Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supplementary Information

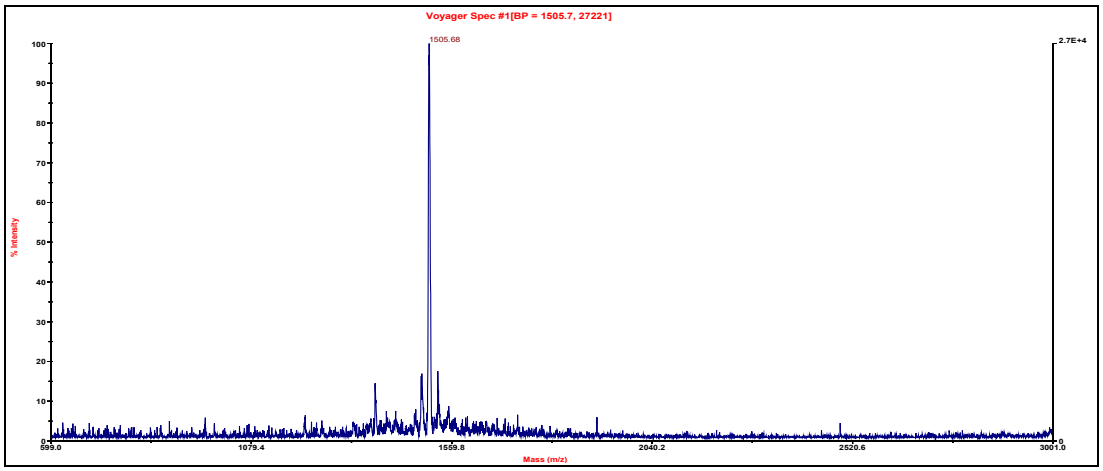
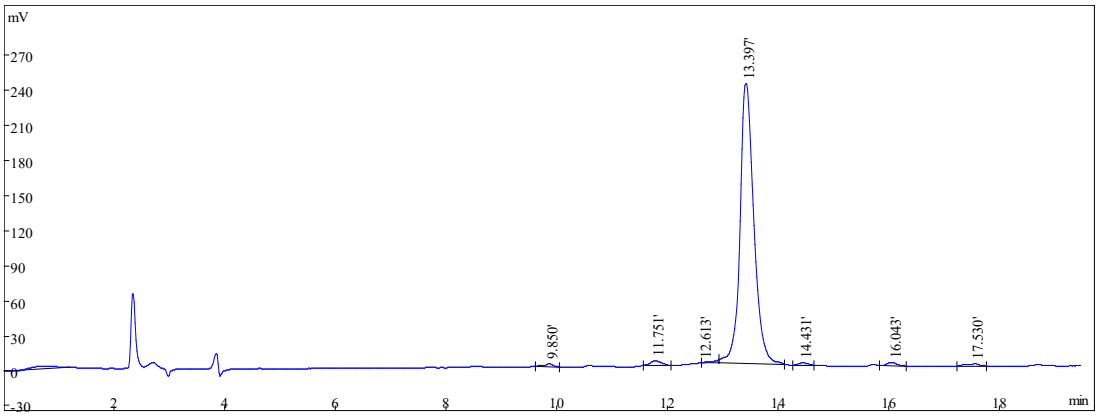


Fig. 1 Mass spectrometry. Oligopeptide molecular weight was 1505.7 Da.



Peak Results

Rank	Time	Conc.	Area	Height
1	14.059	0.1106	10208	1058
2	14.482	96.78	8930526	852180
3	14.958	0.291	26848	2957
4	15.424	1.287	118748	13162
5	16.310	1.302	120182	12635
6	17.199	0.222	20483	2682
Total		100	9226995	884674

Fig. 2 High-Performance Liquid Chromatography. The oligopeptide purity was 95.29%.

