

## Supporting Information

### **Modulating Surface Charges of Bismuth Tantalum Oxychloride Nanoplates for Promoting Photogenerated Charge Separation**

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## **Experimental Procedures.**

### **1. Sample preparation**

Faceted  $\text{Bi}_4\text{TaO}_8\text{Cl}$  (BTOC) photocatalyst was synthesized via flux method as previously reported.<sup>[1]</sup> In a typical synthesis process, stoichiometric quantities of  $\text{Bi}_2\text{O}_3$  (Beijing Shiji Chemical),  $\text{BiOCl}$  and  $\text{Ta}_2\text{O}_5$  (99.99%, Amresco Chemical) with  $\text{NaCl}$  (99.5%, Sinopharm Chemical) and  $\text{KCl}$  (99.5%, Sinopharm Chemical) (molar ratio of  $\text{NaCl}$  /  $\text{KCl}$  is 1:1) as the flux reagent, were mixed and heated in air at 973 K for 6h. The cooled yellow mixture was washed several times with deionized water and dried at 353 K in the oven. Pd nanoparticles was loaded on the as-prepared  $\text{Bi}_4\text{TaO}_8\text{Cl}$  (BTOC) photocatalyst using photo-deposition and impregnation method. Typically, Pd nanoparticles was loaded through both photo-deposition and impregnation method from a solution of 0.5mg/ml concentration of disodium palladium hexachloride ( $\text{Na}_2\text{PdCl}_6$ ) (99%, Admas Reagent Co., Ltd.).

### **2. Sample pretreatment in acid and alkaline solution**

Individually, acid and alkaline pretreatment of the as-prepared faceted BTOC samples were carried using similar procedure. Typically, 300 mg of the as-prepared faceted BTOC photocatalyst powder was added to 50 mL ultrapure  $\text{H}_2\text{O}$  in 100 mL conical flask, and the pH of the obtained mixture was adjusted to the required pH value using  $\text{NaOH}$  (0.1M) and  $\text{HNO}_3$  (0.1M) as acid and alkaline buffers. Thereafter, the obtained solution was covered with aluminum foil under continuous stirring on a magnetic stirrer for 2 hrs. Afterward, the obtained acid and alkaline modified BTOC samples were washed with distilled water and centrifuge at 5000 rpm and dried at room temperature. The obtained pretreated samples were used for selective in-situ photo-deposition of metals and/or metal-oxide.

### **3. Photo-deposition of metals and metal oxides.**

In a typical Photo-deposition procedure, 100 mg pretreated BTOC photocatalyst powder was added to 10 %  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  solution in a Pyrex reactor, follow by addition of calculated (2 %) concentration of Pd from the prepared stocks solution. The obtained mixture was placed in a cooling water bath system and thoroughly degassed by evacuation pump, and irradiated with 300 W Xe lamp (Ushio-CERMAX LX300, kenko, L42,  $\lambda \geq 420$  nm) from top under constant magnetic stirring for 2hrs. The obtained product formed were collected by centrifuging at 5000 rpm for 1 minute, washed thoroughly with deionized water and dried in oven at 80 °C.

Furthermore, selective photo-deposition of  $\text{MnO}_x$ ,  $\text{RuO}_2$  metal-oxides particles on the pretreated BTOC was carried out using  $\text{MnCl}_2$  and  $\text{RuCl}_3$  as precursors respectively.<sup>[3]</sup> 100 mg of pretreated photocatalyst powder and calculated  $\text{Mn}^{2+}$  or  $\text{Ru}^{3+}$  (2 %) metal precursor solution was added to 100 mL 0.05M  $\text{NaIO}_3$  aqueous solution in a quartz glass vessel connected to a closed gas circulation and evacuation system, and irradiated by 300 W Xe lamp (Ushio-CERMAX LX300) equipped with a 420 nm cutoff filter for 3 h. The precipitates formed were collected by centrifuging at 5000 rpm for 1 minute, and thoroughly washed with deionized water and dried in oven at 80 °C overnight. Photo-deposition of dual cocatalyst ( $\text{Au}/\text{MnO}_x$ ) was carried as previously reported with no substantial change in the procedure. <sup>[3]</sup>

