

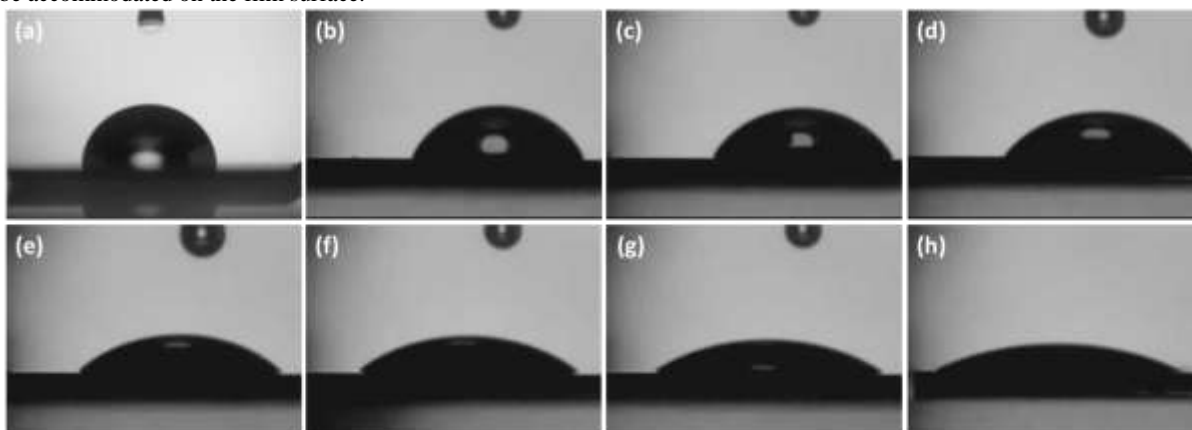
## Supporting Information

# Nitrogen-Functionalised Pyrolytic Carbon Films as Highly Electrochemically Active Electrodes

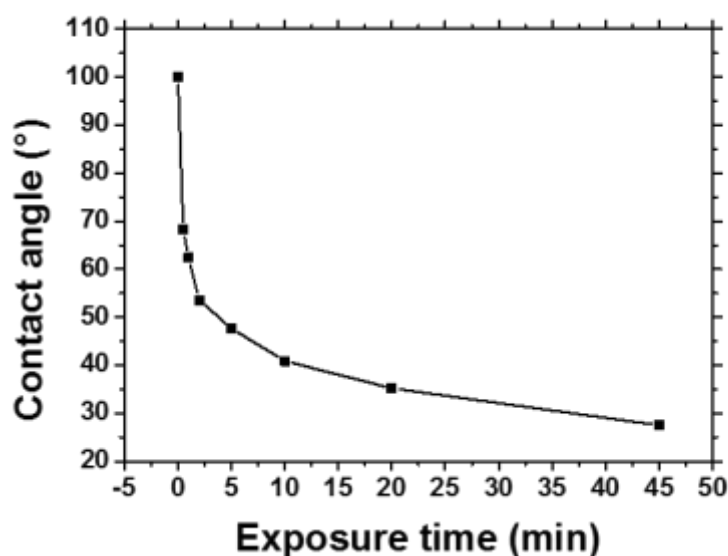
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## Plasma Exposure Time

PyC samples were exposed to  $\text{NH}_3$  plasma for a range of time periods to ascertain the effect, if any, of the plasma treatment time on the properties of the N-PyC films. Shown in Fig.S1 below are water contact angle images for N-PyC after a range of treatment times in  $\text{NH}_3$  plasma. It is clear that the contact angle decreases as the plasma treatment time increases; indicative of the PyC surface becoming functionalised to a greater degree with polar groups. Figure S2 graphically illustrates this relationship between water contact angle and plasma treatment time. From this it is apparent that the surface chemistry of the PyC changes rapidly with plasma treatment but, as the treatment time is increased, the relative effect on the contact angle is increasingly diminished. This occurs as the functionalisation of the PyC film reaches saturation and no further N-groups can be accommodated on the film surface.



