Supporting Information

Synthesis of bismuth vanadate nanoplates with exposed {001} facets and enhanced visible-light photocatalytic properties

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Experimental details

Chemicals: bismuth trichloride ($BiCl_3$), ammonium metavanadate (NH_4VO_3), ethanolamine ($H_2NCH_2CH_2OH$), distilled water, absolute ethanol. All reagents used were analytically pure, and were purchased from Wako Chemical Reagent Company, and were used without further purification.

Preparation of m-$BiVO_4$ nanoplates: in a typical synthesis, 1mmol of $BiCl_3$ was added into 100 ml of distilled water under mild stir, a white suspension was formed immediately due to the hydrolysis of $BiCl_3$. Then, 1mmol of NH_4VO_3 were added into the white suspension, and an orange suspension was formed. The pH value of the orange suspension is 2.21. The pH value quickly reached 6.15, and the suspension changed into light yellow and became a colloid solution when 0.5 ml of 1M aqueous ethanolamine was added into the suspension. The colloid solution was loaded into a Teflon-lined autoclave. The autoclave was sealed, heated in an oven of 160 °C for 12 h, and then naturally cooled to room temperature, and a yellow powder formed, which was then collected, washed with distilled water and ethanol several times to remove ions and possible remnants, and vacuum-dried for further characterization. The schematic illustration of the synthesis procedure is shown in Figure S1.

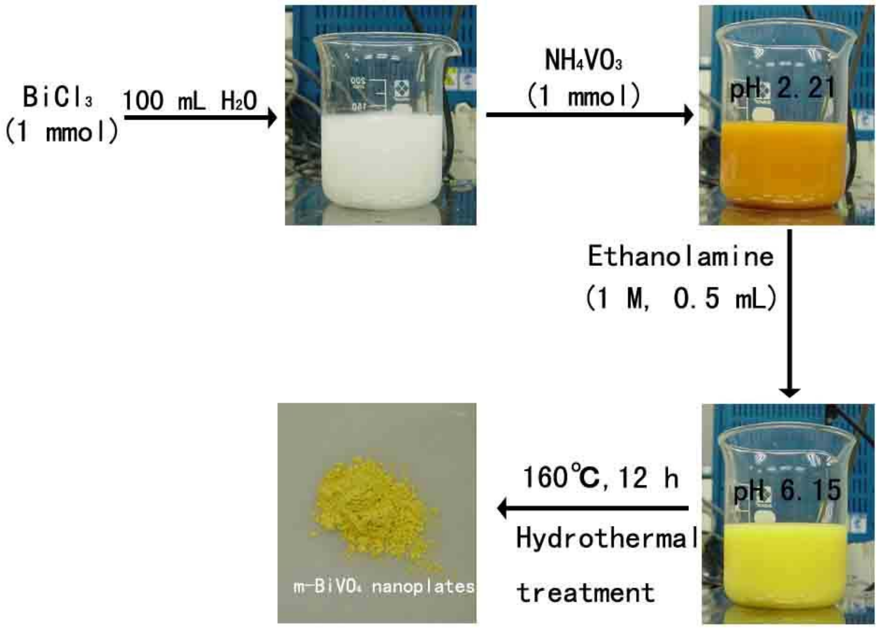


Figure S1. Schematic illustration of the synthetic procedure of the m-$BiVO_4$ nanoplates.

Characterization: XRD patterns of the products were recorded on a Rigaku (Japan) D/max-γA X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54178$ Å). Scanning electron microscopy (SEM) images were recorded with a field emission scanning electron microscopy (JEOL-6700F). Samples for transmission electron microscopy (TEM) analysis were prepared by drying a drop of nanocrystal dispersion in absolute ethanol on amorphous carbon-coated copper grids. Particle sizes, shapes and high-resolution TEM (HRTEM) characterization was performed with a JEOL 2010 operated at 200 kV. UV-vis absorption spectra were recorded with a Shimadzu UV-2500. BET measurements were carried out in Micromeritics, SHIMADZU.

