Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supporting Information

Facet effect of Bi_5O_7I nanocrystals on selective oxidation of benzylamine under visible light

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Experimental section

1. Chemicals

$Bi(NO_3)_2 \cdot 5H_2O$ (99 %, Aladdin), NaI (99 %, Tianjing Fuchen Chemical Reagent Factory), HNO_3 (68 %, Beijing Chemical Reagent Factory), methanol (100 %, Beijing Chemical Reagent Factory), dimethylformamide (DMF) (99.5 %, Tianjing Damao Chemical Reagent Factory), NaOH (96 %, Tianjing Zhiyuan Chemical Reagent Factory), acetonitrile (ACN) (99.9 %, Tianjing Guangfu Chemical Reagent Factory), ethyl acetate (99.5 %, Dongfang Chemical Reagent Factory), benzylamine (99.0 %, Aladdin), toluene (99 %, Aladdin). All of the chemicals used in this experiment were used as received without any further purification.

2. Synthesis of Bi_5O_7I

Bi_5O_7I-010 was obtained by calcining BiOI-pH6 which was synthesized according to a previous work[1], at 400 ^oC in air for 4 h (1 ^oC/min ramp) using a Nabertherm oven.

Bi_5O_7I-001 was synthesized by a hydrothermal method. Typically, 10 mmol of KI in 6 ml deionized water was added with stirring to a solution with 2 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ in 21 ml deionized water, acidified with 2 ml nitric acid. The required amount of 1 M NaOH

solution was added to adjust the pH of the solution to 13. After stirring for 30 min, the solution was poured into a 40 ml Teflon-lined stainless steel autoclave and kept at 160 °C for 2 h under autogenous pressure. The resulting precipitate was collected by centrifugation, washed with absolute ethanol, and dried in an oven at 80 °C overnight. The product obtained was denoted as Bi_5O_7I-001.

Bi_5O_7I-$\bar{3}$10 was prepared by the same calcinations procedure to Bi_5O_7I-010 except using BiOI microflowers as precursor. BiOI microflowers were synthesized according to our recent work[2].

3. Characterization

Powder X-ray diffraction patterns were measured with a Siemens D5005 diffractometer using Cu Kα radiation. The 2θ angle from 10 - 70 ° was scanned at 5 °/min with a dwell time of 1 s/step. Nitrogen adsorption and desorption isotherms were measured at 77 K with a porosimeter (TriStar 3000, Micromeritics). The Brunauer-Emmett-Teller equation was used to calculate the specific surface area. Scanning electron microscopy (SEM) was performed on a Zeiss SUPRA 55 SEM (field-emission) microscope with 20 kV electron beam energy. Transmission electron micrographs were obtained with a HT7700 operated at 100 kV. HRTEM

images were taken on a JEOL-JEM-2100 electron microscope with an acceleration voltage of 300 kV. UV-visible diffuse reflectance spectra (DRS) were measured with a Shimadzu UV-2450 UV-Visible spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurement were conducted on a Thermo ESCALAB spectrometer using a monochromated Al Kα radiation (hc, v=1486.6 eV). The energy calibration of spectrometer was performed using C 1s peak at 284.85 eV.

4. Photocatalytic activity test

The photocatalytic amine oxidation was performed in a glass tube, as atmospheric air was used to supply O_2. 100 mg photocatalyst was suspended in 5 ml acetonitrile containing 0.1 mmol benzylamine. A 15 W Philips fluorescent lamp was irradiated from the side of the tube (the distance of lamp and tube is 2.5 cm) at room temperature. After a certain time, 0.2 ml suspension was sampled and filtered with a syringe filter. The filtrates were analyzed by a GC (HP N6950) with a HP-5 column and a FID detector. The suspension was further analyzed by GCMS (Shimadzu GCMS-QP5000).