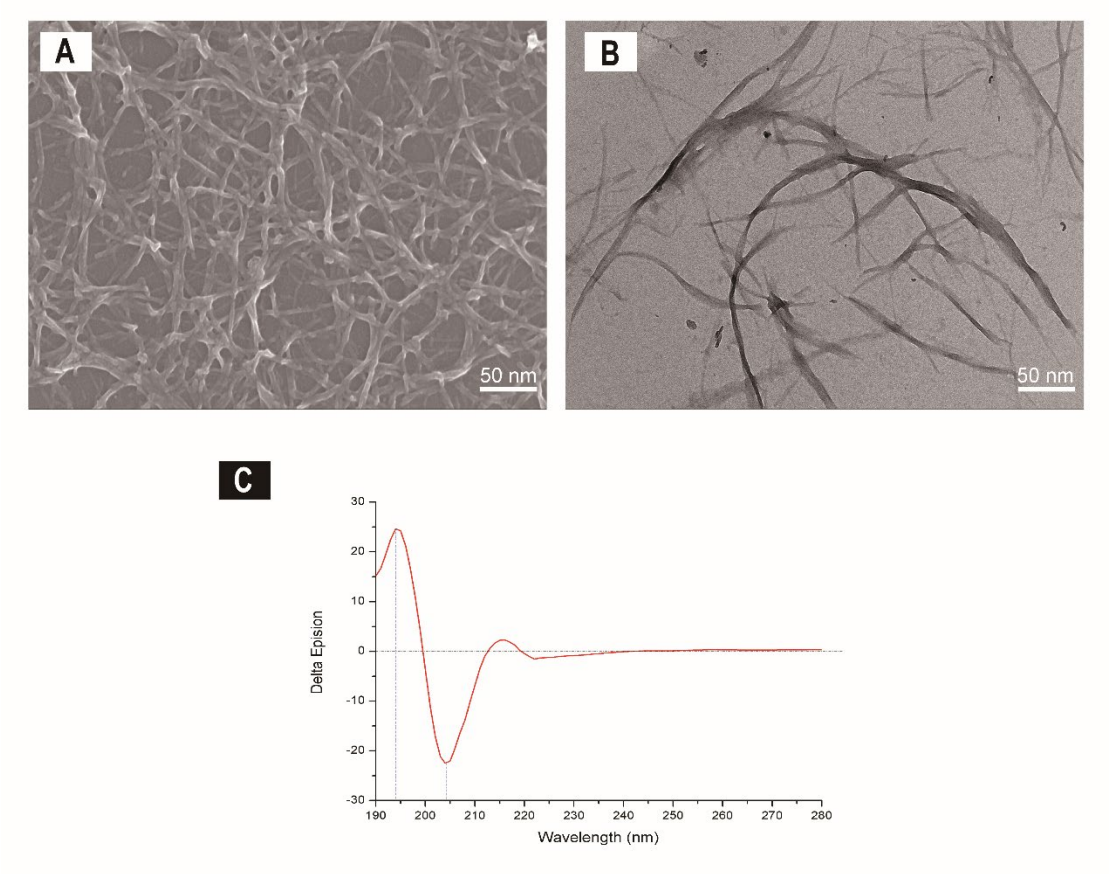


Fig. 3 The self-assembly of the oligopeptide. (A), SEM image (B), TEM image. The oligopeptide self-assembled into the filamentous architectures with a diameter of about 10 nm in the presence of Ca^{2+}. (C), The circular dichroism spectrum of the self-assembled oligopeptide. The spectrum showed negative and positive bands at approximately 205 and 194 nm, respectively. This observation represents a typical helix structure of the self-assembled oligopeptide.[1]

