Plant Extract-Based Liquid Phase Exfoliation Enables One-Step Green Production of Two-Dimensional Heterostructure Nanohybrids Capable of Dramatic Improvement of Polymer Properties

Yingjie Bu, Rhudith B. Cabulong, Beom Soo Kim*

Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea

*Corresponding author E-mail: bskim@chungbuk.ac.kr

Table S1. Summary of hybrid composites reported in the literature.

No.	Hybrid type	Precursor materials	Preparation method	Application	Reference
1	Aluminum-h-BN-GNP	H-BN and graphene	ultrasonic dispenser for 1 h	Automotive and aerospace applications	1
2	Aluminum alloys-h-BN-GNP	h-BN and graphite	Hummer's method	Corrosion protection	2
3	GO/BN hybrid membranes	GO and amino groups functionalized BN	heated to 80 °C for 2 h	Electronic devices heat transfer materials	3
4	Mxene-PSZ-ABN	Mxene and h-BN	crosslinked at 160 ◦C for 12 h	Thermally conductive materials	4
5	Graphene/BNN	Graphene and BNN	stirring and sonication	Sensor	5
6	f-BNNS-Ti_3C_2Tx/PBI composite	Functionalized BNN and Mxene	ball milling and thermal reaction	Thermal conductivity	6
7	RGO-h-BN/STG	h-BN and RGO	ultrasonication, ball grinding and quartz tube reactor	Thermal transport performance	7
8	Graphene/h-BN	BNN and graphite	CVD method (graphene growth on the BNN surface)	Oxygen reduction reaction	8
9	EP/GNS/BNOH aerogel	BNOH and GO	mixing and thermal reaction	Thermal insulation	9
10	GO/BNN PVA film	GO and BNN	stirred at room temperature for 3 days	Thermal conductive polymers	10
11	Epoxy/ graphene/ boron nitride	Graphene and BN	ultrasonication for 1 h	High thermal conductivity material	11
12	Polystyrene-BNN-graphene	BNN and graphene	sonication for 1 h	Thermal conductive	12

				polymeric	

No.	hybrid type	Precursor materials	Preparation method	Application	Reference
13	Brophene-graphene aerogel	Borophene and GO	mixing individual materials	Sensors	[13]
14	Mxene/GO	GO and Mxene	mixing GO with Mxene at room temperature for 6 h	Supercapacitors	[14]
15	Graphene/ BNN	Graphene and BNN	sonication and hydrothermal treatment	Insulating composites	[15]
16	Mxene/BNN	Mxene and BNN	sonication for 20 min	Electronic devices	[16]
17	BNN/GO	BNN and GO	mixed	Electronic systems	[17]
18	Graphene/ Mxene	GO and Mxene	mixed	Flexible electronics	[18]
19	EP/BN-PDA-MXene composites	BNN and Mxene	stirring for 24 h	Fireproof material	[19]
20	BNN/GO	GO and BNN	ball-milled for 8 h	Battery	[20]
21	TPU/BNN/ GO	GO and BNN	oxidized BN was reacted with grafted GO	H_2 gas barrier coating applications	[21]
22	Silicone rubber/BNN/ GO	Functionalized BNN and graphene	sonication for 1 h	Thermally conductive	[22]
23	GO/graphene film	GO and graphene	stirred for 24 h	Flexible device	[23]
24	BNOH–GNP/TPU Hybrid	NaOH modified BNN and graphene	mixed	Wearable cooled smart clothes	[24]
25	BNN/FFG	h-BN and graphite	sonication for 24 h using tannic acid	Biocompatible	[25]

