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Supporting information

Synthesis, Characterization and Photoelectrochemical properties of HAP

Gang Li,[a] Jianwei Miao,[b] Jun Cao,[c] Jia Zhu,[c] Bin Liu[b]* and Qichun Zhang[a]*

[a] School of Materials Science Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, E-mail: qczhang@ntu.edu.sg
[b]School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore. E-mail: liubin@ntu.edu.sg
[c]Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, 100875 Beijing, China

General methods

Glyoxal solution (40 wt. % in H_2O), Sodium Acetate (anhydrous, 99%), Ethylene glycol (anhydrous, 99.8%) and 1,2,4,5-Benzenetetramine tetrahydrochloride (technical grade) were purchased from Aldrich company. Other solvents were directly used without further purification. 2,3,7,8-Phenazinetetramine hydrochloride was synthesized according to our reported procedure.[1]

Solution NMR spectra were taken on a Bruker Advance 400 spectrometer. Electrochemistry was carried out with a CHI 600C potentiostat, employing glassy carbon (diameter: 1.6 mm; area 0.02 cm^2), a platinum wire and Ag/AgCl (Ag/Ag^+) as working electrode, counter electrode, and reference electrode, respectively. Tetrabutyl-ammonium Hexafluorophosphate (0.1M) in DMF was used as an electrolyte at room temperature under Argon. The potential was externally calibrated against the ferrocene/ferrocenium couple assuming HOMO of Fc/Fc^+ to be 4.88 eV, [1] the Potential of Fc in our measured condition was 0.56 V. HR-MS (ESI) spectra were recorded on a Waters Q-Tof premierTM mass spectrometer. UV-Vis spectrum was recorded using a Shimadzu UV-2501 spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q500 Thermogravimetric Analyzer at a heating rate of 10 ^oC/min up to 700 ^oC.

Synthesis protocols

1,4,6,8,11,13-hexazapentacene (HAP, 1): 2,3,7,8-Phenazinetetramine hydrochloride (200 mg, 0.678 mmol), Glyoxal solution (3 mL, 26.15 mmol), sodium acetate (112 mg, 1.36 mmol) were dispersed into ethylene glycol (30 mL) under an atmosphere of argon. The mixture was heated to

190 ^{o}C for 48 hours. After cooling to room temperature, 200 ml methanol was added, the precipitate was filtered and washed with water, 2M HCl, acetone, ethylene acetate, yielded compound **HAP** (160 mg, 83%) as a brown solid. ^{1}H NMR (400 MHz, TFA-*d*, δ ppm) 8.97 (s, 4H), 8.00 (s, 4H). ^{13}C NMR (100 MHz, TFA-*d*, δ ppm) 140.09, 139.19, 135.69, 104.21. MS-HRMS: $C_{16}H_8N_6$ calcd, 284.0810 (M^+), found 284.0815 (M^+). Elemental analysis: $C_{16}H_8N_6$, calcd, C 67.60, H 2.84, N 29.56, found C 67.88, H 2.90, N 29.22.

Electrode Preparation

To prepare the photoelectrodes, 10 mg of **HAP** was first ground using a marble mortar and pestle, and then added into 1 ml of 98% ethanol (Merck). The as-prepared solution was placed on a 60˚C hotplate stirrer overnight to ensure that the **HAP** was completely dissolved in the solution. Meanwhile, the fluorine-doped tin oxide (F:SnO_2, Tec 15, 10Ω/□, Hartford Glass Company) were cleaned thoroughly by sonication in 5% detergent for 30 min first and then rinsed with de-ionized water (DI water) for several times, which were followed by sonication in DI water for 15 min. The sonication in DI water process was repeated for three times. Before coating with **HAP**, the FTO substrates were cleaned with UV-ozone plasma for 15 min to remove the organic residues. After that, 10 µl of the 10 mg/ml **HAP** solution was dropped onto the surface of FTO substrate, which was masked by a 3M scotch tape with an exposed area of 1.0 × 1.0 cm^2, and then dried in air at 60˚C on a hotplate.

