Electronic Supplementary Information (ESI)

Title: Controlled self-assembly and templated metallization of fibrinogen nanofibrils

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Materials and Methods:

1. Preparation of fibrinogen (Fg) nanofibrils

Human plasma Fg solution (purchased from Merck KGaA, Darmstadt, Germany; contains >95% clottable protein) was diluted to different concentrations: 200, 50, 20, 5, and 1 ng/μL with ultrapure water. For the preparation of Fg fibrils, Fg solutions with different concentrations were first incubated in a water-bath at 37 ºC for half an hour, after that, the Fg solutions were mixed with ethanol (95%) with various ratios, from 4:1 to 1:4 (v/v). Amyloid-like fibrils formed after the mixed solutions were incubated in the water-bath at 37 ºC for one hour.

2. Metallization of Fg nanofibrils

Some metallic ions, such as Ag^+, $AuCl_4^-$, $PtCl_6^{2-}$, can be adsorbed onto the protein templates by changing the pH value higher or lower than the isoelectronic point of proteins. The metallization of Fg nanofibrils in the present study was conducted by two different strategies reported by Dujardin *et al.* and Richter *et al.*.[1, 2]

Strategy one: 40 μL $HAuCl_4$ (10 Mm, in H_2O) was mixed with 200 μL formed Fg fibrils solution, and the mixed solution was kept at dark for half an hour, then 50 μL $N_2H_4 \cdot H_2O$ (1 mM, in H_2O) was

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added into the mixed solution to synthesize Au NPs. For the measurement of metallized fibrils with Au NPs by the first method, a 15 μL droplet of solution was placed on a copper grid, and the dried sample was immersed into the 1% phosphotungstic acid (PTA) for 1 minute and then dried in air for the TEM measurement.

Strategy two: 200 μL formed Fg nanofibrils was mixed with 40 μL $HAuCl_4$ solution (10 mM, in H_2O) to prepare Fg fibrils/$AuCl_4^-$ composites; then the mixed solution (20 μL) was dropped onto the carbon-coated copper grid and reduced with $NaBH_4$ (1%, v/v, in H_2O) for 10s, and then dried in air for the TEM measurement.

3. Preparation of AFM and TEM samples

Tapping mode atomic force microscopy (AFM) was carried out using a Nanoscope IV multimode scanning force microscope (Digital Instruments, Santa Barbara, CA). New cleaved mica and clean silicon were used as substrates for AFM. 20 μL solution of Fg was dropped onto the mica and dried in air.

Transmission electron microscopy (TEM) observations were conducted with a JEOL 3010 instrument operated at 300 kV. For the imaging of Fg fibrils and fibrils/$AuCl_4^-$ composites, a 20 μL droplet of the solution was placed on a carbon-coated 400 mesh copper grid, and the excess liquid was absorbed by filter paper. The dried samples with the TEM grid were immersed into the 1% PTA for 2 minutes and then dried in air for the TEM measurement.

Reference

(1) E. Dujardin, C. Peet, G. Stubbs, J. N. Culver and S. Mann, *Nano Lett.*, 2003, **3**, 413.

(2) J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke and H. K. Schackert, *Adv. Mater.*, 2000, **12**, 507.

