# **Electronic Supplementary Information**

# Transforming collagen wastes into doped nanocarbons for sustainable energy applications

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**Fig. S1** XRD patterns of the carbon materials derived by heating collagen waste at different temperatures and time. a) 500 °C for 8 h; b) 750 °C for 8 h; c) 1000 °C for 4 h; d)1000 °C for 8 h.



The increase in the crystallinity of the carbon materials with the increase in temperature and time of heat treatment is evident from the gradual appearance and sharpening of both diffraction peaks and in particular (101) peak.

Carbon materials		% C	% O	% N	% H	% Other
Temperature	Type of					elements
(°C)	analysis					(S and other
						impurities)
	XPS	77.94	6.17	12.79	-	3.10
500	CHNS	72.21	-	13.56	3.05	4.94
	XPS	81.58	9.84	7.21	-	1.37
750	CHNS	78.72	-	8.45	1.60	1.40
	XPS	79.68	15.41	2.86	-	2.05
1000	CHNS	78.56	-	3.12	0.55	1.41

**Table S1** Atomic composition of the carbon materials derived by heating collagen waste at different temperatures for 8 h characterized through XPS and elemental (CHNS) analysis

Elemental analysis of the collagen waste from goat skins revealed the presence of C, N, H and S close to 41.5, 14.7, 7.1 and 0.2%, respectively. The atomic composition of the carbon materials derived from different temperatures of treatment of collagen waste predominantly compose of carbon, oxygen and nitrogen in the range of 72-82, 6.2-15.4 and 2.9-13.6%, respectively as analyzed through XPS and elemental analysis (Table S1). The presence of other elements such as S and impurities (Na, Ca and Cl are the possible major impurities present in the collagen waste) in the range of 1.4-4.9% was also noted. It is evident that the amount of oxygen in the carbon materials increases while that of nitrogen decreases as the temperature of treatment of collagen waste increases. It is interesting to note that the amount of nitrogen in the carbon materials and

the decreasing trend of nitrogen as a function of the treatment temperature as analyzed from the XPS analysis is consistent with the values obtained from the CHNS analysis (Table S1). These results confirm the fact that the nitrogen and oxygen act as defects or (natural) doping atoms in the carbon matrix synthesized in this study.

#### **XPS** Analysis

The deconvolution of O(1s) peaks resulted in a strong peak at 530.9 eV and a broad peak at 534.4 eV, which are assigned to C=O group and -O-COO- group, respectively for the carbon materials derived from low temperature treatment (500 °C) of collagen waste (Fig. 2b). Higher temperature (750 and 1000 °C) treatment of collagen waste leads to carbon materials with peaks at 531±0.1, 532.3±0.1 and 535.7±0.2 eV. The strong appearance of 531 eV peak in the carbon materials prepared from high temperature treatment suggests the prevalence of C=O and O=C-OH groups in comparison to C-N bonds, as also envisaged in the analysis of C(1s) spectra. The peak at 532.3±0.1 eV can be assigned to C-OH group while the peak at 535.7±0.2 eV corresponds to either C-O-O- or N-O groups.<sup>1</sup> The N(1s) peak was deconvoluted into three peaks in all the carbon materials (Fig. 2c). Low temperature treatment (500 °C) of collagen waste provides carbon materials with binding energies at 397.3, 399.2 and 401.9 eV. The lower energy contributions of the N(1s) spectrum (397.3 and 399.2 eV) are attributed to pyridine-like nitrogen atoms on the edge of graphene lattice only bonded to two C atoms and the broad and weak peak at 401.9 eV is assigned to highly coordinated N atoms substituting inner C atoms (quaternary N) on the graphene layers and bonded to three C atoms.<sup>2,3</sup> Carbon materials derived from collagen waste when treated at higher temperature (750 and 1000 °C) exhibit peaks at 398.8±0.5,

400.9±0.1 and 403.2±0.2 eV, of which lower energy contribution is assigned to pyridine-like nitrogen atoms in graphitic lattice as above and higher energy contributions (400.9 and 403.2 eV) are assigned to highly coordinated N atoms substituting inner C atoms on the graphene layers. It is evident that the formation of graphitic nitrogen substituting inner C atoms on the graphene layers increases while the pyridinic nitrogen contribution decreases as the treatment temperature increases. Further, it is evident that the strength of peaks in N(1s) core spectra reduced by many folds when the temperature increased to 1000 °C. It is possible that certain nitrogen functionalities could be converted into nitrogen gas (N<sub>2</sub>) in anoxic conditions at high temperature and escape.<sup>4</sup>

### **FT-IR Analysis**

**Fig. S2** FT-IR spectrum of the carbon materials derived by heating collagen waste at different temperatures and time. a) 500 °C for 4 h. b) 500 °C for 8 h. c) 750 °C for 4 h. d) 750 °C for 8 h. e) 1000 °C for 4 h. f)1000 °C for 8 h.