5. Photoelectrochemical measurements

Transient photocurrent response of photocatlysts were monitored by CHI660E electrochemical workstation with a conventional three-electrode cell. The working electrodes were fabricated by using as-prepared catalyst coated on indium tin oxide (ITO) glass. 10 mg catalyst was dissolved in 1mL ethanol, and 10µl naphthol was added to prepare the solution. The sample was evenly coated on the conductive glass with an area of 1 cm x 1 cm, and the sample area was 1 cm x 0.8 cm. The measurement processes were performed in 0.5 M Na_2SO_4 aqueous solution, Ag/AgCl electrode (saturated KCl solution) and Pt wire were used as reference electrode and counter-electrode, respectively. The quantum yield was calculated based on the number of benzylamine converted divided by the total incoming photons from the lamp (4.99×10^{16} photons/s). The electrochemical impedance spectroscopy of photocatlysts were monitored by CHI660E electrochemical workstation with a conventional three-electrode cell. The working electrodes were fabricated by using as-prepared catalyst coated on Glassy carbon electrode (GCE). 10 mg catalyst was dissolved in 970 µl ethanol, and 30 µl naphthol was added to prepare the solution. The working electrode is prepared by dropping 10 µl of solution onto a GCE. The measurement processes were performed in 0.5 M Na_2SO_4 aqueous solution, Ag/AgCl electrode (saturated KCl solution)

and Pt wire were used as reference electrode and counter-electrode, respectively.

6. DFT calculation

The first-principles calculations were executed adopting the pseudopotential plane wave method based on density functional theory (DFT) and investigated by the Vienna Ab-initio Simulation Package (VASP). The interaction between electrons was described by Perdew Burke Ernzerhof (PBE) of generalized gradient approximation (GGA). The ultra-soft pseudopotential was utilized to approximately depict the interaction between the inside and outside of the delocalization and the truncation energy of plane wave was set up to 500 eV for calculation; the k-point was set to 2 x 3 x 1. The energy convergence in the geometry optimization and single point energy calculation were set to 1×10^{-4} eV and 1×10^{-5} eV, respectively. The lattice parameters of Bi_5O_7I: a = 16.265, b = 5.3439, c = 23.020, $\alpha=\beta=\gamma = 90^{o}$.

The supercell structure was established on the cell. The (010), (001) and ($\bar{3}$10) facet were cut respectively, a vacuum layer with a thickness of 10 Å was set up on the surface, and the surface structure was geometrically optimized. Then, the adsorption system was established, the adsorption particles were introduced at the surface respectively, and the geometric optimization of the adsorption system was performed to

minimize the total energy of the system to obtain the ground state electronic structure and make the model closer to reality. After the structure was optimized, the energy of the system were calculated.

Supplementary Figures and Tables

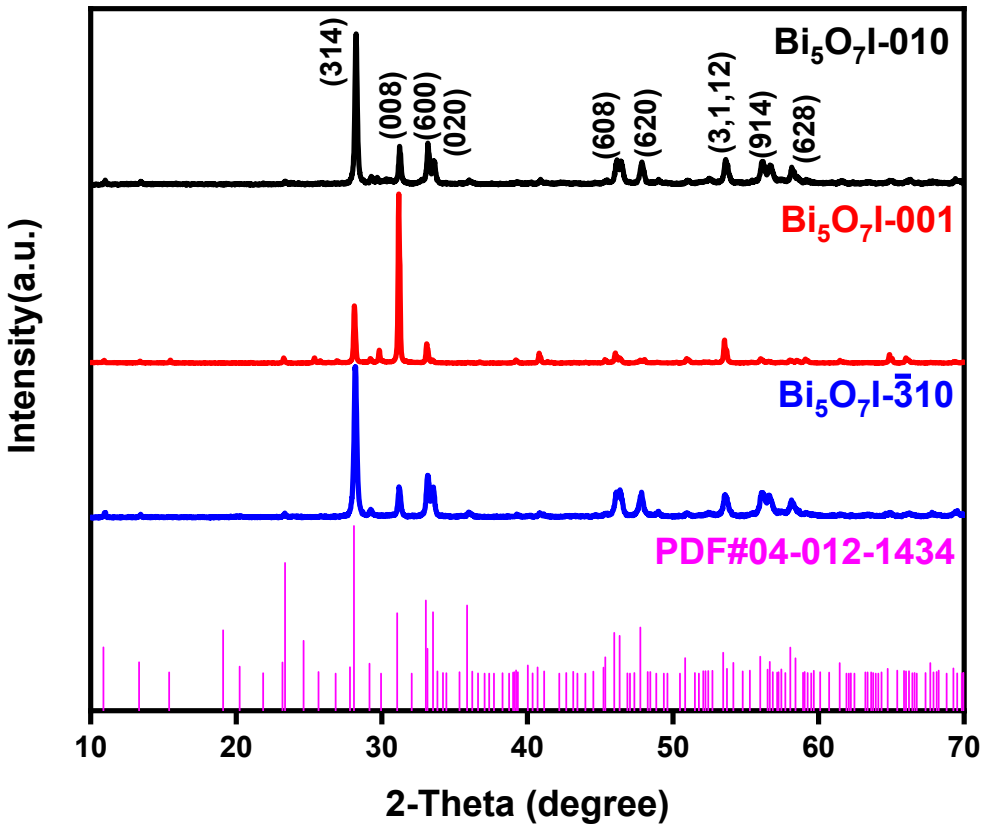

Fig. S1 XRD patterns of the Bi_5O_7I samples.

