Supporting information

Stereoselective Assembly of Amino Acid-Based Metal-Biomolecule Nanofibers

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Experimental section

Materials:

Copper(II) sulfate pentahydrate ($CuSO_4$•$5H_2O$), sodium hydroxide (NaOH) were purchased from Beijing Beihua Fine Chemicals Co., Ltd (Beijing, China). L-Aspartic acid (L-Asp), D-Aspartic acid (D-Asp), L-Glutamic acid (L-Glu), D-Glutamic acid (D-Glu), L-2-Aminoadipic acid (L-Ami) and D-2-Aminoadipic acid (D-Ami) were purchased from Sigma-Aldrich Chemical Co., Ltd. All the reagents were of analytical grade and used without further purification. The water used in all experiments was treated by the Millipore Milli-Q purification system.

Synthesis of the several nanofibers at low concentration

For the synthesis of discrete amino acid-based nanofibers, 2 ml 14 mM $CuSO_4$ aqueous solution was added into 2 ml 14 mM deprotonated amino acid solution. After matured for a certain period of time, glue nanofibers were obtained.

Synthesis of gels or precipitates at high concentration

For the synthesis of gels or precipitates, 2 ml 70 mM $CuSO_4$ aqueous solution was added into 2 ml 70 mM deprotonated L-Asp, D-Asp and LD-Asp solutions, respectively. 2 ml 280 mM $CuSO_4$ aqueous solution was added into 2 ml 280 mM deprotonated L-Glu, D-Glu and LD-Glu solutions, respectively. 2 ml 280 mM $CuSO_4$ aqueous solution was added into 2 ml 280 mM deprotonated L-Ami, D-Ami and LD-Ami solutions, respectively. After matured for a certain period of time, opaque blue gels or precipitates would form. The formation of gels or precipitates at high concentrations can be identified by the inverted tube method.

Characterizations and measurements

SEM images were recorded by using a scanning electronic microscopy (SEM, JSM-6700F, JEOL, Japan). EDS element mappings were obtained through energy dispersive spectroscope (EDS) attached to SEM. TEM images were recorded by using a transmission electron microscope (TEM, JEM-2100(UHR)). XPS spectra were recorded by an X-ray photoelectron spectroscopy (XPS, ESCALAB, 250Xi). FTIR spectra were obtained on a FTIR spectrometer (FT/IR-660, JEOL, Japan). X-ray powder diffraction patterns were recorded on an X-ray diffraction (XRD, Empyrean, Netherlands). Solid state CD spectra were recorded on a solid state circular dichroism

spectroscopy (JASCO J185). Thermogravimetric analysis (TGA) was performed on a TA instrument (SDT Q600).

The conversation rates of the several assembly process were calculated (eq.1) by measuring the decrease of UV-vis absorption at 727 nm, 702 nm and 733 nm, which was the maximum UV-vis absorption wavelength of Cu(II)-Asp complexes, Cu(II)-Glu complexes and Cu(II)-Ami complexes, respectively.

$$\text{Conversation rate } (\%) = 100(C_0 - C)/C_0 \qquad \text{eq.1}$$

C_0 was the initial concentration of the Cu(II)-amino acid complexes, C was the concentration of the remaining Cu(II)-amino acid complexes in the solution as a function of time. For the measurement of C, the Cu(II)-amino acid complexes solution was separated from the mixture by a syringe with a filter head.

