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 °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 °C). The samples of irradiated BAs-Ag⁺ and BAs-Au³⁺ hydrogels or solutions for FESEM, TEM, and HRTEM characterizations were corresponding BAs-Ag⁺ and BAs-Au³⁺ 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-Ag⁺ systems: 2 equivalents of BAs and 1 equivalent of AgNO₃ were dissolved in pure water of a certain volume, respectively. Two solutions were mixed, leading to the formation of BAs-Ag⁺ hydrogel or solution systems of various BAs-Ag⁺ concentrations.

BAs-Au³⁺ systems: Two solutions, BAs solution of certain concentration and 0.02428 M HAuCl₄ stock solution, were mixed by certain volumes, resulting in the formation of BAs-Au³⁺ hydrogel or solution systems of various BAs-Au³⁺ 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:\textsuperscript{S1} 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:

Fig. S1 Photographs of SC-M$^{n+}$ hydrogel or solution systems (100 mM SC and 50 mM M$^{n+}$)

Fig. S2 Photographs of SDOC-M$^{n+}$ hydrogel or solution systems (100 mM SDOC and 50 mM M$^{n+}$)

Fig. S3 Photographs of SCDOC-M$^{n+}$ hydrogel or solution systems (100 mM SCDOC and 50 mM M$^{n+}$)
**Fig. S4** Photographs of SLC-\textsuperscript{M} hydrogel systems (20 mM SLC and 10 mM M\textsuperscript{+})

**Fig. S5** Photographs of SGC-\textsuperscript{M} hydrogel or solution systems (100 mM SGC and 50 mM M\textsuperscript{+})

**Fig. S6** Photographs of STC-\textsuperscript{M} solution systems (100 mM STC and 50 mM M\textsuperscript{+})
Table S1: Effect of molar ratio of SC to Au\(^{3+}\) on the gelation and on the formation of Au NPs of SC-Au\(^{3+}\) system

<table>
<thead>
<tr>
<th>adding (V_{\text{HAuCl}_4} / \mu\text{L})(^a)</th>
<th>(n_{\text{SC}} / n_{\text{Au}^{3+}})</th>
<th>gelation, Y/N(^a)</th>
<th>forming Au NPs, Y/N(^a)</th>
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<tbody>
<tr>
<td>10</td>
<td>82.4:1</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>20</td>
<td>42.1:1</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>30</td>
<td>27.5:1</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>70</td>
<td>11.8:1</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>80</td>
<td>10.3:1</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>90</td>
<td>9.2:1</td>
<td>Y (partial gel)</td>
<td>Y</td>
</tr>
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<td>8.2:1</td>
<td>Y (partial gel)</td>
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<td>7.5:1</td>
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<td>120</td>
<td>6.9:1</td>
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<td>Y</td>
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<tr>
<td>130</td>
<td>6.3:1</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>140</td>
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<td>Y</td>
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<td>5.5:1</td>
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<td>160</td>
<td>5.2:1</td>
<td>Y</td>
<td>N</td>
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<tr>
<td>200</td>
<td>4.1:1</td>
<td>Y</td>
<td>N</td>
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</table>

\(^a\) The concentration of SC is 100 mM and the volume of SC solution is 200 \(\mu\text{L}\); the concentration of stock Au\(^{3+}\) solution is 24.3 mM; “Y/N” represents “Yes or No”.

Electronic Supplementary Material (ESI) for Soft Matter
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Table S2: Effect of molar ratio of SDOC to Au\(^{3+}\) on the gelation and on the formation of Au NPs of SDOC-Au\(^{3+}\) system\(^a\)

<table>
<thead>
<tr>
<th>adding (V_{\text{HAuCl}_4} / \mu\text{L})(^a)</th>
<th>(n_{\text{SDOC}} / n_{\text{Au}^{3+}})</th>
<th>gelation, Y/N(^a)</th>
<th>forming Au NPs, Y/N(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>82.4:1</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
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<td>42.1:1</td>
<td>N</td>
<td>Y</td>
</tr>
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<td>Y</td>
</tr>
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<td>40</td>
<td>20.6:1</td>
<td>Y</td>
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<td>Y</td>
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<td>100</td>
<td>8.2:1</td>
<td>Y</td>
<td>N</td>
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\(^a\) The concentration of SDOC is 100 mM and the volume of SDOC solution is 200 \(\mu\text{L}\); the concentration of stock Au\(^{3+}\) solution is 24.3 mM; “Y/N” represents “Yes or No”. 

