33COO}$  is the energy of C<sub>17</sub>H<sub>33</sub>COO<sup>-</sup>.

#### DFT calculation of the density of surfaces

Surface properties are closely related to the surface atomic structures, and Ga-Zn-O terminated surfaces are considered to be more stable because of relative lower surface energy, To investigate the electronic structural changes due to different exposed plane, both the (100) and (111) surfaces are constructed by the periodic ( $2 \times 2$ ) slab models which involve 16 units of ZnGa<sub>2</sub>O<sub>4</sub> (112 atoms), while (110) surface is simulated by a ( $2 \times 1$ ) slab model containing 84 atoms. The total density of states (TDOS) as well as partial density of states (PDOS) are calculated to give qualitative insight into the bonding interaction variations among three crystal planes as shown in Figure S0.



**Figure S0.** (a) Total density of states (TDOS) plots for {111}, {110} and {100} surface of ZnGa<sub>2</sub>O<sub>4</sub>. (b)-(d) Partial density of states (PDOS) of Zn, Ga, O for {111}, {110}and {100} surface of ZnGa<sub>2</sub>O<sub>4</sub>, respectively.

#### Calculation of surface area normalized rate constants of dye decomposition:

The measured rate constants were normalized to the BET surface area measured for each

sample to determine the intrinsic photocatalytic performance of the ZnGa<sub>2</sub>O<sub>4</sub> nanostructures.

The calculations were using the equation  $\ln \frac{C0}{C} = kt$ . The results summarized in Table S1 demonstrate that the trend in facet-dependent photocatalytic performance is {Coe} > {100} > {110}.

 Table S1. Summary of the normalized rate constants.

sample	Surface(m <sup>2</sup> ·g <sup>-1</sup> )	Measured rate	Surface area normalized
		constant (min <sup>-1</sup> )	rate constant (min <sup>-1</sup> ·m <sup>-2</sup> )
ZGO-100	9	0.0215	2.39×10 <sup>-3</sup>
ZGO-110	96	0.0598	0.62×10 <sup>-3</sup>
ZGO-Coe	30	0.1116	3.72×10 <sup>-3</sup>

## **S2** Supplementary Figures



Figure S1. SEM image and the corresponding size distribution of the ZGO-Coe nanoprisms.



**Figure S2.** (a) AFM image and (b) the corresponding height profiles. The height profiles from 1 to 4 in (b) correspond to the lines from 1 to 4 in (a).



**Figure S3**. HRTEM images of the ZGO-Coe nanoprisms: (a) top view with clear lattice fringes with an lattice spacing of 0.29 nm confirms the exposed facets are {111} facets. (b) side view with clear lattice fringes with lattice spacing of 0.48 nm and 0.41 nm corresponds to (111) and (200) planes, confirms the exposed side facets are {110} facets.



Figure S4. XPS spectra of ZGO-Coe: (a) survey, (b) Ga 2p, (c) Zn 2p and (d) O 1s.



Figure S5 (a, c) SEM images of the nanosheet-assembled microspheres and nanocubes. (b, d) TEM images of  $ZnGa_2O_4$  nanosheet-assembled microspheres and nanocubes, with the insets showing the corresponding SAED patterns.



Figure S6. XRD patterns of the ZGO-Coe, ZGO-100, and ZGO-110 samples.



**Figure S7.** TEM images showing temporal evolution of the ZGO-Coe nanoprisms from nanocrystals with a reaction time of (a) 1h, (b) 2h, (c) 5h, (d) 18h. The scale bars are 200 nm.



**Figure S8.** Schematic illustration of the formation of ZGO-Coe nanoprisms, ZGO-110 microflowers and ZGO-100 nanocubes.



Figure S9. FT-IR spectra of ZGO-Coe before and after washing by cyclohexane and ethanol.



Figure S10. Cycling test of photocatalytic H<sub>2</sub> evolution for ZGO-Coe nanoprisms.



**Figure S11.** Typical fluorescence spectral changes observed during UV illumination of ZGO-Coe in terephthalic acid solution ( $4 \times 10^{-4}$  mol L<sup>-1</sup>, excitation at 315 nm). Inset shows the formation of 2-hydroxyterephthalic acid as a result of the reaction between terephthalic acid and •OH.



**Figure S12.** Phenol photodecomposition over three types of ZnGa<sub>2</sub>O<sub>4</sub> photocatalysts under Xe lamp irradiation.



TOC