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UV grafting: surface modification of cellulose nanofibers without the use of organic solvents

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The effect of polymerization time and monomer concentration on the DG

The purpose of this part is to reveal that the DG of CNF-*g*-PMMA was directly related to the duration of the reaction and the concentration of the monomer. A linear fit (DG *versus* time) gave an equation of $y = 0.0238x – 0.3181$ ($R^2 = 0.993$), suggesting that the DG increased linearly with polymerization time. The x-intercept is 13.4 min. Therefore, we considered that there was an induction period of current UV grafting and the value was approximately 13 min. In the case of DG *versus* monomer concentration, a power function, $y = 0.9254x^{1.4247}$, fitted the data well. We will determine the kinetics of UV grafting in the future study.

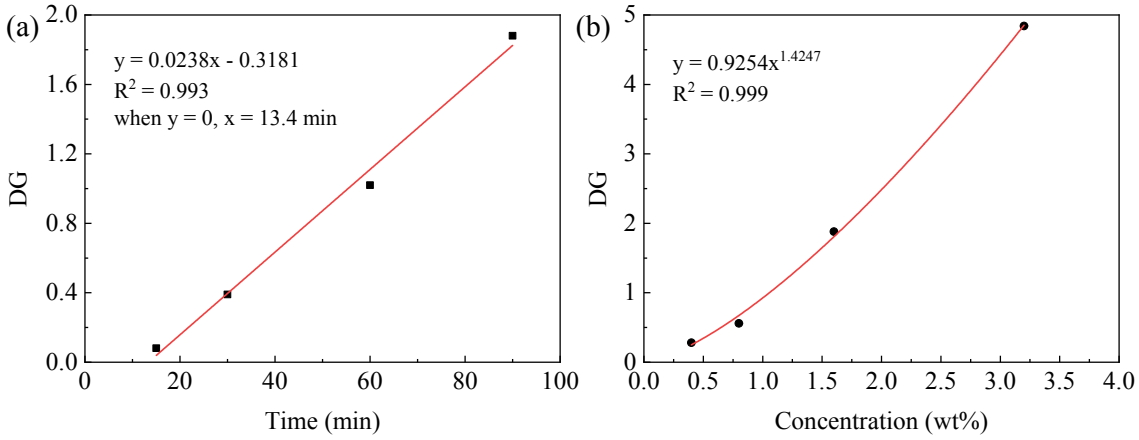

Fig. S1 UV grafting of PMMA from the surfaces of CNFs. (a) DG as a function of polymerization time. (b) DG as a function of monomer concentration.

Comparison of UV grafting with other methods

Table S1. Comparison of UV grafting with other polymer grafting methods concerning to CNF-*g*-PMMA

method	pre-treatment	polymerization condition	post-treatment	DG	homopolymer	Ref.
CAN initiation	None	0.2 wt% aqueous suspension, pH=1; CAN as initiator	centrifugation; washed with acetone and THF	0.6-1	25-44%	1
SI-ATRP	Immobilization of initiator in DMF	Bacterial cellulose membrane in DMF/H_2O; Cu(I)Br and PMDETA as catalyst	washed with DMF and water	0.59-8.87	none	2
UV grafting	None	0.2 wt% aqueous suspension; UV radiation	filtration	0.28-4.84	none	current work

THF: tetrahydrofuran; PMDETA: N,N,N′,N″,N″-pentamethyldiethylenetriamine;
DMF: N, N-dimethylformamide

As prepared CNF-*g*-PMMA suspensions

After UV grafting, the as prepared CNF-*g*-PMMA suspensions look like homogeneous until the DG reached 4.84 (Fig. S2). However, the microscope images showed that aggregation occurred even the DS is low (Fig. S3). The aggregation of CNF-*g*-PMMA may facilitate the dewatering which is an important issue for CNF materials.[3]

