

Supplementary information

Interfacial self-assembly of cellulose-based polyelectrolyte complexes: pattern formation of fractal “trees”

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1. Synthesis and characterization of four PECs.

Fig. 1 schematically shows the synthesis of four PECs and their dissolution in NaOH. Fig. 1 shows that there are COOH groups in obtained PEC solids. PECs solids are re-dispersed in NaOH by re-ionization of these COOH groups into COONa groups. Fig. 2 shows the $\eta_{sp}/c \sim c$ curves of CMCNa and PDMC solutions with 0.005 M HCl at 30 °C and their intrinsic viscosity ($[\eta]$) and overlap concentration (c^*) were shown in Table 1. It is seen from Table 1 that the CMCNa and PDMC concentrations in PEC fabrication are slightly above and below their overlap concentrations, respectively.

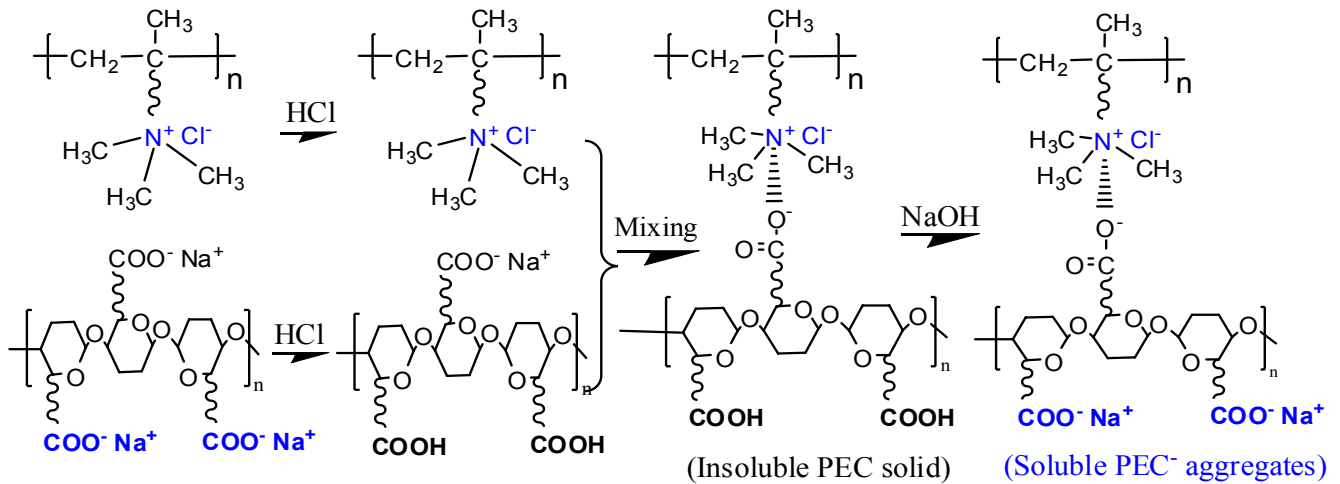


Fig. 1. A schematic diagram of the formation of CMCNa-PDMC PEC aggregate. Fabrication of soluble PEC aggregates between CMCNa and cationic cellulose, PDPA and chitosan is the same as that of CMCNa-PDMC.

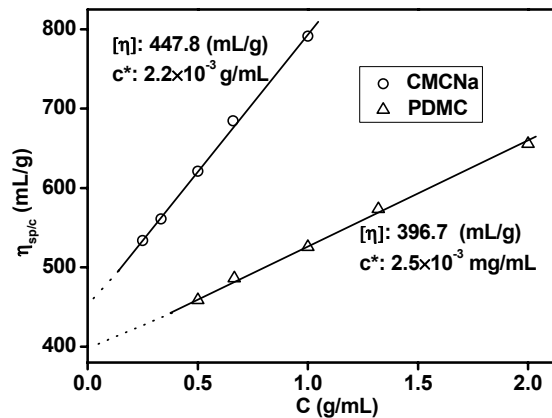


Fig. 2 $\eta_{sp}/c \sim c$ curves of CMCNa and PDMC solutions with 0.005 M HCl at 30 °C.

Table 1. Concentrations of CMCNa and PDMC solutions and their overlap concentrations (c^*). C^* is calculated based on the equation $c^* = 1/[\eta]$.

