Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Polymer Grafting on Cellulose Nanocrystals Initiated by Ceric Ammonium Nitrate: Is It Feasible under Acid-Free Conditions?

Yunxiao Liu, Yunjie Lu, Hui Zhang, Xinran Liu, Zhengqing Kong, Lijuan Zhou*, Heng Liu and Jianming Zhang*

Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-Plastics, Qingdao University of Science & Technology, Qingdao City 266042, People's Republic of China

Basic characterization of CNCs:

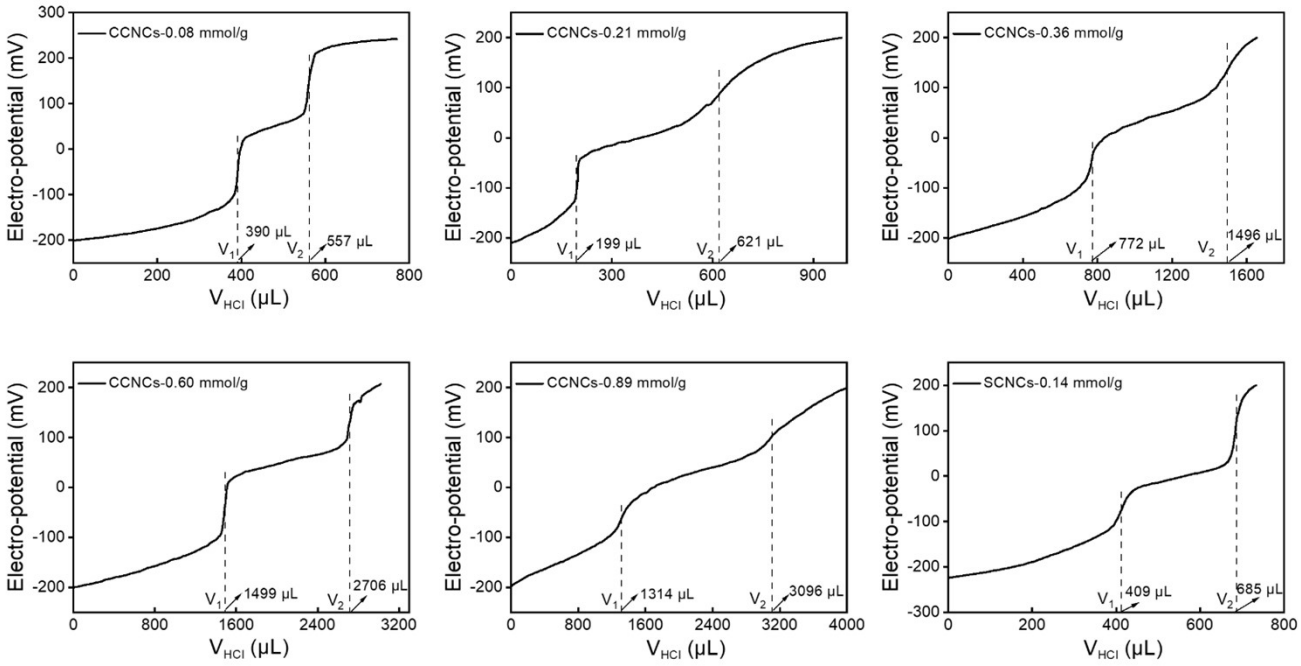

Fig. S1 Electro-potential titration curves of CCNCs and SCNCs.

Table S1. Carboxyl content and yield of CCNCs prepared under different reaction times.

