Supplementary Information

Single-crystal $NaY(MoO_4)_2$ thin plates with dominant {001} facets for efficient photocatalytic degradation dyes under visible light irradiation

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Experimental Section

I. Reagents and Purity. Na_2MoO_4, $Y(NO_3)_3$, and nitric acid were purchased from Shanghai Chemical Reagents Company, P. R. China. H_2O was ultrapure water. All reagents used in experimental process were analytically pure.

II. Synthesis of the Products. In a typical procedure for the synthesis of $NaY(MoO_4)_2$ thin plates, 2 mmol of $Y(NO_3)_3$ was dissolved into 40 mL of ultrapure water. Next, 16 mmol of Na_2MoO_4 was introduced into the solution under stir. After that, the pH value of the solution was adjusted to 4.3 by diluted nitric acid drop by drop. The solution was agitated for 5 min. Then it was poured into a stainless steel autoclave with a Teflon-liner of 50 mL capability and heated at 180 ^oC for 20 h. After the autoclave was cooled to room temperature, the resulting white products were separated centrifugally and washed with ultrapure water and then absolute ethanol for

several times. The products were dried under vacuum at 60 ^{o}C for 4 h. As to $NaY(MoO_4)_2$ octahedrons, octahedrons truncated by {001} planes, quasi-cubes, tetragonal prisms, and thin plates with a thickness of *ca*.150 nm, they were synthesized in a manner similar to that for thin plates except that the amounts of $NaY(MoO_4)_2$ were 4, 6, 8, 10, and 14 mmol, respectively.

III. Characterization. Powder X-ray diffraction (XRD) was carried out with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm) at a scanning rate of 8^{o}/min in the 2θ range from 10 to 70^{o}. Field emission scanning electron microscopy (FE-SEM) images were taken on a Nova NanoSEM 200 scanning electron microscope (FEI Inc.). High-resolution transmission electron microscopy (HRTEM) images and selected area electronic diffraction (SAED) patterns were performed with a JEOL JEM 2010 HRTEM, using an accelerating voltage of 200 kV. The optical diffuse-reflectance spectra were recorded on a Lambda 950 (Perkin Elmer) using $BaSO_4$ as a reference. The Brunauer-Emmett-Teller (BET) surface area was measured with a ASAP2020 specific surface area and porosity analyzer. Total organic carbon (TOC) was monitored with an Elementar Liqui II analyzer. Prior to injection into the TOC analyzer, the samples were centrifuged to remove any particles. All experiments were carried out at least twice.

IV. Photosensitized Degradation Properties Study. The photosensitized activities of $NaY(MoO_4)_2$ octahedrons, cubes, and thin plates were evaluated by degradation of rhodamine B (RhB) under visible-light irradiation from 500 W Xe light (CHF-XM500, purchased from Beijing Trusttech Co., Ltd) equipped with a 400 nm cutoff filter. In every experiment, 100 mg of solid catalysts were added to 100 mL of a RhB solution (10^{-5} mol/L). Before illumination, the solution was magnetically stirred in the dark for 2 h to ensure the establishment of an adsorption-desorption equilibrium between the samples and RhB. After that, the solution was exposed to visible-light irradiation under magnetic stirring. At given time intervals, 3mL aliquots were sampled and centrifuged to remove the catalysts particles. Then, the filtrates were analyzed by recording variations of the absorption band maximum (553 nm) in the UV-vis spectra of RhB by using a Shimadzu UV2501PC spectrophotometer. For photocatalytic degradation of methylene blue, indigo, and alizarin green, their experimental processes are similar to that of RhB.

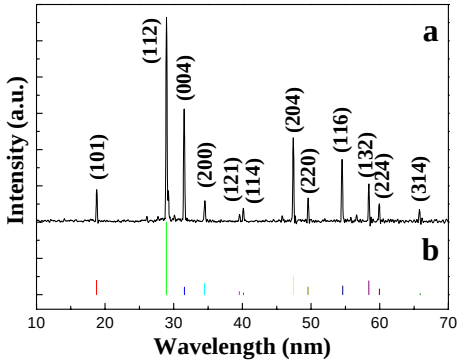
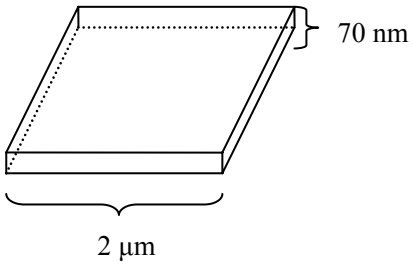


Fig. S1 (a) Powder XRD pattern of the products hydrothermally synthesized at 180 ^{o}C for 20 h and (b) standard XRD pattern obtained from JCPDS No. 82-2369.

