Electronic Supplementary Information

$BiVO_4$@ TiO_2 Core-shell Hybrid Mesoporous Nanofibers towards Efficient Visible-light-driven Photocatalytic Hydrogen Production

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Experimental Section

Synthesis of mesoporous $BiVO_4$ nanofibers

The mesoporous $BiVO_4$ nanofibers were fabricated by a foaming-assisted electrospinning method. In a typical procedure, 0.5 g PVP was firstly dissolved in a mixed solvent containing 2 g DMF, 3 g acetic and 1 g ethanol. Then the obtained mixture was vigorously stirred for 3 h to make the PVP be completely dissolved. After that, 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and $Vo(acac)_2$ were added into the above solution, followed by being magnetically stirred for 2 h. Subsequently, 1 g diisopropylazodiformate (DIPA, $C_8H_{14}N_2O_4$) used as the foaming agent was introduced to the solution and stirred for another 2 h. The resultant solution was transferred into a plastic injector with a stainless-steel needle serving as an anode and a low-speed rotating cylinder acting as the collector (cathode). An electrical potential of 20 kV was applied for the electrospinning. The as-spun precursor fibers weres dried at room temperature overnight. Finally, the precursor was calcined at 500 ℃ for 1 h with a heating rate of 5 ℃ min^{-1}, followed by furnace cool to ambient temperature.

Synthesis of mesoporous $BiVO_4$@TiO_2 hybrid nanofibers

The as-synthesized mesoporous $BiVO_4$ nanofibers were then loaded into a Cambridge Nanotech S200 atomic layer deposition (ALD) system for the deposition of TiO_2. Each ALD cycle consisted of a 0.05 s pulse of H_2O, followed by a 0.10 s pulse of isopropyl titanate (Sigma-Aldrich, 99.999%). A 25-s purge under a constant 0.05 L min^{-1} flow of research-grade Ar was performed between each pulse. When idle, the ALD system maintained a continuous Ar purge under a base pressure of 2.7×10^{-1} Torr. The ALD process was fixed at 30, 50, 80 and 100 cycles of pulsed precursors to tailor the thicknesses of the deposited TiO_2 layer around the mesoporous $BiVO_4$ nanofibers. The obtained samples are referred to as $BiVO_4@TiO_2^n$ (the number of n refers to the given cycles of ALD).

Microstructural Characterization

The products were examined using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan). Transmission electron microscopy (TEM) images were collected under a JEM-2100F electron microscopy (JEOL, Japan), together with energy-dispersive X-ray spectroscopy (EDX, Quantax-STEM, Bruker, Germany). The obtained products were characterized with X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) with Cu $K\alpha$ radiation (λ=1.5406 Å). The optical properties were tested on an ultraviolet-visible spectrophotometer (U-3900 spectrophotometer, Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250XI electron spectrometer under ultrahigh vacuum condition. All of the binding energies ere calibrated by using surface adventitious carbon (C 1s at 285.4 eV) as a reference.

Photocatalytic hydrogen production measurements

The photocatalytic activity of the resultant products was evaluated for hydrogen evolution in the absence of co-catalysts, which was performed in an inner-irradiation quartz annular reactor with a 300-W Xenon lamp (CEL, HUL300), a vacuum pump, a gas collector, a recirculation pump and a water-cooled condenser. The as-synthesized samples (0.05 g) were suspended in a mixture with a deionized water and methanol solution (40 mL, 3:1) by an ultrasonic oscillator. The mixture was then transferred into the reactor and desiccated under a vacuum pump. A Xenon lamp with a 420-nm cut-off quartz optical filter was utilized as the light source, and the cooling water was circulated through a cylindrical Pyrex jacket located around the light source to maintain the reaction temperature. The reactor was sealed with ambient air during irradiation, and the hydrogen evolution was monitored by online gas chromatography (GC, 7900) equipped with a Porapak-Q column, high-purity nitrogen carrier and a thermal conductivity detector (TCD).

