Supplementary Information

Assembly of Peptides in Mica-graphene Nanocapillaries Controlled by Confined Water

Jinjin Zhang,[‡a,b] Limin Zhou,[‡b,c] Qiqige Du,[b] Zhiwei Shen,[b,c] Jun Hu*[a,b] and Yi Zhang*[a,b]

[a]Shanghai Synchrotron Radiation Facility, Zhangjiang Lab, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China.

[b]Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China.

[c]University of Chinese Academy of Sciences, Beijing 100049, China

[‡]These authors contributed equally to this work.

*To whom correspondence should be addressed. Email: zhangyi@sinap.ac.cn; hujun@sinap.ac.cn

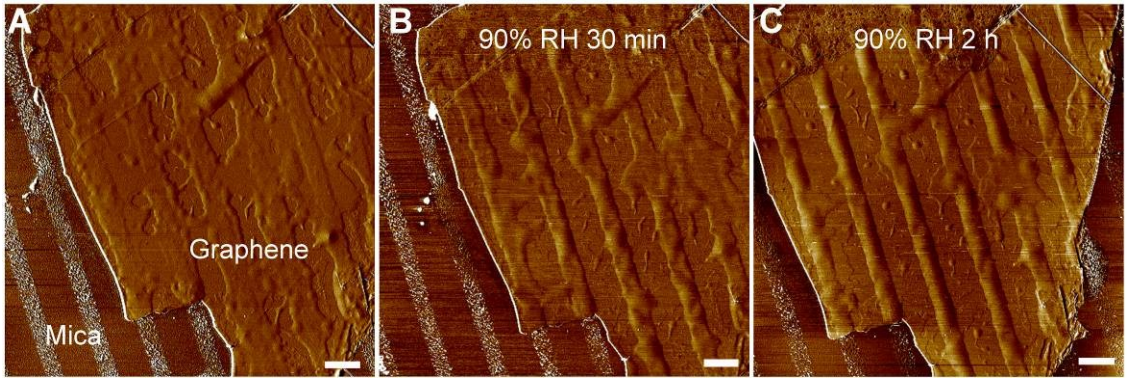

Fig. S1 *In situ* AFM phase images of the GAV-9 peptide confined between the mica-graphene nanocapillary in a relative humidity (RH) of 90%. (A) GAV-9 strips generated by D-μCP method before incubation. (B, C) Peptide hydrogels formed under a 90% RH environment, which were maintained within 30 min (B) and 2 h (C). Different phase contrasts were observed among the graphene, unconfined peptide strips and mica surface, reflecting the different surface properties. On the contrary, the phase images show no obvious difference on the graphene plateau, indicating the AFM tip interacted with the same graphene surface, and these peptide strips were underneath the graphene sheet. Scale bars represent 1 um for all images.

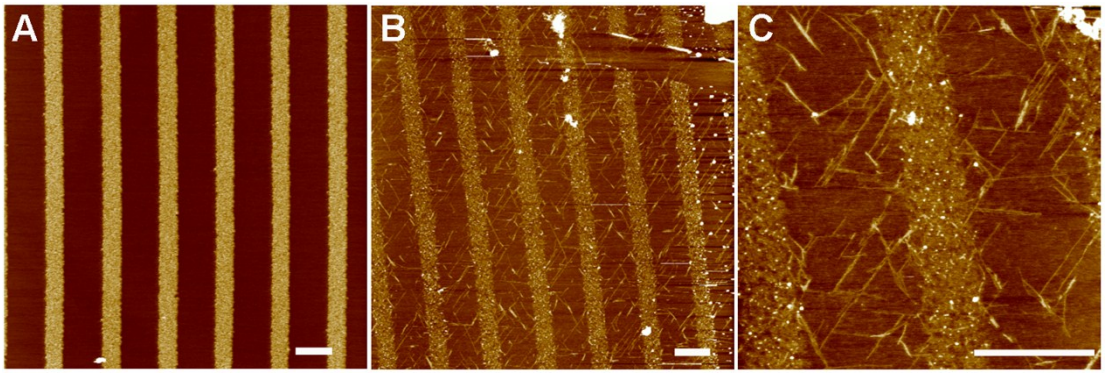

Fig. S2 AFM observations of the self-assembling process of GAV-9 peptide strips on the bare mica surface under a 90% RH environment. (A) D-μCP generated GAV-9 strips before incubation. (B) Peptide nanofilaments formed under a RH of 90% within 4 h. (C) Zoom-in AFM image of the nanofilaments shown in (B). Scale bars represent 1 um for all images.

