Supplementary Information.

Diazonium coupling reaction

The tyrosine residues of silk were modified with a diazonium salt. Under these conditions, all the tyrosine residues, representing 5.26% of amino-acid residues in the silk proteins, should be modified.10 mL of 10% w/v silk solution prepared in borate buffer (100 mM sodium tetraborate decahydrate, 150 mM NaCl, pH 9) was then combined with 3.968 mL of the stock diazonium salt solution. The coupling reaction was left for 30 min and excess diazonium salts removed by passing the reaction mixture through a PD10 desalting column (GE healthcare, Sephadex G25M, Buckinghamshire, UK) previously equilibrated with distilled water. The progress of the diazonium coupling reaction was checked by UV-Vis spectrometry with a UNICAM UV-Vis spectrophotometer scanning between 190 and 600 nm. When complete, the diazo-coupled silk solution was lyophilised.

EDC/NHS activation procedure

The lyophilised diazo-coupled silk was first dissolved in LiBr (100 mg silk/10 mL LiBr, 9M). This solution was desalted on a PD10 desalting column pre-equilibrated with PBS buffer (pH 4.5) to ensure that coupling occurred at the N-terminus of the peptide thus enabling a better activity of activated species. The diazo-coupled silk dissolved in PBS buffer was then activated with 0.5 mg/mL EDC and 0.7 mg/mL NHS and mixed for 15 min at room temperature. The activated silk protein was purified on a PD10 desalting column pre-equilibrated with PBS to remove unreacted coupling agents. One mg peptide was added per mL activated silk protein solution. The silk-peptide solution was mixed at room temperature for two hours, purified on a PD10 desalting column pre-equilibrated with distilled water, and lyophilised overnight (Virtis apparatus, Biopharma process systems, Winchester, Hampshire, UK; T_c = -63.3°C).

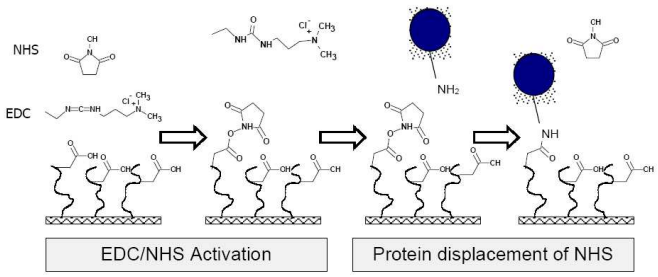

Figure S1. EDC/NHS mediated amine coupling. Peptides are represented in blue (http://www.thermo.com).

Genetically Produced chimeras.

The nucleotide strands were annealed in the presence of T4 ligase buffer by heating to 95^{o}C and cooling to 20^{o}C at a rate of 0.1^{o}C/s. For the insertion of the Pep 1 sequence into the pET30-silk (6mer or 15mer) vector, the plasmid was first digested with the restriction enzyme *SpeI* (New England Biolabs, Beverly, MA, USA) and then dephosphorylated with Calf Intestinal Phosphatase (New England Biolabs, Beverly MA, USA). After gel extraction of the digested vector using the Qiaquick gel extraction kit (Qiagen, Valencia, CA), the Pep1 insert sequence was ligated into the digested pET30-silk vector using T4 DNA ligase (New England Biolabs, Beverly, MA, USA). The insertion of the Pep1 DNA sequence into the pET30-silk vector was verified by sequencing using the T7 and T7 term primers (Tufts Core Facility).

Plasmid vector containing Pep1 and silk-coding DNA sequences was transformed into RY *E. coli* cells.[26] using heat shock transformation. The transformed *E. coli* cells were plated in sterile conditions on LB agar containing kanamycin (50 μg/mL; Sigma-Aldrich, St Louis, MO, USA) as selection marker and incubated overnight at 37°C.

One single transformed colony was incubated in a medium containing 5 mL LB media and kanamycin (50 μg/mL) and put at 37°C for 6-8 hours. This log phase culture (10 μL) was then used to inoculate 1L sterile Hyper Broth medium (Athena Enzyme Systems, Baltimore,

