

Electronic Supplementary Information (ESI)

Catechol-Driven Self-Assembly to Fabricate Highly Ordered Glycoadjuvant Patterns

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Materials.

Chloroauric acid hydrated ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) was purchased from Shanghai Shi Wu Chemical Reagent Science and Technology Co, LTD. Silicon wafers ($375 \pm 20 \mu\text{m}$, $100 \pm 0.3 \text{ mm}$, p-doped, (100)-oriented) were purchased from Guangzhou Semiconductor Materials Laboratory. FeCl_3 (AR) and trisodium citrate dehydrate (99%) was purchased from Shanghai Macklin Biochemical Co, LTD. CTAB@GNRs was purchased from Guangzhou Clusterbiophoton Biotechnology Co, LTD. 2-Cyanoprop-2-yl- α -dithionaphthalate (CPDN),^[S1] N-3,4-dihydroxybenzenethyl methacrylamide (DMA)^[S2] and 2-(methacrylamido) glucopyranose (MAG)^[S3] were synthesized according to previously reported method. PMMA template was provided by Prof. Zhijun Hu laboratory.

Characterization.

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the obtained glycopolymer was determined on an Agilent PL-GPC 50 gel permeation chromatography (GPC) equipped with a refractive index detector, using a $5 \mu\text{m}$ Guard, $5 \mu\text{m}$ MIXED-D column with PMMA standard samples and 0.05 mol L^{-1} lithium bromide solution in DMF used as the eluent operated at $50 \text{ }^\circ\text{C}$. The ^1H NMR spectra of the glycopolymer were recorded on an INOVA 300 MHz nuclear magnetic

resonance instrument using D₂O as the solvent and tetramethylsilane (TMS) as an internal standard. Ultraviolet-visible (UV-visible) absorption spectra were recorded on a Shimadzu (Kyoto, Japan) UV-3600. The size and zeta potential of gold nanoparticles (AuNPs) was measured using Dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern Instruments Ltd). Transmission Electron Microscope (TEM, FEI Tecnai G-20) operating at 200 KV. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 6700 infrared spectrophotometer (Thermo scientific, U.S.A.) equipped with an ATR accessory (ZnSe crystal, 45°). Morphology and energy dispersive X-ray spectroscopy of AuNPs were measured by a S4800 scanning electron microscopy (SEM, Hitachi, Japan). Patterns were observed by optical microscopy with polarized light (Leica DM2700 P, Germany). Raman spectrum were detected by a confocal Raman microscope (InVia reflex, Renishaw, U.K.).

Preparation of glycopolymer.

N-3,4-dihydroxybenzenethyl methacrylamide (DMA) and 2-deoxy-2-(methacrylamido) glucopyranose (MAG) were prepared using our reported method. A typical process for the photopolymerization is as follows: MAG (335 mg, 1.36 mmol), DMA (150 mg, 0.68 mmol), CPDN (4.6 mg, 0.017 mmol) were added to 1.5 mL DMSO in 5 mL ampoule. After deoxidizing by argon for 15 min, the ampoule was sealed and polymerized under sunlight. At the designed time, the ampoule bottle was opened and the mixture was diluted with 2 mL THF and precipitated into 250 mL petroleum ether. The product was obtained by filtration and dried to keep constant weight under vacuum.

Preparation of glycopolymer@AuNPs.

1.5 mg glycopolymer (PDMA_{26-co}-PMAG₅₃) was dissolved in ultrapure water (4.95 mL), then the solution was added HAuCl₄·4H₂O aqueous solution (50 μL, 12.11 mg/mL) on a shaker at 25 °C ($n_{\text{catechol}}/n_{\text{HAuCl}_4} = 1.8/1$), and the resulting solution was dialysis for 48 h to remove unreacted HAuCl₄ and glycopolymer.

Preparation of glycoadjuvant@AuNPs.

1.5 mg glycopolymer (PDMA_{26-co}-PMAG₅₃) and CpG (0.3 mg) were dissolved in ultrapure water (4.95 mL), HAuCl₄·4H₂O aqueous solution (50 μL, 12.11 mg/mL) on

a shaker at 25 °C ($n_{\text{catechol}}/n_{\text{HAuCl}_4} = 1.8/1$), and the resulting solution was dialysis for 48 h.

Pre-preparation of silicon wafer.

