Electronic Supplementary Information

Amorphous Titanic Acid Electrode: Its Electrochemical Storage of Ammonium in a New Water-in-Salt Electrolyte

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Experimental

Synthesis of Materials

The synthesis of the precursor $Ti(OH)_4$ was performed in a similar method to literature.[10] In a typical synthesis, 1 mL $TiCl_4$ was added to 50 mL of DI water slowly under constant stirring. An aqueous ammonia solution was then added dropwise until the pH reached 9, yielding a $Ti(OH)_4$ gel mixture. The particles were then separated by centrifuge, which were calcined at 110 ^{o}C and 450 ^{o}C for 12 hours, yielding $TiO_{1.85}(OH)_{0.30}\cdot 0.28H_2O$ and TiO_2 anatase powder, respectively.

Materials Characterization

The crystal structure of all materials was characterized by powder X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.5406 Å) in a Rigaku Ultima IV Diffractometer. The morphologies were determined using scanning electron microscopy (SEM) using a FEI NOVA 230 high resolution scanning electron microscope. Thermal gravimetric analysis (TGA) was performed on a Shimadzu TGA-50 instrument in air at a temperature ramp of 5 °C min^{-1} from room temperature to 700 ^{o}C. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a Nicolet™ iS™ 10 spectrometer on powder samples and free-standing film electrodes. Brunauer–Emmett–Teller (BET) analysis was conducted in a Micromeritics TriStar II instrument using N_2 at an isotherm of 77.3 K. Density measurements were performed on a Mettler Toledo XS64 balance using the Archimedes Principle. pH measurements were done on a Schott Instruments Lab 850 pH probe, which was calibrated using pH = 4 and pH = 7 buffers prior to testing.

Electrochemical Characterization

All the half-cell tests were performed in three-electrode Swagelok configuration cells using an aluminum and titanium rod as the negative and positive current collectors, respectively. The working electrode was prepared by mixing active material ($TiO_{1.85}(OH)_{0.30}\cdot 0.28H_2O$ or TiO_2), super P carbon-45 (TIMCAL) and polyvinylidene fluoride with a mass ratio of 7:2:1 in N-Methyl-2-pyrrolidone (NMP). The homogeneous slurry was then cast on aluminum foil followed by drying at 80 °C for 12 h. The active mass loading was approximately 1.3 mg cm^{-2}. Activated carbon (AC) free-standing film electrodes were prepared by mixing AC, super P carbon-45 (TIMCAL), and polytetrafluoethylene (PTFE) with a mass ratio of 7:2:1 in 2-propanol followed by rolling for use as the counter electrode. Free-standing electrodes used in Ex-Situ FTIR measurements were prepared using the same method, replacing AC with the active material to be tested (titanic acid/TiO_2). An Ag/AgCl electrode (saturated KCl) was used as the reference electrode, with filter paper as the separator. All electrodes were stored in a desiccator in between testing.

Cyclic voltammetry (CV) was carried out on an EC-Lab VMP3 instrument. Galvanostatic charge/discharge (GCD) measurements were conducted on both EC-Lab VMP3, and Maccor 3000 systems. All electrolyte stability tests were performed in beaker cells with AC electrodes housed in titanium mesh as a counter electrode. The working electrode was aluminum foil for negative potentials, and titanium foil for positive potentials, using an Ag/AgCl reference electrode. The capacitive contribution of the CV curves was calculated in accordance with literature.[27]

Electrolyte conductivity experiments were carried out using electrochemical impedance spectroscopy (EIS) on a Biologic EC-Lab VMP3. The test cell consisted of two parallel copper foil electrodes on either side of a 1 cm x 1 cm x 0.5 cm electrolyte reservoir. The room temperature (25 °C) electrolytes were transferred to the test cell tested at a frequency range of 200 kHz to 100 Hz. The uncompensated resistance from the Nyquist plot was assumed to be dominated by electrolyte resistance and used to calculate conductivity.

