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A Redox-active 2D Covalent Organic Frameworks with Pyridine Moieties Capable of Faradic Energy Storage

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Experimental

Synthesis of TaPa-Py COF and DAB-TFP COF

Both COFs were prepared under solvothermal conditions. Briefly, in case of **TaPa-Py** COF 1,3,5-triformylphloroglucinol (TFP) (63 mg, 0.3 mmol) monomer was reacted with diaminopyridine (DAP) (96 mg, 0.45 mmol) while for DAB-TFP COF synthesis, p-diaminobenzene (DAB, 34 mg, 0.142 mmol) and TFP (20 mg, 0.096 mmol) were treated in a special glass tube using 1,4-dioxane (1.5 mL) as solvent. A 3 M acetic acid (0.5 mL) solution was added. The reactants were first dispersed by ultrasonication for 5 min, then froze and degassed under partial vacuum (100 mTorr). The tubes were then flame sealed and placed in an isotherm oven for 2 days at 120 ^{o}C. Finally, the resulting COFs materials were filtered out and washed with 1,4-dioxane and acetone for several times and dried under vacuum at 150 °C for 12 h.

Characterization

Surface morphology of the materials was carried out on Hitachi S4800 scanning electron microscopy (SEM). Transmission electron microscope (TEM) images were obtained on a FEI Tecnai G2 T20 electron microscope operated at 200 Kv. Powder X-ray diffraction(XRD) patterns were recorded on a Pananlytical X'Pert-pro MPD X-ray power diffractometer by using Cu kα radiation (λ= 0.154056 nm). Fourier transform infrared (FTIR) spectra were collected on a Spectrum One in the spectral range of 400-4000 cm^{-1} using the KBr disk method. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 Xi. XPS system of Thermo Scientific, where the analysis chamber was 1.5×10^{-9} mbar and the X-ray spot was set to 500µm. The BET (Brunauer-Emmett-Teller) surface area of the materials was measured using a Micromeritics ASAP 2420 system instrument.

Electrochemical measurements

Electrochemical studies were carried out in a conventional three-electrode and two-electrode symmetric supercapacitor setup under room temperature in 1M H_2SO_4 aqueous solution as the electrolyte. Briefly, in three-electrode system COF film on carbon paper as the working electrode, platinum (Pt) foil and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. The working electrode was prepared by mixing 65 wt% active material, 10 wt% PVDF binder and 25 wt% carbon black in an agate mortar. Then an appropriate amount of ethanol was added to this mixture to make slurry, which was subsequently coated on carbon paper and dried in an oven at 100 °C for 10 h. The electrochemical performance of the electrodes ware studied on a CHI660D electrochemical workstation using cyclic voltammetry (CV) under a potential in the range from -0.3 to 0.4. Galvanostatic charge-discharge (GCD) curves in the potential range from -0.3 to 0.35 at different current densities from 0.5A to 5A. The EIS measurements were obtained using the classic three electrodes setup at an applied potential of 0 V with 5 mV of signal amplitude and frequency range of 1 Hz to 10^5 Hz. Nyquist plots were collected at room temperature.

While in a traditional two-electrode system the electrodes were prepared as follows; First the active materials (65 wt%), carbon black (25 wt%, Super P conductive) were grinded in an agate mortar. Then polytetrafluoroethylene binder (10 wt%, 60% in water, and diluted to 6% before use) was added and sonicated for 10 minutes. After that material films were made on a hot plate using glass rod. These films were then cut into circular tablets with diameter of 12 mm and dried under vacuum at 120 °C for 12 h. Two electrodes with exactly the same mass were pressed onto stainless steel circular disc (diameter of 15 mm). These two electrodes separated by common filter paper (Whatman) were soaked into 1M H_2SO_4 electrolyte prior to measurement for 40 min, allowing the electrolyte to impregnate into the electrode pores and then assembled into a coin-type cell. All solutions were prepared with deionized water purified with a Milli-Q system (18.2 M Ω cm). The electrochemical performance of the assembled devices ware studied on a CHI660D electrochemical workstation using cyclic voltammetry (CV) at various scan rates, Galvanostatic charge-discharge (GCD) curves at different current densities from 0.5A to 10A.

We have calculated the specific capacitance of both COFs materials in three as well in two electrode system using CV using the following equation.

