

# Supramolecular hydrogels for *in situ* creating gold and silver nanoparticles

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**Electronic Supplementary Information (ESI)**

## Chemicals and characterizations

All chemicals at AR grade were purchased from Sangon (Shanghai) and Guoyao group (China). Field emission scanning electron microscopy (FESEM) experiments were carried out on HITACHI S-4800 working at an accelerating voltage of 20 kV. For FESEM characterization, xerogel samples were prepared by freeze-drying the original hydrogels under vacuum at  $-80\text{ }^{\circ}\text{C}$ . Transmission electron microscopy (TEM) experiments were performed on HITACHI H-7650 system. High resolution transmission electron microscopy (HRTEM) experiments were carried out on Tecnai F30 (300 KV). UV-vis absorption spectra were recorded on a Varian Cary 300 absorption spectrophotometer. A light incubator used to simulate room light for the photoreduction is a SaFe light incubator system of PGX-250B (Ningbo; the illuminance was set to be 8000 lux in all irradiation experiments, and temperature was kept to be at  $25\text{ }^{\circ}\text{C}$ ). The samples of irradiated BAs- $\text{Ag}^+$  and BAs- $\text{Au}^{3+}$  hydrogels or solutions for FESEM, TEM, and HRTEM characterizations were corresponding BAs- $\text{Ag}^+$  and BAs- $\text{Au}^{3+}$  hydrogels or solutions under irradiation of the light incubator for 24 h. Rheological experiments were performed with an AR 2000 rheometer (TA Instruments) using a Peltier plate with a diameter of 40 mm.

## Gel preparation and rheology

Gel preparation:

BAs- $\text{Ag}^+$  systems: 2 equivalents of BAs and 1 equivalent of  $\text{AgNO}_3$  were dissolved in pure water of a certain volume, respectively. Two solutions were mixed, leading to the formation of BAs- $\text{Ag}^+$  hydrogel or solution systems of various BAs- $\text{Ag}^+$  concentrations.

BAs- $\text{Au}^{3+}$  systems: Two solutions, BAs solution of certain concentration and 0.02428 M  $\text{HAuCl}_4$  stock solution, were mixed by certain volumes, resulting in the formation of BAs- $\text{Au}^{3+}$  hydrogel or solution systems of various BAs- $\text{Au}^{3+}$  concentrations.

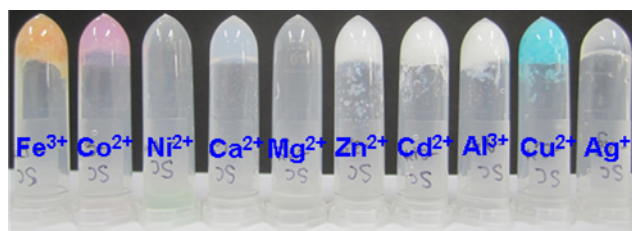
Photoreduction: All irradiated samples were carefully and uniformly placed in a light

incubator used to simulate room light for photoreduction (a SaFe light incubator system of PGX-250B, and temperature was kept to be 25 °C and illuminance was set to be 8000 Lux). Samples were taken to test at different time interval.

Rheological experiments were conducted as follows:<sup>S1</sup> the samples of rheological experiments were prepared in cylindrical sample vials with the bottle neck removed so as to minimize pre-shear. The as-prepared gels were carefully loaded onto a stainless steel plate of 40 mm diameter of an AR 2000 Rheometer (TA Instruments). All tests were run at a gap of 1 mm between two parallel plates and 1 Hz oscillation frequency. The temperature of the rheometer system was kept to be at 30 °C.

#### **References:**

**S1:** M.-O. M. Piepenbrock, N. Clarke and J. W. Steed, *Soft Matter*, 2011, **7**, 2412.



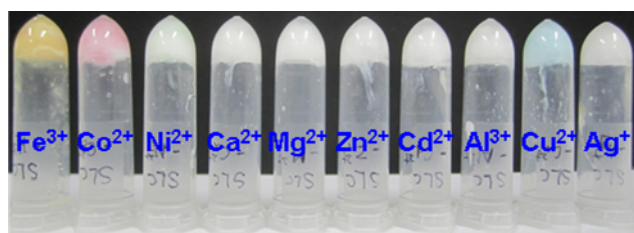
**Fig. S1** Photographs of SC-M<sup>n+</sup> hydrogel or solution systems (100 mM SC and 50 mM M<sup>n+</sup>)