Samples	APS (g)	Temperature (℃)	Reaction time (h)	Carboxyl content (mmol/g)	Yield (%)
$CCNCs_{0.08}$	42.5	80	2	0.08	42.07
$CCNCs_{0.21}$	42.5	80	3	0.21	48.98
$CCNCs_{0.36}$	42.5	80	4	0.36	50.32
$CCNCs_{0.60}$	42.5	80	6	0.60	48.65
$CCNCs_{0.89}$	42.5	80	8	0.89	47.23

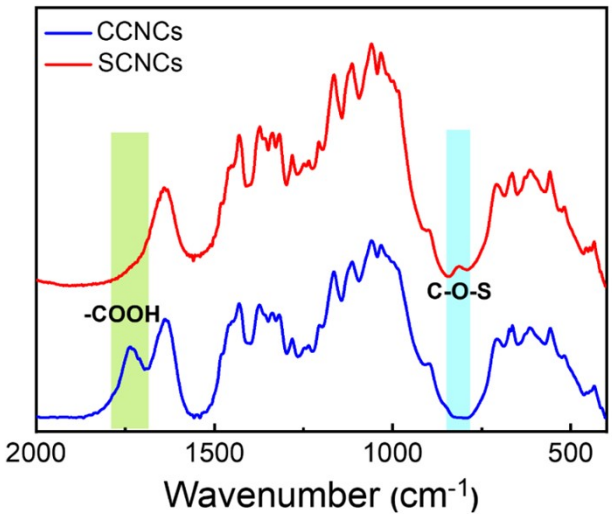

Fig. S2 FT-IR of CCNCs and SCNCs.

Grafting results of SCNCs and CCNCs systems:

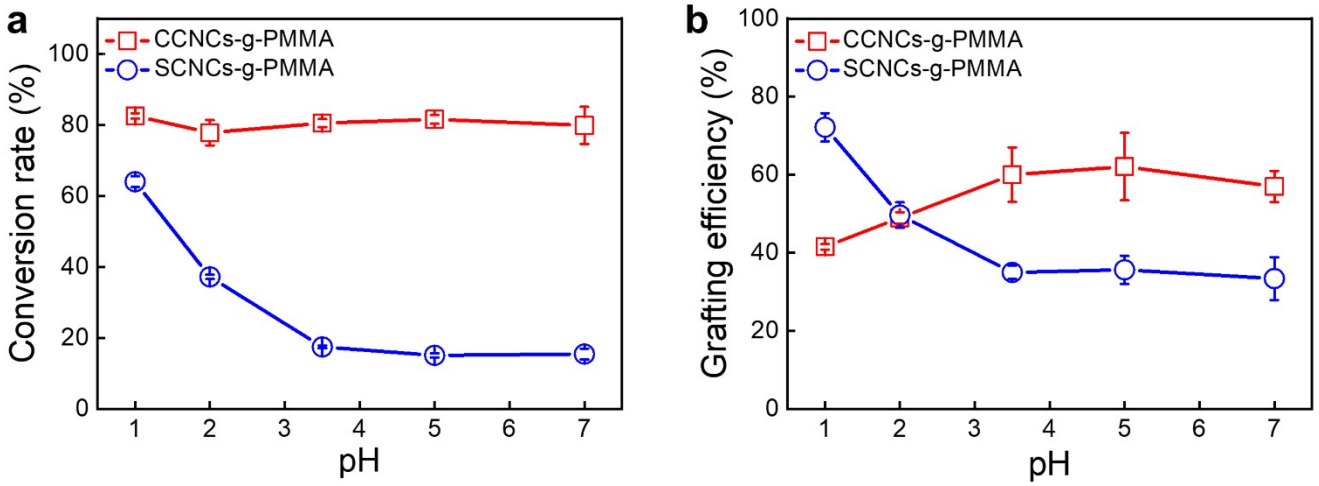

Fig. S3 (a) Monomer conversion rate and (b) grafting efficiency of CCNCs and SCNCs system at pH 1-7.