First, cut the silicon wafer into a piece of 0.5 x 0.5 cm. Then, put silicon wafers immersing into a solution ($v_{\text{H}_2\text{SO}_4} : v_{\text{H}_2\text{O}_2} = 3/1$) and ultrasonically cleaned for 45 min, then rinse with ultrapure water to remove H_2SO_4 and H_2O_2 . Afterwards, the silicon wafers were ultrasonically cleaned in ultrapure water, ethanol, acetone and ethanol each for 20 min, and dried with argon flow.

Preparation of citrate@AuNPs.

According to the method of G Frens,^[S4] 15 nm gold nanoparticles was synthesized by trisodium citrate dihydrate. First, solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.1 mg/mL) and trisodium citrate dihydrate (10 mg/mL) was prepared. Then, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solution (100 mL) was heated to boiling, and sodium citrate (3.5 mL) was added under high stirring and keep boiling 20 min. Finally, the solution was naturally cooled to room temperature and filtered by 0.22 μm water phase filtration membrane. The obtained solution of 15 nm gold nanoparticles was stored at 4 °C in the dark.

Citrate@AuNPs and CTAB@GNRs mixed with glycopolymer.

Citrate@AuNPs (1mL) and CTAB@GNRs (1mL) were mixed with glycopolymer (0.3 mg) for 24 h at 25 °C, respectively. The molar ratio of catechol and nanoparticles is 1.8:1, which is the same as glycopolymer@AuNPs. Afterwards, the resulting solution was dialysis for 48 h.

Glycopolymer@AuNPs and Fe^{3+} ion.

FeCl_3 was added to prepared glycopolymer@AuNPs with five molar ratio ($n_{\text{catechol}}/n_{\text{Fe}^{3+}} = 1/1, 1/5, 1/10, 1/20, 10/1$), respectively. And then, the sample with the molar ratio of $n_{\text{catechol}}/n_{\text{Fe}^{3+}} = 1/1$ was chosen to monitor the size evolution.

Nanoparticles self-assembly on silicon wafers and PMMA template.

A simple evaporative self-assembly method was utilized to prepare the patterns and arrays of AuNPs. First, the prepared solution of glycoadjuvant@AuNPs was diluted by 10 and 50 times, respectively. Then, a drop of prepared nanoparticles solution (10 μL) was dripped onto silicon surface and kept stationary under dry air atmosphere for

24 h to evaporate the water at 25 °C. Then, the patterns were formed on silicon surface. And a drop of glycoadjuvant@AuNPs solution (10 μL) was dripped onto PMMA template and kept stationary under dry air atmosphere at 25 °C for 24 h to evaporate the water.

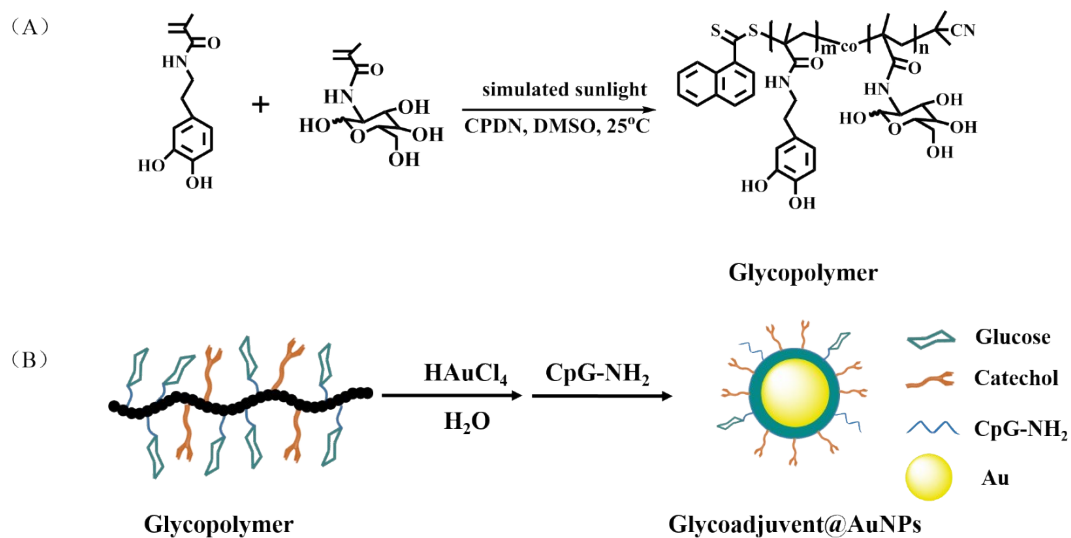


Figure S1. (A) Preparation of glycopolymer by RAFT polymerization, (B) Preparation of glycoadjuvant@AuNPs.