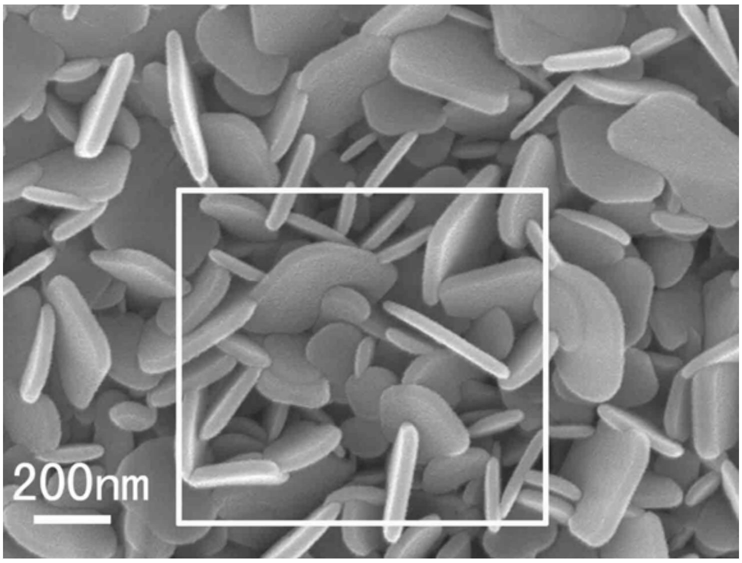
Photocatalytic Activity Test of m-$BiVO_4$ nanoplates

1. Photocatalytic degradation of Rhodamine B: the photocatalytic activities of the m-$BiVO_4$ nanoplates were first evaluated by degradation of Rhodamine B in an aqueous solution under visible light from a 300W Xe lamp (CERMAX LX−300; ILC Technology) equipped with cutoff filter L42 (Hoya Optics) and a water filter. The photocatalyst (0.1 g) was added into 100 mL RhB aqueous solution (12 mg L^{-1}) in a Pyrex reactor at room temperature under air. Before light was turned on, the solution was continuously stirred for 30 min in dark to ensure the establishment of an adsorption–desorption equilibrium. The concentration of RhB during the degradation was monitored by colorimetry using a UV-vis spectrometer (Shimadzu UV-2500). The light intensity was measured by a spectroradiometer (USR-40D, Ushio), and the value is about 28 mW/cm^2.

2. Photocatalytic oxidation of water for O_2 generation: the photocatalytic activity of the as-obtained m-$BiVO_4$ nanoplates employed to oxidize water for generation of O_2 was measured on a closed system equipped with an online gas chromatograph (SHIMADZU, GC–8A). The visible light source was a 300W Xe lamp (CERMAX LX−300; ILC Technology) equipped with cutoff filter L42 (Hoya Optics) and a water filter. Typically, m-$BiVO_4$ nanoplates (0.1 g) were dispersed in $AgNO_3$ aqueous solution (270 mL, 0.017 M). The gas composition was recorded every 30 min with an online gas chromatograph. The light intensity was measured by a spectroradiometer (USR-40D, Ushio), and the value is about 28 mW/cm^2.

Photo-Electrochemical Measurements

The spin-coating method was employed to make the photoelectrode. In a typical process, 20 mg of as-synthesized BiVO4 nanoplates was added into 10 ml ethanol, formed a uniform suspension. As in a standard spin-coating process, the ethanol suspension was dropped onto a piece of FTO (fluorine tin oxide) glass, while spinning at a high speed of 150 rps. The film was then allowed to dry in an oven at 70 °C for 1 h. Finally, the film was annealed by heating in air at 400 °C for 30 min. Photo-electrochemical measurements were carried out using a conventional three-electrode, single-compartment glass cell fitted with a synthesized quartz window using a potentiostat. The quartz electrolytic cell was filled with 0.1 M Na_2SO_4. The m-$BiVO_4$ nanoplate electrode served as the working electrode. The potential was swept linearly at a scan rate of 10 mV/sec. The illuminated area of the working electrode is 1 cm^2. A 300W Xe lamp (CERMAX LX−300; ILC Technology) was used as the visible-light source. The counter and reference electrodes were a platinumblack wire and saturated calomel electrode (SCE), respectively. The light intensity was measured by a spectroradiometer (USR-40D, Ushio), and the value is about 200 mW/cm^2. The photoelectrochemical experiment was performed using an electrochemical system (CHI-660B).