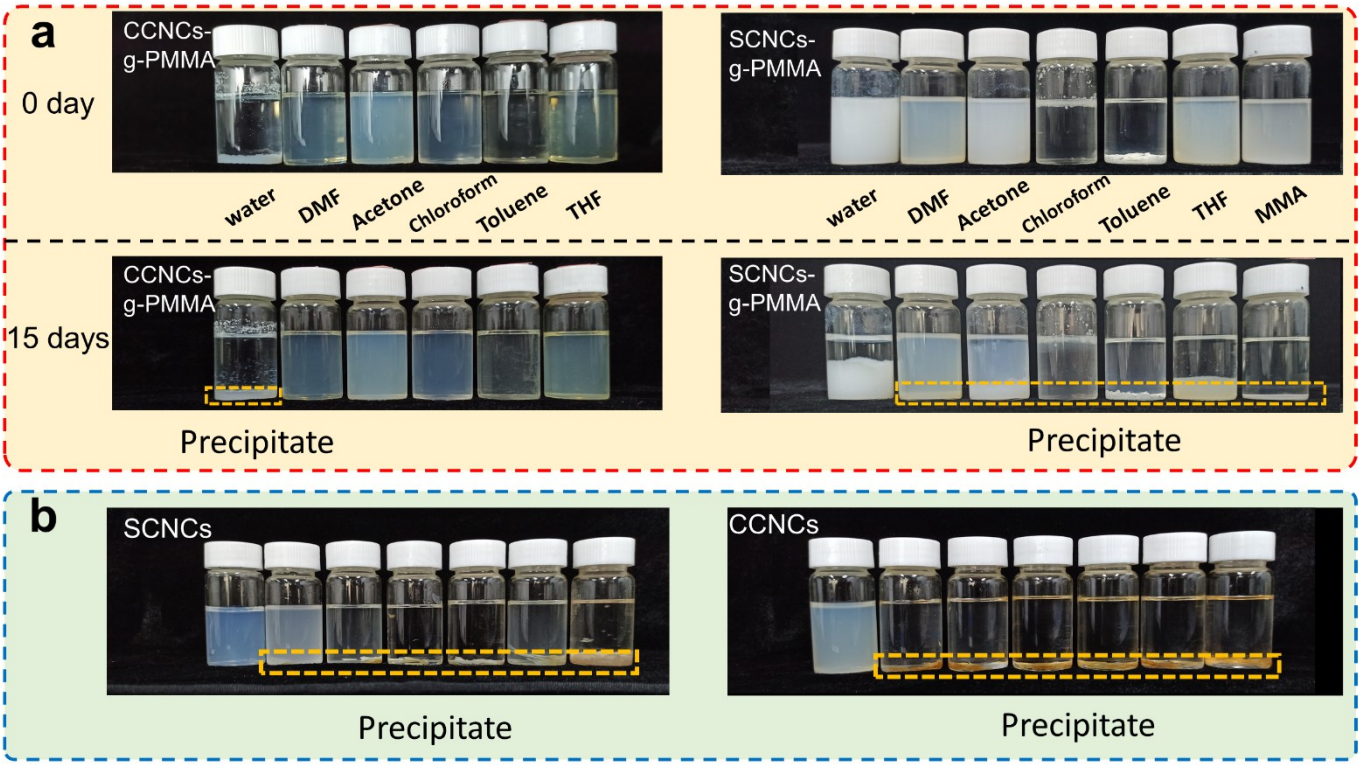

Fig. S4. (a) Photographs of redispersed CCNCs-g-PMMA (left) and SCNCs-g-PMMA (right) in different solvents. The dispersions at 0 day (top) and standing for 15 days (down) were exhibited. (b) Photographs of redispersed SCNCs (left) and CCNCs (right) in different solvents (From left to right are water, DMF, acetone, chloroform, toluene, THF and MMA). The concentration of CNCs-g-PMMA and CNCs is 0.5 wt%.

