Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

**Supplementary Information**

# Pd-Decorated *m*-$BiVO_4$/BiOBr Ternary Composite with Dual Heterojunction for Enhanced Photocatalytic Activity

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## MATERIALS AND METHODS

### Chemicals

Hexadecyltrimethylammonium bromide (CTAB, ≥99.0% (AT), Sigma), ammonium metavanadate ($NH_4VO_3$, ACS, 99.0% minimum, Alfa Aesar), bismuth(III) nitrate hydrate ($Bi(NO_3)_3$•$xH_2O$, Puratronic, 99.999% (metals basis), Alfa Aesar), palladium(II) acetate ($Pd(CH_3COO)_2$, 99.9%, Acros organics), Rhodamine B (RhB, ≥95% (HPLC), Sigma), 4-chlorobiphenyl (PCB3, AccuStandard), tetrachloro-m-xylene (TCMX, AccuStandard), hexane (Omnisolv, 98.5%, EMD Millipore) and ethyl alcohol (ACS/USP grade, 200 proof, Pharmaco-Aaper) were used as received. High purity deionized water (18.2 MΩ·cm) was used during the particle preparation.

### Photocatalyst synthesis

The *m*-$BiVO_4$/BiOBr composite was synthesized by a modified surfactant assisted aqueous route. Briefly, 117 mg $NH_4VO_3$ was dissolved in 10 mL of water at 90 °C, stirred vigorously for 10 min, and then cooled down to room temperature. The $NH_4VO_3$ solution was added dropwise into a two-neck flask containing 20 mL of 0.05 M CTAB solution under vigorous stirring (500 rpm) at 60 °C. Next, 970 mg $Bi(NO_3)_3$•$xH_2O$ was added to 10 mL of water and stirred for 10 min at room temperature. Afterwards, the formed white suspension was added dropwise into the two-neck flask, the temperature was set to 80 °C, and the mixture was stirred for 16 h. Finally, the *m*-$BiVO_4$/BiOBr yellow product was filtered and washed with water and ethanol for several times and dried in air at room temperature. To deposit Pd nanodomains on the material, 220 mg of *m*-$BiVO_4$/BiOBr composite was dispersed in 290 mL of ethanol; then, 22 mg of $Pd(CH_3COO)_2$ was added and stirred overnight in the dark. Finally, the greenish product was filtered, washed with ethanol several times and dried in air at room temperature.

## Characterization

Morphological investigations of the samples were carried out on a Philips XL30 field-emission environmental SEM equipped with an Oxford energy-dispersive X-ray detector and running at 20 kV, while TEM experiments were performed using a JEOL JEM-1400 TEM running at 80 kV. HRTEM, dark-field STEM, and EDS elemental mapping were conducted on an FEI Tecnai F30 running at 300 kV, and equipped with an EDAX energy dispersive x-ray spectrometer with a 30 mm$^2$ Si(Li) detector. X-ray photoelectron spectroscopy measurements were carried out using an electron spectrometer manufactured by OMICRON Nanotechnology GmbH (Germany). The photoelectrons were excited both by MgKα (1253.6 eV) and AlKα (1486.6 eV) radiation. Spectra were recorded in the Constant Analyser Energy mode of the EA125 energy analyzer with 30 eV pass energy resulting in a spectral resolution of ~1 eV. Samples in the form of fine powder were pressed into pellets. Data were processed using the CasaXPS software package [N. Fairley, www.casaxps.com, 2006] by fitting the spectra with Gaussian-Lorentzian product peaks after removing a Shirley or linear background. Chemical states were identified using XPS databases [C.D. Wagner, A.V. Naumkin, A. Kraut-Vass, J.W. Allison, C.J. Powell, J.R. Rumble Jr., NIST X-ray Photoelectron Spectroscopy Database, Version 3.4, National Institute of Standards and Technology, Gaithersburg, MD 2003; (http://srdata.nist.gov/xps/), J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben: Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp. Eden Prairie, Minnesota, USA, 1992]. X-ray powder diffraction (XRD) patterns were obtained in a Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer using CuKα radiation ($\lambda$= 0.15418 nm), a graphite monochromator, and a proportional counter. Silicon powder (NIST SRM 640) or corundum was used as internal standard, and the scans were evaluated with profile-fitting methods. The UV-vis DRS measurements were performed on a Shimadzu UV-2600 spectrophotometer.

