

## Electronic Supplementary Information (ESI)

### Rational Design of Charge Shunt: Modification upon Crystal Facet Engineering of Semiconductor Photocatalysts

*Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou 350002, P. R. China. Fax: +86-591-8377-9239; Tel: +86-591-8377-9239; E-mail: [liuping@fzu.edu.cn](mailto:liuping@fzu.edu.cn).*

#### Experimental Section

##### Materials :

Bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , >99.0%) ammonium vanadate ( $\text{NH}_4\text{VO}_3$ , >99.9%), ammonia water ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 26-28 wt%), nitric acid ( $\text{HNO}_3$ , 26-28 wt%), ethanal absolute ( $\text{CH}_3\text{CH}_2\text{OH}$ ) and methanal absolute ( $\text{CH}_3\text{OH}$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). GO was purchased from Nanjing XFNANO, INC. All materials were analytical grade and used without any purification process. Deionized (DI) water used in the synthesis came from local sources.

##### Synthesis of $\text{BiVO}_4$ :

$\text{BiVO}_4$  with {110} and {010} facets exposed was synthesized by a hydrothermal procedure. Typically, 36 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and equal amount of  $\text{NH}_4\text{VO}_3$  were dissolved into 300 mL  $\text{HNO}_3$  solution (2M) and the pH value of the solution was then adjusted to 2.0 with ammonia solution under stirring until formation of an orange precipitate. After about 2h aging, the orange precipitate at the bottom of the beaker was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 24h and then allowed it cool down. A vivid yellow powder was separated by filtration, washed with DI water for several times. Then the products were dried at 60 °C overnight in vacuum oven.

##### Synthesis of $\text{BiVO}_4/\text{GO}$ :

$\text{BiVO}_4/\text{GO}$  was synthesized through a evaporation-induced self-assembly process. Briefly, 1 g  $\text{BiVO}_4$  powders and 20 mg GO were put into 100 mL ethanol and 50 mL DI water respectively, and ultrasound treated for 1h to disperse the samples evenly. Then the obtained 50mL GO solution was dropped into the  $\text{BiVO}_4$  solution under vigorous stirring and the obtained mixtures were kept stirring for 12h without sealing in a fuming hood. Then, the residual solution was dried in a 60 °C water bath with stirring. Lastly, the obtained sample was further kept overnight to let the GO combine tightly with  $\text{BiVO}_4$  polyhedrons.

**Synthesis of BiVO<sub>4</sub>/RGO:**

The BiVO<sub>4</sub>/RGO composites have been fabricated by a mild photoreduction process. In detail, 100 mg BiVO<sub>4</sub>/GO was dispersed into a breaker containing 80 mL DI water and 20 mL methanol. Then, the solution was irradiated with full-wave band light for 2h with stirring. Collected the precipitate and washed it with DI water. The final product was dried in a vacuum oven.

**Characterization:**

The crystal structures of the as-prepared samples was identified by X-ray diffraction using X-ray powder diffraction (XRD) patterns were carried out on a Bruker D8 ADVANCE X-ray diffractometer, with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm), which operated at 40 kV and 40 mA. The scan rate was 0.5 ( $2\theta \cdot s^{-1}$ ). Scanning electron microscopy (SEM) images were obtained using a HITACHI SU8000 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images were collected with a TecnaiG2F20 S-TWIN with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) investigation was recorded on a Thermo Scientific ESCA Lab 250 system, with a monochromatic Al K $\alpha$  as the X-ray source, hemispherical analyzer, and sample stage with multi-axial adjustability to obtain the composition on the surface of samples. UV-Vis diffuse reflectance spectroscopy (DRS) was measured by a Carry 500 UV-Vis spectrophotometer, during which BaSO<sub>4</sub> was served as the background. The nitrogen adsorption and desorption isotherms were characterized using a Micrometrics ASAP 2020 analyzer at 77K after the as-prepared samples were degassed at 180 °C for 300min in a vacuum. A Bruker model A300 spectrometer equipped with a xenon lamp (with 400 nm cut filter) was used for measurements of the electron spin resonance (ESR) signals of radicals spin trapped by 3,4-dihydro-2,3-dimethyl-2H-pyrrole-1-oxide (DMPO). The settings were center field, 3512.000 G; microwave frequency, 9.85 GHz; and power, 2.01 mW. The photoluminescence (PL) spectra were obtained using an Edinburgh Analytical Instrument FL/FSTCSPC920 spectrophotometer.