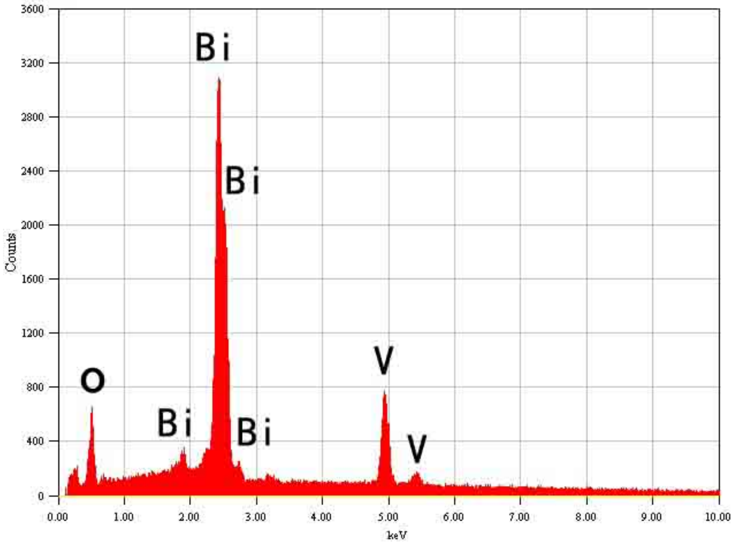
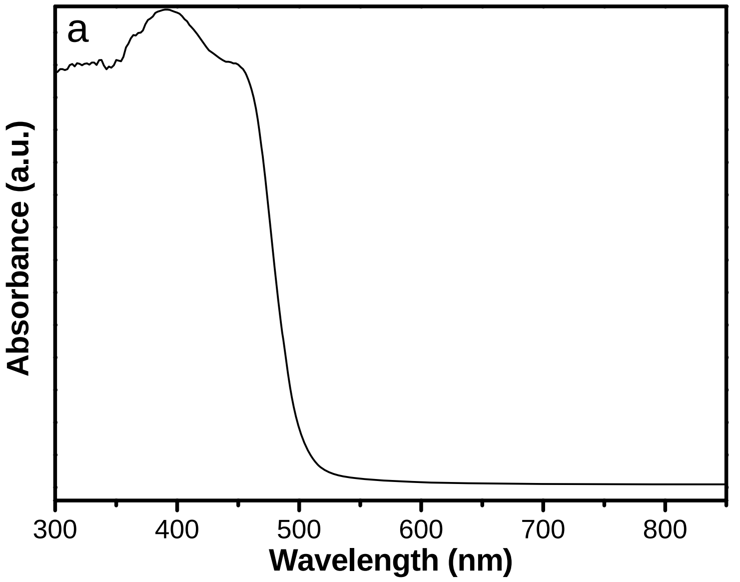


Figure S2. Energy dispersive spectra (EDS) spectrum of the as-obtained m-$BiVO_4$ nanoplates.



