Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

In situ modification of $BiVO_4$ nanosheets on graphene for boosting photocatalytic water oxidation

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1. Supplementary Note

The reaction mechanism under two synthetic strategies

Conventional synthesis strategy:

$$BiCl_3 + H_2O + GO \xrightarrow{\text{Hydrolysis}} 2H^+ + 2Cl^- + BiOCl/GO$$

$$BiOCl/GO + VO_3^- \xrightarrow{\text{Hydrothermal}} \text{impure-}BiVO_4/Graphene$$

In situ modification strategy:

$$BiCl_3 + Cl^- + CTA^+ + GO \xrightarrow{\text{Self-assembly}} BiCl_4^- - CTA^+/GO$$

$$BiCl_4^- - CTA^+/GO + VO_3^- + H_2O \xrightarrow{\text{Hydrothermal}} 4Cl^- + CTA^+ + 2H^+ + \text{ultrapure-}BiVO_4/Graphene$$

2. Supplementary Figures

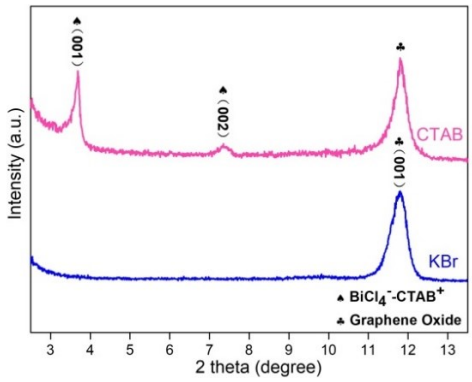

Fig S1. Small-angle X-ray scattering patterns for different intermediate products prepared with CTAB or KBr assistance.

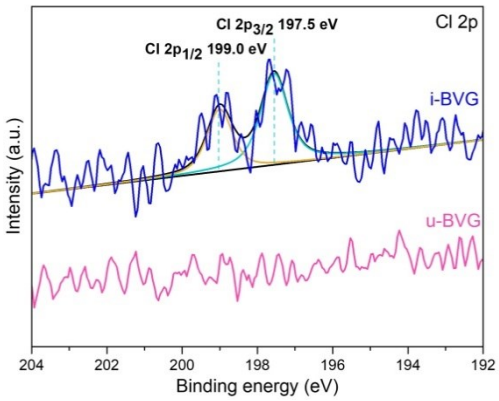

Fig S2. High-resolution Cl 2p XPS spectra for the i-BVG and the u-BVG. Different from the u-BVG, the photoelectron peaks at 199.0 eV and 197.5 eV are assigned to the Cl $2P_{1/2}$ and Cl $2P_{3/2}$ peaks, respectively, indicating that the Cl is as Cl^- anions in the i-BVG.