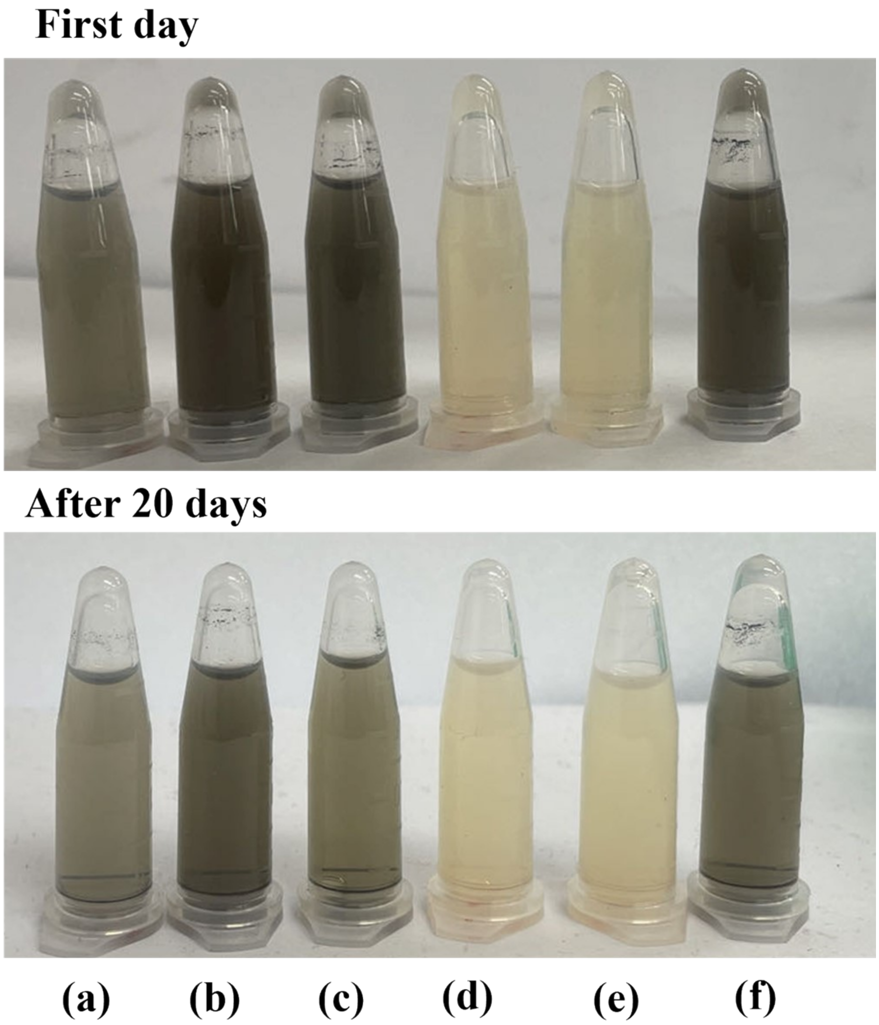

Fig. S1. Digital picture of sample (a) BNN/FFG; (b) FFG/FFB; (c) FFG/MXene; (d) BNN/FFB; (e) BNN/MXene; and (f) FFB/MXene liquid stored water dispersions after sonication.

