Supporting Information

Integrated Ternary Bioinspired Nanocomposites *via* Synergistic Toughening of Reduced Graphene Oxide and Double-Walled Carbon Nanotubes

Shanshan Gong,[a†] Wei Cui,[a†] Qi Zhang,[a†] Anyuan Cao,[c] Lei Jiang[a] and Qunfeng Cheng[a,b*]

[a]Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment

BeiHang University Beijing 100191, P.R. China

[b]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, P.R. China

[c]Department of Materials Science and Engineering, College of Engineering

Peking University, Beijing 100871, P. R. China

[†]These three authors contributed equally to the work

[*]Correspondence should be addressed to Qunfeng Cheng, E-mail: cheng@buaa.edu.cn

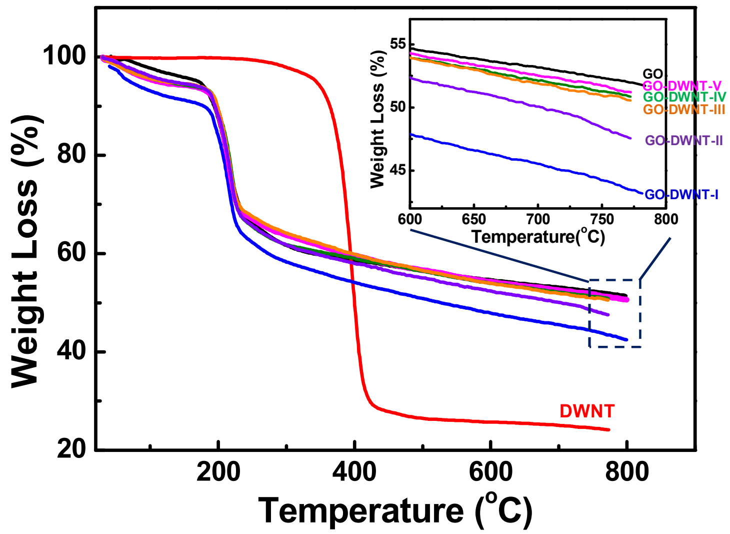

Figure S1. TGA curves of GO, DWNTs, and GO-DWNT hybrid layered materials. The curves were obtained under atmosphere of argon with a temperature rising rate of 10°C·min^{-1}.

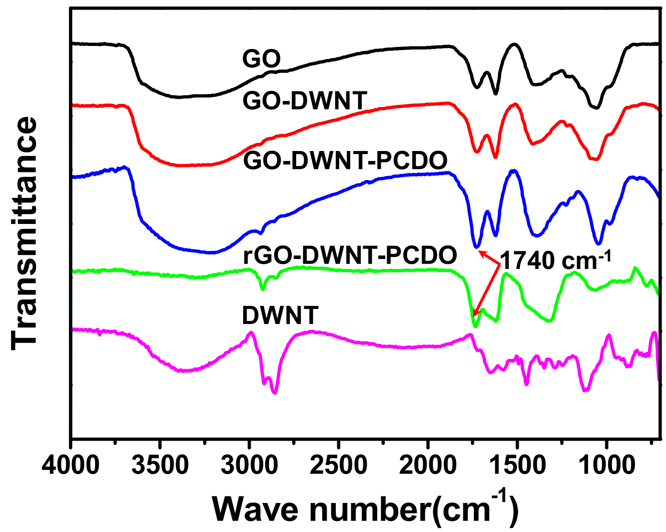

Figure S2. FTIR spectra of pure GO film, DWNT film, GO-DWNT hybrid layered materials, GO-DWNT-PCDO, and rGO-DWNT-PCDO nanocomposites. The peaks at 1740 cm^{-1} of GO-DWNT-PCDO and rGO-DWNT-PCDO are corresponding to the stretching vibration of the C=O moiety in the ester groups proves the successful introduction of PCDO on GO nanosheets. On the other hand, this characteristic peak is kept intact after HI reduction, further confirming the strong esterification between PCDO and GO nanosheets.[1]

