

## ---Supporting Information---

### **Ultrathin Corrugated Nanowire TiO<sub>2</sub> as a Versatile Photoanode Platform for Boosting Photoelectrochemical Alcohol and Water Oxidation**

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## Experimental Section

### Synthesis of Spherical nanocrystalline particulate TiO<sub>2</sub> (NPTiO<sub>2</sub>)

Anatase TiO<sub>2</sub> nanocrystallites paste were synthesized according to a procedure that was modified from a previously reported sol-gel method.<sup>1</sup> 60 mL deionized water and 0.42 mL concentrated HNO<sub>3</sub> (about 70%) was mixed in an Erlenmeyer flask at room temperature. With vigorous stirring, 10 mL titanium tetraisopropoxide Ti(*i*-OPr)<sub>4</sub> was added dropwise into the flask in 10-20 min. A powdery white precipitate was observed and the mixture was then heated to 90-96 °C for roughly 7 hours till the volume of the solution reached 18 mL. During this time, the precipitate dissolved and become translucent grayish blue. The solution was then transferred into a 25 mL acid digestion bomb and heated at 200 °C for 12 hours. After cooling to room temperature, the resulting glue-looking substance was stirred continuously for at least 12 hours after adding 1.0 g of finely ground carbowax.

Spherical nanocrystalline particulate TiO<sub>2</sub> film (NPTiO<sub>2</sub>) were deposited by sol-gel spin coating method onto glass substrates. The above prepared paste diluted 5 times with water was dropped onto pre-FTO substrate, which was rotated at 3000 rpm for 60 s by using SETCAS LLC KW-4A spin coater. The films were then allowed to dry for about 30 min. They were then transferred into a box furnace and heated under air at 450 °C for 30 min. The films were either used immediately or stored in the dark at 70 °C. The thick of film is about 800 nm as measured in cross section by SEM, as shown in

Fig. S1.

**Spectroelectrochemistry** was performed on a CHI 760E electrochemical workstation and Agilent Cary 60 spectrometer. A typical three electrode cell was used with FTO|TiO<sub>2</sub>|RuP as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. N<sub>2</sub> degassed acetonitrile with 0.1 M TBAP was used as the supporting electrolyte. Spectra at specific potentials were recorded once the spectra after multiple scans stabilized.

### Figure S1-S8

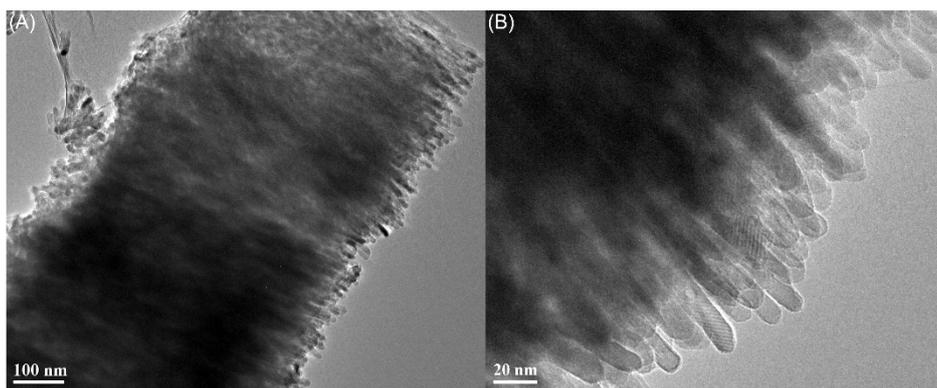


Fig. S1 TEM images of TiO<sub>2</sub> arrays reacted for 48 h (the smooth ultrathin nanowire TiO<sub>2</sub> arrays, UW-TiO<sub>2</sub> arrays).

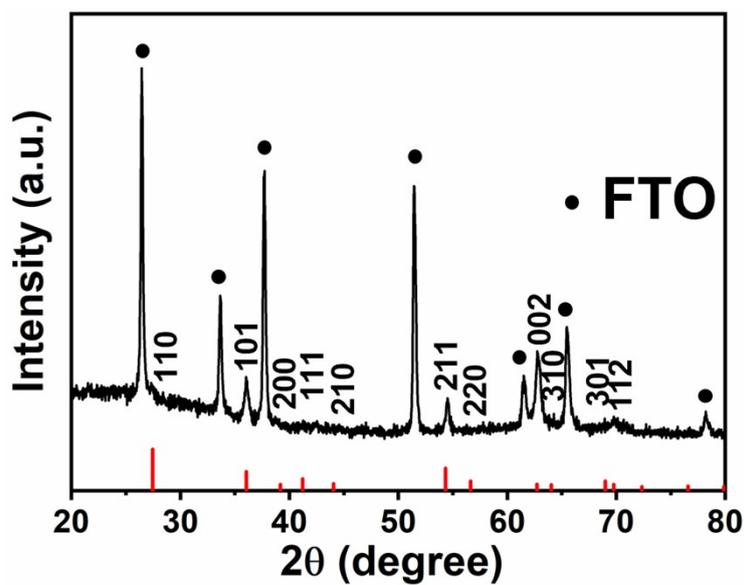


Fig. S2 XRD pattern of UCW-TiO<sub>2</sub>.