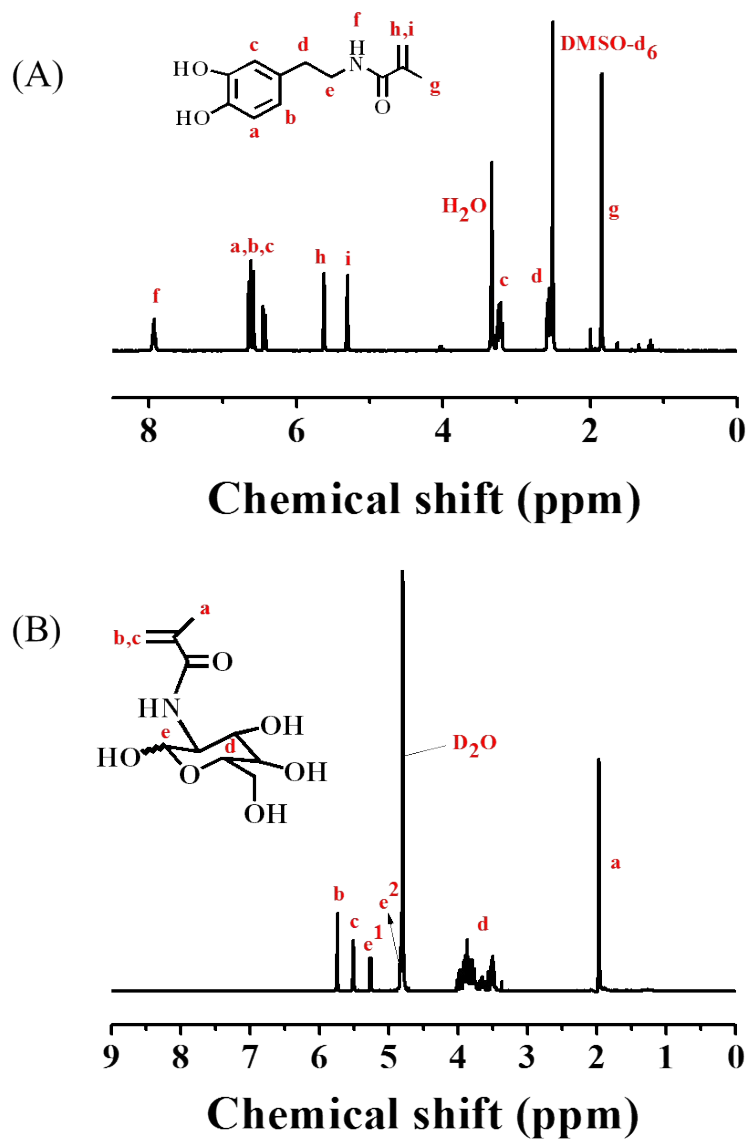
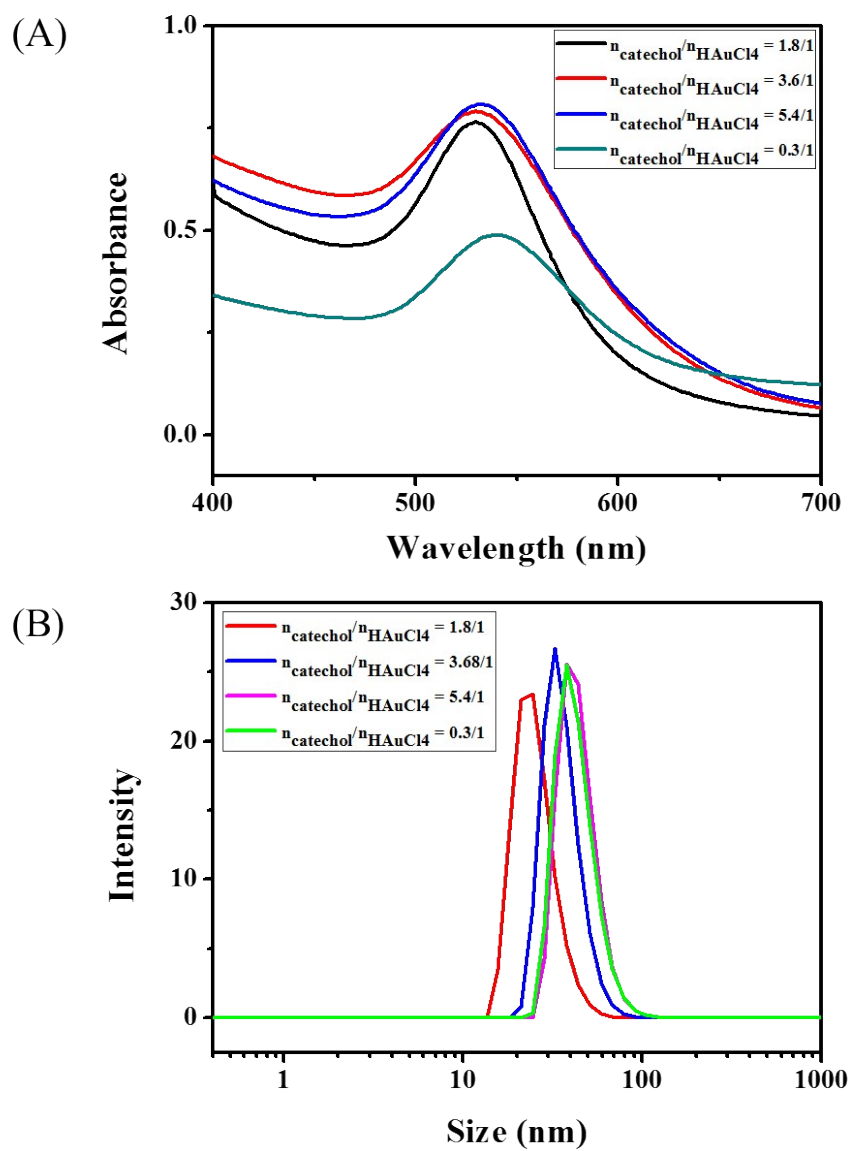