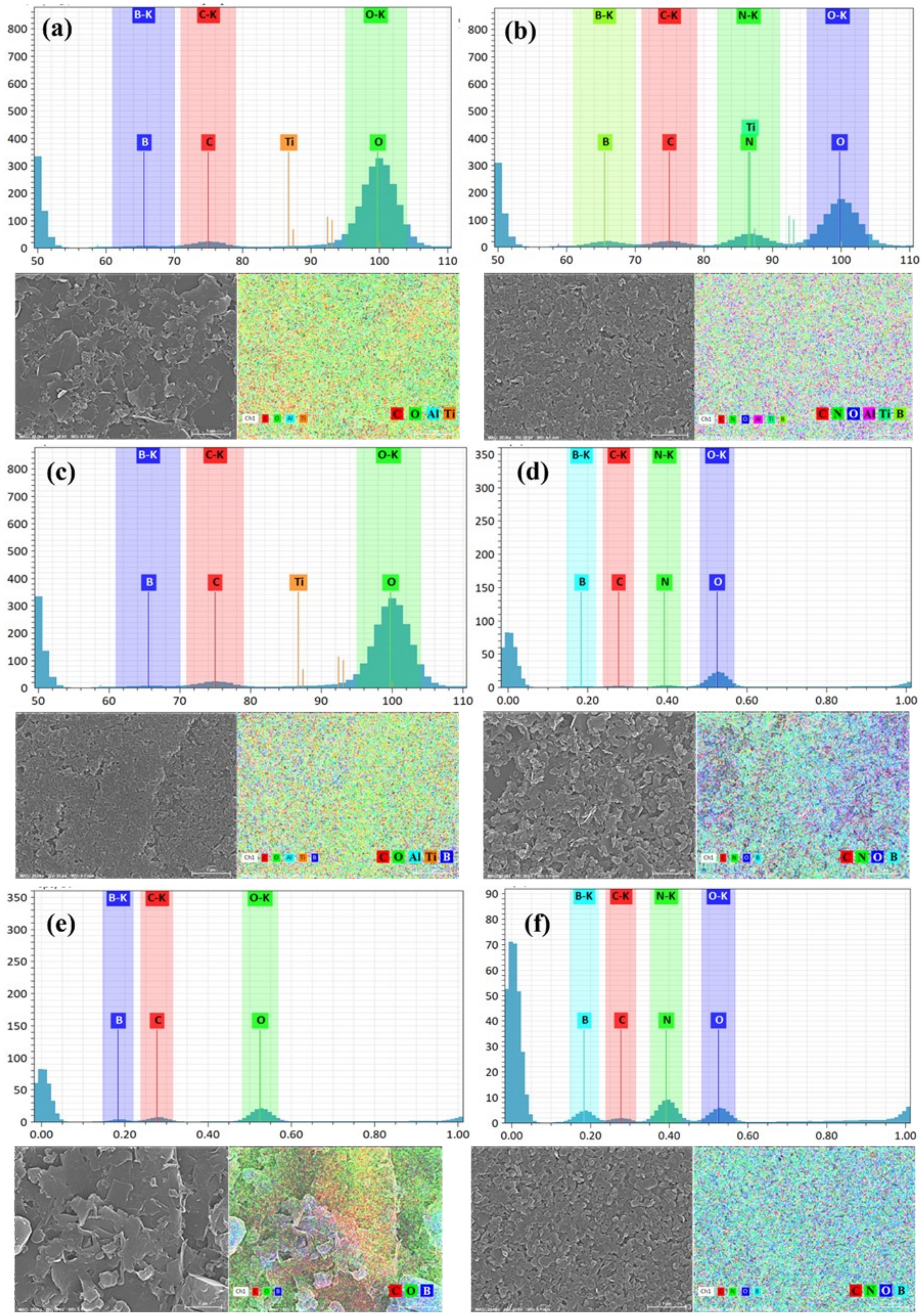

Fig. S2. EDS analysis of (a) FFG/MXene, (b) BNN/MXene, (c) FFB/MXene, (d) BNN/FFG, (e) FFG/FFB, and (f) BNN/FFB.

Table S2. Elemental composition of hybrids through EDS analysis.

Sample	Atomic %					
	C	O	B	N	Al	Ti
FFG/MXene	24.81	73.03			0.34	1.82
BNN/MXene	13.59	34.53	35.96	15.04	0.06	0.82
FFB/MXene	16.51	59.36	22.3		0.35	1.48
BNN/FFG	13.82	45.4	28.86	11.92		
FFG/FFB	33.85	30.1	36.05			
BNN/FFB	10.51	13.75	44.35	31.39		

Table S3. Elemental composition of nanomaterials and hybrids through XPS analysis.

Sample	Atomic %					
	C	O	B	N	Al	Ti
FFG	78.18	21.82				
BNN	47.07	19.03	15.16	18.74		
MXene	42	36.58			1.08	20.34
FFB	45.92	35.98	18.10			
BNN/FFG	19.64	38.49	25.85	16.02		
BNN/FFB	40.25	18.37	18.79	22.6		
FFG/MXene	70.19	28.07				1.74
BNN/MXene	34.86	18.67	19.95	25.81		0.71
FFG/FFB	83.00	11.24	5.77			
FFB/MXene	46.26	37.9	12.98			2.86