Photoelectrochemical Measurements

Photoelectrochemical measurements were carried out with an Autolab PGSTAT302G work station by using a typical three-electrode setup. To fabricate the photoanodes, the products were coated on the FTO glass through spin-coating. The prepared photoanodes were used as the working electrode, with a Pt plate and an Ag/AgCl electrode using as the counter and reference electrodes, respectively. The illumination was carried out under a 300-W xenon lamp and a 420-nm cut-off quartz optical filter with a typical illuminating area of 1 cm^2 for all measurements. All experiments were performed in 0.5 M Na_2SO_4 electrolyte solution. The scan rate of linear sweep voltammetry (LSV) curves was measured with a scan rate of 25 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was recorded with a frequency range from 10^{-1} to 10^5 Hz under a 10 mV amplitude at an open-circuit voltage.

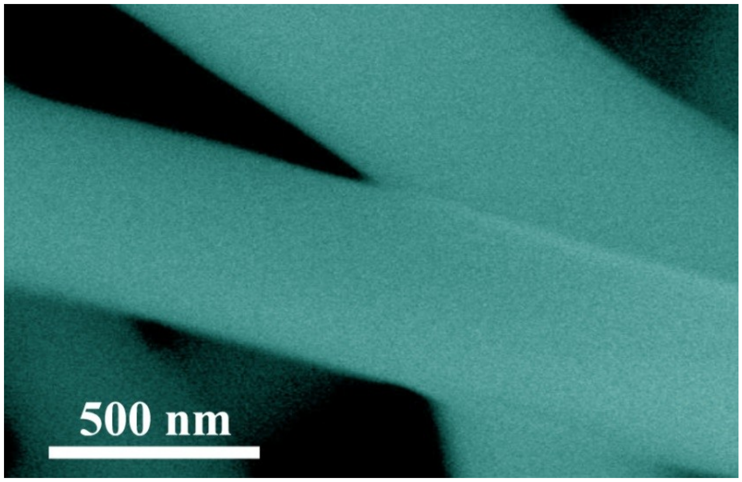

Fig. S1. Typical SEM image of as-spun $BiVO_4$ polymer nanofibers

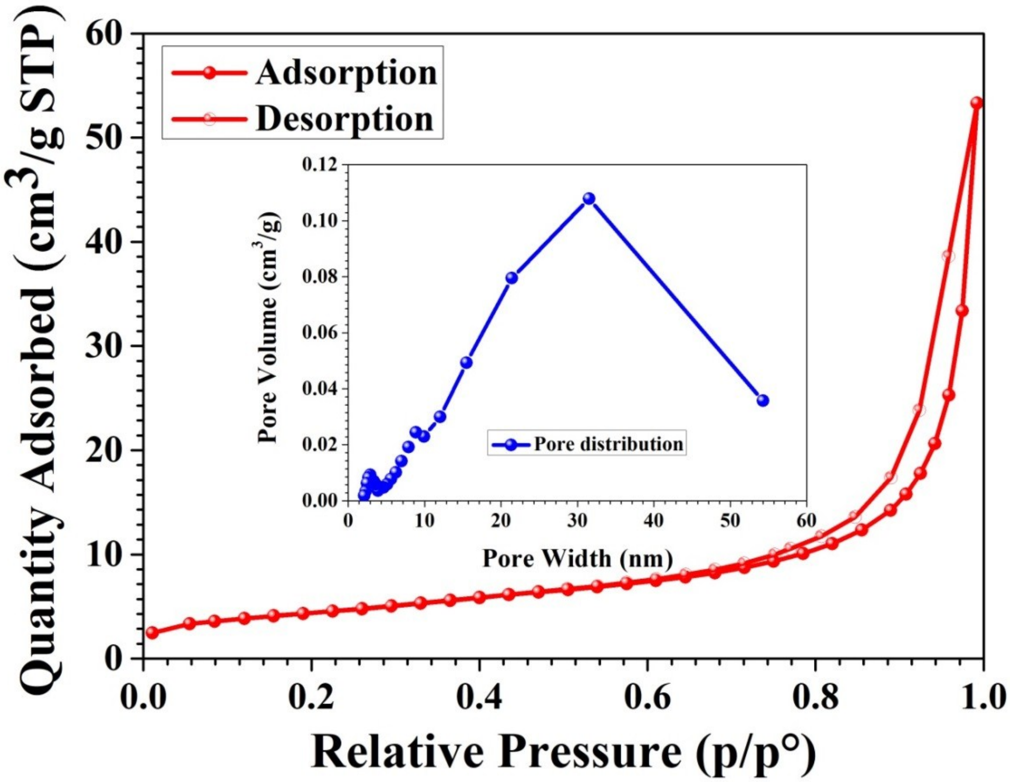

Fig. S2. N_2 adsorption and pore distribution (the inset) of the mesoporous $BiVO_4$ nanofibers.

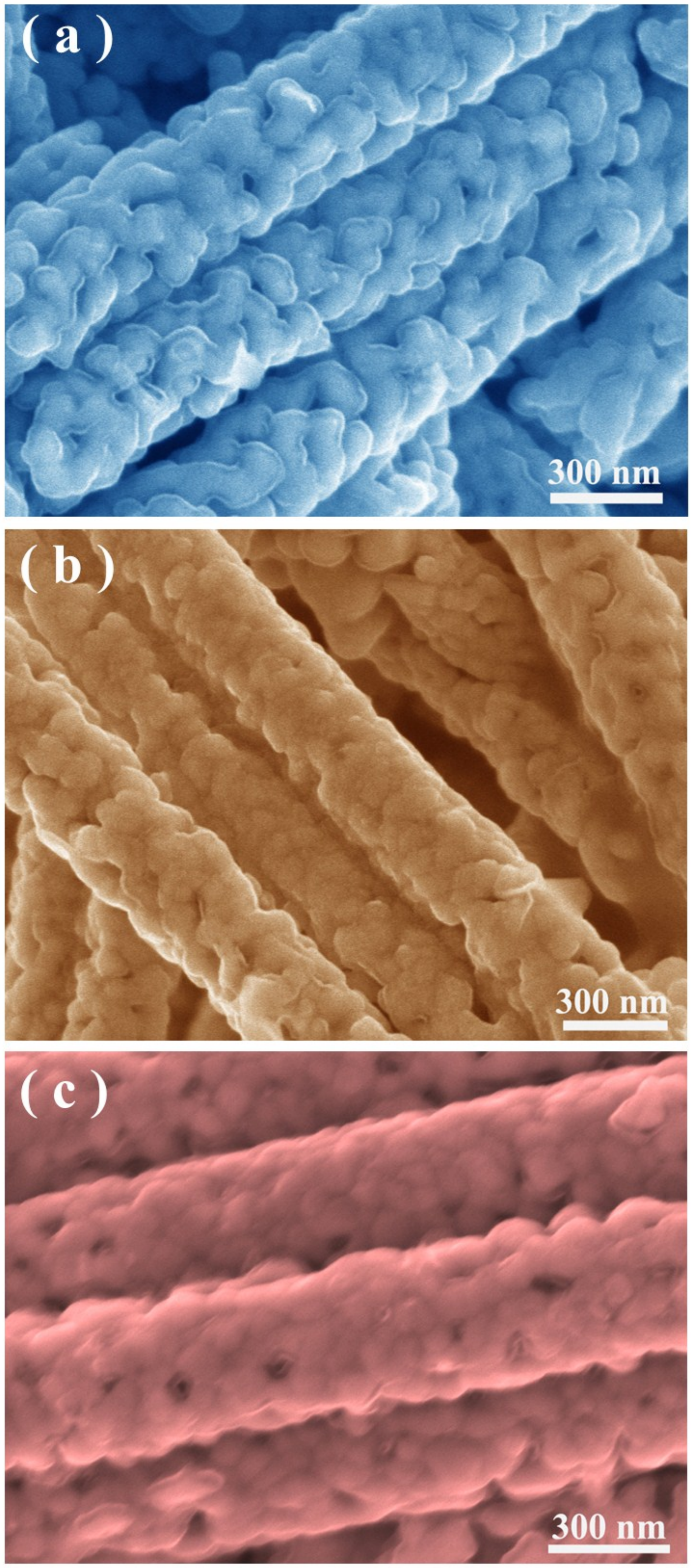

Fig. S3. Typical SEM images of $BiVO_4$@TiO_2 core-shell nanofibers with different TiO_2 ALS cycles: (a) 30, (b) 80 and (c) 100.