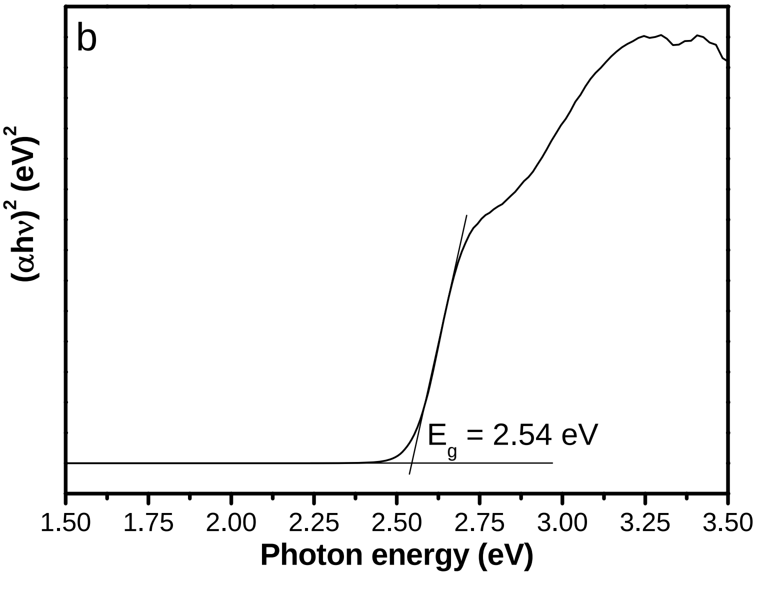


Figure S3. (a) UV-Vis diffuse reflectance spectrum of the as-obtained m-$BiVO_4$ nanoplates. (b) The plots of $(\alpha h\nu)^2$ versus hν, by which the values of the energy band gaps of the as-obtained m-$BiVO_4$ nanoplates.