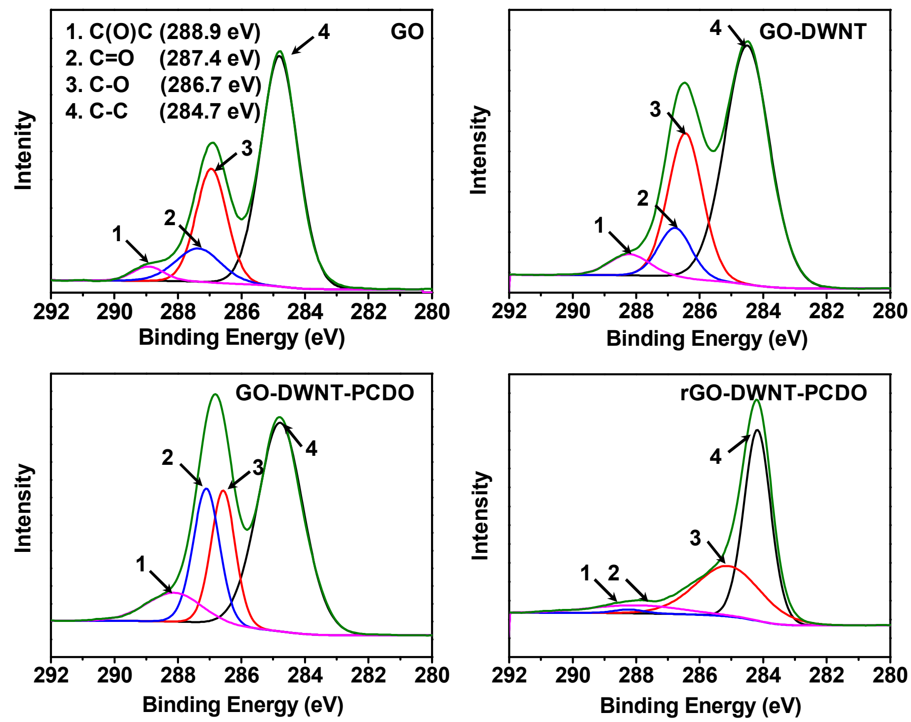

Figure S3. XPS spectra of pure GO film, GO-DWNT hybrid layered materials, GO-DWNT-PCDO, and rGO-DWNT-PCDO nanocomposites. The broad C_{1s} peak of the pure GO film can be fitted into four peaks with the binding energy at 284.7, 286.7,287.4, and 288.9 eV, corresponding to the C-C, C-O, C=O, and C(O)O groups, respectively. After covalent cross-linking with PCDO, the peak intensity of C=O and C-O of the GO-DWNT-PCDO nanocomposites is significantly increased. After HI reduction, the ratio of O_{1s} to C_{1s} is significantly decreased, indicating that the residual groups on the GO nanosheets have been removed.[1]