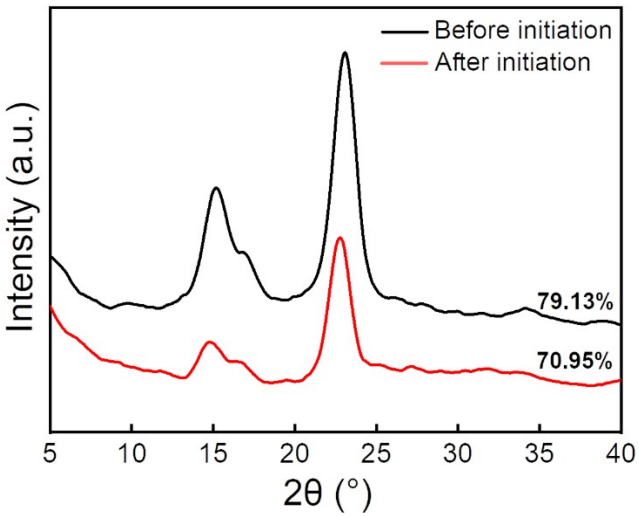

Fig. S5. XRD profile of SCNCs before and after CAN initiation under strong acid conditions.

Initiation mechanism of CAN in CCNCs system under acid-free conditions:

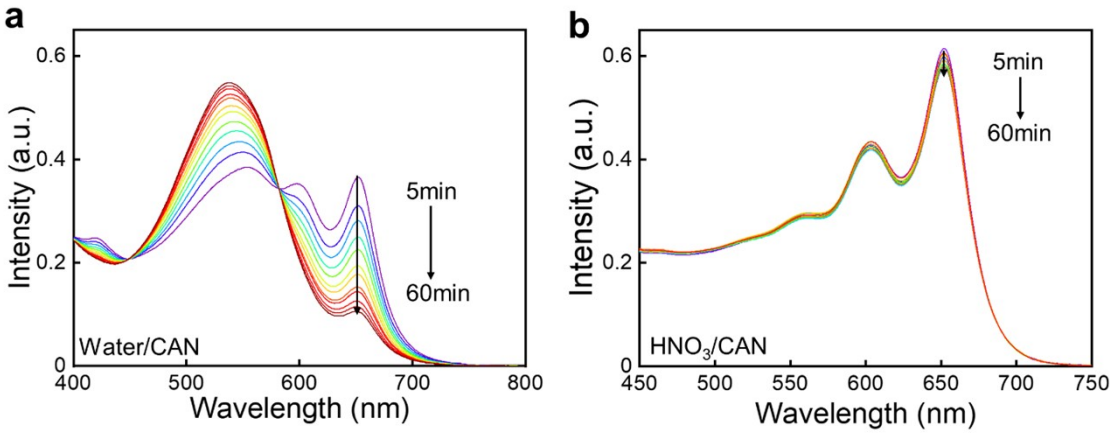

Fig. S6. UV−vis spectra of (a) CAN water solution and (b) CAN in HNO_3 solution at different storage times. (Arsenazo III as chromogenic reagent)

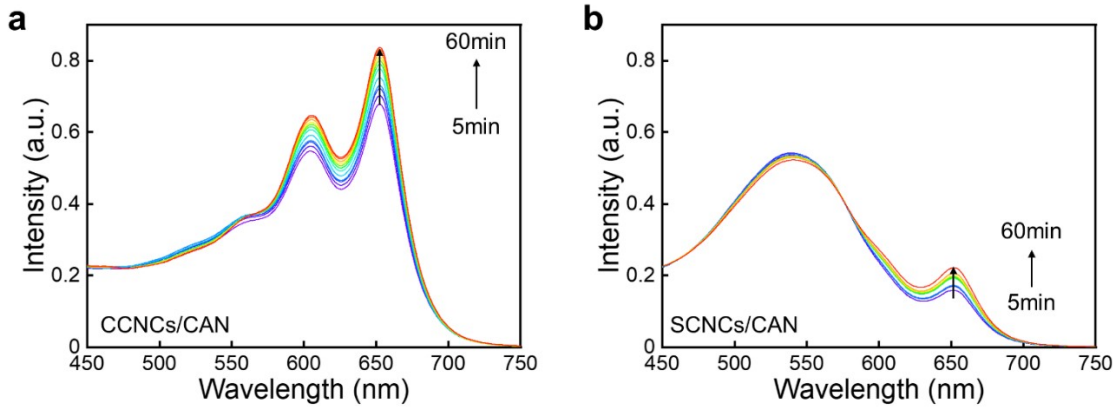

Fig. S7 UV−vis spectra of (a) CCNCs/CAN and (b) SCNCs/CAN mixture at different initiation times. (Arsenazo III as chromogenic reagent)