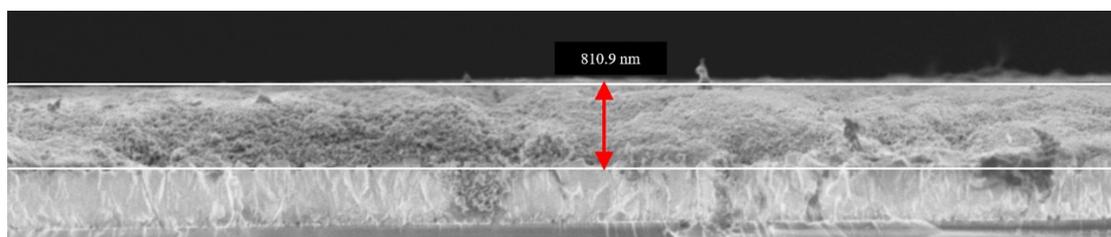


Fig. S3 Side-view of the SEM image of NPTiO<sub>2</sub> on FTO.

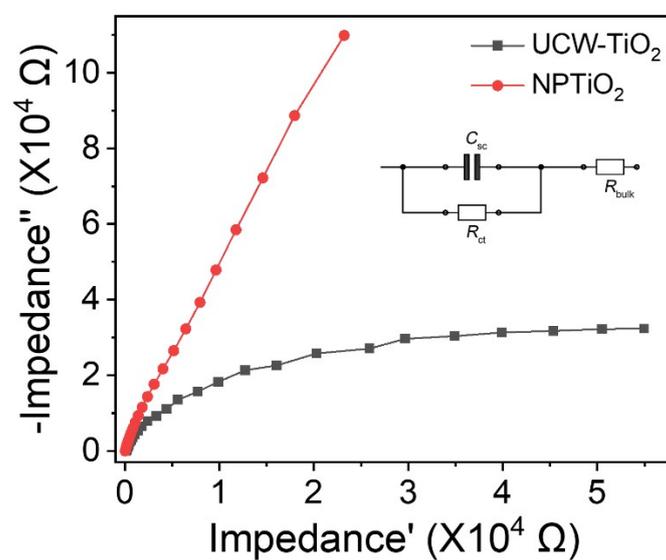


Fig. S4 Electrochemical impedance spectroscopy of UCW-TiO<sub>2</sub> and NPTiO<sub>2</sub> under white light illumination in 0.1 M tetrabutylammonium perchlorate (TBAP) acetonitrile solution.

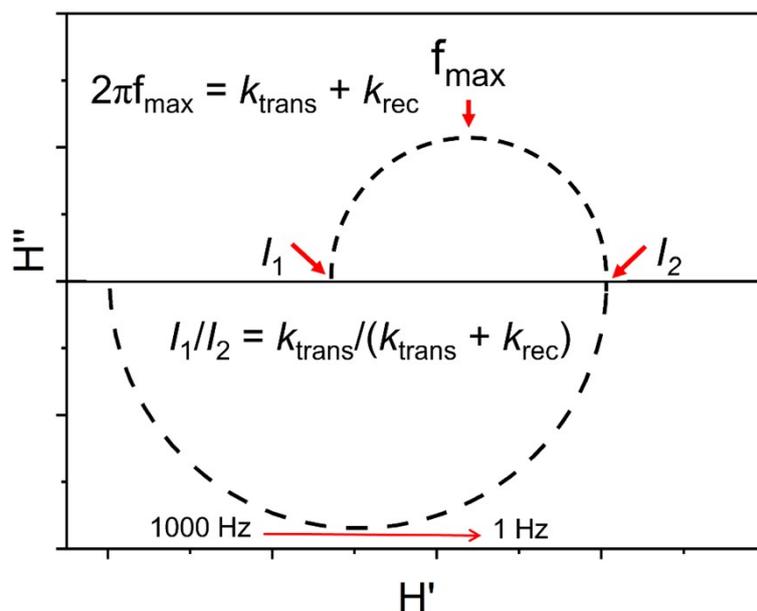


Fig. S5 A calculated example of IMPS spectrum, various properties (e.g. charge transfer rate constant, surface recombination rate constant) can be obtained based on the multiple points of such spectrum.