Figure S2. The ^1H -NMR spectrum of the two monomers, (A) DMA, (B) MAG.



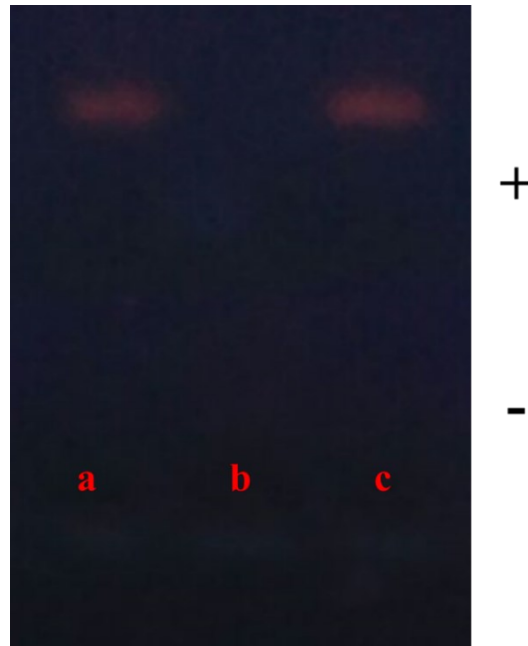


Figure S4. Characterization of glycoadjuvant@AuNPs by agarose gel electrophoresis, (a) CpG, (b) glycoadjuvant@AuNPs, (c) mixture of CpG and glycopolymer@AuNPs.

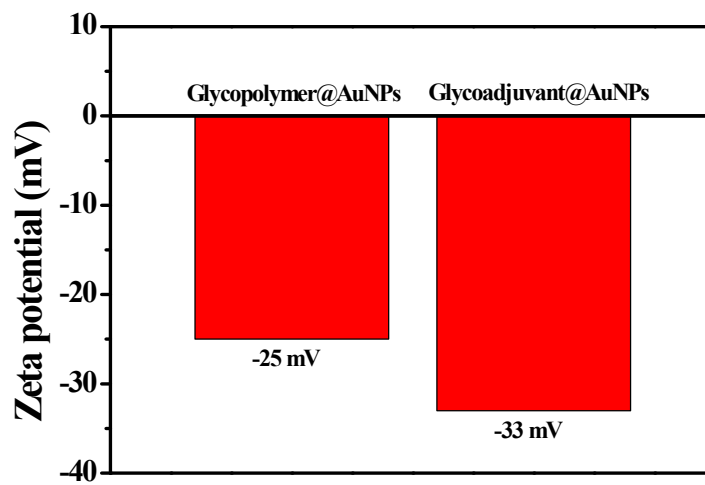


Figure S5. Zeta potential values of glycopolymer@AuNPs and glycoadjuvant@AuNPs.

