Electronic Supplementary Information (ESI)

$BiVO_4$ Tubular Structures: Oxygen Defect-Rich and Largely Exposed Reactive {010} Facets Synergistically Boost Photocatalytic Water Oxidation and the Selective N=N Coupling Reaction of 5-amino-1H-tetrazole

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Experimental Section

Reagents: Bismuth nitrate pentahydrate (AR 99%) were obtained from Aladdin Industrial corporation. Ammonium metavanadate (AR), sodium hydroxide (AR) and ethanol absolute (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Analytical grade sodium dodecylbenzensulfonate(SDBS) and nitric acid were purchased from Chengdu Kolong Chemical Reagent Co., Ltd and Nanjing Chemical Reagent Co., Ltd, respectively. Analytical grade sodium dimethyldithiocarbamate were obtained from Chengdu Aikeda Chemical Reagent Co., Ltd. All chemicals were used as received, unless otherwise stated. Deionized water was prepared with a Milli-Q puritysystem (18.2 MΩ).

Synthesis of $BiVO_4$ nanotube: For the synthesis of $BiVO_4$ nanotube, 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 0.5 g SDBS were dissolved in a nitric acid solution (noted as A solution). 2 mmol NH_4VO_3 were dissolved in a sodium hydroxide solution (noted as B solution). Then B solution was added into the A solution under vigorous stirring. After 30 min stirring, and the pH value of solution was then adjusted to 6.5 with 2M sodium hydroxide solution. The final 40 ml solution was transferred into a 100 ml Teflon-lined autoclave and maintained at 180 ℃ for 10 h, followed by naturally cooling to room temperature. The resulting solid products were collected through centrifugation at 12000 rpm for 5 min and were washed with deionized water and ethanol for several times, and finally dried in vacuum at 60°C for 12h.

Bulk $BiVO_4$ $BiVO_4$ sample: the reference sample was obtained by the solid-state reaction (SSR) of raw materials of Bi_2O_3 and V_2O_5 at 900 ^{o}C for 12 hours.

Characterizations: X-ray diffraction (XRD) was conducted on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 0.15406 nm), where the data was collected in the 2θ range of 20–80° at a step size of 0.02°. SEM images of solid products were measured on a Nova Nanosem 200 system operated at an acceleration voltage of 15 kV. Both transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on JEOL-3010 instrument. XPS was performed on a spectrometer from Kratos Axis Ultradld, using Mono Al Kα (1486.71eV) radiation at a power of 120 W (8 mA, 15 kV). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon. UV-vis diffuse reflectance spectra were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan), where fine $BaSO_4$ powder was used as a reflectance standard. The Brunauer–Emmett–Teller(BET) surface areas of the samples were measured by nitrogen adsorption using a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). Tapping-mode atomic force microscopy (AFM) images were obtained on DI Innova Multimode SPM platform. The transient time-resolved photoluminescence decay measurements were recorded on a fluorescence spectrometer (FLS920, Edinburgh Instruments Ltd, UK).

Photocatalytic H_2O splitting test: Photocatalytic activity in O_2 production was evaluated using a 400 mL Pyrex flask with a closed gas circulation and evacuation system. A 300 W Xe lamp with a UV-cut off filter ($\lambda \geq 420$ nm) was employed as the light source. In a typical experiment, 100.0 mg as-prepared photocatalyst powders was dispersed by using magnetic stirring in the 270 mL aqueous solution using 0.05 M $AgNO_3$ as the sacrificial reagent. Before irradiation, the suspension was pumped to remove any dissolved oxygen in order to guarantee that the reaction system was under anaerobic condition. Typically, amount of evolved gas was determined using a gas chromatograph (Shimadzu GC-2014C, argon carrier) equipped with a thermal conductivity detector (TCD).