Supplemental Figures

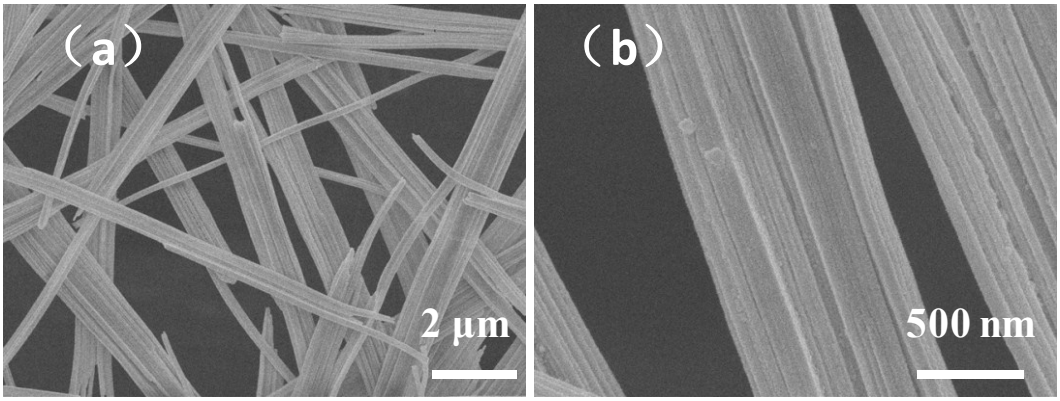

Figure S1: (a, b) SEM images of the Cu(II)-Asp nanofibers, The images showed that many Cu(II)-Asp nanowires combined together to form the 1-D Cu(II)-Asp nanofibers

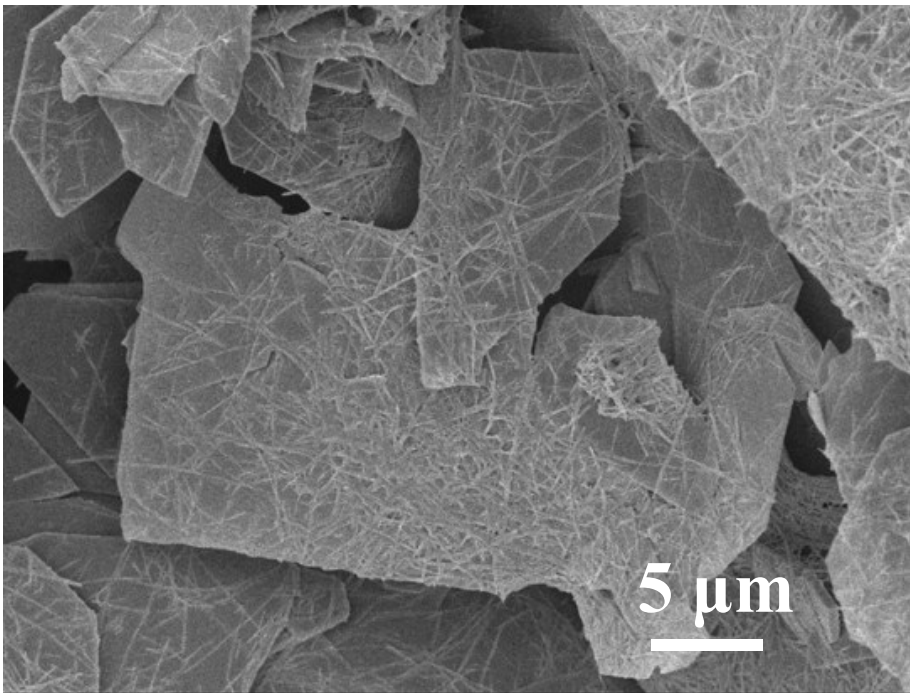

Figure S2: SEM images of the 2-D Cu(II)-LD-Glu microsheets formed when the concentration of the reactants was 35 mM. The microsheets were composed of 1-D Cu(II)-LD-Glu nanofibers