#### 4. Characterizations

The as-prepared samples were characterized by X-ray power diffraction (XRD) on a Rigaku D/Max- 2500/PC powder diffractometer. Each sample powder was scanned using Cu-K $\alpha$  radiation with an operating voltage of 40 kV and current of 200 mA and a scan rate of 10°/min was applied to record the XRD patterns in the range of 10-80° at a step size of 0.02°. UV-visible (UV-vis) diffuse reflectance spectra were recorded on a UV-vis spectrophotometer (JASCO V-550) equipped with an integrating sphere, scanning range, 200-700 nm, scanning rate, 200 nm/min. The morphologies and the shapes of the as-prepared samples were examined by scanning electron microscopy (SEM, Quanta 200 FEG, FEI) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2000EX). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG ESCALAB MK2 spectrometer with monochromatized Al-K $\alpha$  excitation. Raman spectra were collected using 532 nm diode-pumped solid-state laser (Changchun New Industries Optoelectronics Technology Co., Ltd.) and a commercial Raman spectrometer (Invia, Renishaw plc.). The Isoelectric point (IEP) and the surface charge were determined using Melvern sizer (Nano-ZS90 model). The contact angle (CA) was determined using a commercial Contact Angle metre (DSA100).

#### 5. Photocatalytic reactions O<sub>2</sub> evolution Reaction

Photocatalytic O<sub>2</sub> evolution reactions of BTOC, Pd/BTOC-S, Pd/BTOC-T and Pd-BTOC-R were carried out in a closed gas circulation and evacuation system using a 300 W Xe lamp (Ushio-CERMAX LX300) with an optical cut-off filter (kenko, L42, 420 nm) as the light source. Specifically, 100 mg of the photocatalyst powder was added to 100 mL H<sub>2</sub>O, 5.0 mM, Fe (NO<sub>3</sub>)<sub>3</sub> or 10 mM AgNO<sub>3</sub> aqueous solution and the solution was thoroughly degassed by evacuation pump. The temperature of the reactor was maintained at 15 °C by a water-cooling system, and the O<sub>2</sub> gas evolved was quantified using an online gas chromatograph (Shimadzu GC-8A, TCD, Ar carrier).

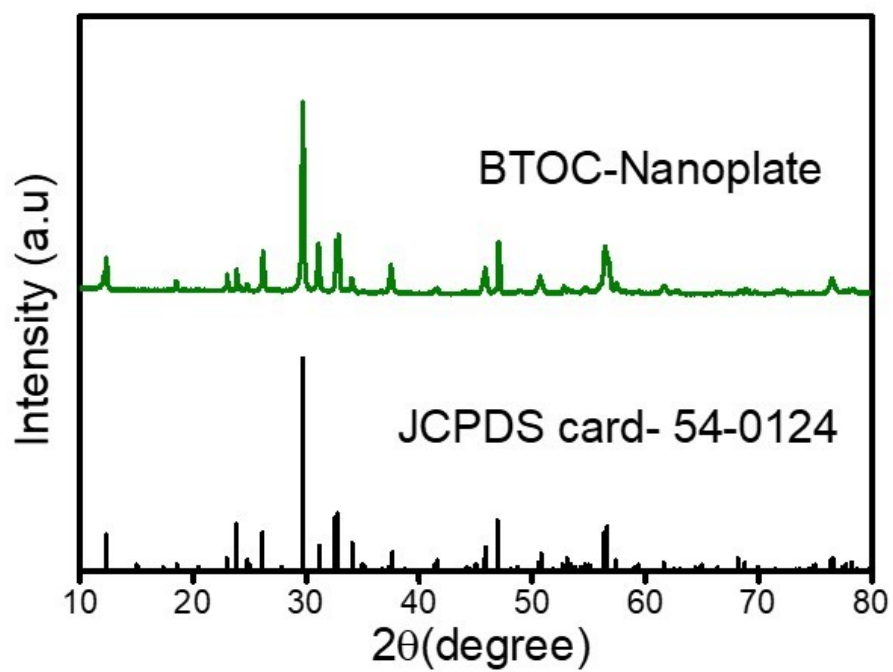
#### 6. Photocatalytic reactions H<sub>2</sub> evolution Reaction

Photocatalytic H<sub>2</sub> evolution reactions for BTOC, Pd/BTOC-S, Pd-BTOC-T and Pd-BTOC-R were carried out in a closed gas circulation and evacuation system using a 300 W Xe lamp (Ushio-CERMAX LX300) and an optical cutoff filter (kenko, L42, 420 nm). In a more precise procedure, 100 mg photocatalyst powder was dispersed in (10 vol%, 100 mL) aqueous methanol solution in a Pyrex reactor cell, and thoroughly degassed by evacuation pump in order to drive off the air inside. The amount of evolved H<sub>2</sub> was determined by an on-line gas chromatograph (Agilent, TCD, Ar carrier).