$Cs= \int Idv/2vm \Delta V$

where Cs is the specific capacitance ($F\ g^{-1}$), $\int Idv$ is the integrated area under the CV curve loop; ν is the scan rate ($V\ s^{-1}$); m is the mass of the electroactive material (g); ΔV is the voltage window (V):

The specific capacitance (C, F/g) was also calculated from the slop of discharge curve using the formula:

In the three-electrode measurement, the specific capacitance is calculated from charge-discharge profiles using the following equation:

$Cs = (I\Delta t)/(m\Delta V)$

For two-electrode symmetric system the following equation is used to calculate the specific capacitance:

$Cs= 2\times I\times dt/m\times\Delta V$, Where Cs (F/g) is specific capacitance of the supercapacitor, I (unit: A) corresponds to the discharge current, ΔV (unit: V) is the potential window, Δt (unit: s) is the discharge time, and m (unit: g) refers to the mass of active materials on one electrodes.

Differential pulse voltammetry (DPV) of TaPa-Py COF:

The experimental conditions for differential pulse voltammetry were pulse amplitude 50 mV, pulse width 50 ms and scan rate 20 mV. Other calculations were made according to the literature.[1]

Buffer Solution:

In order to maintain proper ionic strength and proton exchangeability Britton-Robinson (BR) aqueous universal buffer solutions with different pH were prepared by mixing appropriate volumes of acids and basic buffer components. The acidic buffer component comprises 0.04 M phosphoric acid, 0.04 M boric acid, and 0.04 M acetic acid. The basic buffer component is 0.2 M sodium hydroxide solution.[2]

Additional figures

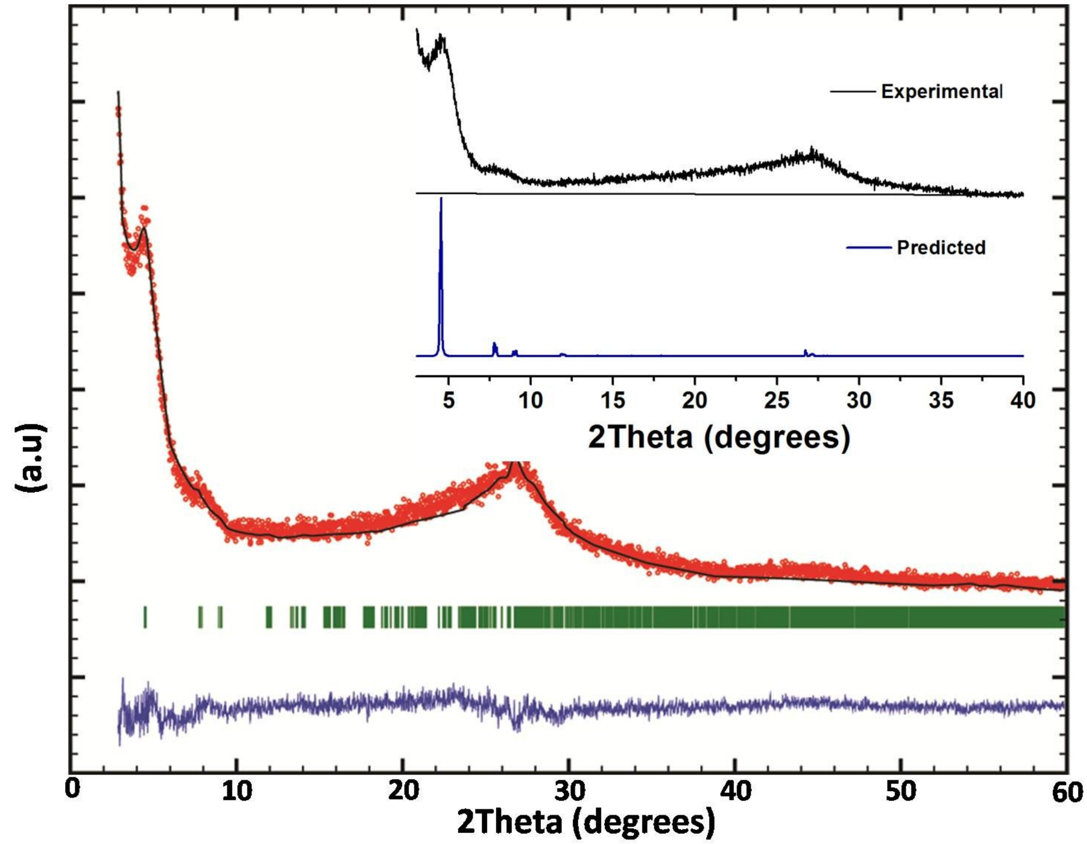

Figure S1. Experimental (black) and predicted (blue) PXRD patterns of TaPa-Py COF (inset). Experimental (red dots), Pawley refined (superimposed black line) and a difference plot (blue).