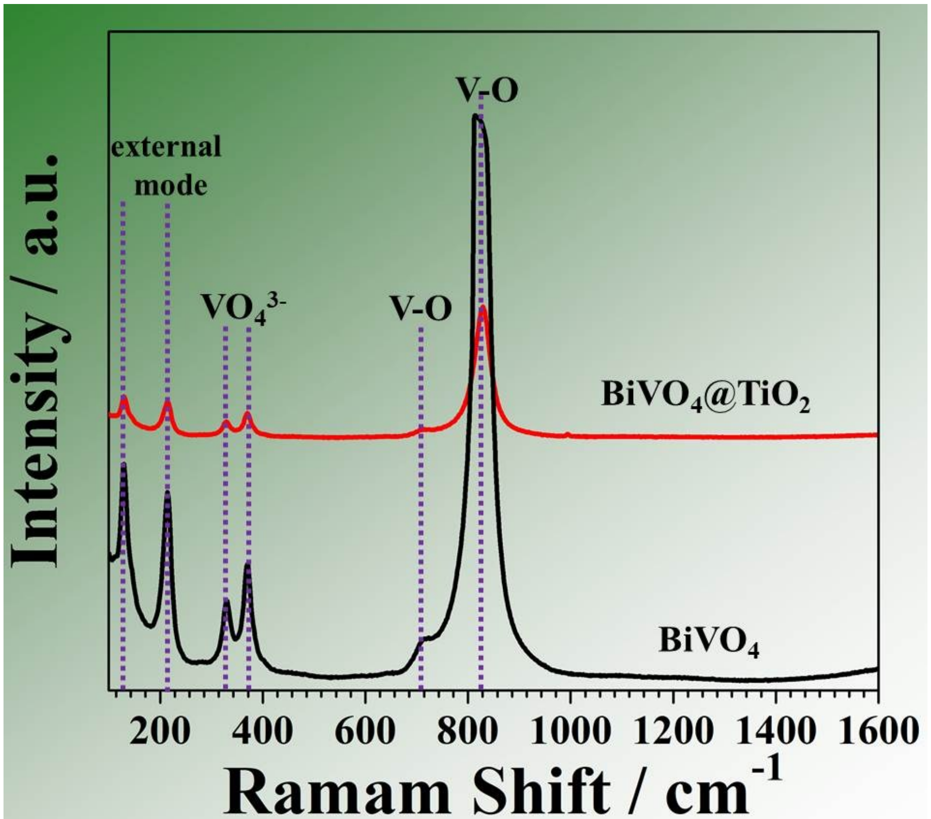

Fig. S4. Representive Raman spectrum of pure $BiVO_4$ and $BiVO_4@TiO_2$ core-shell nanofibers.

