Supplementary Information



1. SEM analysis of SAN/CATH precursor fibres

Fig. S1 Secondary electron micrographs and fibre diameter histograms (40 fibres) of electrospun SAN/CATH composite fibres obtained at different applied voltages (15, 17, 20 and 22 kV).

 C_{FU} is a measure of fibre diameter distribution and it approaches unity when the distribution is uniform.¹

$$C_{FU} = \frac{A_w}{A_n}$$
(S1)

$$A_n = \frac{\sum n_i d_i}{\sum n_i}, \ A_w = \frac{\sum n_i d_i^2}{\sum n_i d_i}$$
(S2)

 d_i is the fibre diameter and n_i is the number of fibres with a diameter d_i .

Applied voltage	AFD	SD	
(kV)	(nm)	(nm)	C_{FU}
15	386.1	119.3	1.12
17	328.2	81.9	1.08
20	302.2	65.5	1.07
22	274.0	54.3	1.05

Table S1. AFD, SD and C_{FU} of precursor fibres

2. The degradation mechanism of CATH

The degradation mechanism of CATH is as follows:

$$C_0(CH_3COO)_2.4H_2O \longrightarrow C_0(OH)(CH_3COO) + CH_3COOH + 3H_2O$$
 (S3)

$$Co(OH)(CH_3COO) \longrightarrow 0.5CoO + 0.5CoCO_3 + 0.5H_2O + 0.5CH_3COCH_3$$
(S4)

$$6CoO + O_2 \longrightarrow Co_3O_4 \tag{S5}$$

$$6CoCO_3 + O_2 \longrightarrow 2Co_3O_4 + 6CO_2 \tag{S6}$$

3. FTIR spectra of precursors and peak assignments

The common peaks 3421, 3489, 3435 and 3455 cm⁻¹ are due to OH stretching in the respective spectrum. The peaks 3028, 3090, 3023 and 3026 cm⁻¹ and the peaks 2928, 2932 and 2925 cm⁻¹ are associated with the symmetric and asymmetric vibrations of C-H in CH_2 and CH_3 , respectively in the corresponding spectra. The peak 2239 cm⁻¹ corresponds to C=N stretching in the case of SAN and SAN/CATH composite, but its intensity is decreased when the fibres are heated at 423 K. In SAN, the peaks 1,600 and 1450 cm⁻¹ arise due to the stretching of C=C bond in styrene ring. The peak at 1493 is due to -CH₂- deformation and the peak at 1356 cm⁻¹ is due to CH₃ deformation. The peaks 1065, 1029 and 908 cm⁻¹ are due to C-H in plane deformation, and those at 760, 701, 537 and 458 cm⁻¹ are due to C-H out of plane deformation in styrene ring,

respectively.² In CATH, the peaks at 1532 and 1420 cm⁻¹ are due to C=O in ionized acetate and C-H deformation in the acetate, respectively. The peaks between1023 and 551 cm⁻¹ are due to CH deformation.



Fig. S2 FTIR spectra of SAN, CATH, SAN/CATH composite fibres and SAN/CATH composite fibres heated at 423 K.

4. Theoretical prediction in Raman shift with grain size

Assuming that the grains in the Co_3O_4 nanofibres are spherical, then according to the Heisenberg's uncertainty principle,³

$$\Delta x \Delta p \ge \frac{h}{2}$$
(S7)
$$p^{2} = 2mE, \quad E = h \frac{c}{\lambda}, \quad h = \frac{h}{2\pi} , \quad (S8)$$
$$\Delta p = -\frac{\Delta \lambda}{2\lambda}$$
(S9)

$$-\frac{\Delta x \Delta \lambda}{2\lambda} \ge \frac{h}{4\pi} \tag{S10}$$

Where, Δx is the standard deviation of position and Δp is the standard deviation of momentum of the phonons. *h* is the Planck's constant, *p* is the momentum of phonons, *m* is the mass of the phonons, *c* is the velocity of light, λ is the wavelength of phonons and *E* is the energy of phonons.

 $\frac{h}{4\pi}$ is a constant and it is always positive, therefore Δx should be negative if there is a

hypsochromic shift in the wavenumber or a bathochromic shift in wavelength, similarly, Δx should be positive if there is a bathochromic shift in wavenumber or a hypsochromic shift in wavelength. Therefore, it is confirmed that the shift in the Raman spectra of the fibres calcined at different temperatures are due to the change in its grain size.

Calcination temperature	FWHM of Raman peaks	Shift in maximum intensity peak
(K)	(cm ⁻¹)	with respect to Co_3O_4 single crystal ⁴
773	28.15	1.9
873	19.71	5.5
973	17.89	8.6

Table S2 Raman peak analysis

5. Determination of grain size from XRD analysis

In Williamson-Hall method the Scherrer formula is modified to account the micro-strain induced broadening of the peaks due to the crystal imperfections or distortions. The Williamson-Hall equation is,

$$\beta_{hkl}\cos\theta = \left(\frac{k\lambda}{D}\right) + 4\varepsilon\sin\theta$$
 (S11)

Where, β_{hkl} is the full width at half maximum of the XRD peaks, k is a constant whose value is 0.9, D is the grain size, λ is the wavelength of the x-rays used for the analysis, ε is the induced strain and θ is the Bragg angle. The grain size was calculated from the 'y' intercept of the linear fit of the plot of $\beta cos \theta vs. 4sin\theta$ (Fig. S3). The slope of the linear fit is the lattice strain. The grain size and the lattice strain were calculated for the Co₃O₄ fibres obtained at different calcination temperatures



Fig. S3 Williamson-Hall plot for determining crystallite size and lattice strain in Co_3O_4 nanofibres obtained at 873 K.

Since grain growth is a diffusion controlled process, it can be explained by Arrhenius equation,

$$D = A \exp\left(-E_a/RT\right) \tag{S12}$$

Where, D is the average grain size, A is the pre-exponential factor, E_a is the activation energy for atomic/ionic diffusion around the grain boundary, R is the universal gas constant, and T is the absolute temperature. Considering E_a as 36.09 kJ mol⁻¹ [ref. 5] and R as 8.314 J K⁻¹ mol⁻¹ for a calcination temperature of 773 K, which has a crystallite size of 19.8 nm, the value of the constant 'A' in Eqn. S12 is calculated as 5.44×10^3 nm.K⁻¹. The value of A was used to calculate the crystallite sizes for the samples calcined at 873 and 973 K. The influence of temperature on the grain sizes is revealed, even though there is a difference between the actual (XRD) and calculated grain sizes of the fibres.

6. Estimation of band gap and Urbach energy

 Co_3O_4 is a p-type semiconductor and its optical band gap can be obtained by the following equation,

$$(\alpha h \nu)^2 \propto (h \nu - E_g)$$
(S13)

Where, α is the absorption coefficient, hv is the photo energy, E_g is the band gap, and n is either 1/2 for an indirect transition or 2 for a direct transition. The band gap energy was calculated by finding the x-intercept of the linear part in the plot $(\alpha h v)^2 vs h v$.



7. H_2 evolution



Fig. S5 Variation in the quantity of evolved H₂ with respect to current

8. O₂ evolution



Fig. S6 Variation in the quantity of evolved O2 with respect to current

References

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