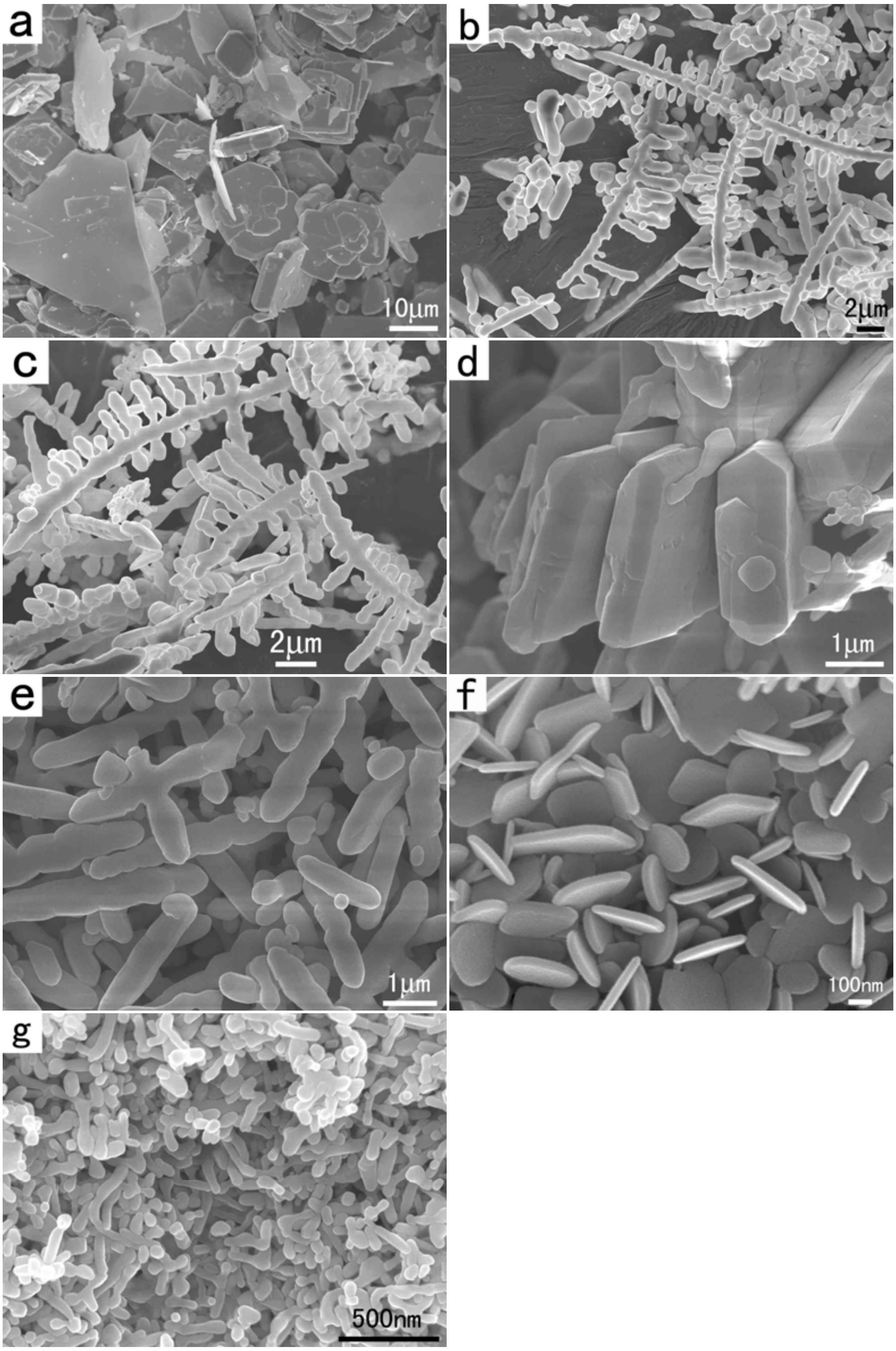


Figure S4. (a)–(g) FESEM images of the products obtained at pH values of 1.0, 2.0, 3.0, 4.0, 5.0, 6.15, and 7.0, respectively.

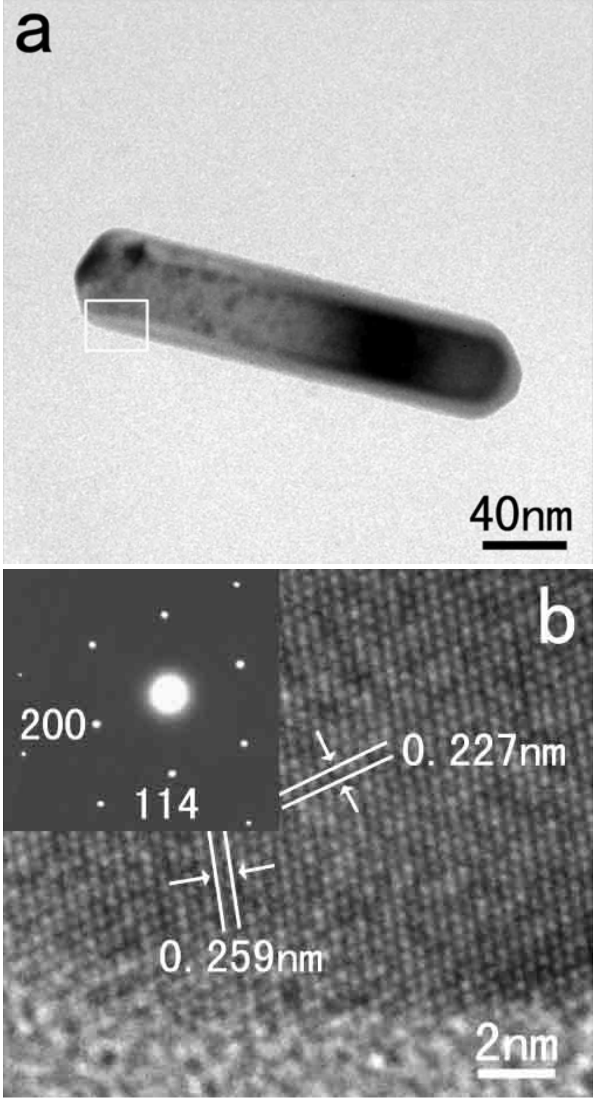


Figure S5. (a) TEM image of one single m-$BiVO_4$ nanorod. (b) HRTEM image and SAED pattern taken from the white frame area indicated in Figure S6a. From the HRTEM image and the corresponding SAED pattern we can see that the nanorod is grown along the [100] direction.