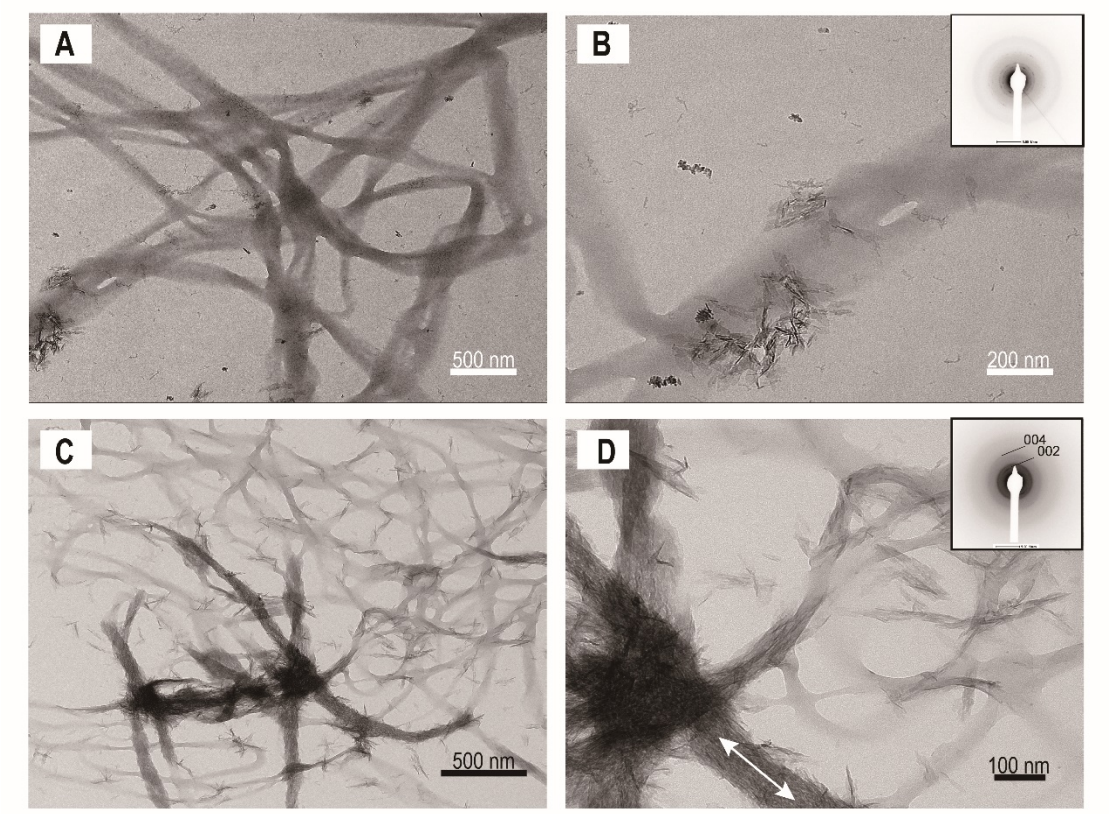


Fig. 4 Mineralized collagen fibrils in control group after 48 h.

(A)**,** Low magnification. (B), High magnification. A few apatite crystallites were randomly distributed on the surface of collagen fibrils. The collagen fibrils alone did not influence the distribution or organisation of the crystallites.

Mineralized collagen fibrils in positive group (pASP) after 48 h.

(C), Low magnification. (D), High magnification. The pASP achieved partial intrafibrillar mineralization and a few extrafibrillar mineralisation.