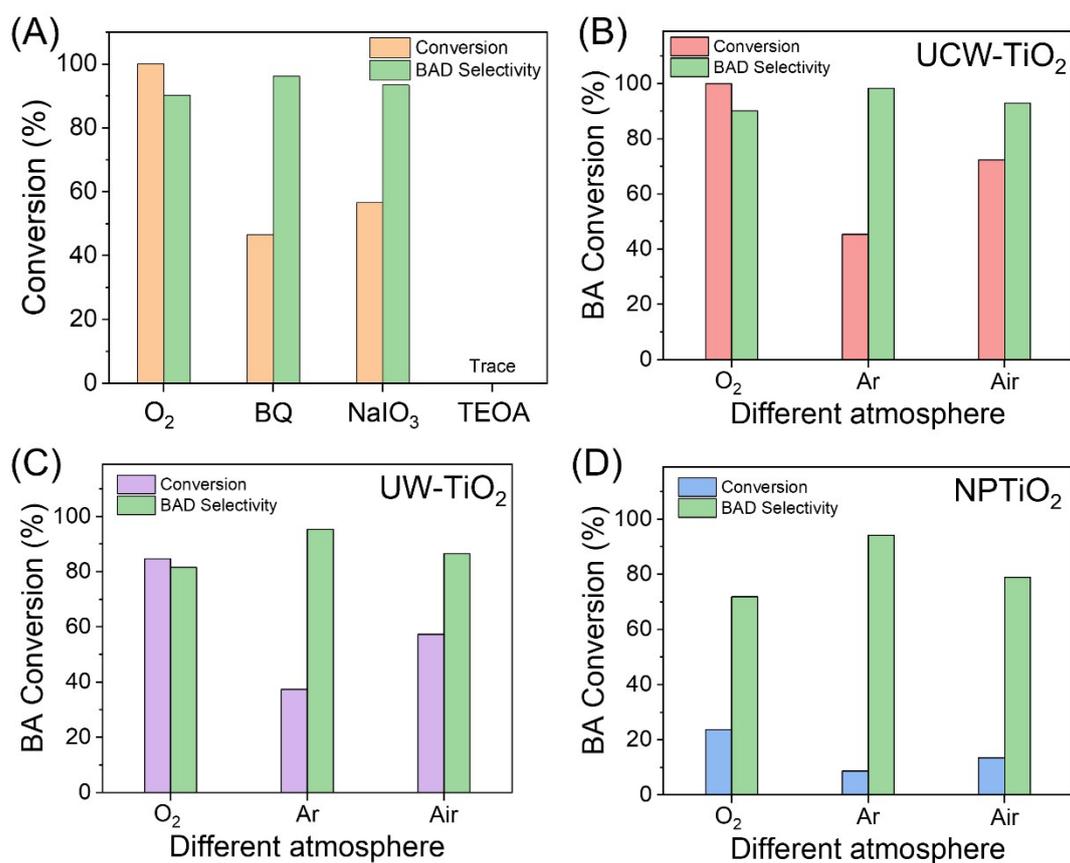


Fig. S6 (A) PEC BA oxidation reaction over a UCW-TiO<sub>2</sub> photoanode in the presence of various radical scavengers for 15 h, BQ as a O<sub>2</sub><sup>-</sup> radical scavenger, 5 mM; NaIO<sub>3</sub> as an e<sup>-</sup> scavenger, 30 mM; TEOA as a h<sup>+</sup> scavenger, (10% v/v). (B-D) Conversion and corresponding selectivity of BAD under different reaction atmospheres (argon, air, and O<sub>2</sub>) at the same reaction time.

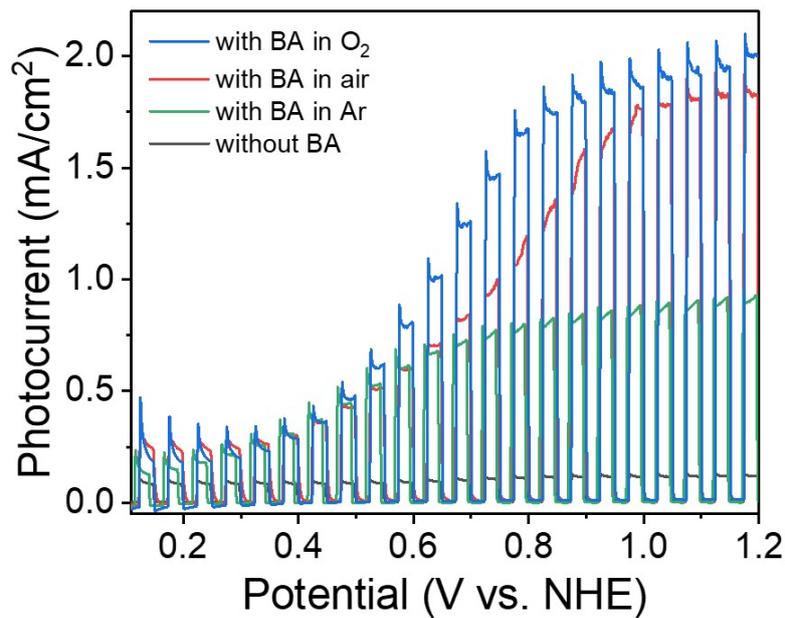


Fig. S7 The chopped photocurrent responses of the UCW-TiO<sub>2</sub> photoanode for BA oxidation under different reaction atmosphere (argon, air, and O<sub>2</sub>).