## Rhodamine B and 4-chlorobiphenyl degradation

Photocatalytic activities of the samples were measured by following the degradation of RhB and PCB3 in water at room temperature. All experiments were carried out using a Sol1A Class ABB 94061A solar simulator (Newport Corporation, USA) with 100 mW cm$^{-2}$ power output produced by a 1000-W xenon lamp. In the RhB degradation experiments, 20 mg of photocatalyst was dispersed in 18 mL of water, and then 2 mL of RhB solution (100 mg L$^{-1}$) was added in the dark. After stirring for 30 s in the dark, the suspension was exposed to irradiation. At given time intervals, a 0.5-mL aliquot was taken and centrifuged to separate the particles. The visible spectra of the supernatants were measured using a Shimadzu UV-2600 spectrophotometer. To study the stability of the *m*-$BiVO_4$/BiOBr/Pd photocatalyst for multiple cycles, the photocatalytic degradation of RhB was conducted as described above, but taking only one 200-μL sample after 10 min of irradiation. Subsequently, the reaction was conditioned under the solar simulator irradiation for 30 min to eliminate any carbonaceous residues from the catalyst active sites. At the end of 30 min, the irradiation was stopped and a fresh amount of 4 gL$^{-1}$ RhB solution was injected into the reaction to attain 10 mgL$^{-1}$ as the starting concentration. Then, the reaction was irradiated in the same manner, and the entire process was repeated for 12 consecutive cycles.

In PCB3 degradation experiments, 50 mg of photocatalyst was dispersed in 50 mL of 15 μM PCB3 solution. The suspension was exposed to irradiation, and at given time intervals 0.5 mL of the suspension was taken and combined with 0.5 mL hexanes in order to extract the PCB and degradation products. Reaction progress analysis was conducted via GC-MS (Agilent 5975C GC-MS, Santa Clara, CA) using TCMX as an internal standard.

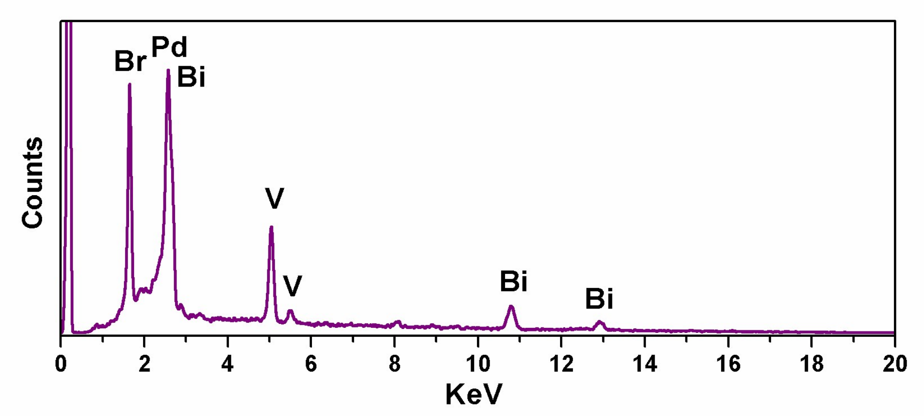
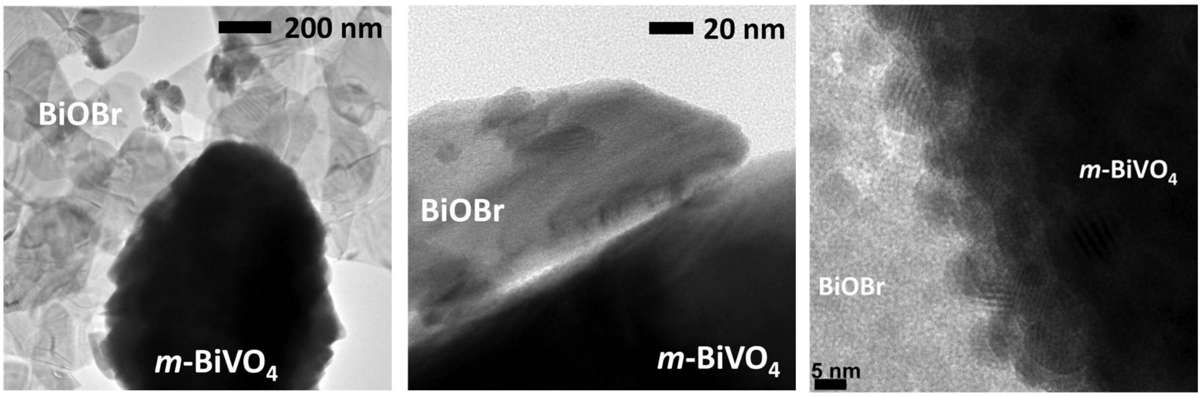