**Photocatalytic activity measurement:**

The photo-degradation of RhB in aqueous solution was done in a Pyrex glass vessel. Typically, 20 mg of the photocatalyst was dispersed into 60 mL of a RhB aqueous solution ( $5 \text{ mg} \cdot \text{L}^{-1}$ ) in the Pyrex glass vessel. Before light illumination, all suspensions were kept in the dark for 60min with stirring to ensure the adsorption–desorption equilibrium had been established. Then the suspension was illuminated under a 300 W Xe lamp with a 420 nm band-pass filter. and the photodegradation came into

operation. During the process of photodegradation, the concentrations of RhB in the suspension, collected at interval 20min, was detected respectively by a Cary-50 UV-Vis spectrophotometer. The normalized temporary concentration changes ( $C/C_0$ ) of RhB solution during the photo-degradation are proportional to the normalized maximum absorbance ( $A/A_0$ ) and derived from the changes in the dye's absorption profile (554 nm for RhB) at a given time interval.

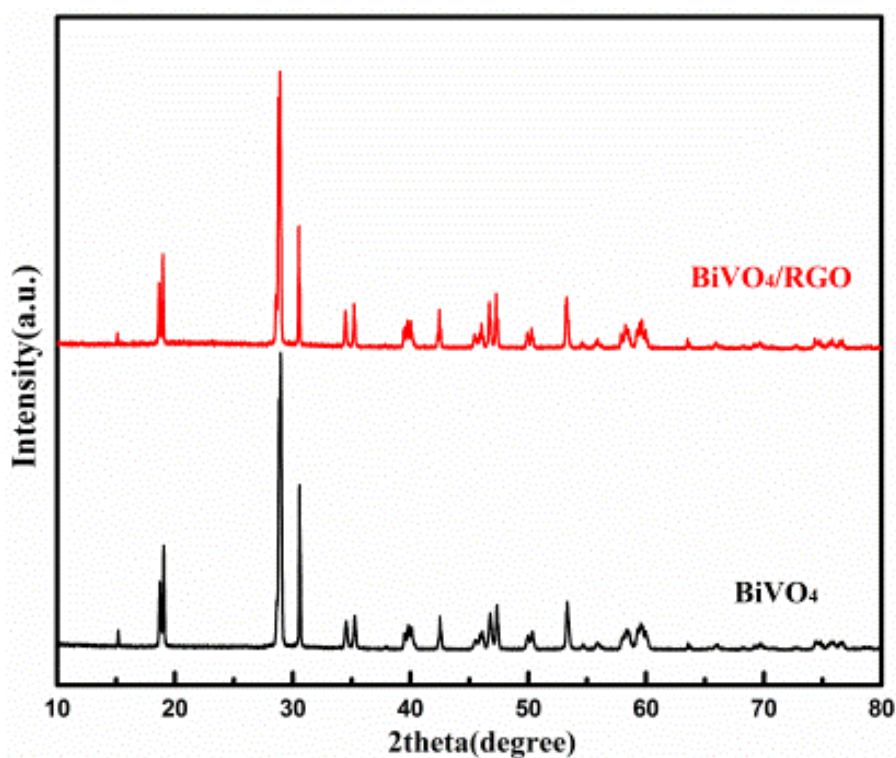


Fig. S1 XRD patterns of pure BiVO<sub>4</sub> and BiVO<sub>4</sub>/RGO composites.