Polyelectrolytes	Concentration for PEC fabrication	Overlap concentration (C^*)
CMCNa	2.4×10^{-3} g/mL	2.2×10^{-3} g/mL
PDMC	2.07×10^{-3} g/mL	2.5×10^{-3} g/mL

Fig. 3 shows the experimental phenomenon. Turbidity immediately occur in CMCNa solution upon the adding of cationic polyelectrolyte (Fig. 3a), and macroscopically visible PECs solids precipitate out when the ionic complexation endpoint was reached (Fig. 3b). The PECs precipitates are white in their swelled state (Fig. 3c) and weak yellow in dry state (Fig. 3d). PECs were re-dispersed in NaOH after being washed and dried thoroughly (Fig. 3e). Four cationic polyelectrolytes used in this study are poly (2-(Methacryloyloxy) ethyl trimethylammonium chloride) (PDMC), cationic cellulose (Cationic cellulose), poly(diallyldimethylammoniumchloride) (PDDA) and chitosan (CS). Elemental analysis of four PECs in Table 2 shows that CMCNa contents in all the four PECs are larger than 50 mol % and this is in accordance with the FT-IR results.

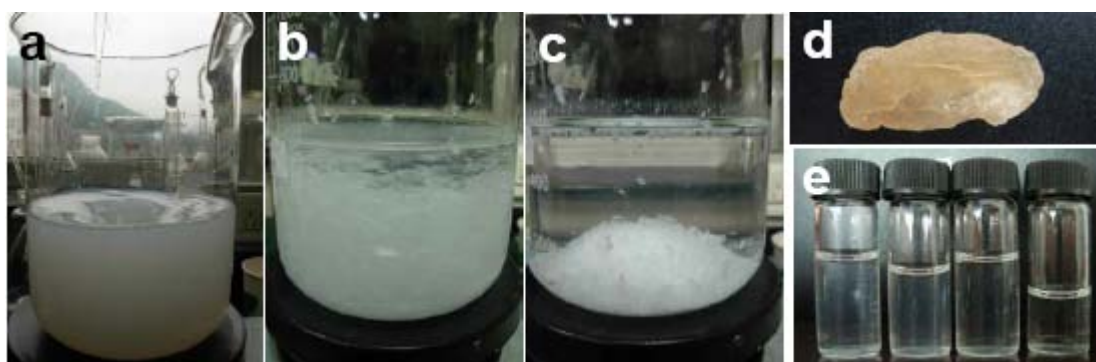


Fig. 3 Optical photographs of (a) 0.01 M CMCNa (400 mL) added with 50 mL of 0.01 M PDMC; (b) reaching the endpoint of ionic complexation after adding 150 mL of 0.01 M PDMC; (c) 1 min after stopping the stir; (d) dried CMCNa-PDMC PECs; (e) four PECs dispersions (0.02 wt%; from left to right: CMCNa-PDMC, CMCNa-Cationic cellulose, CMCNa-PDDA and CMCNa-CS respectively).

Table 2 Elemental analysis results of four PECs

PEC samples	[HCl] (M)	C (wt %)	N (wt %)	H (wt %)	CMCNa (mol %)
CMCNa-PDMC	0.005	48.07	1.92	6.28	71.5
CMCNa-PDDA	0.005	49.63	1.99	6.39	72.4
CMCNa-CS	0.009	43.21	1.25	5.11	81.1
CMCNa-cationic cellulose	0.009	---	---	---	---

2. Dynamics of water evaporation at 30 °C.

Fig. 4 shows the weight loss of 0.06 mL of CMCNa-PDMC PEC dispersion (0.02 wt %) on silicon wafer (drying temperature: 30 °C). It is seen from Fig. 4 that ca. 260 mins are required to dry the PEC dispersion.

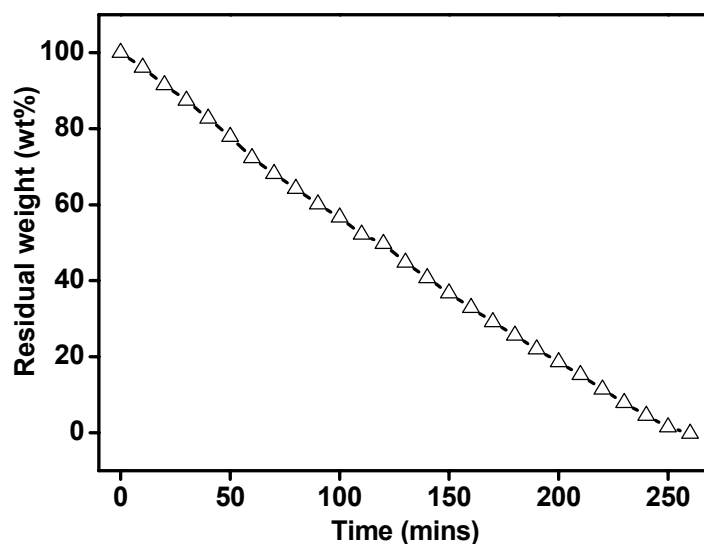


Fig. 4 Weight loss of 0.06 mL of CMCNa-PDMC PEC solution (0.02 wt %) on silicon wafer with drying time at 30 °C.