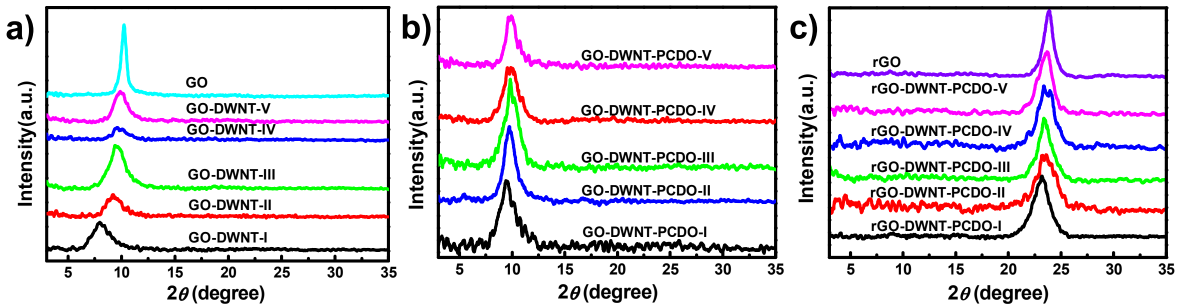

Figure S4. XRD spectrum of a) GO-DWNT hybrid layered materials, b) GO-DWNT-PCDO, and c) rGO-DWNT-PCDO nanocomposites, respectively. The interlayer distance (d-spacing) of pure GO film is 8.9 Å, which is consistent with the previous reports.[17] For GO-DWNT-I hybrid layered materials, the d-spacing gradually increases to 10.90 Å. After esterification with PCDO, the d-spacing of GO-DWNT-PCDO nanocomposites slightly decreases but is still larger than the d-spacing of pure GO film. This is because the covalent cross-linkings between GO nanosheets and PCDO molecules further densify GO-DWNT hybrid layered materials. After HI reduction, the d-spacing of rGO-DWNT-PCDO ternary nanocomposites is dramatically decreased due to the removal of the residual chemical groups on the GO nanosheets. The d-spacing details of GO-DWNT, GO-DWNT-PCDO, and rGO-DWNT-PCDO nanocomposites are listed in Table S2.

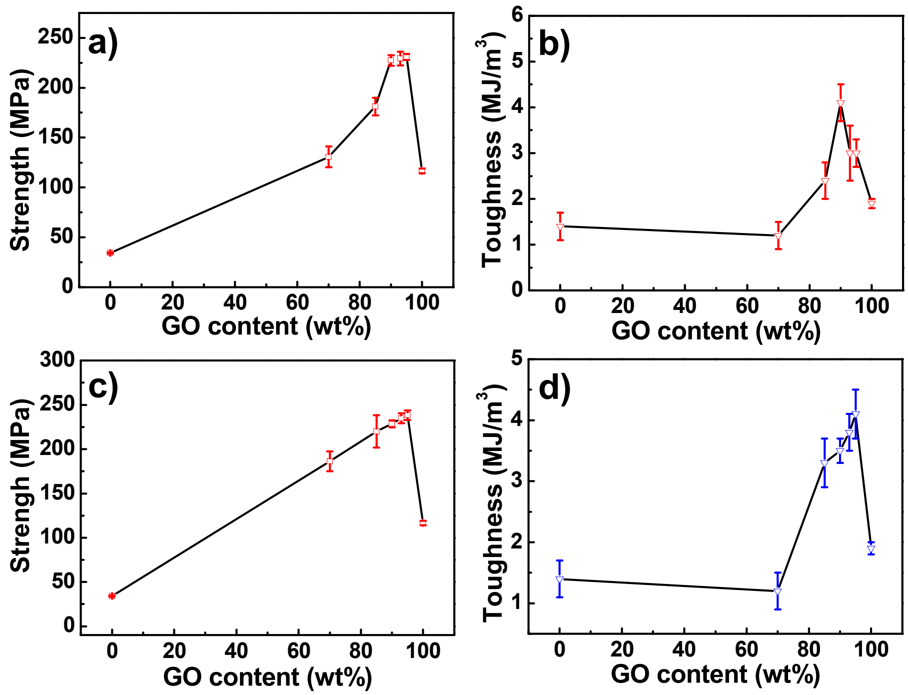

Figure S5. The stress and toughness of the prepared samples increased with GO contents: a) and b) binary GO-DWNT hybrid layered materials; c) and d) GO-DWNT-PCDO nanocomposites.