The CNCs/CAN mixture with different initiation time was added in 5% KI solution. The I^{-1} was oxidized to I_2 due to the oxidability of Ce^{4+}. The as-formed yellow mixture had UV absorption at 288 and 352 nm. The UV-vis absorption spectra were carried out in the range of 250-500 nm to evaluate the relative amount of Ce^{4+}.

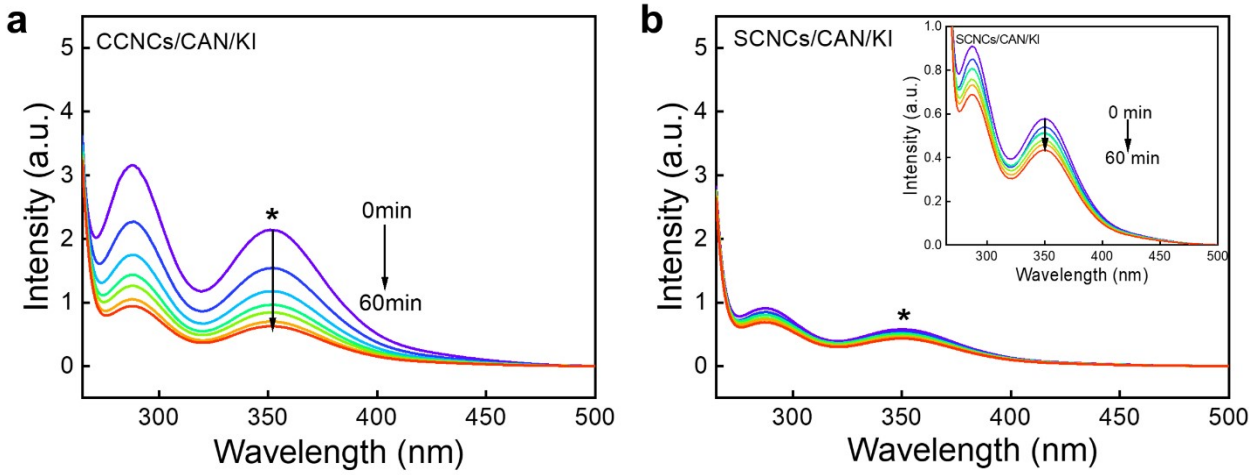

Fig. S8 UV−vis spectra of (a) CCNCs/CAN and (b) SCNCs/CAN mixture for different initiation times. (Iodimetry)

In CCNCs system, the absorption peak intensity at 352 nm is much higher than SCNCs when the initiation is 0 min, indicates that the hydrolysis of Ce^{4+} is inhibited in CCNCs system. The absorption peak intensity at 352 nm decreases with the increase of the initiation time in CCNCs system, which indicates that the concentration of Ce^{4+} in the system decreases because of its participation in the initiation reaction. In SCNCs system, the absorption peak intensity at 352 nm barely reduction with the extension of initiation time, which indicates that the Ce^{4+} almost no initiating effect.[1]

Table S2. Zeta potential and electrical conductivity of undialyzed and dialyzed CCNCs, and the difference in grafting effect under acid-free conditions.