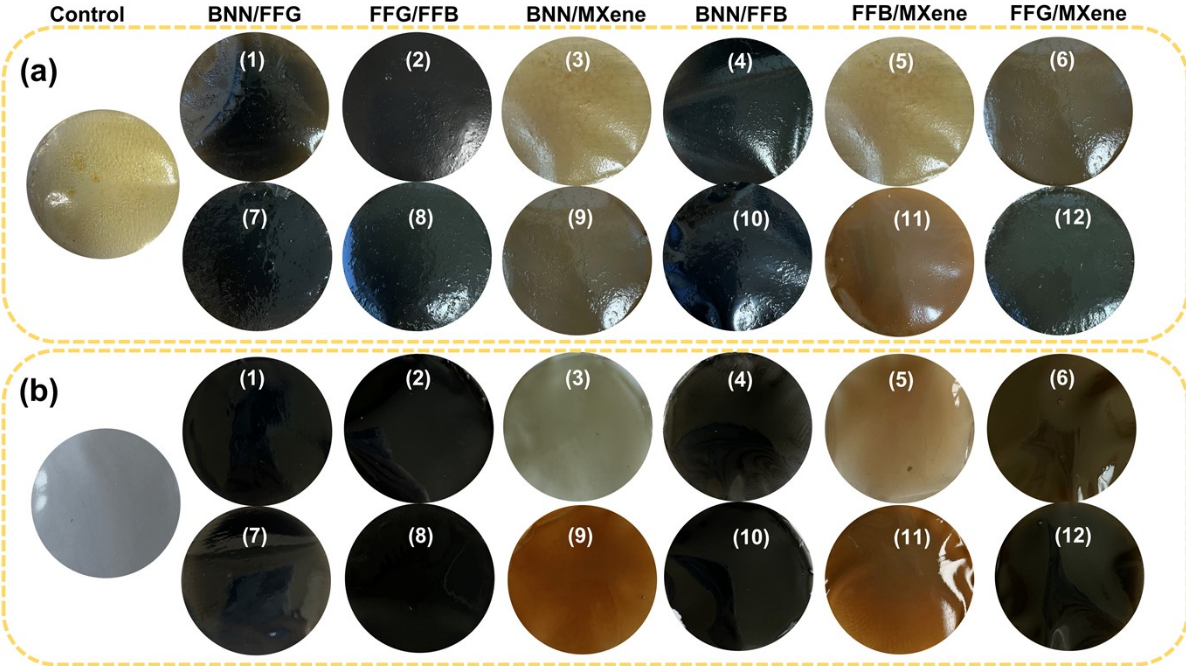

Fig. S3. Images of (a) chitosan films containing 1 wt% hybrids (a1-a6) and mixtures (a7-a12); (b) PVA films containing 1 wt% hybrids (b1-b6) and mixtures (b7-b12).

Table S4. Cost of the solvents retrieved from Sigma-Aldrich as of January 2024.

Solvent	*Quantity used*	*Sigma price (KRW)*	*Cost (KRW)/100ml*	*Cost (USD)/100ml (Rate 0.00076)*
Coffee Waste	100 ml	501.75/ 1000 ml	50.175	0.038
Gallnut Powder	100 ml	801.75/ 1000 ml	80.175	0.061
Acetone	100 ml	71,456/500 ml	14,292.1	10.862
DMF	100 ml	91,553/250 ml	36,624.2	27.834
Ethanol	100 ml	103,400/1000 ml	10,340	7.858
DMSO	100 ml	581,189/1000 ml	58,118.9	44.170
IPA	100 ml	80,869/500 ml	16,173.8	12.292

Table S5. Cost of the solvent by calculation.

	Quantity used	**Price (KRW)** (*including power consumption*)	**In detail**
Coffee Waste Powder	10 g	501.75/1000 ml	Electric brewing kettle power: 300 W Centrifuge power: 2.7 kW Electricity bills: 111.5 KRW
Gallnut Powder	10 g	801.75/1000 ml	

The life cycle assessment (LCA) has an important role in investigating the potential environmental impacts of new technologies to develop an understanding of their potential environmental burdens by considering all activities from raw material acquisition through production, use, and final disposal. Due to the complexity of the raw material and limited database resources, utilizing existing graphite and graphene databases as reference, we performed a LCA of the technology described herein including activities from raw material extraction and processing to graphene production. The functional unit is the procedure required to prepare 1 g of graphene. The system boundaries of this study represent a cradle-to-gate perspective. This process includes the first step of coffee extract preparation, the second step of sonication, centrifugation, washing, and drying to obtain graphene. The general scheme of the LCA system boundaries is shown in **Fig. S4**. The methods of IPCC 2021 GWP 100a V1.02

was considered for this LCA, and the software SimaPro was used for the calculations. We include three impact categories: energy use, biogenic, and land transformation. For all other processes, inventory data was obtained from the Ecoinvent database.