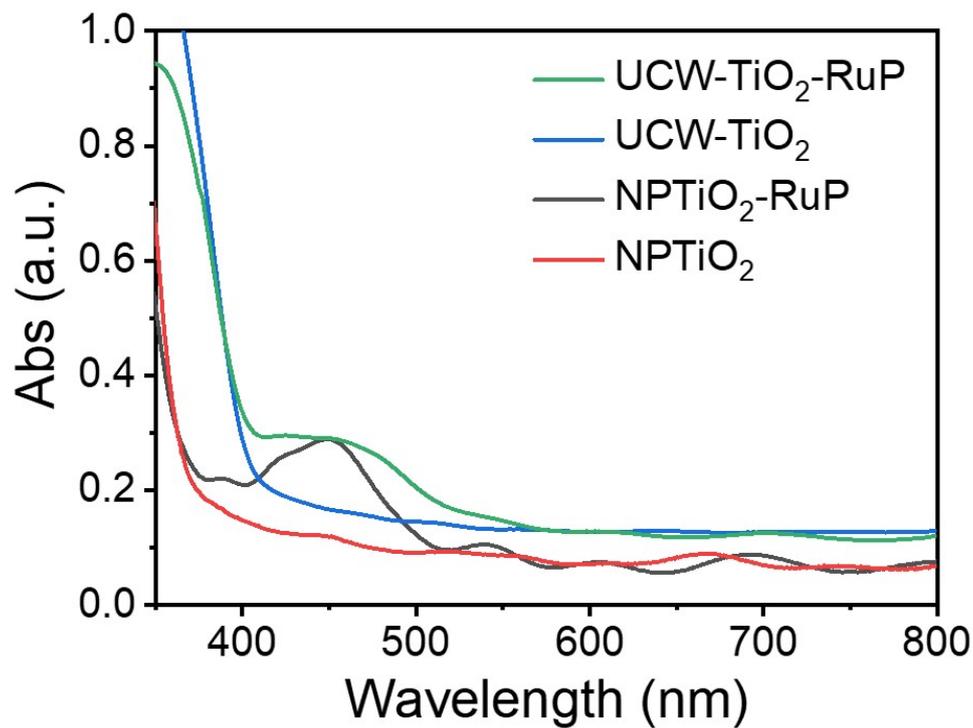
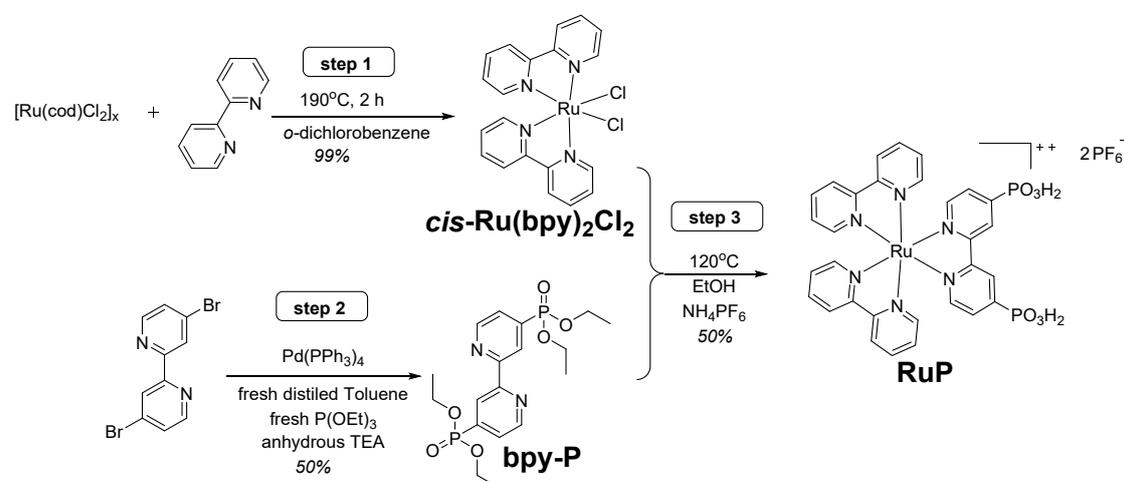


Fig. S8 UV-Vis spectra of NPTiO<sub>2</sub> and UCW-TiO<sub>2</sub> electrodes on FTO: pristine NPTiO<sub>2</sub> (red line) and UCW-TiO<sub>2</sub> (blue line), RuP sensitized UWTiO<sub>2</sub> (green line), and NPTiO<sub>2</sub> (black line).

Table S1 Comparison of the conversion, selectivity of BA molecules with different substituents over UCW-TiO<sub>2</sub> photoanodes.

Substrate	Conversion (100%)	Selectivity (100%)	Time (h)
4-methylbenzyl alcohol	91.5	92.1	10
4-Methoxybenzyl alcohol	92.6	90.7	10
4-bromobenzyl alcohol	86.3	89.7	10
4-Nitrobenzyl alcohol	83.7	87.5	10

### Synthesis of [Ru(4,4'-(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>-2,2'-bipyridine)(2,2'-bipyridine)]<sup>2+</sup> (RuP)



Scheme S1: photosensitizer **RuP** synthesis.

