Supplementary material (ESI) for Journal of Materials Chemistry

Speedy Fabrication of Free-standing Layer-by-Layer Multilayer Films by Using Polyelectrolyte Complex Particles as Building Blocks

Qiang Zhao Jinwen Qian, Quanfu An,* Binyang Du[*]

1. ζ potential, viscosity and FT-IR of PEC nanoparticles.
2. Optical micrographs concerning the preparing and dissolving of PDDA-CMCNa PEC solid.
3. Optical micrographs of the free-standing LbL multilayer film peered off from the QCM quartz.
4. Versatility of the free-standing LbL film fabrication method.

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[*] Corresponding authors. E-mail: qianjw@zju.edu.cn (J.W. Qian), duby@zju.edu.cn (B. Y. Du).

1. ζ potential, viscosity, and FT-IR of PEC nanoparticles.

From Fig. 1, it can be seen that the ζ potential of PDDA/CMCNa PEC^- and PDDA/ PSSNa PEC^+ nanoparticles were -18.8 mv and 22.3 mv, respectively. From Fig. 2, it can be seen that the $\eta_{sp}/c \sim c$ curves of both PEC^- and PEC^+ gives a typical polyelectrolyte behavior, confirming the charged character of both PEC nanoparticles. The η_{sp}/c value of PEC^+ is much lower than that of PEC^- due to the relatively lower molecular weight of PSSNa.

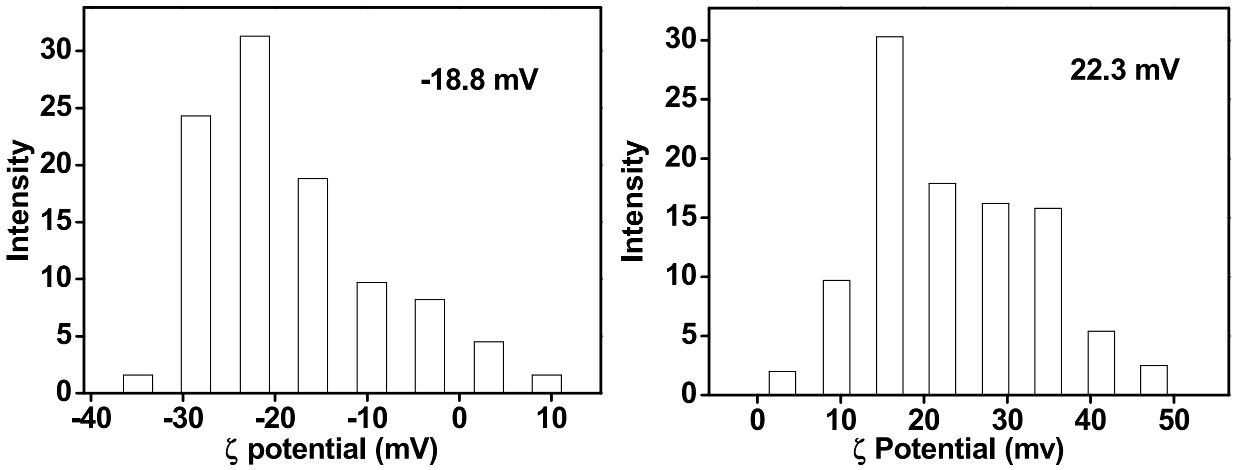


Fig. 1 ζ potential of PDDA/CMCNa PEC^-, and PDDA/PSS PEC^+, respectively.

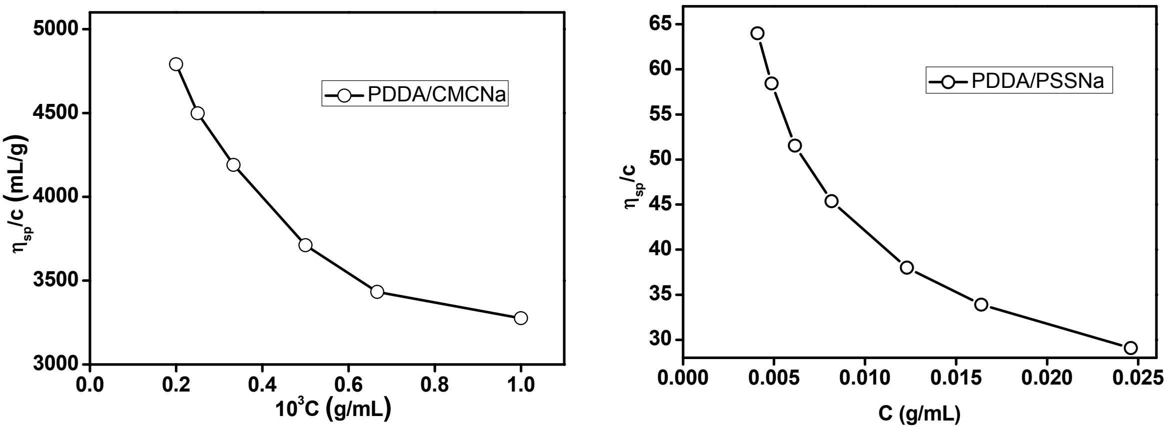
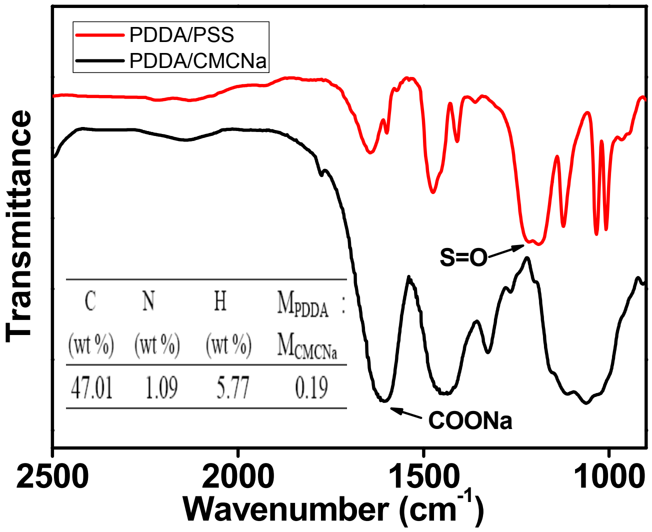