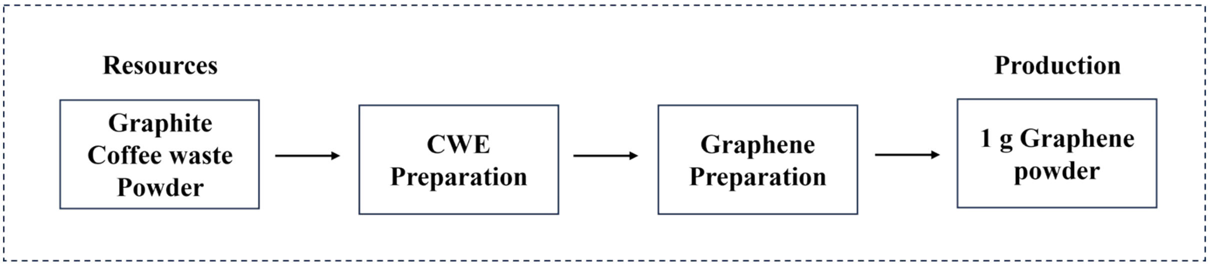

Fig. S4. Flowchart describing the cradle-to-gate life cycle of graphene produce.

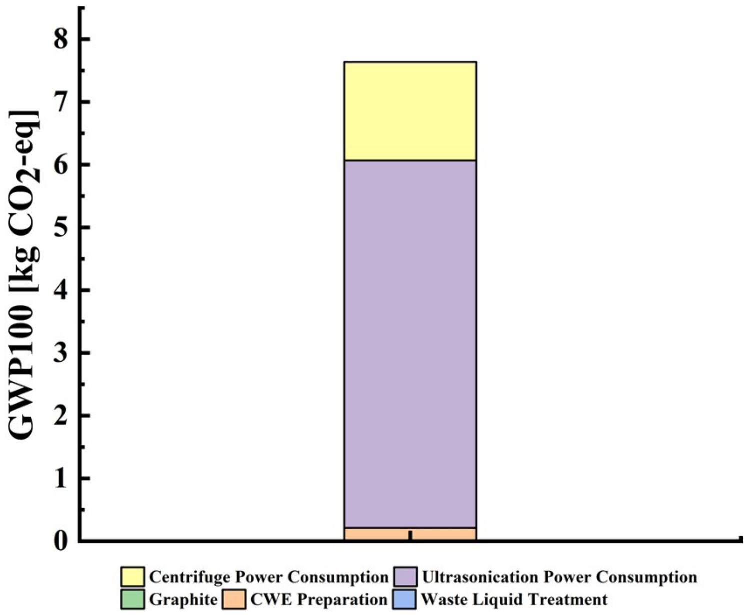

Fig. S5. Life cycle global warming potential of graphene production.

Table S6. Input data for the process.

Process1-input		Electrical Power
Coffee Waste Powder	10 g	
Distilled Water 1 L	1000 g	
Electric kettle power consumption	0.3 kWh	300 W
Process1-output		
CWE	1000 ml	
Process2-input		
CWE	1000 ml	
Graphite	10 g	
Sonication power consumption	8.4 kWh	350 W
Centrifuge consumption	2.25 kWh	2.7 kW
Process2-output		
Graphene	1 g	
Unexfoliated graphite	9 g	
Solvent	1000 ml	

Table S7. Numerical results presented for LCA analysis.

