ADVANCED MATERIALS

Supporting Information

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A Stable Polyaniline-Benzoquinone-Hydroquinone Supercapacitor

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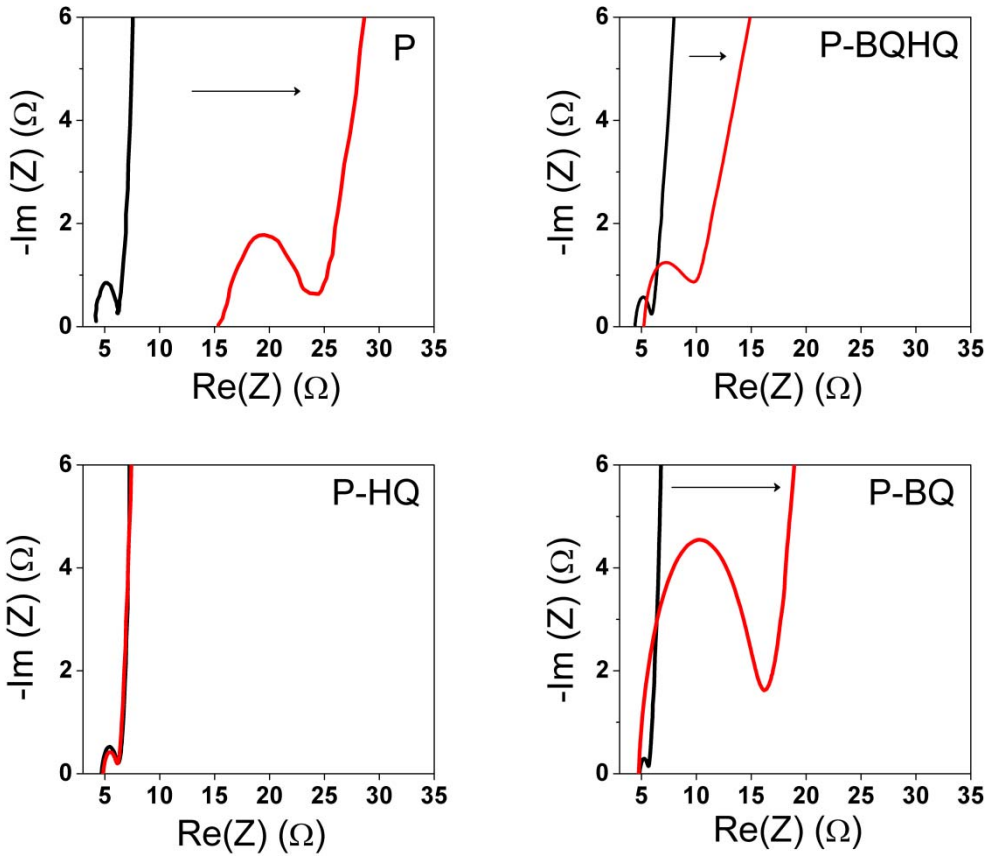

Figure S1. AC-impedance measurements of the supercapacitors (0.0 V, 25 mA). The Nyquist plots are shown for the P (20,000 cycles), P-BQHQ (50,000 cycles), P-HQ (50,000 cycles), and P-BQ (20,000 cycles) supercapacitors before (black curves) and after (red curves) cycling.

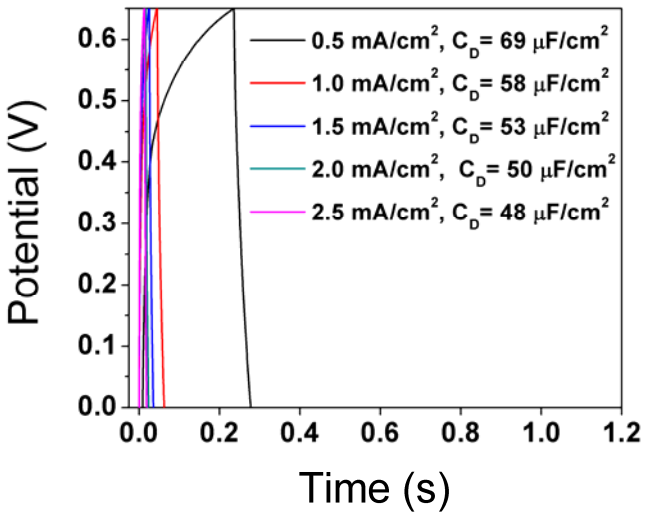

Figure S2. Galvanostatic charge-discharge curves of the Pt-HQBQ reference 2-electrode supercapacitor devices with BQHQ (73 mM, 1:1) and H_2SO_4 (1M) AcOH (30%) as supporting electrolyte at low rates (0.5-2.5 mA/cm^2). These measured areal capacities are three orders of magnitude lower than the capacities measured in polymer-quinone supercapacitors.