The percentages of {001} facets were estimated on the basis of the total surface area of thin plates. The percentages of {001} facets are approximately calculated as follows.



$$\{001\}\% = \frac{\text{Surface area of } \{001\} \text{ planes}}{\text{The total surface area of thin plate}} \times 100\%$$

$$= \frac{2 \times 2 \times 2}{4 \times 2 \times 0.07 + 2 \times 2 \times 2} \times 100\%$$

$$= 93\ \%$$

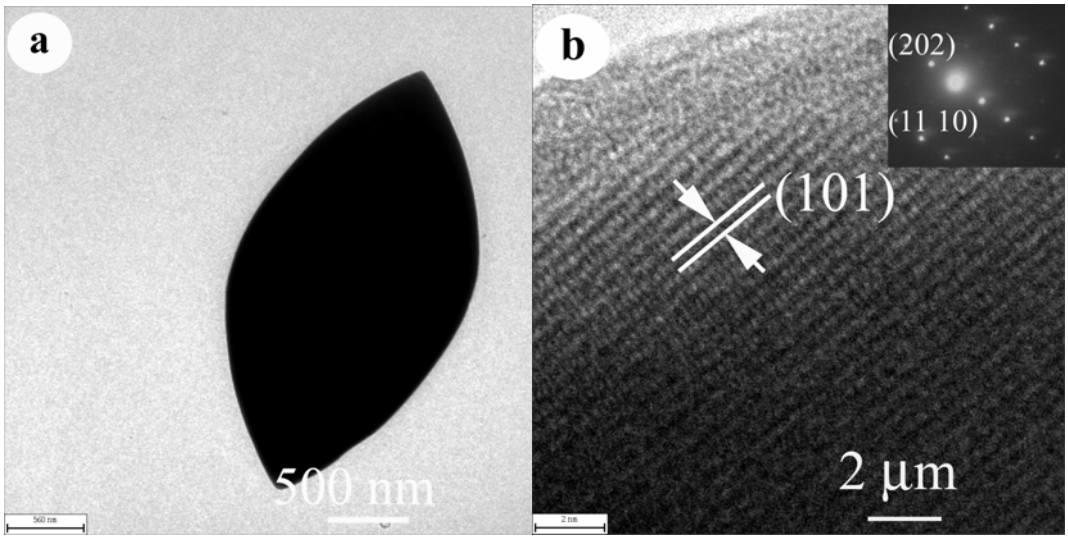


Fig. S2. (a) TEM image of an individual octahedron. (b) HRTEM image and SAED pattern performed on the octahedron.

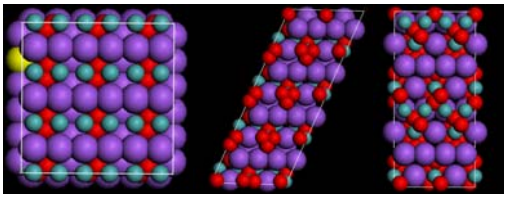


Fig. S3. Surface cleavage of a $NaY(MoO_4)_2$ crystal: (001) plane (left), (101) plane (middle), and (100) plane (right). The red, blue, and purple spheres represent O, Mo, and Y or Na, respectively.