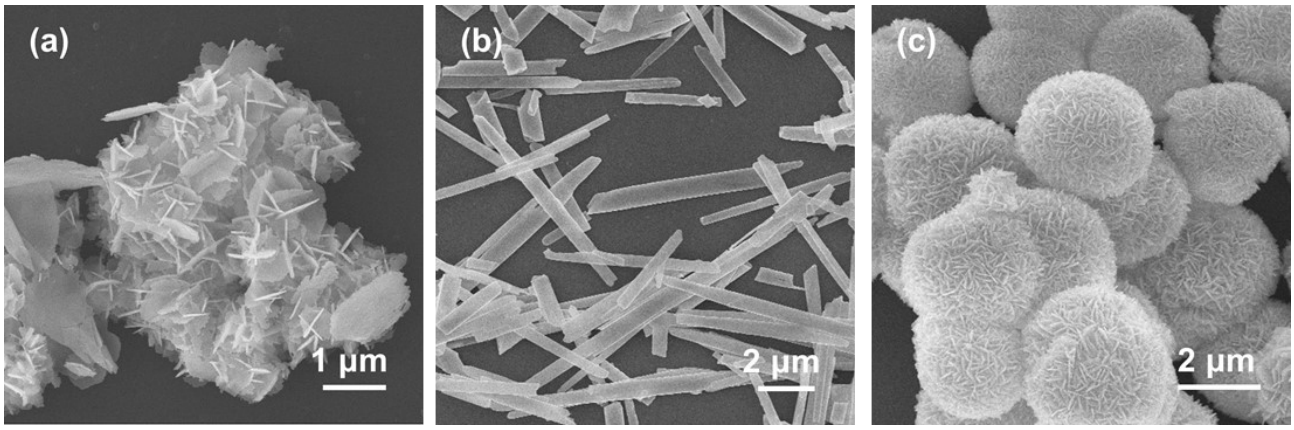

Fig. S2 SEM images of (a) Bi_5O_7I-010, (b) Bi_5O_7I-001, (c) Bi_5O_7I-$\bar{3}$10.

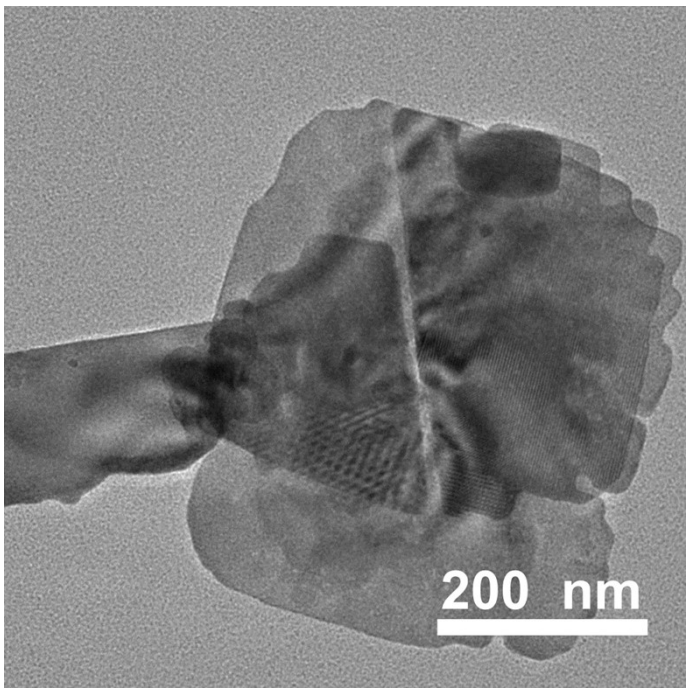

Fig. S3 The TEM image of the reused Bi_5O_7I-010.