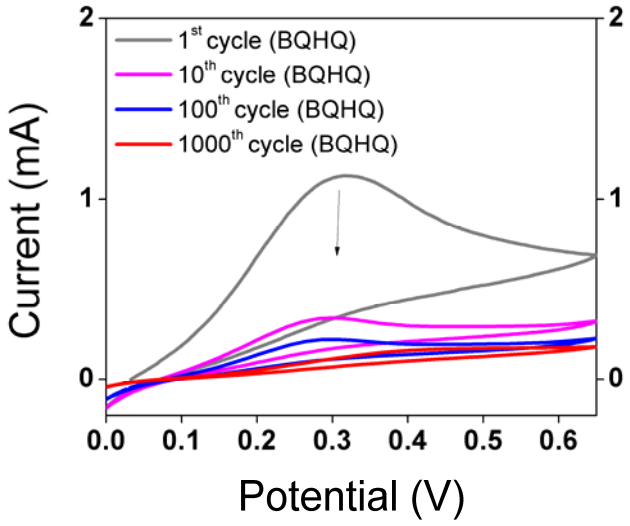

Figure S3. Cyclic voltammetry (25mV/s) of the Pt-HQBQ 2-electrode supercapacitor devices with BQHQ (73 mM, 1:1) and H_2SO_4 (1M) AcOH (30%) as supporting electrolyte. The current response drops rapidly after the first few cycles.

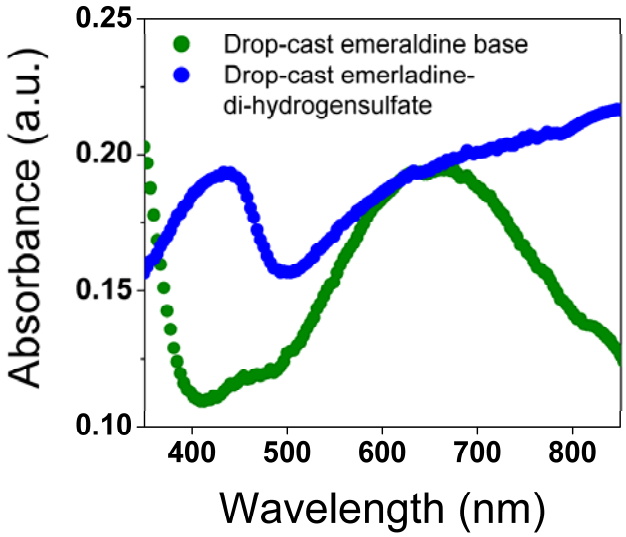

Figure S4. UV-VIS-NIR absorption spectra of polymers obtained by drop-casting the various polymer suspensions on transparent ITO substrates. The films were prepared identically to the polymer-electrodes on Pt substrates. Films of the polyaniline emeraldine-base were prepared by suspending emeraldine-base (20 mg) in H_2O/DMSO (1:1, 400 uL). After sonication (45min), 2 uL of the blue suspension was drop cast on ITO. The films were kept at 40°C (1h) and at room temperature (6h) to obtain the dry emeraldine-base films. The metallic emeraldine-di-hydrogensulfate film was prepared identically to the supercapacitor electrodes. The green emeraldine-di-hydrogensulfate suspension (2 uL) was drop cast on ITO and dried as described above. UV-VIS-NIR absorption spectra were recorded between 350-850 nm. The blue spectra (Figure S4) correspond to the emeraldine-base and the green spectra to the acid-doped emeraldine-di-hydrogensulfate. The metallic polyaniline emeraldine-di-hydrogensulfate (green curve) exhibits a characteristic polaron-absorption band approaching a

maxima at ~850 nm. There is a second absorption maximum at ~440 nm and an absorption minimum at ~495 nm. This is in sharp contrast to the absorption spectra of the undoped emeraldine-base (blue spectra) where the characteristic absorption maximum is observed at ~650 nm tailing down to 1000 nm. An absorption minimum is located at ~410 nm. The values agree well with the values in the literature.[1]