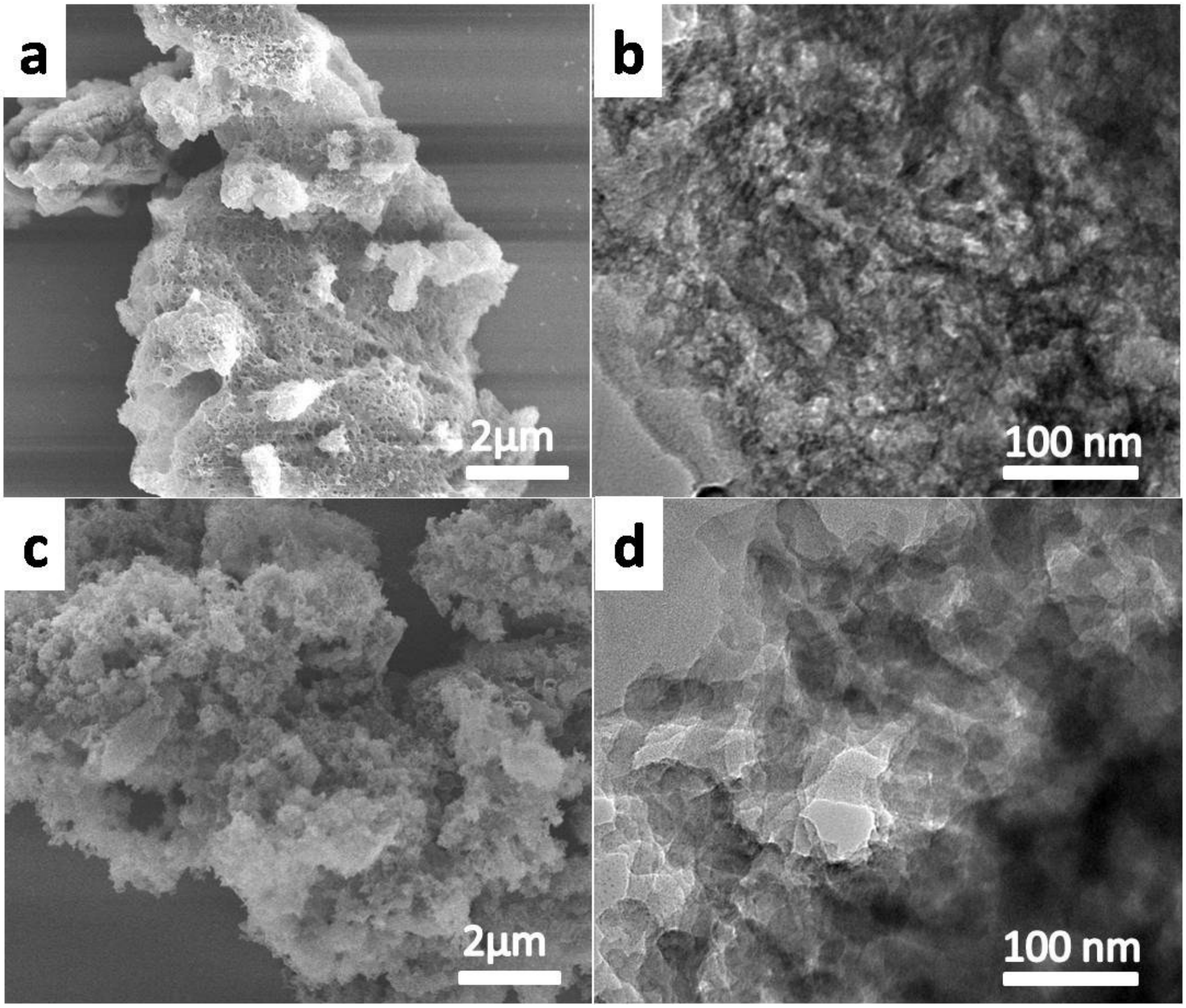

Figure S2. SEM and TEM images of TaPa-Py COF (a,b) and DAB-TFP COF (c,d)