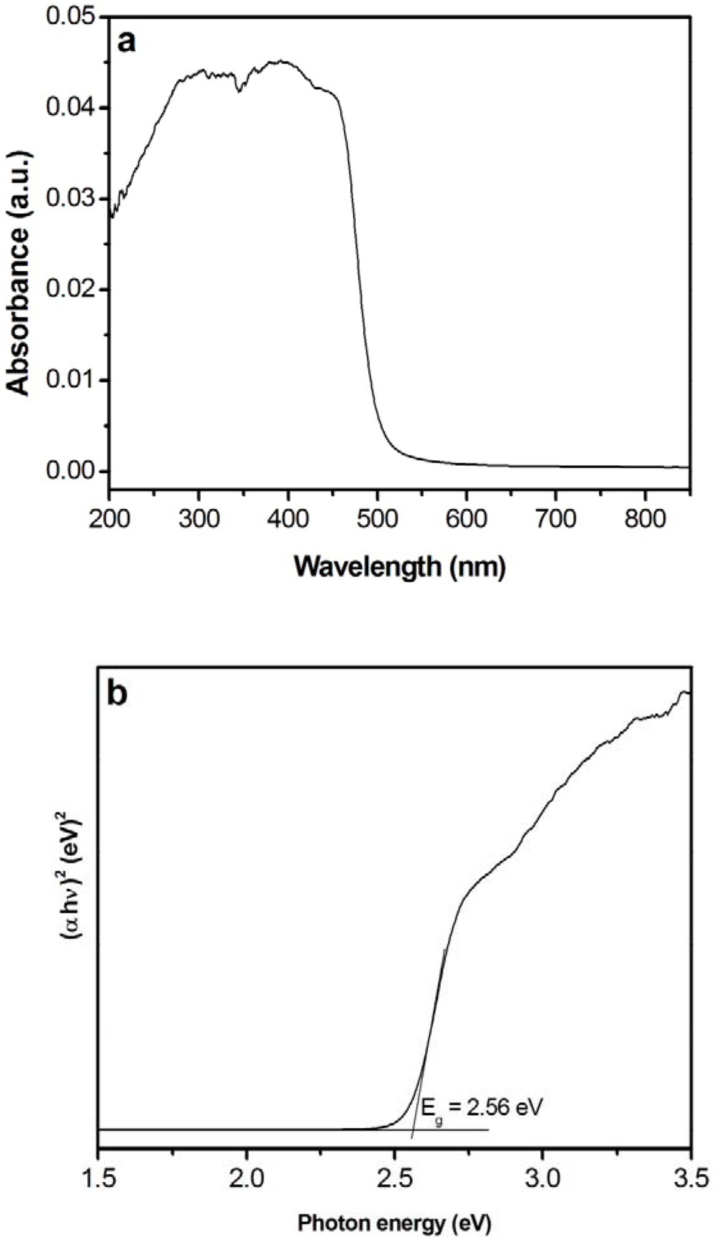


Figure S6. (a) UV-Vis diffuse reflectance spectrum of the as-obtained m-$BiVO_4$ nanorods. (b) The plots of $(\alpha h\nu)^2$ versus hν, by which the values of the energy band gaps of the as-obtained m-$BiVO_4$ nanorods.