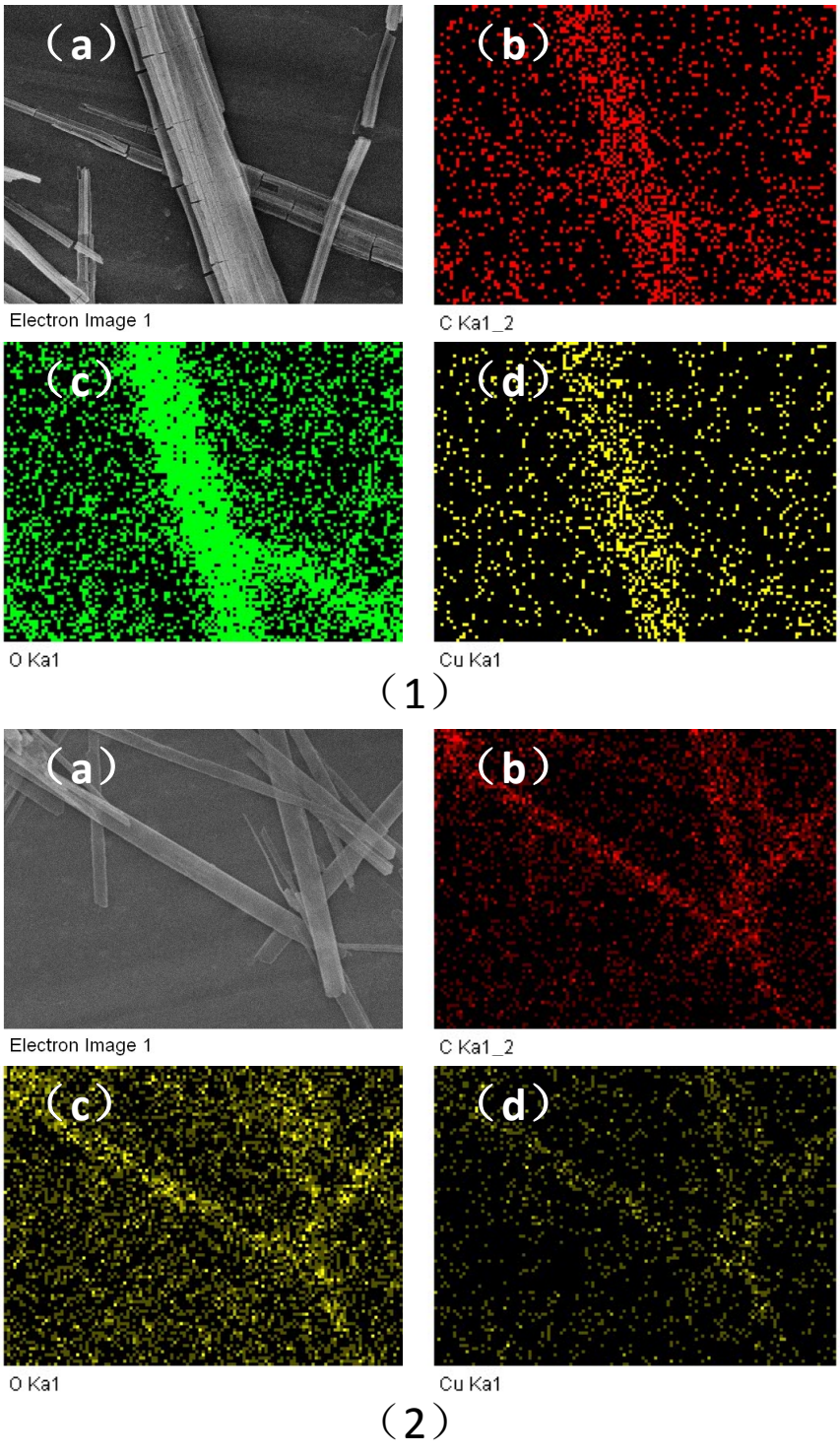

Figure S3. SEM images and EDS element mappings (C (red), O (green), Cu(II) (yellow)) of the (1) Cu(II)-Asp nanofibers and (2) Cu(II)-Ami nanofibers. The Cu(II)-LD-Glu nanofibers were too slim to obtain clear EDS element mappings, so the EDS element mappings of the Cu(II)-LD-Glu nanofibers were not given here.

