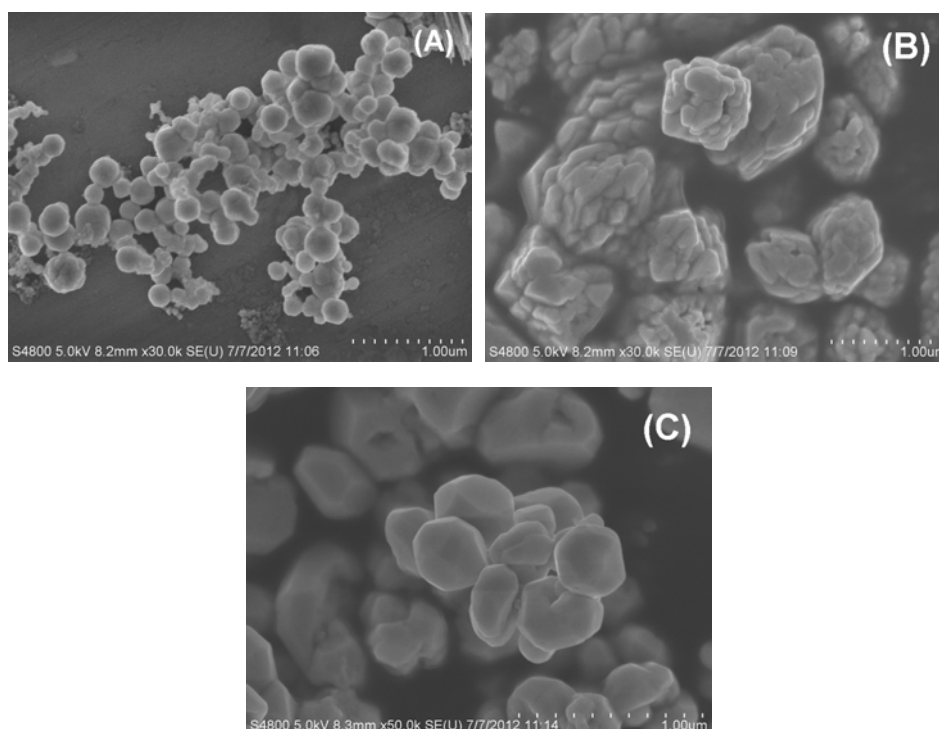


## Tandem Photocatalytic Oxidation of Rhodamine B over Surface Fluorinated Bismuth Vanadate Crystals

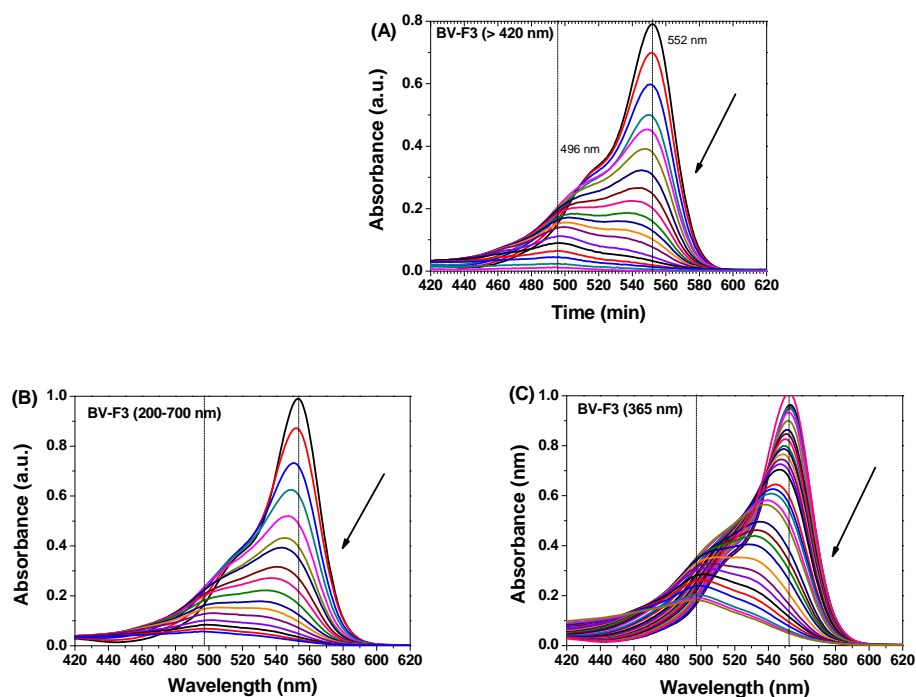
Shengwei Liu, Kai Yin, Wanshu Ren, Bei Cheng, Jiaguo Yu\*