The Ruthenium phosphate photosensitizer synthesis was synthesized via three steps as illustrated in above Scheme S1, which was referred to reported with slight modification<sup>2</sup>. The only slight modification was step 3 with NH<sub>4</sub>PF<sub>6</sub> as additive. The NH<sub>4</sub>PF<sub>6</sub> not only provided exchangeable polyfluoro anion PF<sub>6</sub><sup>-</sup> that facilitated precipitation, but also provided Brønsted acid NH<sub>4</sub><sup>+</sup> that smoothly hydrolyzed the PO(OEt)<sub>2</sub> group into -PO(OH)<sub>2</sub>.<sup>2</sup> Protocol details were the following. Into a 25 mL round bottle layered *cis*-Ru(*bpy*)<sub>2</sub>Cl<sub>2</sub> (120 mg, 0.25 mmol), *bpy*-P (92 mg, 0.25 mmol), NH<sub>4</sub>PF<sub>6</sub> (163 mg, 1 mmol), and dissolved by EtOH (15 mL). The resultant thin bottle

was bubbled by nitrogen flow for half an hour, and sealed, stirred and heated at 120 °C for 10 hours. After finished, the mixture was concentrated under reduced pressure, dried under vacuum. The afforded crude mixture was purified by several crystallization via MeOH/Et<sub>2</sub>O, which afforded the desired **RuP** in red solid (120 mg, 50%). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 8.72 (t, *J* = 10.2 Hz, 1H), 8.59 – 8.43 (m, 2H), 8.01 (dd, *J* = 16.2, 8.4 Hz, 2H), 7.93 – 7.85 (m, 1H), 7.78 (t, *J* = 5.8 Hz, 2H), 7.54 (dd, *J* = 11.2, 5.5 Hz, 1H), 7.39 – 7.29 (m, 2H); <sup>31</sup>P NMR (162 MHz, D<sub>2</sub>O) δ 6.7 (m, -PO(OH)<sub>2</sub>), -144.66 (penta, *J* = 1393.4 Hz, PF<sub>6</sub><sup>-</sup>). The NMR spectra were in good agreement with the literature<sup>2</sup>.

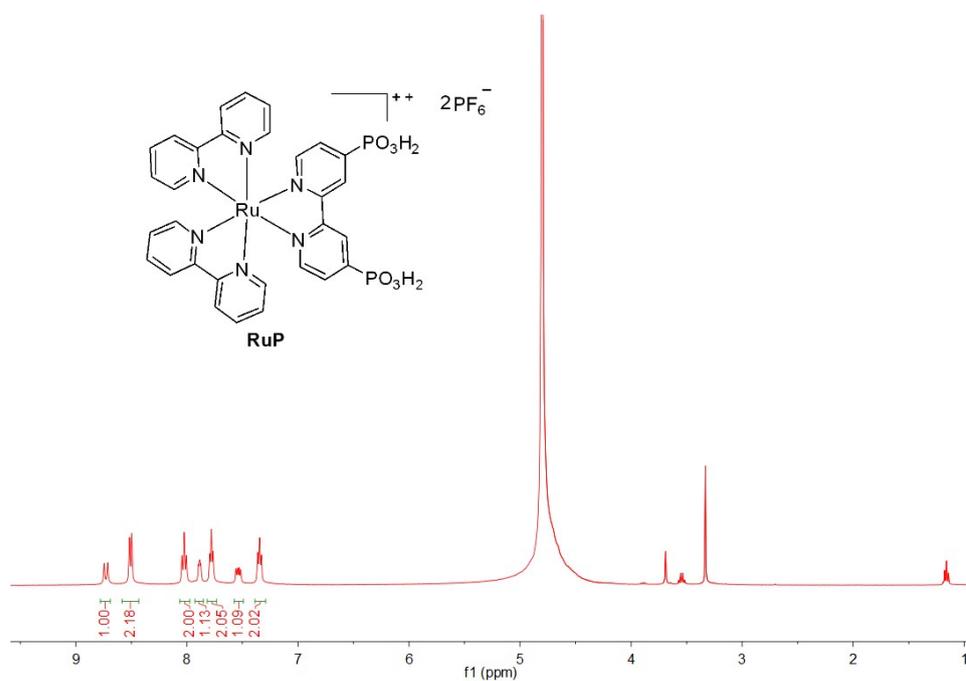


Fig. S9 <sup>1</sup>H NMR spectrum of RuP.

