Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Additive-Free Aqueous-Based Graphene Inks for 3D Printing Functional Conductive Aerogels

Elnaz Erfanian[a,b], Milad Goodarzi[c], Gabriel Banvillet[b], Farbod Sharif[a], Mohammad Arjmand[c], Orlando J. Rojas[b,d,e], Milad Kamkar[f*], and Uttandaraman Sundararaj[a*]

[a] Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, AB T2N 1N4, Canada

[b] Bioproducts Institute, Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, BC V6T 1Z4, Canada

[c] Nanomaterials and Polymer Nanocomposites Laboratory, School of Engineering, University of British Columbia, Kelowna, BC, V1V 1V7 Canada

[d] Department of Chemistry and Department of Wood Science, University of British Columbia, Vancouver, BC V6T 1Z4, Canada

[e] Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FIN-00076 Aalto, Espoo, Finland

[f] Department of Chemical Engineering and the Waterloo Institute for Nanotechnology University of Waterloo, 200 University Avenue West Waterloo ON N2L 3G1, Canada

* Corresponding author: u.sundararaj@ucalgary.ca , Milad.kamkar@uwaterloo.ca

S.1. X-ray diffraction (XRD) spectra

To address the difference in interlayer spacing, we have utilized Bragg's Law, which is specifically designed for this purpose. Bragg's Law allows us to calculate the spacing between crystal planes (d-spacing) using the angles of diffracted X-rays. The calculations based on Bragg's Law have been included in SI to accurately reflect the changes in interlayer spacing due to intercalation.

The calculation results based on Bragg's law ($n\lambda = 2d\sin\theta$) for the interlayer spacing before and after different intercalations are as follows considering the $\lambda = 1.54$ Å

Graphite (002) d-spacing considering first-order diffraction ($2\theta = 26.48°$): 3.36 Å

N-2min (002) d-spacing considering first-order diffraction ($2\theta = 13.60°$): 6.51 Å (93.8% enhancement in d-spacing)

Elec (002) d-spacing considering first-order diffraction (2 θ = 13.54°): 6.53 Å (94.3% enhancement in d-spacing)

P-2min (002) d-spacing considering first-order diffraction (2θ = 13.42°): 6.59 Å (96.1% enhancement in d-spacing)

S-2min (002) d-spacing considering first-order diffraction (2θ = 13.39°): 6.61 Å (96.7% enhancement in d-spacing)

These results indicate that intercalation significantly increases the interlayer spacing of graphene, suggesting successful insertion of ions between the graphene layers. The differences in spacing also imply variations in the degree of intercalation depending on the used acid in the first step.

Table S1. Raman data of graphite and electrochemical and sulfuric, nitric, and phosphoric acid samples

	G (cm^{-1})	D (cm^{-1})	I_D/I_G	I_{2D}/I_G
Graphite	1587.6	-	-	0.547
El	1588	1349.5	1.04	0.108
P-2min	1585	1351	0.61	0.175
S-2min	1584.5	1349.5	1.2	0.090
N-2min	1592.5	1341.3	1.25	0.087

Table S2. Zeta potential of the ECGs.