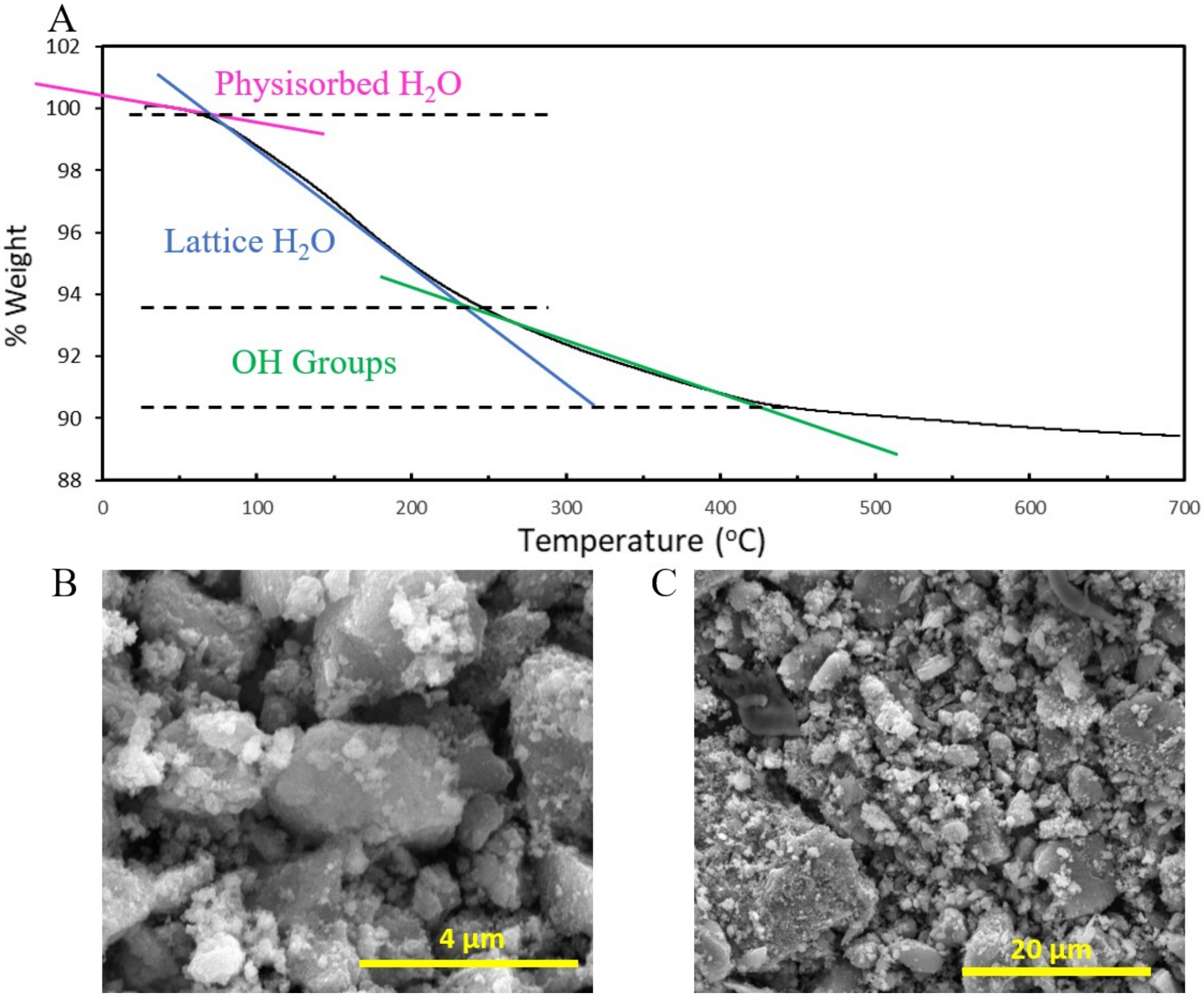

Figure S1. (A) TGA of the titanic acid powder at a temperature ramp of 5 ˚C min^{-1} in air. (B, C) SEM images of the titanic acid sample at various magnifications.