Photoelectrochemical Measurements

The photoelectrochemical tests were performed using an electrochemical workstation (CHI 760E). A three-electrode set-up, with a platinum plate (1 × 2 cm^2) and a saturated calomel electrode (SCE, in 3 M KCl) as the counter and reference electrodes, respectively, was used to study the photovoltage response (illuminated open circuit potential). Meanwhile, the photocurrent test was carried out using a two-electrode set-up, in which the working electrode **HAP** and the counter electrode (Pt) were short-circuited. Sodium phosphate buffer (pH = 7.0) was used as the electrolyte throughout the photoelectrochemical tests. Prior to each measurement, the electrolyte was deaerated by purging it with argon continuously for 30 minutes. A 300 W xenon lamp (Newport) coupled to an AM 1.5G filter was used as the standard light source. The illumination intensity of the surface of electrode was ~100 mW/cm^2, calibrated using a standard silicon photodiode.

Mott-Schottky Plot

The Mott-Schottky plot of the **HAP** electrode was obtained using impedance-potential technique. The capacitance of the semiconductor-electrolyte interface was collected at 1000 Hz, with 10 mV AC voltage amplitude, in the same electrolyte (0.5 M sodium phosphate buffer, pH 7.0) and

setup for PEC measurements. To convert the measured voltage into the voltage vs. the reversible hydrogen electrode (RHE), the following calculation was performed:

$$V_{RHE}=V_{Ag/AgCl} + V^{0}_{Ag/AgCl} + 0.059 \times pH$$

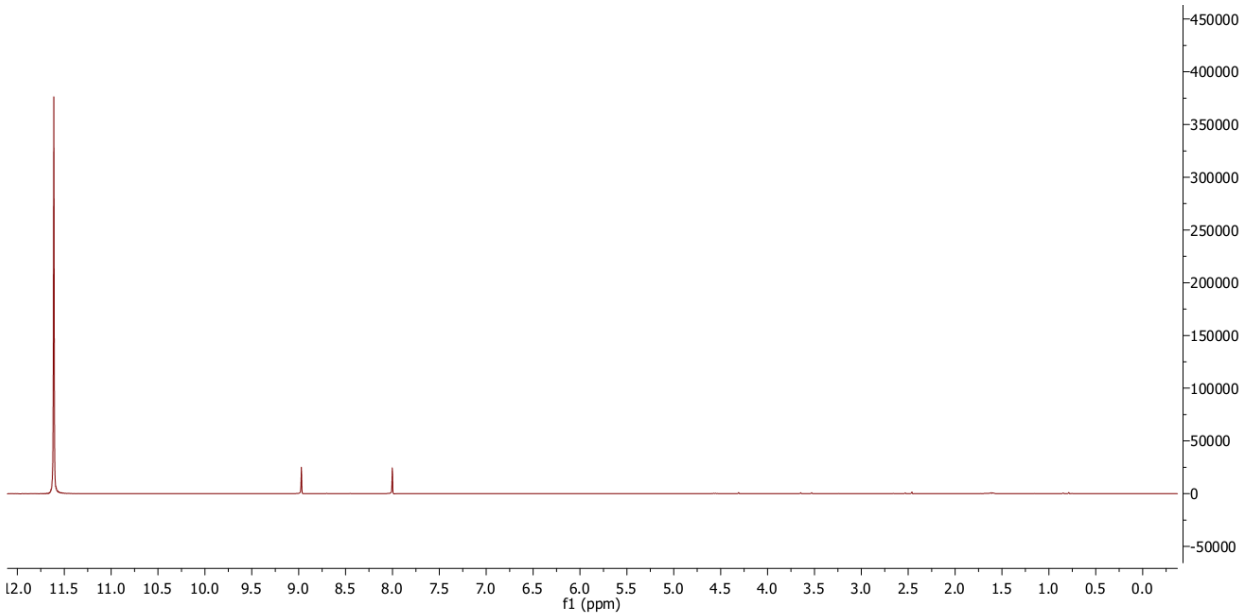


Figure S1. ^{1}H NMR spectrum of **HAP**.