State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, Luoshi Road 122#, Wuhan 430070, P. R. China, Fax: 86-027-87879468; Tel: 86-027-87871029; E-mail: [jiaguoyu@yahoo.com](mailto:jiaguoyu@yahoo.com)



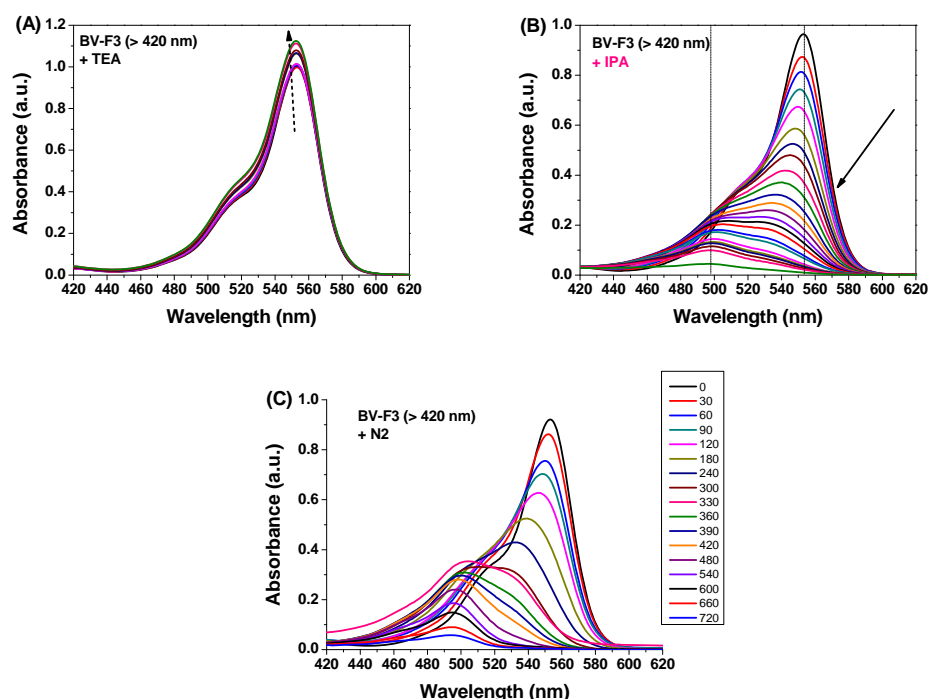
**Figure S1** SEM images of the time-dependent morphology evolution of sample BV-F3. (A) Before hydrothermal treatment,  $\text{BiVO}_4$  spherical aggregates are obtained; (B) after hydrothermal treatment for 3 h, smaller polyhedral crystals evolved within the  $\text{BiVO}_4$  spherical aggregates; (C) after hydrothermal treatment for 7 h, larger polyhedral crystals are isolated.

Normally, the formation of single microcrystals follows the typical dissolution-recrystallization (Ostwald ripening) mechanism. The time-dependent evolution experiments of sample BV-F3 basically supported the dissolution-recrystallization mechanism. As shown in Figure S1, amorphous  $\text{BiVO}_4$  aggregates gradually evolved into increasingly larger  $\text{BiVO}_4$  polyhedra.