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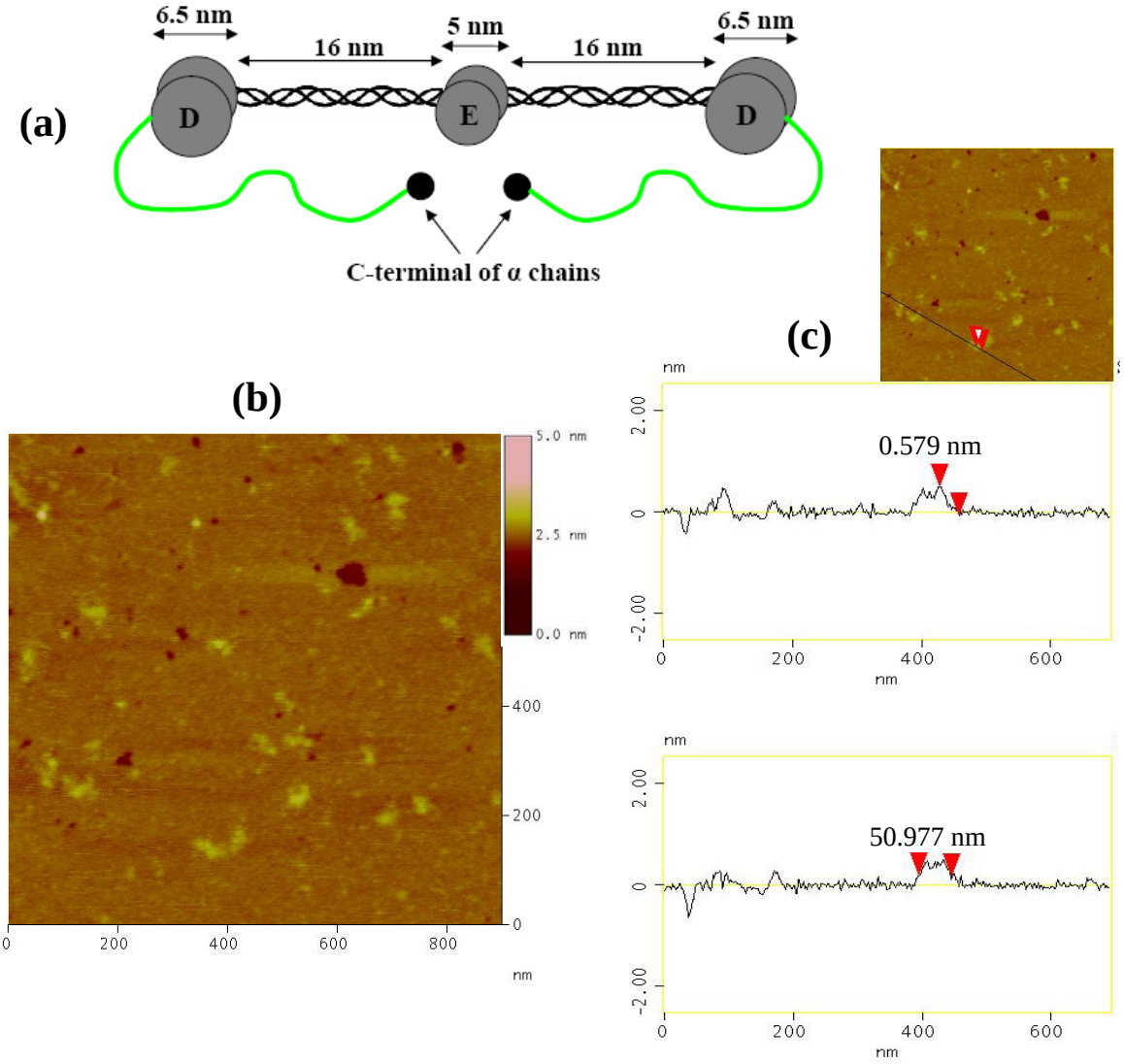

Fig. S1 (a) Scheme of the structure of human plasma Fg, which is based on our previous work (P. Cacciafesta, A. D. L. Humphris, K. D. Jandt and M. J. Miles, *Langmuir*, 2000, **16**, 8167) ; (b) AFM height image of 5 ng/μL Fg (at 37 ºC) solution on the new cleaved mica; (c) Section analysis of single Fg molecule, which shows the height is about 0.58 ± 0.12 nm and length is 50.98 ± 3.57 nm.

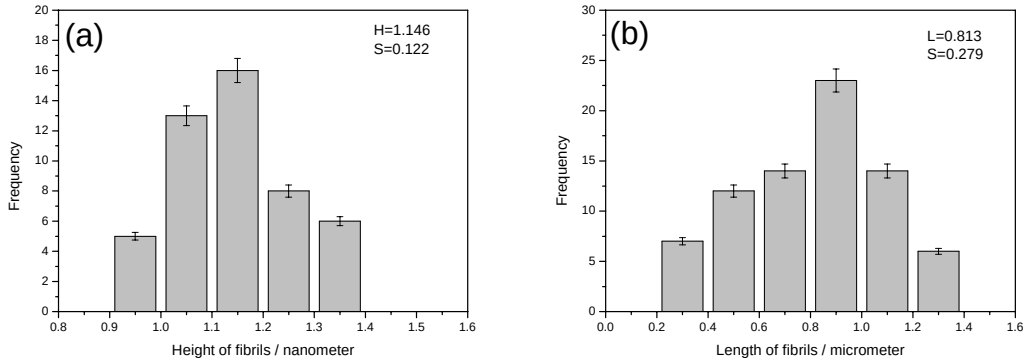

Fig. S2 Histograms of the height (a) and length (b) of the Fg fibrils formed when the ratio of Fg (20 ng/μL) with ethanol was 1:2, as that in Fig. 2c in the manuscript.