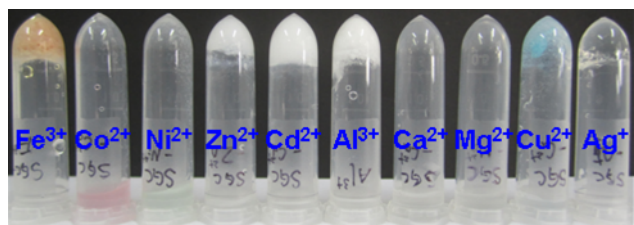
**Fig. S2** Photographs of SDOC-M<sup>n+</sup> hydrogel or solution systems (100 mM SDOC and 50 mM M<sup>n+</sup>)



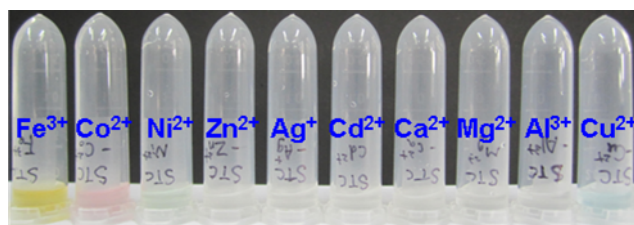
**Fig. S3** Photographs of SCDOC-M<sup>n+</sup> hydrogel or solution systems (100 mM SCDOC and 50 mM M<sup>n+</sup>)



**Fig. S4** Photographs of SLC-M<sup>n+</sup> hydrogel systems (20 mM SLC and 10 mM M<sup>n+</sup>)



**Fig. S5** Photographs of SGC-M<sup>n+</sup> hydrogel or solution systems (100 mM SGC and 50 mM M<sup>n+</sup>)



**Fig. S6** Photographs of STC-M<sup>n+</sup> solution systems (100 mM STC and 50 mM M<sup>n+</sup>)

**Table S1:** Effect of molar ratio of SC to Au<sup>3+</sup> on the gelation and on the formation of Au NPs of SC-Au<sup>3+</sup> system<sup>a</sup>

adding V <sub>H<sub>Au</sub>Cl<sub>4</sub></sub> / μL <sup>a</sup>	n <sub>SC</sub> / n <sub>Au<sup>3+</sup></sub>	gelation, Y/N <sup>a</sup>	forming Au NPs, Y/N <sup>a</sup>
10	82.4:1	N	Y
20	42.1:1	N	Y
30	27.5:1	N	Y
70	11.8:1	N	Y
80	10.3:1	N	Y
90	9.2:1	Y (partial gel)	Y
100	8.2:1	Y (partial gel)	Y
110	7.5:1	Y	Y
120	6.9:1	Y	Y
130	6.3:1	Y	Y
140	5.9:1	Y	Y
150	5.5:1	Y	Y
160	5.2:1	Y	N
200	4.1:1	Y	N

<sup>a</sup> The concentration of SC is 100 mM and the volume of SC solution is 200 μL; the concentration of stock Au<sup>3+</sup> solution is 24.3 mM; “Y/N” represents “Yes or No”.

**Table S2:** Effect of molar ratio of SDOC to Au<sup>3+</sup> on the gelation and on the formation of Au NPs of SDOC-Au<sup>3+</sup> system<sup>a</sup>

adding V <sub>H<sub>Au</sub>Cl<sub>4</sub></sub> / μL <sup>a</sup>	n <sub>SDOC</sub> / n <sub>Au<sup>3+</sup></sub>	gelation, Y/N <sup>a</sup>	forming Au NPs, Y/N <sup>a</sup>
10	82.4:1	N	Y
20	42.1:1	N	Y
30	27.5:1	N	Y
40	20.6:1	Y	Y
50	16.5:1	Y	Y
60	13.7:1	Y	Y
70	11.8:1	Y	Y
80	10.3:1	Y	N
90	9.2:1	Y	N
100	8.2:1	Y	N

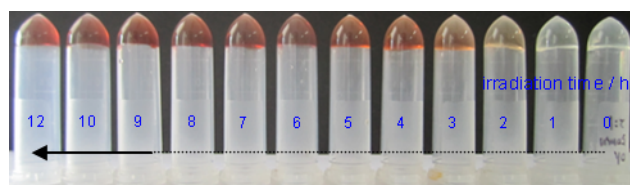
<sup>a</sup> The concentration of SDOC is 100 mM and the volume of SDOC solution is 200 μL; the concentration of stock Au<sup>3+</sup> solution is 24.3 mM; “Y/N” represents “Yes or No”.