MD) with kanamycin (50 μg/mL). The culture was incubated overnight at 30°C (Incubator shaker series 25, New Brunswick Scientific, Edison, New Jersey, USA). The next day, the temperature was increased to 37°C and the bacteria growth was followed by spectrophotometry (λ = 600 nm). Once an appropriate absorbance value reached (Abs. ≈ 1), the culture was induced by the addition of IPTG (0.5 mM, Sigma-Aldrich, St Louis, MO, USA) and incubated for 4 hours. The culture was then centrifuged (7600 rcf, 15 min, 10°C; Dupont Instrument, Sorvall RC-5B refrigerated superspeed centrifuge) and bacterial cells collected were lysed. 1L lysis buffer B was prepared with 100 mM NaH_2PO_4 ($NaH_2PO_4.H_2O$; MW 137.99 $g.mol^{-1}$), 10 mM TrisBase (MW 121.1 $g.mol^{-1}$) and 8 M urea (60.06 $g.mol^{-1}$). Buffer B was filtered through a 0.22 μm sterile filter and adjusted to pH 8 using NaOH (3M) before use. Elution buffer C and purification buffers, D and E, were obtained after pH adjustment of lysis buffer B to 6.3, 5.9 and 4.5 respectively. 4 mL of buffer B was added per g of *E. coli* cell pellet and mixed for 1 hour. A second centrifugation step was performed (7600 rcf, 20 min) to pellet the insoluble cellular debris. 1 mL of Ni-NTA resin (Qiagen, Valencia, CA) was added per 4 mL supernatant from the lysed cells and gently stirred overnight. After incubation, fusion protein was purified onto glass columns, eluted with buffer B (pH 8), C (pH 6.3), D (pH 5.9) and finally buffer E (pH 4.5). All eluates were collected for further protein purification study using SDS-PAGE (Bis-Tris 1 mm Gels, Invitrogen, Carlsbad, CA). The purified silk-pep1 recombinant protein was dialyzed for two days in acetate buffer (10 mM, pH 4.5) to promote protein refolding, then against deionised water until reaching a conductivity value less than 2 μS/cm and finally freeze-dried.

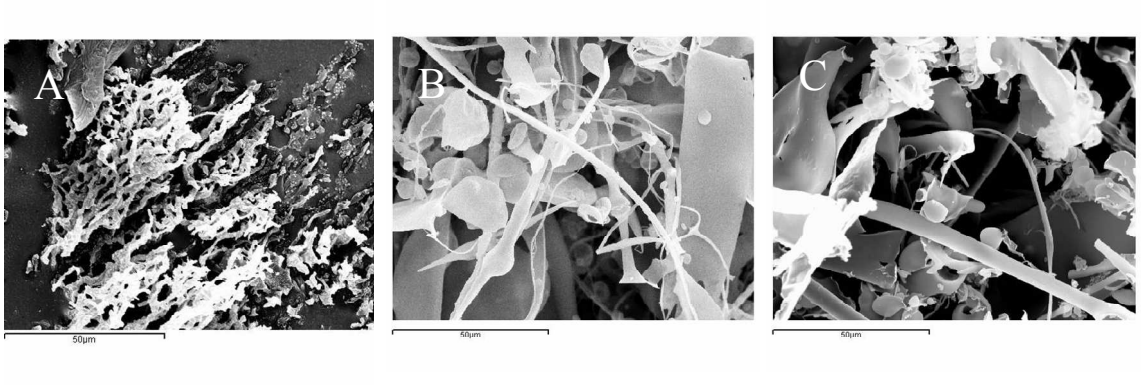

Figure S2. SEM images of non-silicified biomolecules (A) Silk. (B) 6 mers. (C) 15 mers. Scale bars for all proteins 50µm.