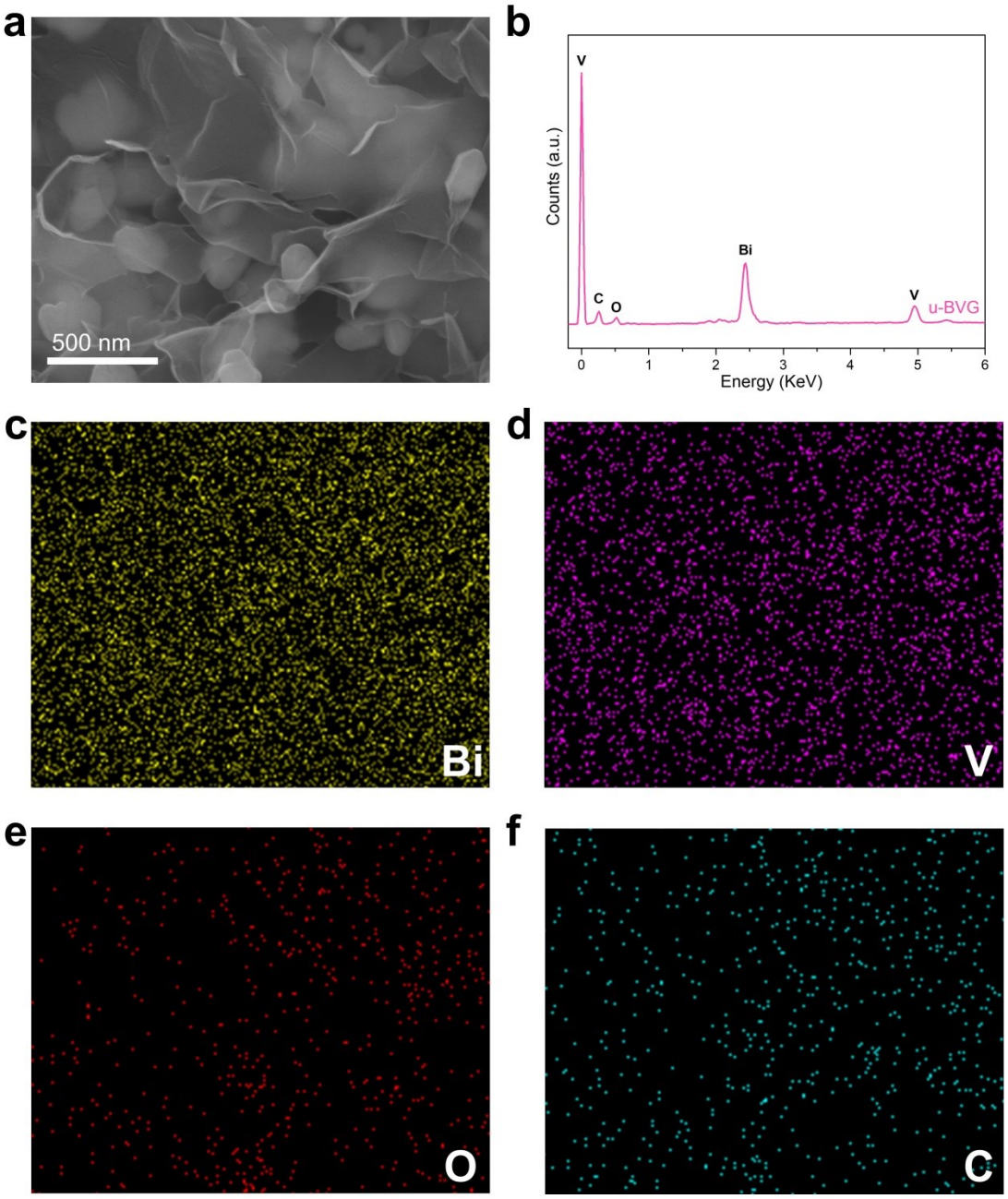

Fig S3. Characterizations of the physical structure for the u-BVG. a) SEM image and b) the corresponding EDS spectra, here the EDS spectra clearly show that bismuth (Bi), vanadium (V), oxygen (O), and carbon (C) are the main constituent elements in accord with c-f) the elemental mapping images, and the elemental mapping images confirm the homogeneous distribution of Bi, V, O, and C.

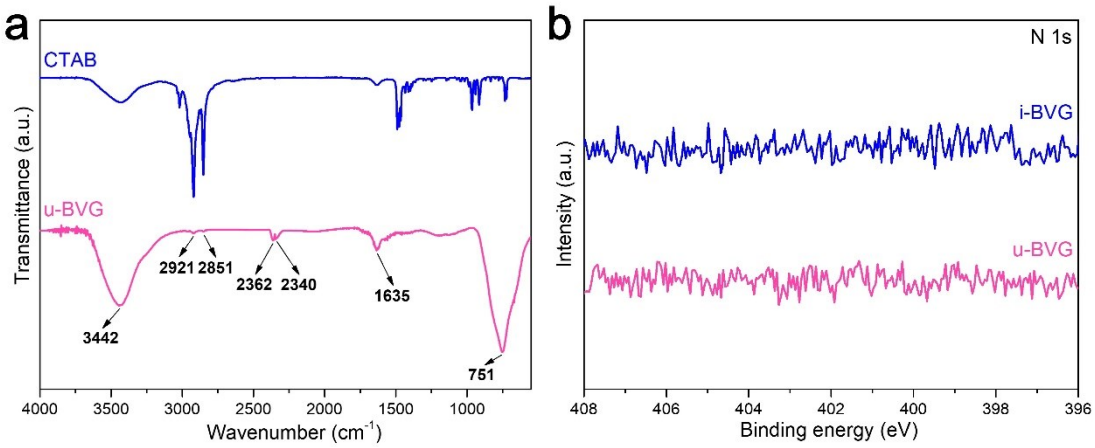

Fig S4. a) FT-IR spectra for the CTAB and the u-BVG. b) High-resolution N 1s XPS spectra for the i-BVG and the u-BVG. As shown in Figure S4a, it can be clearly found that CTA^+ cations are thoroughly removed by comparison. For the u-BVG, FT-IR bands at 3442 cm^{-1} and 1635 cm^{-1} are resulted from the bending vibration of adsorbed H_2O molecules, whereas the bands at 2362cm^{-1} and 2340 cm^{-1} are due to the trace CO_2 impurity. In addition, it can be seen that the representative absorptions of the graphene composition are at 2921 cm^{-1} and 2851 cm^{-1} representing $-CH_2-$ stretching vibration, the peak at 751 cm^{-1} is attributed to the υ_3 asymmetric stretching vibration of the VO_4 unit $\upsilon_3(VO_4)$[1]. Moreover, Figure S4b provides N 1s XPS spectra, it is observed that the residual CTA^+ cations on the u-BVG are rare as the i-BVG without the introduction of CTAB during the synthesis process, which further implies that most of CTA^+ cations could be thoroughly removed by washing after the synthesis process.