The Photocatalytic coupling reaction of 5AT into SZT test: The reaction process was conducted in Pyrex flask with about 50 mL. In a typical experiment, 100mg as-prepared photocatalyst powders was dispersed by using magnetic stirring in the 22 mL 0.03 M Na_2CO_3-0.1 M 5AT aqueous solution with or without using 0.05 M $AgNO_3$ as the sacrificial reagent. 300 W Xe lamp with a UV-cut off filter ($\lambda \geq 420$ nm) was used as the light source. The temperature of the reaction solution could be maintained at approximately 293 K by continuous cooling with refrigerated circulating water. During the reaction process, 1.5mL was continually removed from the reaction cell at 180 min intervals under 420 nm light irradiation for subsequent SZT concentration was determined at the characteristic absorption peak of 418 nm by UV-vis spectrophotometric. The absorption spectrum shows that 0.2 M Na_2CO_3-0.1 M 5AT water solution has no characteristic absorption peak at range of 380-525 nm, whereas the standard SZT solution exhibits an obvious absorption peak at 418 nm (shown in Fig. S7, ESI†).

Computational detail: The optimization of monoclinic scheelite $BiVO_4$ unit cell has been carried out by means of VASP code[1,2] with the projector augmented wave (PAW) pseudopotentials.[3] The Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA) was adopted for the exchange correlation.[4] The bulk lattice parameter of $BiVO_4$ are relaxed and optimized using 400 eV as the cutoff energy for basis function and 6×6×3 Monkhorst-Pack type of k-points sampling. According to the experiment parameters of monoclinic scheelite $BiVO_4$,[5] β angle, which should be 90.383°, was set as 90° for simplification. The calculated lattice parameters for a unit cell are $a = 5.1773$Å, $b = 11.7609$Å, $c = 5.1450$Å, $\beta = 90^{\circ}$, which is in good agreement with the experiment data in reference 5. The (010) surface was presented by a slab model repeated periodically with a vacuum region of 15 Å.

References

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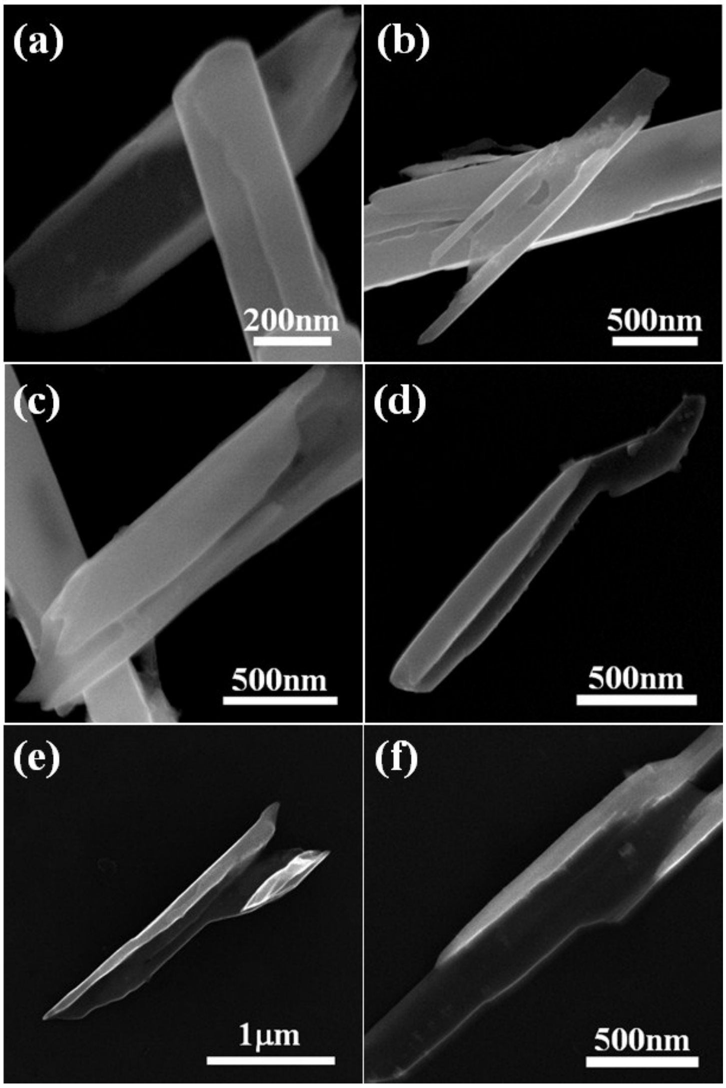

Fig. S1 FE-SEM images of curling nascent lamellar sheets, which did not completely develop into well-defined nanotubes.