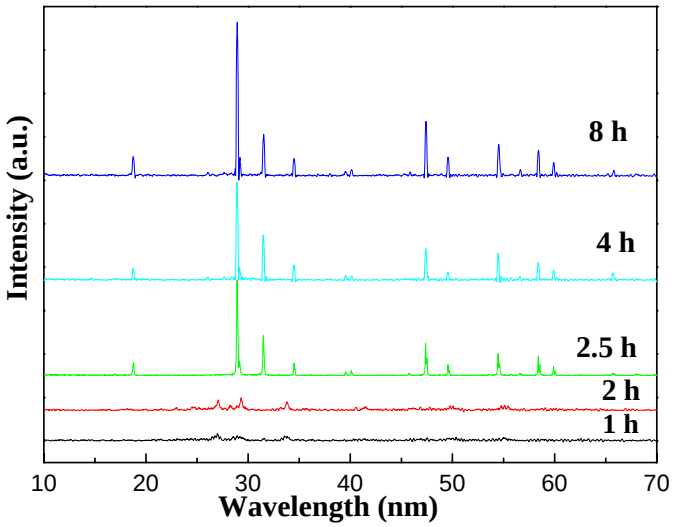


Fig. S4. XRD patterns of the samples synthesized with 16 mmol of Na_2MoO_4 at 180 ^oC for 1, 2, 2.5, 4, and 8 h.

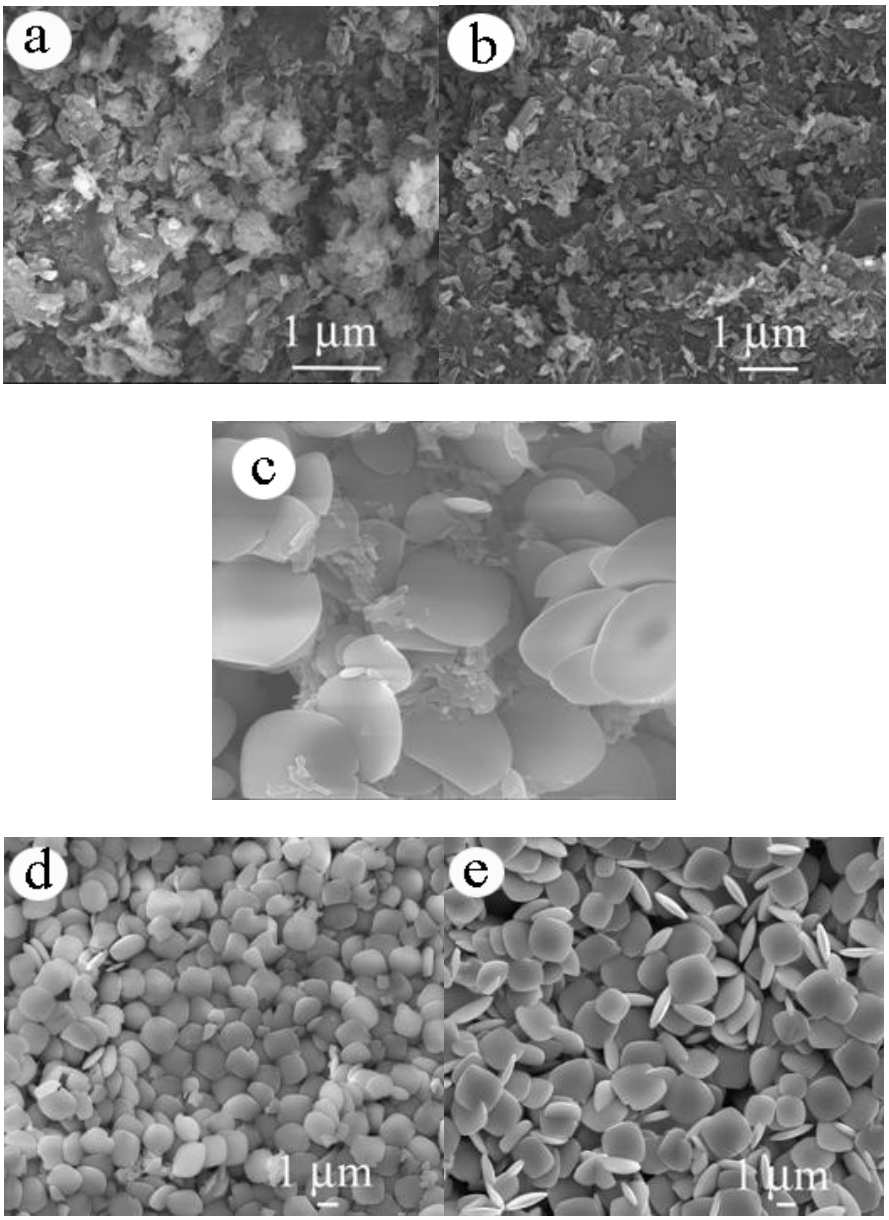


Fig. S5. FE-SEM images of the samples hydrothermally synthesized with 16 mmol of Na_2MoO_4 for different time periods: (a) 1 h, (b) 2 h, (c) 2.5 h, (d) 4 h, and (e) 8 h.

