Significantly Improved Charge Collection and Interface Injection in 3D $BiVO_4$ based Multilayered Core-Shell Nanowire Photocatalyst

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1. Experimental section

1.1 Synthesis of the ITO@BVO photocatalyst

ITO NW arrays directly grown on ITO glass substrates (1.1 mm in thickness, >86% transmittance, 8 Ω per square, Nippon) through a standard CVD method according to our previous publication [1]. Simply, ITO glass substrates coated with Au catalyst layer were placed at the outlet of tube furnace. A mixture of indium and tin metal powder was used as the source materials, which was placed at the center of the quartz tube. Then the tube furnace was heated to 700 °C and kept for 30 min under a constant mixed gas flow of Ar (50 sccm) and O_2 (0.3 sccm). After that, the furnace was cool down to room temperature and the samples were taken out. Then the BVO nanoparticles were deposited onto the ITO NW arrays using a facial ED method [2-3]. In a typical process, 35 mM $VOSO_4•2H_2O$ (>98, Wuxi Zhanwang Chemical Co., Ltd., China) was dissolved in 30 mL deionized water and the pH value was adjusted to 0.5 with conc. HNO_3 (2 mL). Then, 10 mM $Bi(NO_3)_3•5H_2O$ (AR, Tianjin Fengyue Chemical Co. , Ltd. , China) was added into the solution and 2 M NaAC (AR, Shanghai Kefen Chemical Reagent Co. , Ltd. , China) was used to stabilize the Bi ions. After being stirred for 10 min, the pH value was adjusted to 4.7 with HNO_3 (1.6 mL). An ED process was performed at a constant current density (12.5 mA cm^{-2}) at room temperature using an electrochemical workstation (RSE5000). A saturated silver/silver chloride electrode (Ag/AgCl) was used as the reference electrode, titanium (Ti) foil as the counter electrode and the ITO NW arrays as the working electrode. The solution was purged by Ar during the whole deposition procedure. After deposition, the samples were rinsed with deionized water and dried at 500 °C for 2 h with a heating rate of 2 °C min^{-1}. To remove vanadium pentoxide, the samples were treated with 1 M KOH for 20 min and dried at 60 °C in vacuum oven.

The bare BVO film as the reference sample was prepared by an ED method with FTO as the substrate. The solution and the deposition parameter were the same as that of ITO@BVO.

1.2 Synthesis of rGO-ITO@BVO and Co-pi/rGO-ITO@BVO photocatalyst

The rGO catalyst layer was coated onto the ITO@BVO NW arrays with the CV reduction ED method as described in our previous publication [1]. Typically, rGO solution with a density of 0.1 mg mL^{-1} was used as the electrolyte and the scan voltage is between –1.5 and 0.6 V at a rate of 20 mV s^{-}

[1]. Cobalt phosphate (Co-pi) was deposited on the surface of rGO-ITO@BVO using photo-assisted ED method [4]. Typically, the prepared rGO-ITO@BVO electrode was immersed into 0.1 M phosphate buffer solution (pH=7) containing 0.15 mM cobalt nitrate. A constant potential (0.3 V vs. Ag/AgCl) was applied for 600 s under AM 1.5 simulated illumination. The resulting films were rinsed with deionized water and dried in vacuum oven.

1.3 Material Characterization

The morphology of the samples was investigated by field emission scanning electron microscope (FE-SEM, Hitachi S-4800), and high-resolution transmission electron microscope (HRTEM, FEI Tecnai F30). Elemental analysis was performed by X-ray photoelectron spectroscope (XPS), which is carried out on Kratos AXIS Ultra DLD XPS instrument equipped with an Al Kα source (hv = 1486.6 eV). Energy-dispersive X-ray (EDX) spectroscopy equipped to the TEM (in-situ) was also performed to confirm their chemical compositions. X-ray diffraction (XRD, Philips, X' per pro, Cu kα 0.154056 nm) was employed to characterize the crystal structure of the samples. Optical absorption spectra of the photocatalysts between 350 nm and 800 nm were recorded using a spectrophotometer (U-3900H, HITCHI), operating in absorption mode. The TS-SPV measurement was carried out based on the pulse laser (wavelength of 532 nm and pulse width of 5 ns) from an Nd: YAG laser (Lab-130-10H, Newport, Co.). The structure of the sample chamber is a sandwich-like structure of FTO/sample/FTO. The TS-SPV signal was recorded by a 1 GHz digital phosphor oscilloscope (DPO 410B, Tektronix). The TS-SPV measurements were carried out in air at ambient temperature.