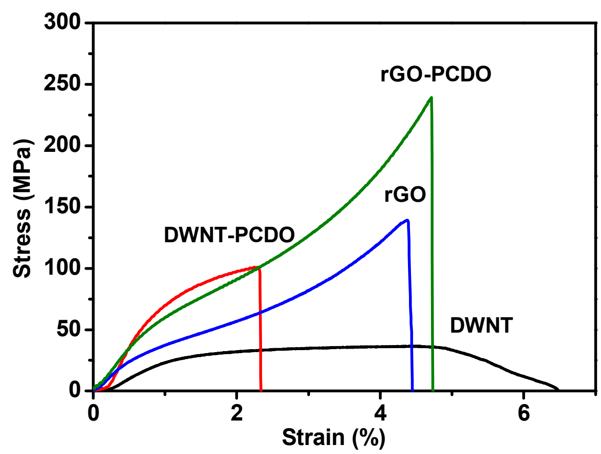

Figure S6. The stress-strain curves of DWNT, DWNT-PCDO, rGO, and rGO-PCDO materials. After PCDO cross-linking, the tensile strength of DWNT and rGO films have been dramatically enhanced.

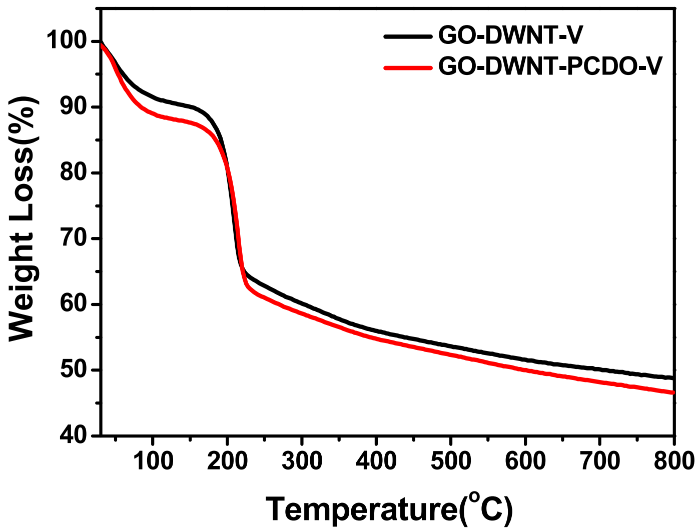

Figure S7. TGA curves of GO-DWNT-V, and GO-DWNT-PCDO-V. The curves were obtained under atmosphere of argon with a temperature rising rate of 10°C·min^{-1}. The PCDO content in the GO-DWNT-PCDO-V is about 2.24 wt%.