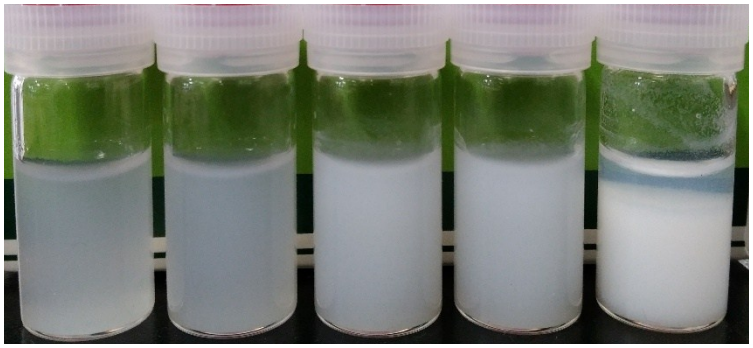

Fig. S2 As prepared CNF-*g*-PMMA suspensions which were stored for one week. From left to right: CNF-*g*-PMMA0.28, CNF-*g*-PMMA0.56, CNF-*g*-PMMA1.24, CNF-*g*-PMMA1.88 and CNF-*g*-PMMA4.84.

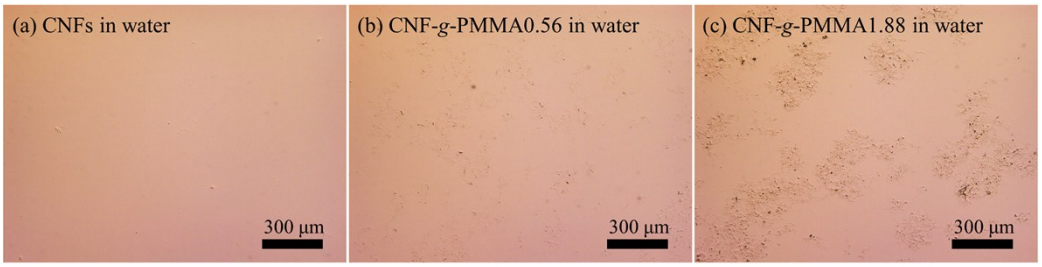

Fig. S3 Microscope images of CNFs (a), CNF-*g*-PMMA0.56 (b) and CNF-*g*-PMMA1.88 (c).

CNF-*g*-PMMA4.84

After UV grafting, the as prepared CNF-*g*-PMMA4.84 suspension separated, as shown in Fig. S5a. Both the supernatant and sediments showed the nanofiber-nanoparticle structures (Fig. S5 b–e). The supernatant had the same size as those of CNF-*g*-PMMA1.84 (Fig. S5c) while the sediments showed increased size (Fig. S5e). However, we did not observe any PMMA microparticles even in the image with lower magnification (Fig. S5d). Therefore, CNFs may be a good template for preparation of unique nanostructures via UV grafting.

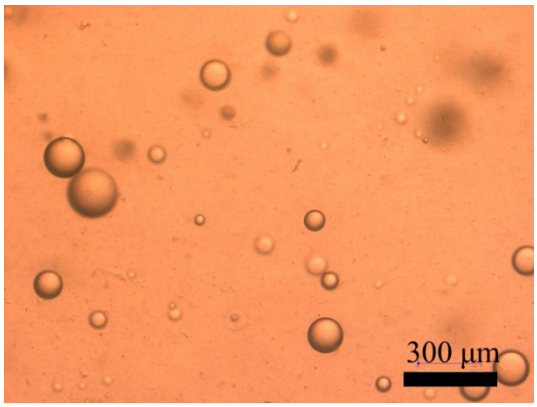

Fig. S4 Microscope image of a CNF suspension containing 3.2 wt% MMA during UV grafting.