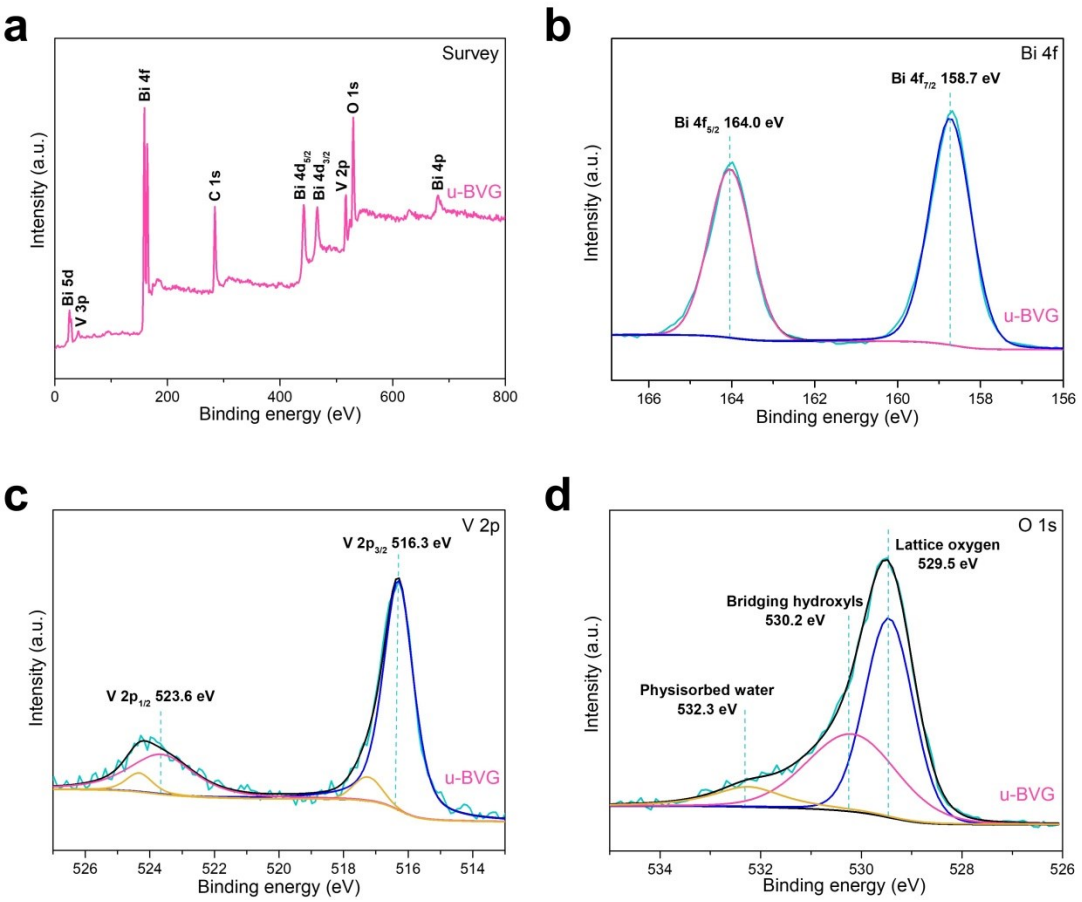

Fig S5. Characterizations of the chemical statue for the u-BVG. a) XPS survey spectra and high-resolution XPS spectra of b) Bi 4f, c) V 2p, and d) O 1s. The XPS survey spectra in Figure S5a show that the u-BVG is primarily composed of bismuth (Bi), vanadium (V), oxygen (O), and carbon (C), which further confirms the u-BVG contains only ultrapure $BiVO_4$. For the u-BVG, Figure S5b is Bi 4f spectra, the peaks located at 164.0 eV and 158.7 eV are assigned to the Bi $4f_{5/2}$ and Bi $4f_{7/2}$ peaks, respectively, confirming that the bismuth species in the sample are Bi^{3+} cations. Figure S5c is V 2p spectra, the photoelectron peaks at 523.6 eV and 516.3 eV are assigned to the V $2P_{1/2}$ and V $2P_{3/2}$ peaks, respectively, indicating that the vanadium species are V^{5+} cations in the sample, and the other two small peaks represent the V-C bonds[2]. Figure S5d is O 1s spectra, first two peaks at 529.5 eV and 530.2 eV are

assigned respectively to lattice oxygen and bridging hydroxyls[3, 4], which corresponds to the O^{2-} anions in the sample, however, the peak at 532.3 eV belongs to physisorbed water because the open metal sites on the u-BVG surface have strong interaction with the surrounding water[5].