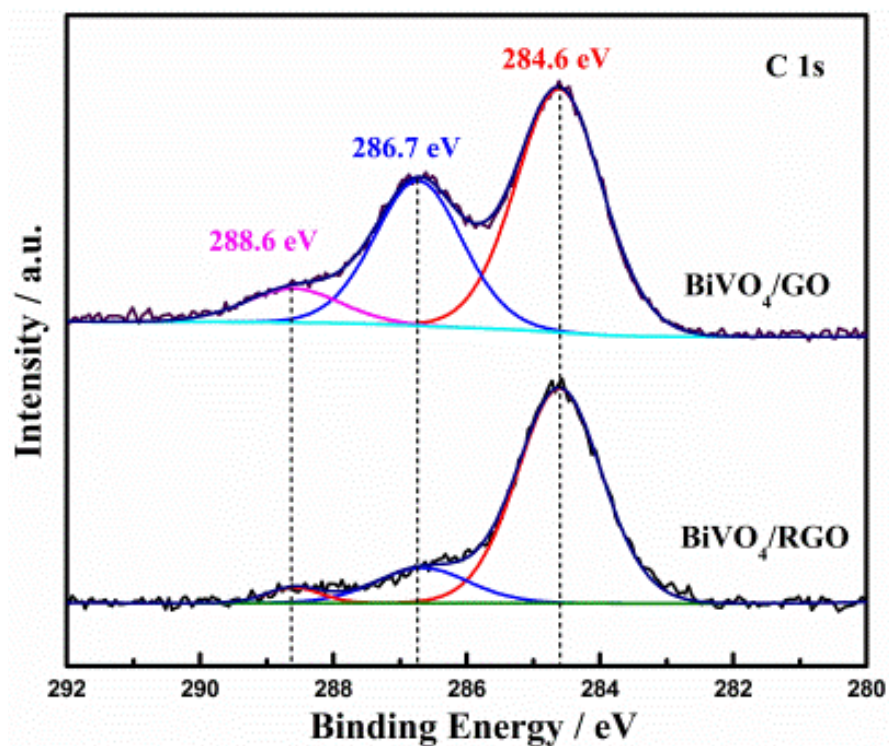


Fig. S2 XPS spectra of C 1s of the BiVO<sub>4</sub>/GO and BiVO<sub>4</sub>/RGO.

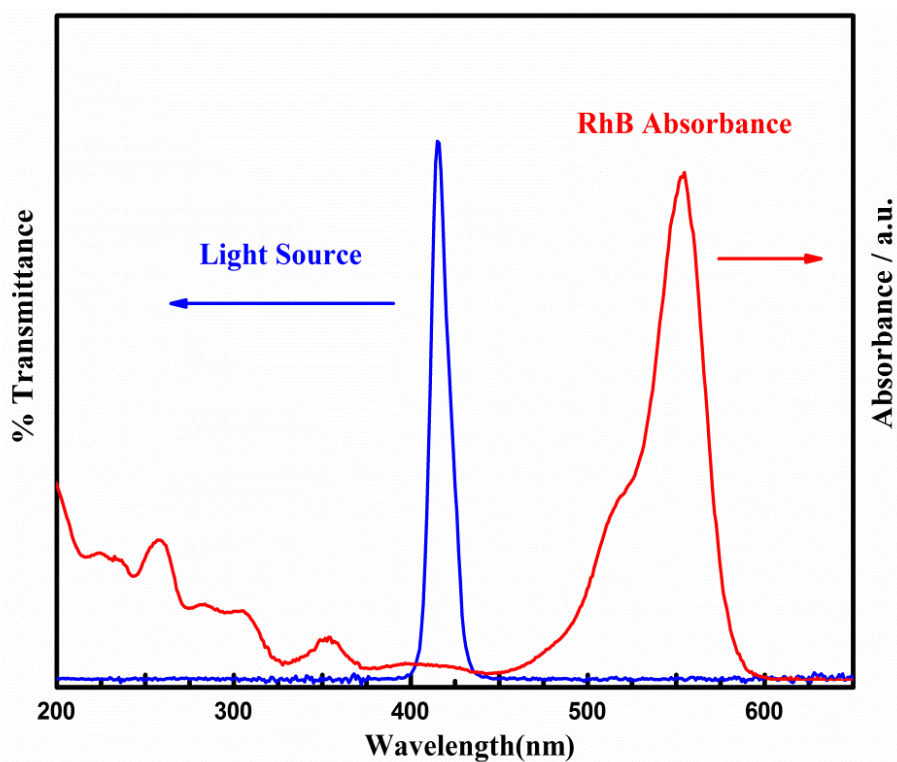


Fig. S3 Blue curve: Transmission spectrum of visible source with 420 nm pass filter.  
Red curve: RhB absorption spectrum (arbitrary scale).