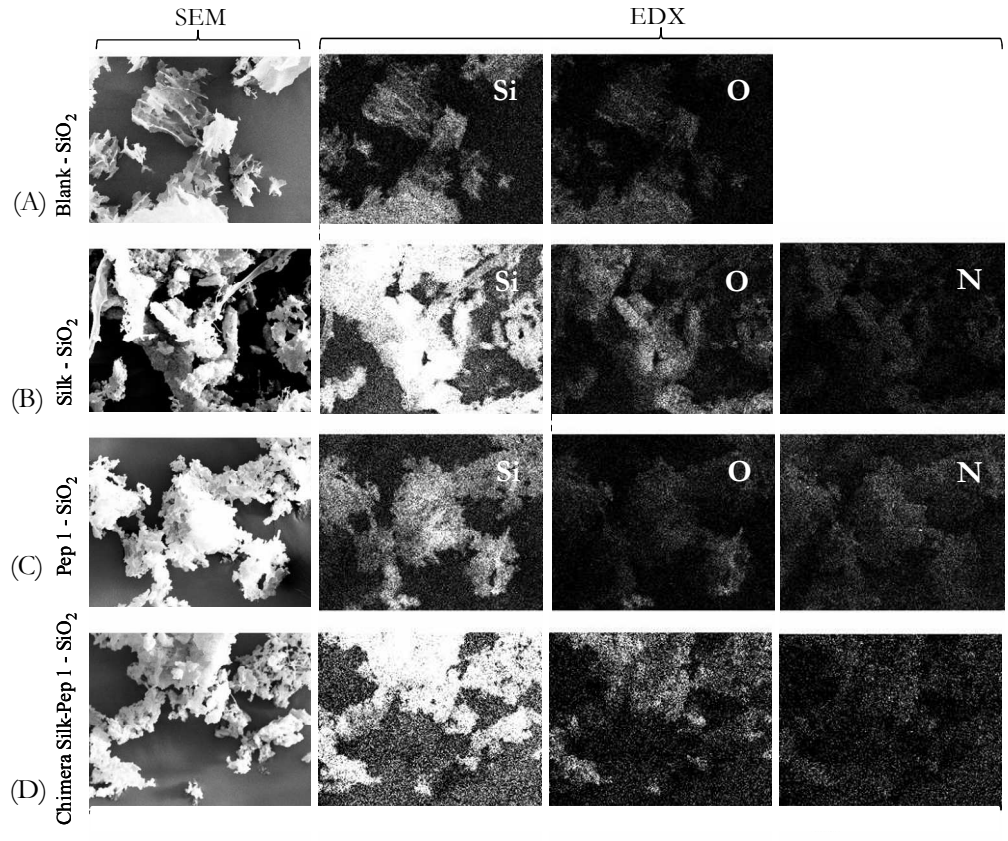

Figure S3. EDX elemental analysis of silicified biomolecules (+ SiO_2, 30 mM in the condensing system). (A) Blank + SiO_2. (B) Silk + SiO_2. (C) Pep1 + SiO_2. (D) Chemical Chimera silk-Pep1 + SiO_2. After 24h silica condensation and direct lyophilisation.