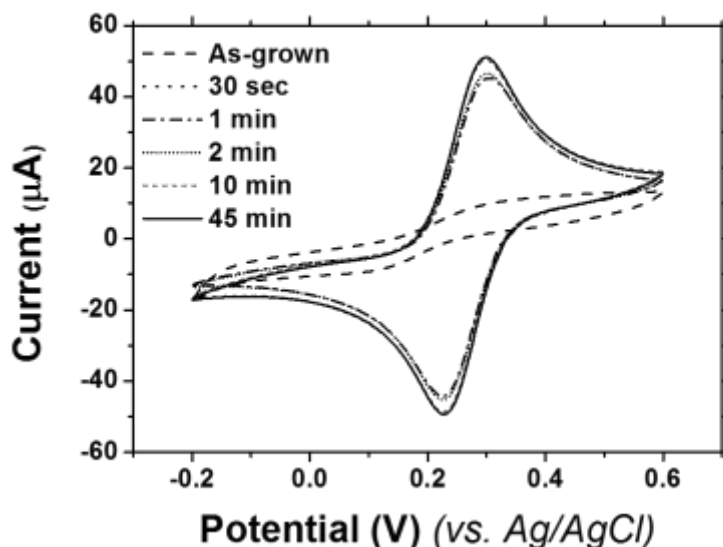
**Figure S1** Water contact angles for as-grown PyC and N-PyC for a range of plasma exposure times (b) 30 seconds, (c) 1 minute, (d) 2 minutes, (e) 5 minutes, (f) 10 minutes, (g) 20 minutes, (h) 45 minutes.



**Figure S2** Graphical representation of effect of increased plasma treatment time on contact angle.

The influence of the plasma treatment time on the electrochemical properties of the N-PyC films was also investigated using the ferri-ferro-cyanide redox couple. It was found that even after very short exposure times, as short as 30 seconds, the N-PyC exhibited massively enhanced electron transfer kinetics compared to the as-grown PyC. Increased plasma exposure

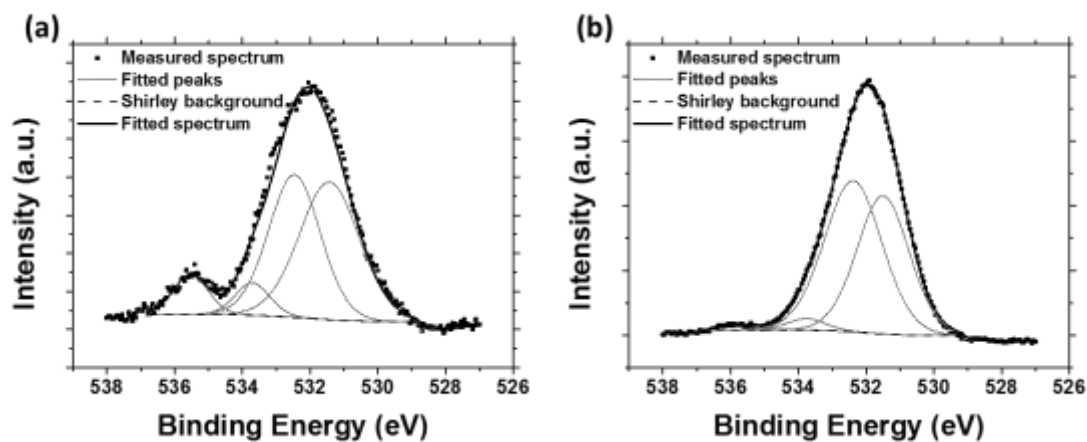
times only caused minimal further changes to the electron transfer kinetics. These further changes to electrochemical behaviour were small to the extent that calculating the heterogeneous electron transfer kinetic rate constant ( $k^0$ ) became impractical. Fig. S3 below shows voltammetric data for a selection of plasma exposure times and illustrates the minimal changes observed with increasing exposure time. For the measurements used in the main body of the text, such as XPS and full electrochemical characterisation, 45 minute plasma treatments were used to ensure that the N-PyC films were well functionalised.



