

Modulation of electrical charge transfer in cornstarch-based films through carbonized polymer dots and their validation as electrodes in triboelectric nanogenerators

Supporting information:

FT-IR Characterization of coffee ground-based carbonized polymer dots

The surface functional groups of CPDs derived from ground coffee were analyzed using FT-IR spectroscopy, as shown in Figure S1. The band centered at approximately 3344 cm^{-1} is attributed to N–H vibrations of amines and O–H vibrations of hydroxyl groups; this band may also correspond to other functional groups such as alcohols or phenols, which is consistent with the presence of up to 14 types of phenolic compounds in ground coffee [1]. The peak around 2978 cm^{-1} corresponds to C–H stretching vibrations of methylene groups; these peaks are characteristic of the CPDs [2]. A low-intensity band at approximately 1649 cm^{-1} can be attributed to overlapping contributions from C=O stretching vibrations and C=C stretching in conjugated or aromatic domains. The bending vibration signals at 1467 cm^{-1} and 1397 cm^{-1} are attributed to N–H and C–N groups. These results indicate the presence of a hybrid polymer/carbon structure comprising carbonyl, amide, and other functional groups [3]. On the other hand, a nearby peak at 1044 cm^{-1} is associated with C–O stretching vibrations. Finally, the absorption band at 600 cm^{-1} is assigned to out-of-plane bending vibrations of aromatic C–H bonds [4].

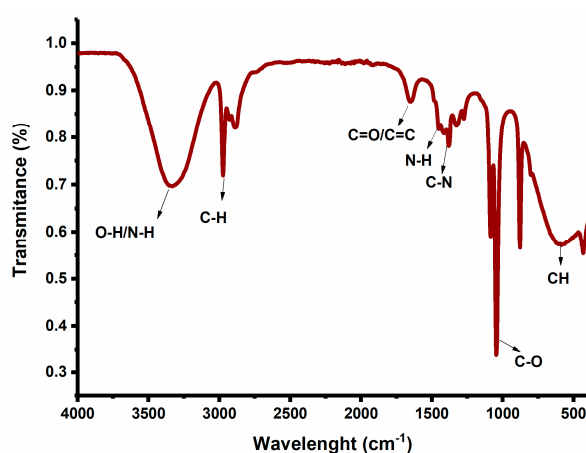


Figure S1. FT-IR spectrum of coffee ground-based CPDs

FT-IR of cornstarch and composite cornstarch films

Figure S2 shows the FT-IR analysis, which provides insight into the reorganization of cornstarch chains during polymer formation and reveals the molecular differences that arise when different concentrations of CPDs are incorporated into the polymeric films. The peak at 3300 cm^{-1} corresponds to O–H stretching present in cornstarch and glycerol, while the peak at 2934 cm^{-1} is attributed to C–H stretching. The band at 1651 cm^{-1} corresponds to C=O stretching; however, it is also associated with O–H bending of absorbed water. The peak at 1154 cm^{-1} corresponds to C–C vibrations, and the peak at 1024 cm^{-1} is assigned to C–O stretching of the C–O–C groups in the anhydroglucose units of cornstarch. Additionally, the band at 917 cm^{-1} is attributed to the vibrational modes of the D-glucopyranosyl ring [5, 6]. The FT-IR spectra of the cornstarch film and the films containing CPDs show the same characteristic vibrational modes, indicating that the starch, glycerol, and CPDs possess similar functional groups, without generating new bands or causing significant alterations in the structure of the cornstarch films.

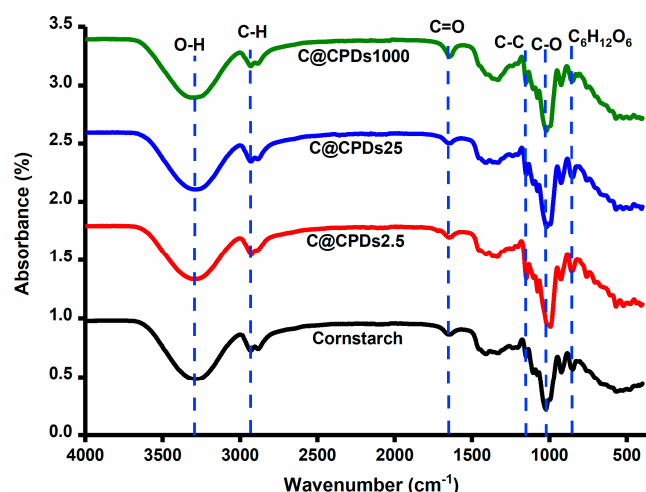


Figure S2. FT-IR spectroscopy of the polymeric films with different concentrations of CPDs.