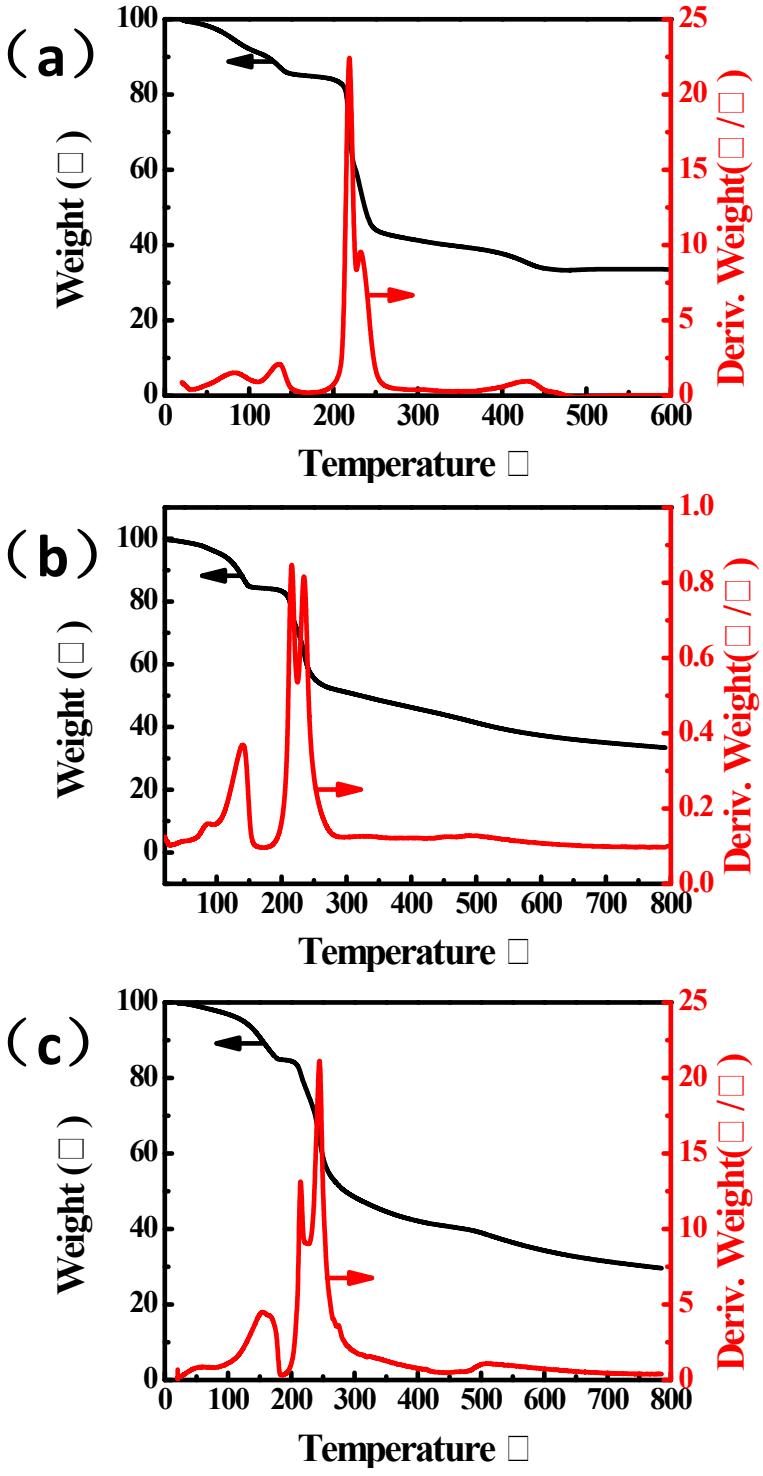

Figure S4. TGA curves of (a) Cu(II)-Asp nanofibers, (b) Cu(II)-LD-Glu nanofibers and (c) Cu(II)-Ami nanofibers.