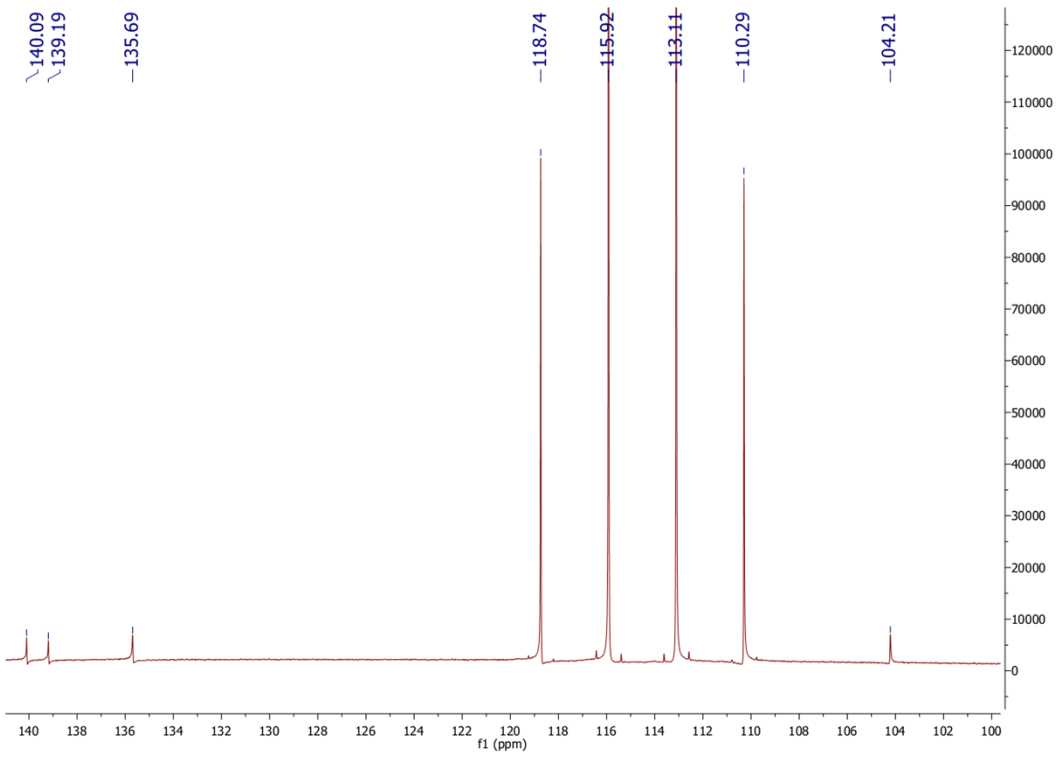


Figure S2. ^{13}C NMR spectrum of **HAP**.

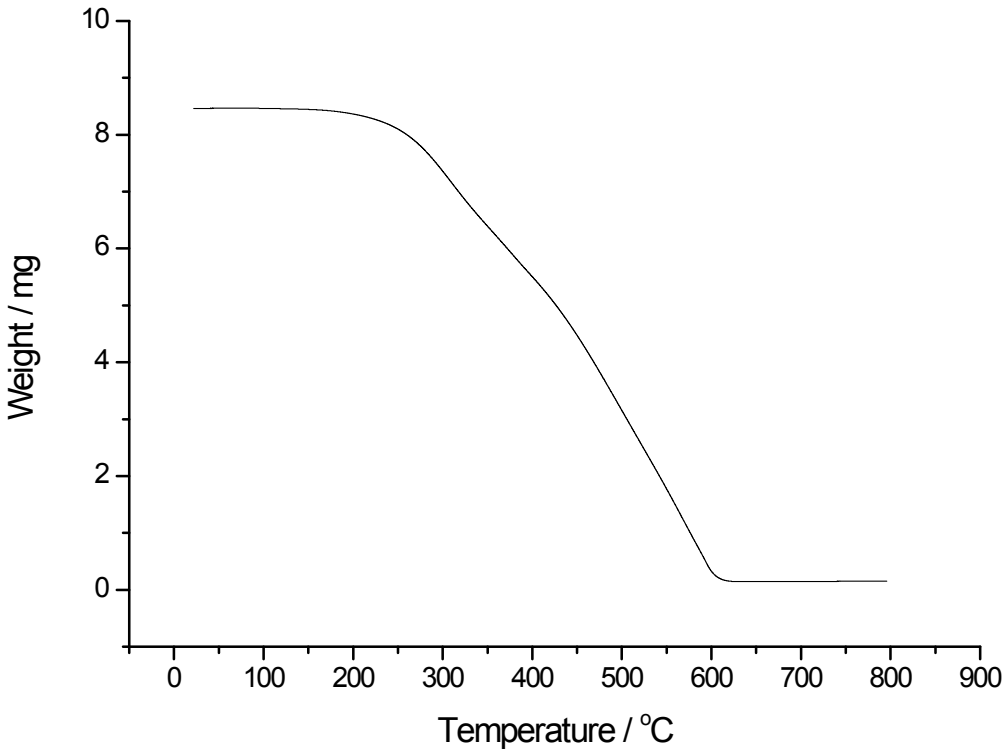


Figure S3. TGA plot of **HAP**.