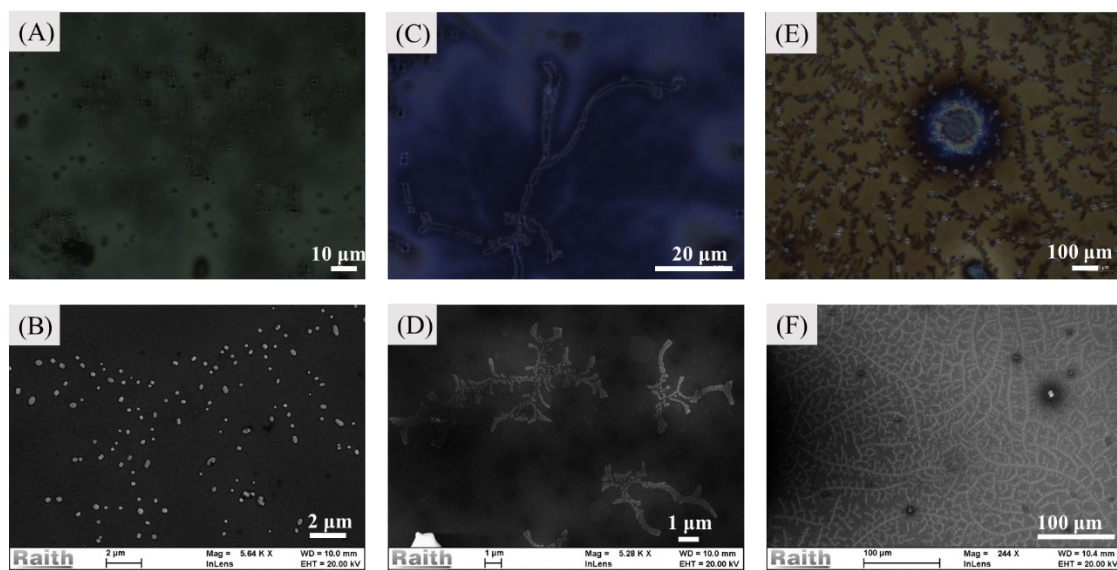


Figure S6. Glycoadjuvant@AuNPs self-assemble at different concentrations. (A) Polarized image, (B) SEM image of glycoadjuvant@AuNPs. Concentration of AuNPs is 0.00116 mg/mL. (C) Polarized image, (D) SEM image of glycoadjuvant@AuNPs. Concentration of AuNPs is 0.0058 mg/mL. (E) Polarized image, (F) SEM image of glycoadjuvant@AuNPs. Concentration of AuNPs is 0.058 mg/mL. Solvent evaporation temperature is 25 °C.