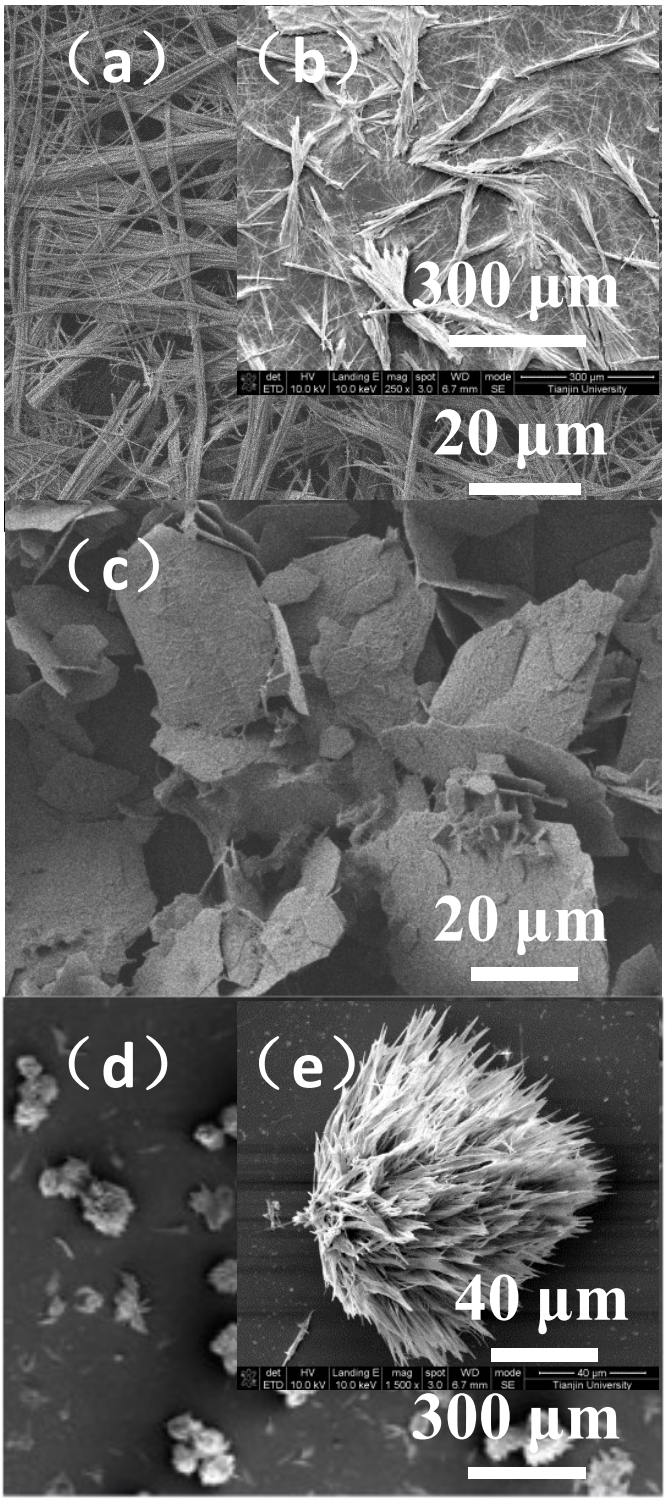

Figure S5. SEM images of (a, b) Cu(II)-Asp gel, (c) Cu(II)-LD-Glu gel and (d, e) Cu(II)-Ami precipitate using reactants with high concentrations.