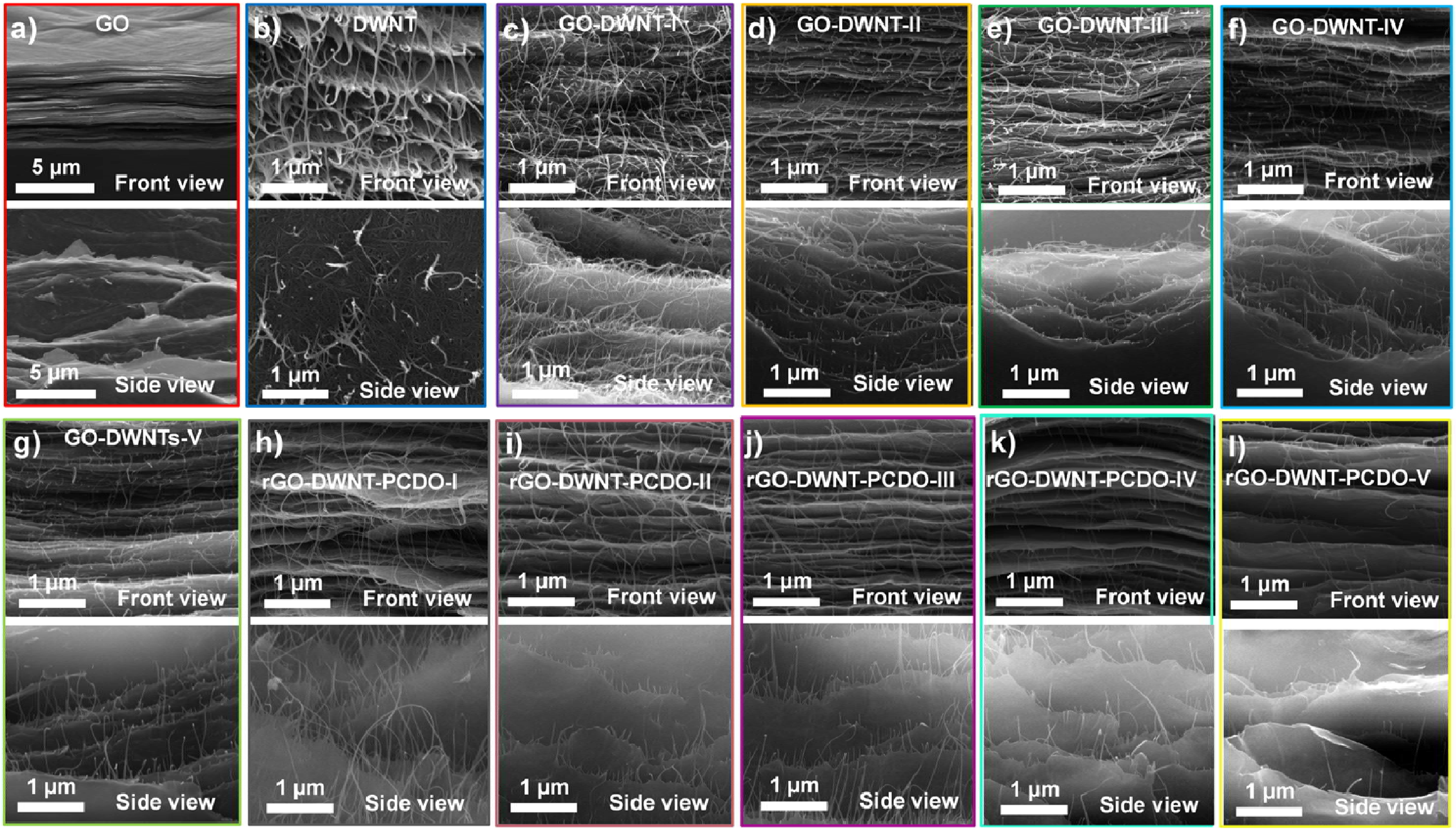

Figure S8. The fracture morphology of GO film, DWNT film, and binary GO-DWNT hybrid layered materials; and rGO-DWNT-PCDO nanocomposites: a) GO film; b) DWNT film; c)–g) binary composites shown in order from GO-DWNT-I to GO-DWNT-V; h)–l) ternary bioinspired nanocomposites shown in order from rGO-DWNT-PCDO-I to rGO-DWNT-PCDO-V.

