Electronic Supplementary Information (ESI)

Controlled Growth of Hexagonal Zn₂GeO₄ Nanorod on Carbon Fibers for Photocatalytic Oxidation of p-Toluidine

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Experimental section

Materials

Carbon fibers (CFs) are 12 k fiber tows supplied by Lanzhou Carbon Factory, China. GeO₂, Zn(CH₃COO)₂•2H₂O were purchased from Aladdin Reagent Co., Ltd.. Other solvents were Shanghai Chemical Co., Ltd.. Milli-Q water was utilized through the whole experiment. All chemicals were analytical grade and used without further purification.

Activation of carbon fibers

CFs were firstly washed by acetone and deionized water to remove the impurity substances on the surface. Then, CFs were immersed in 7% sodium hypochlorite aqueous solution for 24 h. Finally, the soaked CFs was washed with deionized water and absolute ethanol consecutively. The activated carbon fibers were obtained after dried at 80 °C for 6 h.

Preparation of Zn₂GeO₄/ACFs composites

In a typical synthesis procedure, 0.13 g GeO₂ and 0.55 g $Zn(CH_3COO)_2 \cdot 2H_2O$ were firstly dissolved in 35 mL mixed solvent (deionized water : ethanol = 1:6) with stirring. After stirring for 1h, the mixture' solution was transferred in a 50 mL Teflon-lined stainless steel autoclave. Then, the CFs were immersed in the mixture solution and heated at 170 °C for 24h. After autoclave cooled to room temperature, the CFs was collected and washed with deionized water and absolute ethanol for five times. Finally, the Zn_2GeO_4/CFs products were obtained by drying at 60 °C for 12h. The $Zn_2GeO_4/graphene$ composites were prepared under the same conditions except from using graphene to replace CFs.

Characterization

Microstructures of the as-synthesized products were analyzed with a SIEMENS Diffraktometer D5000 X-ray diffractometer using Cu K α radiation source at 35 kV, with a scan rate of 2° min⁻¹ in the 20 range of 10-80°. The morphologies were investigated by Hitachi-S4800 field emission scanning electron microscopy (FE-SEM) equipped with an energy dispersive X-ray spectrum (EDS) at an accelerating voltage of 10 kV and JSM-2100 transmission electron microscopy (TEM). The TEM samples were prepared by detaching Zn₂GeO₄ nanorods from the CFs substrates using an ultrasonic cleaner with a power of 100 W (KQ-400KDE, Kunshan ultrasonic instrument). UV-Vis diffuse reflectance

spectra were recorded with a UV-vis spectrometer (U -3010, Hitachi).

Computational methods

Surface energies of various facets for Zn_2GeO_4 had been investigated using density functional theory (DFT) calculations. Simulations were performed using Cambridge Sequential Total Energy Package (CASTEP). The electron-ion interaction was described by generalized gradient approximation (GGA) and the Perdaw, Burke and Ernzerhof (PBE) functional. All the calculations employed a plane-wave basis set with a cut off energy of 340 eV. The surface energies of Zn_2GeO_4 facets had been investigated using a 2×2 slab model with a thickness of 5. All atoms were constrained before geometry optimization excepting the top layer of atoms containing the stoichiometry of Zn, Ge and O atoms. A 10 Å vacuum layer was used to minimize interactions between surfaces of adjacent slabs. Surface energies are calculated by taking the difference between the energy of our slab and the same amount of Zn_2GeO_4 formula units in the bulk, divided by the surface area of the slab (including both sides of the slab):

$$\gamma = 1/(2S) \times [E_{slab} - n E_{bulk}]$$
(1)

In which E_{bulk} is the total energy per formula unit of bulk Zn_2GeO_4 . E_{slab} is the total energy of the given supercell containing n formula units of Zn_2GeO_4 . S is the base area of the supercell.