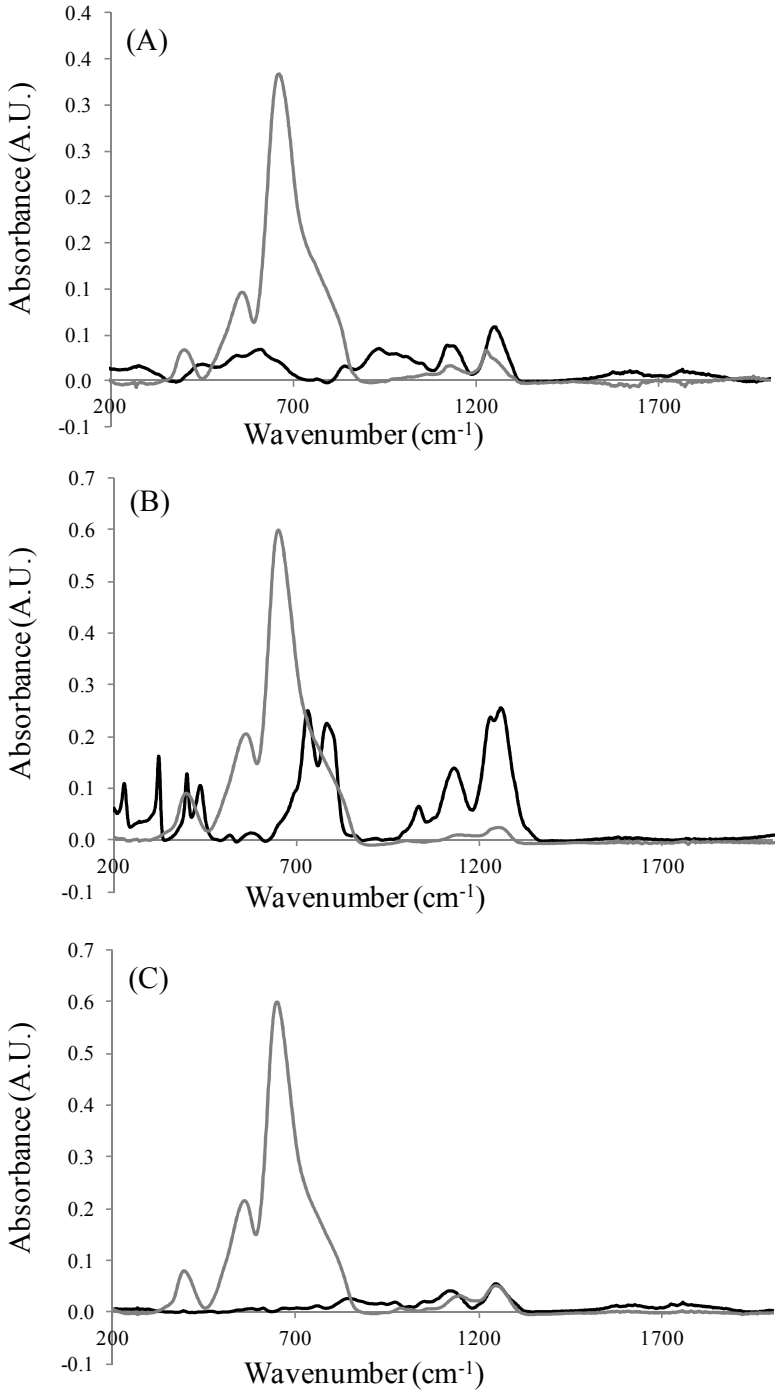

Figure S4. ATR-FTIR spectra for non silicified (black) and silicified biomolecules (grey). (A) Silk, (B) Pep1, (C) Chimera silk-Pep1.

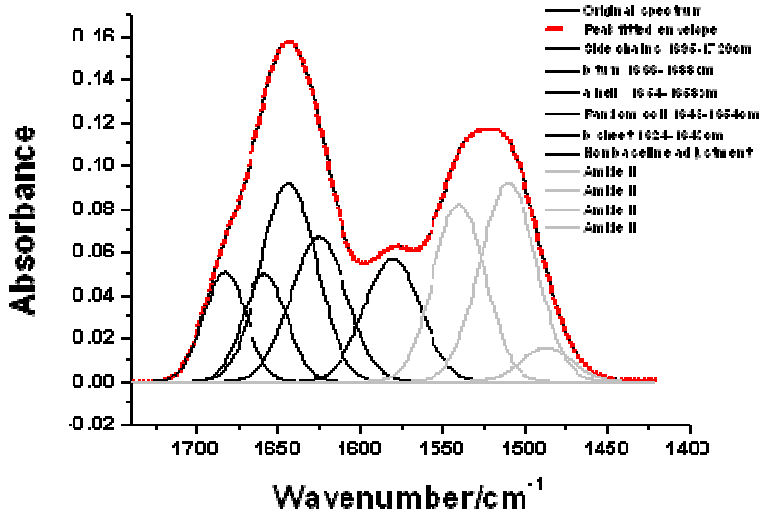

Figure S5) a. Example of amide I band curve fitting of standard α lactalbumin

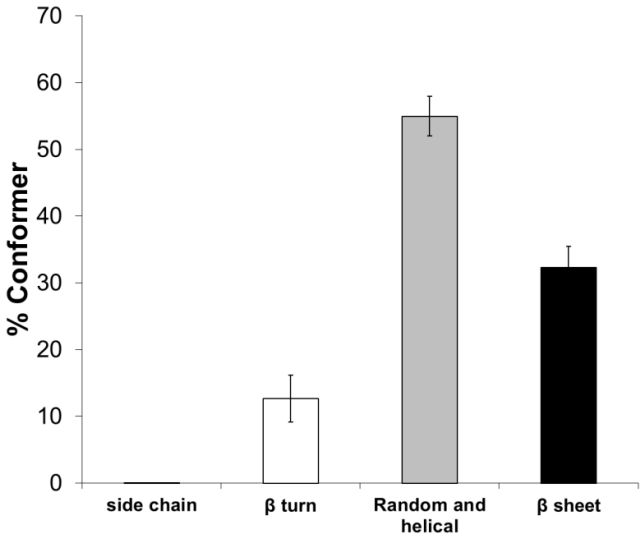

Figure S5)b. Statistical analysis of 5 repeats (sampling, data collection and analysis) of α lactalbumin

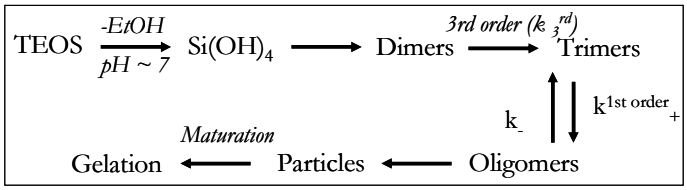

Figure S6 Kinetic constants determination upon silica condensation.