1.4 Photocatalytic water-splitting performance evaluation

Photocatalytic performances of the photocatalysts were evaluated in a three-electrode configuration. We used the samples as working electrode, Ag/AgCl as reference electrode, Pt foil as counter electrode and 0.5 M Na_3PO_4 with pH of 10.5 as electrolyte. Simulated solar illumination was provided by a 500 W Xe lamp equipped with an AM 1.5 G filter and the incident photo-intensity was calibrated to 100 mW cm^{-2} by a standard silicon solar cell. Liner sweep voltammetry (LSV) was carried out in a potential range from – 0.6 to 0.8 V vs. Ag/AgCl with scanning rate of 50 mV s^{-1} in dark and under simulated solar illumination. Electrochemical impedance spectroscopy (EIS) measurements were performed in light condition (AM 1.5) from 100 kHz to 0.05 Hz.

The practical amount of oxygen produced in the photocatalytic process has been measured by using a dissolved oxygen probe immersed in the solution. Typically, the photocatalysts as the working electrodes were sealed in a quartz cell with 0.5 M Na_2SO_4 solution (80 mL) as electrolyte. High-purity nitrogen gas was employed to bubble through the electrolyte before the experiment. During the experiment, the samples were illuminated by visible light with working area of 0.5 cm^2, at 0.6 V vs. Ag/AgCl. The amount of oxygen produced was quantitatively detected with an Ocean Optics fluorescence-based oxygen sensor (NFSC 0058) by putting the needle probe into the electrolyte, near to the working electrode, and the irradiation was lasted for 10 min.

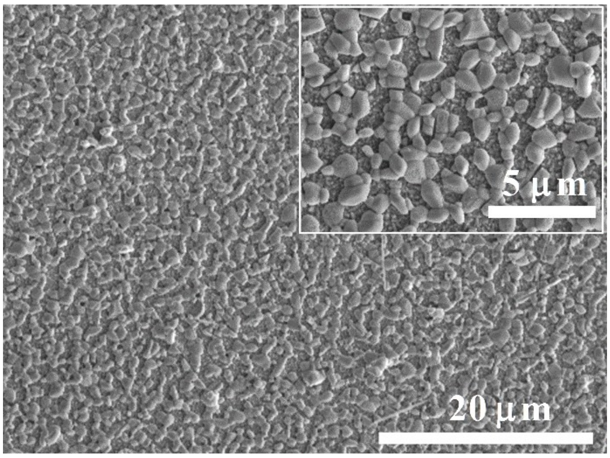

Figure S1. The SEM image of bare BVO on FTO substrate.

2. XPS analysis

The surface electronic states and chemical composition purity of the nanocomposites were analyzed by X-ray photoelectron spectroscopy (XPS). Figure S1a, b, c and d show the Bi 4f, V 2p, In 3d and C 1s core level XPS scans at higher resolution over smaller energy windows. As shown in Figure S4a and b, compared with pure BVO, the Bi 4f and V 2p peaks of ITO@BVO show no shift, which implies the ITO@BVO is a simple composite. The peaks at binding energy of 164.5 and 159.2 eV are ascribed to Bi 4f $_{5/2}$ and Bi 4f $_{7/2}$, which confirm the existence of Bi^{3+}. The V 2p peaks at 524.5 and 517.1 eV, corresponding with the reported value of V5+, which indicates the high purity of BVO. The In 3d spectrum exhibits two peaks at 444.9 eV ($3d_{5/2}$) and 452.5 eV ($3d_{3/2}$), which can be assigned to In_2O_3 (Figure S1c). The shape peak at 284.5 eV of C 1s spectrum should attribute to the C-C, while the other peaks at 285.6 and 288.1 eV are corresponding to the C-OH and carboxylic groups O=C-O, respectively. The low intensity of C–OH and O–C–O indicates that the GO has been reduced to rGO (Figure S1d).