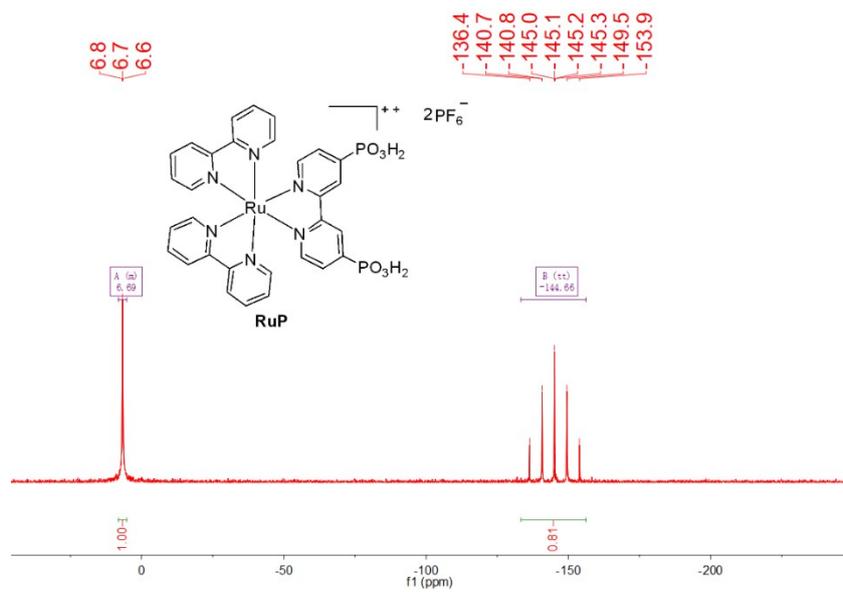
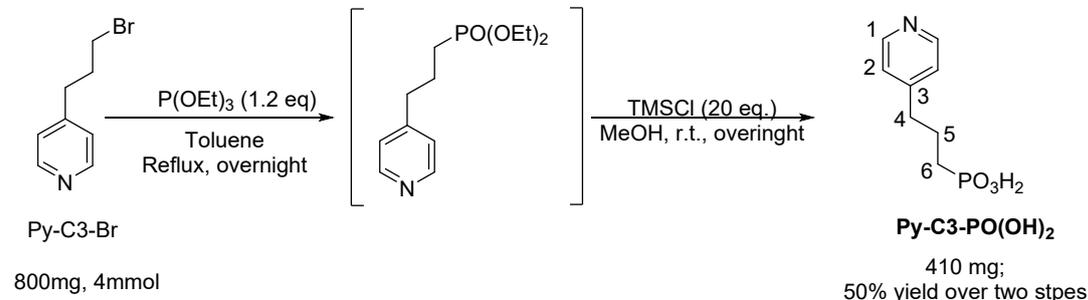


Fig. S10 <sup>13</sup>C NMR spectrum of RuP.

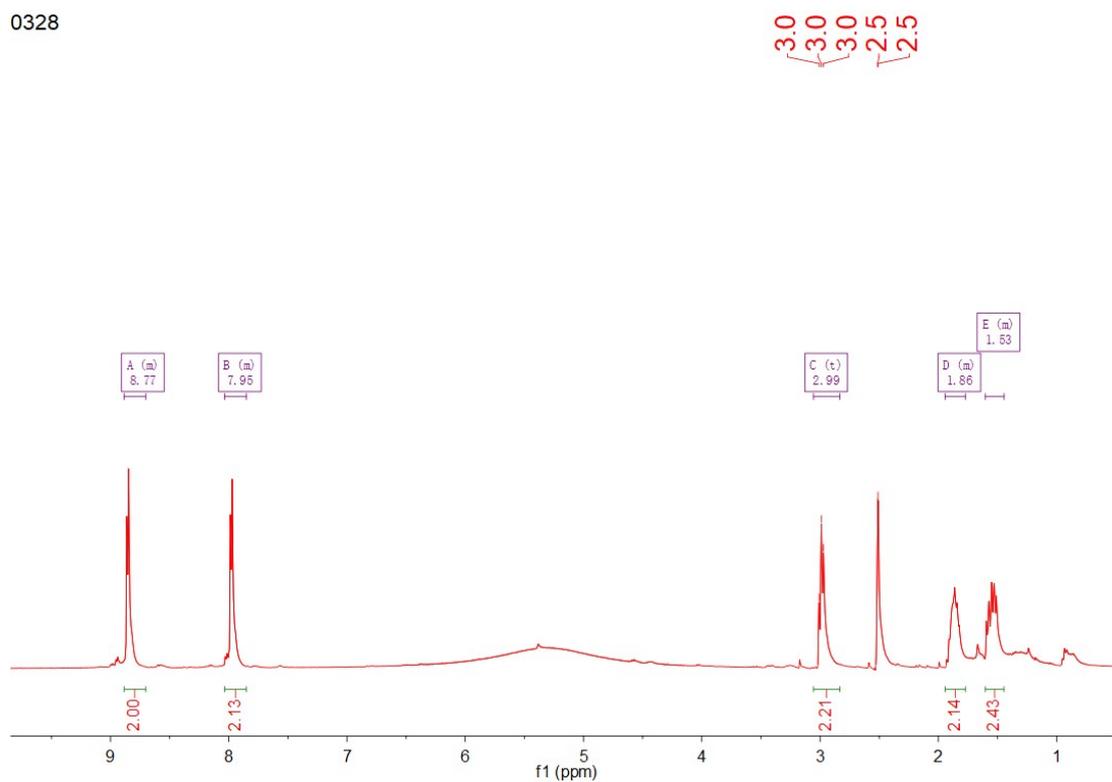
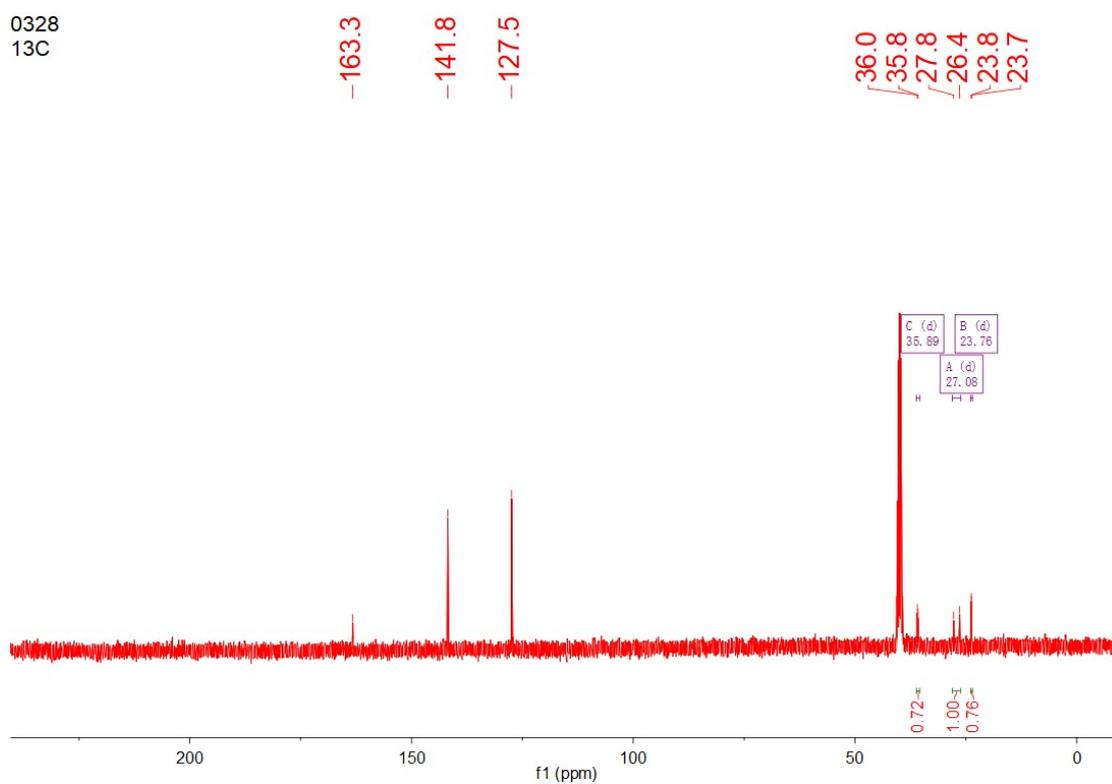
**Synthesis of phosphate-containing ligand (3-(pyridin-4-yl)propyl)phosphonic acid (Py-C3-PO(OH)<sub>2</sub>)**