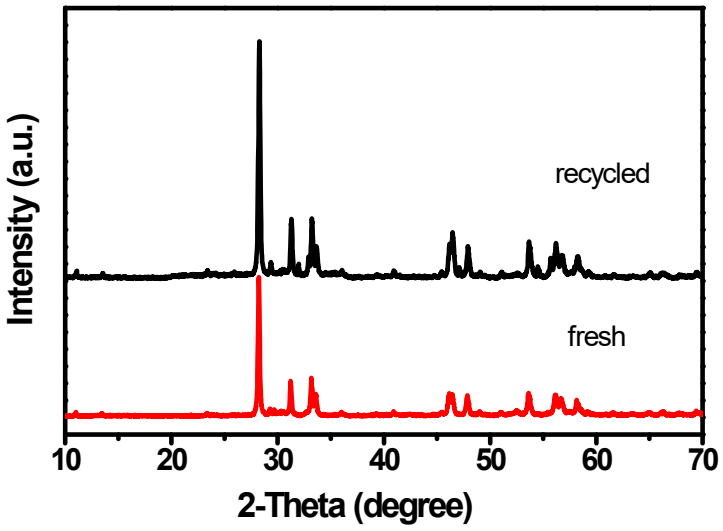

Fig. S4 The XRD pattern of the fresh and recycled Bi_5O_7I-010.

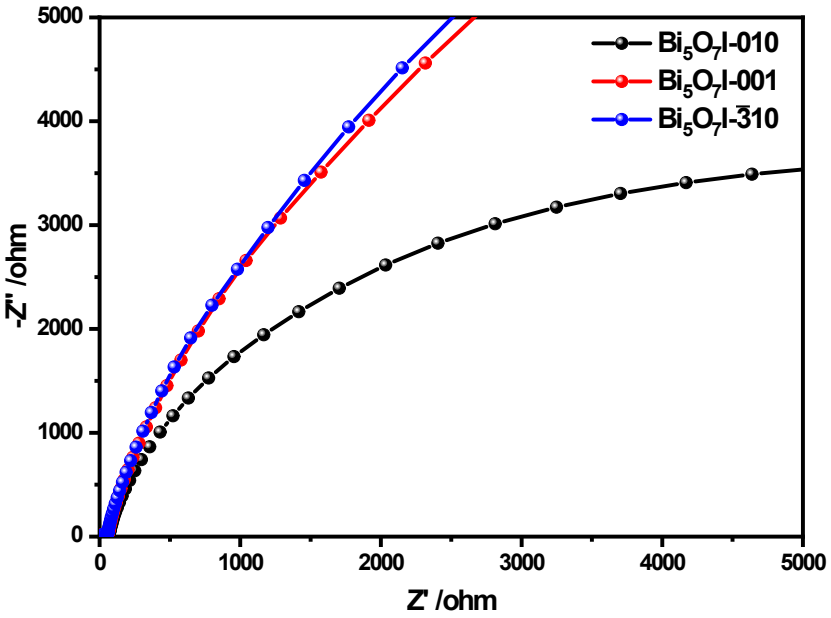

Fig. S5 The Electrochemical impedance spectroscopy of Bi_5O_7I samples.