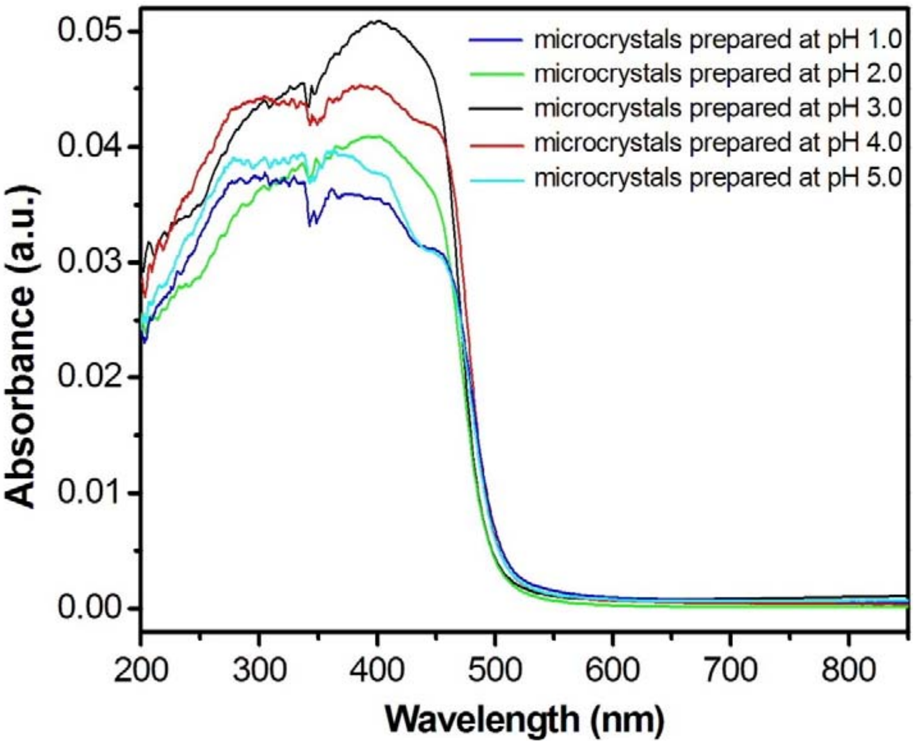


Figure S7. UV-Vis diffuse reflectance spectrum of the as-obtained m-BiVO$_4$ microcrystals.

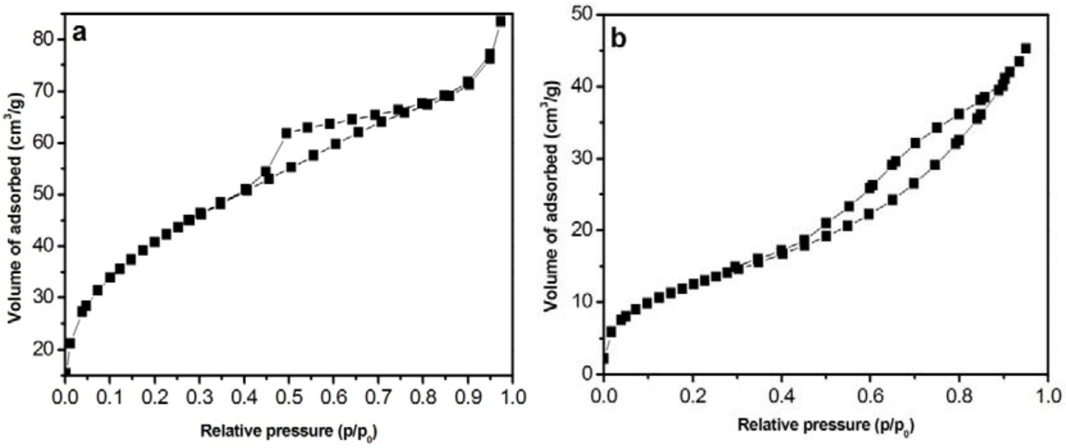


Figure S8. Nitrogen adsorption-desorption isotherm plot of the as-synthesized nanorods (a) and nanoplates (b) samples, respectively.

Table 1. The morphology and specific surface area of the samples prepared at different Ph values.