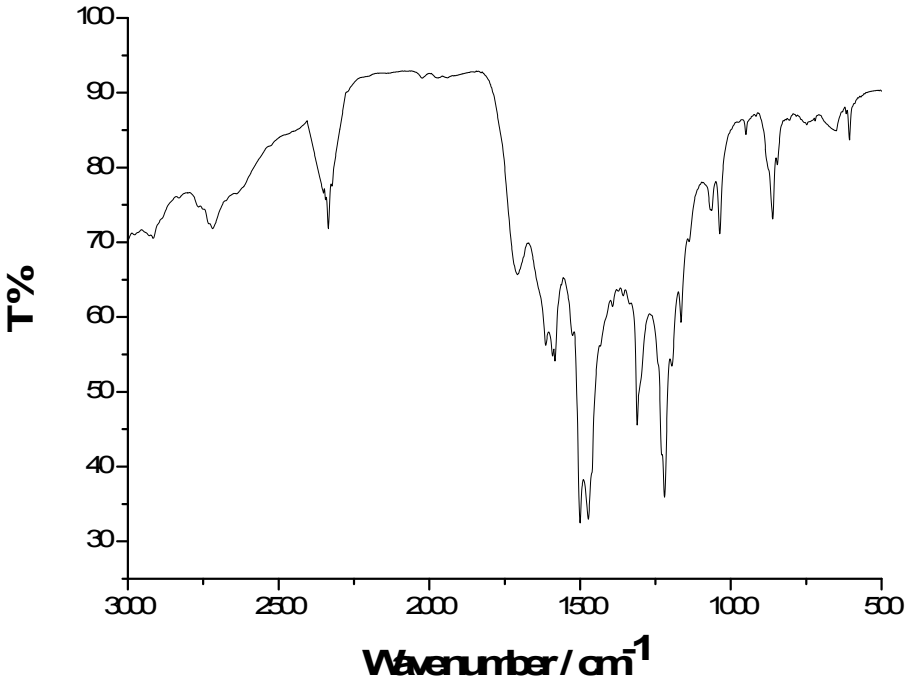


Figure S4. FT-IR spectrum of **HAP**

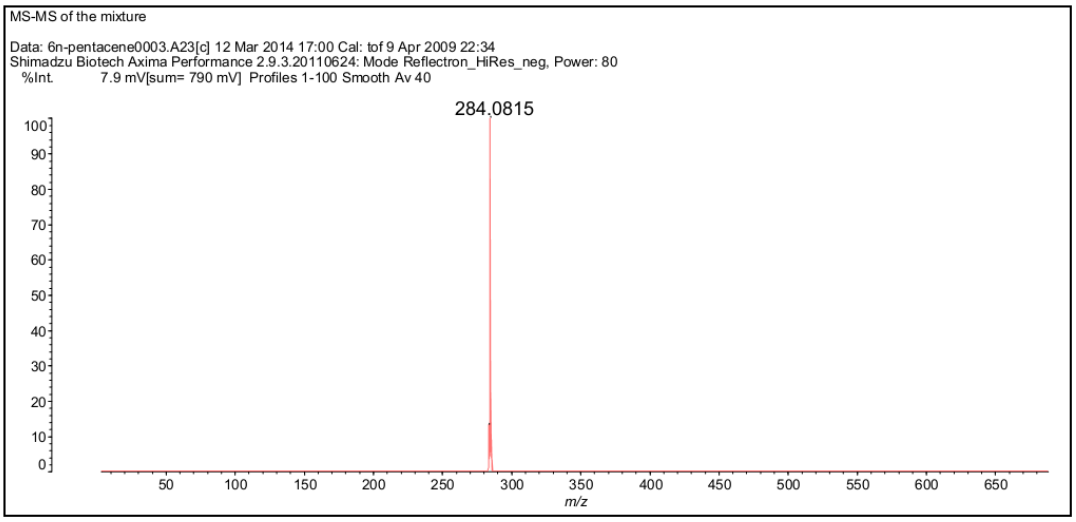
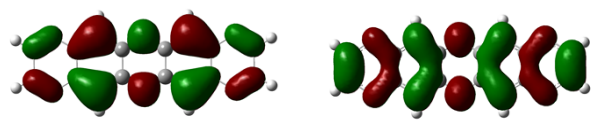


Figure S5. HRMS plot of **HAP**.