Fig. 2 η_{sp}/c curves for PDDA/CMCNa PEC^- and PDDA/PSSNa PEC^+ in water at 30 °C.

From Fig. 3, it can be seen that the negative charge of PDDA/CMCNa PEC^- was due to the COONa groups in PECs. This is because there are residual COOH groups in PDDA/CMCNa PECs, and these COOH groups were ionized when dissolved in NaOH. Elemental analysis inserted in Fig. 3 shows that the average mole ratio of PDDA monomer to CMCNa monomer is 0.19. Elemental analysis of PDDA/PSSNa PEC is not given since no precipitate was obtained when mixing PDDA and PSSNa solution. However, it has been known that the composition of PDDA/PSSNa PEC is dependent on its mixing ratio.[1]



C (wt%)	N (wt%)	H (wt%)	M_{PDDA} : M_{CMCNa}
47.01	1.09	5.77	0.19

Fig. 3 FT-IR spectrum of PDDA/PSS PEC, PDDA/CMCNa PEC and elemental analysis results of PDDA/CMCNa PEC.

2. Optical micrographs concerning the preparing and dissolving of PDDA-CMCNa PEC solid.

Fig. 4 shows the optical photographs of CMCNa solution added with different amount of PDDA and PDDA@MWCNTs, respectively. It can be seen that turbidity happens upon the adding of PDDA or PDDA@MWCNTs solution (Fig. 4a, d), indicating that ionic complexation happens. When the endpoint of ionic complexation is reached, the PEC solid precipitates out at the bottom of the beaker (Fig. 4c, f). These solids are dried and re-dissolved in aqueous NaOH solution to form stable dispersion (Fig. 4i).

Fig. 4 Optical photographs of (a,b) 400 mL CMCNa (0.01m) added with 50 and 175 mL PDDA (0.01 M), respectively, (c) depositing of b for 5 mins, (d, e) 400 mL CMCNa (0.01m) added with 50 and 190 mL PDDA@MWCNTs, respectively, (f) depositing of e for 5 mins, (g, h) PDDA-CMCNa PEC solid and PEC/MWCNTs nanocomposite, (i) 0.1 wt% PEC and PEC/MWCNTs solution, respectively (the aqueous PEC dispersion are stable in months).

3. Optical micrographs of the free-standing LbL multilayer film peered off from the QCM quartz.

As seen from Fig. 5, the multilayer film is clearly visible on QCM quartz crystal by naked eyes (Fig. 5a). However, it is difficult to directly peer off the multilayer film from the quartz crystal (Fig. 5b), and only small pieces of cracked multilayer film was obtained (Fig. 5c and 5d). The difficulty in peeling off the multilayer film is caused by the strong electrostatic interaction between the PDDA and quartz substrate. This phenomenon is inherent for polyelectrolyte multilayer films driven by electrostatic force. Thus, a post-treatment is required to peel off the multilayer film from the substrate.