Impact category	Unit	Total	Raw material acquisition and preparation process		Product Manufacturing Process		Waste disposal process
			CWE Preparation	Graphite	Ultrasonication power consumption	Centrifuge power consumption	Waste liquid treatment
GWP100 - fossil	kg CO2-eq	7.6256609	0.21029009	0.000715934	5.8479882	1.5664254	0.000241294
GWP100 - biogenic	kg CO2-eq	0.007679042	0.000243815	6.94E-07	0.005839832	0.001564241	3.05E-05
GWP100 - land transformation	kg CO2-eq	0.004165862	1.16E-04	1.36E-06	0.003192853	8.55E-04	3.13E-07
Total Carbon Footprint		7.637505805	0.210650012	0.000717988	5.857020886	1.568844869	0.000272068
Percentage		100%	2.76%	0.01%	76.69%	20.54%	0.00%

References

(1) Şenel, M. C.; Gürbüz, M. Synergistic Effect of Graphene/Boron Nitride Binary Nanoparticles on Aluminum Hybrid Composite Properties. *Adv. Compos. Hybrid Mater.* **2021**, *4* (4), 1248–1260. https://doi.org/10.1007/s42114-021-00209-0.

(2) Liu, X.; Chen, S.; Zhang, Y.; Liu, M.; Emori, W.; Shao, Y. Preparation of Graphene Oxide–Boron Nitride Hybrid to Reinforce the Corrosion Protection Coating. *Corros. Rev.* **2021**, *39* (2), 123–136. https://doi.org/10.1515/corrrev-2020-0051.

(3) Li, Y.; Lin, H.; Mehra, N. Identification of Thermal Barrier Areas in Graphene Oxide/Boron Nitride Membranes by Scanning Thermal Microscopy: Thermal Conductivity Improvement through Membrane Assembling. *ACS Appl. Nano Mater.* **2021**, *4* (4), 4189–4198. https://doi.org/10.1021/acsanm.1c00528.

(4) Lee, S.; Kim, J. Incorporating MXene into Boron Nitride/Poly(Vinyl Alcohol) Composite Films to Enhance Thermal and Mechanical Properties. *Polymers* **2021**, *13* (3), 379.

https://doi.org/10.3390/polym13030379.

(5) Jerome, R.; Sundramoorthy, A. K. Preparation of Hexagonal Boron Nitride Doped Graphene Film Modified Sensor for Selective Electrochemical Detection of Nicotine in Tobacco Sample. *Anal. Chim. Acta* **2020**, *1132*, 110–120. https://doi.org/10.1016/j.aca.2020.07.060.

(6) Liu, Z.-J.; Yin, C.-G.; Cecen, V.; Fan, J.-C.; Shi, P.-H.; Xu, Q.-J.; Min, Y.-L. Polybenzimidazole Thermal Management Composites Containing Functionalized Boron Nitride Nanosheets and 2D Transition Metal Carbide MXenes. *Polymer* **2019**, *179*, 121613. https://doi.org/10.1016/j.polymer.2019.121613.

(7) Liang, W.; Ge, X.; Ge, J.; Li, T.; Zhao, T.; Chen, X.; Zhang, M.; Ji, J.; Pang, X.; Liu, R. Three-Dimensional Heterostructured Reduced Graphene Oxide-Hexagonal Boron Nitride-Stacking Material for Silicone Thermal Grease with Enhanced Thermally Conductive Properties. *Nanomaterials* **2019**, *9* (7), 938. https://doi.org/10.3390/nano9070938.

(8) Kumar Rastogi, P.; Rani Sahoo, K.; Thakur, P.; Sharma, R.; Bawari, S.; Podila, R.; N. Narayanan, T. Graphene–hBN Non-van Der Waals Vertical Heterostructures for Four- Electron Oxygen Reduction Reaction. *Phys. Chem. Chem. Phys.* **2019**, *21* (7), 3942–3953. https://doi.org/10.1039/C8CP06155F.

(9) Yang, W.; Wang, N.-N.; Ping, P.; Yuen, A. C.-Y.; Li, A.; Zhu, S.-E.; Wang, L.-L.; Wu, J.; Chen, T. B.-Y.; Si, J.-Y.; Rao, B.-D.; Lu, H.-D.; Chan, Q. N.; Yeoh, G.-H. Novel 3D Network Architectured Hybrid Aerogel Comprising Epoxy, Graphene, and Hydroxylated Boron Nitride Nanosheets. *ACS Appl. Mater. Interfaces* **2018**, *10* (46), 40032–40043. https://doi.org/10.1021/acsami.8b15301.