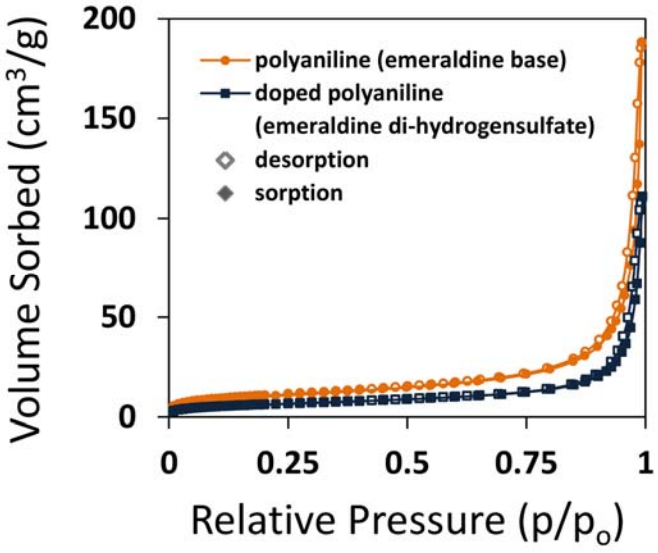

Figure S5. N_2 sorption analysis of the polyaniline powder before and after doping. To analyze the surface area of the drop-cast films, polyaniline base was doped identically to the material used for drop-casting. The resulting doped polyaniline emeraldine di-hydrogensulfate was filtered over a mixed cellulose-ester membrane with 50 μm pore size. The green solid was washed with water and dried in vacuum at 45° for one hour and 8 hours at room temperature. Prior to BET analysis, the powders were ground with a mortar and pestle and degassed with N_2 for 18 hrs at room temperature. Doping results in a decrease of the BET surface area from 36.56 $m^2\ g^{-1}$ to 22.09 $m^2\ g^{-1}$. The BET surface areas are multipoint surface areas calculated from the adsorption branch between 0.05 p/p_o and 0.35 p/p_o. Surface area analysis of the powders was done on a Micromeritics TriStar Porosimeter at 77 K.

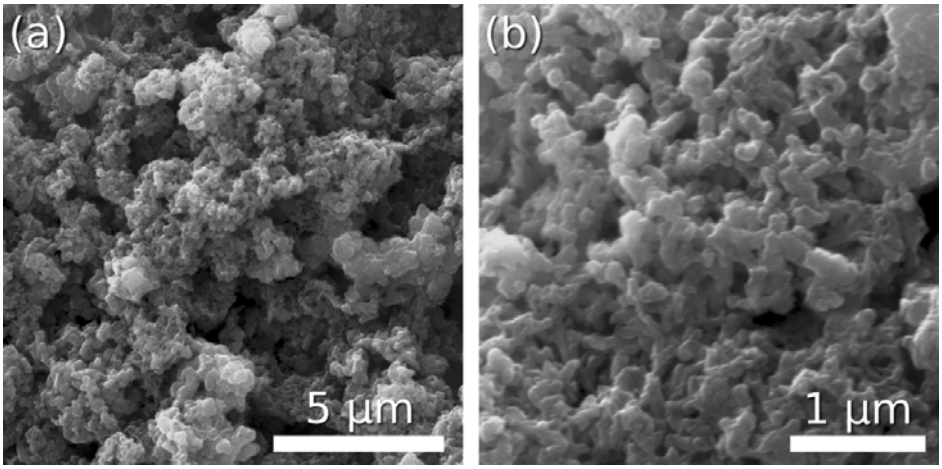

Figure S6. Scanning electron microscopy (SEM) images were obtained using an FEI XL40 Sirion on drop-cast films of acid-doped emeraldine at (a) low and (b) high magnification. The drop-cast electrode film of the emeraldine-di-hydrogensulfate is largely composed of a network of interpenetrating particles creating a porous network, although some agglomeration is noticeable (Figure S6a). The particles of the conventional polyaniline in the film are 100 nm – 300 nm wide and exhibit a low aspect ratio (Figure S6b). The high porosity of the film results in high electrochemical response.

Calculations[2-4]

The cell capacitance (capacitance) is obtained from the inverse of the slope of the voltage-time discharge curves and the constant discharge current according to Formula 1.

$$C_{Cell}(t) = \frac{I}{dV/dt} \qquad \textbf{Formula 1}$$

The specific capacitance C_s per electrode mass was calculated according Formula 2. C_{Cell} (F) is the measured cell capacitance and $m_{electrode}$ is the mass of polymer (based on the mass of the emeraldine-base). The mass of the polymer for the thinner electrodes (~10μm) is 0.125 mg and 1.0 mg for the thicker electrodes (~67μm).

$$C_S(t) = 2 \times \frac{C_{Cell}\,(t)}{m_{electrode}} \qquad \textbf{Formula 2}$$

References

[1] W. S. Huang, A. G. MacDiarmid, *Polymer* **1993,** *34*, 1833-1845.

[2] R. Kötz, M. Carlen, *Electrochim. Acta* **2000**, *45*, 2483-2498.

[3] M. D. Stoller, R. S. Ruoff, *Energy Environ. Sci.* **2010**, *3*, 1294-1301.

[4] V. Khomenko, E. Frackowiak, F. Béguin, *Electrochim. Acta* **2005**, *50*, 2499-2506.