

Supplementary Information

Gold nanoparticle-conjugated heterogeneous polymer brush-wrapped cellulose nanocrystals by combining different controllable polymerization techniques for theranostic applications

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Preparation of cellulose nanocrystals (CNCs).

CNCs were obtained from cotton wool, which was first dispersed in 64 wt% sulfuric acid in water and then incubated at 45 °C under mechanical stirring for 35 min to allow cotton hydrolysis. The resulting precipitation was re-suspended with cold water and washed thrice by successive centrifugation at 10,000 rpm and 10 °C for 20 min. Dialysis against deionized (DI) water using a dialysis membrane (MWCO 3500) for one week was performed to remove free acid in the dispersion. The suspension was then filtered via membranes with pore sizes of 0.45 µm to remove residual aggregates prior to lyophilization.^{S1}

Syntheses of S,S'-Bis(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate as chain transfer agent (CTA).

The CTA was synthesized as described in the other articles.^{S2} Carbon disulfide (27.4 g), chloroform (107.5 g), acetone (52.3 g), tetrabutylammonium hydrogen sulfate (2.41 g), and mineral spirits (120 mL) were added into a 1 L jacketed reactor cooled with water under nitrogen. Then sodium hydroxide (50%, 201.6 g) was added dropwise. The reaction was stirred overnight no more than 25 °C. Water (900 mL) was added to dissolve the solid, and concentrated HCl (120 mL) was added consecutively to acidify the aqueous layer (caution! gas, mercaptan odor). After stirred 30 min with nitrogen purge, the produced solid was filtered and washed thoroughly with water, followed by lyophilization. The crude product was purified by recrystallizations from acetone to afford a yellow crystalline solid. As shown in Fig. S1, the ¹H NMR and ¹³C NMR spectra were consistent with the Lai's report.^{S2} ¹H NMR (DMSO-*d*₆, ppm from TMS): 1.59 (s, 12H), 12.91 (s, 2H). ¹³C NMR (DMSO-*d*₆): 25.76, 57.25, 176.26, 220.50.

Table S1. Characterization of CNC-based vectors.

Sample	Reaction Time	M_n (g/mol) ^c		PDI ^c
		PPEGEEMA	PDMAEMA	
CNC-PPEG/Br ^a	6 h	4.7×10 ³		1.21
CNC-g-PDMA1 ^b	5 min		4.2×10 ³	1.19
CNC-g-PDMA2 ^b	15 min		6.4×10 ³	1.23
CNC-g-PDMA3 ^b	30 min		7.7×10 ³	1.27

^aSupernatant of RAFT polymerization after centrifugation was used for GPC assay.

^bHydrolyzed with H₂SO₄ for 3 h at 45 °C to cleave PDMAEMA side chains.

^cDetermined from GPC results. PDI=weight average molecular weight/number average molecular weight, or M_w/M_n .

Table S2. XPS analysis of the bi-functional CNC-based initiator.

Sample	Peak area (cps.eV)	
	N 1s	Br 3d
pristine CNC	0	0
CNC-NH ₂	0	1809
CNC-Br	2721	1367
CNC-Br/ACVA	4476	368

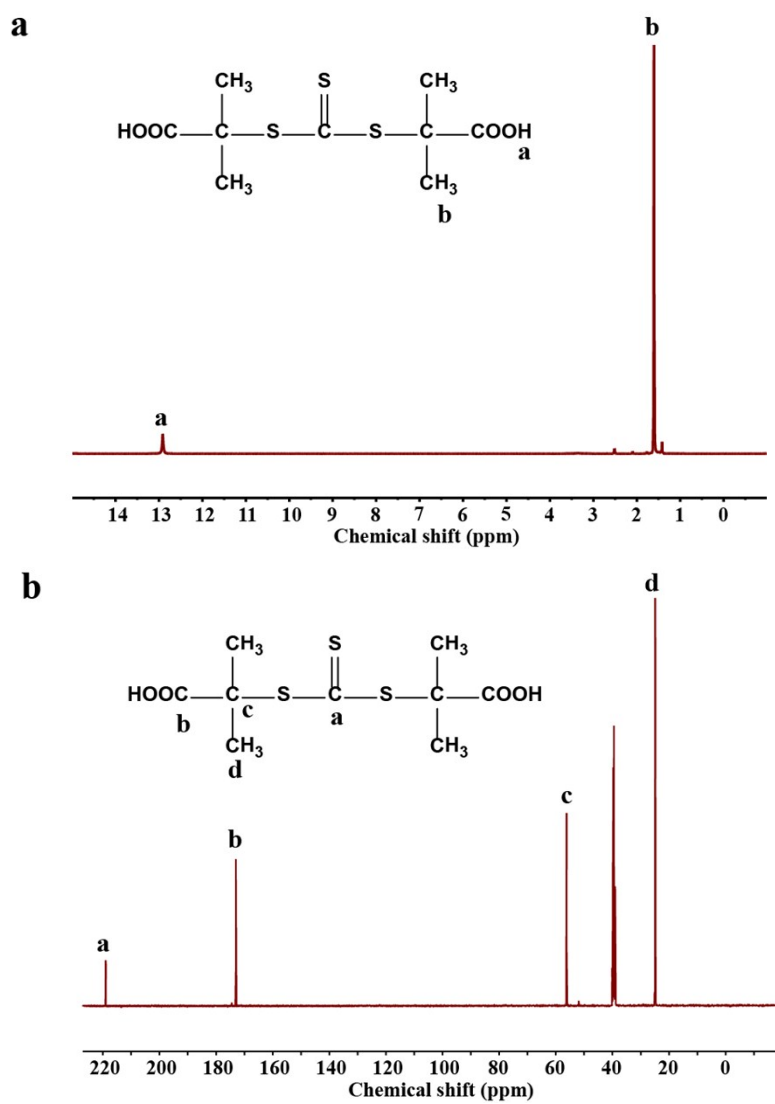


Fig. S1 (a) ^1H NMR spectrum and (b) ^{13}C NMR spectrum of *S,S'*-Bis(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate in $\text{DMSO-}d_6$.

