Supporting Information

Synthesis of Janus Au@BCP nanoparticles via UV light-initiated RAFT polymerization-induced self-assembly

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Experimental Section

Materials
Hydrogen tetrachloroaurate trihydrate (99.9 %), sodium citrate trisodium dihydrate were purchased from Aladdin. 4-Vinylpyridine (4VP) was distilled under vacuum after dried with CaH₂. Styrene was passed through a column of activated basic alumina prior to use. AIBN was recrystallized from methanol twice and stored at 3°C prior to use. S-1-dodecyl-S-(α,α’-dimethyl-α”-acetic acid) trithiocarbonate (DDMAT) was synthesized according to the literature reported by Lai et al. Methanol was distilled before use. Other reagents were used as received. The UV light source is a UV nail gel curing lamp (λ_{max} = 365 nm) which equipped with 4×9 W bulbs. The intensity of the light was measured as 2.50 mW cm⁻² by a UV radiometer.

Synthesis of P4VP-CTA
The P4VP-CTA was prepared by thermal initiated RAFT solution polymerization in THF at 80 °C. A typical polymerization procedure is described as follows: 4VP (4.24 g, 40 mmol), DDMAT (72 mg, 0.2 mmol) and AIBN (6.40 mg, 0.04 mmol) were dissolved in 10 mL THF. The solution was degassed by bubbling with nitrogen for 30 min, and then placed in a preheated oil bath at 80 °C. The polymerization was stopped by immersing in liquid nitrogen and exposing to air after 6 h. The resulting polymer was purified by precipitation into excess n-hexane for three times and dried under vacuum at 40 °C overnight. The polymer was characterized by \(^1\)H NMR and GPC.

Synthesis of citrate-capped AuNPs
The AuNPs was prepared by sodium citrate reduction of HAuCl₄. All glassware was cleaned with aqua regia, repeatedly washed with nanopure water and dried before use. In a typical experiment, HAuCl₄ aqueous solution (0.246 mL, 1.22 × 10⁻⁴ mol) and a sodium citrate aqueous solution (3 mL, 4.35 × 10⁻⁴ mol) were added into 100 mL boiling water under vigorously stirring in a 250 mL flask. The mixture was refluxed for 30 minutes until the solution reached a wine red color. After cooled to room temperature, the colloidal suspension was stored at room temperature. The TEM results were shown in Figure S2.

Preparation of polymer-tethered Au@P4VP
The method is modified by the report in literature. A 30 mL of the original citrate-capped AuNPs were centrifuged (8500 rpm, 30 min) to remove the excess sodium citrate. The concentrated AuNPs were redispersed in 2 mL H₂O. Then, a mixture of 25 mg P4VP-CTA dissolved in 15 mL methanol was added to the concentrated AuNPs under sonification at room temperature for 1 h. After incubated for 24 h, the solution was concentrated by centrifugation at 10000 rpm for 30 min. The centrifugation–redispersion procedure was repeated twice in order to exchange the solvent with methanol. Finally, the dispersion was concentrated to 2 mL and stored in refrigerator before use.
Preparation of Janus Au@P4VP-b-PS nanoparticles

In UV light-initiated RAFT polymerization, the glass bottle charged with reaction mixture was placed in a UV curing lamp, which was equipped with a magnetic stirring apparatus and a blowing air device for keeping constant temperature. The reaction mixture was deoxygenated by three freeze-pump-thaw cycles and filled with N₂ gas. Then the mixture was irradiated under UV irradiation. A typical experiment was conducted as follows: Au@P4VP (200 μL), P4VP (4.0 mg, 5.88 × 10⁻⁴ mmol), styrene (0.909 g, 8.7 mmol), AIBN (0.02 mg, 1.21 × 10⁻⁴ mmol) with a molar ratio of P4VP/St/AIBN = 5:14800:1 were dissolved in 3.2 mL methanol. The polymerization was conducted under UV light for 9 h and then stopped by exposing to air.

For the kinetics study, the hybridization process of Janus Au@P4VP-b-PS via UV light-initiated RAFT PISA was monitored by TEM, in situ UV-vis spectroscopy and in situ ¹H NMR spectroscopy. The evolution of Janus Au@BCPs during photo-polymerization was recorded by TEM observation at timed intervals (e.g., 1 h, 3 h, 4 h, 5 h, 7 h and 9 h). The evolution of the UV-vis absorption spectra of the mixture with the molar ratio of P4VP/St/AIBN = 5:14800:1 in methanol were recorded after the solution exposed to the UV light at different time intervals. The evolution of ¹H NMR spectra of the mixture in d₄-methanol during the polymerization was recorded at different time intervals after a NMR tube exposed to the UV light.