#### 7. Zeta potential measurement

The surface charge of the pristine acidic and alkaline pretreated BTOC samples was measure in solution of different pH adjusted using 0.1M NaOH and 0.1M HNO<sub>3</sub> buffer solution. Typically, 10 mg pretreated BTOC sample powder was added to 20 mL ultrapure water in a 50 mL conical flask, thereafter, and obtained mixture was ultrasonicated for 2 minutes. Thereafter, the pH of the obtained solution was adjusted to the require value using 0.1M NaOH and 0.1M HNO<sub>3</sub> buffer solution. The obtained solution concentration was further diluted by a factor of 2, by transferring 4 mL of the stock solution into a 10 mL test tube and make up to 8 mL mark with

ultrapure water. Measurable amount of the obtained diluted solution was taken by a pipette into a polystyrene disposable zeta cell for measurement. Machine parameters for measurements: temperature (25°C), viscosity (0.887) dielectric constant (78.5), RI value (1.330), absorbance (0.01), zeta run (12), dispersant (H<sub>2</sub>O) in a (Nano-ZS90 model).



**Fig. S1** The X-ray diffraction patterns of the as-prepared BTOC nanoplate with the JCPDS standard card No. 54-0124.

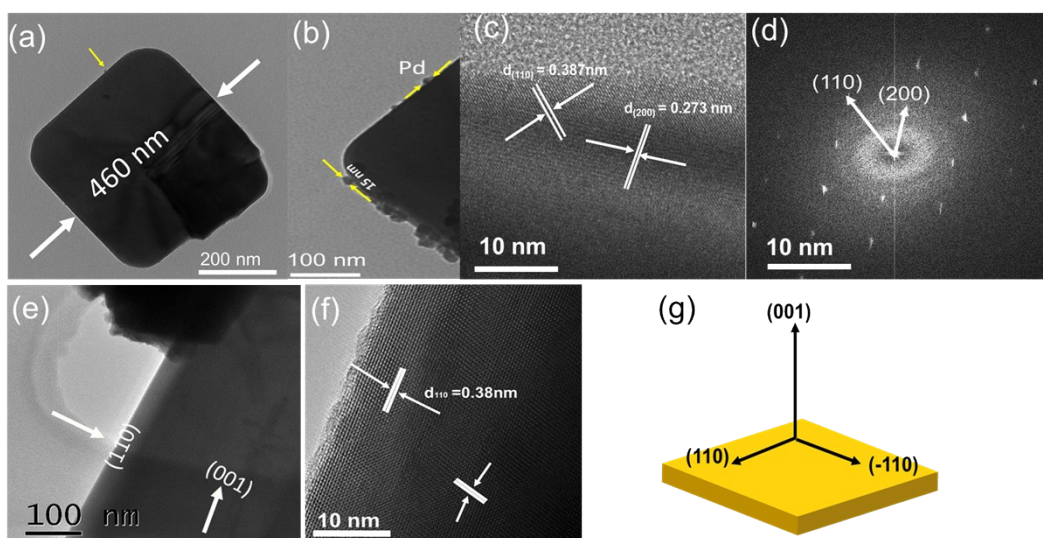
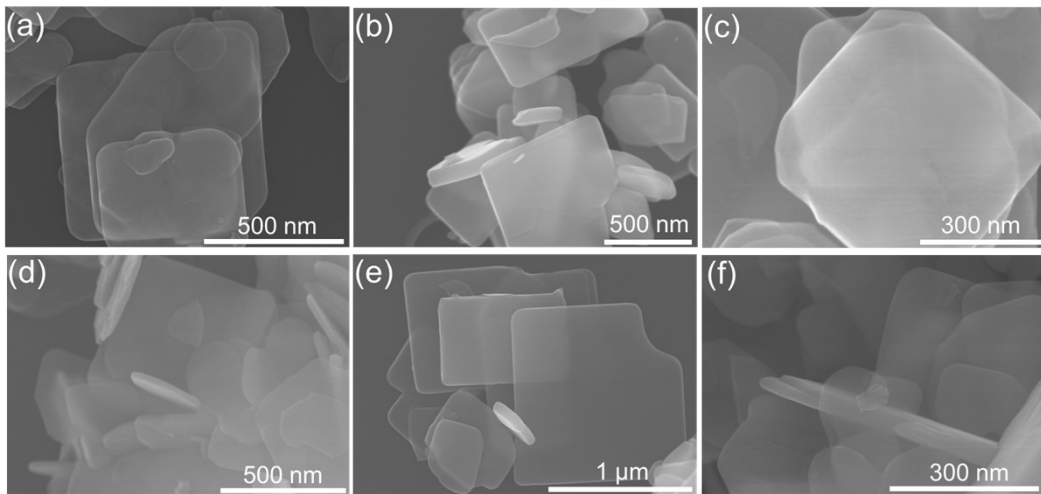
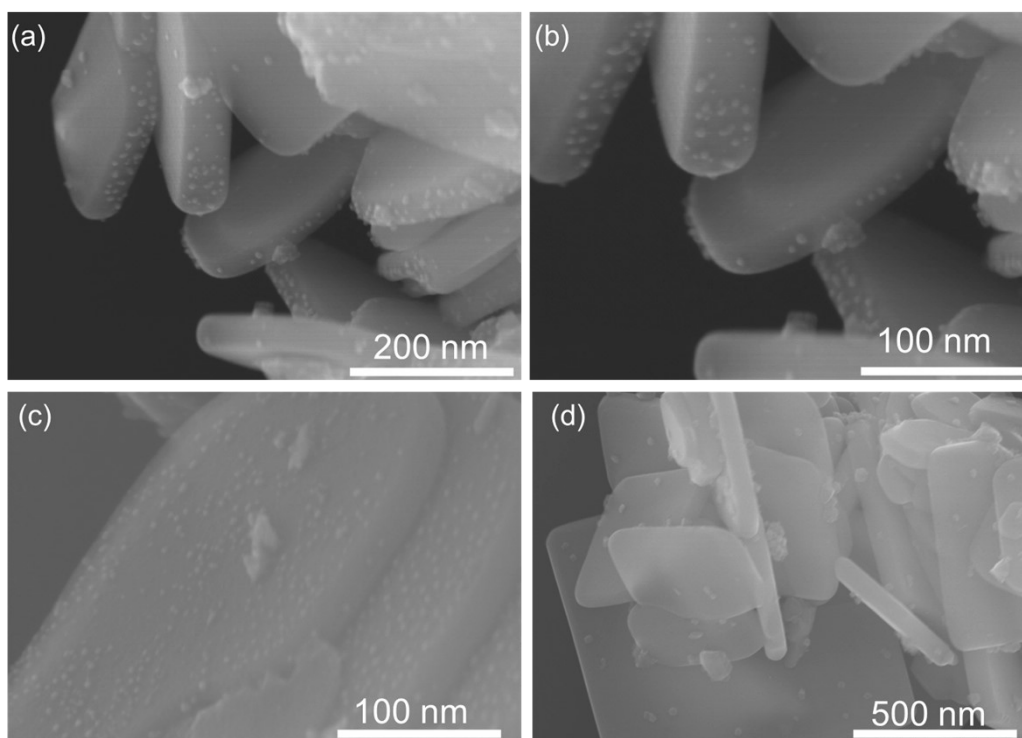