Sample	Zeta potential
P-2min	-40 ± 1.2
S-2min	-63±1.5
N-2min	-47 ± 1
El	-35 ± 1

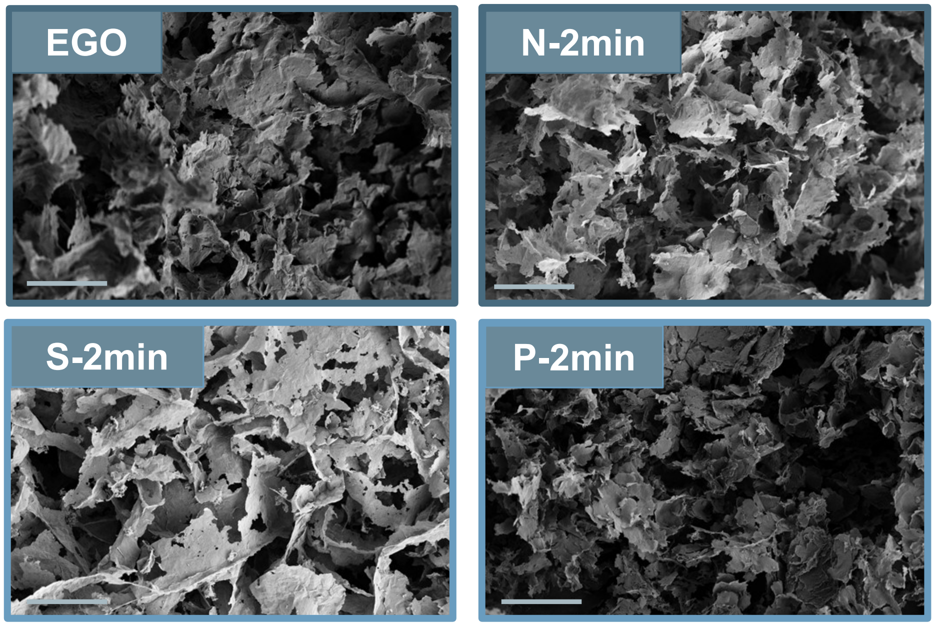

Figure S1. SEM images of synthesized graphene. Scale bar corresponds to 40 µm.

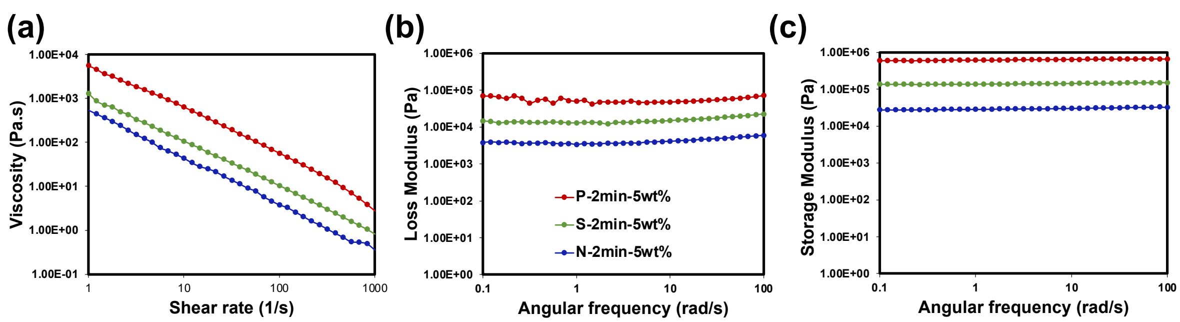

Figure S2. Rheological properties of the inks at 5wt.% at 22°C. (a) Apparent viscosity versus shear rate. (b,c) Loss modulus (G″) and storage modulus (G′) versus angular frequency at a fixed strain of 0.1%.

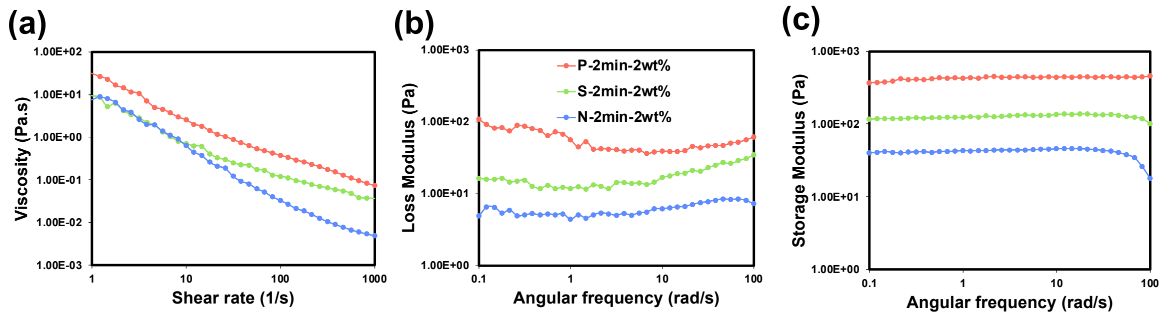

Figure S3. Rheological properties of the inks at 2wt.% at 22◦C. (a) Apparent viscosity versus shear rate. (b,c) Loss modulus (G′′) and storage modulus (G′) versus angular frequency at a fixed strain of 0.1%.