Characterizations

The ¹H NMR spectra were recorded in CDCl₃ using trimethylsilane as an internal reference at room temperature on a Bruker AVANCE III 400 MHz NMR spectrometer in 5 mm diameter tubes. The number average molecular weight (Mₙ) and molecular weight distributions (Mₚ/Mₙ) were assessed by Waters 1515 GPC equipped with refractive index detector at 40 °C. DMF was used as eluent at a flow rate of 1.0 mL/min. TEM images were performed with a JEOL JEM-2100F microscope at an accelerating voltage of 200 kV. SEM images were captured on a S4800 at an accelerating of 5 kV. The UV-vis absorption spectra were conducted on a Perkin Elmer Lambda 950 with wavelength from 300 nm to 800 nm. The XPS measurements were carried out using an XPS Kratos Axis Ultra instrument. The power was 120 W and the X-ray spot size was set to 700×300 μm. The XPS spectra were calibrated relative to the reference energy value of the C 1s core level at 284.8 eV.
Data analysis

**Figure S1.** The GPC curve of P4VP in DMF elution.

**Figure S2.** TEM image of citrate-capped AuNPs.
**Table S1.** Experimental recipe using citrate-capped AuNPs as seeds to prepare hybrid nanoparticles by UV-light initiated RAFT PISA.

| entry | Au@citrate$^a$ | P4VP  | St    | AIBN  | methanol |
|-------|----------------|-------|-------|-------|----------|
| 1     | 200 μL         | 4 mg  | 0.1 mL| 0.02 mg| 3.2 mL   |

$^a$The citrate-decorated AuNPs is concentrated in water and stored at 5 °C before use. Experimental condition: UV light intensity: $I_{365}$ nm = 2.50 mW cm$^{-2}$, irradiation time: 9 h, 25 °C.

**Figure S3.** SEM image of nanoparticles obtained using citrate-capped AuNPs as seeds in methanol.
Figure S4. The evolution of UV-vis spectra of Au@P4VP upon UV irradiation at different times in methanol.

Table S2. Experimental recipes using Au@P4VP as seeds to prepare hybrid nanoparticles by UV-light initiated RAFT PISA.

| entry | Au@P4VP<sup>a</sup> | P4VP | St | AIBN | methanol |
|-------|---------------------|------|----|------|----------|
| 1     | 200 μL              | 4 mg | 0.1 mL | 0.02 mg | 3.2 mL  |

<sup>a</sup> The Au@P4VP is dispersed in methanol and stored at 5 °C before use. Experimental condition: UV light intensity: $I_{365 \text{ nm}} = 2.50 \text{ mW cm}^{-2}$, irradiation time: 9 h, 25 °C.
Figure S5. TEM image of Janus Au@P4VP-\textit{b}-PS nanoparticles obtained using polymer-tethered Au@P4VP as seeds in methanol after 9 h polymerization.

Figure S6. SEM image of Janus Au@P4VP-\textit{b}-PS nanoparticles obtained using polymer-tethered Au@P4VP as seeds in methanol after 9 h polymerization. (Note: those nanoparticles which only see the micelles part is because the Au@P4VP part is displayed on the bottom side.)
Figure S7. The GPC curve of P4VP-b-PS obtained by Janus Au@BCPs in DMF elution.
Figure S8. TEM images of the intermediates obtained at different polymerization times: 1 h, 3 h, 4 h, 5 h, 7 h and 9 h.
Figure S9. The evolution of $^1$H NMR spectra during UV light-initiated RAFT PISA in $d_4$-methanol at (a) 0 h, (b) 1 h, (c) 3 h, (d) 4 h, (e) 5 h, (f) 7 h and (g) 9 h.
Table S3. Experimental recipes by tuning concentrations of Au@P4VP seeds, P4VP and styrene to prepare hybrid nanoparticles by UV-light initiated RAFT PISA.

| entry | Au@P4VP$^a$ | P4VP  | St   | AIBN  | methanol |
|-------|-------------|-------|------|-------|----------|
| 1     | 200 μL      | 5 mg  | 0.15 mL | 0.02 mg | 3.2 mL   |
| 2     | 200 μL      | 4 mg  | 0.10 mL | 0.02 mg | 3.2 mL   |
| 3     | 400 μL      | 4 mg  | 0.10 mL | 0.02 mg | 3.2 mL   |

$^a$ The Au@P4VP is concentrated in methanol and stored at 5 °C before use. Experimental condition: UV light intensity: $I_{365 \text{nm}} = 2.50 \text{ mW cm}^{-2}$, irradiation time: 9 h, 25 °C.

Figure S10. UV-vis spectra of hybrid nanoparticles obtained via UV light-initiated RAFT PISA with different recipes: (a) the mixture of Janus Au@BCPs and free micelles, (b) the bigger Janus Au@BCPs and (c) the smaller Janus Au@BCPs.
References

1. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.
2. W. M. Wan, C. Y. Hong and C. Y. Pan, *Chem Commun*, 2009, **39**, 5883-5885.
3. H. Wang, X. Song, C. Liu, J. He, W. H. Chong and H. Chen, *ACS Nano*, 2014, **8**, 8063-8073.
4. A. M. Percebom, J. J. Giner-Casares, N. Claes, S. Bals, W. Loh and L. M. Liz-Marzán, *Chem Commun*, 2016, **52**, 4278-4281.
5. N. Guarrotxena, O. Garcia and I. Quijada-Garrido, *Scientific reports*, 2018, **8**, 5721.