Sample	Morphology	Specific surface area (m^2/g)
Prepared at pH 1.0	irregular large particles	0.3
Prepared at pH 2.0	hyperbranched microcrystals	5.6
Prepared at pH 3.0	hyperbranched microcrystals	7.7
Prepared at pH 4.0	polyhedral microcrystals	2.8
Prepared at pH 5.0	rod-like microcrystals	3.8
Prepared at pH 6.15	nanoplates	21.4
Prepared at pH 7.0	nanorods	67.5

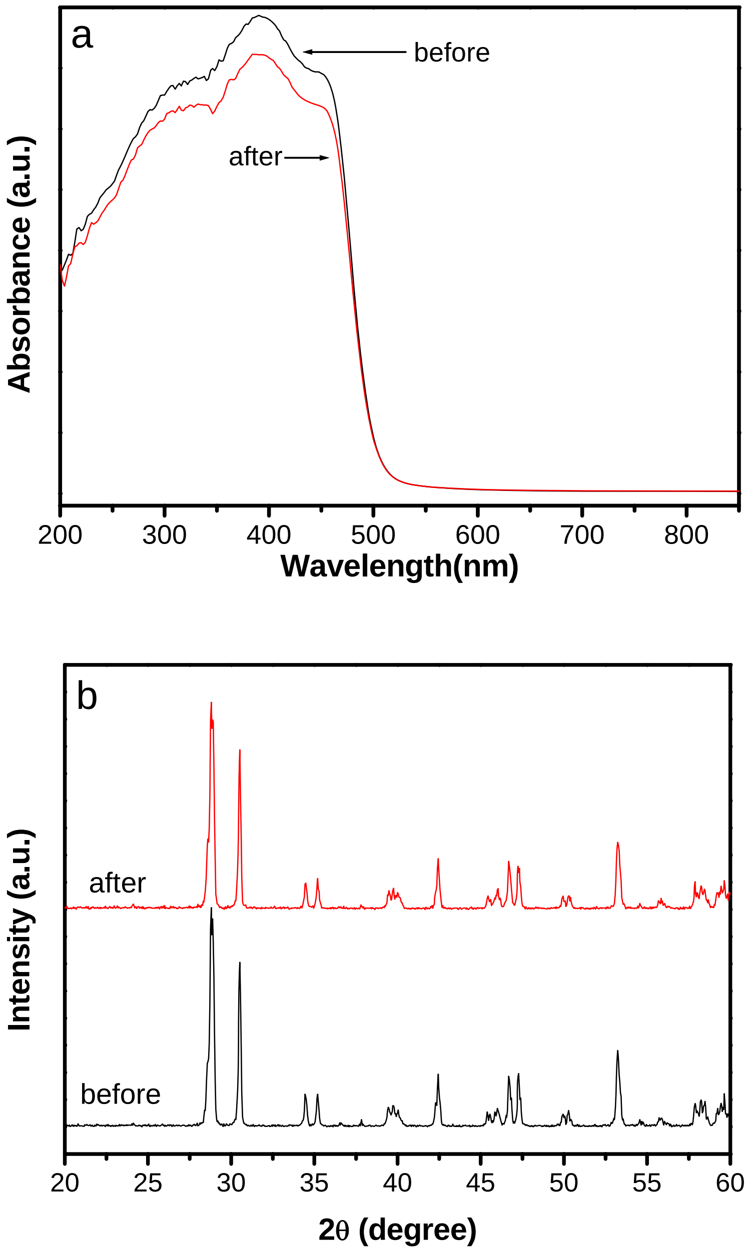


Figure S9. (a) UV-Vis diffuse reflectance spectrum and (b)X-ray diffraction (XRD) patterns of the m-$BiVO_4$ nanoplates before and after reaction for degradation of Rhodamine B over under visible light irradiation ($\lambda > 420$ nm). Light source: 300 W xenon lamp. These results confirm that the sample is relatively stable upon light irradiation.