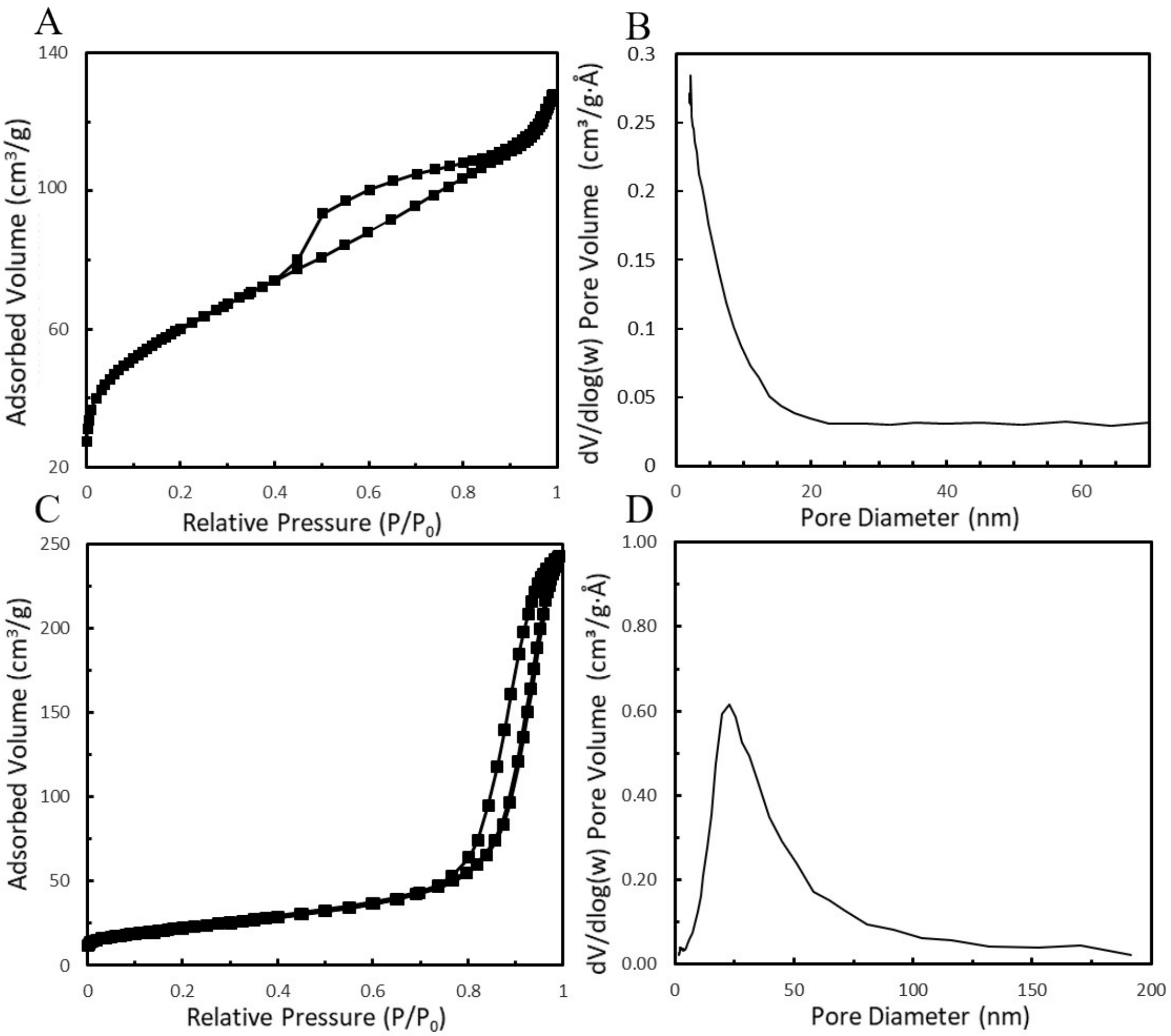

Figure S2. BET data of titanic acid and TiO_2 samples (A) N_2 absorption/desorption isotherms of titanic acid. (B) Pore size distribution of titanic acid. (C) N_2 absorption/desorption isotherms of TiO_2. (D) Pore size distribution of TiO_2.