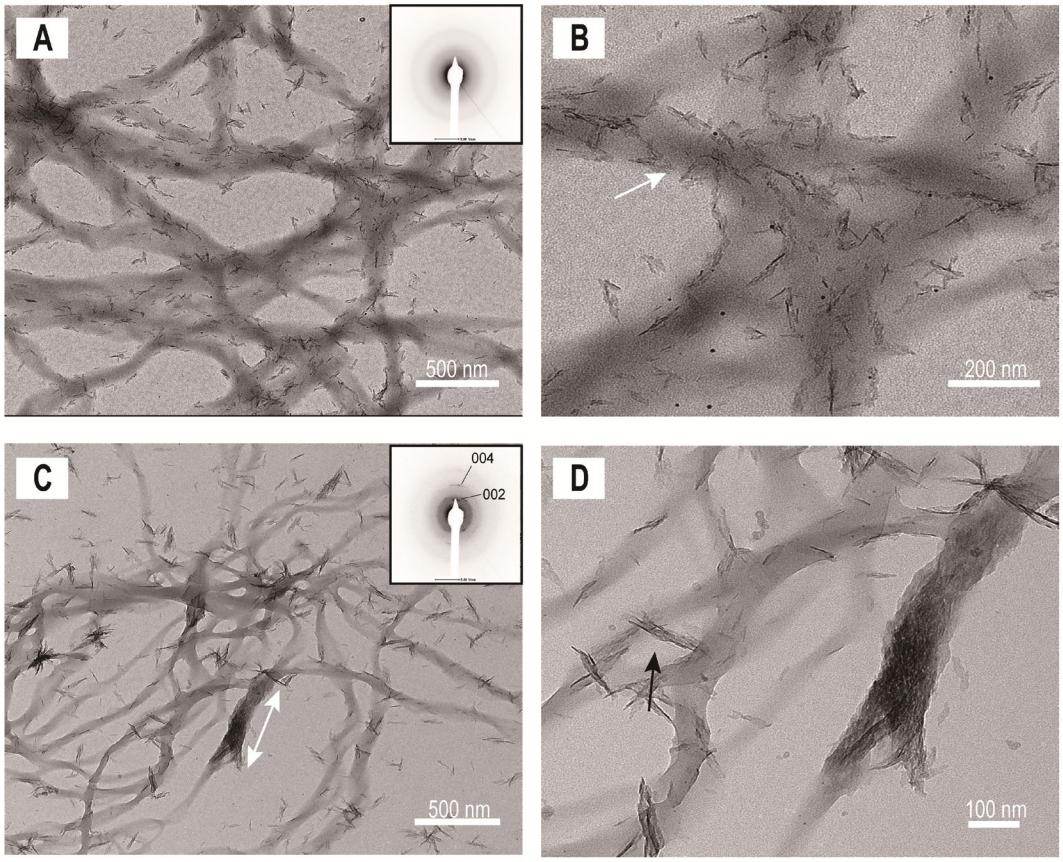


Fig. 5 Collagen mineralisation induced by the peptide lacking the capacity of self-assembly. (A)**,** Low magnification after 24 h. (B), High magnification after 24 h. Plate-like minerals was randomly distributed on the surface of collagen fibrils. Those minerals were comparable to the precursors.

(C), Low magnification after 48 h. (B), High magnification after 48 h. The peptide lacking the capacity of self-assembly achieved a few intrafibrillar and extrafibrillar mineralisation.

