

Supporting information

Preparation of hexagonal GeO_2 particles with particle size and crystallinity controlled by peptides, silk and silk-peptide chimeras

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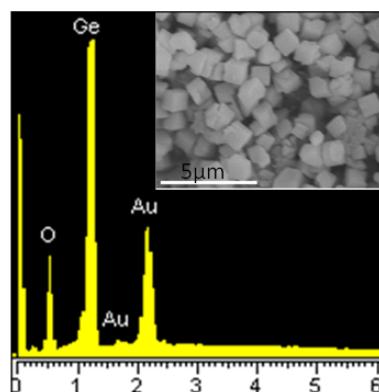


Figure S1. EDX composition of GeO_2 -silk material synthesised at pH6 (SEM inserted image). The EDX results confirmed that the precipitated material contained germanium and oxygen. The peaks associated with Au resulted from the gold coating that was used for imaging. As the characteristic $K\alpha$ and $L\alpha$ X-rays for Ge ($K\alpha$ 9.874, $L\alpha$ 1.188) and Au ($L\alpha$ 9.712, M 2.120) are very similar, the study focused only in the range from 0 to 2.120 KeV to identify the two elements.

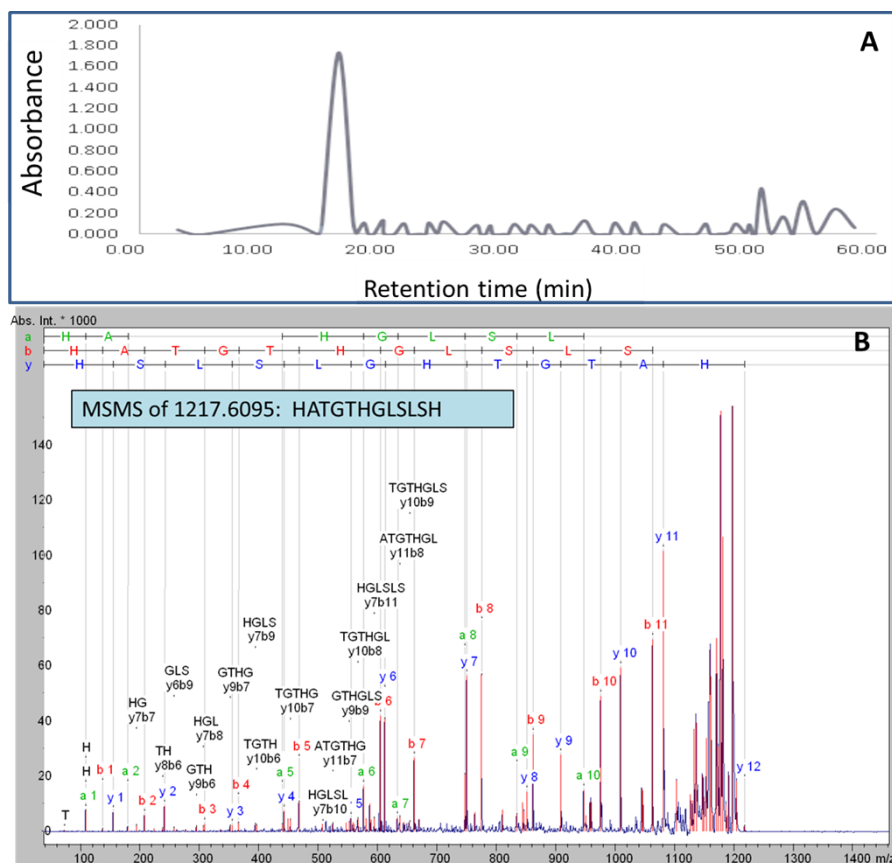


Figure S2. Peptide Ge28 (HATGTHGLSLSH – MW: 1216.59 g/mol (ExPASy)) characterisation: A) RP-HPLC chromatogram (> 85% purity) and B) MS-MS: the peak at 1217.61 g/mol was attributed to MH^+ ion.

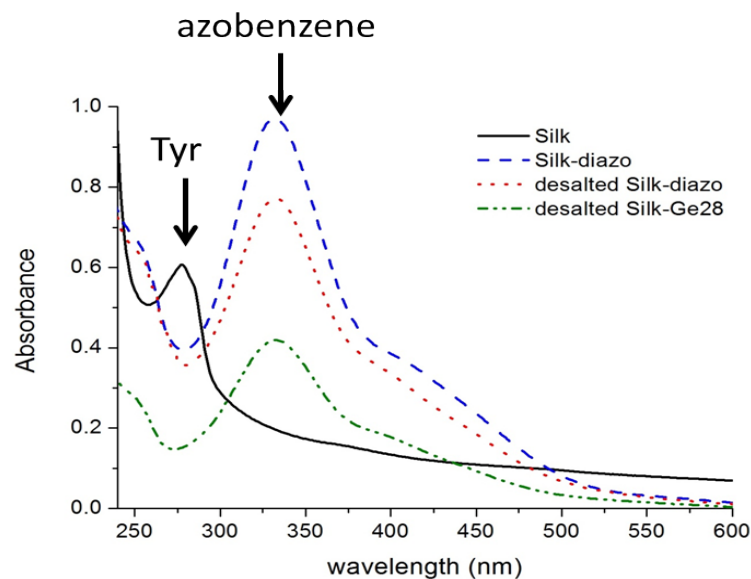


Figure S3. UV-Vis absorption spectra of silk solutions before and after the diazo coupling and after the EDC/NHS peptide binding reaction demonstrating the efficiency of the coupling process.¹ Native silk shows an absorbance band at 280 nm due to the tyrosine groups. This band decreases upon diazonium salt coupling, while a new band at 325 nm with a shoulder 390 nm from azobenzene was observed in the diazo-coupled silk. After desalting, the band at 325 nm decreased as a result of the elimination of unbound diazonium salt. After coupling the Ge28 peptide to the silk-diazo protein, the 325 nm absorbance peak also decreased, possibly as a result of the changes in the electron delocalisation of the aryl azo group (azobenzene) after incorporation of the electron-donor amine group from the peptide.

1. A. R. Murphy, P. S. John and D. L. Kaplan, *Biomaterials*, 2008, **29**, 2829-2838.

Table S.1. Wavenumber values corresponding to the Ge-O-Ge antysymmetric vibrations for germania synthesis with no additive and in the presence of biomolecules.

	Additive used	Ge-O-Ge vib (cm ⁻¹)
Buffer-pH6	No additive	870, 961
	Ge28	874, 961
	15mer silk	875, 961
	native silk	875, 961
	silk-Ge28 10%	876, 961
	silk-Ge28 50%	876, 961
water	No additive	880, 961
	Ge28	878, 961
	15mer silk	881, 961
	native silk	880, 961
	silk-Ge28 10%	879, 961
	silk-Ge28 50%	878, 961