CCNCs type	Zeta potential (mV)	Electrical conductivity (μS/cm)	Grafting yields (%)	Grafting efficiency (%)	Conversion rate (%)
Undialyzed	-25.31	352	255.60±34.51	56.99±3.99	79.90±5.22
Dialyzed	-40.58	28	257.75±13.93	59.41±2.81	77.65±7.86

Valence state of cerium ion on CCNC surface:

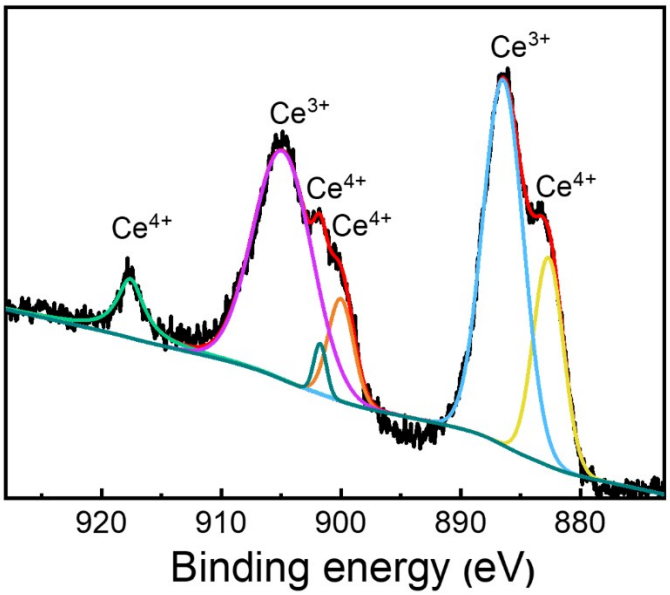

Fig. S9 XPS high-resolution Ce 3d spectra of CCNCs after initiated by CAN.[2]

Effect of CAN concentration on grafting yields:

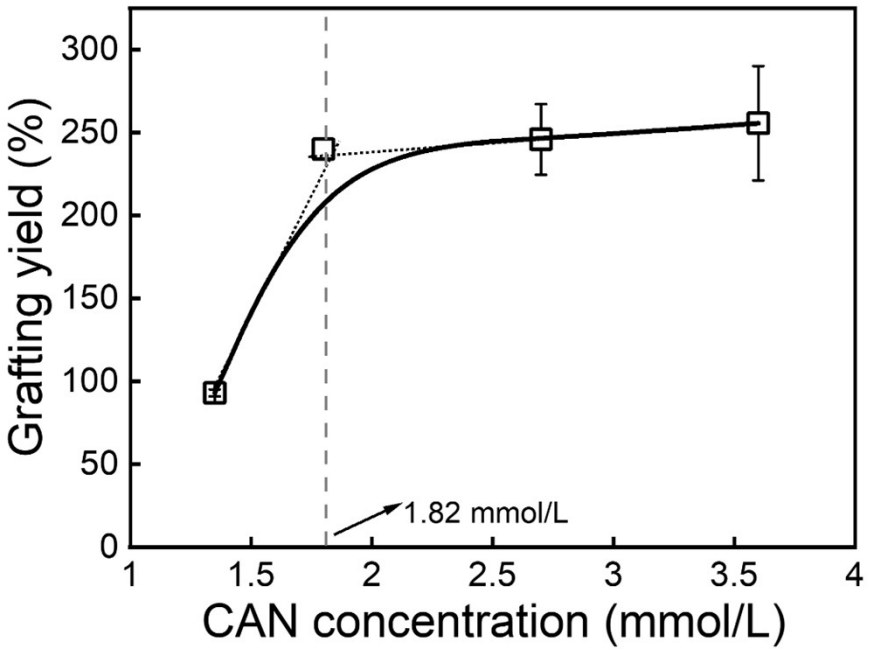

Fig. S10 Effect of initiator concentration on grafting yields of PMMA on CCNCs.

1. C. Liang, C F. Huang, N. Mohanty, and RM. Kurakalva, Chemosphere, 2008, 73(9):1540-1543.
2. J. He, Y. Xu, W. Wang, B. Hu, Z. Wang, X. Yang, Y. Wang and L. Yang, Chemical Engineering Journal, 2020, 379, 122431.