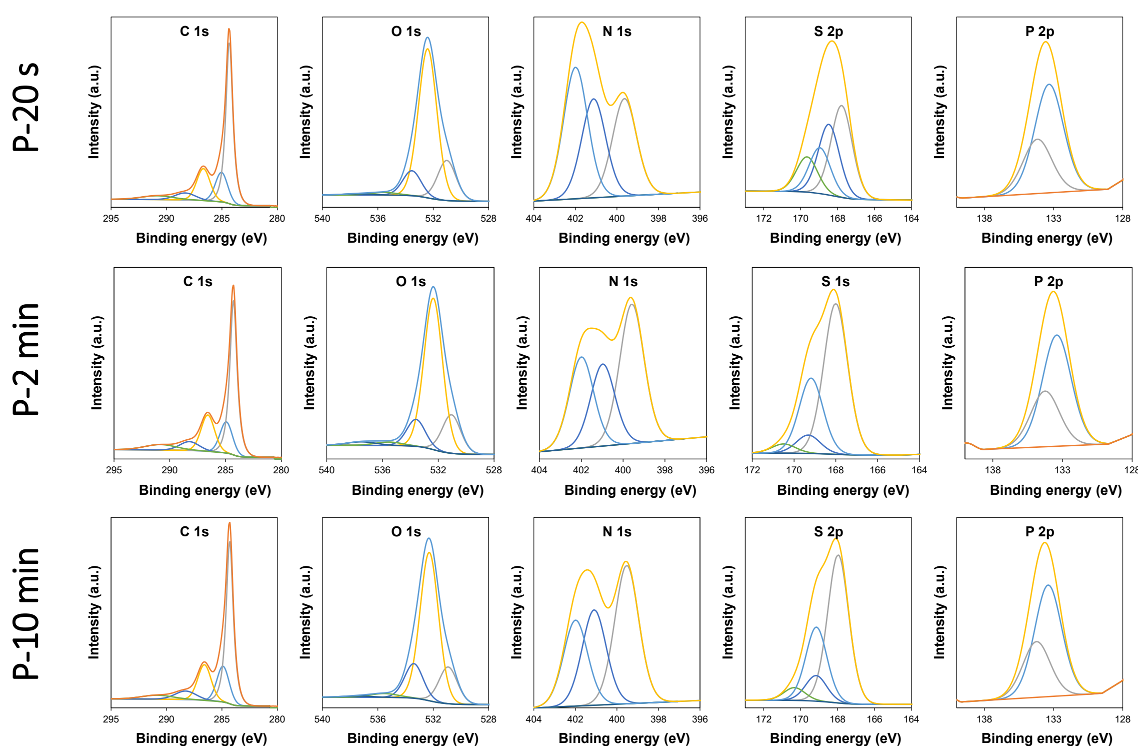

Figure S4. High resolution of C 1s, O 1s, N 1s, S 2p and P 2p of pre-treated graphenes with phosphoric acid at different times.

Table S3. Atomic composition derived from XPS spectra of pre-treated ECGs with phosphoric acid as intercalant agent at different times

	P2p (at%)	**S2p (at%)**	**C1s (at%)**	**N1s (at%)**	**O1s (at%)**
P-20sec	0.1	0.4	83.9	1.1	14.5
P-2min	0.1	0.3	83.3	1.0	15.3
P-10min	0.1	0.3	83.4	0.9	15.3