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Supporting Information

Decoupling half-reactions of electrolytic water splitting by integrating a polyaniline electrode

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EXPERIMENTAL

Chemicals. Aniline (99.5%), ammonium peroxodisulfate (AR), hydrochloric acid (37.5%), hydrazine hydrate (98%), ethanol (99.8%), ammonium hydroxide (28%) and sulfuric acid (98%) were obtained from Sigma-Aldrich. All the chemicals were used as received without further purification. Black Pearl 2000 was purchased from Cabot Corporation. Ti-mesh, Pt-coated Ti-mesh electrode and RuO_2/IrO_2-coated Ti-mesh electrode were purchased from Baoji Zhiming Special Metal Co., LTD. All electrolyte solutions were prepared with deionized water (18.2 MΩ·cm) unless stated otherwise.

Apparatus. Scanning electron microscopy (SEM) images were obtained at Hitachi S-4800 (Hitachi, Japan). Transmission electron microscopy (TEM) images, high resolution TEM (HRTEM) images and selected area electron diffraction (SAED) images were obtained using Tecnai G^2 F20 S-Twin.

FT-IR spectra were obtained on a Nicolet 6700 spectrometer (Thermo Fisher Nicolet, USA) with KBr pellets. Raman spectra were recorded on a confocal microscope laser Raman spectrometer (Rainshaw invia). The excitation source was a helium-neon laser with a wavelength of 532 nm. Powder X-ray diffraction (XRD) was measured by Bruker D8 Foucs via ceramic monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 40 mA.

Electrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua Corp., Shanghai, China). The three-electrode system consisted of a working electrode, a platinum plate counter electrode, and a saturated calomel reference electrode (SCE, ~0.244 V *vs.* NHE). Prior to each measurement, the platinum plate counter electrode was routinely treated by soaking in 1 M hydrochloric acid to remove any impurity. Unless stated otherwise, all potentials in cyclic voltammetry and linear scan voltammetry were reported *vs.* RHE with 80% *iR* compensation and Galvanostatic charge-discharge experiments were conducted without *iR* compensation. The current denisty and discharge capacity were calulated on the basis of pure PANI. All experiments were performed at 22 ± 2 °C.

The electrochemical impedance spectroscopy (EIS) data was recorded under an open-circuit potential over a frequency range from 0.01 Hz to 1 MHz at the amplitude of the sinusoidal voltage of 5 mV. The explicit Nyquist plots were obtained based on the EIS data. Before the linear scan voltammetry and chronopotentiometry tests with the $RuO_2/IrO_2||PANI||Pt$ electrolyzer, the PANI electrode was pretreated by holding the potential at 0.4, 0.5, 0.6, 0.7 and 0.8 V vs. RHE, respectively, in a standard three-electrode setup until the current approaches zero.

Procedure. *Preparation of the PANI material.* The PANI material was synthesized by the chemical oxidative dispersion polymerization of aniline in HCl aqueous solution under stirring, where ammonium peroxodisulfate was used as the oxidant and MnO_2 as the initiator in an ice water bath (< 5 ^{o}C). In detail, 600 mL of 1.0 M HCl aqueous solution, 50.0 g of aniline (0.55 mol) and 1.4 g of MnO_2 were added into a flask. The mixture was stirred for 30 min in an ice bath. Then, 125 g of ammonium peroxodisulfate was added into the suspension for 80 times in 3 h under stirring. Polymerization of aniline was carried out at < 5 °C for 4 h and 2 g of conductive agent carbon black was added into the suspension. The resultant PANI dispersion was then dewatered by vacuum filtration and washed repeatedly with deionized water and ethanol to ensure the complete removal of the inorganic salts. Finally, 5% aqueous ammonia was used to obtain the purified PANI by de-doping. After being dried under vacuum at 50 °C, the purified PANI material was collected.

Preparation of the PANI electrode. To evaluate the electrochemical redox behavior of PANI, the PANI working electrode was prepared as follows: a total of 8 mg of the electrocatalyst and 80 μl of 5 wt% Nafion solution were dispersed in 1 ml of 4:1 (v/v) water/ethanol by 30 min sonication. Five microliters of the electrocatalyst suspension were dropped onto the glassy carbon (0.071 cm^2) electrode, which was allowed to dry at 50 ^{o}C for 30 min in the oven.