3. CMCNa-PDMC fractal “trees” observed by TEM.

Fig. 5 shows the CMCNa-PDMC fractal “trees” observed by transmission electron microscopy (TEM). The fractal “tree” in Fig. 5 is formed by drying CMCNa-PDMC PEC dispersion on Cu grid (400 mesh), which were commonly used for TEM support. It can be seen that fractal “trees” can also form on Cu grids.

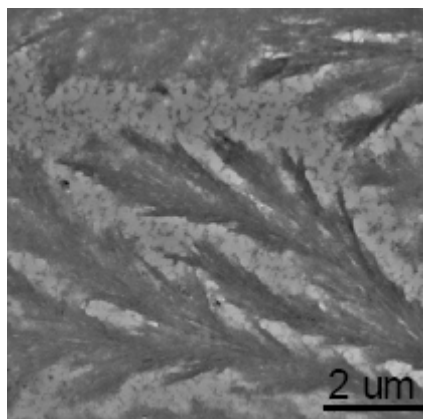


Fig. 5 TEM observation of drying 0.02 wt % CMCNa-PDMC PEC aqueous dispersion at 30 °C.

4. Applications of cellulose-based fractal structures.

Herein, we show three applications of cellulose-based fractal structures (Sections 4.1~4.3).

4.1 PEC aggregates for bottom-up nanofabrication: fast fabrication of Layer-by-layer (LbL) free-standing multilayer films.

A defect free free-standing multilayer film (ca. 2.5 μm thick) can be obtained (Fig. 6) by LbL depositing CMCNa-PDMC PEC aggregates with PDDA-PSS PEC aggregates for only 25 bi-layers. Thus, using PEC aggregates as LbL building components is timesaving for bottom-up nanofabrication. More importantly, multiwall carbon nanotubes (MWCNTs) can be encapsulated into the PEC aggregates. Using these PEC aggregates that loaded with functional nano-fillers as LbL building blocks offers a new pathway for tailoring the functionality of their free-standing multilayer films and solution cast films. For

example, solution cast PEC film made from PEC aggregates that encapsulating 7 wt% MWCNTs show 3.5 times higher tensile strength (Fig. 7). These films have potential in manifold applications like fuel cell membrane, separation membrane and sensors. Thus, the formation of PEC aggregates is promising in bottom-up nanofabrication and as functional nano-container.

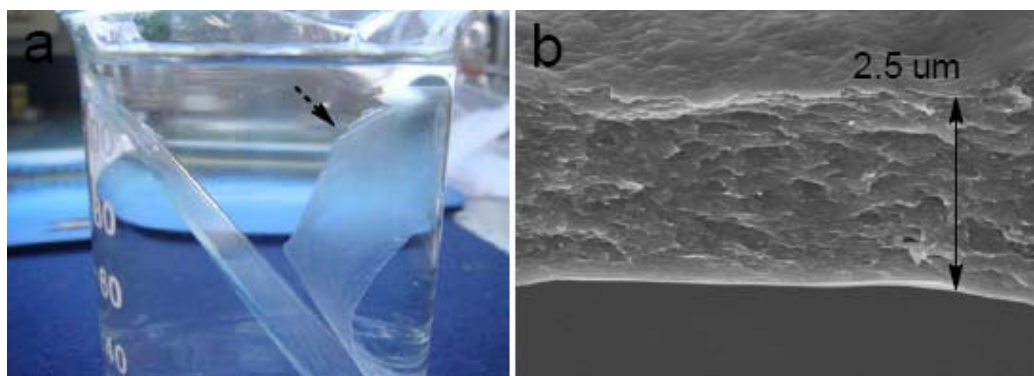


Fig. 6. A free-standing multilayer film constructed from CMCNa-PDMC PEC aggregates (a) optical photographs of peering off the film from the substrate (b) FESEM cross-section view.