The interaction energies between graphene and Zn_2GeO_4 facets was estimated by molecular dynamics (MD) simulations carried out with a commercial software package called Materials Studio developed by Accelrys Inc. The condensed phase optimization molecular potentials for atomistic simulation studies (COMPASS) module in the Materials Studio software was used to conduct force-field computations. For graphene, a surface model containing two layers of C atoms were established and optimized. After optimization, the C supercell was constructed according to the area of various facets by cutting a Zn_2GeO_4 unit cell. A 0 Å vacuum layer was added to the supercell to establish 3-dimensional (3D) structure (Fig. S1). The each facets of Zn_2GeO_4 with a thickness of various value (here, thickness=3) were optimized and added to C supercell. A 30 Å valcuum layer was added to the surface of Zn_2GeO_4 facets, which a new 3D structure containing C supercell and Zn_2GeO_4 facets. Before MD simulation, all the atoms of new 3D structure were constrained until calculating its total energy. Here, the MD simulation for each case study was performed long enough to observe several cycles of thermal vibration. The interval of each MD simulation step was 5 fs. All calculations were carried out at the initial temperature of 443 K, using a constant number of particles, constant volume, and constant temperature (NVT) ensembles. Generally, the interaction energy is estimated from the difference between the potential energy of the composites system and the potential energies for the Zn_2GeO_4 and the corresponding graphene model as follows:

$$\Delta E = E(total) - [E(graphene) + E(Zn_2GeO_4)]$$
(2)

Where E(total) is the total potential energy of the composite, E(graphene) is the energy of the of graphene without the Zn_2GeO_4 , and $E(Zn_2GeO_4)$ is the energy of the Zn_2GeO_4 without the graphene. In other words, the interaction energy can be calculated as the difference between the minimum energy and the energy at an infinite separation of the graphene and the Zn_2GeO_4 .



Fig. S1 The 3D structural model for investigating the interactions between graphite surface and various facets of Zn_2GeO_4 crystal with a thickness of 3. a:(300), b:(220), c:(113), d:(410), e:(223), f:(333).

Photocatalytic oxidation of p-toluidine

The photocatalytic activity of as-prepared catalysts was evaluated by the photocatalytic oxidation of p-toluidine in the mixed solution (H₂O/CH₃CN=1:1 in volume). The photocatalytic oxidation of p-toluidine was performed in a photochemical reaction equipment with a 300 W mercury lamp as the light source. In each experiment, 0.05 g catalysts were added into 30 mL of p-toluidine solution (0.02 mol·L⁻¹). Before light irradiation, the mixed solution was placed in the dark for 30 min to ensure the adsorption-desorption equilibrium. The temperature of solution was maintained below 283 K by a flow of cooling water during the photocatalysis. The concentrations (C) of p-toluidine after an appropriate irradiation time were measured by LC-MS technique (Agilent LC 1100 instrument equipped with a UV detector set at λ = 270 nm). The mobile phase for HPLC was a mixture of water and acetonitrile in a ratio of 50:50 (v/v).

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Crys	tal face	E (total)∕ kcal∙mol ⁻¹	E (graphene)/ kcal·mol ⁻¹	<i>E</i> (Zn ₂ GeO ₄)/ kcal·mol ⁻¹	Surface energy/ J m ⁻²
(3	300)	7984.19	36984.17	-28994.31	1.83
(2	220)	-32008.56	10777.36	-43775.53	1.20
(1	113)	93021.25	173874.94	-80826.77	1.56
(4	410)	-58479.64	27337.58	-85791.79	1.96
(2	223)	94410.46	106698.98	-12265.48	1.36
(3	333)	868.31	8311.15	-7423.53	0.57

Table S1. The calculated E (total), E (graphene), E (Zn₂GeO₄) and surface energy for each 3D model



Fig. S2 The surface energy of various facets of rhombohedral Zn₂GeO₄.



Fig. S3 The interaction energies for graphene surface and various facets of rhombohedral Zn₂GeO₄.



Fig. S4 The photocurrent transient response plots and electronchemical impedance spectra (EIS) of as-prepared samples.