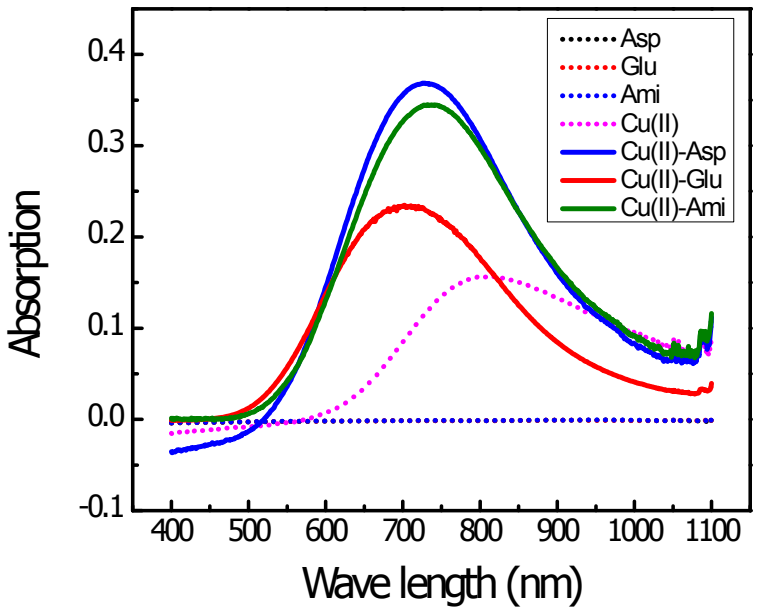

Figure S6. UV-vis spectra of the several amino acids, Cu(II) and the several Cu(II)-amino acid complexes solutions. The concentration of all the solutions used here for the recording of the UV-vis spectra was 14 mM.

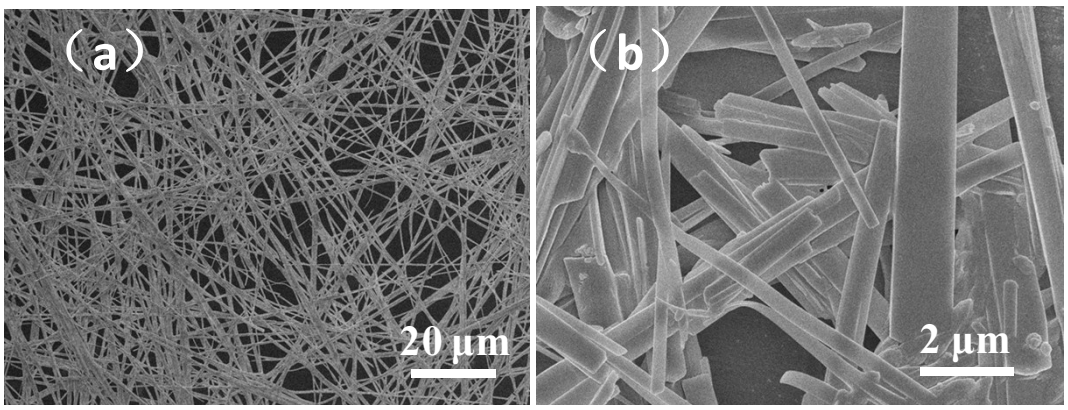

Figure S7. SEM images of (a) Cu(II)-Asp nanofibers and (b) Cu(II)-Ami nanofibers. The images showed that the Cu(II)-Asp nanofibers were significantly longer than the Cu(II)-Ami nanofibers.

Supplemental Table

Table S1. Element contents of the corresponding nanofibers measured by XPS.

Element	Atomic%					
	Cu(II)-Asp		Cu(II)-LD-Glu		Cu(II)-Ami	
	Measured	(Theoretical)	Measured	(Theoretical)	Measured	(Theoretical)
C	44.57	(40.00)	52.01	(45.45)	54.27	(50.00)
O	37.01	(40.00)	32.38	(36.36)	32.40	(33.33)
N	9.80	(10.00)	8.61	(9.09)	7.46	(8.33)
Cu	8.62	(10.00)	7.00	(9.09)	5.86	(8.33)
Totals	100.00	(100.00)	100.00	(100.00)	100.00	(100.00)