XPS characterization of the compounds and cornstarch base-film

Table S1. C 1s spectrum adjustment parameters of the films

Sample	Assignment	BE (eV)	FWHM (eV)	Area (%)
Cornstarch	C–C / C=C	284.8	1.30	34.12
	C–O	286.3	1.35	32.77
	C=O / O–C–O	287.7	1.72	6.64
	O–C=O	289.0	1.86	2.77
C@CPDs2.5	C–C / C=C	284.6	1.30	26.4
	C–O / C–N	286.2	1.30	38.2
	C=O / O–C–O	287.6	1.51	7.1
	O–C=O	288.9	1.85	2.2
C@CPDs25	C–C / C=C	284.7	1.31	32.9
	C–O / C–N	286.2	1.32	34.0
	C=O / O–C–O	287.6	1.88	5.6
	O–C=O	289.0	1.94	2.0
C@CPDs1000	C–C / C=C	284.9	1.28	40.9
	C–O / C–N	286.4	1.35	23.2
	C=O / O–C–O	287.8	1.82	5.1
	O–C=O	289.1	1.81	2.4

The high-resolution C 1s spectra of cornstarch and cornstarch composite films were deconvoluted into four main contributions (Table S1). For pristine cornstarch, the components located at ~284.8 eV, ~286.3 eV, ~287.7 eV, and ~289.0 eV were assigned to C–C/C=C, C–O, C=O or O–C–O, and O–C=O environments, respectively, in agreement with the chemical structure of polysaccharides. Although a low nitrogen content was detected in the survey spectrum (1.8 at.%), no distinct C–N contribution was resolved in the C 1s region of cornstarch due to the strong overlap between C–N and C–O signals and the minor contribution of nitrogen-containing species.

For cornstarch composites, the component centered at ~ 286.2 – 286.4 eV was attributed to overlapping C–O and C–N contributions, reflecting the incorporation of nitrogen-containing functional groups from the carbon quantum dots. The peak at ~ 287.6 – 287.8 eV remains dominated by carbonyl-type species (C=O/O–C–O), with a possible minor contribution from nitrogen-containing environments. The relative area of the C–O/C–N component increases at low and intermediate CPDs contents, indicating enhanced interfacial interactions between the starch matrix and the functionalized CPDs. At higher CPDs loadings, an increase in the C–C/C=C contribution is observed, which is attributed to the greater exposure of carbon-rich sp^2 domains at the surface, consistent with surface enrichment effects commonly observed in carbon-based composites.

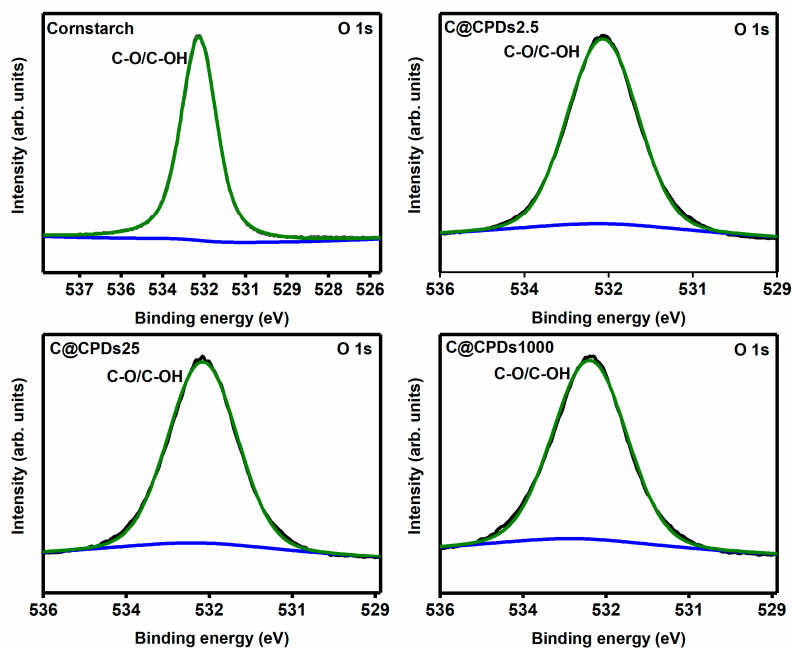


Figure S3. High-resolution O 1s XPS spectra of pristine cornstarch and cornstarch composite films.