**Figure S3** Voltammogram showing variation of N-PyC voltammetric response to different plasma exposure times in 1 mM ferri/ferrocyanide in background electrolyte of 0.1 M KCl.

### Further XPS Analysis

As reported in the main body of the text, the oxygen content of the PyC films did not appreciably change after plasma treatment. Nonetheless, high resolution scans were taken of the O1s spectral region for both as-grown and N-PyC samples to gain further insight into the nature of the oxygen moieties present via fitting of spectral contributions to the measured spectrum. Hydroxyl groups are found at  $\sim 533.6$  eV, carbonyl groups at  $\sim 532.4$  eV and carboxyl groups at 531.6 eV.<sup>1</sup> Chemisorbed oxygen was also observed at  $\sim 535.5$  eV.<sup>2</sup> Of note is that the hydroxyl signal is reduced after the plasma treatment process. This is consistent with the observed C1s spectrum in the main text, where the hydroxyl contribution is reduced in N-PyC compared to the as-grown film. Previous studies have shown that a similar  $\text{NH}_3/\text{H}_2$  plasma treatment can reduce oxygen moieties on carbon materials.<sup>3,4</sup> Here it is proposed that the hydroxyl groups are reduced by the plasma mixture and are replaced with amine groups whose presence is confirmed in the analysis of the N1s spectral region in the main body of the text.

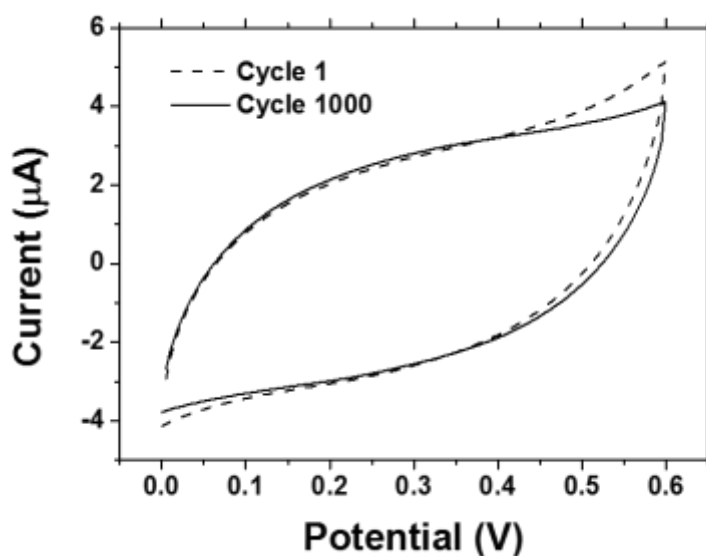


**Figure S4** O1s core level spectrum for (a) as-grown PyC and (b) N-PyC with fitted spectral contributions.

### N-PyC Electrochemical Stability

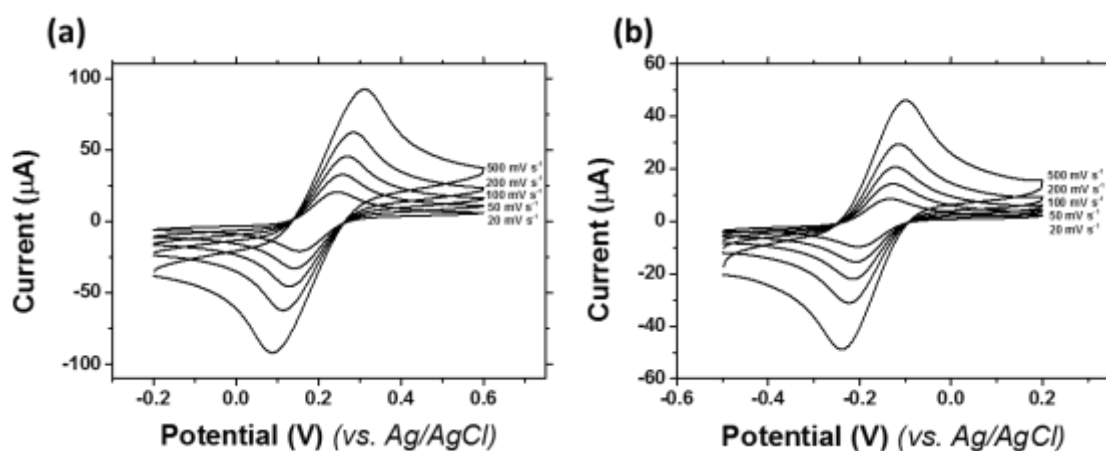
The cycling stability of the N-PyC electrode was investigated by repeated cyclic voltammetry in a background electrolyte of