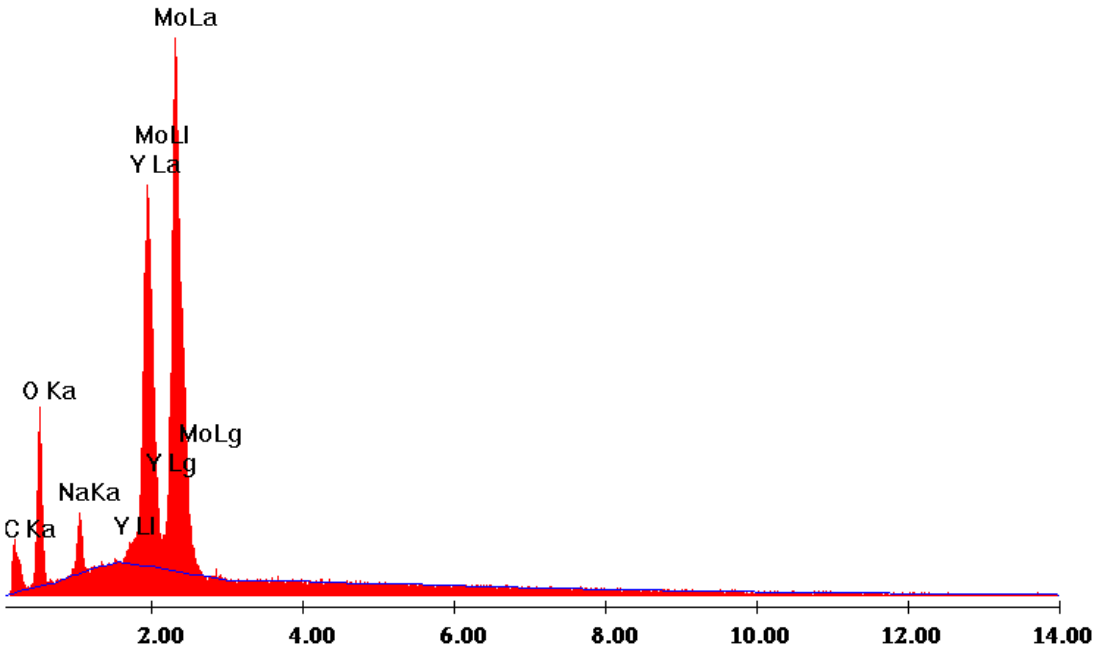


Fig. S6. EDX spectrum of solid precursors hydrothermally obtained at 180 ^{o}C for 2 h.

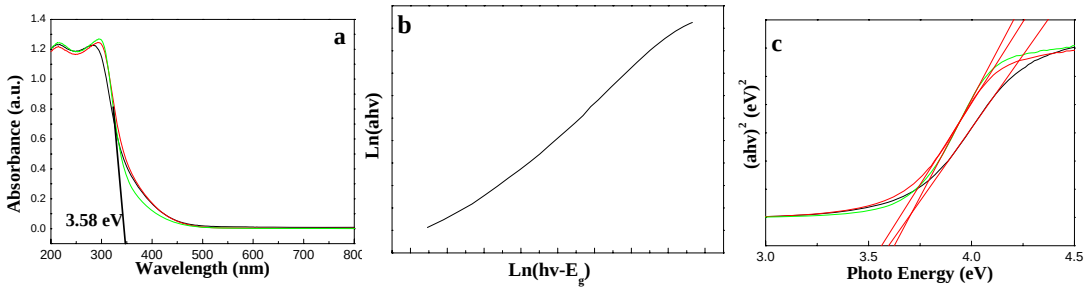


Fig. S7. The determination of the band gap of $NaY(MoO_4)_2$ octahedrons, cubes, and thin plates.