FT-IR spectra of the carbon materials were analyzed using Perkin-Elmer spectrophotometer. The carbon samples were ground finely using KBr powder and pressed into pellets. The pellets were analyzed over the range of 400-4000 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup> with an average of 25 scans.

The chemical bonding, functionalities and structure of the formed carbon materials can be traced through FT-IR spectroscopy (Fig. S2). The absorption bands corresponding to the conjugated structure occurs at lower frequencies. Especially, graphene like carbon-carbon and nitrogen substituted carbon double bonds such as C=C and C=N species (1550-1650 cm<sup>-1</sup>), carboxy COO<sup>-</sup> (~1410 cm<sup>-1</sup>) and alkoxy C-O (1000-1070 cm<sup>-1</sup>) bonds are observed in our carbon materials derived from different temperature treatment of collagen waste.<sup>5,6</sup> It is interesting to mention that the appearance of carbonyl groups (C-O) is noted only in the carbon materials derived from high temperature treatment (750 and 1000 °C), which is in agreement with the XPS results where it has been shown that the formation of C=O groups and diminution of pyridinic nitrogen contribution increases as the temperature of treatment increases. The sharp peaks around 2900 and 2855 cm<sup>-1</sup> corresponds to the asymmetric C-H stretching of -CH<sub>3</sub> and symmetric vibrations of -CH<sub>2</sub> groups.<sup>7</sup> All the spectra show a broad absorption band around 3200-3600 cm<sup>-1</sup>, which can be assigned to the N-H stretching of amine or O-H stretching of the hydroxyl groups.<sup>6</sup> The intensity of the O-H stretching band increases gradually as the treatment temperature increases beyond 500 °C thereby providing further proof for the formation of C-OH groups in the carbon materials derived from higher temperature treatment (750 and 1000 °C).

### **SEM Analysis**

Fig. S3 (a) SEM micrograph and (b) particle size distribution of carbon material derived by heating collagen waste at 1000 °C for 8 h.



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SEM micrographs of sonicated carbon samples show presence of agglomerated spheroidal nanocarbon particles with an average size of  $\sim 41$  nm. This is comparable to the size observed for the polyhedral and spherical onion-like particles in HRTEM images (Fig. 3).

### **EPR** Analysis

**Fig. S4** EPR spectra of select carbon materials derived by heating collagen waste at different temperatures and time. a) 500 °C for 4 h. b) 500 °C for 8 h. c) 1000 °C for 8 h.

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Electron paramagnetic resonance measurements were recorded at room temperature ( $25\pm2$  °C) using Bruker-EMX EPR spectrometer operated at a frequency of 9.521 GHz with modulation 12

amplitude of 3.00 G and a power level of  $\sim$ 3.20 mW. Diphenyl picryl hydrazine (DPPH) with a g value of 2.0036 (±0.0002) was used a standard to calibrate the magnetic field.

The EPR measurement gives details on the structural transformation of the carbon materials formed during thermal treatment of collagen waste. EPR spectra of the select carbon materials obtained in this work are shown in Fig. S4. It is observed that all the carbon materials derived from different temperature and time exhibit a slightly broad EPR signal with *g*-value ranging from 1.999 to 2.0322. Even at low temperature treatment (500 °C) for 4 h, the *g*-value is not far from the value of free spin of g=2.0023, indicating a paramagnetic behavior. The EPR signal of the carbon material becomes broader as the temperature increases, implying the gradual conversion of the spin system towards the nature of conduction carriers.<sup>8</sup> In addition, the *g*-value is found to increase as the temperature and heating time increases. For the carbon material derived from high temperature and longer duration of treatment (1000 °C for 8 h), the EPR signal is broader and noisy with a very high *g*-value implying the presence of conduction  $\pi$ -electrons delocalized over the aromatic rings, suggesting a ferromagnetic behavior. Such observation has been made earlier for the polyhedral carbon onions.<sup>9</sup> This shows that the EPR results are in good agreement with the HRTEM and magnetization results.

**Fig. S5.** Room temperature M(H) curve of pristine collagen waste probed using a vibrating sample magnetometer



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