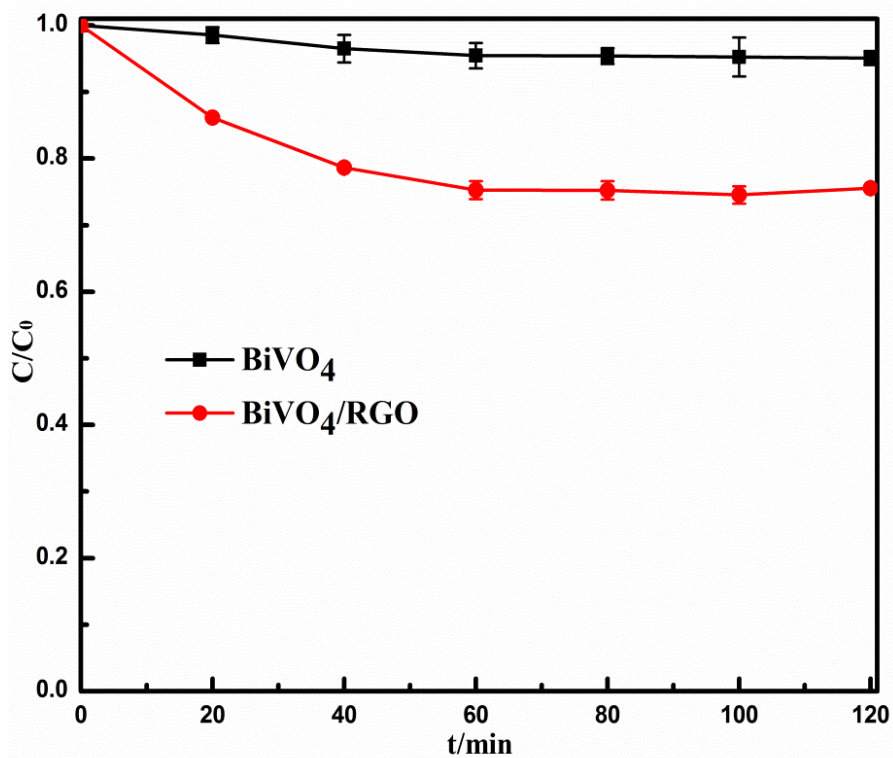


Fig. S4 Dark absorption curves of aqueous solutions of RhB in the presence of bare  $\text{BiVO}_4$  and  $\text{BiVO}_4/\text{RGO}$  composite.

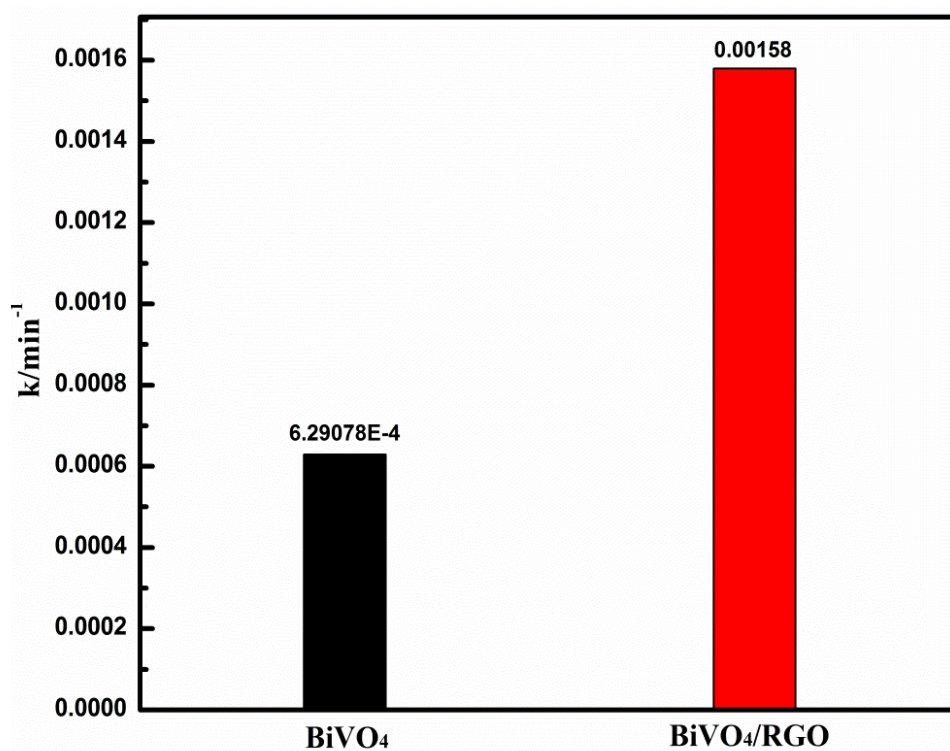


Figure S5. The normalized reaction rate constants with surface area for photocatalytic degradation of RhB over samples over  $\text{BiVO}_4$  and  $\text{BiVO}_4/\text{RGO}$ .