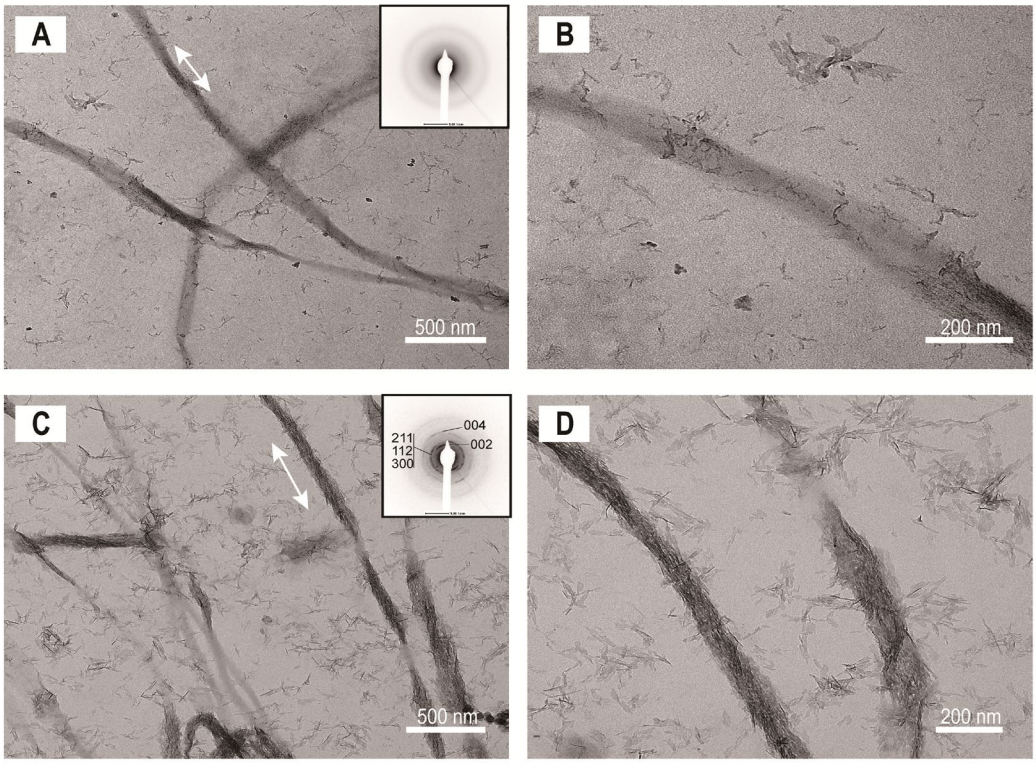


Fig. 6 Collagen mineralisation formed by the oligopeptide without introducing $CaCl_2$ to trigger self-assembly. (A)**,** Low magnification after 24 h. (B), High magnification after 24 h. The filamentous minerals were similar to that formed by introducing $CaCl_2$. (C), Low magnification after 48 h. (B), High magnification after 48 h. After 48 h, intrafibrillar and extrafibrillar mineralisation were also achieved.