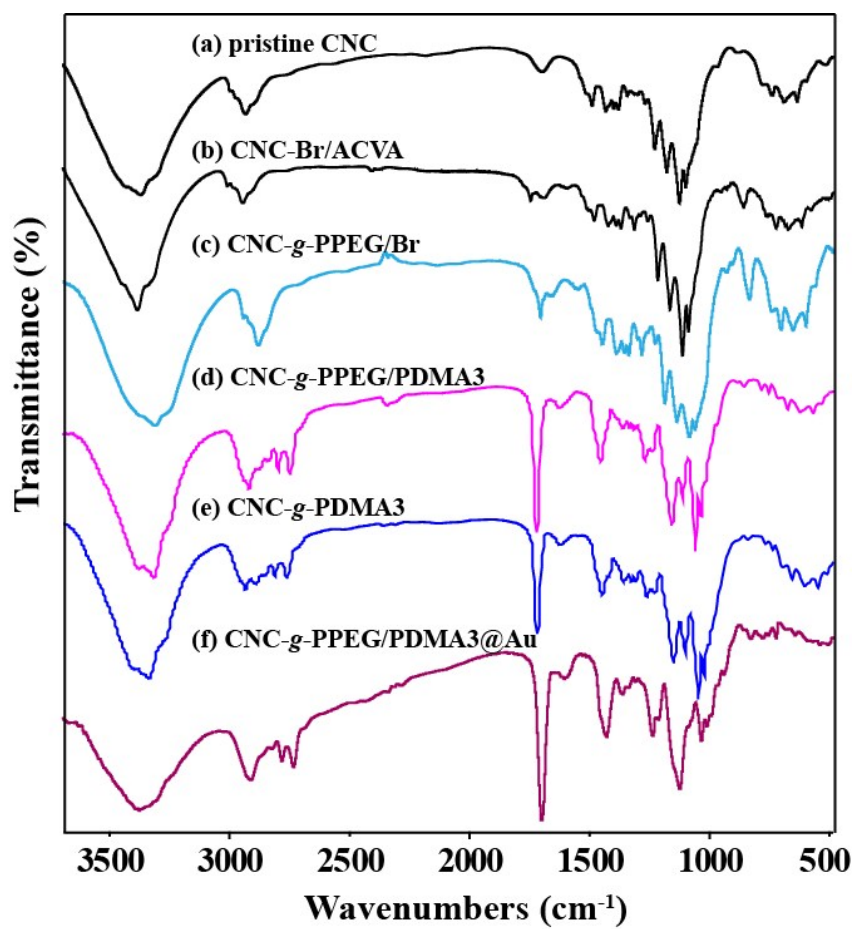


Fig. S2 FTIR spectra of (a) pristine CNC, (b) CNC-Br/ACVA, (c) CNC-*g*-PPEG/Br, (d) CNC-*g*-PPEG/PDMA3, (e) CNC-*g*-PDMA3 and (f) CNC-*g*-PPEG/PDMA3@Au.

XRD measurement.

Fig. S3 shows the XRD patterns of the pristine CNC and CNC-*g*-PPEG/PDMA3@Au. The XRD pattern of the pristine CNC shows five peaks at 14.7°, 16.5°, 20.5°, 22.8°, 34.5°, indexed to (101), (10 $\bar{1}$), (121), (002), and (040) reflections of CNC, respectively.^{S3} The XRD pattern of the CNC-*g*-PPEG/PDMA3@Au exhibits additional four peaks appeared at around 38.5°, 44.7°, 64.6° and 77.8°, corresponding to the (111), (200), (220), and (311) planes of fcc Au.^{S4} The XRD patterns confirm the existence of Au NPs on the CNC in the nanocomposites.

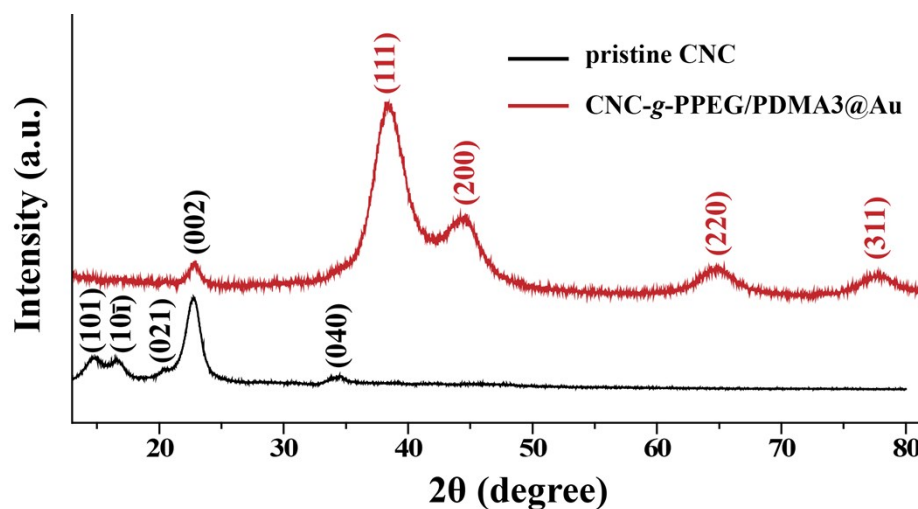


Fig. S3 XRD patterns of the pristine CNC and CNC-*g*-PPEG/PDMA3@Au.

Notes and references

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