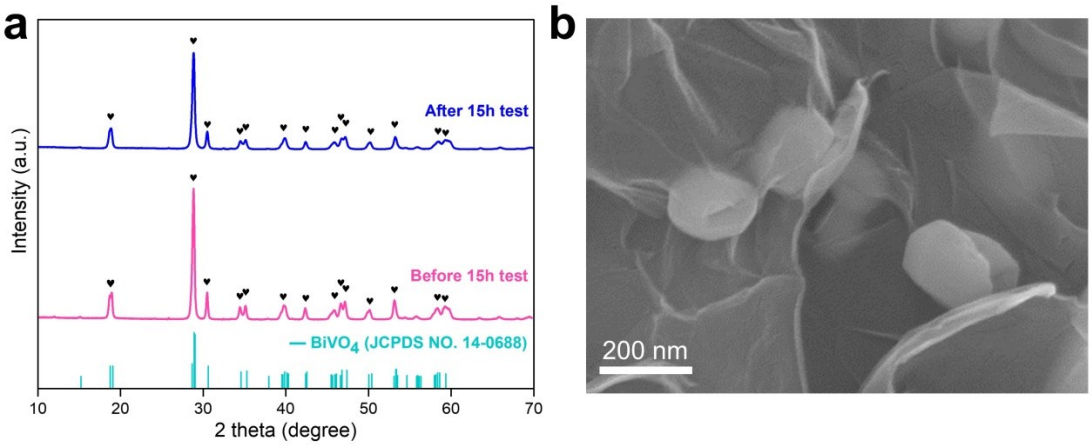

Fig S6. **Characterizations for the u-BVG after photocatalytic water oxidation cycle tests. a) XRD patterns before and after the continuous 15 h tests and b) SEM image after the 15 h cycle tests.** As shown in Figure S6a, the XRD patterns of u-BVG could be still indexed to monoclinic-$BiVO_4$ (JCPDS No. 14−0688) after 15h photocatalytic test, demonstrating its excellent phase structure stability. In addition, the SEM image in Figure S6b exhibits that its microstructure and morphology do not show any obvious change after the same process, further demonstrating its favorable photostability.

3. Supplementary Table

Table S1 Comparison of apparent quantum efficiency of u-BVG with the well-known photocatalysts reported in the recent references.

Photocatalyst	Light Source	Sacrificial Agent	AQE (%)	Reference
u-BVG	**300 W xenon lamp**	**0.15 M $Fe(NO_3)_3$**	**19.8 (420 nm)**	**This work**
$C_8N_2H_4$	150 W xenon lamp	0.2 M $AgNO_3$	3.8 (420 nm)	*Energy & Environmental Science.* **2018**, *11*, 1617-1624
BP/$BiVO_4$	320 W xenon lamp	0.1 M $AgNO_3$	0.89 (420 nm)	*Angewandte Chemie International Edition.* **2018**, *57*, 2160-2164
$PbCrO_4$	300 W xenon lamp	0.02 M $AgNO_3$	1.0 (420 nm)	*RSC Advances.* **2015**, *5*, 1452–1455
$SrTiO_3$:La,Rh/ Au/$BiVO_4$	300 W xenon lamp	0.02 M $AgNO_3$	5.9 (418 nm)	*Journal of Catalysis.* **2015**, *328*, 308–315
30-facets $BiVO_4$ polyhedron	300 W xenon lamp	0.02 M $NaIO_3$	18.3 (430 nm)	*Advanced Materials.* **2018**, *30*, 1703119
CDs/$BiVO_4$QDs	300 W xenon lamp	Absence	0.63 (420 nm)	*Nanoscale.* **2016**, *8*, 17314-17321

$SrTiO_3/Ag_3PO_4$	300 W xenon lamp	0.02 M $AgNO_3$	16.2 (420 nm)	*ACS Catalysis.* **2014**, *4*, 3020−3026
Mo-doped Bi_2WO_6	300 W xenon lamp	0.02 M $Na_2S_2O_8$	3.1 (420 nm)	*Journal of Materials Chemistry A.* **2016**, *4*, 13242-13250
$SiC/BiVO_4$	300 W xenon lamp	0.04 M $FeCl_3$	1.04 (420 nm)	*Chemical Engineering Journal.* **2015**, *281*, 102–108

4. Supplementary References

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