According to the equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α, h, ν, A, E_g, and n are the absorption coefficient, Planck's constant, the incident light frequency, proportionality constant, the band-gap energy, and an integer, respectively. Among them, n depends on the characteristics of the optical transition in a semiconductor, i.e., direct transition (n = 1) or indirect transition (n = 4). Using the approximate E_g value of 3.58 eV (Fig. S7a), plot ln(αhν) vs ln(hν - E_g), and then determine the value of n with the slope of the straightest line near the band edge. The obtained n value equals 1 (Fig. S7b), suggesting $NaY(MoO_4)_2$ is direct semiconductor. The band-gap energy of the samples can be thus estimated from a plot of $(\alpha h\nu)^2$ versus the photon energy (hν). The estimated band-gap energies of the as-obtained $NaY(MoO_4)_2$ octahedrons, cubes, and thin plates were about 3.63, 3.60, and 3.56 eV from the absorption onsets (Fig. S7c), respectively.

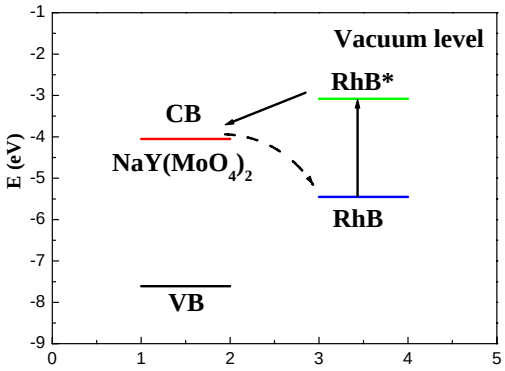


Fig. S8. The energy diagrams of RhB and $NaY(MoO_4)_2$. The solid arrows indicate the charge separation and the dotted arrow indicates the charge recombination.

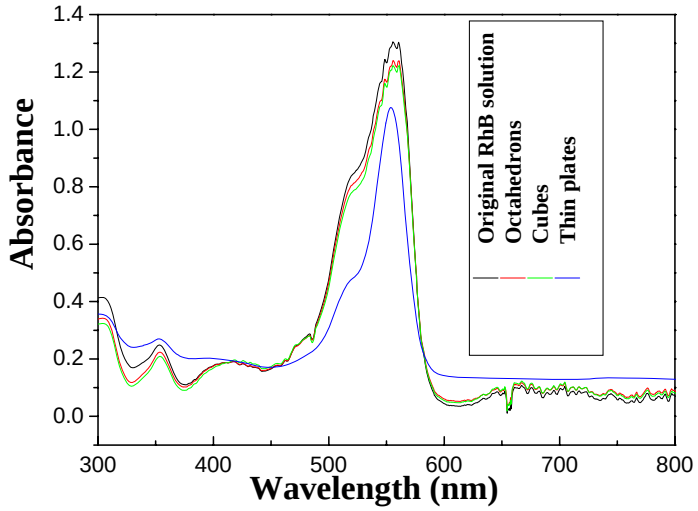


Fig. S9. Uv-vis absorption spectra of original RhB solution and in the presence of octahedrons, cubes, thin plates after adsorption-desorption equilibrium.

The influence of reaction temperature and more amount of Na_2MoO_4 on morphology of the final products

As shown in Fig. S10a and S10b, when 20 and 24 mmol of Na_2MoO_4 were employed, the average thickness of $NaY(MoO_4)_2$ thin plates were *ca*. 55 and 40nm, respectively. Reaction temperature somewhat affects the thickness and diameter of the final products when it is 160 and 200 ^oC, respectively. (See Fig. S10c and S10d).

