Supporting Information

Feeding Single-Walled Carbon Nanotubes or Graphene to Silkworms for Reinforced Silk Fibers

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This supporting file includes:

- Supporting Tables: Table S1 to S6
- Supporting Figures: Figure S1 to S3
- Supporting Discussions related to Table S1-S6 and Figure S1, S3

The sequence is the same as they are mentioned in the main text.

Table S1. Average Diameter of Degummed Silk Fibers

sample	average diameter [μm]
control-S	8.8 ± 0.5
SWNT1-S	8.7 ± 0.6
SWNT2-S	8.7 ± 0.5
GR1-S	8.8 ± 0.6
GR2-S	8.8 ± 0.5

Table S1 shows the average diameters of different silk fibers. The diameters of more than 30 single degummed fibers for each sample were measured, showing that feeding of SWNTs and GR does not have apparent influence on the diameter of fibers.

We have raised 20 silkworms for each group sample. And, for each cocoon obtained from one silkworm, 5 degummed fibers were randomly selected and measured. Therefore, the average mechanical properties were measured from 100 fibers for each group. We obtained the average properties of each cocoon and then obtained the average mechanical properties of each kind of sample according the average data of 20 cocoons. The detailed data are shown in Table S2-S6.

Table S2. Mechanical Properties of Degummed Control-S Fibers

cocoon n.	fracture strength [GPa]	elongation at break [%]	toughness modulus [MPa]
1	0.28	10.88	23.8
2	0.29	8.46	23.2
3	0.35	10.35	30.1
4	0.43	10.67	29.6
5	0.45	8.66	20.7
6	0.42	11.76	30.6
7	0.31	10.89	22.8
8	0.23	10.10	23.1
9	0.42	11.01	24.4
10	0.37	7.69	18.2
11	0.41	11.24	24.1
12	0.43	13.05	28.3
13	0.31	7.12	16.9
14	0.46	8.06	21.1
15	0.45	7.09	17.6
16	0.32	12.04	23.1
17	0.33	7.31	20.3
18	0.29	4.67	15.7
19	0.28	5.65	20.8
20	0.25	11.02	19.8
average	0.36	9.39	22.7
standard deviation	0.07	2.29	4.3

Table S3. Mechanical Properties of Degummed SWNT1-S Fibers

cocoon n.	fracture strength [GPa]	elongation at break [%]	toughness modulus [MPa]
1	0.40	12.11	42.28
2	0.74	14.36	56.68
3	0.69	10.19	48.25
4	0.51	15.52	49.27
5	0.46	11.03	39.51
6	0.65	15.39	59.72
7	0.76	19.72	57.31
8	0.46	12.78	42.11
9	0.41	9.39	39.67
10	0.80	13.59	59.41
11	0.57	14.56	57.22
12	0.58	10.59	42.46
13	0.45	12.27	43.25
14	0.79	15.67	58.41
15	0.69	9.08	39.09
16	0.76	12.89	56.21
17	0.45	11.08	43.66
18	0.49	12.18	40.32
19	0.51	8.28	41.26
20	0.61	11.02	48.67
average	0.59	12.59	48.24
standard deviation	0.14	2.75	7.80

Table S4. Mechanical Properties of Degummed SWNT2-S Fibers

cocoon n.	fracture strength [GPa]	elongation at break [%]	toughness modulus [MPa]
1	0.33	7.31	13.45
2	0.22	3.60	8.22
3	0.30	8.44	12.69
4	0.34	4.42	10.27
5	0.29	6.53	11.27
6	0.21	3.46	7.49
7	0.26	6.20	9.59
8	0.31	7.64	13.67
9	0.25	6.38	10.68
10	0.28	6.03	11.73
11	0.27	5.77	10.34
12	0.31	4.42	10.11
13	0.24	4.51	9.21
14	0.26	4.87	9.55
15	0.34	8.45	11.83
16	0.32	7.59	10.59
17	0.36	6.41	10.29
18	0.29	6.19	9.89
19	0.22	3.26	7.68
20	0.25	3.69	8.03
average	0.28	5.76	10.33
standard deviation	0.04	1.65	0.65