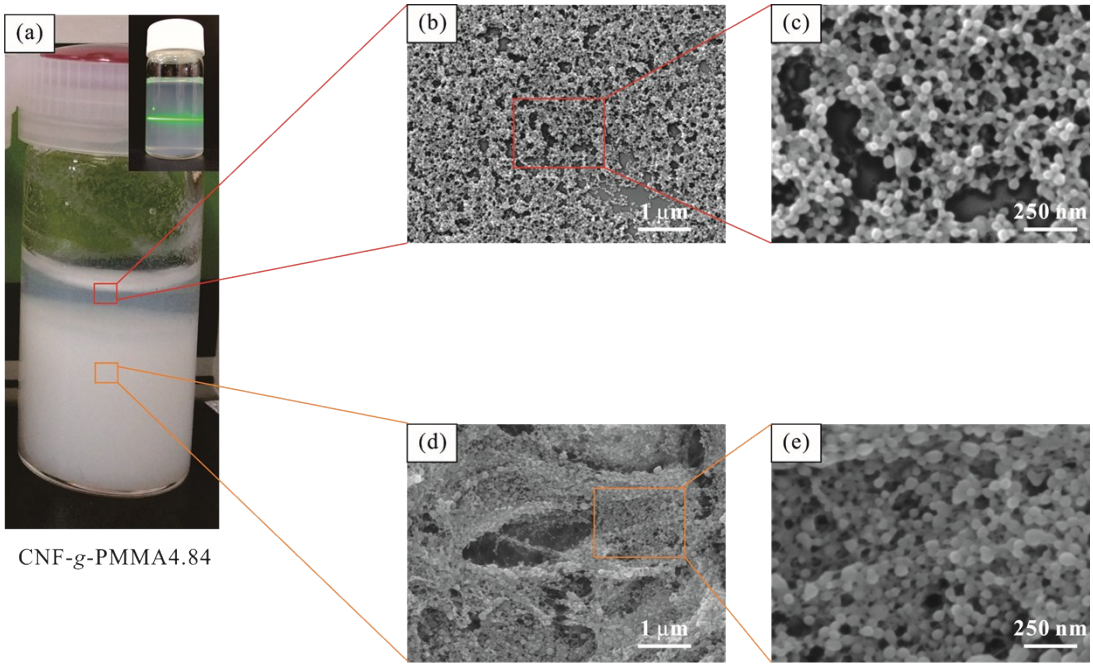

Fig. S5 (a) As prepared CNF-*g*-PMMA4.84 suspension stored for one week. Inserted photo: the sediments were diluted and ultrasonicated. (b–c) SEM images of the supernatant. (d-e) SEM images of the sediments.

Chemical composition of CNFs

Table S2 shows the chemical composition of CNFs used in the current study. The sugar composition of the CNFs was determined from ion chromatography analysis after acid hydrolysis. The hemicellulose is mainly glucomannan and xylan. The lignin content was measured by the Klason lignin method.

Table S2. Chemical composition of CNFs

sample	sugar composition with respect to total sugars, %					Klason lignin content, %
	glucose	mannose	xylose	galactose	arabinose	
CNFs	88.2	9.8	1.6	0.2	0.2	0.4

UV grafting of other nanocelluloses

2,2,6,6-tetramethylpiperidine-1-oxyl radical-oxidized CNFs (TOCN) and cellulose nanocrystals (CNCs) were used to the versatility of UV grafting for other nanocelluloses. Compared with the CNFs, the hydrochloric acid hydrolyzed CNCs had higher crystallinity and less hemicellulose content. On the other hand, TOCN had charged groups (COONa). During UV grafting, the concentration of nanocellulose and MMA were 0.2 wt% and 0.8 wt%. Other conditions were the same with the preparation of CNF-*g*-PMMA0.56. PMMA grafted TOCN (TOCN-g-PMMA) and CNC (CNC-g-PMMA) were obtained (see FT-IR spectra in Fig. S6). The areas of the bands ascribed to C=O of PMMA indicated that the reactivity was: TOCN > CNFs >CNCs.

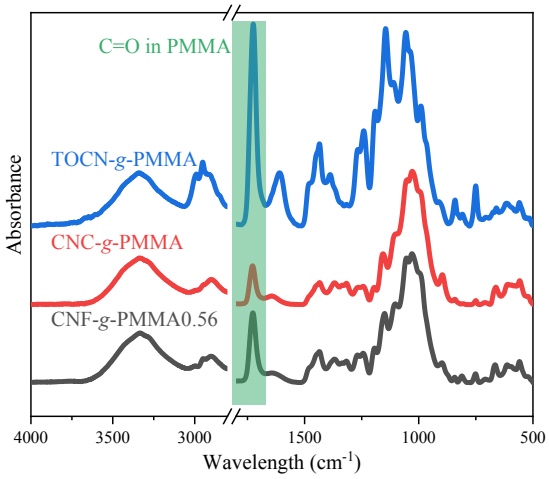

Fig. S6 FTIR spectra of the TOCN-g-PMMA, CNC-g-PMMA and CNF-*g*-PMMA0.56 samples, which were normalized over the range 1316–1315 cm^{-1}.