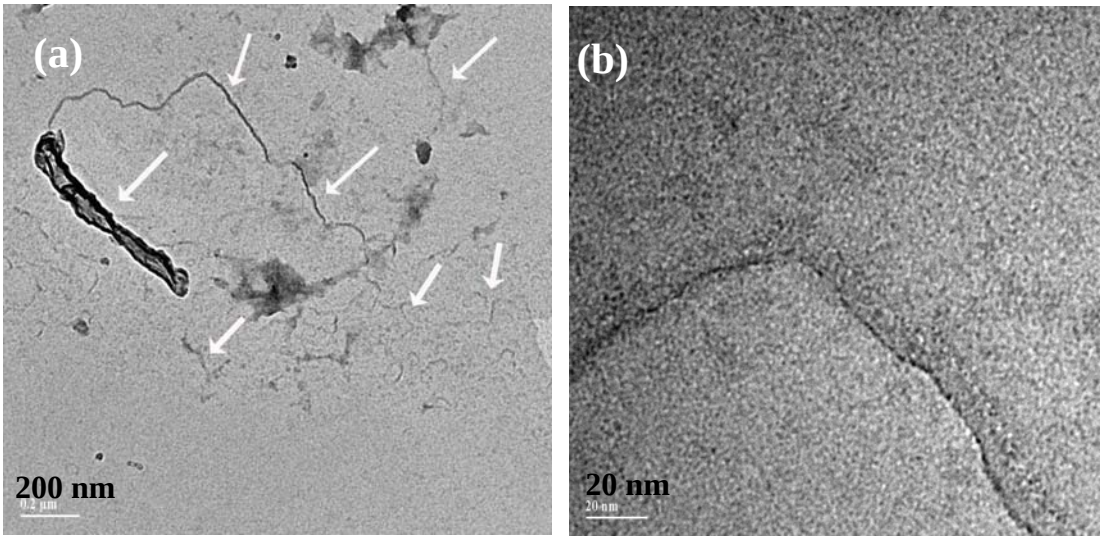

Fig. S3 (a) TEM image of the Fg fibrils formed when the ratio of Fg (20 ng/μL) with ethanol was 1:2, as that in Fig. 2c in the manuscript. (b) High-resolution TEM image of fibrils. The width of the fibrils is about 10 nm. The Fg nanofibrils were indicated by arrows in Fig. S3a.

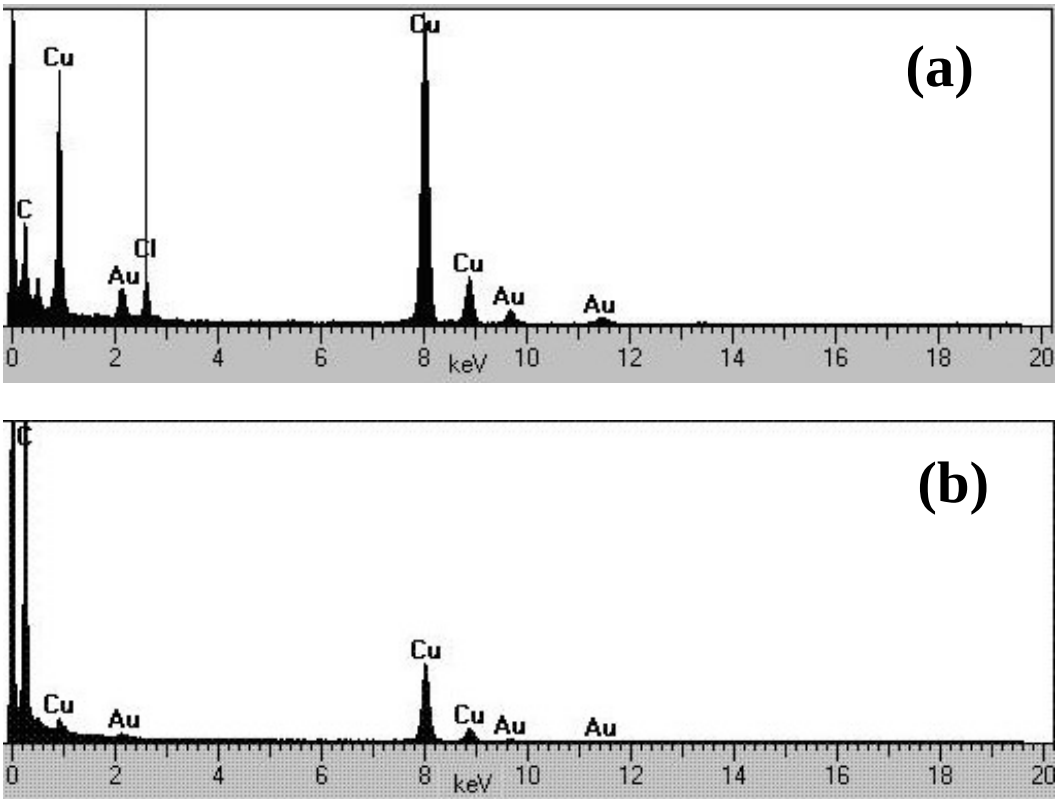

Fig. S4 (a) TEM-EDX spectroscopy analysis of Au NPs prepared by the first strategy, the Au NPs were shown in Fig. 4b; (b) TEM-EDX spectroscopy analysis of Au NPs prepared by the second strategy, the Au NPs were shown in Fig. 4c and d.