Table S5. Mechanical Properties of Degummed GR1-S Fibers

cocoon n.	fracture strength [GPa]	elongation at break [%]	toughness modulus [MPa]
1	0.55	11.40	39.65
2	0.45	12.30	30.58
3	0.41	13.95	32.59
4	0.64	11.60	41.21
5	0.61	6.23	36.41
6	0.57	13.34	45.11
7	0.38	7.39	31.69
8	0.51	7.33	35.63
9	0.48	8.14	38.46
10	0.68	12.34	49.21
11	0.74	11.01	46.47
12	0.68	8.72	36.01
13	0.67	8.46	35.06
14	0.41	8.59	32.68
15	0.62	12.41	38.57
16	0.56	14.38	45.21
17	0.63	8.90	35.68
18	0.51	7.79	32.16
19	0.58	14.21	42.36
20	0.69	8.11	35.99
average	0.57	10.33	38.04
standard deviation	0.11	2.62	5.38

Table S6. Mechanical Properties of Degummed GR2-S Fibers

cocoon n.	fracture strength [GPa]	elongation at break [%]	toughness modulus [MPa]
1	0.51	7.21	7.02
2	0.26	2.95	5.21
3	0.24	4.56	6.29
4	0.39	3.53	7.18
5	0.23	5.30	6.97
6	0.12	2.98	6.04
7	0.28	3.01	5.31
8	0.20	3.38	7.25
9	0.28	2.76	5.28
10	0.26	3.28	6.62
11	0.24	2.98	5.27
12	0.39	3.27	7.42
13	0.16	5.42	6.45
14	0.13	5.71	7.01
15	0.37	3.19	5.92
16	0.29	6.83	7.49
17	0.41	3.92	7.29
18	0.45	3.19	6.97
19	0.24	3.05	6.11
20	0.21	2.46	4.98
average	0.28	3.95	6.40
standard deviation	0.11	1.39	0.84

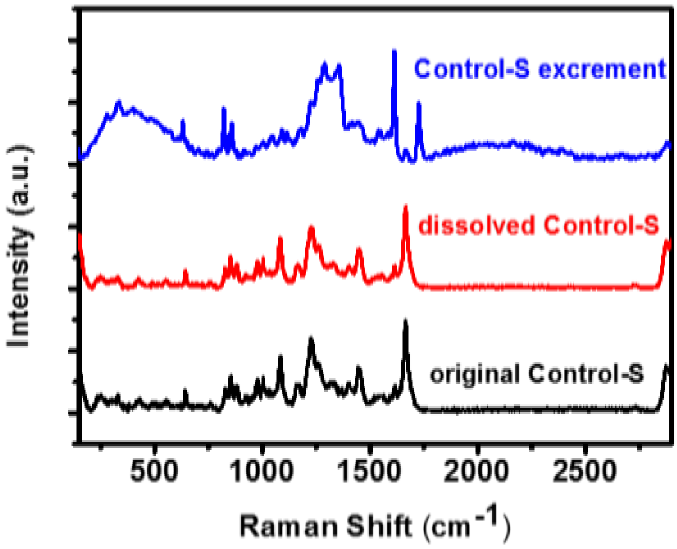

Figure S1. Raman spectra of the as-obtained Control-S silk fiber, films prepared from dissolved Control-S solution and the excrements of the control group silkworms.

The Raman spectra of the as-obtained silk fibers and the film prepared from dissolved Control-S silk fibers show bands at 1084, 1227 and 1665 cm^{-1}, which can be attributed to the typical β-sheet conformation in silk fibroin. No D-band or G-band of nanocarbons can be found in either the Control-S or the excrements of controls group silkworms. These results indicate the exclusion of possible contamination of the cocoons, further confirming that SWNTs or GR are incorporated into as-spun SWNT1-S, SWNT2-S, GR1-S, and GR2-S through the natural feeding process.