Scheme S2: synthetic route to (3-(pyridin-4-yl)propyl)phosphonic acid (Py-C3-PO(OH)<sub>2</sub>)

4-(3-bromopropyl)pyridine (**Py-C3-Br**) was synthesized according to the corresponding reference<sup>3</sup>. While the bromide was phosphonated via Arbuzov reaction with P(OEt)<sub>3</sub>, which quantitatively forged the Py-C3-PO(OEt)<sub>3</sub>, and further hydrolysis to the target (3-(pyridin-4-yl)propyl)phosphonic acid [**Py-C3-PO(OH)<sub>2</sub>**] was referred to the related literature<sup>2</sup>, which resulted in colorless to slight yellow oil (410mg, two steps, 60% yield). <sup>1</sup>H NMR (400 MHz, DMSO) δ 8.85 (d, *J* = 6.4 Hz, 2H, H<sub>1</sub>), 7.98 (d, *J* = 6.2 Hz, 2H, H<sub>2</sub>), 2.99 (t, *J* = 7.5 Hz, 2H, H<sub>4</sub>), 1.94 – 1.77 (m, 2H, H<sub>6</sub>), 1.60 – 1.44 (m, 2H, H<sub>5</sub>); <sup>13</sup>C NMR (101 MHz, DMSO) δ 163.28 (C-1), 141.83(C-2), 127.45 (C-3), 35.89 (d, *J* = 15.7 Hz, C-4), 27.08 (d, *J* = 136.9 Hz, C-6), 23.76 (d, *J* = 3.7 Hz, C-5); <sup>31</sup>P NMR (162 MHz, DMSO) δ 25.98 – 24.48 (m).

0328

Fig. S11  $^1\text{H}$  NMR spectrum of (3-(pyridin-4-yl)propyl)phosphonic acid (Py-C3-PO(OH)<sub>2</sub>).0328  
13CFig. S12  $^{13}\text{C}$  NMR spectrum of (3-(pyridin-4-yl)propyl)phosphonic acid (Py-C3-PO(OH)<sub>2</sub>).