**Fig. S1** EDS analysis of the *m*-$BiVO_4$/BiOBr/Pd composite.



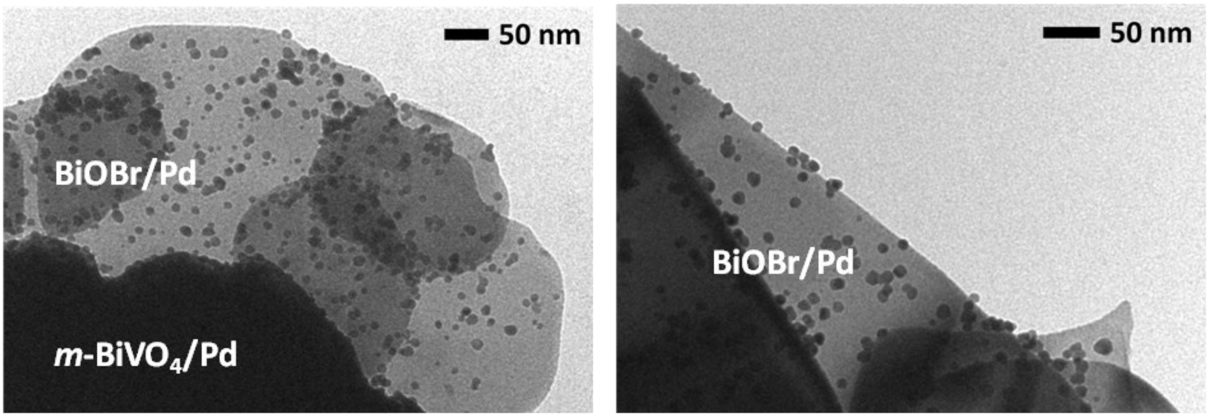
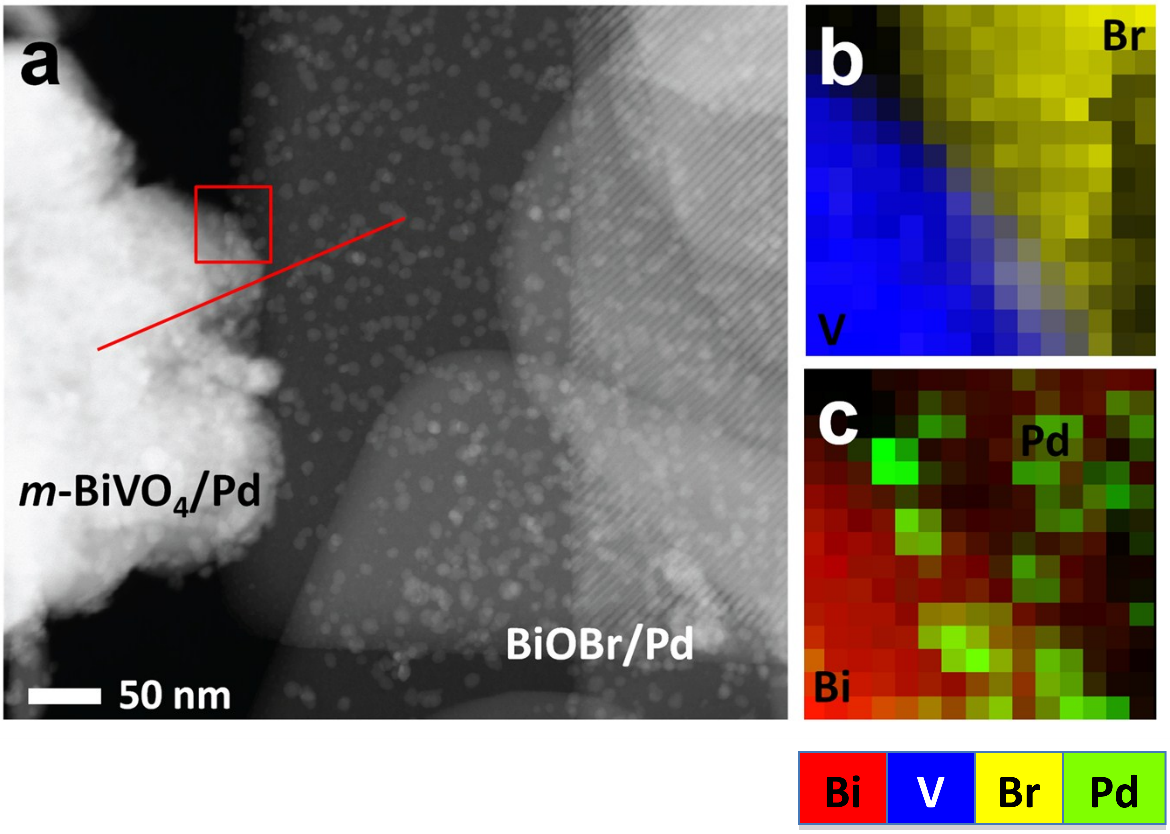