To evaluate the effectiveness of PANI as a redox mediator, the PANI powder was pressed onto the Ti-mesh substrate (2 cm × 2 cm) at the pressure of 10 MPa for 2 mintues. Unless stated otherwise, the mass loading of the PANI electrode for electrochemical measurements in a standard three-electrode setup is approximately 5 mg/cm^2, and the mass loading of the PANI electrode for decoupled water splitting (with PANI as the intermediary electrode) is approximately 50 mg/cm^2.

Figure S1. Photograph of the as-prepared PANI composite.

The as-prepared PANI composite is in the form of dark green powder.

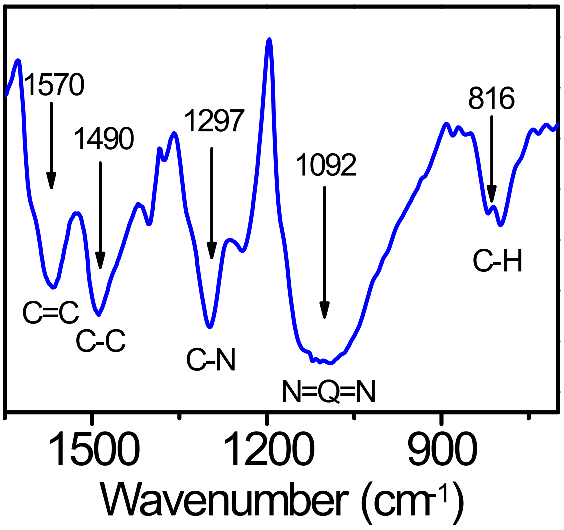

Figure S2. FTIR spectrum of the PANI composite.

In Figure S2, the FT-IR spectrum reveals that it has characteristic bands at 1570 cm^{-1} (C=C stretching of the quinonoid rings), 1490 cm^{-1} (C=C stretching of the benzenoid rings), 1297 cm^{-1} (C-N stretching of the benzenoid rings), 1092 cm^{-1} (N=Q=N stretching of the quinonoid ring), and 816 cm^{-1} (C-H out of the plane bending vibration).

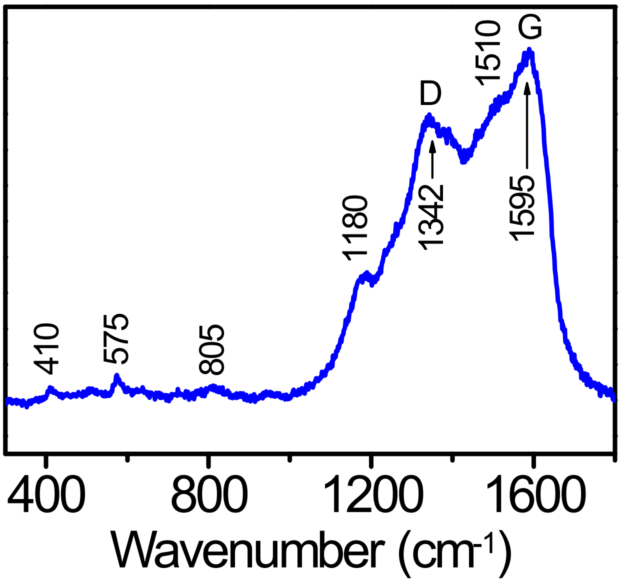

Figure S3. Raman spectrum of the PANI composite.

In Figure S3, the Raman spectrum of the PANI material exhibits two distinct Raman peaks at around 1342 and 1595 cm^{-1}, attributed to the D-band and G-band of the carbon-based material (i.e. the conductive agent carbon black). In addition, a series of Raman peaks appear at around 410, 575, 805, 1180 and 1510 cm^{-1}, respectively, consistent with other PANI materials prepared by similar or different methods.