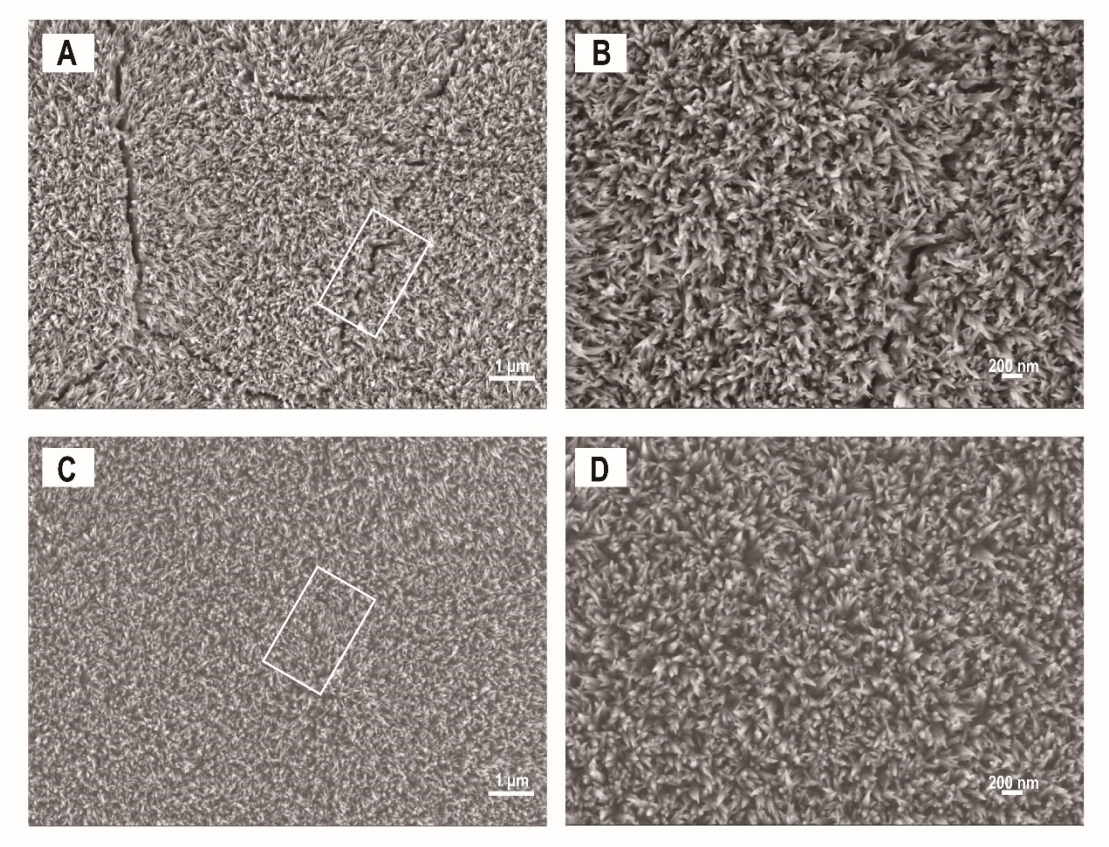
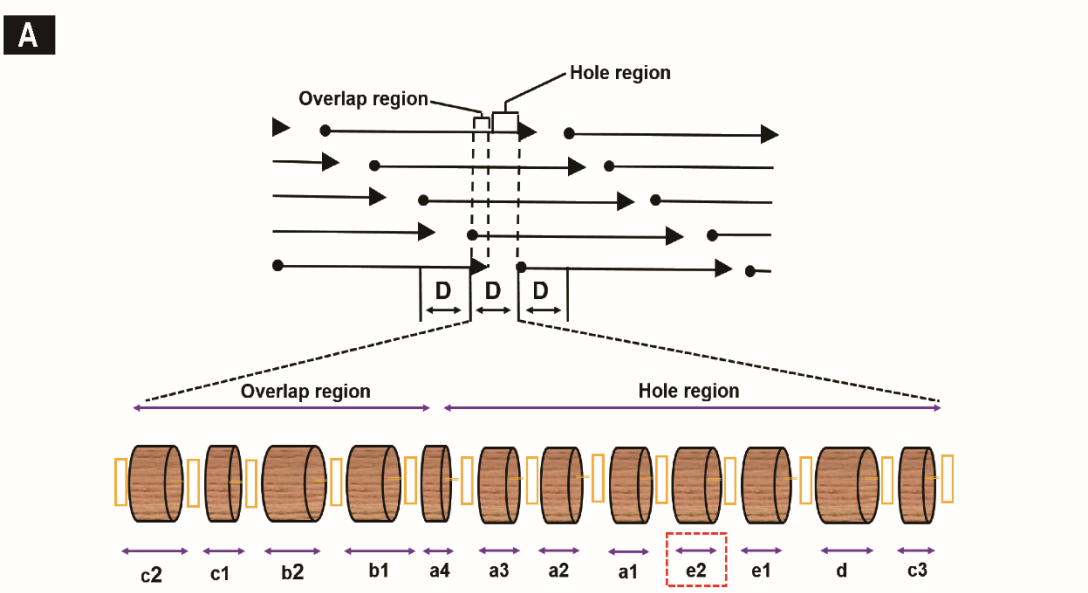


Fig. 7 Surface view of the mineralized dentinal collagen. (A), Surface view in the experimental group. (B), Magnification of A. (C), Surface view in the control group. (D), Magnification of C.