**Table S3:** Effect of molar ratio of SLC to Au<sup>3+</sup> on the gelation and on the formation of Au NPs of SLC-Au<sup>3+</sup> system <sup>a</sup>

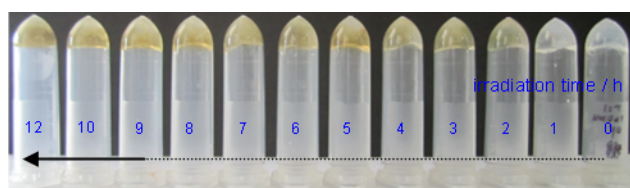
adding V <sub>H<sub>Au</sub>Cl<sub>4</sub></sub> / μL <sup>a</sup>	n <sub>SLC</sub> / n <sub>Au<sup>3+</sup></sub>	Gelation, Y/N <sup>a</sup>	forming Au NPs, Y/N <sup>a</sup>
10	42.1:1	N	Y
20	20.6:1	N	Y
30	13.7:1	N	Y
40	10.3:1	Y	Y
50	8.2:1	Y	Y
60	6.9:1	Y	Y
70	5.9:1	Y	Y
80	5.2:1	Y	N
90	4.6:1	Y	N
100	4.1:1	Y	N

<sup>a</sup> The concentration of SLC is 25 mM and the volume of SLC solution is 200 μL; the concentration of stock Au<sup>3+</sup> solution is 24.3 mM; “Y/N” represents “Yes or No”.

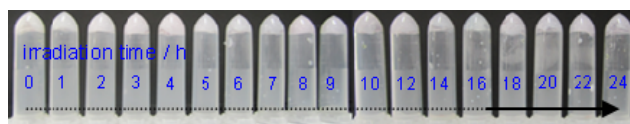




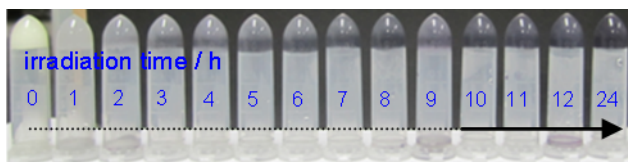
**Fig. S7** Photographs of color change of the SGC-Ag<sup>+</sup> supramolecular hydrogel under irradiation of the controllable light incubator with increasing irradiation time (from 0 to 12 h). SGC concentration is 100 mM, and Ag<sup>+</sup> concentration is 50 mM.



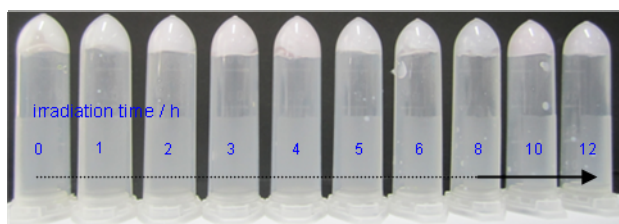
**Fig. S8** Photographs of color change of the SCDOC-Ag<sup>+</sup> supramolecular hydrogel under irradiation of the controllable light incubator with increasing irradiation time (from 0 to 12 h). SCDOC concentration is 60 mM, and Ag<sup>+</sup> concentration is 30 mM.



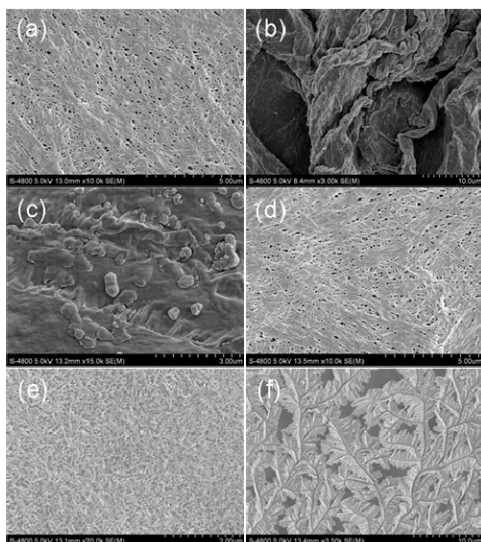
**Fig. S9** Photographs of color change of the SLC-Ag<sup>+</sup> supramolecular hydrogels under irradiation of the controllable light incubator with increasing irradiation time (from 0 to 24 h). SLC concentration is 25 mM, and Ag<sup>+</sup> concentration is 12.5 mM.



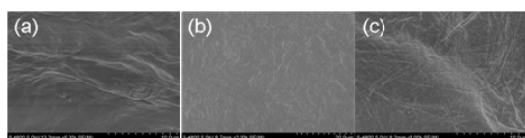
**Fig. S10** Photographs of color change of the SC-Au<sup>3+</sup> supramolecular hydrogel under irradiation of the controllable light incubator with increasing irradiation time (from 0 to 24 h). SC concentration is 100 mM, and Au<sup>3+</sup> concentration is 13.3 mM.