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Table S3: Effect of molar ratio of SLC to \( \text{Au}^{3+} \) on the gelation and on the formation of Au NPs of SLC-Au\(^{3+}\) system\(^a\)

<table>
<thead>
<tr>
<th>adding ( V_{\text{HaAuCl}_4} / \mu\text{L}^a )</th>
<th>( n_{\text{SLC}} / n_{\text{Au}^{3+}} )</th>
<th>Gelation, Y/N(^a)</th>
<th>forming Au NPs, Y/N(^a)</th>
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<td>N</td>
<td>Y</td>
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<td>20.6:1</td>
<td>N</td>
<td>Y</td>
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<td>13.7:1</td>
<td>N</td>
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<td>10.3:1</td>
<td>Y</td>
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<td>50</td>
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<td>5.9:1</td>
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<td>5.2:1</td>
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<td>90</td>
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<td>100</td>
<td>4.1:1</td>
<td>Y</td>
<td>N</td>
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</table>

\(^a\) The concentration of SLC is 25 mM and the volume of SLC solution is 200 \( \mu\text{L} \); the concentration of stock \( \text{Au}^{3+} \) solution is 24.3 mM; “Y/N” represents “Yes or No”.
**Fig. S7** Photographs of color change of the SGC-Ag\(^+\) 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\(^+\) concentration is 50 mM.

**Fig. S8** Photographs of color change of the SCDOC-Ag\(^+\) 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\(^+\) concentration is 30 mM.

**Fig. S9** Photographs of color change of the SLC-Ag\(^+\) 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\(^+\) concentration is 12.5 mM.
**Fig. S10** Photographs of color change of the SC-Au$^{3+}$ 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$^{3+}$ concentration is 13.3 mM.

**Fig. S11** Photographs of color change of the SLC-Au$^{3+}$ 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$^{3+}$ concentration is 5 mM.
**Fig. S12** FESEM images of xerogels originating from the irradiated hydrogel (or solution) of SC-Ag⁺ (gel, a), SDOC-Ag⁺ (gel, b), SCDOC-Ag⁺ (gel, c), SLC-Ag⁺ (gel, d), SGC-Ag⁺ (gel, e), and STC-Ag⁺ (solution, f) systems. Scale bars for (a), (b), (c), (d), (e), and (f) are 5, 10, 3, 5, 2, and 10 μm, respectively.

**Fig. S13** FESEM images of xerogels originating from the irradiated hydrogels of SC-Au³⁺ (a), SDOC-Au³⁺ (b), and SLC-Au³⁺ (c). Scale bars for (a), (b), and (c) are 10, 20, and 10 μm, respectively.
**Fig. S14** FESEM images of xerogels originating from the unirradiated BAs-Ag$^+$ hydrogel of SC-Ag$^+$ (a), SDOC-Ag$^+$ (b), SCDOC-Ag$^+$ (c), SLC-Ag$^+$ (d), SGC-Ag$^+$ (e) systems. Scale bars for (a), (b), (c), (d), and (e) are 5 $\mu$m, 5 $\mu$m, 5 $\mu$m, 50 $\mu$m, and 5 $\mu$m, respectively.

**Fig. S15** FESEM images of xerogels originating from the unirradiated BAs-Au$^{3+}$ hydrogel of (a) SC-Au$^{3+}$, (b) SDOC-Au$^{3+}$, (c) SLC-Au$^{3+}$ systems. Scale bars for (a), (b), and (c) are 10 $\mu$m, 5 $\mu$m, and 5 $\mu$m, respectively.
Fig. S16 TEM images of unirradiated BAs-Ag⁺ hydrogel or solution systems. (a) SC-Ag⁺; (b) SDOC-Ag⁺; (c) SCDOC-Ag⁺; (d) SGC-Ag⁺; (e) STC-Ag⁺.