

## **Electronic Supplementary Information for**

### **Promoting Water Dissociation Performance by Borinic Acid for**

### **Strong-Acid/Base-Free Hydrogen Evolution Reaction**

#### **Experimental**

##### Reagents and instruments

Borinic acid (BA) was synthesized according to the literature.<sup>[1]</sup> Sulfuric acid, acrylic acid, methane sulfonic acid, etc. are all analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd. Tetra-n-butylammonium perchlorate (TBAP) was purchased from Sigma (Sigma-Aldrich, China). The water used in the experiment is bidistilled water. The electrochemical tests were carried out by using the CHI660D electrochemical workstation manufactured by Shanghai Chenhua Instrument Co., Ltd.

##### Glassy Carbon Electrode (GCE) pretreatment

The working surface of the GCE electrode was firstly polished on a polishing cloth with alumina powders (1.0  $\mu\text{m}$ , 0.3  $\mu\text{m}$ , 0.05  $\mu\text{m}$  diameter), and the surface was rinsed with deionized water for 1 min. The polished GCE was then immersed in absolute ethanol, acetone and 10% (volume fraction) aqueous solution of nitric acid for 3 min, and then washed with deionized water.

Electro-activity detection: The polished GCE was placed in a 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6^+$  0.2M KCl mixed solution, and a cyclic voltammetry curve was performed using a three-electrode system at a sweep speed of 50 mV/s in the range of 0.6 to -0.1 V. Cycle voltammetry curve was used to calculate the potential difference ( $\Delta E_p$ ) between the two peaks. The electrode is cleaned when  $\Delta E_p$  is less than 80 mV.

##### Electrochemical Measurements

The electrochemical test method used is cyclic voltammetry. In the three-electrode system, the working electrode is a GCE or platinum electrode, the counter electrode is a platinum plate electrode, and the reference electrode is a saturated calomel electrode (SCE). TBAP was used as electrolyte and added to the mixed solvents of DMF containing  $\text{H}_2\text{O}$ . The solution was purged with nitrogen for 15 min before the test to

remove dissolved oxygen in the solution.

The Nuclear Magnetic Resonance (NMR) spectra were recorded in  $\text{CDCl}_3$  solution on Bruker Ascend TM 400 NMR spectrometer (400 MHz for  $^1\text{H}$ ), using internal tetramethylsilane as a reference.

Fourier transform infrared (FT-IR) spectroscopy were recorded on a TENSOR II FTIR Spectrometer (Bruker, Germany), using KBr pellets. The spectra were recorded from an accumulation of 16 scans in the range of  $4000 - 400 \text{ cm}^{-1}$  and were collected at room temperature.

Raman spectra were recorded on a H2000 (Renishaw, England). The excitation wavelength was 532 nm, and the spectra Scanning range was from  $0$  to  $4000 \text{ cm}^{-1}$ .

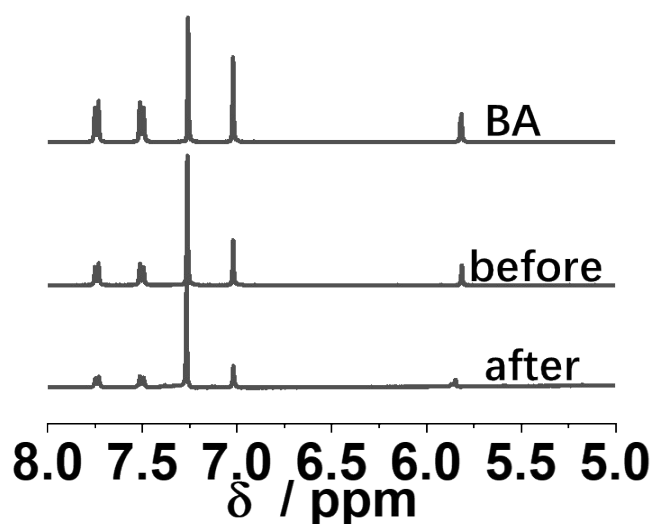


Figure S1. Comparison of the  $^1\text{H}$  NMR spectra of BA, BA+TBAP (before electrolysis reaction) and BA+TBAP (after electrolysis reaction) in  $\text{CDCl}_3$

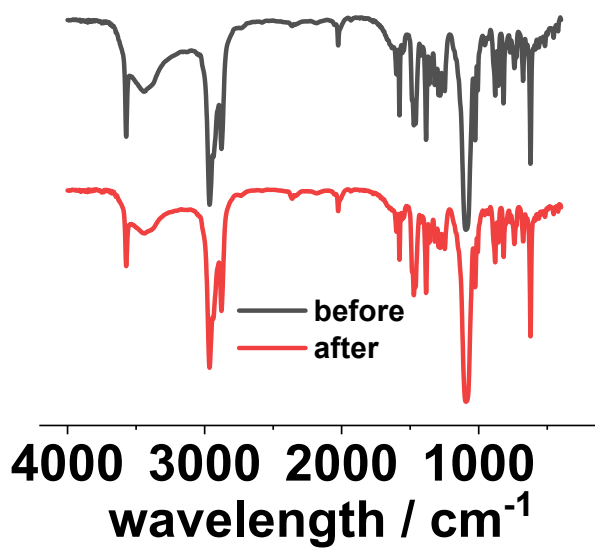


Figure S2. Comparison of the IR spectra of BA+TBAP before and after electrolysis reaction.

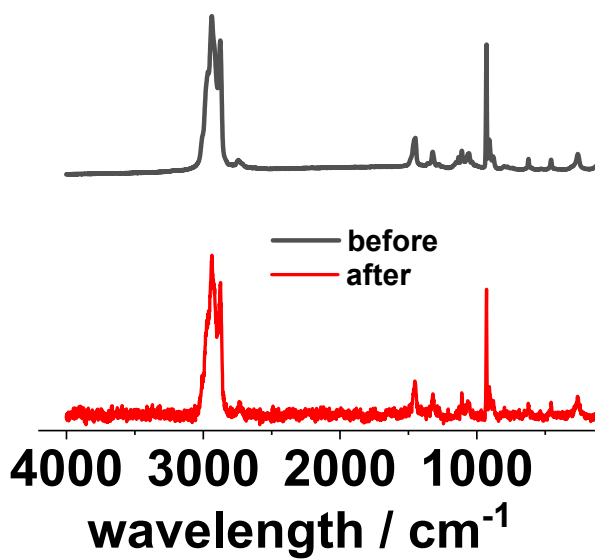


Figure S3. Comparison of the Raman spectra of BA+TBAP before and after electrolysis reaction.

#### Reference

- [1] Wan, W. M.; Cheng, F.; Jäkle, F. *Angew. Chem. Int. Ed.* **2014**, *53*, 8934.