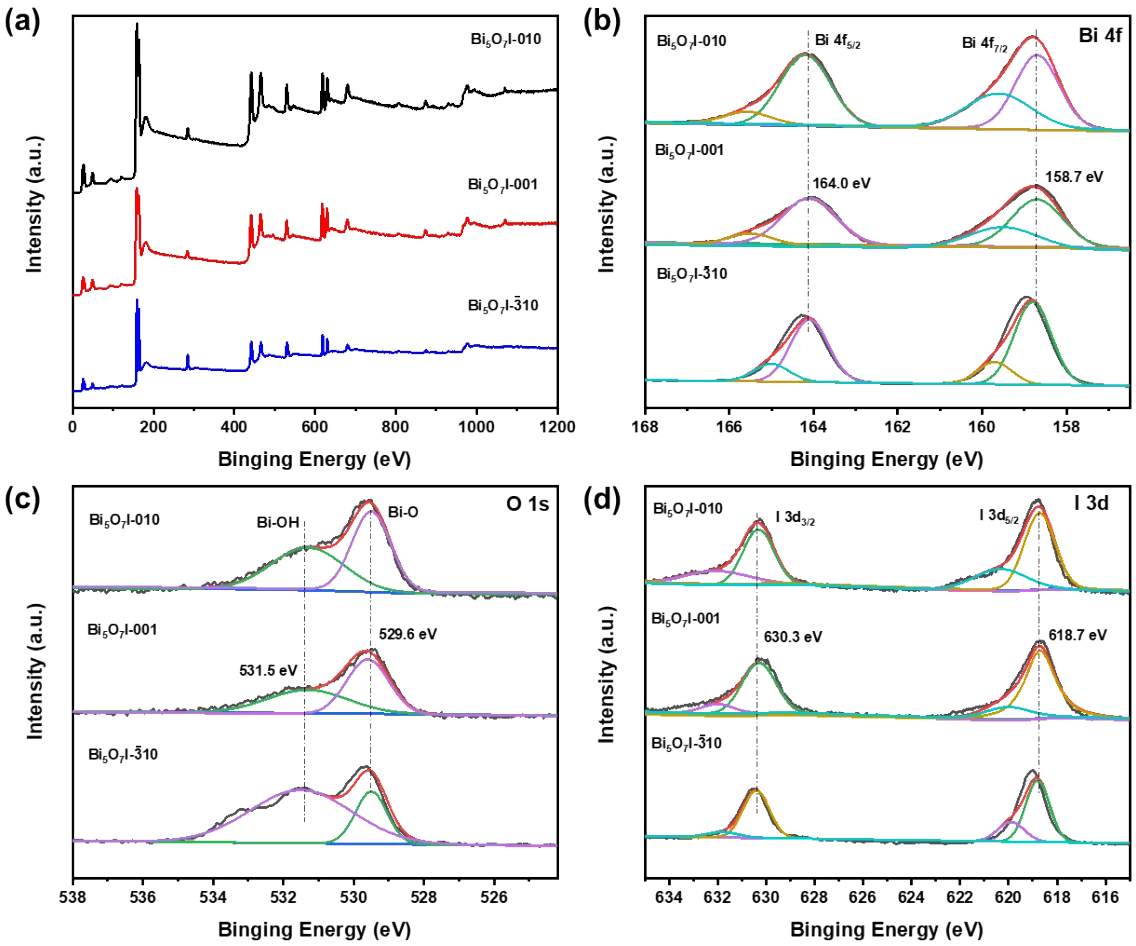

Fig. S6 (a) the XPS of Bi_5O_7I-010, Bi_5O_7I-001 and Bi_5O_7I-$\bar{3}$10, (b) the HR-XPS of Bi 4f, (c) the HR-XPS of O 1s and (d) the HR-XPS of I 3d for Bi_5O_7I-010, Bi_5O_7I-001 and Bi_5O_7I-$\bar{3}$10