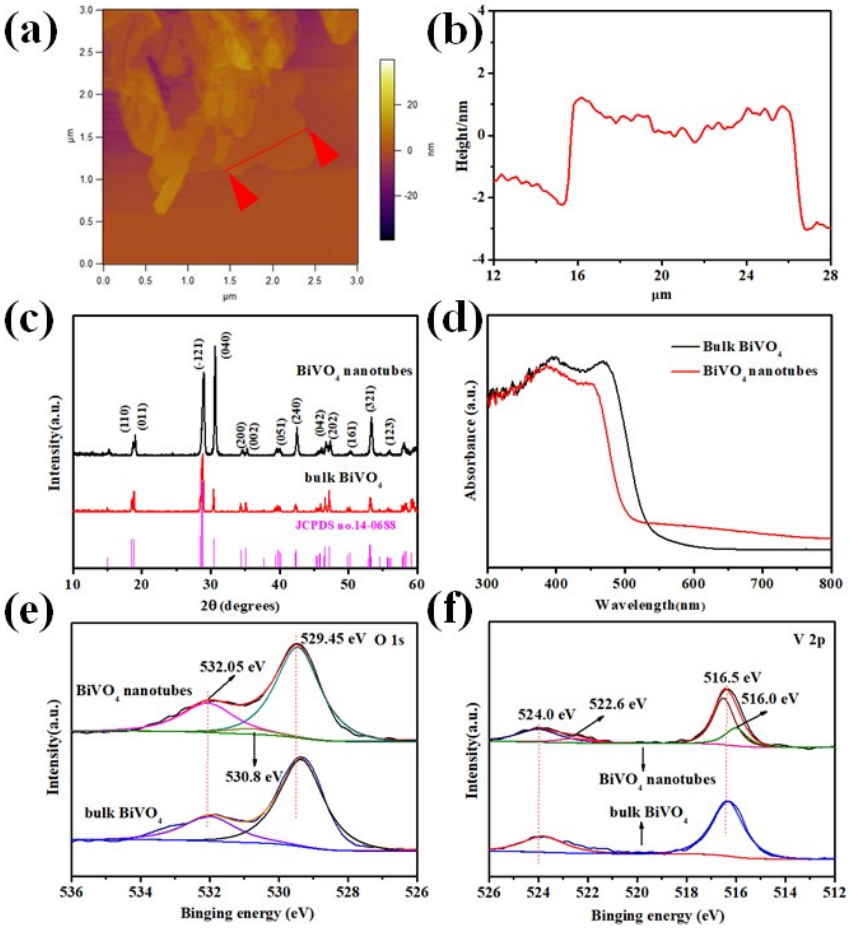

Fig. S2 Characterizations for $BiVO_4$ nanotubes and bulk $BiVO_4$: (a) AFM image of $BiVO_4$ nanotubes, (b) corresponding thickness analysis taken around the red line in (a), (c) XRD patterns, (d) UV/Vis absorption spectra (e) O 1s XPS spectra (f) V 2p XPS spectra.