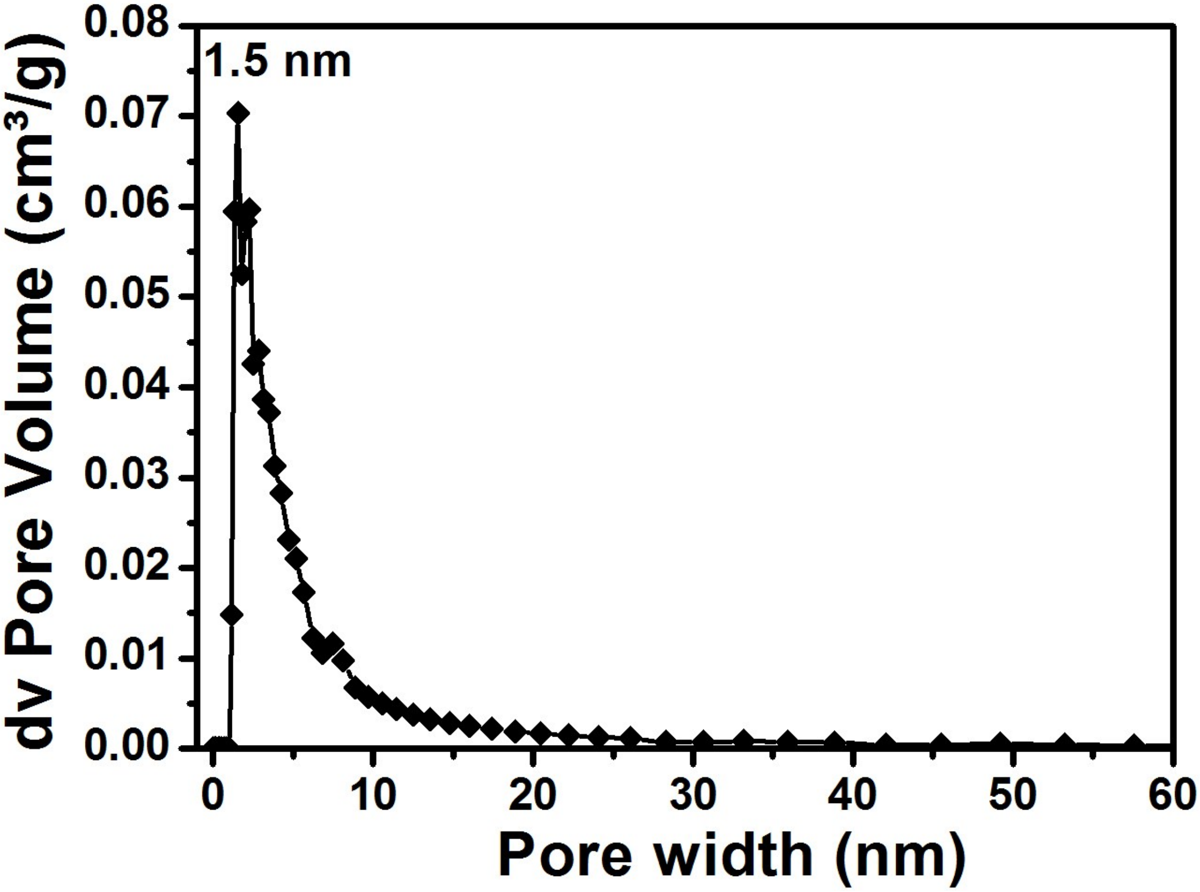

Figure S3. Pore size distribution of TaPa-Py COF

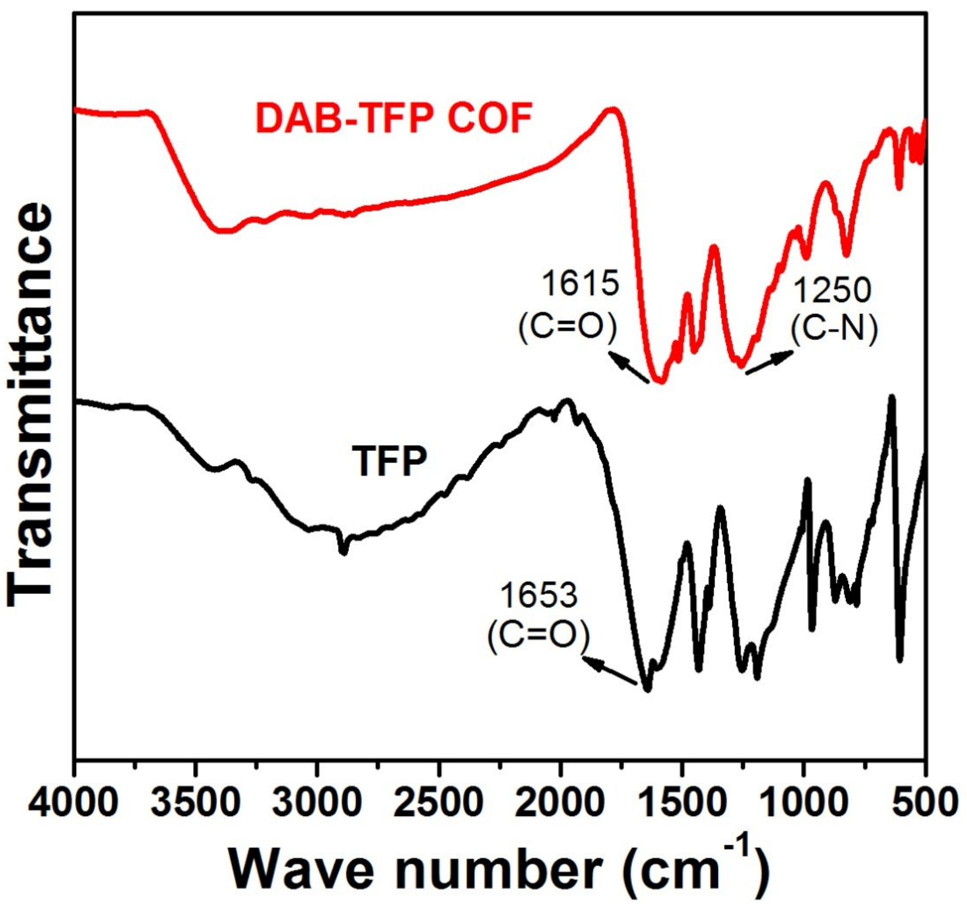

Figure S4. FTIR spectra of TFP monomer (black) and DAB-TFP COF (red)

