Electronic Supplementary Information

Facile sonochemical assisted synthesis of a hybrid red-black

phosphorus/sulfonated porous carbon composite for high-performance

supercapacitors

Arthi Gopalakrishnan^a and Sushmee Badhulika^{a*}

^a Department of Electrical Engineering, Indian Institute of Technology Hyderabad,

Hyderabad 502285, India

*Corresponding author: E-mail: <u>sbadh@iith.ac.in</u>; Phone: 040-23018443, Fax- 04023016032.

Synthesis of R-BP/carbon composite:

The R-BP/carbon composites were synthesized by the direct mixture of R-BP with sulfonated porous carbon under sonication. The porous carbon was synthesized from acorn cupule by carbonization and activation method. The acorn cupule collected from local gardens were cleaned with DI water and ethanol and were subjected to hydrothermal pre-carbonization in diluted sulfuric acid solution. The obtained pre-carbonized material was then activated with KOH (1:3 ratio) and carbonized at 700°C for 1 hr under nitrogen atmosphere. The as obtained product was washed with 30% HCl and DI water simultaneously until the pH reached neutral and dried in oven completely. The obtained sulfur doped or sulfonated porous carbon (SPC) was sonicated with hybrid R-BP (1:1 ratio) with ethanol as solvent under bath sonication for 2 hrs. The mixture was dried in oven to yield hybrid R-BP/SPC composite.



Scheme S1: Synthesis process of hybrid R-BP and hybrid R-BP/SPC composite

Calculations:

The specific capacitance, energy density and power density were calculated as follows:

$$C = \frac{I}{m \left(\frac{dV}{dt}\right)}_{\text{F g}^{-1}} \dots \dots \dots (1)$$

Three-electrode cell :

$$C_{cell} = \frac{2I}{m \left(\frac{dV}{dt}\right)}_{\text{Fg}^{-1} \dots \dots (2)}$$

Two-electrode cell :

where I is the current, m is the mass of carbon material loaded, and dV/dt is the slope of the discharge profile. The energy density (E) and power density (P) were calculated for a two-electrode cell with dt as the discharge time (s):

$$E = \frac{1}{2 * \frac{3600}{1000}} C_{cell} dV^2$$

Wh Kg⁻¹ (3)
$$P = \frac{E}{dt} \times 3600$$

W Kg⁻¹ (4)

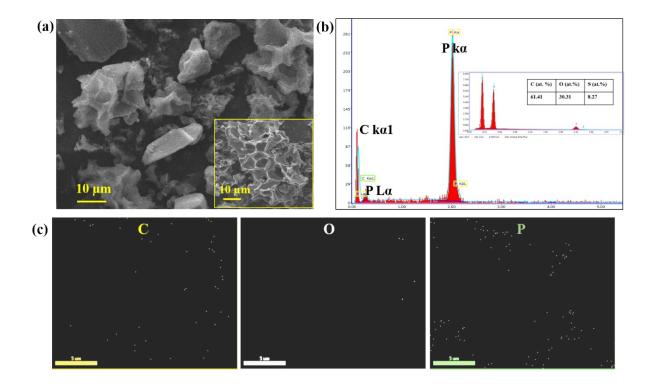


Figure S1: (a) SEM image of R-BP/SPC with inset: Sem image of SPC; (b) EDS spectrum of RBP/SPC with inset: SPC; (c) elemental mapping.

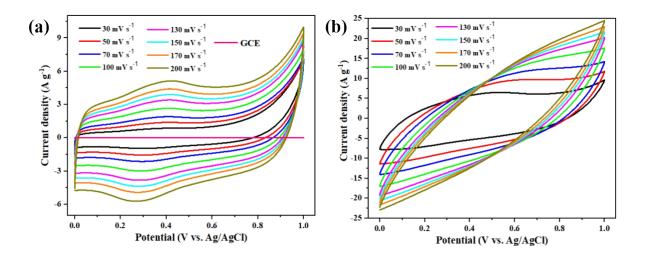


Figure S2: CV curves of (a) R-BP and (b) R-BP/SPC composite.

