Supporting Information

Figure S1. (A) FTIR and (B) ¹H NMR spectra of typical samples: a. CS, b. TCS, and c. TCS-directed gold MCs.



FTIR and ¹H NMR spectra of TCS in comparison of those of CS were used to confirm the successful modification of Cys on the main chain of CS. FTIR spectra of CS and TCS were shown in Figure S1A. From the CS spectrum (curve a), it can be found that the distinctive absorption bands appear at 1662 cm⁻¹ (amide I), 1605 cm⁻¹ (-NH₂ bending), and 1393 cm⁻¹ (amide III). The absorption bands at 1164 cm⁻¹ (asymmetric stretching of the COOOC bridge), 1092, and 1042 cm⁻¹ (skeletal vibration involving the COO stretching) are characteristic of its saccharine structure.^[S1] Compared with CS, the IR spectrum of TCS showed that the new signals at 1632 cm⁻¹ and a weak absorption at 2373 cm⁻¹ were assigned to the acylamino group and S-H vibration, respectively. In addition, the peak at 1605 cm⁻¹ attributed to the unreacted amino groups decreased obviously, indicating that the amino group of CS was partly substituted by the cysteine molecules via the acylamino bond.

The ¹H NMR spectra of original chitosan and modified chitosan are given in Figure S1B. The ¹H-NMR assignment of chitosan was as follows:^[S2] ¹H NMR (D₂O/F₃CCOOD) δ =5.10 (H1), δ =3.09 (H2), δ =3.43~3.81 (H3, H4, H5, H6), δ =1.96 (NHCOCH₃) ppm. The shape of H1 was effected by the near water peak inhibition spectra of H₂O at δ =4.76. Although compared with CS, the ¹H NMR (D₂O/F₃CCOOD) spectrum of TCS did not show that the new signals, we believe the protons of H7 and H8 were overlapped in 3.4~4.4 (H3,

H4, H5, H6, H7) and δ =3.06 (H2, H8). The others were assigned to δ =4.81 (H1) and δ =4.76 (un-inhibited water peak) ppm.

Figure S2 SEM images of: (A) citrate-protected AuNPs in Figure 2A, (B) gold nano chains and islands directed by TCS molecules in Figure 2B, and (C) gold microspheres in Figure 2C dried on a Si substrate.



Table S1. Elemental Analysis and Degree of Substitution of Chitosan and Its Derivatives.

	Molar ratio of Cys/CS	С	Ν	C/N molar ratio	Н	DS
chitosan		40.26	7.40	6.35	7.04	-COCH ₃ 0.18
TCS1	1:2	38.56	7.20	6.24	6.68	0.09
TCS2	1:1	39.08	7.42	6.14	6.71	0.17
TCS3	2:1	33.15	6.38	6.06	7.18	0.23
TCS4	4:1	36.56	7.17	5.95	6.93	0.35

References:

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