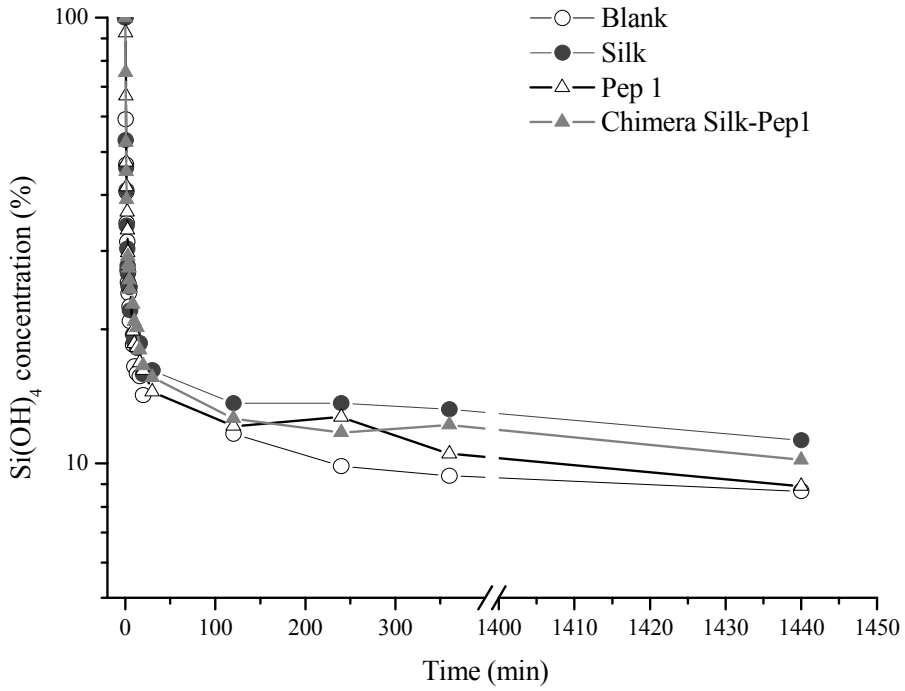

Figure S7. $Si(OH)_4$ concentration (%) upon silica condensation on various biomolecules (silk, peptides, and peptide-silk chimeras).

Table S1. Molecular weight of various trypsin fragments obtained from trypsin autolysis.

Trysin fragment AA sequence	Theoretical MW ($g.mol^{-1}$)	Experimental MW ($g.mol^{-1}$)
VATVSLPR	842.510	842.512
IITHPNFN	955.076	954.400
LGEHNIDVLEGNEQFINAAK	2211.419	2211.110
SGSHFCGGSLINSQWVVSAAHCYKSR	2807.310	2807.300

Table S2. Molecular weight of various Si-peptide fragments (Top) and silk fragments (Bottom) obtained from trypsin proteolysis of Si-peptide-silk chimera.

		Theoretical MW ($g.mol^{-1}$)	Experimental MW ($g.mol^{-1}$)
Peptide R-Pep1	RKSLSRHDHIHHH	1659.832	1659.914
	RKSLSRHDHIHHHHH	1796.974	1796.978
Peptide Pep1	KSLSRHDHIHHH	1503.643	1503.817
1 cleavage site in the Peptide	RK	302.364	n.d.
	KSLSRHDHIHHH	**1503.643**	1507.750
	KSLSRHDHIHHHH	**1640.785**	1640.842
2 cleavage sites in the peptide	KSLSR	589.683	n.d.
	SLSRHDHIHHH	**1375.468**	1375.674
	SLSRHDHIHHHH	**1512.610**	1512.740
3 cleavage sites in the peptide	R	156.189	n.d.
	K	128.175	n.d.
	SLSR	461.508	n.d.
	HDHIHHH	**931.960**	932.420
	HDHIHHHH	**1069.102**	1069.480

n.d.: non detectable

Fibroin	Fragment AA sequence	Theoretical MW ($g.mol^{-1}$)	Experimental MW ($g.mol^{-1}$)
Light Chain-Fibroin[a]	SGNFAGFR	854.912	855.058
	YIAQAASQVHV	1186.329	1186.62
	AWDYVDDTDKSIAILNVQEILK	2549.858	2549.283
Heavy-Chain Fibroin[b]	GYGQGAGSAASSVSSASSR	1686.71	1686.779
	DASGAVIEEQITTKEGYEYAWSSK	2662.752	2663.265
	NCGIPRR	814.959	815.477
	NCGIPRRQLVVK	1382.695	1381.68
	NVRKNCGIPRR	1312.562	1312.619

[a]: Kikuchi et al..[33]

[b]: Ha et al..[31]