Fig. S2 (a) TEM image of BTOC single crystal nanoplate with dimension; (b) TEM image of 0.5 wt.% Pd/BTOC with mark the size of Pd nanoparticles; (c-f) HRTEM images, FFT patterns and TEM image of the as-prepared BTOC nanoplate; (g) Schematic illustrations of the crystal orientation in BTOC with (001) top-facets and (110) lateral side-facets.

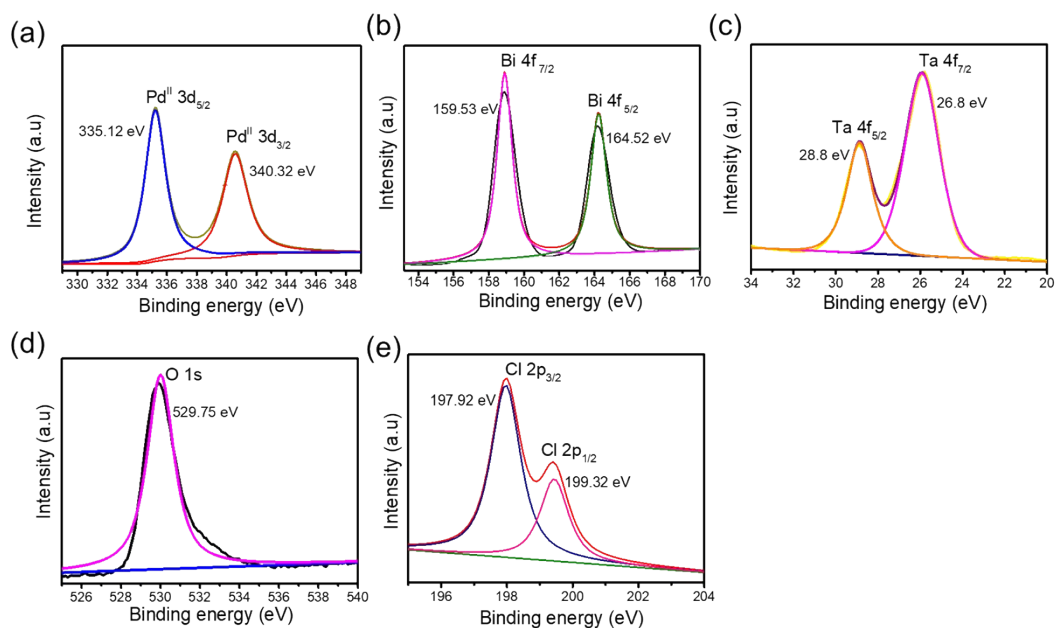


**Fig. S3** SEM images of the acidic and alkaline pretreated BTOC nanoplate samples. (a,b) pH 1.9; (c, d) pH 6.5 and (e, f) pH 10.5.