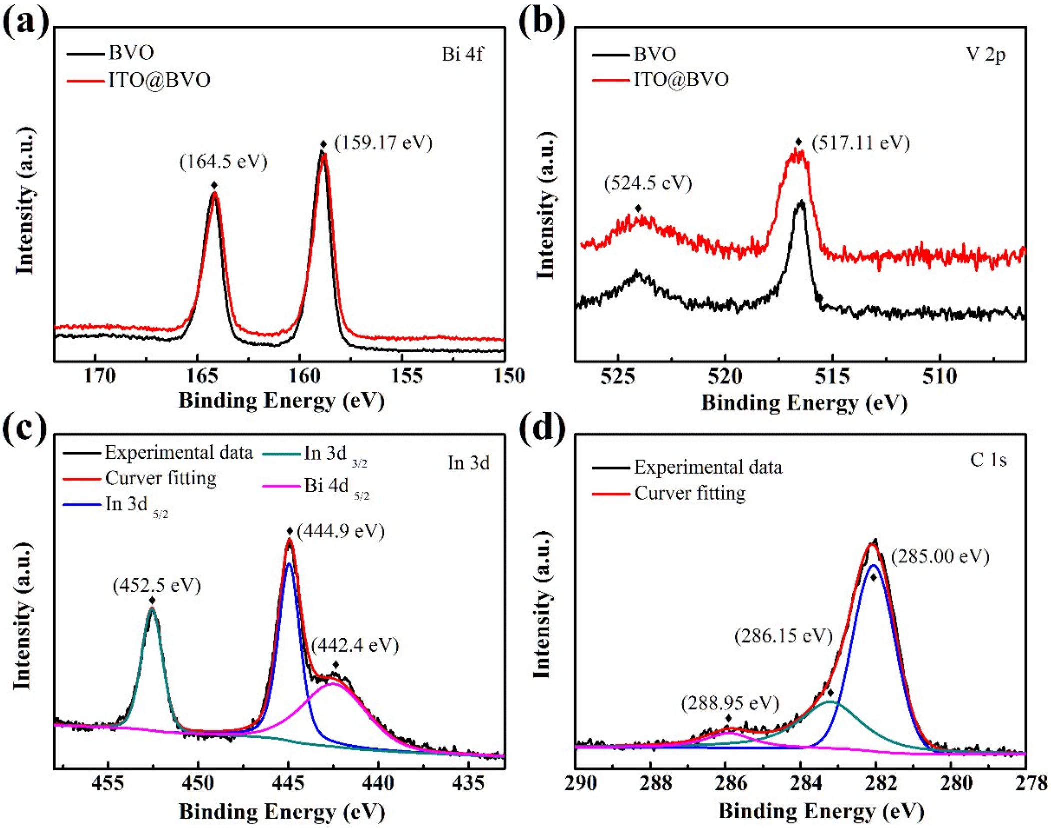

Figure S2. XPS spectra of produced photocatalysts.

3. Supplementary Figures

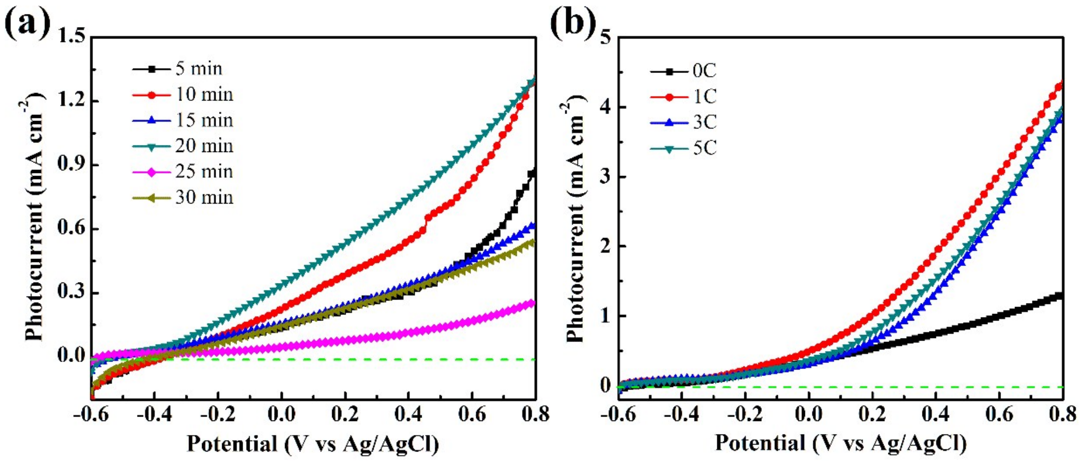

Figure S3. LSV curves of ITO@BVO photocatalysts with different BVO and RGO deposition time (a), (b).