B

e2 bands (molecule 1-4, top to down)

1st e2 band:

α1 chain: HYP-GLY-GLU-ARG-GLY-ARG-HYP-GLY-PRO-HYP-GLY-THR-ALA-GLY-ALA;

α2 chain: LEU-HYP-GLY-GLU-ARG-GLY-ARG-VAL-GLY-ALA-HYP-GLY-PRO-ALA-GLY;

α1 chain: GLY-LEU-HYP-GLY-GLU-ARG-GLY-ARG-HYP- GLY-PRO-HYP-GLY-THR-ALA;

2nd e2 band:

THR-GLY-SER-HYP-GLY-SER-HYP-GLY -PRO-ASP-GLY-LYS -THR-GLY-PRO;

LEU-HYP-GLY-SER-HYP-GLY-ASN-VAL-GLY-PRO-ALA-GLY-LYS-GLU-GLY;

GLY-LEU-THR-GLY-SER-HYP-GLY-SER -HYP-GLY-PRO-ASP -GLY-LYS-THR;

3rd e2 band:

ALA-GLY-ALA-HYP-GLY-ASP-LYS-GLY-GLU-ALA-GLY-PRO-SER -GLY-PRO;

PRO-ALA-GLY-ALA-SER-GLY-ASP-ARG-GLY-GLU-ALA-GLY-ALA-ALA-GLY;

GLY-PRO-ALA-GLY-ALA-HYP-GLY-ASP-LYS -GLY-GLU-ALA-GLY-PRO-SER;

4th e2 band:

HYP-GLY-GLU-SER-GLY-ARG-GLU-GLY-SER -HYP-GLY-ALA-GLU-GLY-SER;

ALA-HYP-GLY-GLU-ALA-GLY-ARG-ASP-GLY-ASN-HYP-GLY -SER-ASP-GLY;

GLY- PRO-HYP-GLY-GLU-SER-GLY-ARG-GLU-GLY-SER-HYP-GLY-ALA-GLU;

Fig. 8 (A), Diagram illustrating the packing pattern of collagen molecules into a microfibrils unit containing five molecules in cross-sectional view. The unit contains collagen molecules that have a total length of about 4.4 D and are staggered laterally by multiples of each D pattern (~67 nm). The e2 band of the hole region is characterized by the presence of only four molecules in the cross-sectional view. The four e2 band of the hole region was reported to be firstly mineralized[2] and thus selected as the

collagen model in the present simulation. (B), The four e2 bands (top to down) are shown from N- to C-terminal (left to right).