HOMO LUMO

Figure S6. Wave functions for the HOMO and LUMO of **HAP**

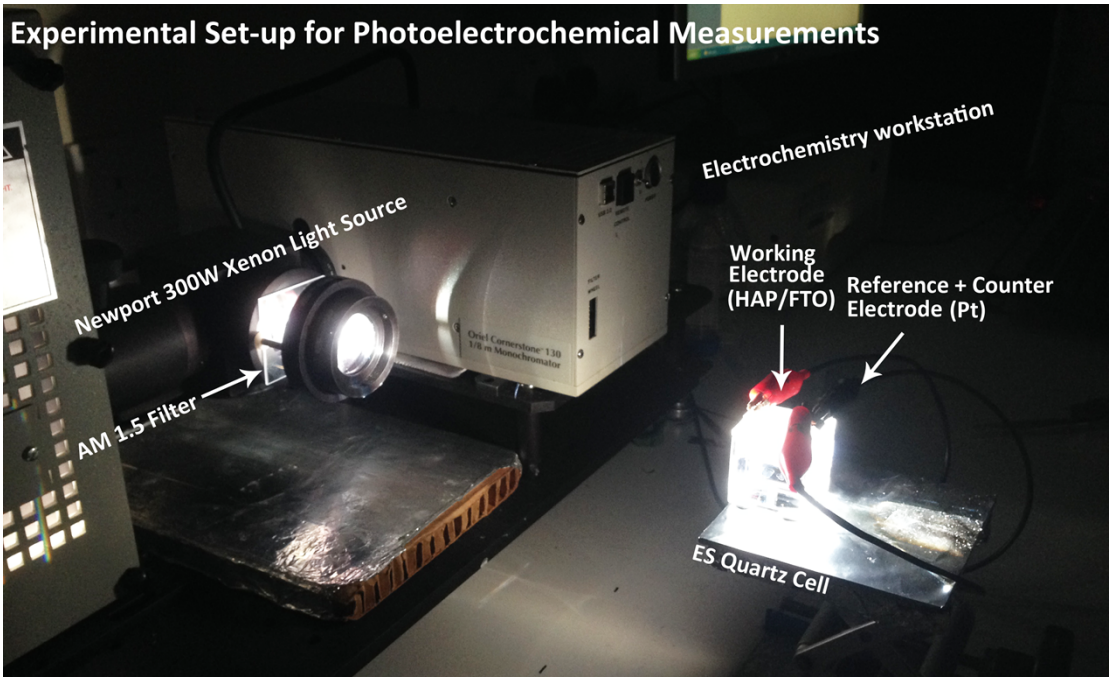


Figure S7. The experimental set-up for photoelectrochemical measurements of **HAP**/FTO photoanodes