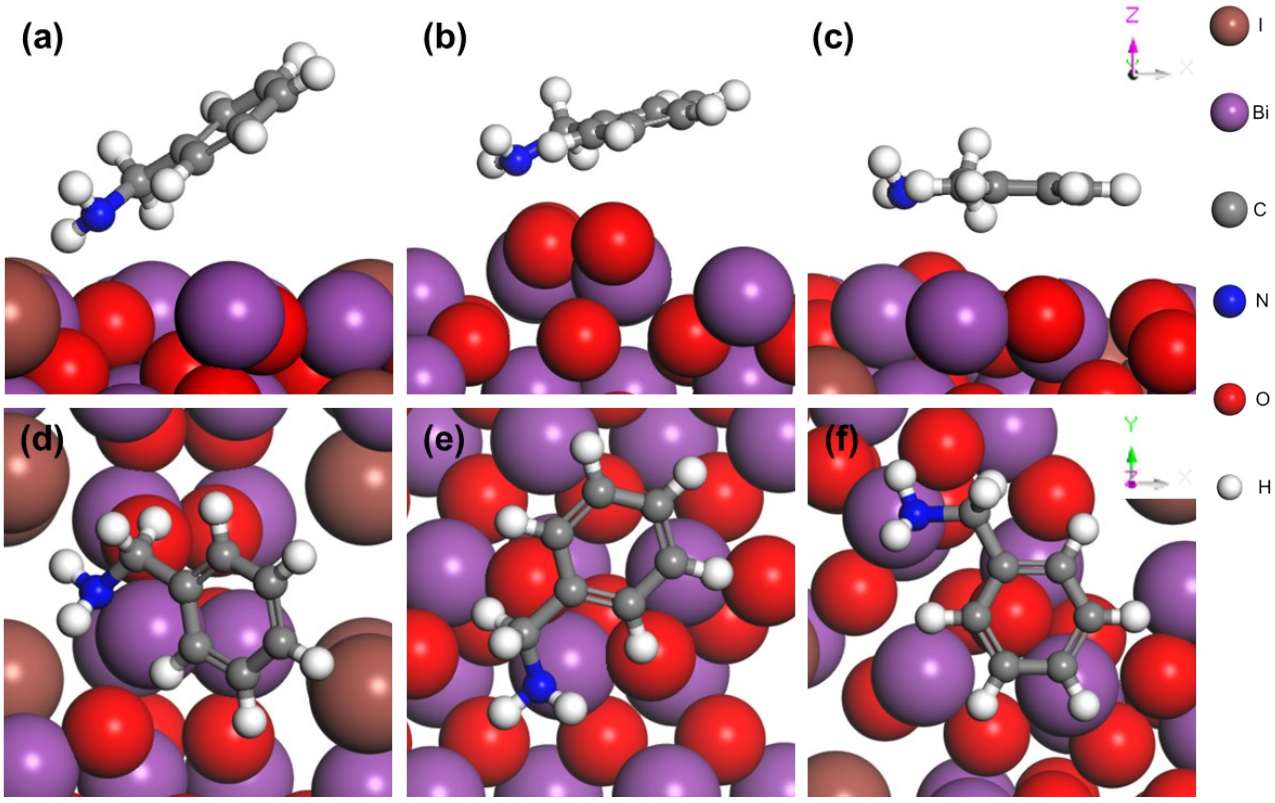

Fig. S7 The illustrations of benzylamine adsorption on facet (010) (a, d), (001) (b, e), ($\bar{3}$10) (c, f), respectively.

Table S1. The surface area of Bi_5O_7I samples

catalyst	Bi_5O_7I-010	Bi_5O_7I-001	Bi_5O_7I-$\bar{3}$10
Surf. Area (m^2 g^{-1})	7.63	2.09	7.11

Table S2. Benzylamine oxidation in the presence of different catalysts

Entry	catalyst	solvent	Conv. (%)	Sel. (%)	AQE[c]
1	no catalyst	ACN	-	-	-
2	BiOI[a]	ACN	32.9	87.7	0.012
3	Bi_5O_7I-010	ACN	100	100	0.037
4	Bi_5O_7I-010[b]	ACN	-	-	-
5	Bi_5O_7I-001	ACN	2.8	100	0.001
6	Bi_5O_7I-$\bar{3}$10	ACN	62.3	93.4	0.023
7	P25	ACN	72.6	92.7	0.027
8	Bi_5O_7I-010	toluene	20.5	100	0.008
9	Bi_5O_7I-010	DMF	64.9	78.1	0.024
10	Bi_5O_7I-010	methanol	37.9	6.03	0.014
11	Bi_5O_7I-010	H_2O	4.6	100	0.002

Condition: 0.1 mmol benzylamine, 100 mg catalyst, 5 ml ACN, 15 W Philips lamp, 18h, 25 ^oC. [a]The precursor of Bi_5O_7I-010 before calcination, synthesized according to our previous work.[1] [b]Without light irradiation. [c]Calculated from the conversion of benzylamine after 18 h.

Table S3. Adsorption energy of benzylamine on different facets

catalyst	Bi_5O_7I-010	Bi_5O_7I-001	Bi_5O_7I-$\bar{3}$10
Adsorption energy (eV)	-1.078	-0.309	-0.412

The adsorption energy of $C_6H_5CH_2NH_2$ on different facets of Bi_5O_7I were calculated by the following formula:

$E_{ads} = E_{photocatalyst+molecule} - E_{photocatalyst} - E_{molecule}$

where $E_{photocatalyst+molecule}$ stands for the free energy of molecule-adsorbed photocatalyst, $E_{photocatalyst}$ for the free energy of photocatalyst, $E_{molecule}$ for the free energy of free molecule.

Reference

1. A. Han, J. Sun, X. Lin, C.-H. Yuan, G. K. Chuah and S. Jaenicke, *RSC Adv.*, 2015, **5**, 88298-88305.
2. A. Han, H. Zhang, G.-K. Chuah and S. Jaenicke, *Appl. Catal., B-Environ.*, 2017, **219**, 269-275.