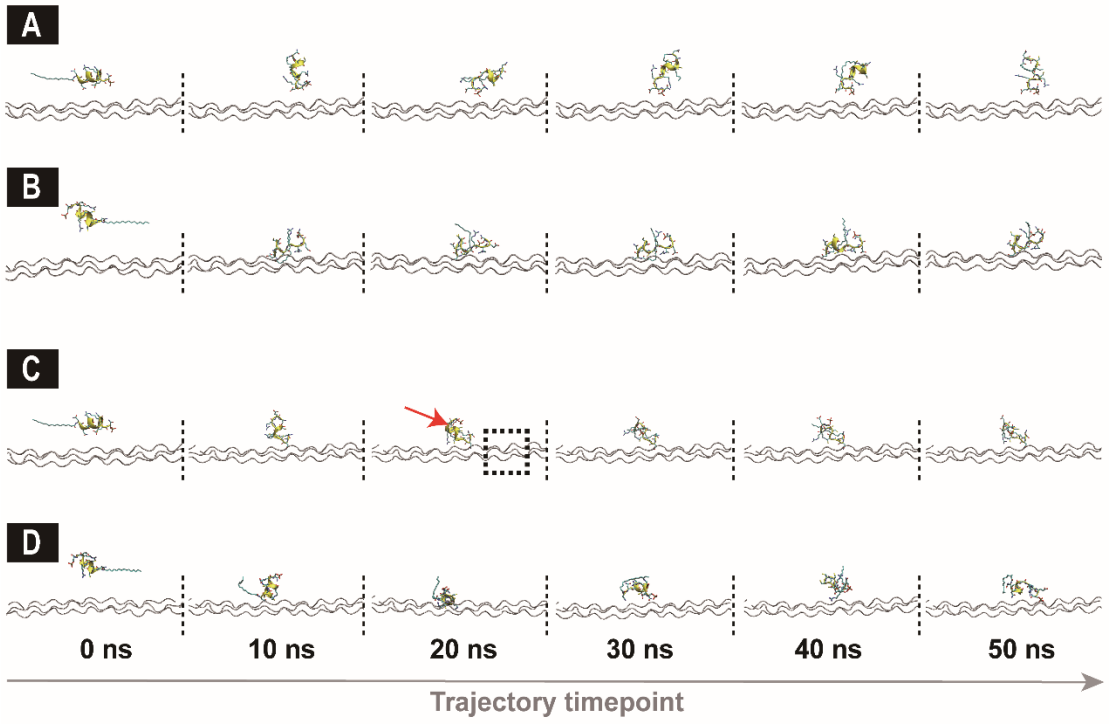


Fig. 9 The simulation of the oligopeptide binding with collagen. (A, B, C, D), Simulation between the oligopeptide and the first, second, third and fourth e2 band, respectively. The oligopeptide was spontaneously adsorbed onto the e2 band of collagen. Red Arrow: Oligopeptide; Black dotted box: the e2 bands

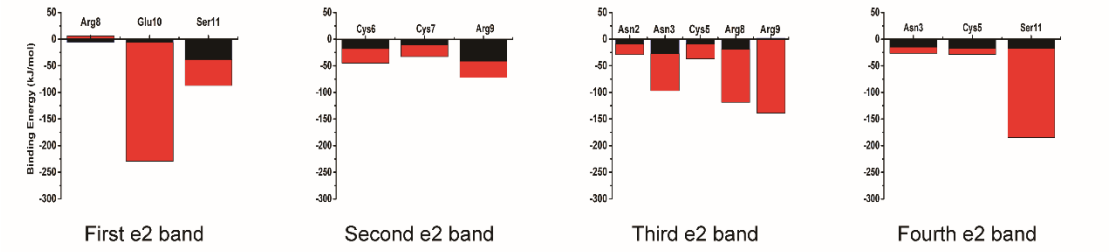


Fig. 10 The key AAs responsible for interacting with collagen. Almost all designed AAs participated in binding with collagen and polar AAs including Arg, Glu, and Ser were the prominent donors.

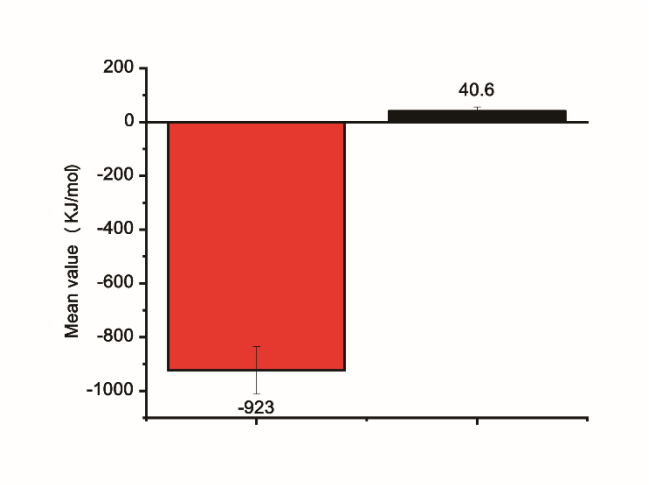


Fig. 11 The binding energy between the oligopeptide and Ca^{2+} during the simulation plateau (40-50 ns).

References

1. K. E. Drzewiecki, D. R. Grisham, A. S. Parmar, V. Nanda and D. I. Shreiber, *Biophysical journal*, 2016, **111**, 2377-2386.
2. F. H. Silver, J. W. Freeman, I. Horvath and W. J. Landis, *Biomacromolecules*, 2001, **2**, 750-756.