Electronic Supplementary Information

Preceramic polymer derived nanoporous carbon hybrid for supercapacitors

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1. Experimental Procedures

1.1 Materials Processing

The preceramic precursor used in the work was a commercially available SiO₂ rich polymethylphenylsilsequioxane polymer H44 (Wacker Chemie, Berghausen, Germany). The precursor was crosslinked at 350°C in a tube furnace. The crosslinked sample, which was a cakey mass, was milled in a high energy mill for 10 minutes (SPEX SamplePrep[®] 8000M, USA). The powder sample was pyrolyzed in an alumina tubular furnace with flowing argon at a heating rate of 2°C min⁻¹ to a pyrolysis temperature 1000 °C (for 2 h) and was labelled as HX. For the production of the template coated H44 hybrid, nanocarbon (N220) with average particle size 25 nm was used. For processing the hybrid, nanocarbon and PMS were taken in the ratio 1:1 (by weight). Required amount of PMS was dissolved in isopropanol. Subsequently, measured amount of nanocarbon was mixed and stirred to make a colloid with the addition of a surfactant (SDS, sodium dodecyl sulphate). The colloid was then crosslinked and pyrolyzed in the same conditions as mentioned for HX. The resulting carbon-ceramic hybrid was labelled as NHX. The etching was performed on the pyrolyzed bulk PMPS (HX) and the nanocarbon-H44 hybrid (NHX) using 20% HF solution in a polypropylene container. The solution was stirred at room temperature and washed by rinsing it with distilled water. The powder was then heated up to 100 °C to remove any residual water. The resulting carbon hybrid was labelled as NHXF.

1.2 Characterisation

The phase analysis of the materials was evaluated by X-Ray diffraction (XRD) (Rigaku, Ultima IV, Japan) with Cu-K α radiation (λ =1.5416 Å) with scan speed of 20 °C min⁻¹ and 25 mA current and 45 kV accelerating voltage. Fourier Transform infrared spectroscopy (FTIR) was performed in the range of 4000-400 cm⁻¹ in a spectrometer (Perkin Elmer, IRL 1600300, Spectrum II). The sample mixed with KBr (Sigma Aldrich) and pressed to a tablet of dia 12 mm. The specific surface area and the pore size distribution (PSD) was determined by the N₂

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adsorption desorption isotherm using the Brunauer-Emmet-Teller (BET) instrument, (Autosorb-1, Quantachrome, USA) at 77 K. Raman analysis was done in the visible range 532 nm laser wavelength (Renishaw) to see the structural change in the graphene sheets after etching. Transmission electron microscopy (TEM, Technai G², FEI, Eindhoven, NL) was performed at an accelerating voltage of 300 kV to observe the microstructural features in the specimen after etching. The sample was dispersed in propanol and drop casted on a copper grid. The electrochemical test was performed on a potentiostat (Autolab PG204) in 6M KOH aqueous solution with a three electrode configuration. The electrode fabrication was done by using nickel foam as a substrate after washing the carbon hybrid (NHXF) in acetone and deionised water in an ultrasonic bath. Acetylene black and polyvinylidene difluoride (PVdF) were used as conducting agent and binder, respectively. The active material, conducting agent and binder were mixed in the weight ratio 80:10:10 ultrasonically in ethanol. The homogenous slurry was dropped onto the foam and dried in the vacuum oven at 80 °C for 2 hours. The Ni foam coated with the active material was used as the working electrode; Pt and Ag-AgCl were used as counter and reference electrode, respectively. Specific capacitance was measured from the cyclic voltammetry (CV) performed in the electrochemical station.

2. Supplementary Discussions

2.1 FTIR Spectroscopy

FTIR spectra of HX gave the typical peaks seen in silicon oxycarbide. The main peak at ~ 1100 cm⁻¹, attributing to the Si-O stretching vibration of Si-O-Si unit. The other two distinct peaks were seen in the 800 and 460 cm⁻¹, assigned to the Si-C stretching and O-Si-O vibrations respectively. The broad band in the range of 3200-3650 cm⁻¹ indicates the presence of Si-OH stretching vibration. A small peak at 1590 cm⁻¹ is attributed to the presence of C=C of the free carbon phase ¹. This indicates the formation of the sp² turbostratic carbon in H44 (aromatic structure) based SiOC pyrolysed at 1000 °C ². This observation was not seen in the XRD, but were visible in the microscopy described below. In the hybrid NHX, we see the summation of spectroscopies of both HX and nanocarbon. The peaks were not that sharp as was seen in HX; this would be due to the presence of carbon from the template for the hybrid (NHX). In the etched hybrid (NHXF), the major effects were the disappearance of the peaks at 1100 and 460 cm⁻¹ (assigned to the Si-O bands), indicating the removal of the silica domains from the SiOC structure. The increase in the intensity of the peak at 1590 cm⁻¹ would be due to the graphitic structures, typically found in HF etched SiOCs.

