**Supplementary Information**

1. **SEM analysis of SAN/CATH precursor fibres**

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>SEM micrographs</th>
<th>Histograms</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td><img src="image1" alt="SEM image" /></td>
<td><img src="image2" alt="Histogram" /></td>
</tr>
<tr>
<td>17</td>
<td><img src="image3" alt="SEM image" /></td>
<td><img src="image4" alt="Histogram" /></td>
</tr>
<tr>
<td>20</td>
<td><img src="image5" alt="SEM image" /></td>
<td><img src="image6" alt="Histogram" /></td>
</tr>
<tr>
<td>22</td>
<td><img src="image7" alt="SEM image" /></td>
<td><img src="image8" alt="Histogram" /></td>
</tr>
</tbody>
</table>

**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).

\[ C_{FU} = \frac{A_w}{A_u} \]  

(S1)
$$A_n = \frac{\sum n_i d_i}{\sum n_i}, \quad A_w = \frac{\sum n_i d_i^2}{\sum n_i d_i}$$  \hspace{1cm} (S2)

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

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

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>AFD (nm)</th>
<th>SD (nm)</th>
<th>(C_{FU})</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>386.1</td>
<td>119.3</td>
<td>1.12</td>
</tr>
<tr>
<td>17</td>
<td>328.2</td>
<td>81.9</td>
<td>1.08</td>
</tr>
<tr>
<td>20</td>
<td>302.2</td>
<td>65.5</td>
<td>1.07</td>
</tr>
<tr>
<td>22</td>
<td>274.0</td>
<td>54.3</td>
<td>1.05</td>
</tr>
</tbody>
</table>

2. **The degradation mechanism of CATH**

The degradation mechanism of CATH is as follows:

$$\text{Co(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Co(OH)(CH}_3\text{COO)} + \text{CH}_3\text{COOH} + 3\text{H}_2\text{O}$$  \hspace{1cm} (S3)

$$\text{Co(OH)(CH}_3\text{COO)} \rightarrow 0.5\text{CoO} + 0.5\text{CoCO}_3 + 0.5\text{H}_2\text{O} + 0.5\text{CH}_3\text{COCH}_3$$  \hspace{1cm} (S4)

$$6\text{CoO} + \text{O}_2 \rightarrow \text{Co}_3\text{O}_4$$  \hspace{1cm} (S5)

$$6\text{CoCO}_3 + \text{O}_2 \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{CO}_2$$  \hspace{1cm} (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 –CH\(_2\)– deformation and the peak at 1356 cm\(^{-1}\) is due to CH\(_3\) 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. 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 between 1023 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$_3$O$_4$ nanofibres are spherical, then according to the Heisenberg’s uncertainty principle,\(^3\)

\[
\Delta x \Delta p \geq \frac{\hbar}{2} \quad \text{(S7)}
\]

\[
p^2 = 2mE, \quad E = \hbar \frac{c}{\lambda}, \quad \hbar = \frac{\hbar}{2\pi} \quad \text{, (S8)}
\]

\[
\Delta p = -\frac{\Delta \lambda}{2\lambda} \quad \text{(S9)}
\]

\[
-\frac{\Delta x \Delta \lambda}{2\lambda} \geq \frac{\hbar}{4\pi} \quad \text{(S10)}
\]

Where, \(\Delta x\) is the standard deviation of position and \(\Delta p\) is the standard deviation of momentum of the phonons. \(\hbar\) is the Planck’s constant, \(p\) is the momentum of phonons, \(m\) is the mass of the phonons, \(c\) is the velocity of light, \(\lambda\) is the wavelength of phonons and \(E\) is the energy of phonons.

\(\frac{\hbar}{4\pi}\) is a constant and it is always positive, therefore \(\Delta x\) should be negative if there is a hypsochromic shift in the wavenumber or a bathochromic shift in wavelength, similarly, \(\Delta x\) 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.

**Table S2** Raman peak analysis

<table>
<thead>
<tr>
<th>Calcination temperature (K)</th>
<th>FWHM of Raman peaks (cm(^{-1}))</th>
<th>Shift in maximum intensity peak with respect to Co$_3$O$_4$ single crystal(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>28.15</td>
<td>1.9</td>
</tr>
<tr>
<td>873</td>
<td>19.71</td>
<td>5.5</td>
</tr>
<tr>
<td>973</td>
<td>17.89</td>
<td>8.6</td>
</tr>
</tbody>
</table>

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,

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

Where, \( \beta_{hkl} \) 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, \( \lambda \) is the wavelength of the x-rays used for the analysis, \( \varepsilon \) is the induced strain and \( \theta \) 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. \( 4 \sin \theta \) (Fig. S3). The slope of the linear fit is the lattice strain. The grain size and the lattice strain were calculated for the Co\(^3\)O\(_4\) fibres obtained at different calcination temperatures.

![Williamson-Hall plot for determining crystallite size and lattice strain in Co\(_3\)O\(_4\) nanofibres obtained at 873 K.](image)

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

\[
D = A \exp\left( - \frac{E_a}{RT} \right) \quad (S12)
\]
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 $36.09 \text{ kJ mol}^{-1}$ [ref. 5] and $R$ as $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ 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 $5.44 \times 10^3 \text{ nm.K}^{-1}$. 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

$\text{Co}_3\text{O}_4$ 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, $\alpha$ is the absorption coefficient, $h \nu$ 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 $(\alpha h \nu)^2$ vs $h \nu$. 

![Graph showing optical properties](image-url)
Fig. S4 Calculation of (a) band gap energy and (b) Urbach energy from UV-Vis-NIR spectra

7. H₂ evolution

![Graph showing H₂ evolution](image)

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

8. O₂ evolution

![Graph showing O₂ evolution](image)

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