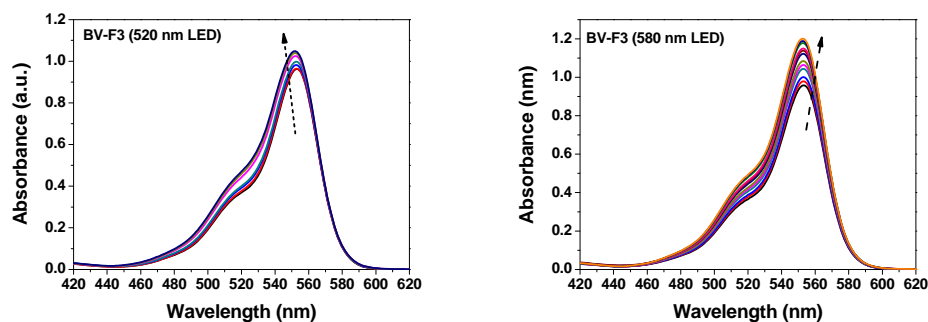
**Figure S2** The photocatalytic oxidation of RhB molecules over BV-F3 photocatalyst under different excitation light source: (A) 350 W xenon lamp with a 420 nm cutoff filter (> 420 nm); (B) 350 W xenon lamp without cutoff filter (200-700 nm); (C) 15W monochromatic 365 nm UV-lamp.

Although the photocatalytic reactivity is varied with (Figure S2 (A)) versus without (Figure S2 (B)) 420 nm cutoff filter, the photocatalytic processes are basically similar whether the cutoff filter is used or not, that is, separate de-ethylation process and subsequent mineralization process. Moreover, using 365 nm UV-lamp as excitation light source (Figure S2 (C)), the photocatalytic processes are also similar. It is indicated that the photocatalytic mechanism for as-synthesized BiVO<sub>4</sub> photocatalyst is the same under light irradiation when excitation wavelength is within the light response range of 200-500 nm.



**Figure S3** The temporal spectral changes of RhB solution over sample BV-F3 under visible light irradiation with 350 W xenon lamp with a 420 nm cutoff filter (> 420 nm) in the presence of different scavengers: (A) tri-ethanolamine (TEA) as hole scavenger; (B) isopropanol (IPA) as  $\cdot\text{OH}$  scavenger; (C)  $\text{N}_2$  as  $\cdot\text{O}_2^-$  scavenger.

The involved active species for photocatalytic RhB oxidation over fluorinated  $\text{BiVO}_4$  photocatalyst was investigated via controlled experiments using different scavengers. Our results were basically consistent with previous reports.<sup>16</sup> Without the incorporation of hole (using triethanolamine as hole scavenger), the photocatalytic oxidation of RhB was almost completely ceased, highlighting the crucial role of hole in initiating the photocatalytic oxidation of RhB molecules. In contrast, without the incorporation of  $\cdot\text{OH}$  (using isopropanol as hydroxy radicals ( $\cdot\text{OH}$ ) scavenger), the photocatalytic oxidation of RhB was not affected too much, ruling out the necessary contribution from  $\cdot\text{OH}$  in photocatalytic oxidation of RhB molecules. In addition, by pumping  $\text{N}_2$  for 30 min, the mineralization process (decrease rate in characteristic peak of rhodamine located at 496 nm) is significantly reduced, highlighting the crucial role of  $\cdot\text{O}_2^-$  in the mineralization process.



**Figure S4** The photocatalytic oxidation of RhB molecules over BV-F3 photocatalyst under 3 W monochromatic LED-lamp: (A) 520 nm; (B) 580 nm.

Using 520 nm and 580 nm LED-lamp as the excitation light source, the absorbance of the treated RhB solution is not decreased with increasing irradiation time, but slightly increased due to the evaporation of water. In this sense, the contribution from DS-initiated pathway is minor for the decomposition of RhB molecules.