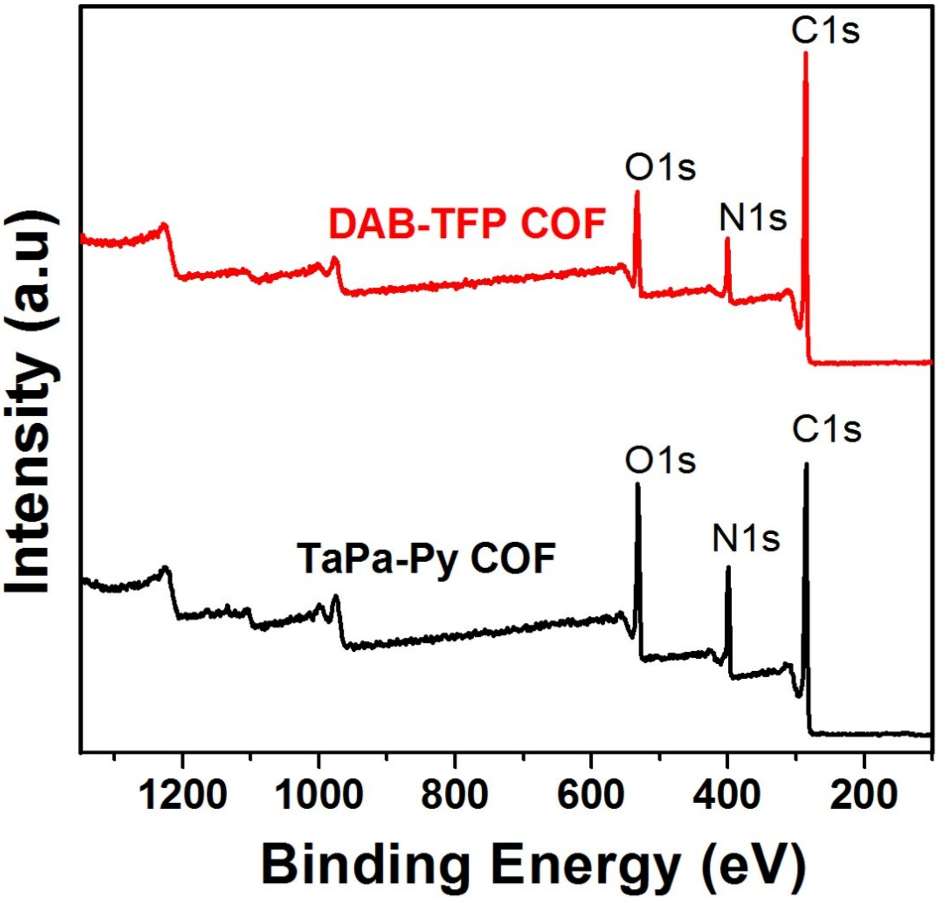

Figure S5. XPS survey spectra of TaPa-Py-COF (black) and DAB-TFP COF (red)

