Electronic Supplementary Information

New Fe-Doped Two-dimensional $BiVO_4$ Nanosheets for Direct Methane Conversion to Methyl Oxygenates

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Preparation of $BiVO_4$ microcrystals

The $BiVO_4$ microcrystals was prepared by dissolving 3.0 mmol $Bi(NO_3)_3{\cdot}5H_2O$ in a 20 mL aqueous solution of 2 M HNO_3 and the resultant solution was denoted as A. 3.0 mmol NH_4VO_3 in a 20 mL aqueous solution of 2 M HNO_3 the resultant yellow solution was denoted as solution B. 3 mmol $C_{18}H_{29}NaO_3S$ (SDBS) in a 20 mL aqueous solution of 2 M HNO_3 and the resultant solution was denoted as solution C. Then, solutions A, B and C were mixed together to form a translucent, yellow solution under vigorous stirring. The pH of the combined solution was adjusted to an acid concentration of 1 M by adding deionized water to prevent the salts from precipitating, and stirred continuously for 2 h. The translucent solution was poured into three different 50 mL Teflon-lined stainless-steel autoclaves until 80% of the volume of each autoclave was occupied. The Teflon-lined stainless-steel autoclaves were sealed and heated in an oven at 150 °C for 5 h. After the hydrothermal treatment, the autoclaves were cooled naturally to room temperature. After cooling, each sample was transferred to a centrifuge tube, centrifuged at 10000 rpm for 5 min during each centrifuging cycle by washing with deionized water for three times and once with absolute ethanol. The vivid yellow precipitate obtained was dried in vacuum at 40 °C overnight and calcined at 250 ^{o}C for 2 h before collecting the yellow powder for activity test.

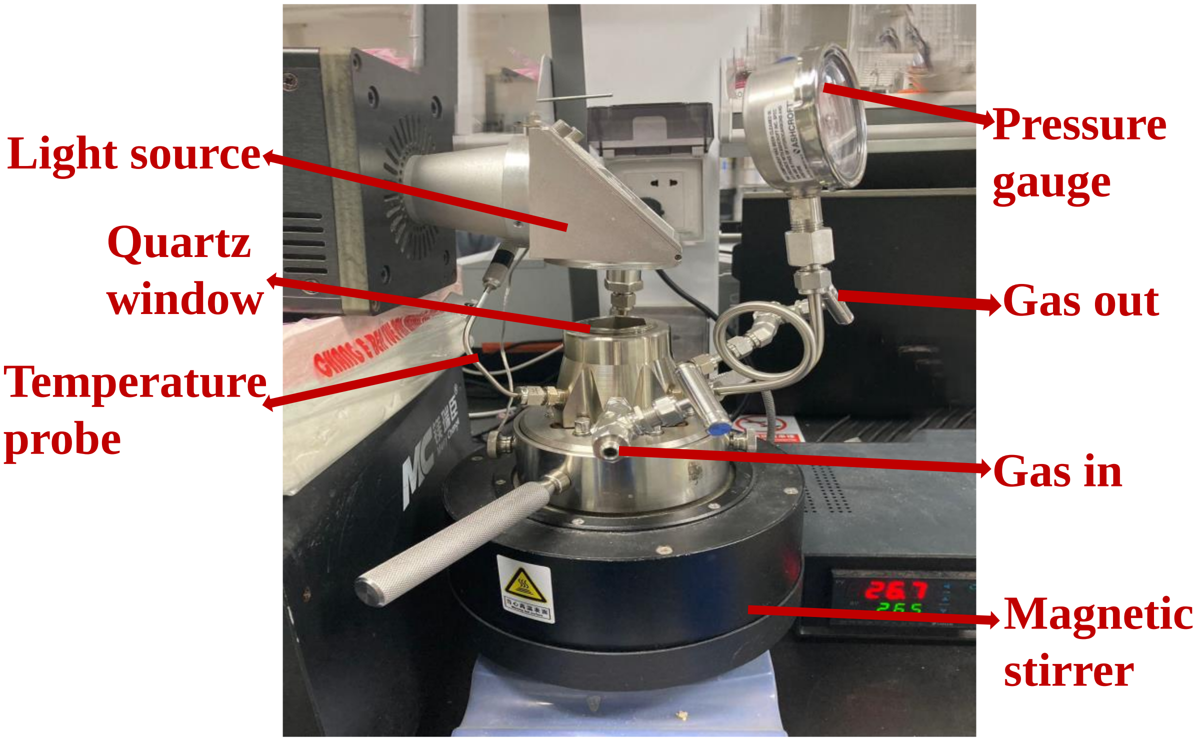

Fig. S1. Batch-type photoreactor experimental set-up

Crystalline structure of $BiVO_4$ microcrystals

Fig. S2 presents the typical XRD pattern of the $BiVO_4$ microcrystals, which can be indexed well with the pure phase of monoclinic scheelite $BiVO_4$ (JCPDC card No. 14-0688). Also, the peak splitting around 19^o and 35^o of the 2θ angles, magnified in the insets gives clear evidence to differentiate the monoclinic phase of the synthesized product from the tetragonal structure (JCPDS No. 14-0133).