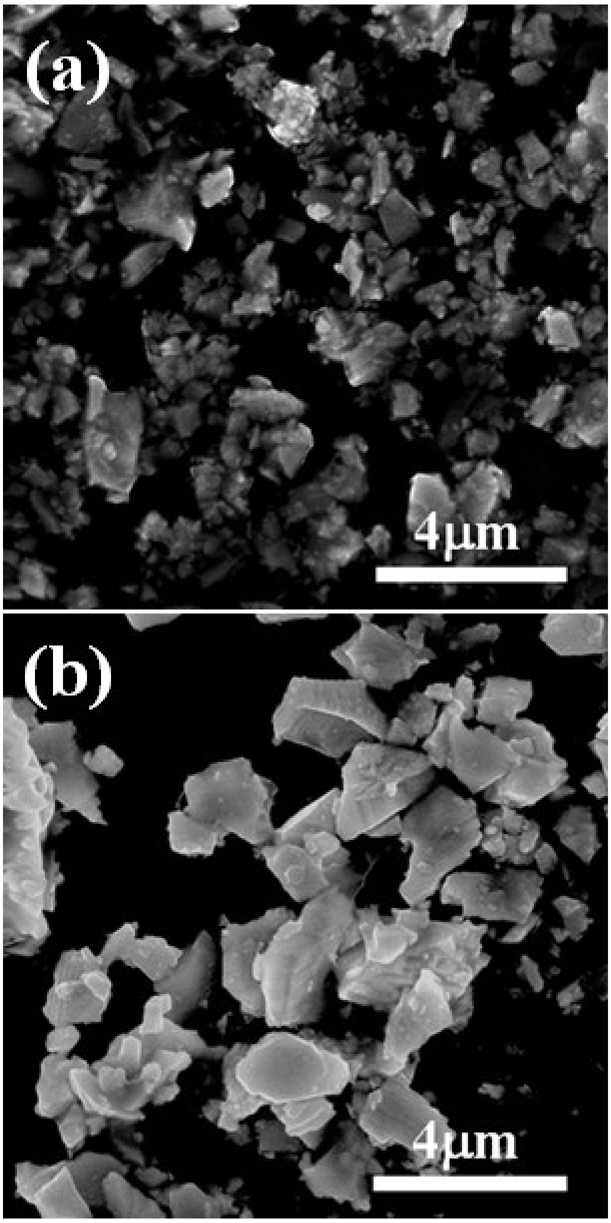

Fig. S3 (a and b) FE-SEM images of bulk $BiVO_4$

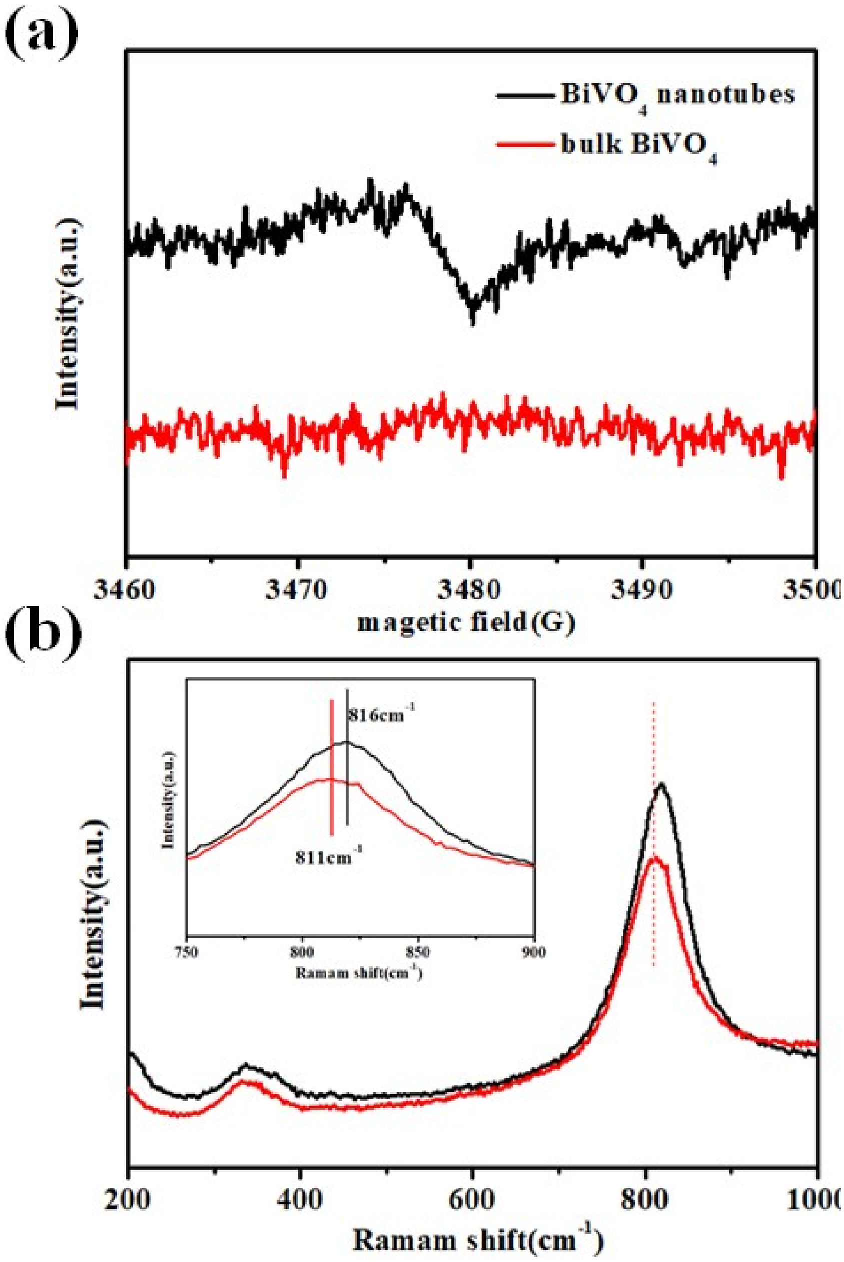

Fig. S4 Characterizations for $BiVO_4$ nanotubes and bulk $BiVO_4$: (a) EPR, (b) raman spectra of $BiVO_4$ nanotubes (black line) and bulk $BiVO_4$ (red line).

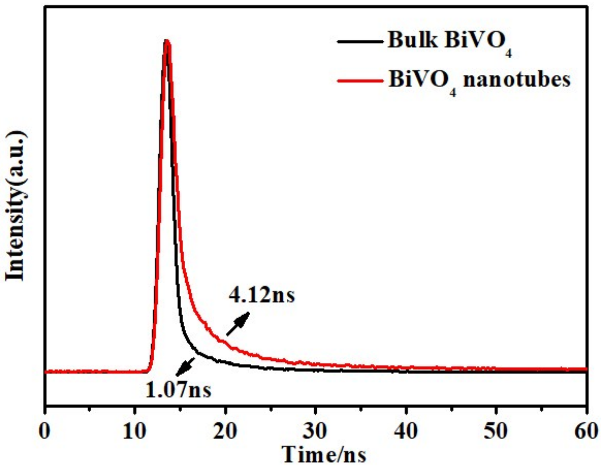

Fig. S5 Time-resolved transient PL decay for $BiVO_4$ of nanotubes and bulk $BiVO_4$.