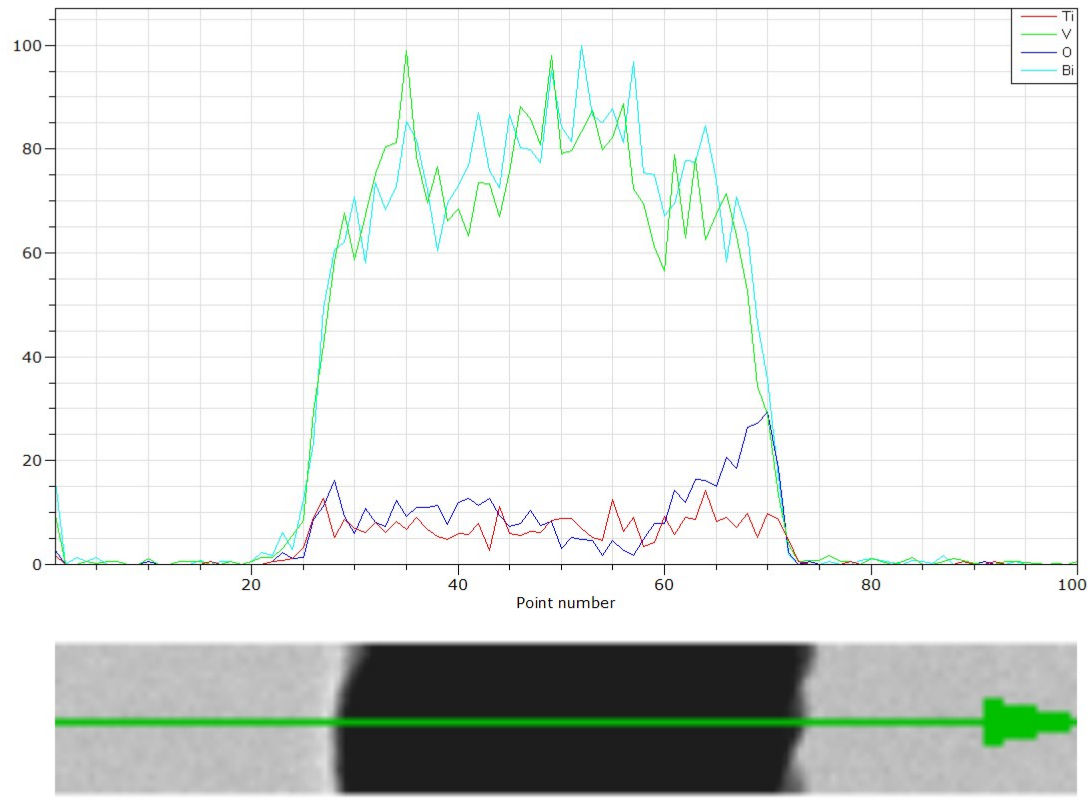

Fig. S5. Typical EDX line scanning of $BiVO_4@TiO_2$ core-shell nanofiber.