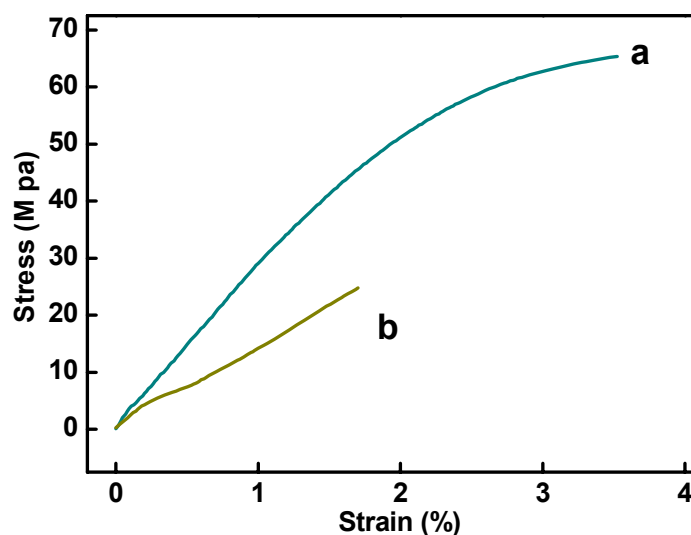


Fig. 7 Mechanical strength of (a) CMCNa-PDDA film encapsulating 7 wt% MWCNT; (b) pristine CMCNa-PDDA film.

4.2 PEC aggregates for high performance separation membranes.

Three dense membranes made of CMCNa-PDMC, CMCNa-PDDA and CMCNa-CS PECs were prepared by casting their concentrated solutions (2 wt %) on a polysulfone ultra-filtration membrane, respectively. From Table 3, it can be seen that the pervaporation performance of membranes made from PECs are 2 ~ 3 times higher as compared with CMCNa membrane. This improvement is probably due to the formation of PEC aggregates and its fractal structure. As shown in Fig. 8, both the surface and cross-section of PEC membrane (CMCNa-PDDA PEC) are composed of needle-shaped PEC aggregates. The space between these PEC aggregates formed ultra-permeable water channel, so that the dehydration performance of PEC membrane is highly improved as compared to CMCNa membrane.

Table 3. Comparison of pervaporation performance of PEC membranes with other membranes for dehydration of isopropanol

PECs Membranes	Water in feed (wt %)	Temperature (°C)	Permeation flux (kg/m ² h)	Separation factor ($\alpha_{\text{H}_2\text{O}/\text{Isopropanol}}$)
CMCNa-PDMC	10	70	3.30	1328.5
CMCNa-PDDA	10	70	2.47	1627.4
CMCNa-CS	10	70	2.11	1249.6
CMCNa	10	70	1.1	1125.2
PERVAP2510 ^a	10	70	0.75	810

a: PERVAP 2510: Commercial membrane from Sulzer Chemtech, Germany. Its performance is from ref: Qiao et.al, *J. Membr. Sci.* 252 (2005) 37-49.

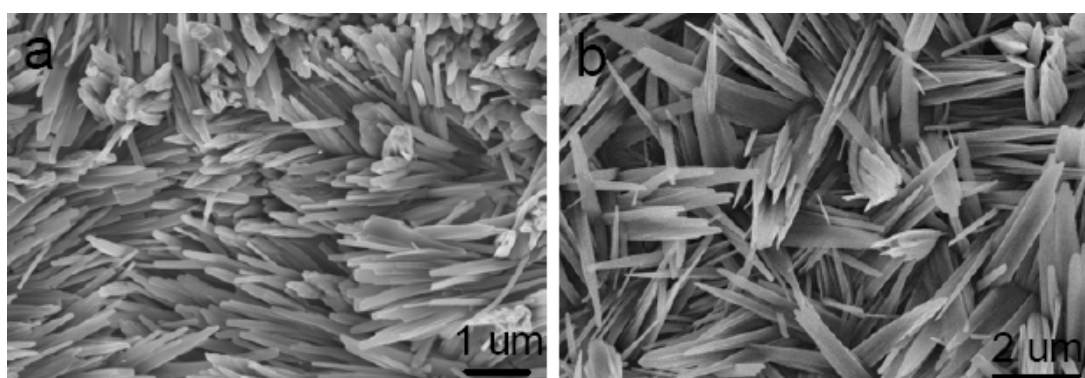


Fig. 8 Cross-section (a) and surface morphology (b) of CMCNa-PDDA PEC membrane.