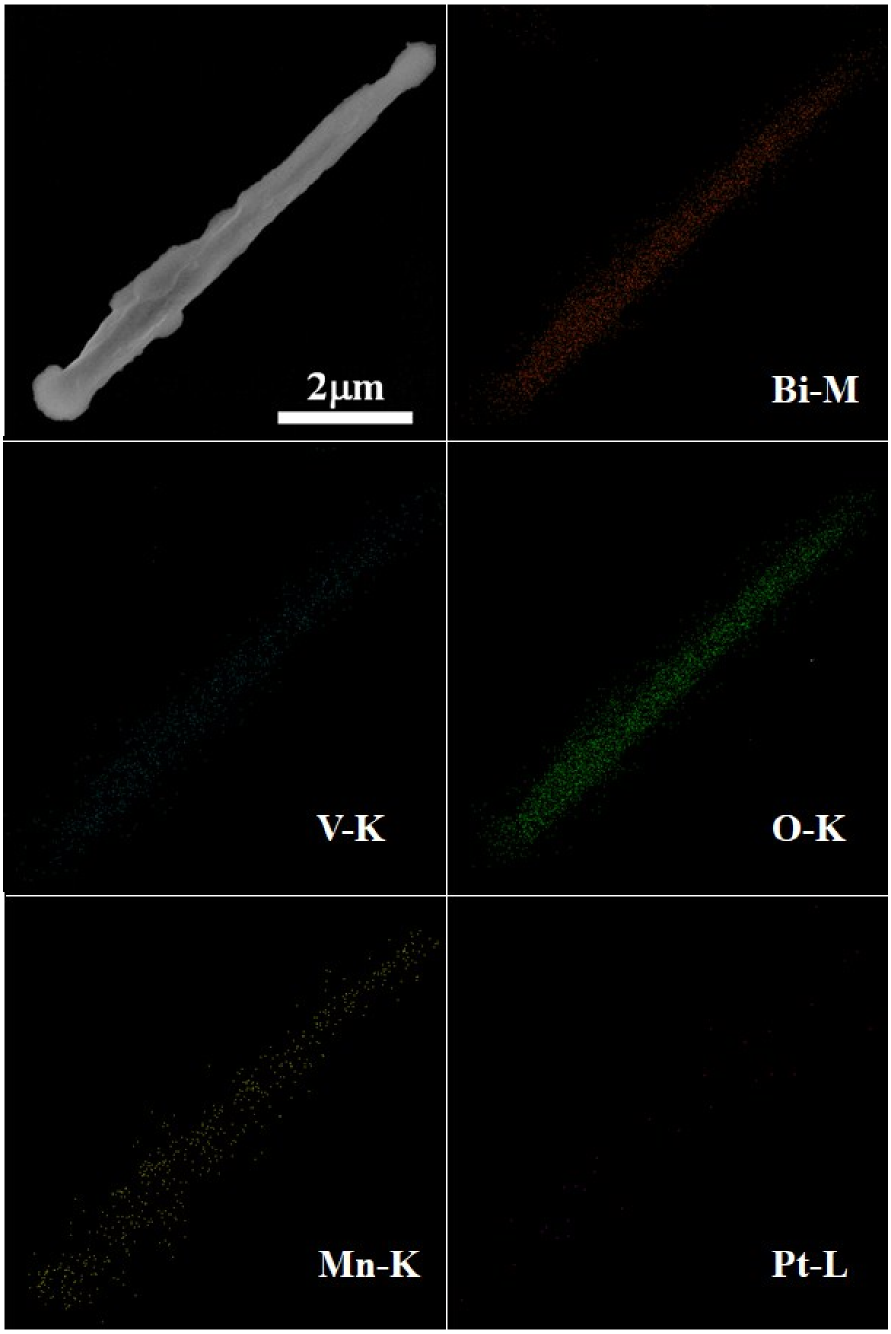

Fig. S6 FE-SEM image and the corresponding elemental mapping of $BiVO_4$ nanotubes coated with MnO_X and Pt.