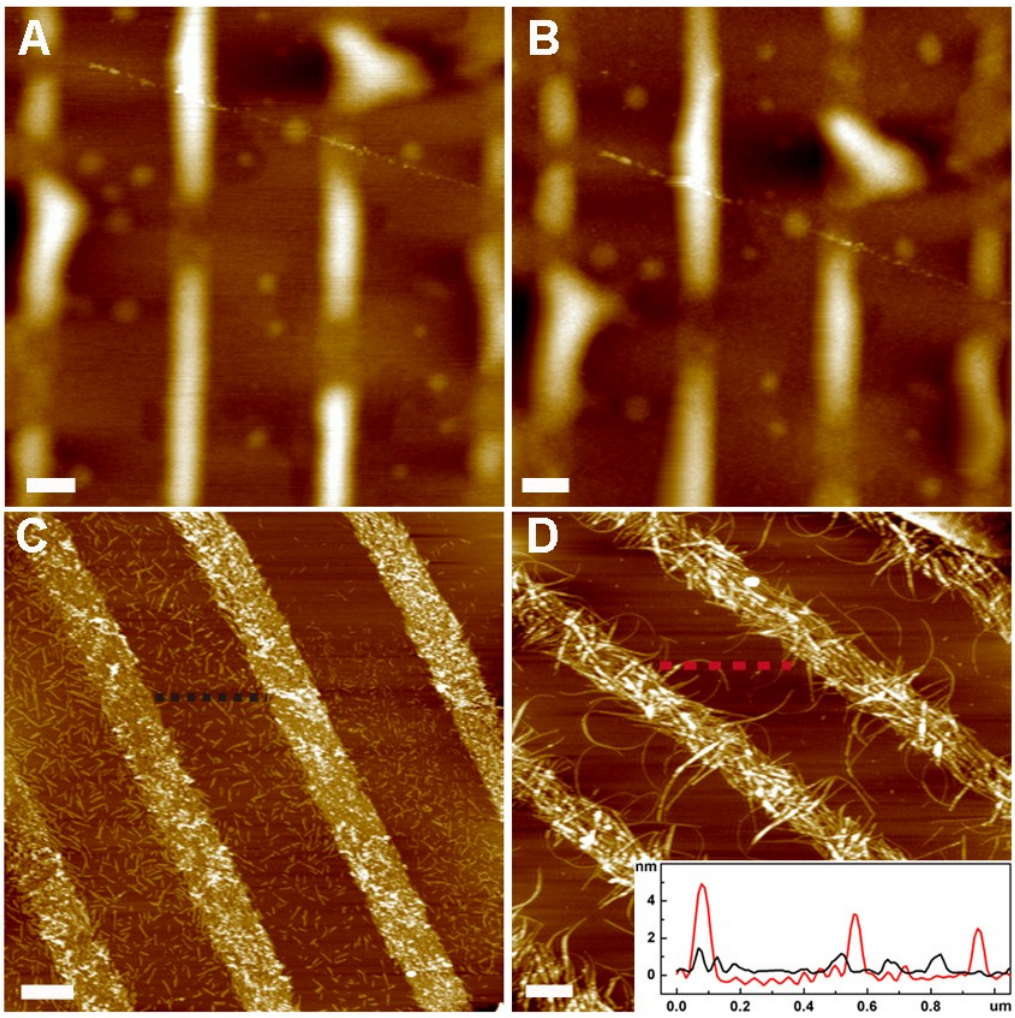

Fig. S3 *In situ* AFM height images of the GAV-9 peptide under the ethanol-saturated atmosphere. (A) GAV-9 peptide hydrogels in the mica-graphene nanocapillary before incubation. (B) GAV-9 peptide hydrogels in (A) after incubation for 48 h. (C) Preformed peptide nanofilaments on the bare mica substrate before incubation. (D) Preformed peptide nanofilaments in (C) after incubation for 48 h. The inset in (D) is the height profile of the fibrils measured along the black and red dashed lines in (C) and (D), respectively. Scale bars: 500 nm.