4.3 Fractal “trees” for surface patterning: toward biological applications.

Fractal “trees” can be a novel method for the surface patterning. Fig. 9 shows that the root mean square surface roughness (RMS) of the fractal “trees” pattern is averagely ca. 110 nm and the PEC layer height is ca.300 ~ 400 nm. Furthermore, the RMS and layer height can be adjusted by the initial PEC concentration. Thus, the ramified structure of CMCNa-CS fractal “trees” is an ideal candidate for cell cultivation due to its large surface roughness and bio-compatibility. Further work on this issue is ongoing in our laboratory.

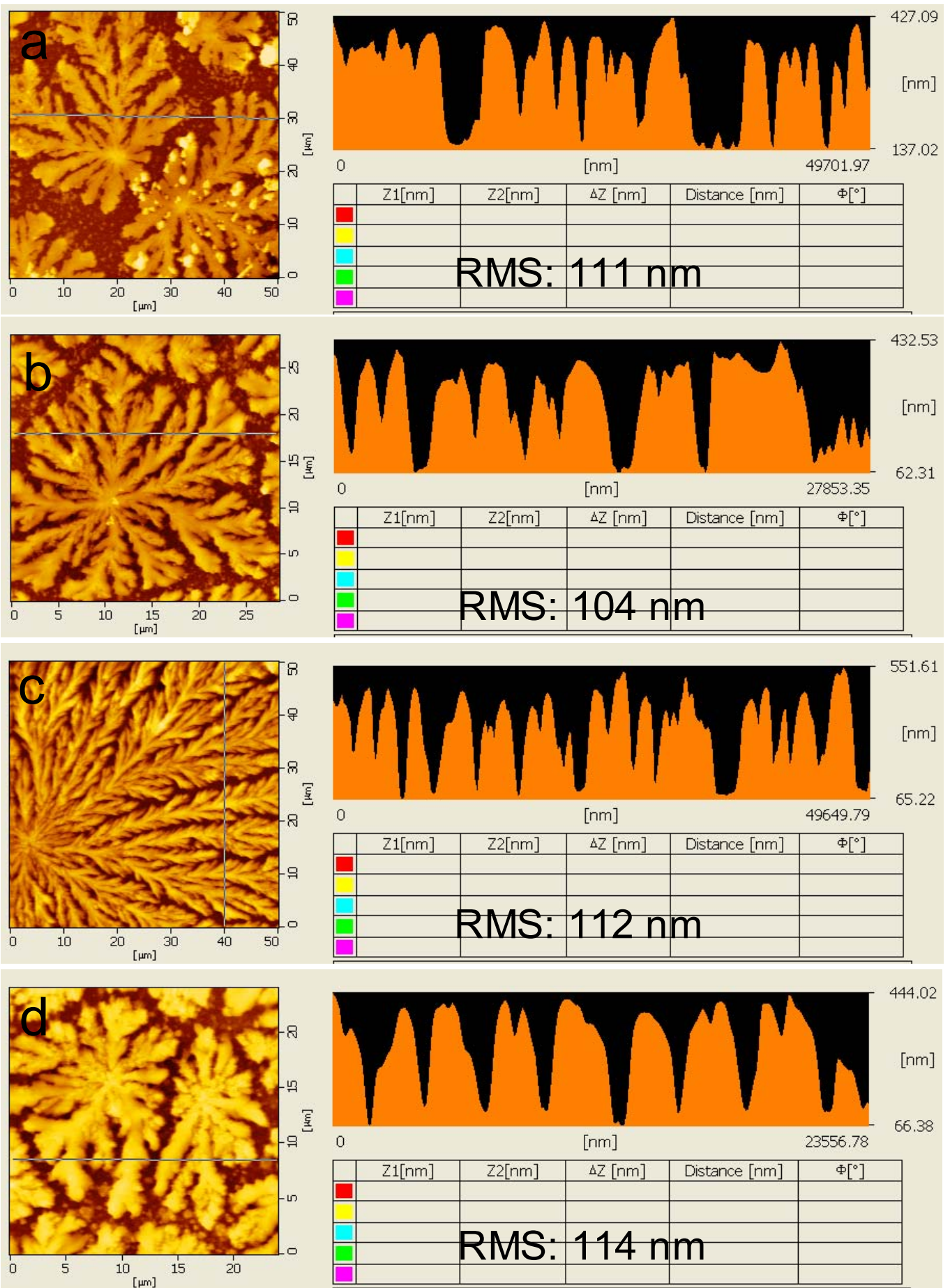


Fig. 9 AFM height analysis of fractal “trees” (a) CMCNa-PDMC; (b) CMCNa-Cationic cellulose; (c) CMCNa-PDDA (d) CMCNa-CS.