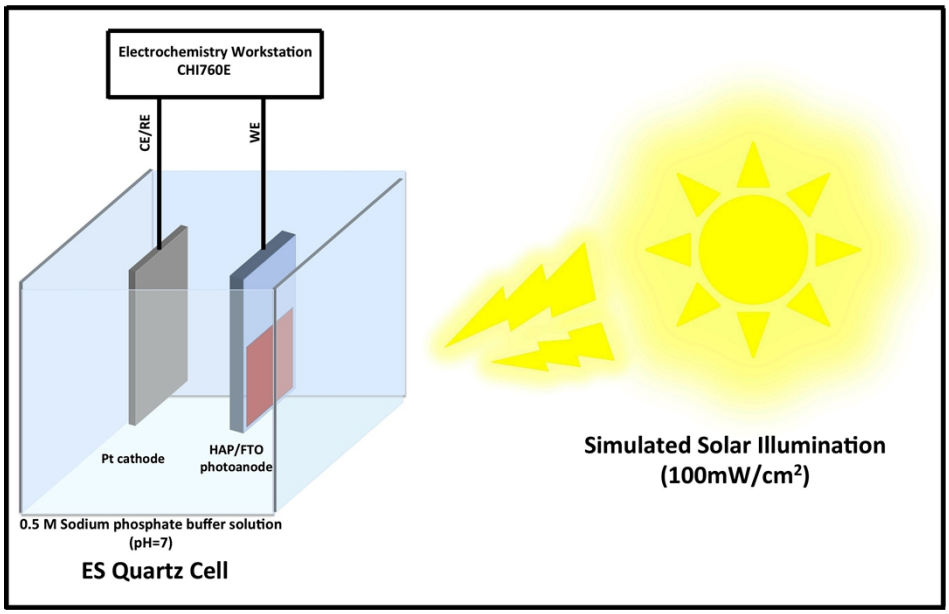


Figure S8. Schematic illustration of the two-electrode set-up for the photocurrent measurements of HAP/FTO photoanode.

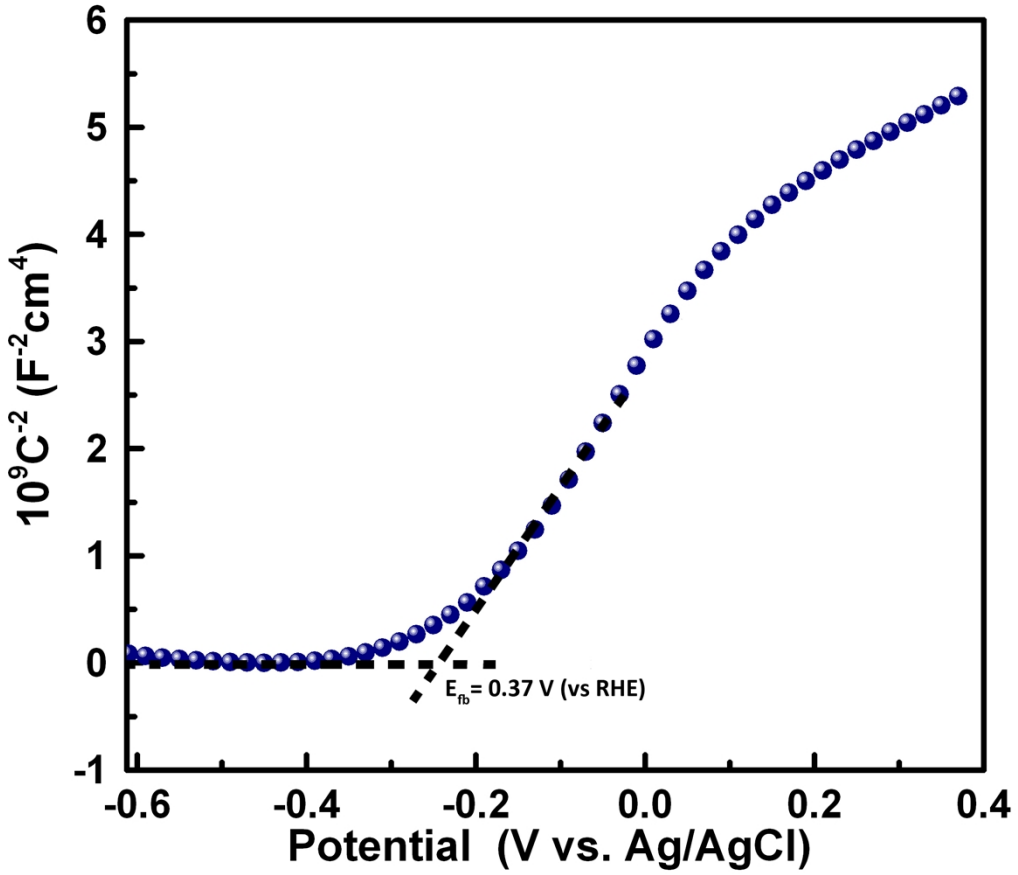


Figure S9. Mott-Schottky plot of **HAP** electrode measured at a frequency of 1000 Hz. The flat-band potential is indicated by the intercept of the dashed lines.

Reference

S1.a) Pavlishchuk, V. V.; Addison, W. A. Inorganica Chimica Acta, 2000, 298, 1. b) Bard, Allen J.; Larry R. Faulkner (2000-12-18). Electrochemical Methods: Fundamentals and Applications (2nd ed.). Wiley.