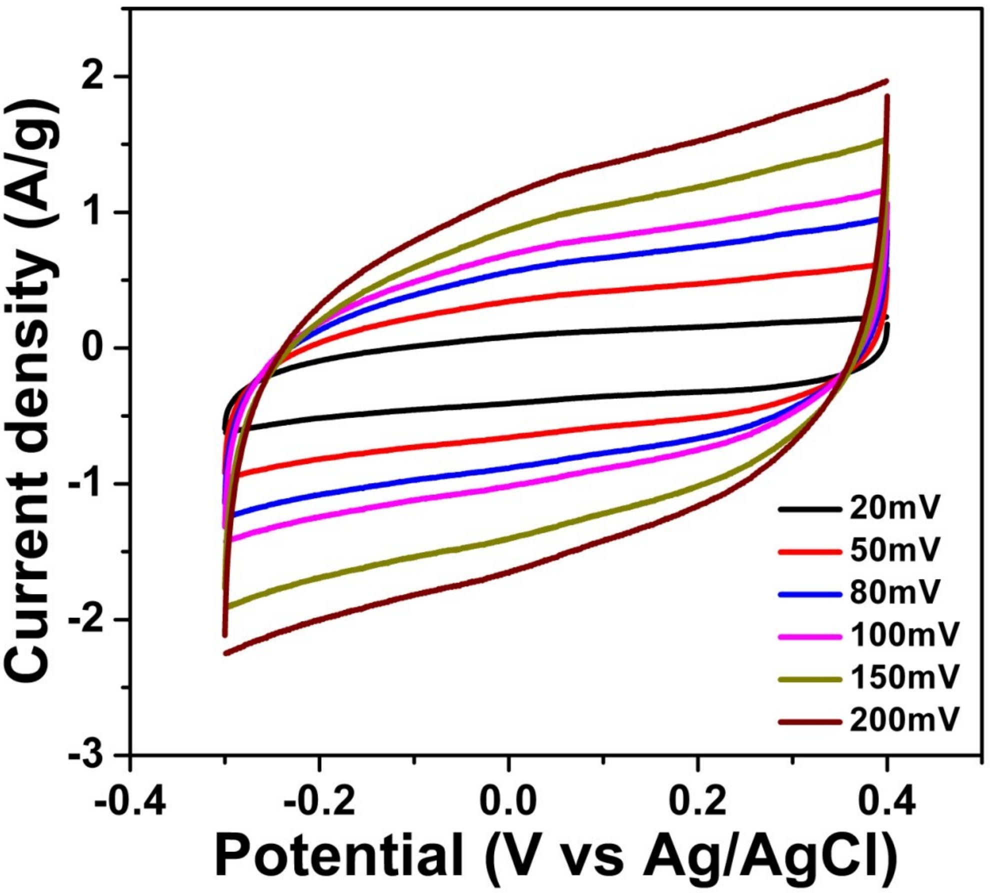

Figure S6. CV curves of DAB-TFP COF at different scan rates

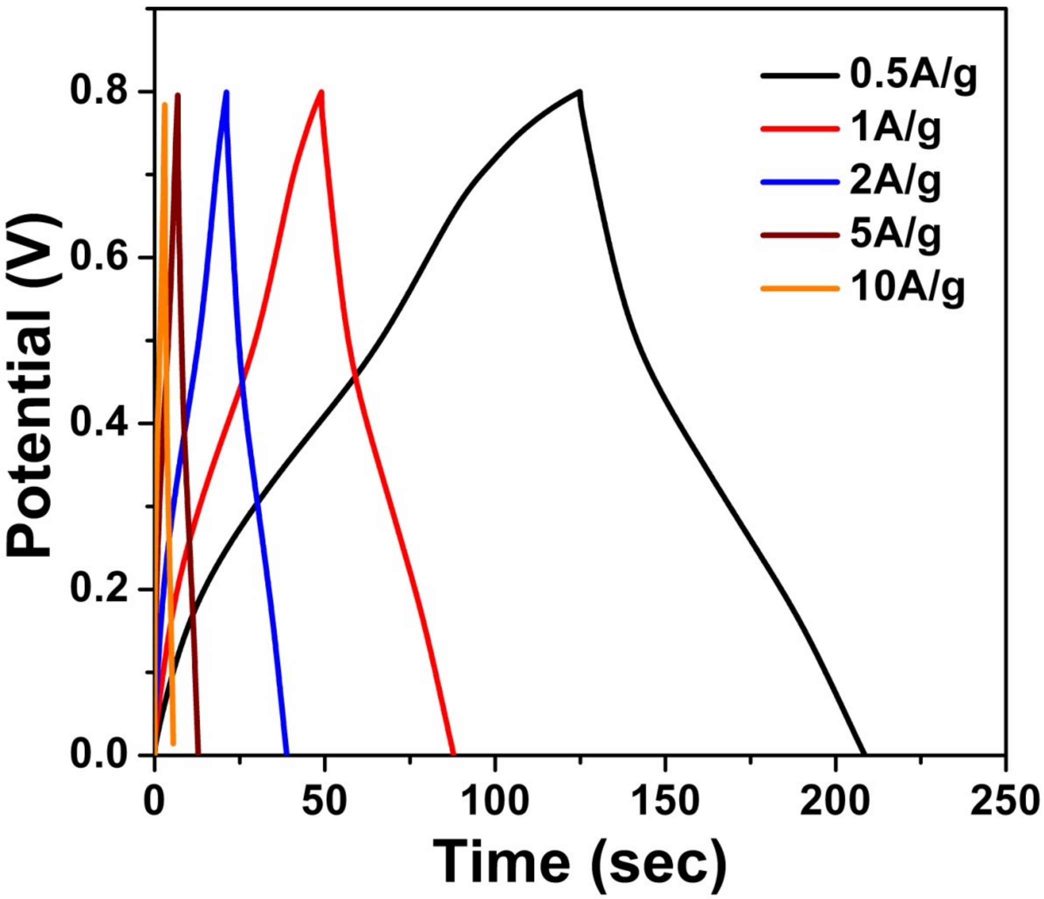

Figure S7. Galvanostatic charge-discharge curves of TaPa-Py COF SC at different current densities

Determination of Pyridine Accessed

(1) Find the mass of the Pyridine in COF on electrode.

TaPa-Py COF mass = 0.8 mg

DAP comprises 51 % of this mass

0.8 mg × 0.51 =0.408 mg of DAP on surface

(2) Convert this mass to moles

4.08×10^{-4} g (mole/107g) = 3.82×10^{-6} mol DAP on surface

(3) Each pyridine is a 2 electron process; determine the number of moles of electrons

3.82×10^{-6} mol DAP (2 mole e^-/mol DAP) =7.63×10^{-6} mol e^-

(4) Determine the maximum coulombs of charge possible to pass

7.63×10^{-6} mol e^- (96485 C /mol e^-) = 736 mC

(5) Integrate the oxidation (or reduction) wave

Example: At 1 mV s^{-1} 19.99 mC of charge is passed

(6) Divide the integrated charge by the theoretical and multiply by 100

19.99 mC /736 mC × 100 =2.716 %

References

1. A. H. Shah, A. Shah, S. U. D. Khan, U. A. Rana, H. Hussain, S. B. Khan, R. Qureshi, A. Badshah, A. Waseem, *Electrochim. Acta*, 2014, **147**, 121.
2. J. E. Reynolds III, M. Josowicz, P. Tyler, R. B. Vegh and K. M. Solntsev, *Chem. Commun.*,2013,**49**, 7788.