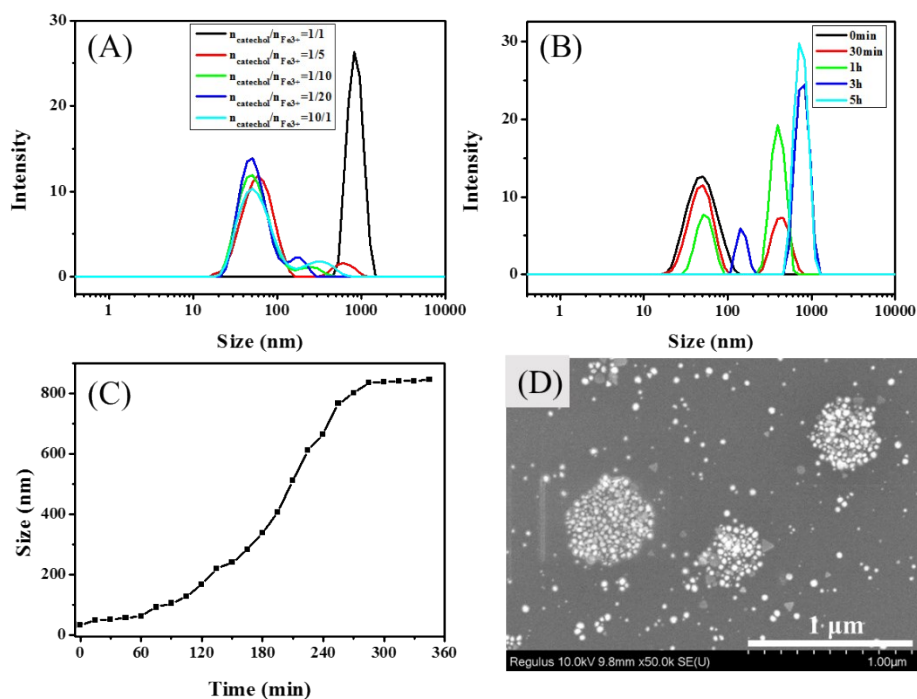


Figure S7. Glycopolymer@AuNPs was mixed with Fe^{3+} . (A) The size of the nanoparticles with five different molar ratios. (B) The dynamic size monitoring of

nanoparticles ($n_{\text{catechol}}/n_{\text{Fe}^{3+}} = 1/1$). (C) The curve of size evolution of nanoparticles ($n_{\text{catechol}}/n_{\text{Fe}^{3+}} = 1/1$) measured by dynamic light scattering. (D) SEM image of nanoparticles ($n_{\text{catechol}}/n_{\text{Fe}^{3+}} = 1/1$) self-assembly on silicon surface. Concentration of AuNPs is 0.058 mg/mL and solvent evaporation temperature is 25 °C.

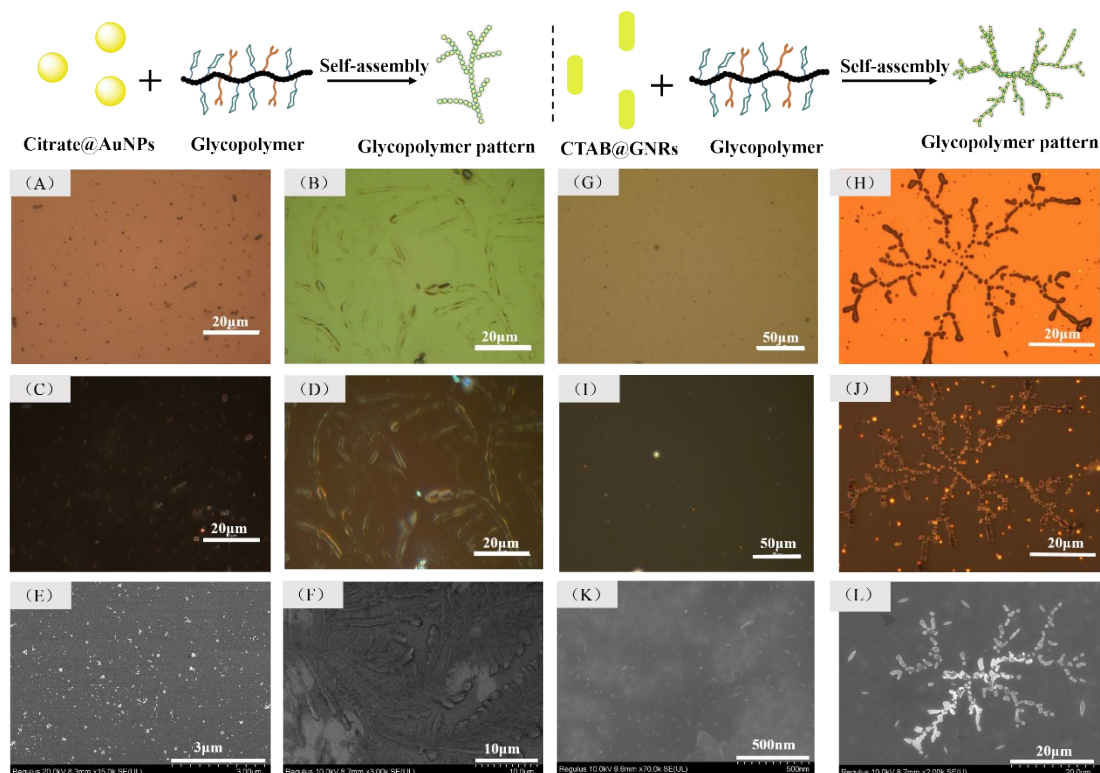


Figure S8. Upper part of the figure is the schematic diagram of citrate@AuNPs and CTAB@AuNPs with the assistance of catechol-containing glycopolymer to form glycopolymer patterns. The OM, POM and SEM were used to monitor the morphology of pattern. Optical images of (A), (B), (G) and (H); POM images of (C), (D), (I) and (J); SEM images of (E), (F), (K) and (L); Concentration of all AuNPs is 0.058 mg/mL, initial concentration of glycopolymer is 0.3 mg/mL and solvent evaporation temperature is 25 °C.