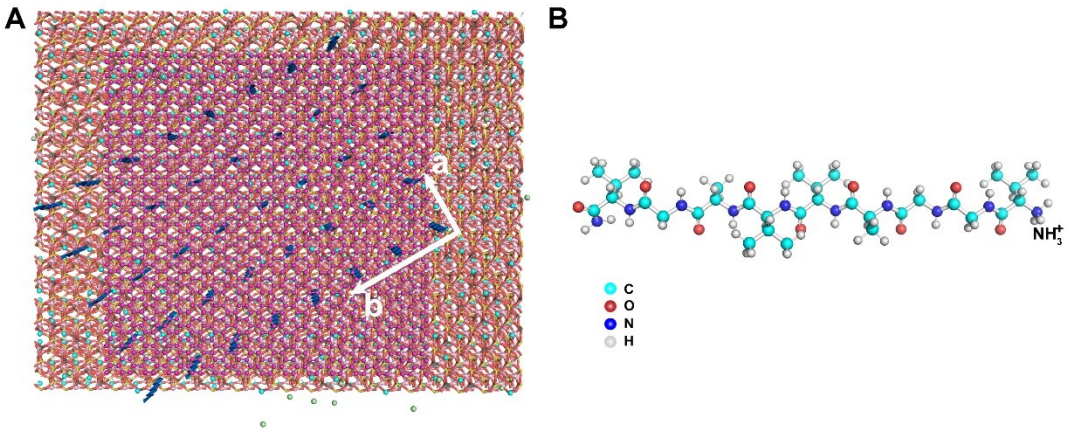

Fig. S4 (A) Top view of initial setup of GAV-9 peptides in the mica-graphene nanocapillary. GAV-9 peptides were sparse packed along the crystallographic axes (i.e., a and b) of mica. (B) Stick-ball model of the positively-charged GAV-9 (NH_2-VGGAVVAGV-$CONH_2$) monomer. The electrostatic interactions between positive N-terminal and negatively charged muscovite mica surface are crucial to pin the GAV-9 peptide monomer on the mica surface.

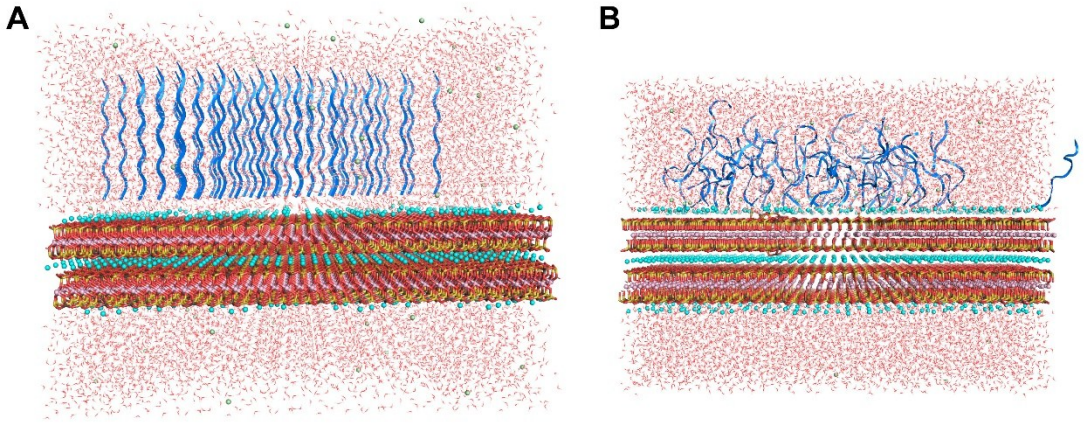

Fig. S5 (A) Initial configuration of the GAV-9 peptides on the mica surface in bulk water without the confinement of a graphene layer. (B) Final configuration at 100ns.With such sparse packing (5 × 8), most of the peptides maintain a “standing up” state but not form highly ordered β-stranded structures.