**Fig. S2** TEM analysis of the *m*-$BiVO_4$/BiOBr and *m*-$BiVO_4$/BiOBr/Pd composite.



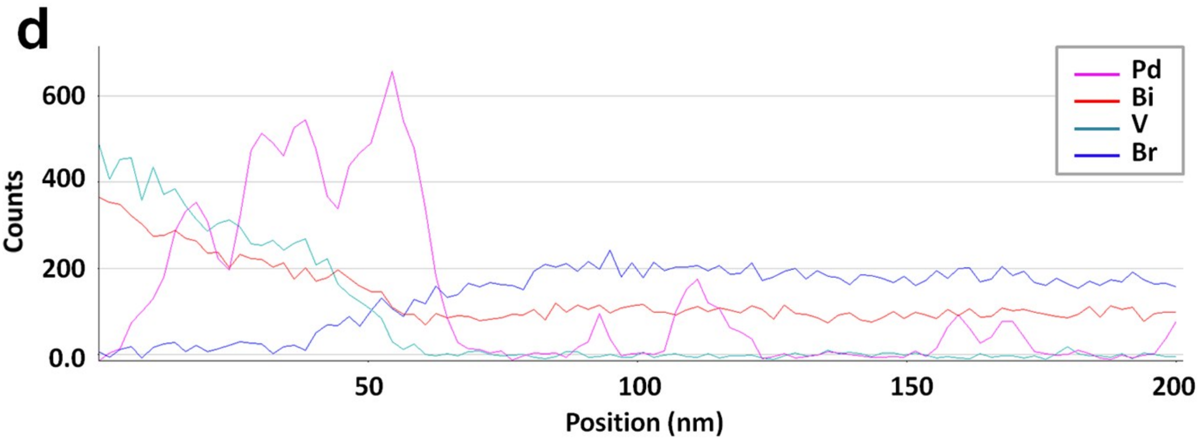


**Fig. S3** (a) Dark field STEM image, (b, c) EDS mapping and (d) EDS line scan performed in STEM mode of the *m*-$BiVO_4$/BiOBr/Pd composite.