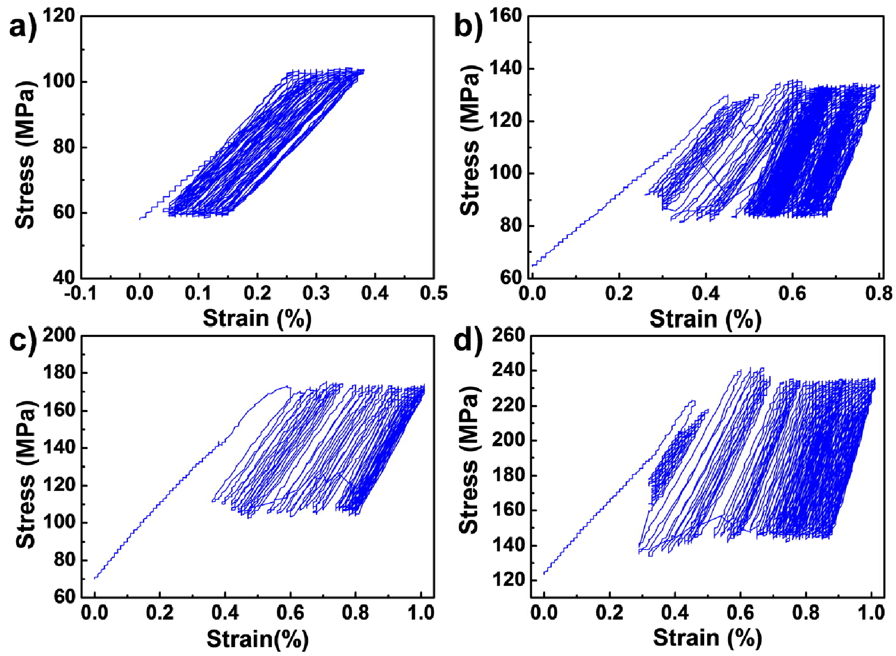

Figure S9. a)–d) The stress-strain fatigue curves of GO film, rGO film, GO-DWNT-V hybrid layered materials, and rGO-DWNT-PCDO-V ternary nanocomposites, demonstrating good fatigue life compared with other ternary poly(vinyl alcohol)–clay–nanofibrillar cellulose nanocomposites.[2]

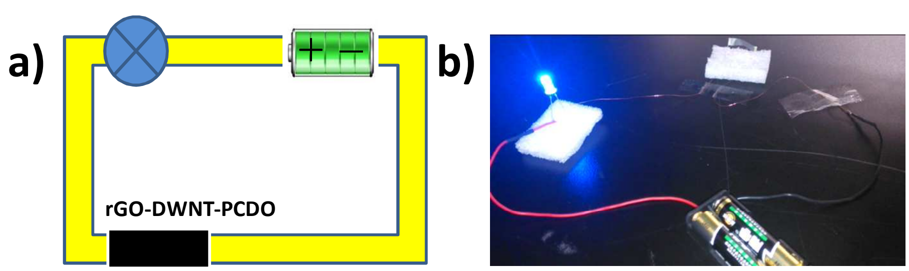

Figure S10. A blue LED light bulb was connected with the power supply, showing that the rGO-DWNT-PCDO ternary nanocomposite cable functioned well for the entire testing period: a) schematics of the circuit; b) the ternary bioinspired nanocomposites as a part of the conductive media connected with the power supply and loaded with a blue LED light bulb.

Table S1. GO and DWNT contents of GO-DWNT hybrid layered materials characterized by TGA.

Sample	GO Content (wt%)		DWNT Content (wt%)	
	Input	by TGA	Input	by TGA
GO-DWNT-I	70%	68.90%	7.50%	7.78%
GO-DWNT-II	85%	84.10%	3.75%	3.98%
GO-DWNT-III	90%	91.70%	2.50%	2.08%
GO-DWNT-IV	93%	92.70%	1.75%	1.83%
GO-DWNT-V	95%	95.60%	1.25%	1.10%

Table S2. The d-spacing of GO-DWNT hybrid layered materials, GO-DWNT-PCDO, and rGO-DWNT-PCDO nanocomposites.

Sample	2θ (°)	*d*-spacing (Å)
GO	10.24	8.65
GO-DWNT-I	8.06	10.90
GO-DWNT-II	9.28	9.51
GO-DWNT-III	9.62	9.17
GO-DWNT-IV	9.68	9.12
GO-DWNT-V	9.92	8.9
GO-DWNT-PCDO-I	9.52	9.28
GO-DWNT-PCDO-II	9.62	9.17
GO-DWNT-PCDO-III	9.72	9.11
GO-DWNT-PCDO-IV	9.80	9.01
GO-DWNT-PCDO-V	9.98	8.85
rGO-DWNT-PCDO-I	23.22	3.83
rGO-DWNT-PCDO-II	23.42	3.79
rGO-DWNT-PCDO-III	23.44	3.78
rGO-DWNT-PCDO-IV	23.52	3.77
rGO-DWNT-PCDO-V	23.60	3.76
rGO	23.86	3.73

Table S3. Mechanical properties of GO film, rGO film, DWNT film, binary GO-DWNT hybrid layered materials, ternary GO-DWNTs-PCDO nanocomposites; and their calculated synergy percentage.