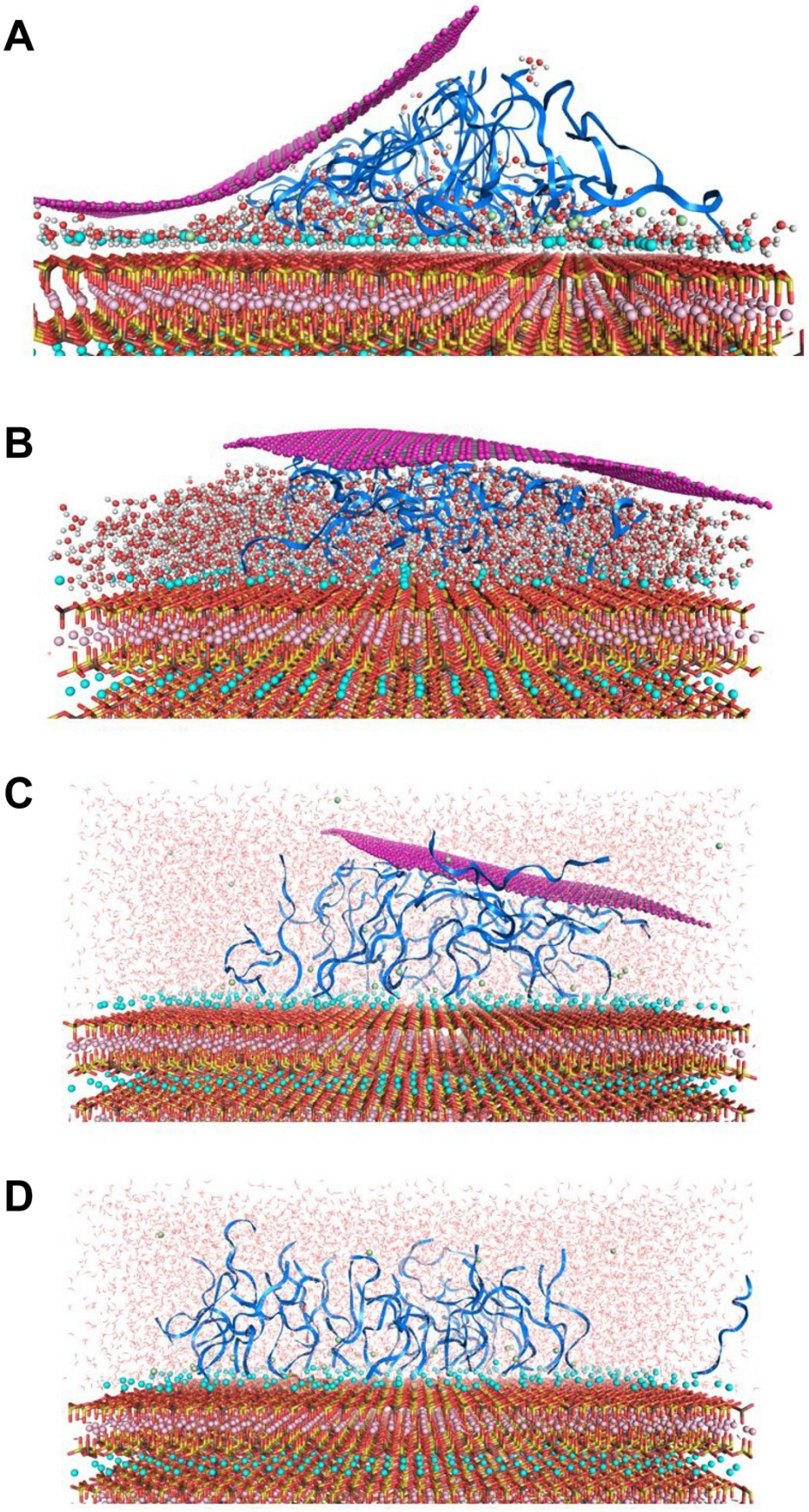

Fig. S6 Magnified images of the final configurations of 1 nm water system (A), 3 nm water

system (B), bulk water system (C) and no confine system (D). Water molecules are found to enter in the distorted peptide assemblies. Peptide hydrogel structures were formed as a result of complicated interactions between peptide and peptide (hydrophobic interaction and electrostatic repulsion), peptide and water (hydrogen bonding), peptide and graphene (hydrophobic interaction), and peptide and the mica substrate (electrostatic attraction).