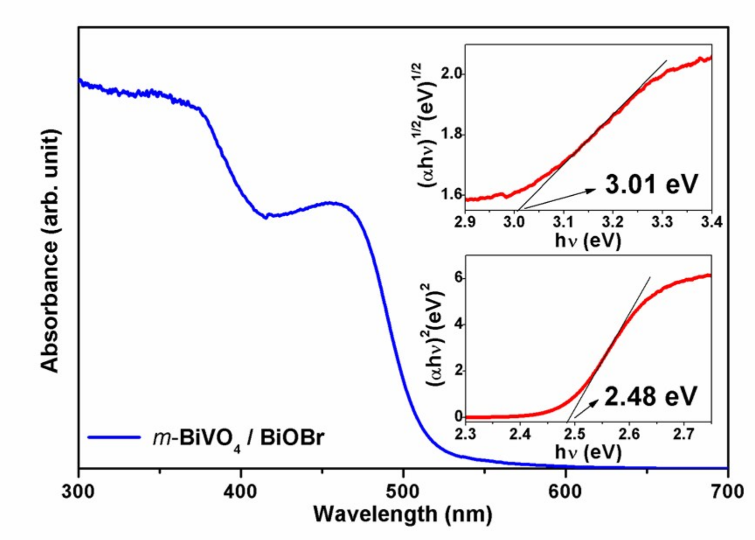


**Fig. S4** UV-vis DRS spectrum and band gap ($E_g$) values of the *m*-$BiVO_4$/BiOBr composite.

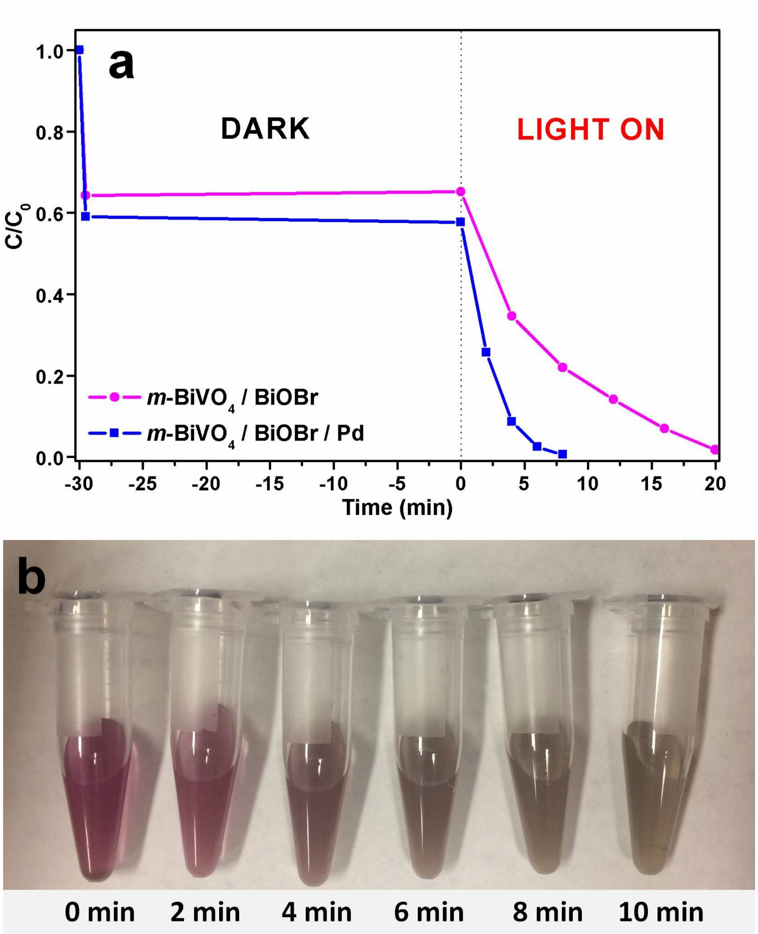
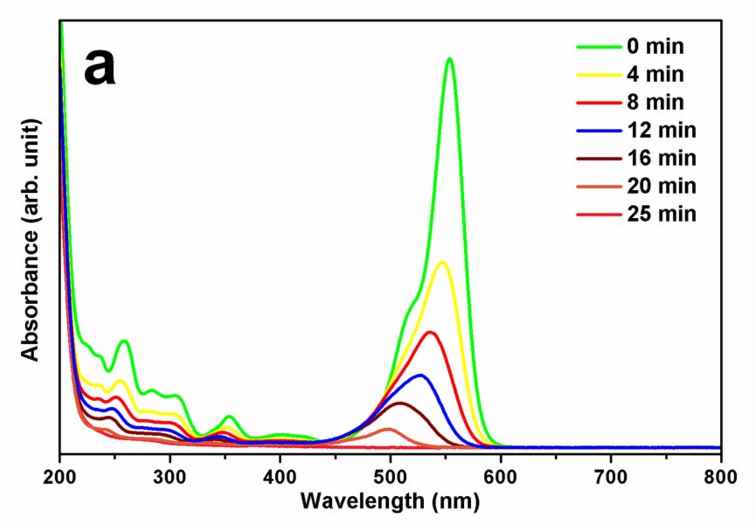


**Fig. S5** (a) Photocatalytic degradation of RhB (10 mg $L^{-1}$) as a function of time and (b) photograph of the *m*-$BiVO_4$/BiOBr/Pd reaction progress.