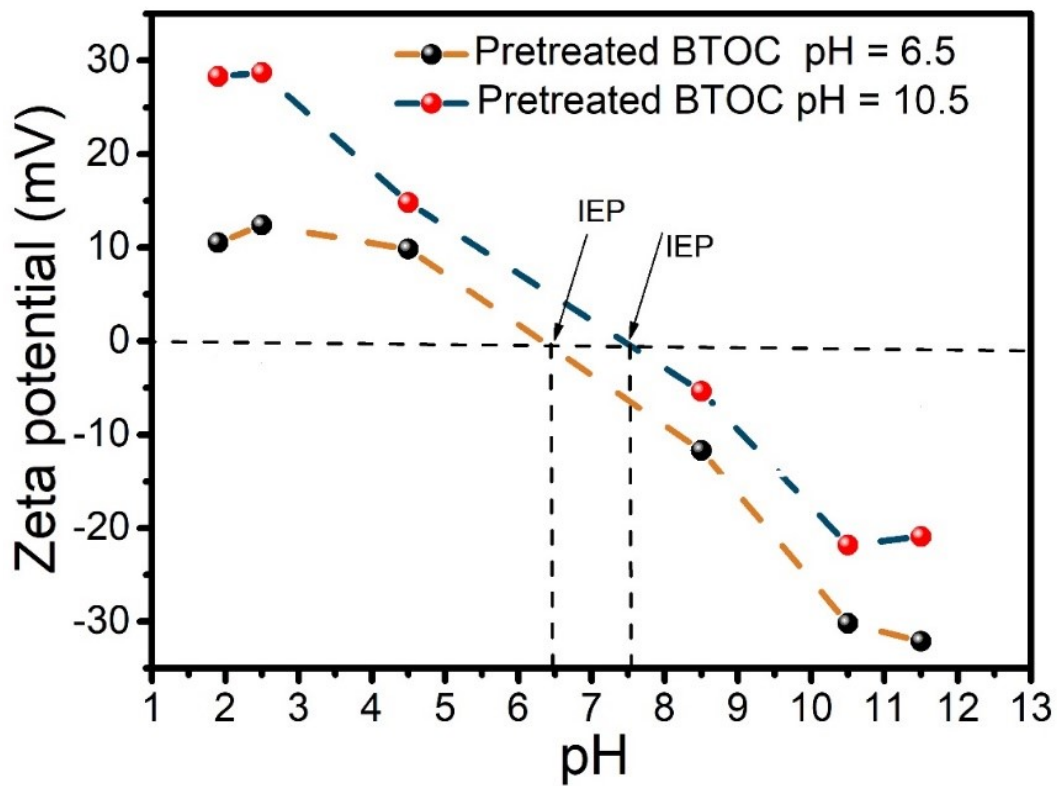




**Fig. S4** SEM images of Selective deposition of Pd nanoparticles under *in-situ* pH adjustment. (a, b) pH 6.5 and (c, d) pH 10.5 photo-deposition.