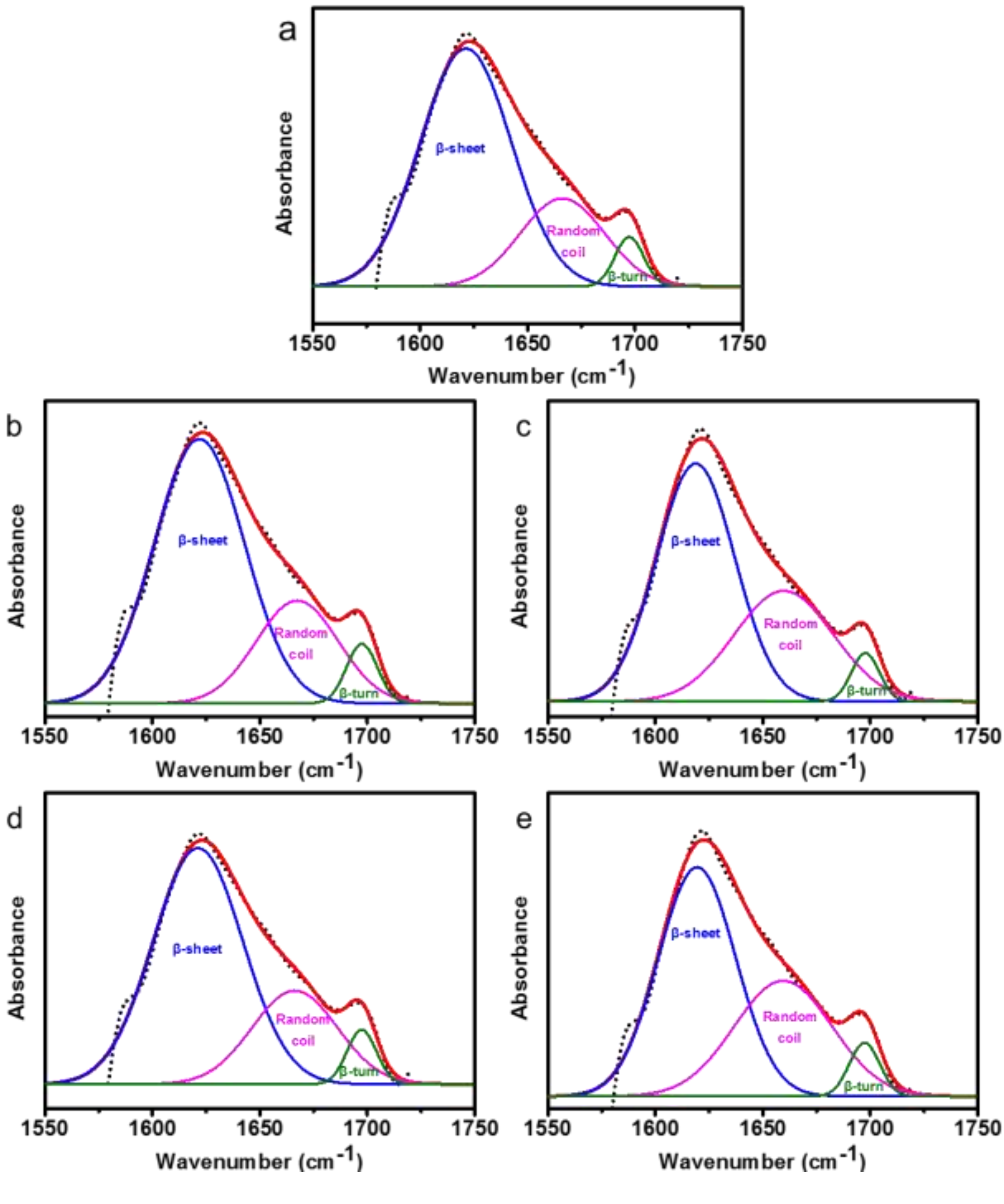

Figure S2. The deconvolution of FTIR spectra in amide I band of (a) control-S, (b) SWNT1-S, (c) SWNT2-S, (d) GR1-S, and (e) GR2-S. The plots show the original spectra (black dotted line), the fitting line (red solid line), and their deconvoluted traces (three smooth Gaussian curves).