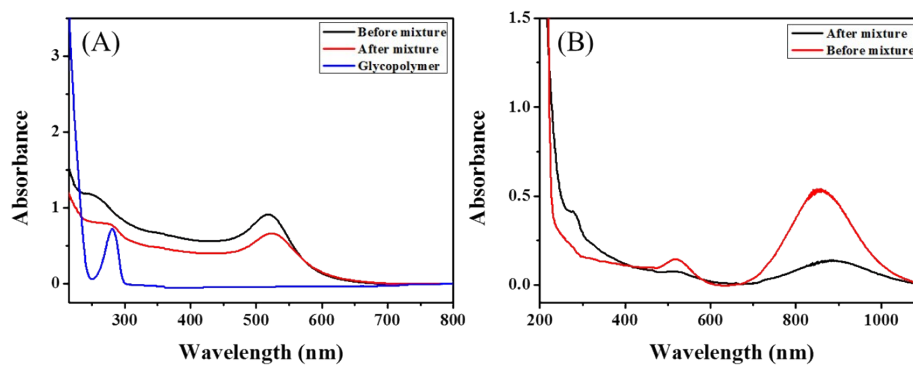


Figure S9. UV-visible absorption spectra. (A) Citrate@AuNPs before and after mixing with catechol-containing glycopolymer. (B) CTAB@GNRs before and after mixing with catechol-containing glycopolymer.

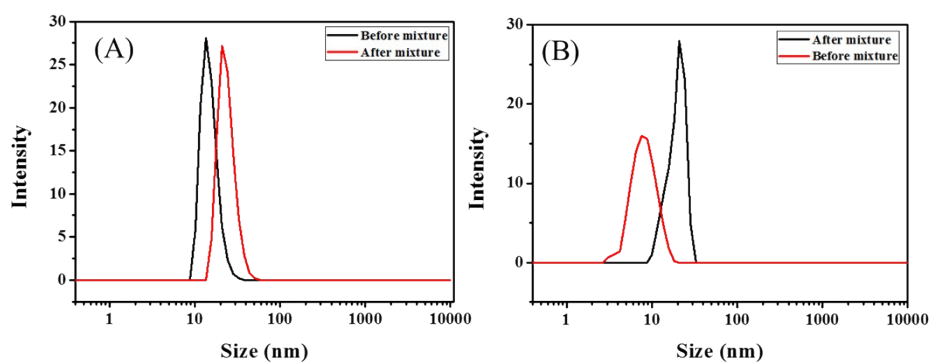


Figure S10. Size of (A) citrate@AuNPs before and after mixing with catechol-containing glycopolymer, (B) CTAB@GNRs before and after mixing with catechol-containing glycopolymer.