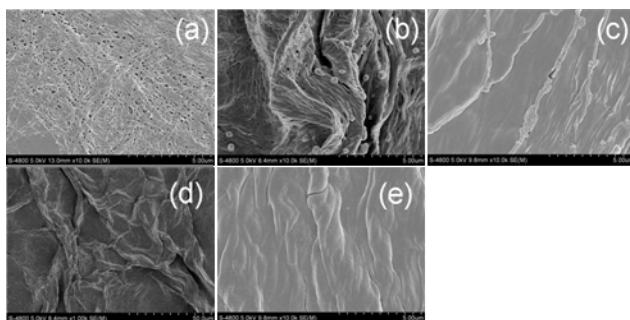
**Fig. S11** Photographs of color change of the SLC-Au<sup>3+</sup> supramolecular hydrogel under irradiation of the controllable light incubator with increasing irradiation time (from 0 to 12 h). SLC concentration is 50 mM, and Au<sup>3+</sup> concentration is 5 mM.



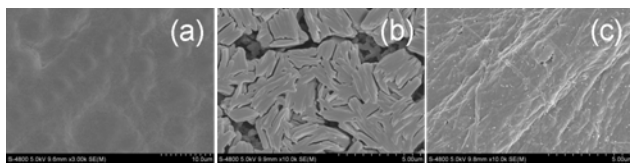
**Fig. S12** FESEM images of xerogels originating from the irradiated hydrogel (or solution) of SC-Ag<sup>+</sup> (gel, a), SDOC-Ag<sup>+</sup> (gel, b), SCDOC-Ag<sup>+</sup> (gel, c), SLC-Ag<sup>+</sup> (gel, d), SGC-Ag<sup>+</sup> (gel, e), and STC-Ag<sup>+</sup> (solution, f) systems. Scale bars for (a), (b), (c), (d), (e), and (f) are 5, 10, 3, 5, 2, and 10  $\mu\text{m}$ , respectively.



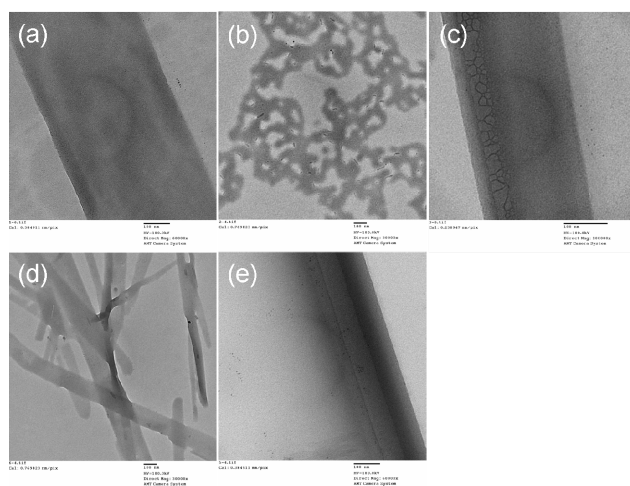
**Fig. S13** FESEM images of xerogels originating from the irradiated hydrogels of SC-Au<sup>3+</sup> (a), SDOC-Au<sup>3+</sup> (b), and SLC-Au<sup>3+</sup> (c). Scale bars for (a), (b), and (c) are 10, 20, and 10  $\mu\text{m}$ , respectively.



**Fig. S14** FESEM images of xerogels originating from the unirradiated BAs-Ag<sup>+</sup> hydrogel of SC-Ag<sup>+</sup>(a), SDOC-Ag<sup>+</sup>(b), SCDOC-Ag<sup>+</sup>(c), SLC-Ag<sup>+</sup> (d), SGC-Ag<sup>+</sup> (e) systems. Scale bars for (a), (b), (c), (d), and (e) are 5  $\mu\text{m}$ , 5  $\mu\text{m}$ , 5  $\mu\text{m}$ , 50  $\mu\text{m}$ , and 5  $\mu\text{m}$ , respectively.



**Fig. S15** FESEM images of xerogels originating from the unirradiated BAs-Au<sup>3+</sup> hydrogel of (a) SC-Au<sup>3+</sup>, (b) SDOC-Au<sup>3+</sup>, (c) SLC-Au<sup>3+</sup> systems. Scale bars for (a), (b), and (c) are 10  $\mu\text{m}$ , 5  $\mu\text{m}$ , and 5  $\mu\text{m}$ , respectively.



**Fig. S16** TEM images of unirradiated BAs-Ag<sup>+</sup> hydrogel or solution systems. (a) SC-Ag<sup>+</sup>; (b) SDOC-Ag<sup>+</sup>; (c) SCDOC-Ag<sup>+</sup>; (d) SGC-Ag<sup>+</sup>; (e) STC-Ag<sup>+</sup>.