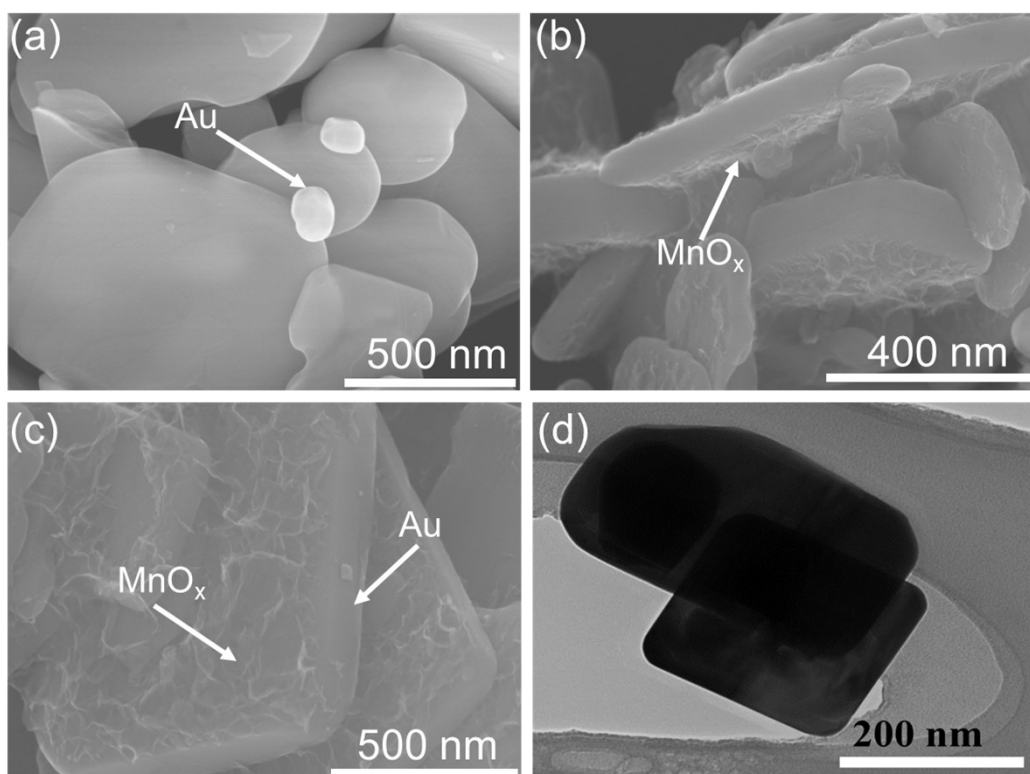


**Fig. S5** High resolution XPS characterization of the obtained Pd/BTOC. (a) Pd 3d, (b) Bi 4f, (c) Ta 4f, (d) O 1s, (e) Cl 2p. The obtained XPS spectrum, show the presence of peaks in feature of spin-orbit splitting according to the literature, referring to the presence of the of Bi<sup>4+</sup> and Ta<sup>4+</sup> as in the bismuth tantalum oxychloride materials. The O 1s XPS measurements reveal only one signals at 529.75±0.1 eV which can be attributed to the oxygen in Bi<sub>4</sub>TaO<sub>8</sub>Cl crystal structure with no adsorbed oxygen due to Pd-O on the surface. Showing that palladium is deposited as Pd metals and not oxide.

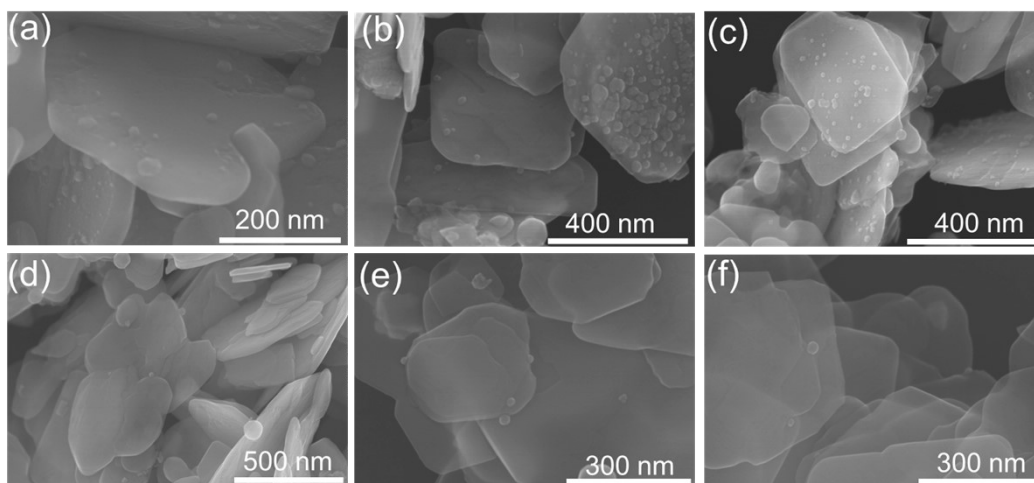


**Fig. S6** Surface charge properties of BTOC exposed {001} top-side facet and {110} lateral-side facet pretreated in acidic and alkaline condition (pH 6.5 and 10.5) as a function of pH of aqueous solution.