0328  
31P

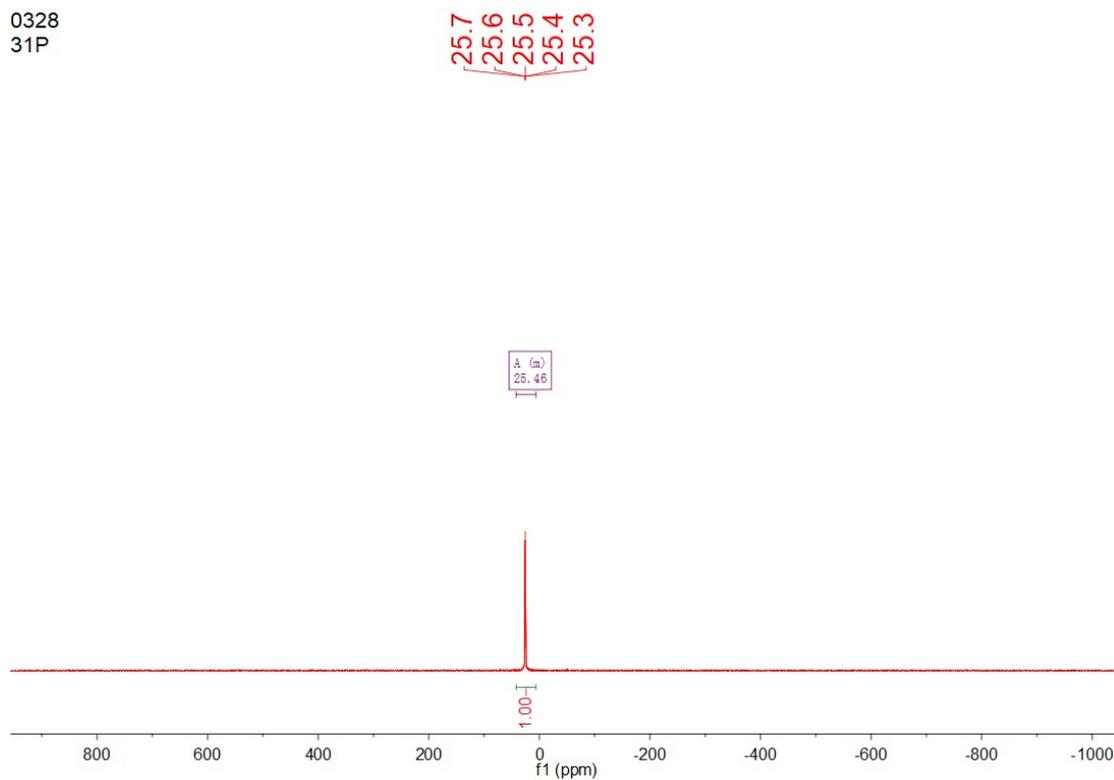
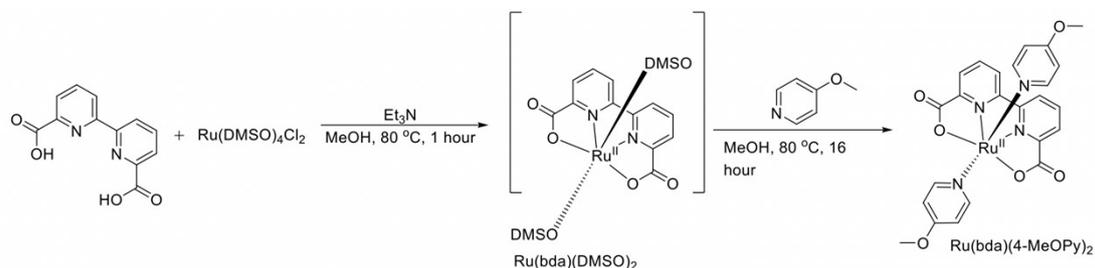


Fig. S13  $^{31}\text{P}$  NMR spectrum of (3-(pyridin-4-yl)propyl)phosphonic acid (Py-C3-PO(OH)<sub>2</sub>).

## Synthesis of water oxidation catalyst (Ru(bda)(4-MeOPy)<sub>2</sub>)

*Synthesis of Water oxidation catalyst (Ru(2,2'-bipyridine-6,6'-dicarboxylate)(4-methoxypyridine)<sub>2</sub>), Ru(bda)(4-MeOPy)<sub>2</sub>*



Scheme S3: synthetic route to Ru(bda)(4-MeOPy)<sub>2</sub>

The compound was synthesized according to previous work of our group.<sup>4</sup> In brief, into a flame-dried Schlenk tube was layered 2,2'-bipyridine-6,6'-dicarboxylic acid (H<sub>2</sub>bda, 97.6 mg, 0.4 mmol), *cis*-Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (193.2 mg, 0.4 mmol), TEA (Triethylamine, 0.5 mL) and methanol (30 mL). The resultant reaction tube was sealed, evacuated, refilled with nitrogen and heated to 80 °C for 1 hour, then an excess of 4-methoxy pyridine (109 mg, 1 mmol) was added via syringe, the mixture was heated at 80 °C overnight. The reaction mixture was concentrated under reduced pressure, and the left residue was applied on silica gel chromatography (DCM/MeOH, 100/1~100/3), which afforded the desired product as dark red solid named Ru(bda)(4-MeOPy)<sub>2</sub> (160 mg, 71%). The complex was stored under nitrogen atmosphere.

## Reference

1. T. A. Heimer, S. T. D'Arcangelis, F. Farzad, J. M. Stipkala and G. J. Meyer, *Inorg. Chem.*, 1996, **35**, 5319-5324.
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