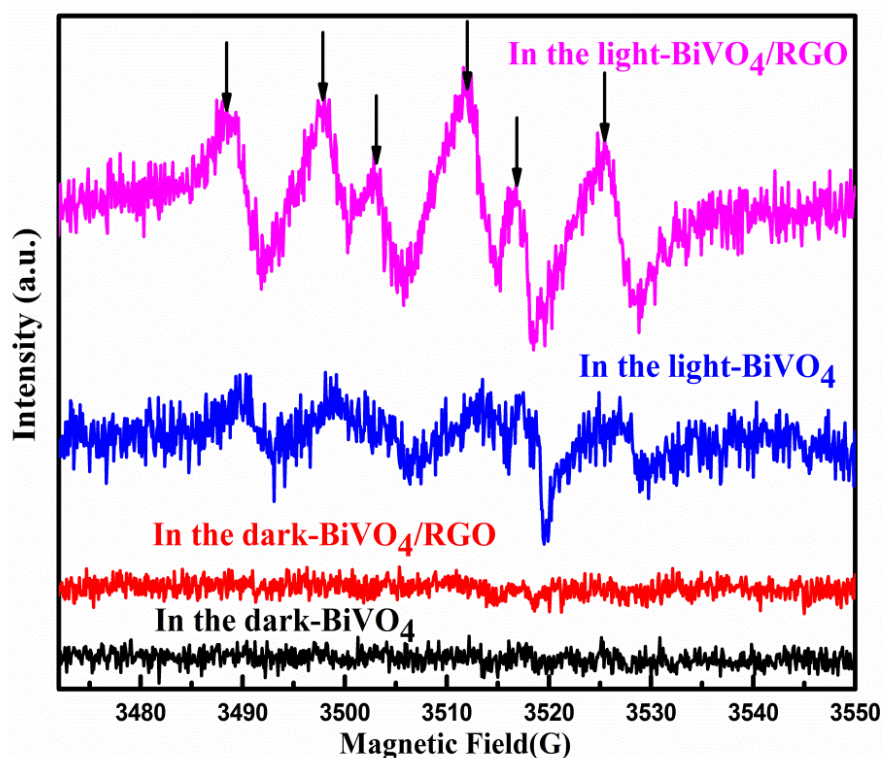


Figure S6. Electron spin resonance (ESR) spectra of radical adduct trapped by DMPO ( $\text{DMPO}\cdot\text{O}_2^-$ ) over the  $\text{BiVO}_4$  or  $\text{BiVO}_4/\text{RGO}$  suspension in the methanol solution without or with the light.

To prove that the photogenerated electrons in  $\text{BiVO}_4$  and  $\text{BiVO}_4/\text{RGO}$  can be scavenged by  $\text{O}_2$  during the photocatalytic process, we employ the ESR spin-trap technique (with DMPO) to probe the superoxide radical ( $\cdot\text{O}_2^-$ ) species generated under the illumination. As shown in figure S6, no obvious ESR signal is observed over both  $\text{BiVO}_4$  and  $\text{BiVO}_4/\text{RGO}$  suspension in the methanol solution in the dark. Notably, the sextet ESR signal which is assigned to  $\text{DMPO}\cdot\text{O}_2^-$ , appears in the presence of  $\text{BiVO}_4$  and  $\text{BiVO}_4/\text{RGO}$  respectively with light irradiation. And the intensity of the sextet ESR signal is much stronger in the presence of  $\text{BiVO}_4/\text{RGO}$  than  $\text{BiVO}_4$  under illumination. These phenomena indicate that the thermodynamic permissibility for transformation of  $\cdot\text{O}_2^-$  from the photoexcited single-electron on CB of  $\{010\}$  facet of  $\text{BiVO}_4$  reduction of  $\text{O}_2$ . Thus, ESR spectra provide evidence of  $\cdot\text{O}_2^-$  formed over the photocatalysts ( $\text{BiVO}_4$  or  $\text{BiVO}_4/\text{RGO}$ ) under the irradiation, and the photogenerated electrons in  $\text{BiVO}_4/\text{RGO}$  can be scavenged more effectively by  $\text{O}_2$  than in bare  $\text{BiVO}_4$  in the aqueous solution. It further confirms the higher utilization rate of photogenerated electrons in  $\text{BiVO}_4/\text{RGO}$ , which may be attributed to the high-efficiency facet-driven charge dual-selectivity-channel separation mechanism. On the other hand, the reduction potential of the transferred electrons from the CB of  $\{110\}$  to the CB of  $\{010\}$ , is no less negative than the reduction potential of electrons on  $\{010\}$  facet of  $\text{BiVO}_4$ . Hence, the transferred electrons are

scavenged by  $O_2$  during the excellently fast migration in graphene is feasible in thermodynamics. That is,  $\bullet O_2^-$  may be primary origin of photoinduced electrons being captured by adsorbed oxygen during the excellently fast migration or on  $\{010\}$  facet of  $BiVO_4$  in  $BiVO_4/RGO$  composite.