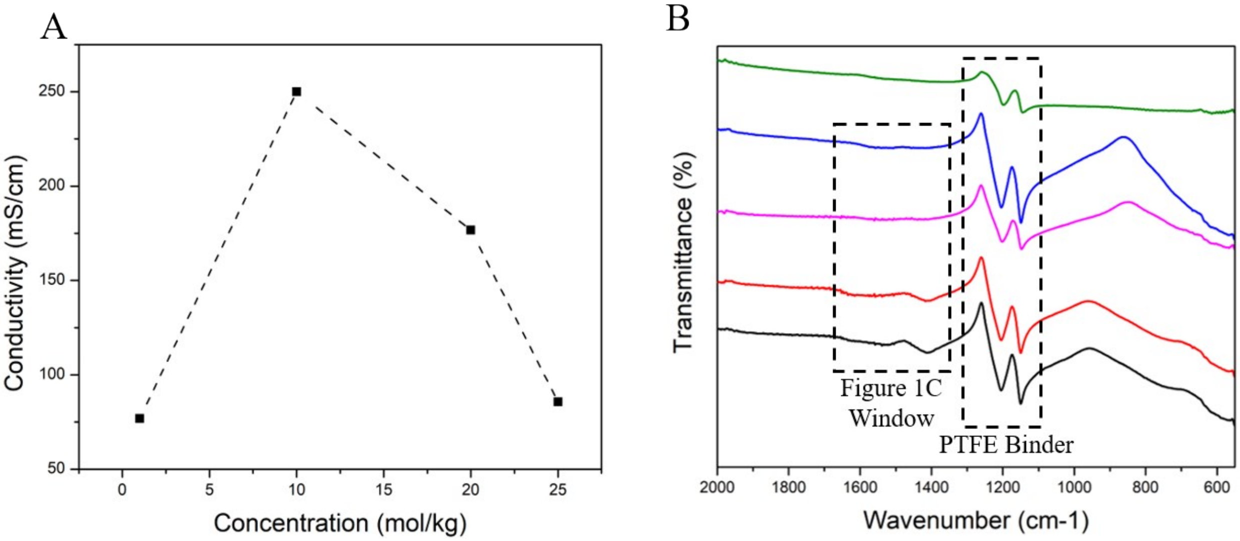

Figure S3. (A) Room-temperature conductivity of the AmAc electrolyte at various concentrations. (B) FTIR spectra of the (i) pristine C45/PTFE film electrode, (ii) pristine TiO_2 film electrode, (iii) ammoniated TiO_2 film electrode, (iv) pristine titanic acid film electrode, (v) ammoniated titanic acid electrode.

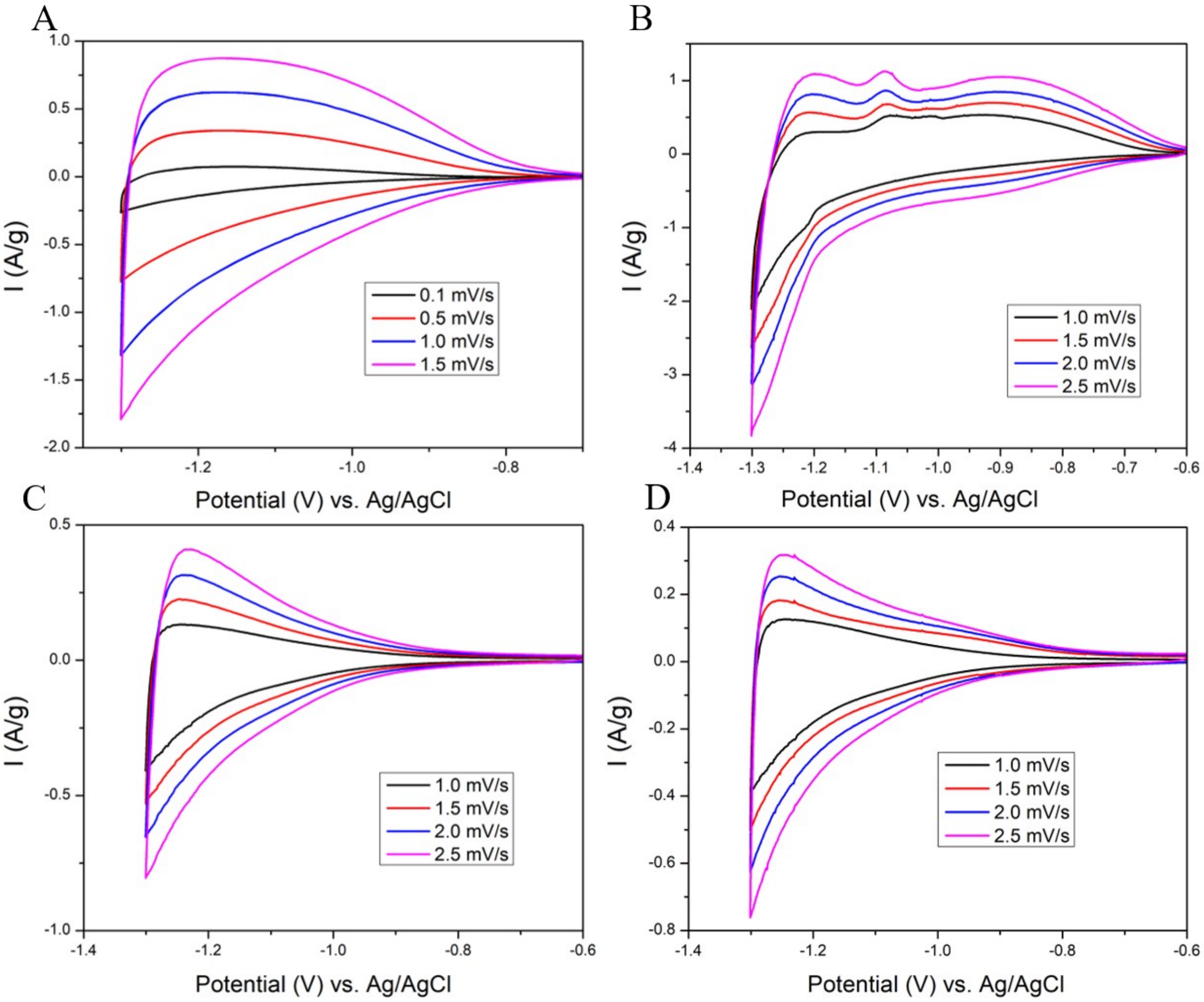

Figure S4. CV curves for the titanic acid electrode at various scan rates in (A) 25 m AmAc, (B) 1 M AmAc. CV curves for the TiO_2 electrodes at various scan rates in (C) 25 m AmAc, (D) 1 M AmAc.