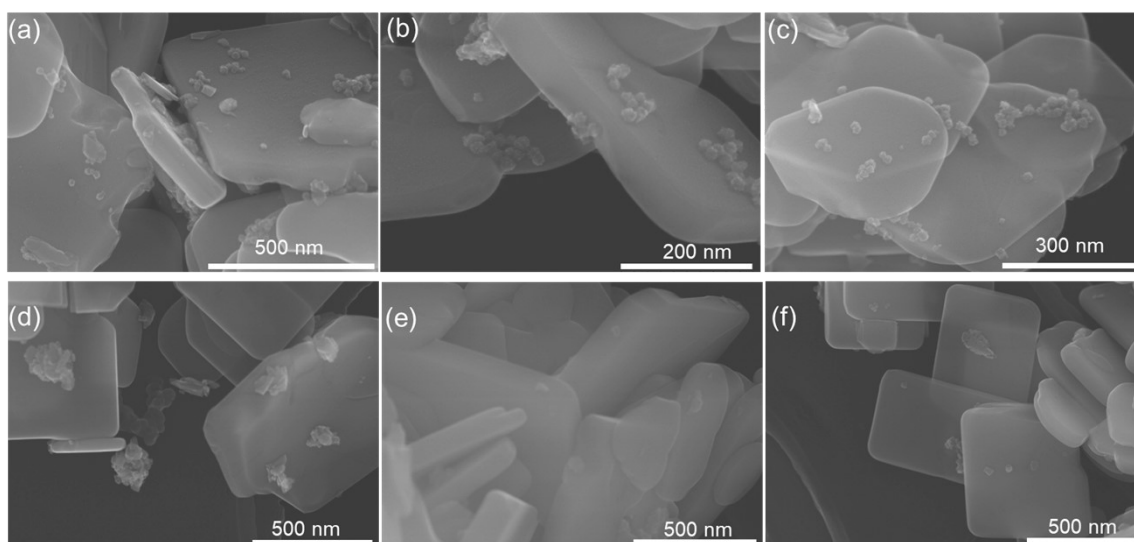
The surface charge of the sample can be said to be significantly dependent on the sample pretreatment condition, as the isoelectric point (IEP) varied.



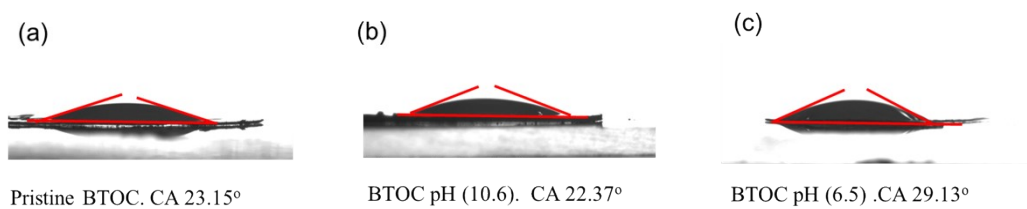
**Fig. S7** SEM images of single and dual metal and metal-oxides cocatalyst photo-deposited on the surface of BTOC. (a) Au/BTOC; (b) MnO<sub>x</sub>/BTOC; (c) Au/MnO<sub>x</sub> and (d) TEM image of BTOC single crystal. The amount of the deposited metals/metal oxides are all 2.0 wt. %.



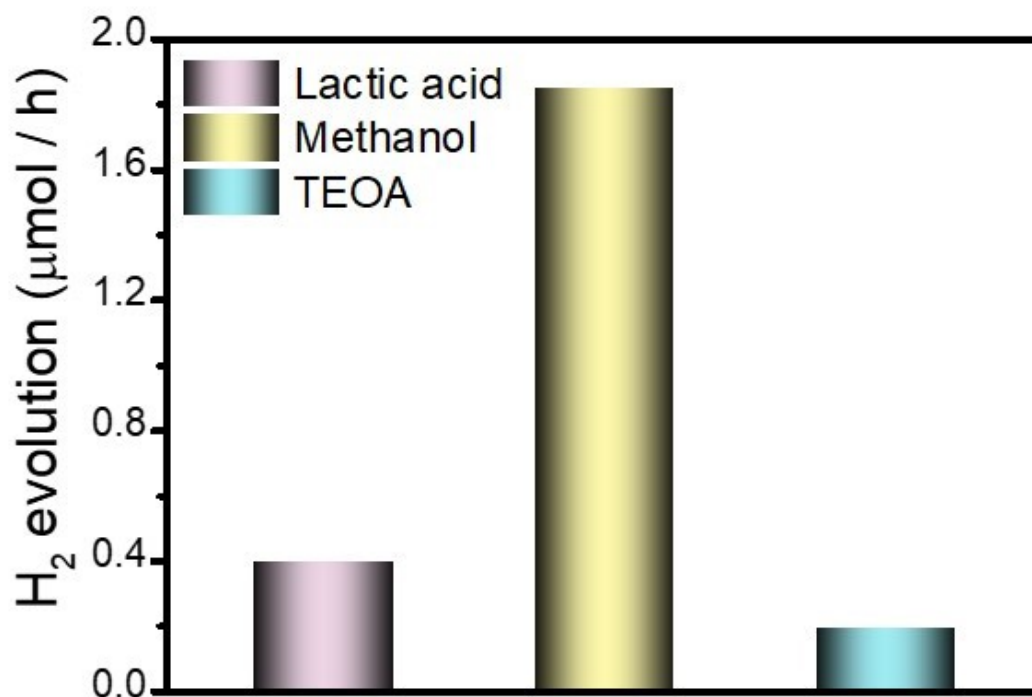
**Fig. S8** SEM images of silver ( $\text{Ag}^+$ ) nanoparticles photo-deposited on the surface of acidic and alkaline at pretreated at pH 10.5 and pH 6.5. BTOC nanoplate semiconductor. (a-c) pH 6.5 and (d-f) pH 10.5. The concentration of  $\text{Ag}^+$  loaded on all the sample is 2.0 wt. %.