1 M KCl for 1000 cycles. Fig. S4 below compares the charging profile of the first scan with that of scan number 1000. It is clear that the performance of the electrode is essentially unchanged; indicating the electrochemical stability of the N-PyC and confirming its suitability for electrode applications.



**Figure S5** Cycling stability of the N-PyC film in 1M KCl comparing voltammetric response of the first scan with that after 1000 cyclic voltammetry cycles. Scan rate is  $200 \text{ mV s}^{-1}$ .

For all voltammetric characterisation presented in the main body of the text, several scan rates were employed. For both the ferri/ferro-cyanide and Ru(III) probes close to ideal quasi-reversible voltammetric responses were observed for all scan rates. This is presented in Fig. S6 below.



**Figure S6** (a) Voltammetric response of N-PyC in 1 mM ferri/ferro-cyanide across a range of scan rates. (b) Voltammetric response of N-PyC in 1 mM hexamine ruthenium (III) chloride across the same range of scan rates. Background electrolyte is 1 M KCl in each case.

## Raman Spectroscopy

Raman spectroscopy was carried out on as-grown PyC and N-PyC films with the resultant spectra shown in Fig. S7. Both samples show spectra typical of heavily defective graphitic carbon systems. However, the small crystallite size and high level of crystalline defects typical of PyC results in suppression of the 2D band and an extremely large, broad D band region, respectively. A detailed description of the Raman spectrum of turbostratic carbon materials such as PyC is dealt with by McEvoy.<sup>5</sup> An important consideration here is that the penetration depth of the Raman laser on carbon systems such as in this study is approximately 30 nm.<sup>6</sup> The plasma treatment only functionalises the surface of the N-PyC and, as such, Raman spectroscopy is not an appropriate technique for measuring such surface changes. As the Raman spectra here are averaged from 10,000 individual spectra measured over a  $30 \times 30 \mu\text{m}$  area of the sample, these are representative of the entire uniform PyC films.

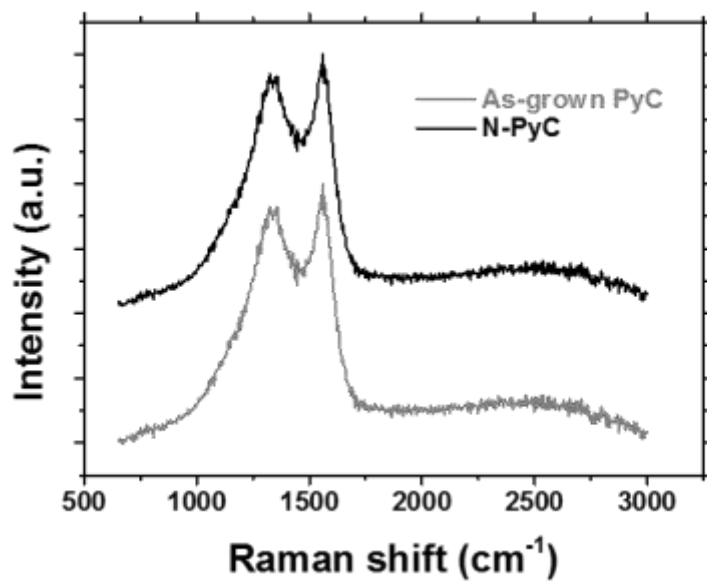


Figure S7 Raman spectra for as-grown PyC and N-PyC

## References

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