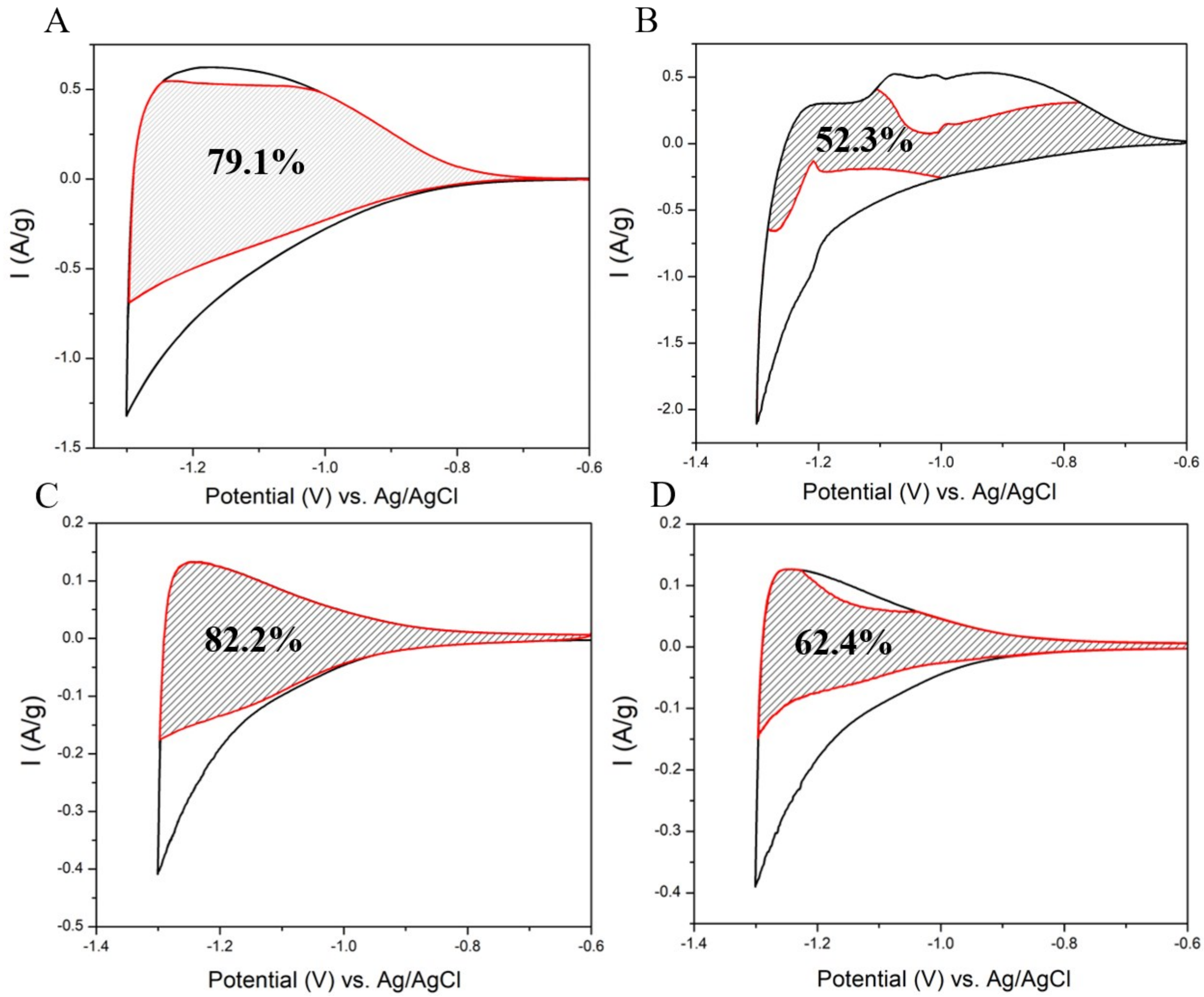

Figure S5. Capacitive current contribution of the titanic acid electrode in (A) 25 m AmAc, (B) 1 M AmAc at 1 mV s^{-1}. Capacitive current contribution of the TiO_2 electrode in (C) 25 m AmAc, (D) 1 M AmAc at 1 mV s^{-1}.