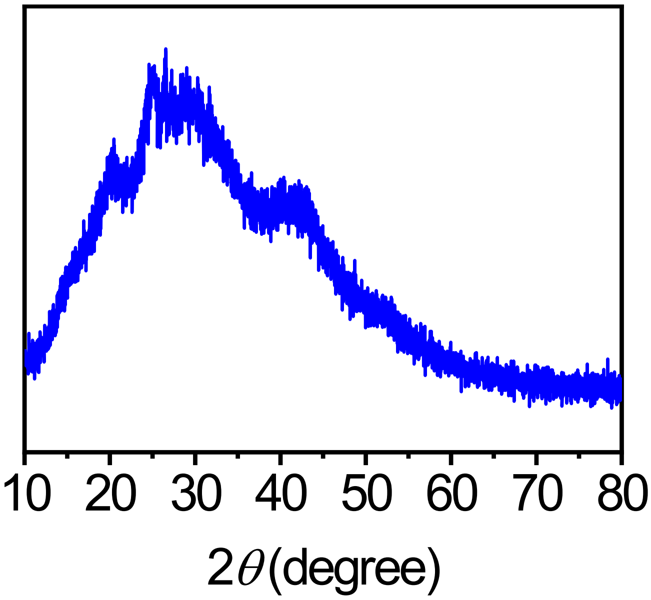

Figure S4. XRD patterns of the PANI composite.

The PANI material was further characterized by XRD technique. As shown in Figure S4, the XRD pattern of the PANI material reveals two broad and weak diffraction peaks at approximately 20.3° and 25.0°, indicating the poor crystalline nature of this material. The other two broad diffraction peaks centered at approximately 27° and 42° are characteristics of carbon-based materials (i.e. the conductive agent carbon black).

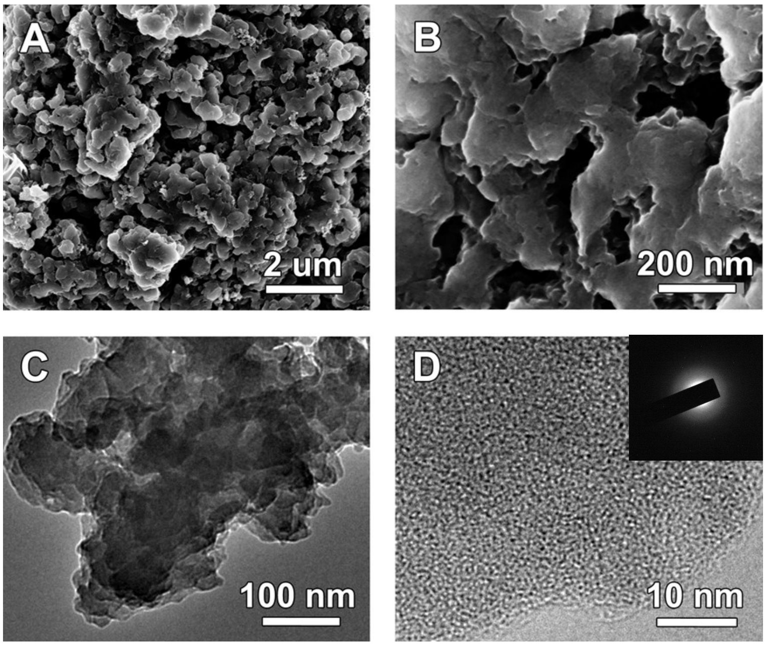

Figure S5. (A, B) SEM images, (C) TEM image, and (D) high-resolution TEM image of the PANI material. The inset in (D) is the selected-area electron diffraction (SAED) pattern of the sample.

In Figures S5A and S5B, the SEM images show that the PANI material has a loose layered structure. In Figure S5C, the TEM image also reveals a layered structure. In Figure S5D, the high-resolution TEM image and the SAED pattern indicate that the material is of poor crystalline structure, consistent with the XRD result.