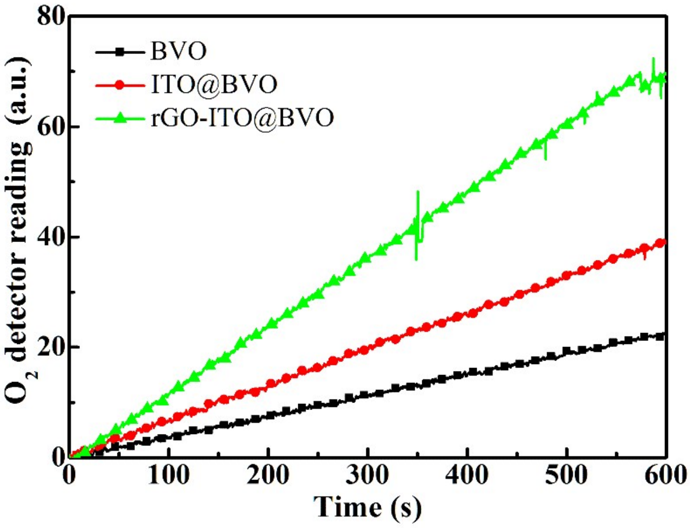

Figure S4. The practical oxygen generation rate of BVO, ITO@BVO and rGO-ITO@BVO photocatalysts.

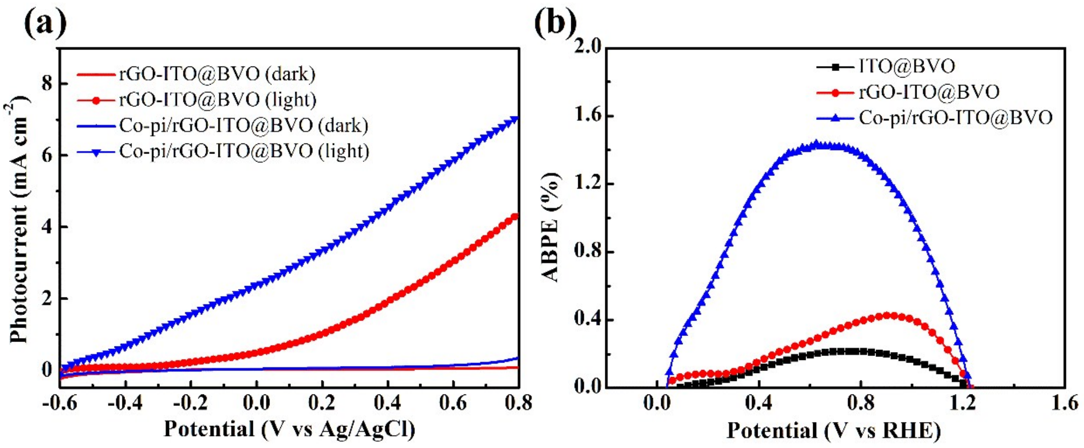

Figure S5. LSV of rGO-ITO@BVO and Co-pi/rGO-ITO@BVO photocatalysts (a); ABPE of ITO@BVO, rGO-ITO@BVO and Co-pi/rGO-ITO@BVO photocatalysts.

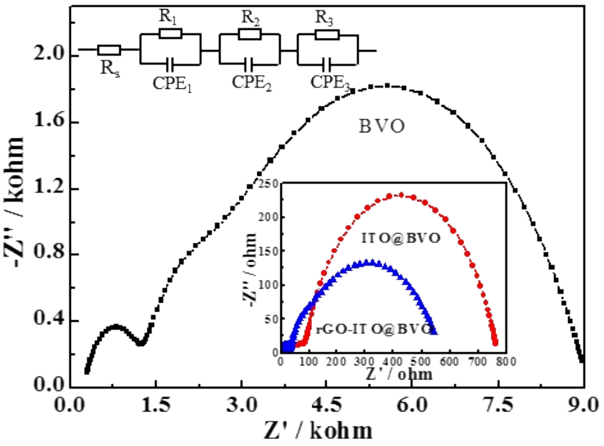

Figure S6. Fitted Nyquist plot of produced photocatalysts, the inset shows the RC model circuit.