(10) Zhang, J.; Lei, W.; Liu, D.; Wang, X. Synergistic Influence from the Hybridization of Boron Nitride and Graphene Oxide Nanosheets on the Thermal Conductivity and Mechanical Properties of Polymer Nanocomposites. *Compos. Sci. Technol.* **2017**, *151*, 252–257. https://doi.org/10.1016/j.compscitech.2017.08.033.

(11) Singh, A. K.; Panda, B. P.; Mohanty, S.; Nayak, S. K.; Gupta, M. K. Synergistic Effect of Hybrid Graphene and Boron Nitride on the Cure Kinetics and Thermal Conductivity of Epoxy Adhesives. *Polym. Adv. Technol.* **2017**, *28* (12), 1851–1864. https://doi.org/10.1002/pat.4072.

(12) Cui, X.; Ding, P.; Zhuang, N.; Shi, L.; Song, N.; Tang, S. Thermal Conductive and Mechanical Properties of Polymeric Composites Based on Solution-Exfoliated Boron Nitride and Graphene Nanosheets: A Morphology-Promoted Synergistic Effect. *ACS Appl. Mater. Interfaces* **2015**, *7* (34), 19068–19075. https://doi.org/10.1021/acsami.5b04444.

(13) Long, C.; Xie, X.; Fu, J.; Wang, Q.; Guo, H.; Zeng, W.; Wei, N.; Wang, S.; Xiong, Y. Supercapacitive Brophene-Graphene Aerogel as Elastic-Electrochemical Dielectric Layer for Sensitive Pressure Sensors. *J. Colloid Interface Sci.* **2021**, *601*, 355–364. https://doi.org/10.1016/j.jcis.2021.05.116.

(14) Zhou, T.; Wu, C.; Wang, Y.; Tomsia, A. P.; Li, M.; Saiz, E.; Fang, S.; Baughman, R. H.; Jiang, L.; Cheng, Q. Super-Tough MXene-Functionalized Graphene Sheets. *Nat. Commun.* **2020**, *11* (1), 2077. https://doi.org/10.1038/s41467-020-15991-6.

(15) Ren, J.; Li, Q.; Yan, L.; Jia, L.; Huang, X.; Zhao, L.; Ran, Q.; Fu, M. Enhanced Thermal Conductivity of Epoxy Composites by Introducing Graphene@boron Nitride Nanosheets Hybrid

Nanoparticles. *Mater. Des.* **2020**, *191*, 108663. https://doi.org/10.1016/j.matdes.2020.108663.

(16) Huang, X.; Wu, P. A Small Amount of Delaminated Ti 3 C 2 Flakes to Greatly Enhance the Thermal Conductivity of Boron Nitride Papers by Assembling a Well-Designed Interface. *Mater. Chem. Front.* **2020**, *4* (1), 292–301. https://doi.org/10.1039/C9QM00616H.

(17) Tsai, M.-H.; Tseng, I.-H.; Chiang, J.-C.; Li, J.-J. Flexible Polyimide Films Hybrid with Functionalized Boron Nitride and Graphene Oxide Simultaneously To Improve Thermal Conduction and Dimensional Stability. *ACS Appl. Mater. Interfaces* **2014**, *6* (11), 8639–8645. https://doi.org/10.1021/am501323m.

(18) Li, B.; Wu, N.; Yang, Y.; Pan, F.; Wang, C.; Wang, G.; Xiao, L.; Liu, W.; Liu, J.; Zeng, Z. Graphene Oxide-Assisted Multiple Cross-Linking of MXene for Large-Area, High-Strength, Oxidation-Resistant, and Multifunctional Films. *Adv. Funct. Mater.* **2023**, *33* (11), 2213357. https://doi.org/10.1002/adfm.202213357.

(19) Yin, L.; Gong, K.; Pan, H.; Guo, L.; Zhou, K. Column-to-Beam Architecture Inspires Interface-Engineered MXene Nanosheet/Boron Nitride Nanosheet/Polydopamine Hybrids for Fire Retardants. *ACS Appl. Nano Mater.* **2022**, *5* (9), 13123–13135. https://doi.org/10.1021/acsanm.2c02902.