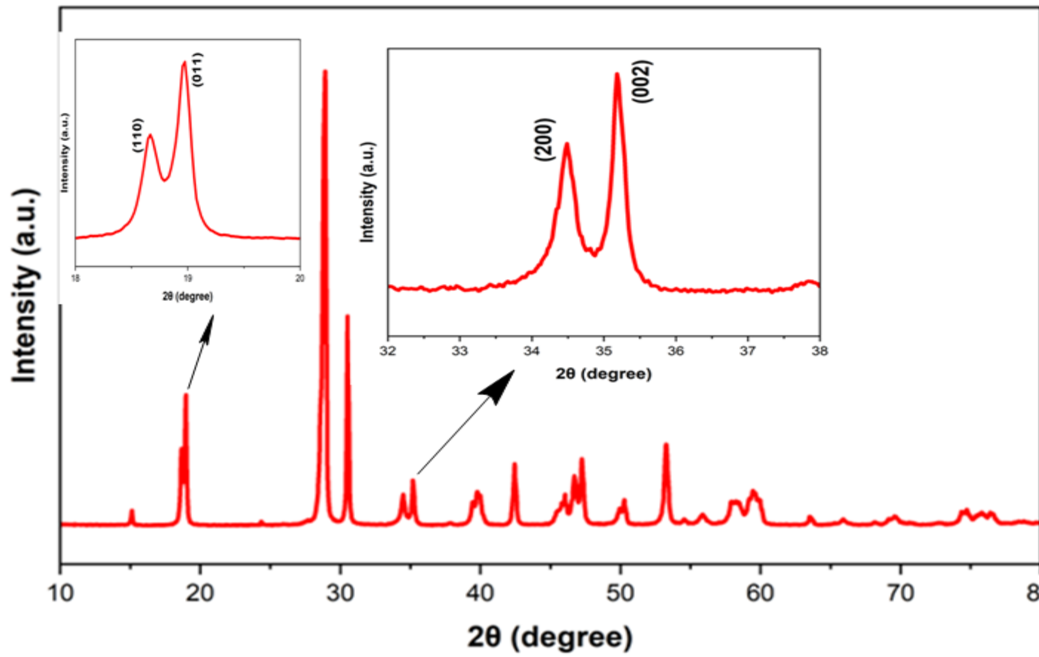

Fig. S2. XRD patterns of $BiVO_4$ microcrystal. Insets are the enlarged views of peaks around 2θ = 19º and 35º.

Photocatalytic performance evaluation

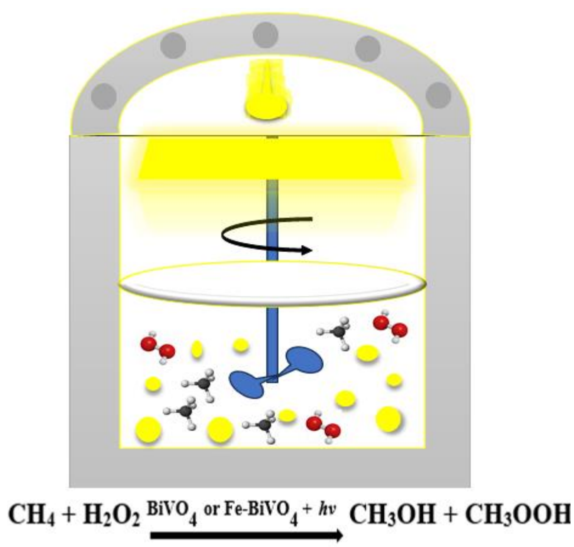

Fig. S3. Schematic illustration of the reaction inside the batch-type reactor vessel.