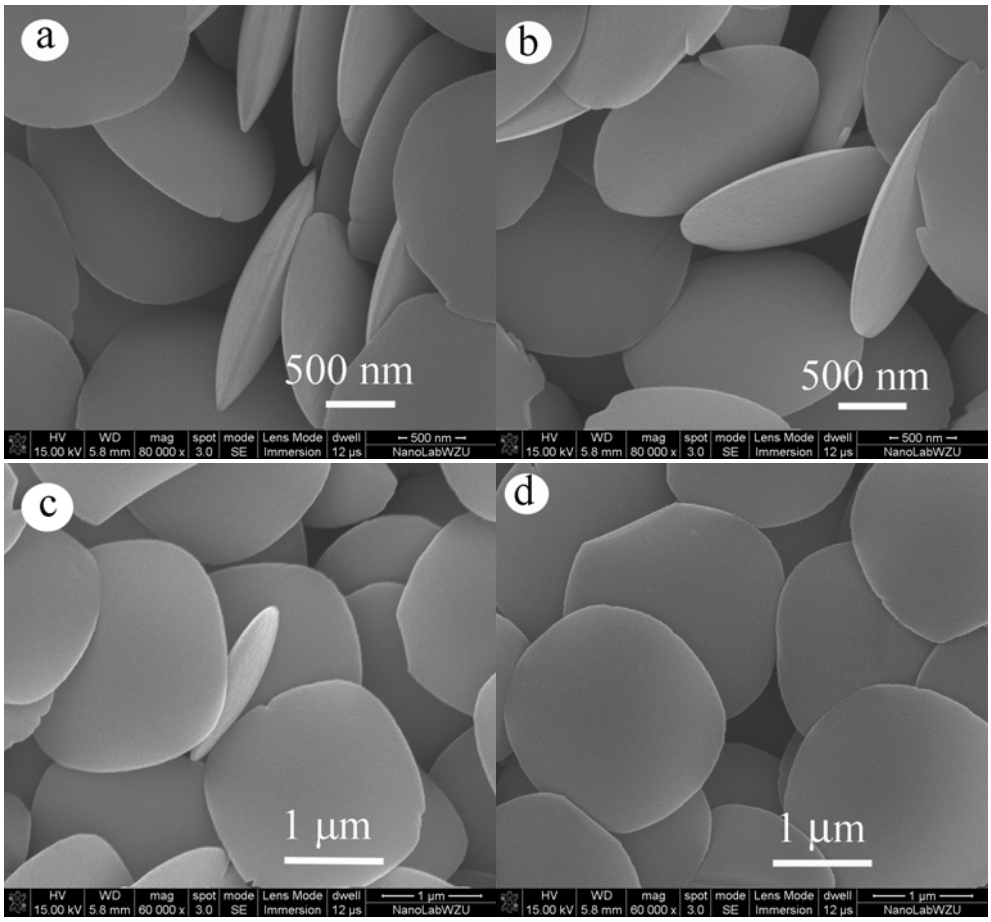
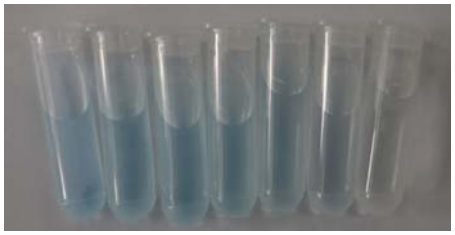


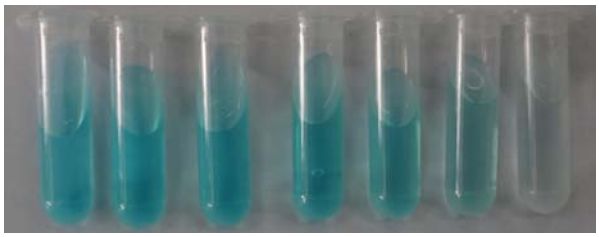
Fig. S10. FESEM images of the products obtained at different reaction conditions: (a) with use of 20 mmol of Na_2MoO_4, (b) with use of 24 mmol of Na_2MoO_4, (c) at 160 ^oC, and (d) 200 ^oC.

The photocatalytic performance of $NaY(MoO_4)_2$ thin plates to different dyes under visible light irradiation



Indigo

Alizarin green



Methylene blue

Rhodamine B

0 min → 15 min → 30 min → 1 h → 2 h → 4 h → 8 h

As seen from photos of the samples degraded for different time period, $NaY(MoO_4)_2$ thin plates showed good photocatalytic performance for degradation of rhodamine B, methylene blue, indigo, and alizarin green.