**Fig. S9** SEM images of Palladium (Pd) metal particles adsorbed in the dark on the surface of acidic and alkaline pretreated BTOC semiconductor (pH 10.5 and pH 6.5). (a-c) pH 6.9 and (d-f) pH 10.5. Calculated 2 wt.% Pd were adsorbed in the dark under a continuous stirring. The concentration of Pd nanoparticles loaded on all the sample is 2.0 wt. %.



**Fig. S10** Water contact angle (WCA) diagram of pristine BTOC and palladium (Pd) modified alkaline and acidic conditions pretreated BTOC samples. (a) pristine BTOC, (b) BTOC at pH 10.5 and (c) BTOC at pH 6.5.



**Fig. S11** Photocatalytic H<sub>2</sub> evolution reaction performs under different electron mediating agent (Lactic acid, Methanol and Triethanolamine). Reaction condition Methanol: 100 mg cat., 10 vol.% CH<sub>3</sub>OH/H<sub>2</sub>O solution, 300 W Xe lamp ( $\lambda > 420$  nm). Reaction condition (Lactic acid): 100 mg cat., 10 vol.% CH<sub>3</sub>CH(OH)COOH/H<sub>2</sub>O solution (10 ml lactic acid), 300 W Xe lamp ( $\lambda > 420$  nm) and Reaction condition triethanolamine (TEOA): 100 mg cat., 10 vol.% TEOA/H<sub>2</sub>O solution, 300 W Xe lamp ( $\lambda > 420$  nm).



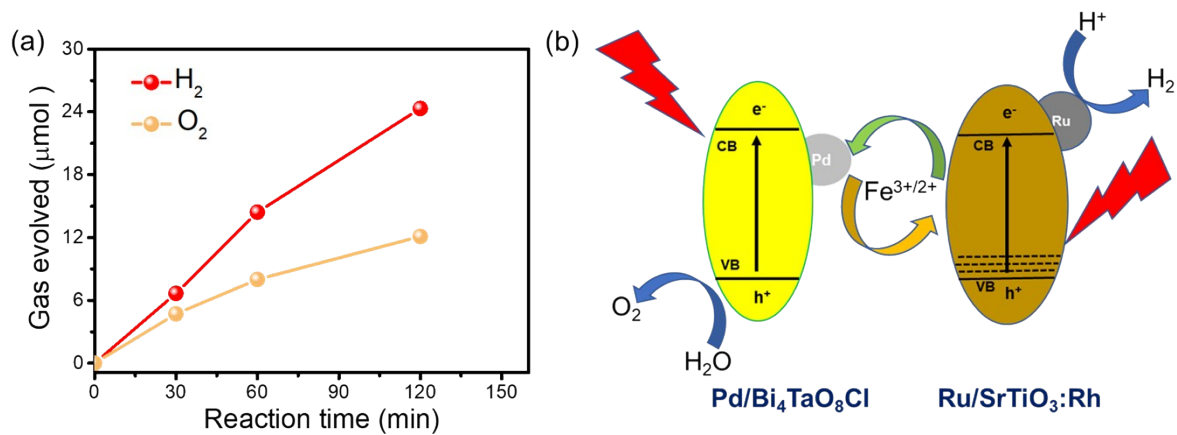


Fig. S12 (a) Time course of Z-scheme water splitting on Pd/Bi<sub>4</sub>TaO<sub>8</sub>Cl coupled with Ru/SrTiO<sub>3</sub>:Rh photocatalyst via Fe<sup>3+</sup>/Fe<sup>2+</sup> redox mediator. Reaction condition: 60 mg Bi<sub>4</sub>TaO<sub>8</sub>Cl, 50 mg Ru/SrTiO<sub>3</sub>:Rh, 100 mL H<sub>2</sub>O, 2.0 × 10<sup>-3</sup> M Fe(NO<sub>3</sub>)<sub>3</sub>, 300 W Xe lamp (λ ≥ 420 nm) and (b) Proposed mechanism of Z-scheme overall water splitting in Fe<sup>3+</sup>/Fe<sup>2+</sup> redox mediator system.

## References

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