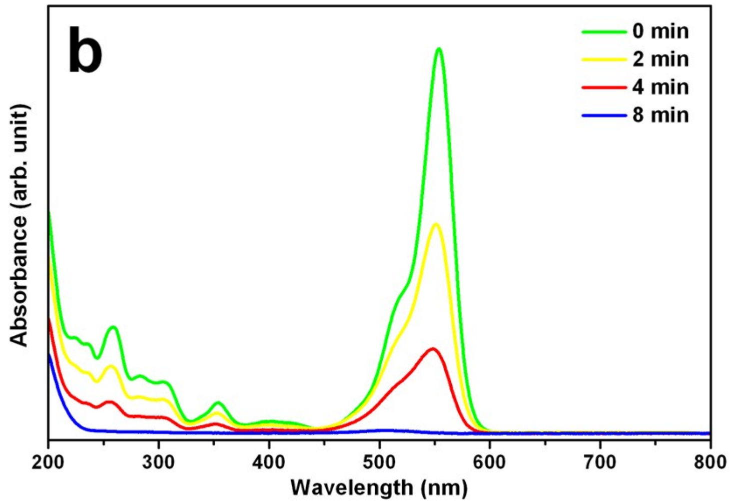


**Fig. S6** UV-vis absorption spectra of RhB in the presence of (a) *m*-BiVO$_4$/BiOBr and (b) *m*-BiVO$_4$/BiOBr/Pd composite.