(20) Sun, Z.; Wang, D.; Lin, L.; Liu, Y.; Yuan, M.; Nan, C.; Li, H.; Sun, G.; Yang, X. Ultrathin Hexagonal Boron Nitride as a van Der Waals' Force Initiator Activated Graphene for Engineering Efficient Non-Metal Electrocatalysts of Li-CO2 Battery. *Nano Res.* **2022**, *15* (2), 1171–1177. https://doi.org/10.1007/s12274-021-3620-8.

(21) Saha, S.; Son, W.; Hoon Kim, N.; Hee Lee, J. Fabrication of Impermeable Dense Architecture Containing Covalently Stitched Graphene Oxide/Boron Nitride Hybrid Nanofiller Reinforced Semi-Interpenetrating Network for Hydrogen Gas Barrier Applications. *J. Mater. Chem. A* **2022**, *10* (8), 4376–4391. https://doi.org/10.1039/D1TA09486F.

(22) Deng, B.; Shi, Y.; Zhang, X.; Ma, W.; Liu, H.; Gong, C. Thermally Conductive and Electrically Insulated Silicone Rubber Composites Incorporated with Boron Nitride−Multilayer Graphene Hybrid Nanofiller. *Nanomaterials* **2022**, *12* (14), 2335. https://doi.org/10.3390/nano12142335.

(23) Wang, S.; Sun, X.; Xu, F.; Yang, M.; Yin, W.; Li, J.; Li, Y. Strong yet Tough Graphene/Graphene Oxide Hybrid Films. *Carbon* **2021**, *179*, 469–476. https://doi.org/10.1016/j.carbon.2021.04.052.

(24) Soong, Y.-C.; Li, J.-W.; Chen, Y.-F.; Chen, J.-X.; Lee Sanchez, W. A.; Tsai, W.-Y.; Chou, T.-Y.; Cheng, C.-C.; Chiu, C.-W. Polymer-Assisted Dispersion of Boron Nitride/Graphene in a Thermoplastic Polyurethane Hybrid for Cooled Smart Clothes. *ACS Omega* **2021**, *6* (43), 28779–28787. https://doi.org/10.1021/acsomega.1c03496.

(25) Deshmukh, A. R.; Chaturvedi, P. K.; Lee, S.-Y.; Park, W.-Y.; Kim, B. S. One-Step Green Production of Biocompatible Functionalized Few-Layer Graphene/Boron Nitride Nanosheet Hybrids Using Tannic Acid-Based Liquid-Phase Exfoliation. *ACS Sustain. Chem. Eng.* **2022**, *10* (29), 9573–9583. https://doi.org/10.1021/acssuschemeng.2c02484.

(26) Occhiuzzi, J.; Politano, G. G.; D'Olimpio, G.; Politano, A. The Quest for Green Solvents for the Sustainable Production of Nanosheets of Two-Dimensional (2D) Materials, a Key Issue in the

Roadmap for the Ecology Transition in the Flatland. *Molecules* **2023**, *28* (3), 1484. https://doi.org/10.3390/molecules28031484.

(27) Paolucci, V.; D'Olimpio, G.; Lozzi, L.; Mio, A. M.; Ottaviano, L.; Nardone, M.; Nicotra, G.; Le-Cornec, P.; Cantalini, C.; Politano, A. Sustainable Liquid-Phase Exfoliation of Layered Materials with Nontoxic Polarclean Solvent. *ACS Sustain. Chem. Eng.* **2020**, *8* (51), 18830–18840. https://doi.org/10.1021/acssuschemeng.0c04191.

(28) D'Olimpio, G.; Occhiuzzi, J.; Lozzi, L.; Ottaviano, L.; Politano, A. Dimethyl 2-Methylglutarate (Iris): A Green Platform for Efficient Liquid-Phase Exfoliation of 2D Materials. *Adv. Sustain. Syst.* **2022**, *6* (11), 2200277. https://doi.org/10.1002/adsu.202200277.