2.2 Transmission Electron Microscopy

TEM was performed on the samples to obtain an understanding on the morphology and microstructure. The high resolution TEM (HRTEM) confirms the layer like, yet disordered, form of the carbon present in the SiOC matrix (Fig. S4a). These structures are similar to turbostratic carbon ribbons with fringes of separation distance ranging between 0.33-0.38 nm. The NHX nanocarbon-SiOC hybrid, on the other hand, exhibited a relatively ordered carbon layer structure, although not fully ordered (Fig. S4b).

The core-shell structure was evident in the NHX sample, with nanocarbon as the template coated by the oxycarbide. The layered coating of the oxycarbide ceramic around the nanocarbon template may have facilitated the better layering of the carbon in the NHX samples.

2.3 Raman Spectroscopy

The Raman spectra confirm the structural changes of the free carbon phase in the oxycarbide matrix before and after etching (Fig. S5, ESI). The experiment was performed in the 1000-2500 cm-1 spectral range. For all of the samples, we see two in-plane modes: the characteristic disorder induced D band at 1335-1360 cm⁻¹ and the graphite G-band near 1585-1610 cm⁻¹. The values of G band closer to 1600 cm⁻¹ suggests the presence of disordered graphitic carbon. The observations seen after HF etching are the narrowing of the G band (FWHM of the G band decreases) and the shift of the G peak to the lower wavenumber. These changes after HF etching suggest the increase in graphitization. The result can be attributed to the release in the strain after the removal of the SiO₂ domains from the SiOC matrix. The I_D/I_G ratio from the spectra also decreased for the NHXF sample, indicating ordering. The HF etching leads to reorganizing of the graphene layers and decreasing the number of defects in the resultant carbon hybrid.

3. Supplementary Figures



Figure S1: XRD assemblage for the silicon oxycarbide ceramic (HX), nanocarbon-ceramic hybrid (NHX), and carbon hybrid (NHXF).



Figure S2: FTIR spectroscopy for the silicon oxycarbide ceramic (HX), nanocarbon (NC), nanocarbon-ceramic hybrid (NHX), and carbon hybrid (NHXF).



Figure S3: (a) Nitrogen sorption isotherms and (b) pore size distribution for the silicon oxycarbide ceramic (HX) and nanocarbon-ceramic hybrid (NHX).



Figure S4: TEM micrographs of oxycarbide HX and hybrid NHX



Figure S5: Raman graphs for the for the oxycarbide (HX), hybrid (NHX), and carbon hybrid (NHXF).



Figure S6: Cyclic voltammograms of the NHXF carbon hybrid up to 1100 cycles at an interval of 100 cycles each. Note that the voltammograms are indistinguishable from each other indicating no decay in capacitance.

4. Supplementary Tables

Sample	Specific surface	Pore volume	Micropore volume	Pore width
	area $(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$	(nm)
HX	2.1	0.00145		10-40
NHX	195	0.179	0.0625	1.4
NHXF	1798	1.20	0.809	1.16

Table S1: Tabulation of the SSA and PSD calculated from the BET and NLDFT methods

Table S2: A comparison of the specific surface area and specific capacitance of the NHXF EDLC electrode produced with the literature.

Material	Electrolyte	Scan Rate	Specific
			Capacitance
		[mV s ⁻¹]	[F g ⁻¹]
Activated Carbon	6M KOH	20	110 ³ , 156.6 ⁴
MWCNT	6M KOH	20	1355
Template-derived	6M KOH	20	2206
carbons			
Carbide derived carbon	$1 M H_2 SO_4$	10	1907
(CDC)			
CDC nanofelts	$1 M H_2 SO_4$	10	1108
Ordered mesoporous	$1 M H_2 SO_4$	10	1759
CDC			
3D PDC-graphene paper	6M KOH	2	269.5210
PANI derived 3D	6M KOH	20	145-16011
graphene sheet			

5. Supplementary References

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