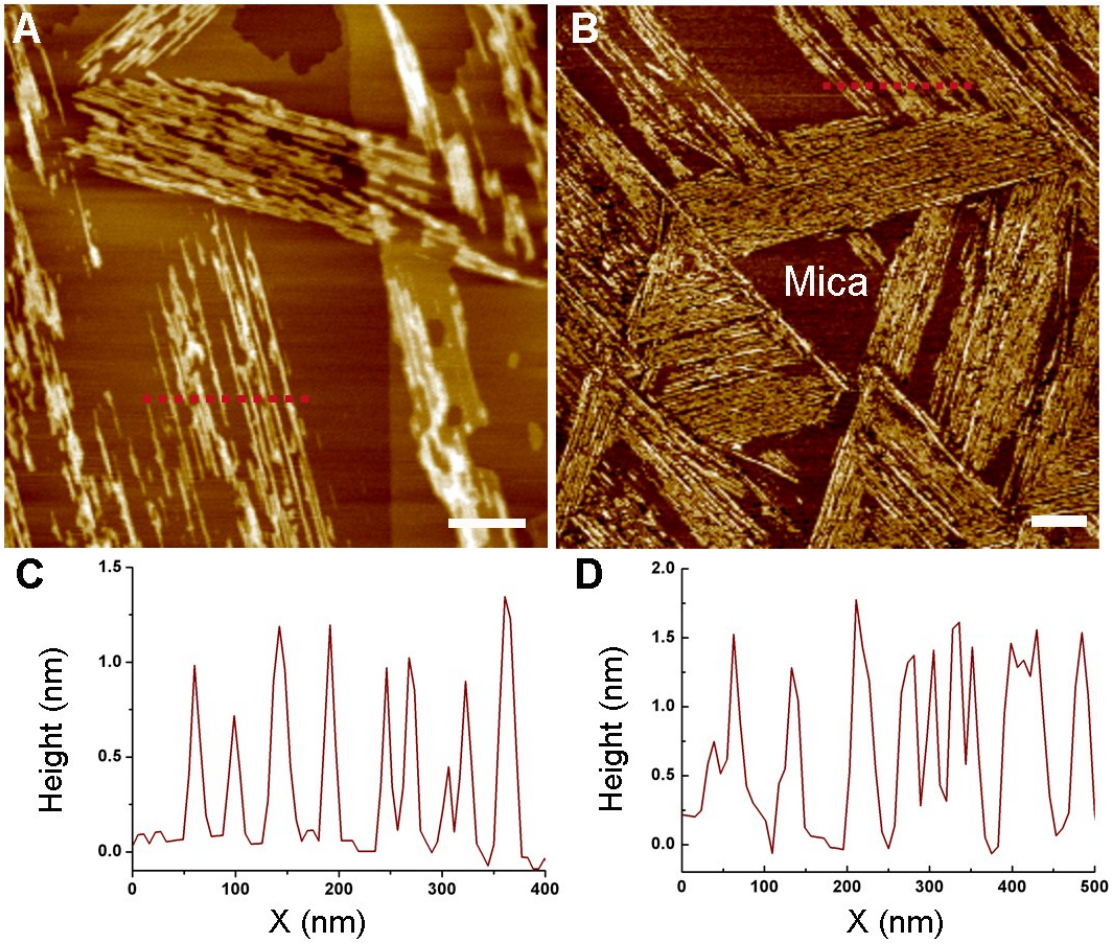

Fig. S7 AFM height images of the confined GAV-9 peptide nanofilaments in the mica-graphene nanocapillaries (A) and the peptide nanofilaments on the bare mica surface (B). (C) (D), the corresponding height profiles of the nanofilaments measured along the red dashed lines labeled in (A) and (B), respectively. Scale bars: 200nm.

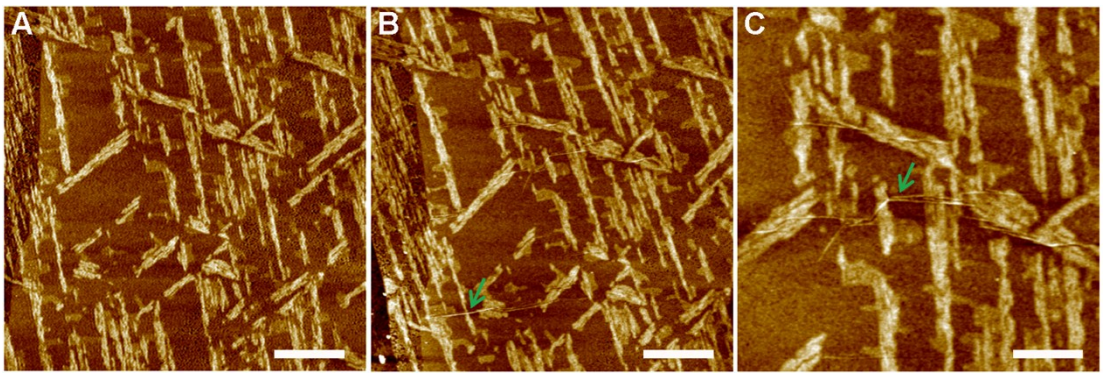

Fig. S8 *In situ* AFM observations of the self-assembling process of the GAV-9 nanofilaments confined between the mica-graphene nanocapillary before (A) and after incubation at a 100% RH for 1h (B). (C) Zoom-in AFM image of the confined nanofilaments shown in (B). Scale bars represent 1 um for (A, B) and 0.5 um for (C).