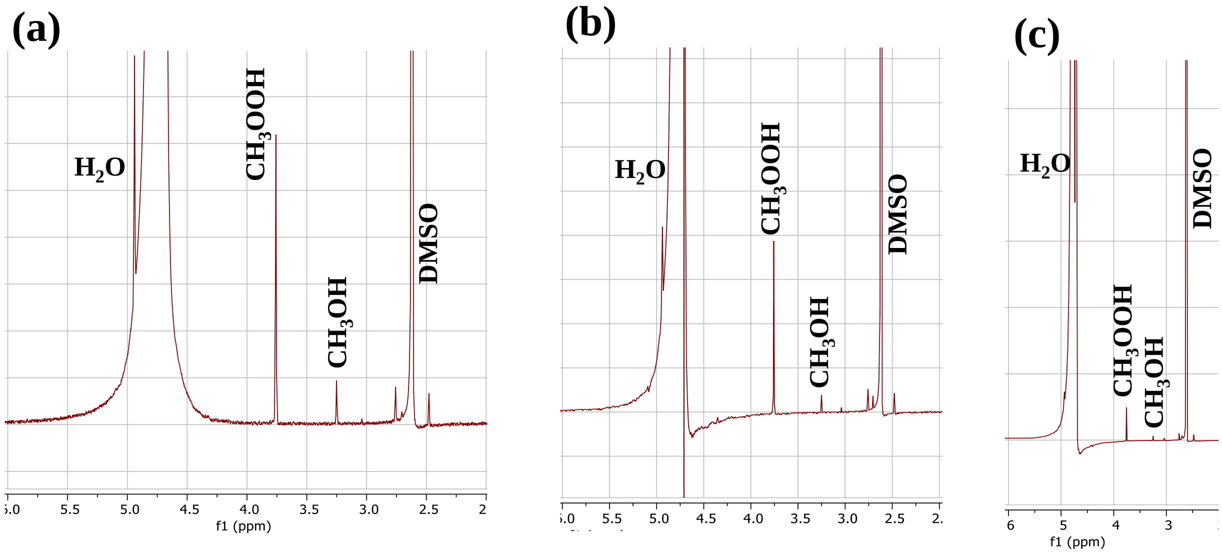

Fig. S4. Representative ^{1}H-NMR spectra collected for the methane oxidation products using 100 μL H_2O_2 as the oxidant under 2 h of light irradiation at 40 ^{o}C for (a) 1.0-Fe-$BiVO_4$ and (b) undoped $BiVO_4$; (c) control experiment without light irradiation.

Table S.1 Summary from literature of the photocatalytic conversion of CH_4 to primary oxygenated products in $BiVO_4$ and other photocatalyst systems in comparison to this work.

Ref. #	Catalyst	Oxidant	Gas	Reaction tempera-ture (ºC)	Reaction time (min)	Light source	Primary oxygenated products selectivity/%	Primary oxygenated products productivity/ $\mu mol g^{-1} h^{-1}$
This work	**Fe-$BiVO_4$ nanosheets**	100 µL H_2O_2	CH_4	40	120	Visible light (≥ 420 nm)	100	217.6
	$BiVO_4$ nanosheets	100 µL H_2O_2	CH_4	40	120	Visible light (≥ 420 nm)	100	149.6
[1]	**WO_3 flowers**	2 mM H_2O_2	20% CH_4 in N_2	50	120	UV-light	-	38.17 ± 3.24
[2]	**q-$BiVO_4$ nanoparticles**	O_2	CH_4	25	180	Visible light (400–780 nm)	96.6	366.67
[3]	**FeOOH/m-WO_3**	1.5 mM H_2O_2	10% CH_4 in N_2	25 ± 1	240	visible-light (420–780 nm)	91.0	211.2
[4]	**Bipyramid $BiVO_4$ microcrystals**	H_2O	10% CH_4 in Ar	65	60	Visible light (350–800 nm)	85.0	111.9
	Thick platelet $BiVO_4$ microcrystals	H_2O	10% CH_4 in Ar	65	60	Visible light (350–800 nm)	85.7	79.2

	Thin platelet $BiVO_4$ microcrystals	H_2O	10% CH_4 in Ar	65	60	Visible light (350–800 nm)	58.2	65.7
[5]	**$FeOx/TiO_2$**	2 mM H_2O_2	20% CH_4 in Ar	25	180	(≤710 nm)	≥90	352
[6]	**$BiVO_4$ + V_2O_5 on beta zeolite**	H_2O	20% CH_4 in He	70	120	450 W Hg lamp	6.4	10.7
	$BiVO_4$ + V_2O_5 on beta zeolite	H_2O	20% CH_4 in He	70	120	450 W Hg lamp + Pyrex filter	100	3.3
[7]	**$BiVO_4$ thick platelets**	H_2O + $NaNO_2$	20% CH_4 in He	55	90	450 W Hg-lamp	≥90	11
	$BiVO_4$ thick platelets	H_2O	20% CH_4 in He	55	90	450 W Hg-lamp	42.0	19.9
[8]	**Bi_2WO_6 flowers**	H_2O	20% CH_4 in He	55	120	450 W Hg-lamp	29.3	15.6
	Bi_2WO_6/TiO_2 composite	O_2	20% CH_4 in He	55	120	450 W Hg-lamp	7.9	10.8
	$BiVO_4$ thick platelets	H_2O	20% CH_4 in He	55	120	450 W Hg-lamp	51.0	20.8

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