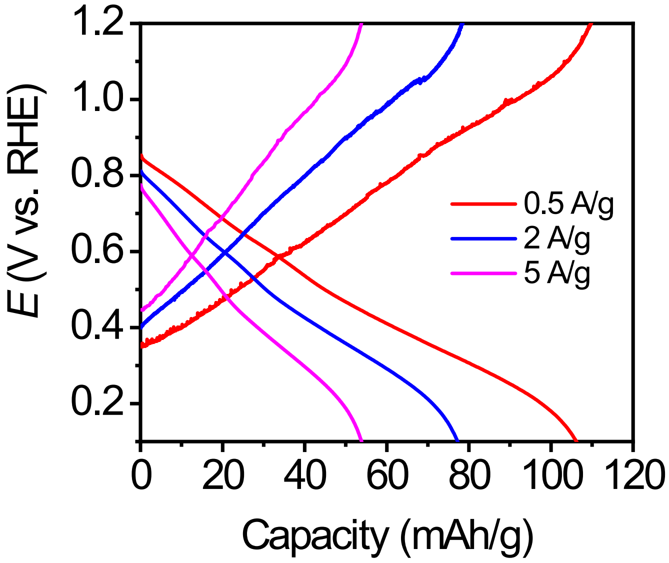

Figure S6. Galvanostatic charge-discharge curves of the PANI electrode at different rates between the voltage of 0.1 and 1.2 V (vs. RHE) in 0.5 M H_2SO_4 solution.

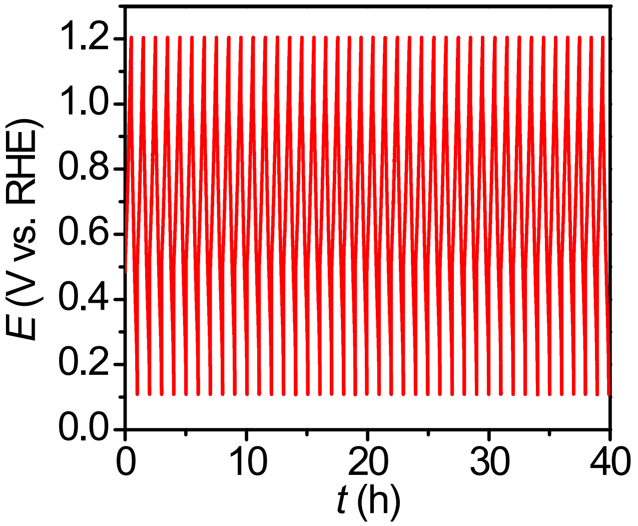

Figure S7. Galvanostatic charge-discharge curves of the PANI electrode at a current density of 0.2 A/g in the range of 0.1 to 1.2 V for 40-cycle test.

Figure S8. Photograph of the decoupled water splitting electrolyzer RuO_2/IrO_2||PANI||Pt. It is constructed with a commercial RuO_2/IrO_2-coated Ti-mesh electrode for the OER (left), a PANI film electrode as the solid-state redox mediator (middle), and a commercial Pt-coated Ti-mesh electrode for the HER (right).

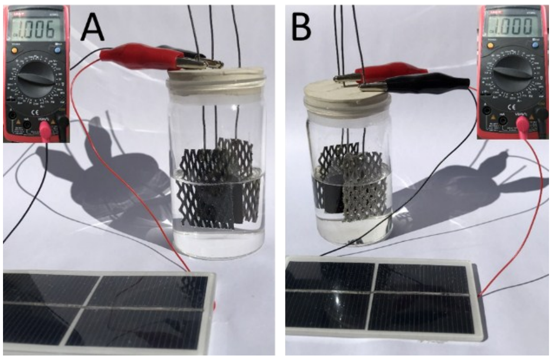

Figure S9. Photograph of the decoupled (A) OER cell and (B) HER cell with the assistance of PANI electrode driven by a commercial Si solar cell (voltage ~ 1.0 V, under natural sunshine). The positive and negative poles of the cell are directly connected to the RuO_2/IrO_2-coated Ti-mesh electrode and PANI electrode in (A) and to PANI electrode and Pt-coated Ti-mesh electrode in (B), respectively.