Figure S3 shows the high-resolution O 1s XPS spectra of pristine cornstarch and cornstarch composite films. All spectra were fitted using a single Gaussian–Lorentzian component centered at ~532.5–532.7 eV (Table S2), attributed to overlapping C–O and C–OH environments characteristic of polysaccharides and oxygen-functionalized carbon materials. No additional oxygen species could be reliably resolved due to the strong overlap of O 1s contributions and the limited chemical shift among different oxygen functionalities. The similar binding energy values observed for cornstarch and CPDs-containing samples indicate that the dominant oxygen chemical environment is preserved upon CPDs incorporation. Minor variations in peak width are observed upon CPDs addition, with a slight increase in FWHM for the C@CPDs1000 sample, suggesting a broader distribution of oxygen environments likely associated with partial CPDs aggregation at high loading.

Table S2. O 1s spectrum adjustment parameters of the films

Sample	Assignment	BE (eV)	FWHM (eV)	Area (%)
Cornstarch	C–O / C–OH	532.6	1.70	21.88
C@CPDs2.5	C–O / C–OH	532.7	1.70	16.30
C@CPDs25	C–O / C–OH	532.5	1.71	15.9
C@CPDs1000	C–O / C–OH	532.7	1.86	19.8

Rectification circuit configuration

The electrical signals generated by the TENG were rectified using a full-wave bridge rectifier assembled on a breadboard with a commercial W02M diode bridge. The alternating output terminals of the TENG were connected to the two AC input terminals of the bridge rectifier, while the positive and negative DC output terminals were connected directly to the oscilloscope for voltage and current measurements. No additional filtering, smoothing, capacitive storage, or signal-conditioning components were incorporated into the circuit. Therefore, the unidirectional signals presented in Figure 9 correspond to the direct full-wave rectification of the alternating electrical output generated by the TENG.

To rigorously verify the authentic triboelectric output of the TENG, the raw AC open-circuit voltage was evaluated using a polarity switching test (Figure S4). Upon swapping the electrode connections between the forward and reverse modes, the output voltage waveform displayed a symmetric 180° phase inversion. This characteristic polarity reversal confirms that the measured electrical response is genuinely driven by the contact–separation triboelectric mechanism rather than background electromagnetic interference or parasitic coupling.

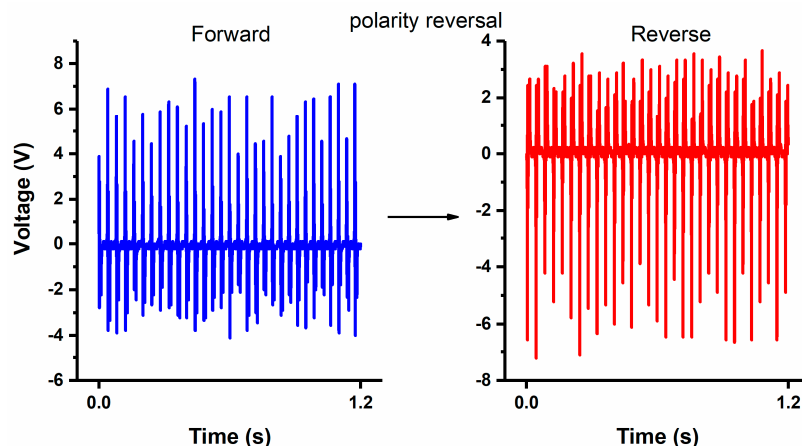


Figure S4. Switching polarity test of the raw AC output. Unrectified open-circuit voltage waveforms recorded under forward (blue) and reverse (red) electrical connections, demonstrating a symmetric 180° phase inversion that confirms the authentic triboelectric origin of the generated signal.

References

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