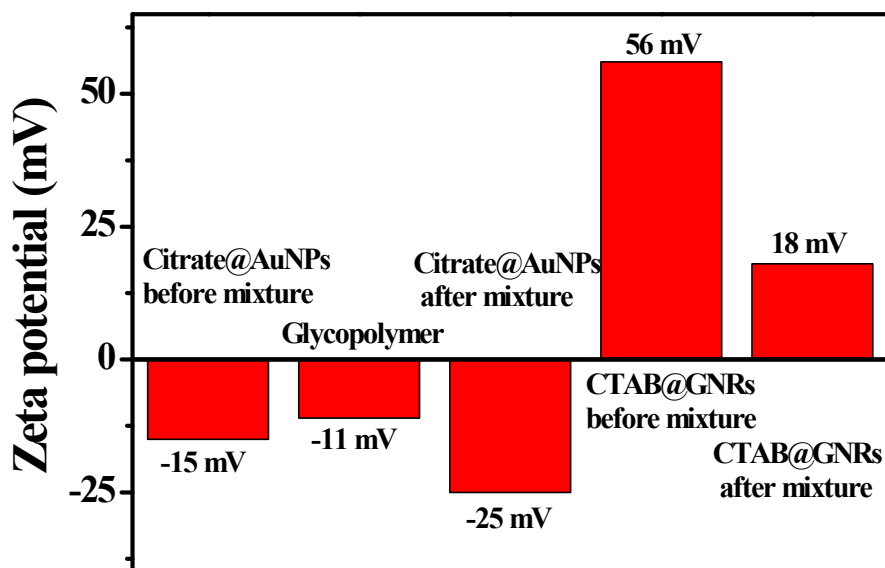


Figure S11. Zeta potential values of glycopolymer, citrate@AuNPs before and after mixing with catechol-containing glycopolymer, and CTAB@GNRs before and after mixing with catechol-containing glycopolymer.

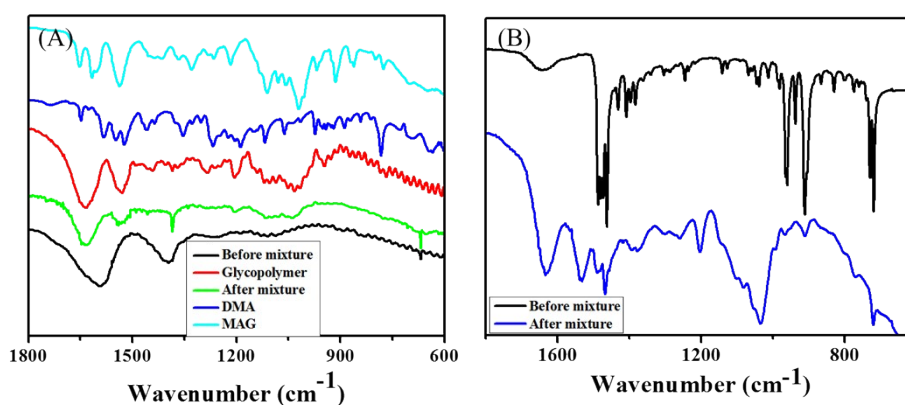


Figure S12. IR spectra. (A) DMA, MAG, glycopolymer, citrate@AuNPs before and after mixing with catechol-containing glycopolymer. (B) CTAB@GNRs before and after mixing with catechol-containing glycopolymer.

Table S1. Position of SERS peaks of dopamine and glucose on the glycopolymer@AuNPs self-assembled on silicon wafer.

	dopamine	glucose
1695 cm ⁻¹	ν_{C-C} ^[S5]	
1328 cm ⁻¹	ν_3 ^[S6]	ω_{CH_2} ^[S7]
1064 cm ⁻¹		ν_{C-O} ^[S7]
938 cm ⁻¹		δ_{CH} ^[S7]
601 cm ⁻¹	ω_{CH} ^[S8]	
515 cm ⁻¹		δ_{C-C-O} ^[S7]
Below 500 cm ⁻¹		endocyclic deformations ^[S9]

δ = bending mode, w = wagging mode, ν = stretching mode.

Table S2. Position of SERS peaks of dopamine and glucose on the glycopolymer@AuNPs self-assembled on PMMA template.

	dopamine	glucose
1701 cm ⁻¹	ν_{C-C} ^[S9]	
1570 cm ⁻¹	ν_{8b} ^[S6]	
1529 cm ⁻¹	ν_{8a} ^[S6]	
1490 cm ⁻¹	ν_{19b} ^[S6]	
1439 cm ⁻¹	ν_{19a} ^[S6]	δ_{CH_2} ^[S7]
1347 cm ⁻¹	ν_3 ^[S6]	ω_{CH_2} ^[S7]
1163 cm ⁻¹		ν_{C-C} ^[S10]
1124 cm ⁻¹		δ_{C-OH} ^[S7]
1076 cm ⁻¹		ν_{C-O} ^[S7]
937 cm ⁻¹		δ_{CH} ^[S7]
838 cm ⁻¹		ν_{C-C} ^[S7]
808 cm ⁻¹	ν_{C-C}, ν_{C-O} ^[S11]	
601 cm ⁻¹	ω_{CH} ^[S8]	
516 cm ⁻¹		δ_{C-C-O} ^[S7]
301 cm ⁻¹		endocyclic deformations ^[S9]

δ = bending mode, w = wagging mode, ν = stretching mode.

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