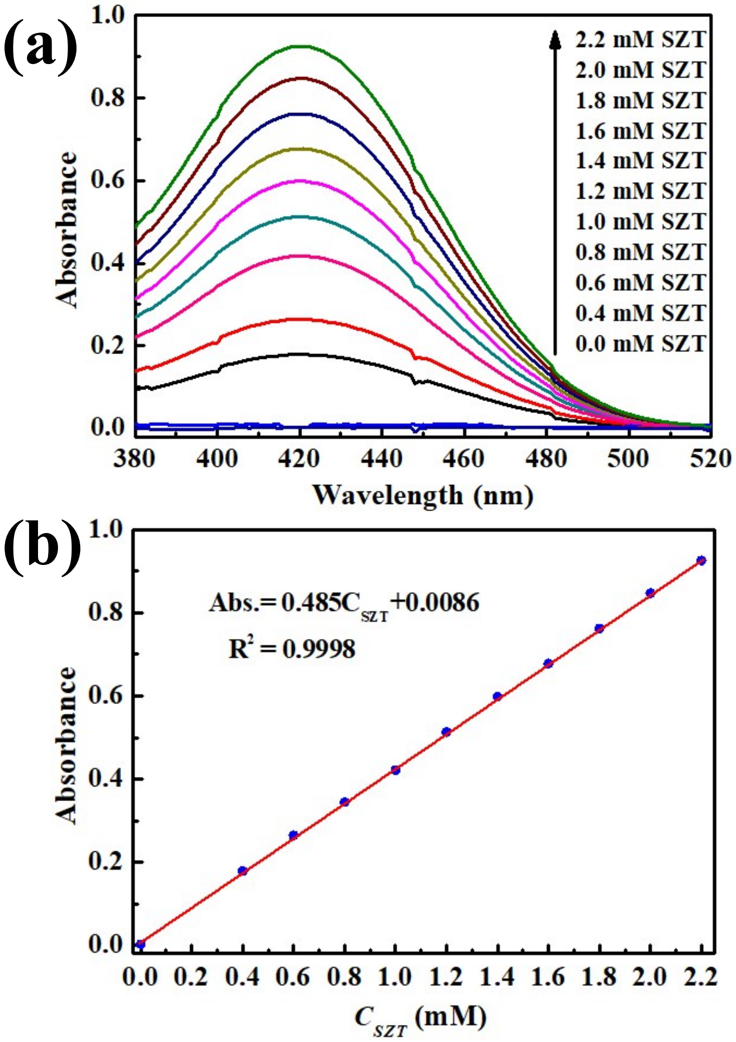

Fig. S7 (a) UV-vis absorbance spectra of 0.2 M Na_2CO_3 water solution containing different concentrations of SZT. (b) Linear relationship between absorbance at 418 nm and concentration of SZT. Copyright permission from Ref.26.

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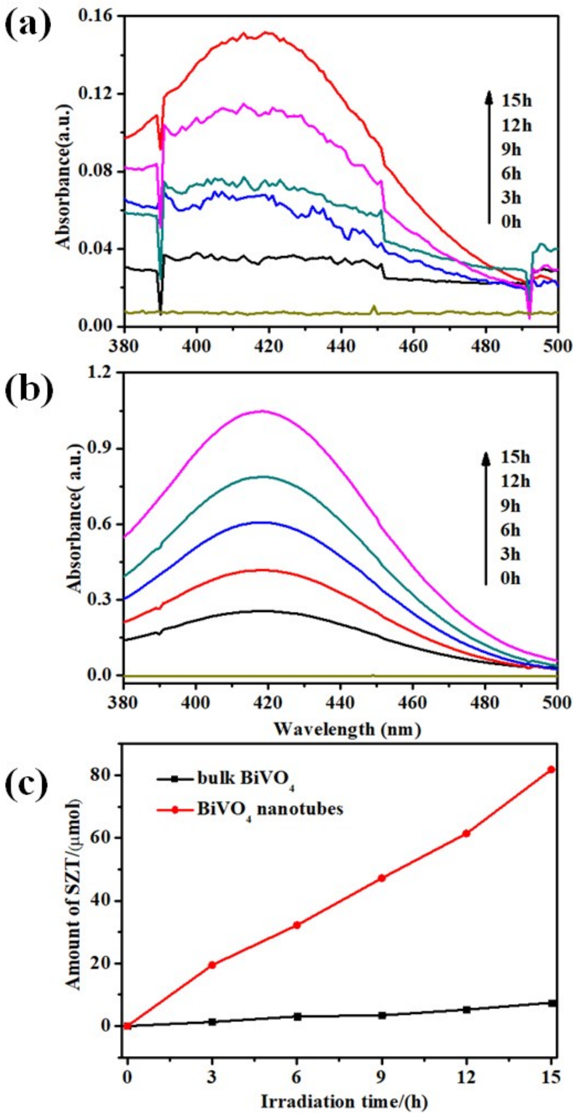

Fig. S8 UV-vis absorbance spectra of 0.03M Na_2CO_3–0.1 M 5AT solution after photocatalytic reaction for (a) buik $BiVO_4$, (b) $BiVO_4$ nanotubes. For accurate measurements, the concentration of solution over $BiVO_4$ nanotubes was diluted to 1.5-fold after 3–15 h photocatalytic reaction for ensuring their absorbance between 0.2–1.0, respectively. (c) Time courses of photocatalytic SZT generation over $BiVO_4$ nanotubes and bulk $BiVO_4$.

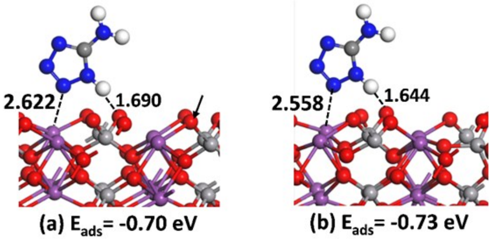

Fig. S9 The stable adsorption configurations for 5AT adsorbed $BiVO_4$ surfaces (a) without and (b) with oxygen vacancy. The corresponding adsorption energy is listed below each structure. The red, purple, gray, blue, dark gray and white balls stand for oxygen, bismuth, vanadium, nitrogen, carbon and hydrogen atoms, respectively.