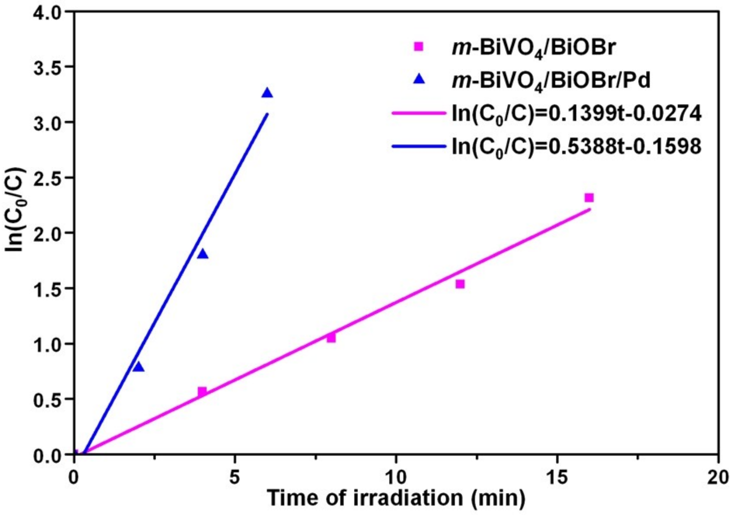


**Fig. S7** Kinetics of RhB degradation.

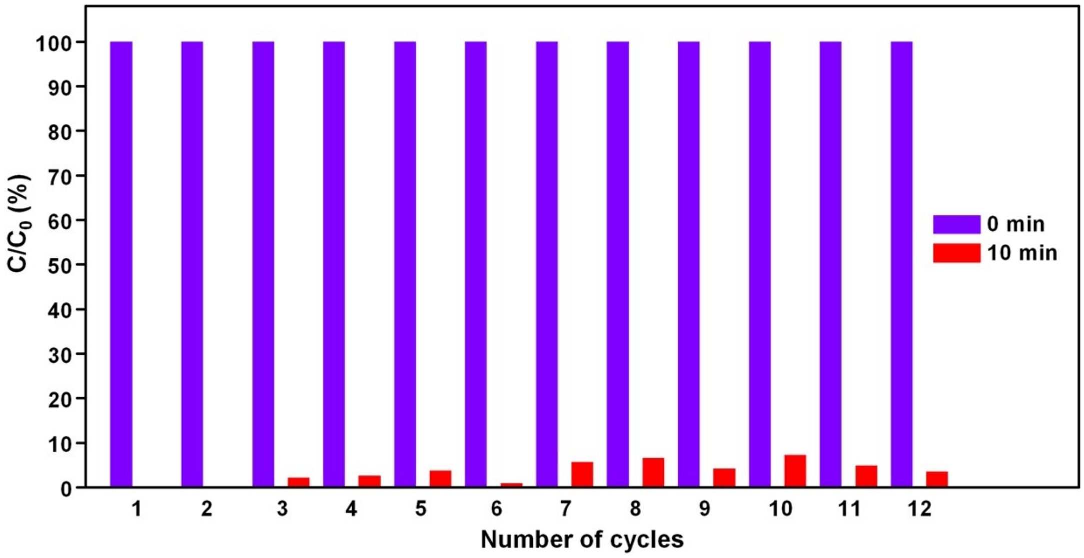


**Fig. S8** Cycling runs in the photocatalytic degradation of RhB (10 mg $L^{-1}$) in the presence of *m*-$BiVO_4$/BiOBr/Pd composite.

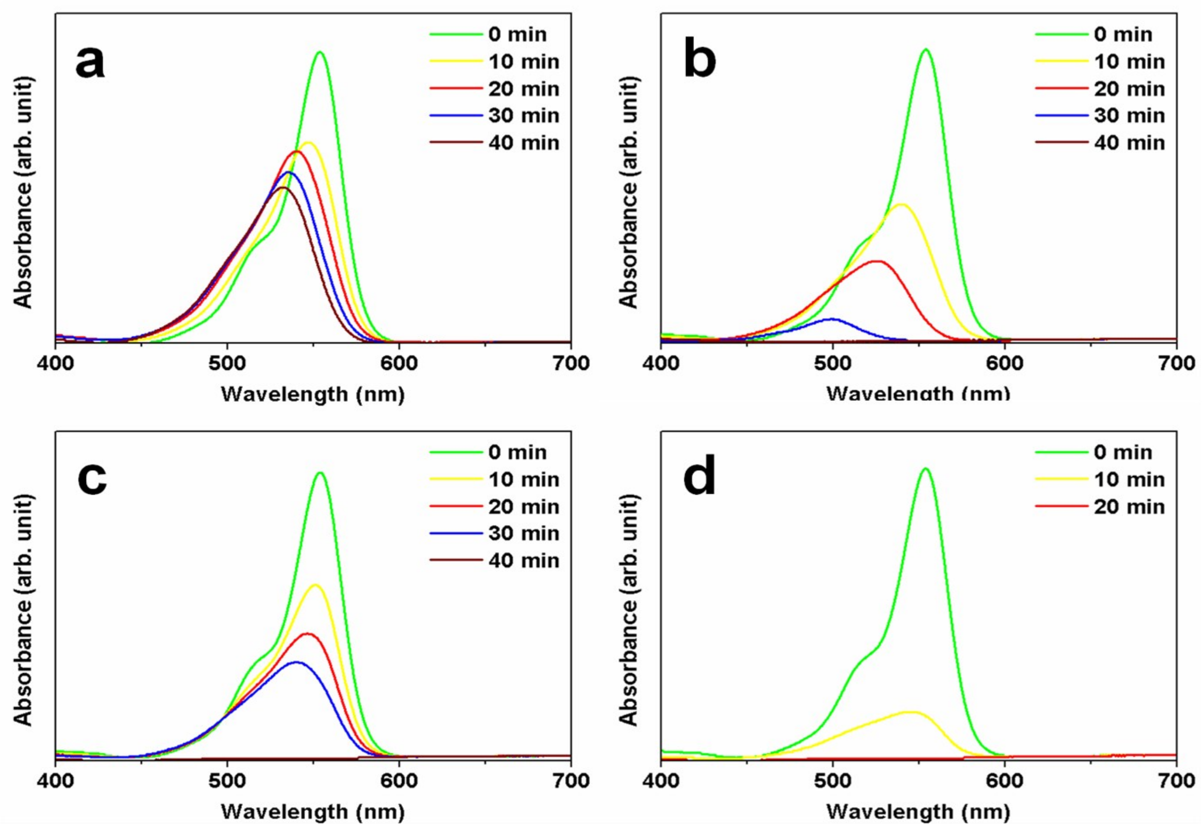


**Fig. S9** UV-vis absorption spectra of RhB in the presence of (a, b) *m*-$BiVO_4$/BiOBr and (c, d) *m*-$BiVO_4$/BiOBr/Pd composite in (a, c) $N_2$-purged and (b, d) air-equilibrated solution.