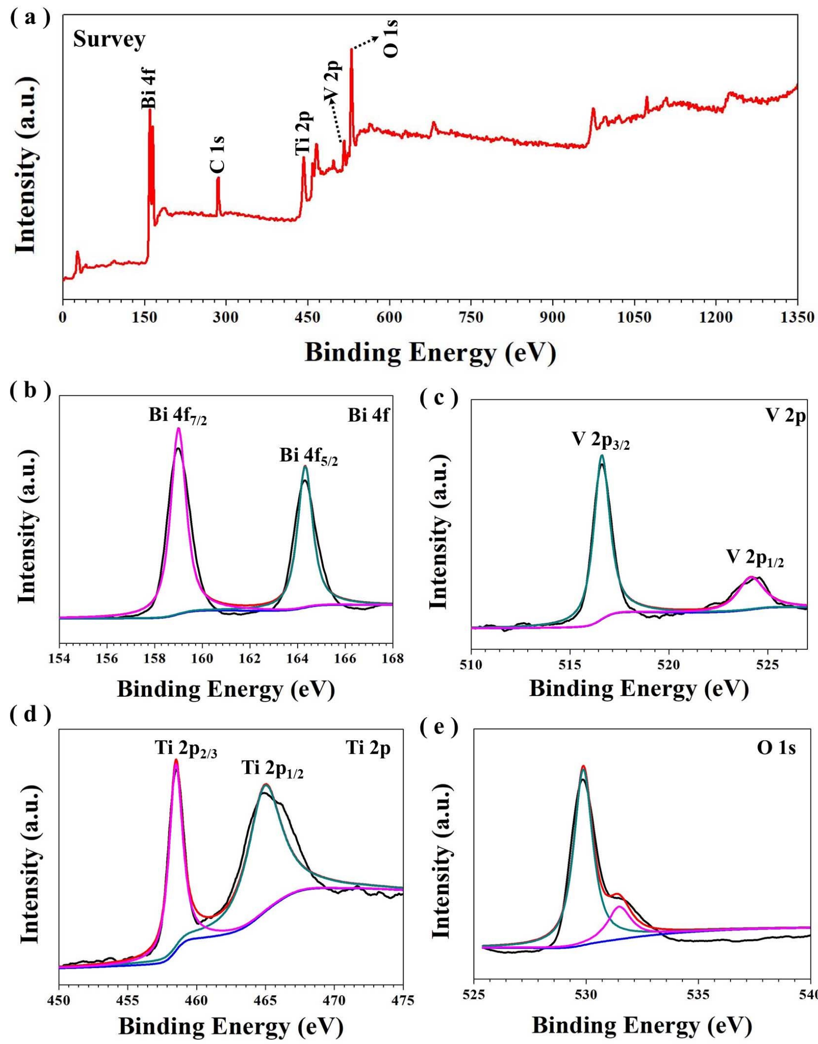

Fig. S6. XPS spectra of the $BiVO_4$@TiO_2 core-shell nanofiber: survey (a), Bi 4f (b), V 2p (c), Ti 2p (d) and O 1s (e).

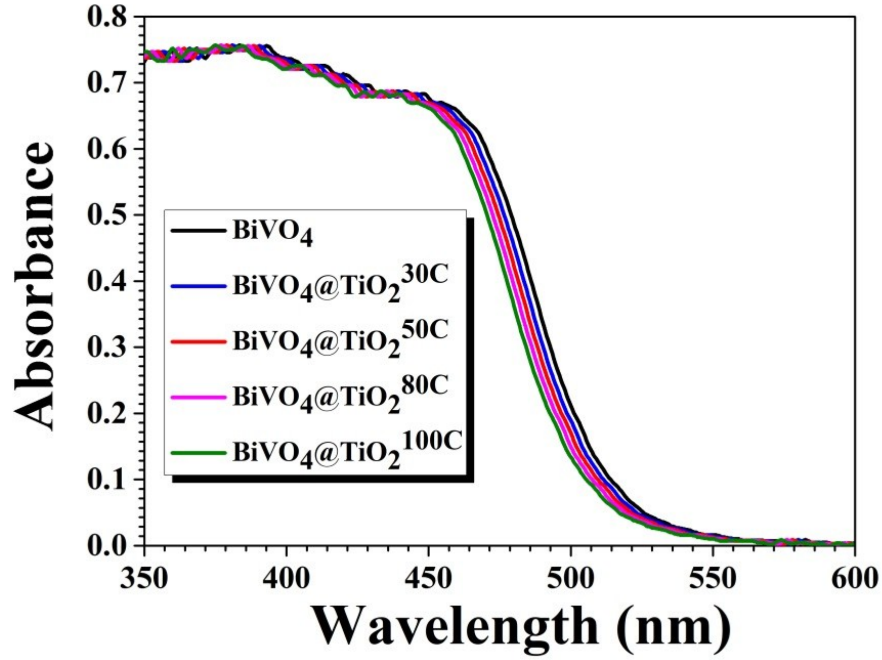

Fig. S7. Typical UV-Vis diffuse reflection spectra of samples with different cycles of ALD TiO_2.

Table S1. Comparison of the related work for photocatalytic H_2 production

Material	**Morphology**	**Cocata lyst**	**Irradiation conditions**	**Reaction solution**	**Activity (μmol h^{-1})**	**Reference**
$BiVO_4$/ TiO_2	Nanoparticles	Pt	300 W xenon light with a 200-400 nm cut off filter	Water+Met hanol	2.2	1
TiO_2/Bi VO_4	Nanoparticles film	Pt	300 W Xe lamp with cutoff filter of 420 nm	Water+Met hanol	6	2
$BiVO_4$/ TiO_2/Ag	Nanoparticles	---	300 W Xe lamp with cutoff filter of 420 nm	Water+Met hanol	4.2	3
TiO_2/Bi VO_4	Nanoparticles	---	300 W Xe lamp	Water	18.1(0.41ml h^{-1})	4
$BiVO_4$ /SnO_2	Screw-like	Pt	500 W xenon light with a 200–400 nm cut off filter	Water+Met hanol	1.16	5
$BiVO_4$/ TiO_2	Mesoporous core-shell nanofibers	---	300 W Xe lamp with cutoff filter of 420 nm	Water+Me OH	6	Current work

References

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