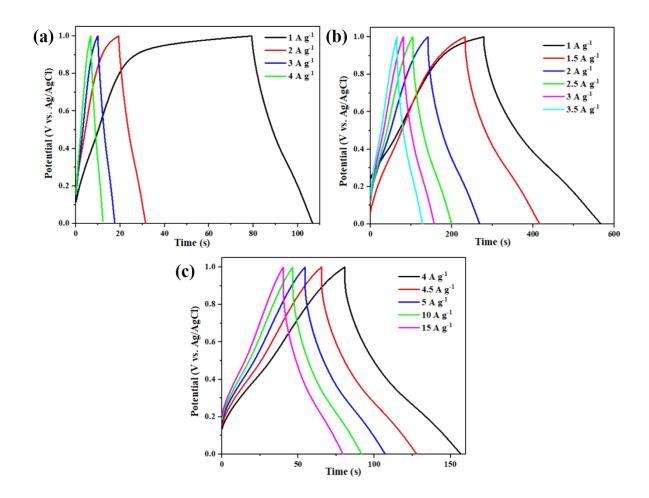


Figure S3: GCD profiles of (a) R-BP; (b-c) R-BP/SPC composite at lower at higher current densities.

The electrochemical impedance spectroscopy was performed to explore the electrode kinetics of R-BP, R-BP/SC and SC. The Nyquist plots of all three electrodes in Fig. S4(a) displays an inclined line in the low frequency region and a depressed semi-circle in the high frequency region indicating its capacitive behaviour and charge transfer resistance (R_{ct}), respectively. The R-BP/SC electrode displays low R_{ct} and steeper tail compared to other electrodes, attributing to its faster kinetics and better capacitive behaviour. Fig. S4(b) gives the Nyquist plot of R-BP/SC electrode before and after 10000 charge/discharge cycles. It shows that there is no change in capacitive behaviour (vertical line) whereas the R_{ct} did not show large difference indicating that charge transfer kinetics was retained.

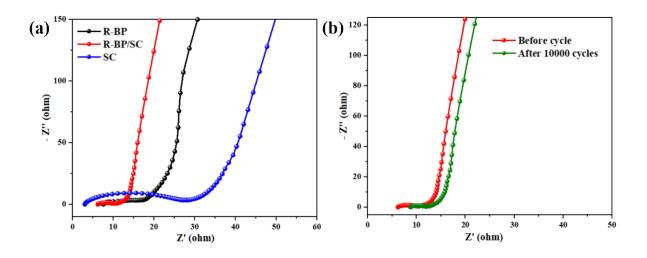


Figure S4: Nyquist plot of (a) R-BP, R-BP/SC and SC; (b) R-BP/SC before and after10000 charge/discharge cycles.

Table S1: Comparison of electrochemical performance of BP based electrodes with R-BP/SPC

 composite for supercapacitors.

Electrode	BP	Synthesis	Electrolyte	Specific	Capacitance	Ref.
material	Precursor	method		Capacitance	retention	
				Cs (F g ⁻¹)	(%) No. of	
					cycles	
BP	Bulk BP	LPE	6M KOH	45.8	84.5%	[9]
				(10 mV s ⁻¹)	10000 cycles	
BP/RP	RP	Sonication	0.1M KOH	60.1	83.3%	[11]
				(0.1 A g ⁻¹)	2000 cycles	

R- BP/SPC	RP	Sonication	1M H ₂ SO ₄	364.5 (0.5 A g ⁻¹)	89% 10000 cycles	This wor
		~		(0.5 A g ⁻¹)	10000 cycles	
BP/PPy	Bulk BP	Sonication	H ₃ PO ₄ -PVA	452	65%	[27]
		milling		(0.3 A g ⁻¹)	175 cycles	
BP/PANI	RP	Shear force	$1 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	354	96%	[26]

 LPE-Liquid phase exfoliation; H₃PO₄-PVA- phosphoric acid-polyvinyl alcohol; PPy- Polypyrrole.