4. Calculation of charge separation and transfer efficiency

To further understand the role of rGO in rGO-ITO@BVO photocatalyst, the η_{trans} and η_{sep} have been calculated based on the following equation:

$$J_{H2O} = J_{abs}\eta_{sep}\eta_{trans} \quad (1)$$

Where J_{H2O} is the measured photocurrent density; J_{abs} is the photo-absorption rate expressed as current density; η_{sep} is the charge separation efficiencies; η_{trans} is charge transfer efficiencies. Previous studies show that Na_2SO_3 can be used as hole scavenger to harvest photoexcited holes with nearly 100% efficiency. With the assuming that η_{trans} is 100%, the photocurrent density in the presence of Na_2SO_3 is obtained by

$J_{Na2SO3} = J_{abs}\eta_{sep}$ (2)

Here J_{Na2SO3} is the photocurrent density in the presence of Na_2SO_3. Hence, the practical η_{trans} can be determined by the following equation:

$\eta_{trans} = J_{H2O}/J_{Na2SO3}$ (3)

The η_{sep} also can be calculated by

$\eta_{sep} = J_{Na2SO3}/J_{abs}$ (4)

Figure S6 is the LSV of ITO@BVO and rGO-ITO@BVO with or without Na_2SO_3 in electrolyte. J_{H2O} and J_{Na2SO3} can be readied from Figure S6.

The absorption current density (J_{abs}) was calculated by the following equation:

$$J_{abs} = \int_{300}^{800} qA\phi d\lambda$$

Where q is the electron charge, ϕ is the AM 1.5 G solar photon flux in $m^{-2} \cdot nm^{-1} \cdot s^{-1}$, A is the fraction of incident light absorbed over the wavelength range (determined from UV-vis experiments) [5].

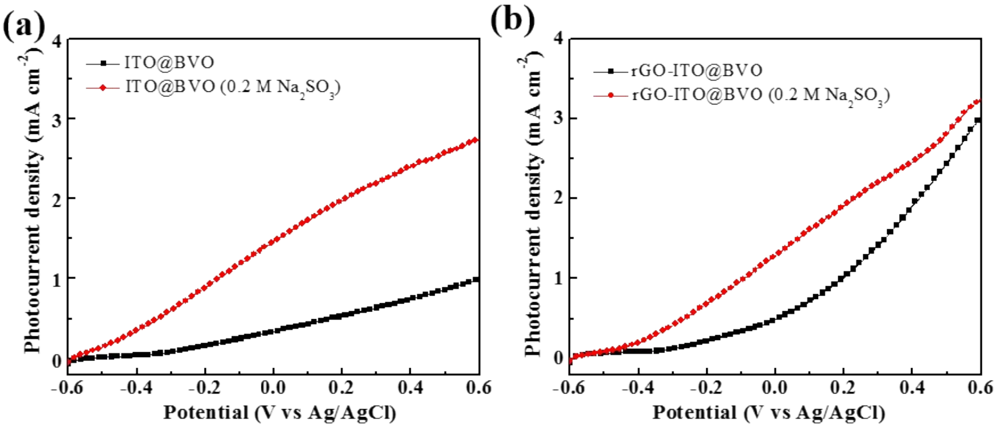

Figure S7. LSV spectra of ITO@BVO and rGO-ITO@BVO photocatalysts with or without Na_2SO_3.

References

1. Zhang, Z.; Gao, C.; Li, Y.; Han, W.; Fu, W.; He, Y.; Xie, E., Enhanced charge separation and transfer through Fe2O3/ITO nanowire arrays wrapped with reduced graphene oxide for water-splitting. *Nano Energy* **2016**, *30*, 892-899.

2. Kuang, Y.; Jia, Q.; Nishiyama, H.; Yamada, T.; Kudo, A.; Domen, K., A Front-Illuminated Nanostructured Transparent BiVO4Photoanode for >2% Efficient Water Splitting. *Adv. Energy Mater.* **2016**, *6*, 1501645.

3. Su, J.; Bai, Z.; Huang, B.; Quan, X.; Chen, G., Unique three dimensional architecture using a metal-free semiconductor cross-linked bismuth vanadate for efficient photoelectrochemical water oxidation. *Nano Energy* **2016**, *24*, 148-157.

4. Pilli, S. K.; Deutsch, T. G.; Furtak, T. E.; Turner, J. A.; Brown, L. D.; Herring, A. M., Light induced water oxidation on cobalt-phosphate (Co-Pi) catalyst modified semi-transparent, porous SiO2-BiVO4 electrodes. *Phys Chem Chem Phys* **2012**, *14*, 7032-7039.

5. Ye, W.; Chen, F.; Zhao, F.; Han, N.; Li, Y., CuWO4 Nanoflake Array-Based Single-Junction and Heterojunction

Photoanodes for Photoelectrochemical Water Oxidation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9211-9217.