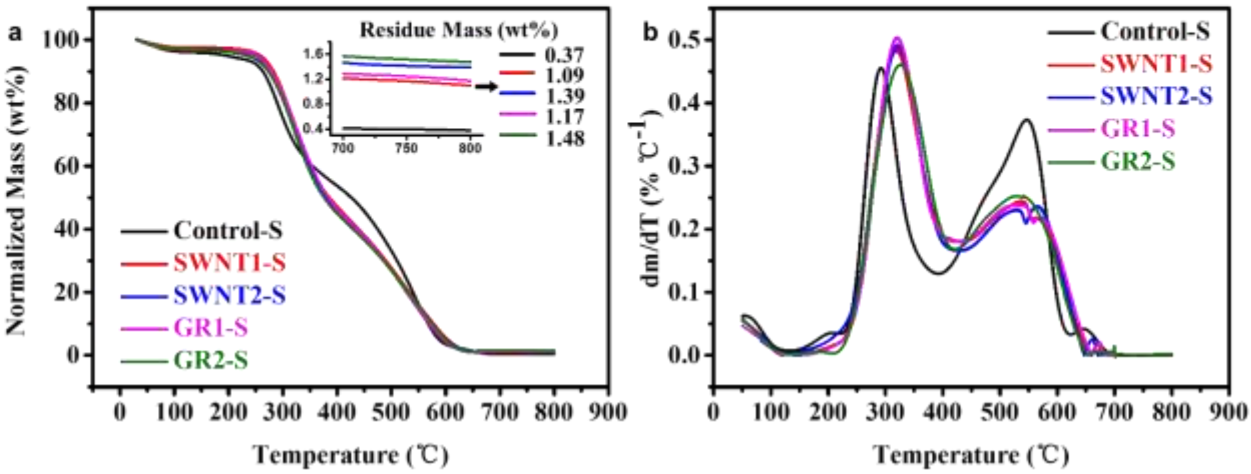

Figure S3. (a) TGA curves and (b) First derivative plots of the TGA of control-S, SWNT1-S, SWNT2-S, GR1-S, and GR2-S fibers. The inset in (a) is a zoom-in of the curves between 700 to 800 ºC and the residual mass are listed.

The thermal degradation of silk fibers was measured by thermogravimetric analysis (TGA) from 30 to 800 ºC in N_2 (99.99%) at a scanning speed of 5 ºC /min. Figure S3 shows the results. The residual water in the silk was removed as the temperature increasing from 30 to 150 ºC and the silk fibers exhibited similar thermal degradation curves with rapid mass decrement from 250 ºC. As shown in Figure S3b, the rapid degradation temperature of control-S fibers is around 290 ºC, in comparison with 320 ºC of SWNT/GR modified silk fibers, indicating the higher thermal stability of SWNT/GR-embedded silk fibers. Besides, as shown in the inset of Figure S3a, the residue mass at 800 ºC are 1.09%, 1.39%, 1.17%, and 1.48% for SWNT1-S, SWNT2-S, GR1-S, and GR2-S, respectively, which are obviously higher than that of control-S (~0.4%), which could also be attributed to the presence of SWNTs or graphene in the silk fibroin matrix. However, since silk fibroin will be transformed into graphitic carbon which has similar structures with SWNTs or graphene, we could not know the exact concentration of SWNTs or graphene in the fibers according to the above TGA results. Besides, it should be noted that higher residue mass is expected if purer N_2 (or

N2 with H_2) is used during this TGA process since the trace O_2 in the gas will result in oxidation of the carbon in the silk fibers and accelerated mass lose.