Sample	Strength (MPa)	Toughness (MJ/m^3)	Synergy percentage (%) of tensile strength
GO	116.5 ± 2.3	1.9 ± 0.1	-
rGO	141.8 ± 10.8	2.8 ± 0.3	-
rGO-PCDO	238.2 ± 8.1	4.0 ± 1.0	-
DWNT	34.1 ± 0.7	1.4 ± 0.3	-
DWNT-PCDO	96.1 ± 4.7	1.6 ± 0.1	-
GO-DWNT-I	130.7 ± 10.4	1.2 ± 0.3	73.6
GO-DWNT-PCDO-I	186.3 ± 11.3	1.2 ± 0.3	147.4
rGO-DWNT-PCDO-I	225.9 ± 17.0	2.7 ± 0.5	156.9
GO-DWNT-II	181.2 ± 8.9	2.4 ± 0.4	140.6
GO-DWNT-PCDO-II	220 ± 18.2	3.3 ± 0.4	192.2
rGO-DWNT-PCDO-II	277.2 ± 21.5	7.0 ± 1.9	215.2
GO-DWNT-III	227.4 ± 5.2	4.1 ± 0.4	202.0
GO-DWNT-PCDO-III	228.6 ± 4.0	3.5 ± 0.2	203.6
rGO-DWNT-PCDO-III	321.4 ± 17.5	8.4 ± 0.7	265.4
GO-DWNT-IV	229.3 ± 7.0	3.0 ± 0.6	204.5
GO-DWNT-PCDO-IV	234.9 ± 5.6	3.8 ± 0.3	212.0
rGO-DWNT-PCDO-IV	353.7 ± 28.3	8.3 ± 0.7	302.2
GO-DWNT-V	230.8 ± 3.1	3.0 ± 0.3	206.5
GO-DWNT-PCDO-V	238.2 ± 5.4	4.1 ± 0.4	216.3

rGO-DWNT-PCDO-V	374.1 ± 22.8	9.2 ± 0.8	325.4

Table S4. The mechanical properties of natural nacre, ternary nanocomposites of rGO-DWNT-PCDO-V , and other GO-based layered materials.

Layered Materials	Stress(MPa)	Toughness(MJ/m^3)	Reference
Nacre	135	1.8	
rGO-PDA	205.0	4.00	[27]
rGO-PCDO	129.6	3.91	[17]
GO-PEI	209.9	0.23	[11]
GO-Borate	185.0	0.14	[10]
GO-GA	101.0	0.30	[26]
rGO-PVA	188.9	2.52	[23]
rGO-SL	300.0	2.80	[24]
GO-PMMA	148.3	2.35	[22]
GO-Ca^{2+}	125.8	0.31	[25]
GO-Mg^{2+}	80.6	0.13	[25]
rGO-PAPB	382.0	7.50	[9]
rGO-DWNT-PCDO-V	374.1	9.20	This work

Table S5. The electrical properties of rGO film, DWNT film, and rGO-DWNT-PCDO nanocomposites.

Sample	Electrical conductivity (S/cm)
rGO	228.3 ± 11.1
DWNT	149.4 ± 15.8
rGO-DWNT-PCDO-I	274.3 ± 6.9
rGO-DWNT-PCDO-II	295.0 ± 3.5
rGO-DWNT-PCDO-III	316.1 ± 6.3
rGO-DWNT-PCDO-IV	336.2 ± 5.1
rGO-DWNT-PCDO-V	394.0 ± 6.8

REFERENCES

1. Cheng, Q.; Wu, M.; Li, M.; Jiang, L.; Tang, Z. Ultratough Artificial Nacre Based on Conjugated Cross-linked Graphene Oxide. *Angew. Chem., Int. Ed.* **2013,** *52*, 3750-3755.

2. Wang, J.; Cheng, Q.; Lin, L.; Jiang, L., Synergistic Toughening of Bioinspired Poly(vinyl alcohol)–Clay–Nanofibrillar Cellulose Artificial Nacre. *ACS Nano* **2014,** *8*, 2739-2745.