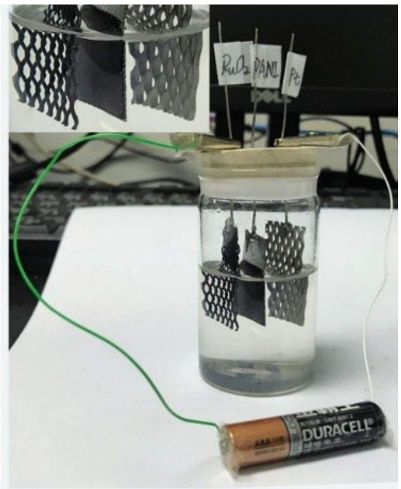

Figure S10. Photograph of the conventional $RuO_2/IrO_2||Pt$ cell driven by a commercial alkaline zinc-manganese dioxide dry battery of ~1.5 V. The positive and negative poles of the battery are directly connected to the RuO_2/IrO_2-coated Ti-mesh electrode and Pt-coated Ti-mesh electrode, respectively. In the absence of the intermediary PANI electrode, water splitting is hardly achieved by the battery even with a voltage of ~1.5 V.

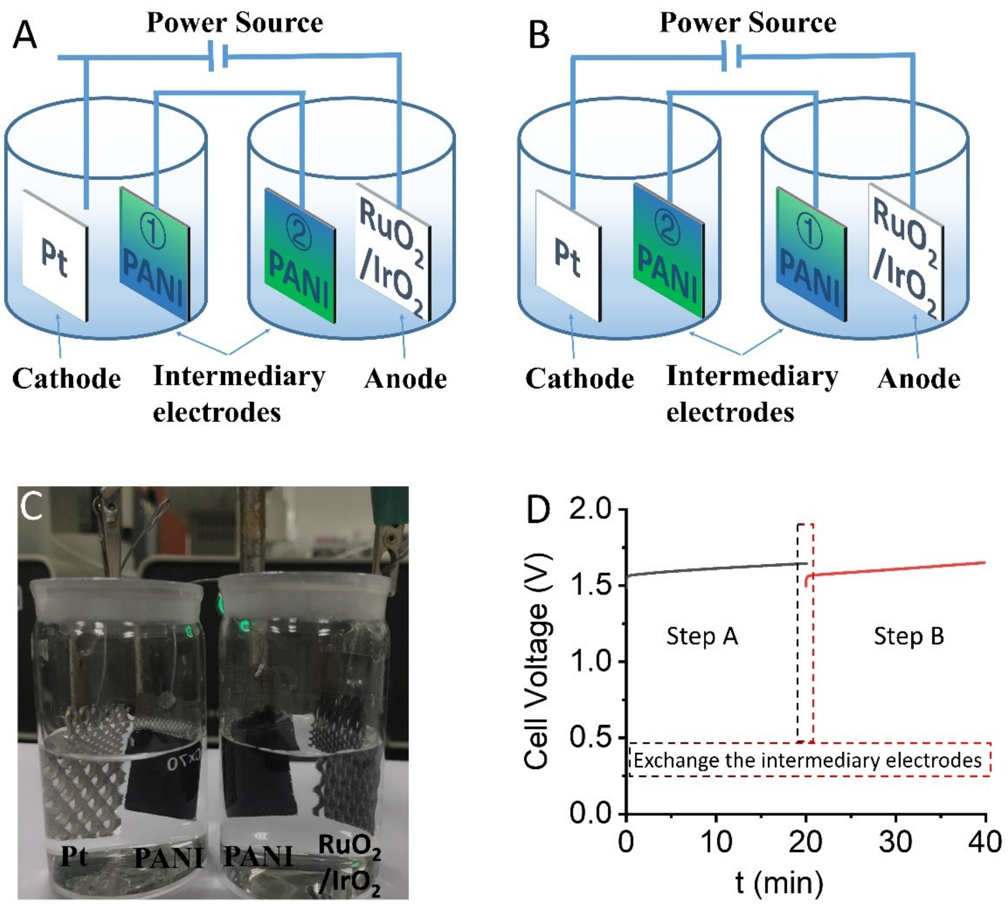

Figure S11. (A) Schematic illustration of water electrolysis with two separate compartments for H_2 and O_2 production, respectively, with the assistance of the intermediary PANI electrodes. (B) The two PANI electrodes are exchanged between the cathode and anode compartments. (C) Corresponding photograph of the electrolysis setup. (D) Chronopotentiometric curves with the assistance of the intermediary PANI electrodes for decoupled HER and OER at two seperate compartments concurrently at 5 mA (0.025 A/g). The rectangle between step A and Step B signifies the exchange of the intermediary PANI electrodes.