Formation of PMMA nanoparticles

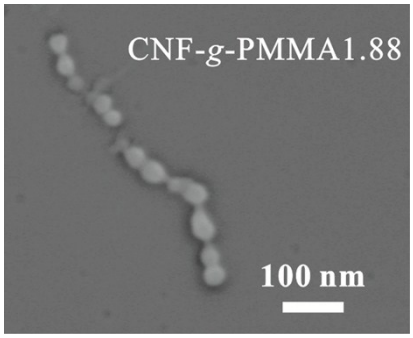

Fig. S7 SEM image of CNF-*g*-PMMA1.88. The arrangement of PMMA nanoparticles in a line probably implied that the particles grew around the surfaces of the CNFs after nucleation.

UV grafting of various polymers from the CNFs

Table S3 shows the UV grafting of various polymers from the CNFs. We can obtain polymer-grafted CNFs with different contact angles. Fig. S8 shows the FT-IR spectra of different polymers grafted CNFs. We also marked the characteristic bands of corresponding polymers in Fig. S8.

Table S3. UV grafting of various monomers from the CNFs and corresponding results

Monomers	conditions of polymerization				grafting degree	contact angle, °
	CNF, wt%	monomer, wt%	T, °C	t, min		
butyl methacrylate (BMA)	0.2	0.4	40	90	1.31	113.4 ± 1.1
2-hydroxyethyl methacrylate (HEMA)	0.2	0.4	40	90	0.59	75.7 ± 1.5
butyl acrylate (BA)	0.2	0.4	40	90	0.88	119.7 ± 1.5
N,N-dimethylacrylamide (DMA)	0.2	0.4	40	90	0.24	/
Acrylonitrile (AN)	0.2	7	40	720	2.1	64.3 ± 2.9
MMA-co-styrene	0.2	0.4-1.2	40	270	0.41	116.5 ± 1.2

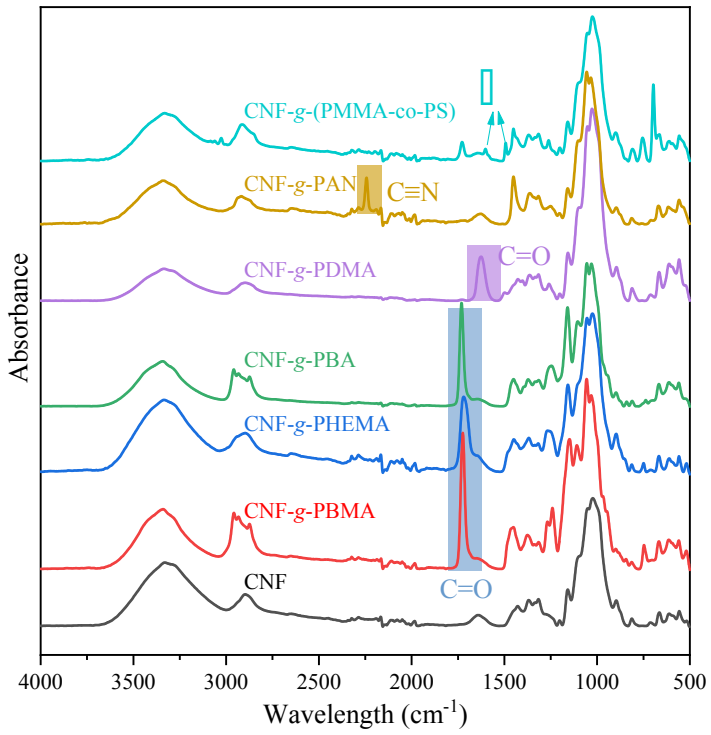

Fig. S8 FTIR spectra of the CNF, CNF-g-PBMA, CNF-g-PHEMA, CNF-g-PBA, CNF-g-PDMA, CNF-g-PAN and CNF-g-(PMMA-co-PS) samples, which were normalized over the range 1316–1315 cm^{-1}. PS: polystyrene.

References

1. Littunen, K.; Hippi, U.; Johansson, L.-S.; Österberg, M.; Tammelin, T.; Laine, J.; Seppälä, J., Free radical graft copolymerization of nanofibrillated cellulose with acrylic monomers. *Carbohydrate Polymers* **2011,** *84* (3), 1039-1047.
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3. Klemm, D.; Kramer, F.; Moritz, S.; Lindstrom, T.; Ankerfors, M.; Gray, D.; Dorris, A., Nanocelluloses: a new family of nature-based materials. *Angew Chem Int Ed Engl* **2011,** *50* (24), 5438-5466.