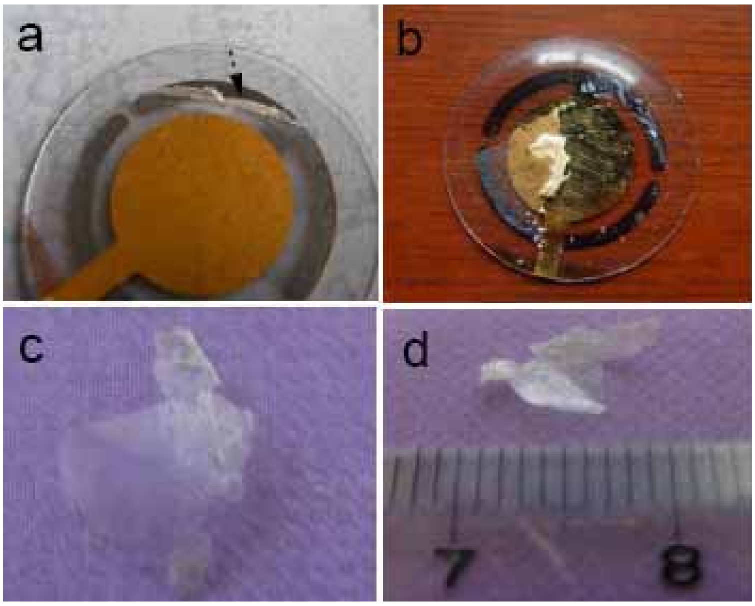


Fig. 5. Optical photographs of $(PDDA/PSS)_3(PEC^-/PDDA)_{10}(PEC^+/PEC^-)_{12}$ LbL multilayer film deposited on QCM quartz cystal (a) initial scratching brim, (b) part of the multilayer films peered off from the quartz crystal, (c ,d) pieces of cracked LbL multilayer films.

4. Versatility of the free-standing LbL film fabrication method.

Fig. 6 shows the optical photographs of peering off $(PDDA/PSS)_3(PEC^+/CMCNa\text{-}PDMC\ PEC^-)_{25}$ multilayer film from the glass slide after the same GA cross-linking. (Note: PDMC = Poly (2-(Methacryloyloxy) ethyl trimethylammonium chloride) (Mw=30 0000 g/mol)). Fig. 7 shows that direct depositing $(CMCNa\text{-}PDDA\ PEC^-/PEC^+)_{20}$ also allows the easy isolation of a large area (9×9 cm^2) multilayer film from the cellulose diacetate (CA) substrate in ethanol.

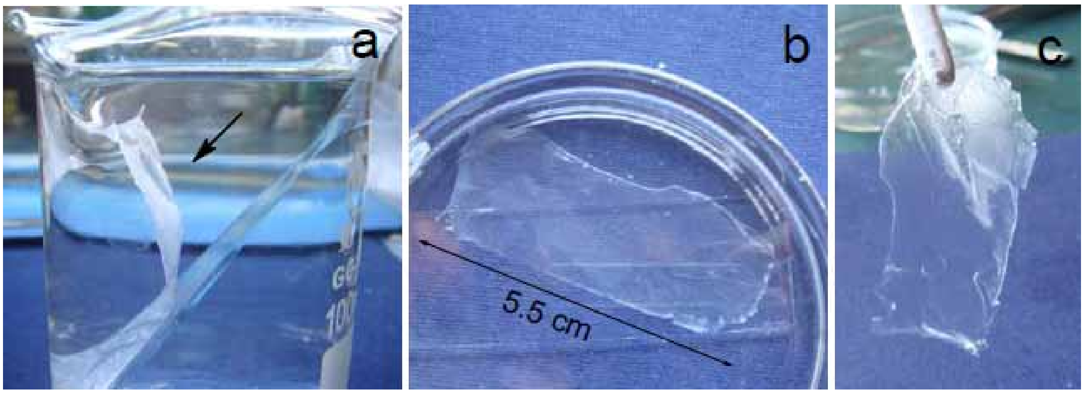


Fig. 6 Optical photographs of $(PDDA/PSS)_3(PEC^+/CMCNa\text{-}PDMC\ PEC^-)_{25}$ multilayer films: (a) peering off the multilayer film after GA cross-linking by tweezers in ethanol, (b) floating in ethanol, (c) in air atmosphere.

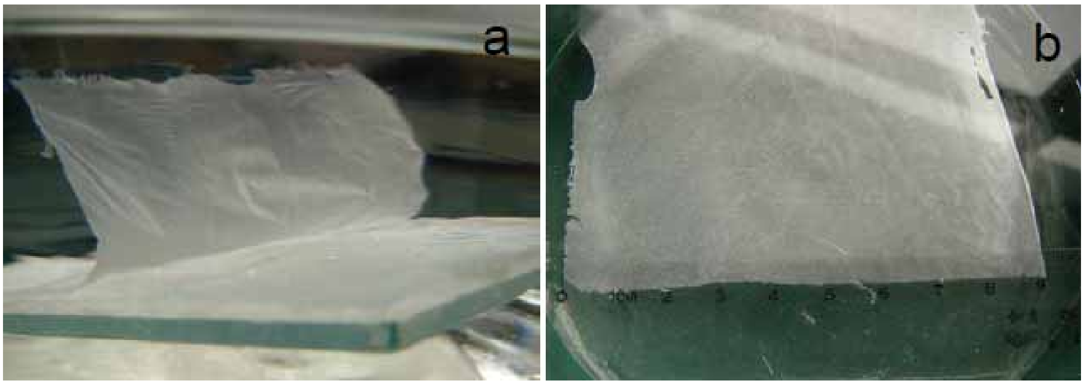


Fig. 7. Large area (CMCNa-PDDA PEC$^-$/PEC$^+$)$_{20}$ LbL multilayer films (a) peering off from CA substrate in ethanol, (b) in air with a size of 9×9 cm^2.

Ref

1 (a) Schuetz, P.; Caruso, F. *Colloids Surf. A.* **2002** *207,* 33-40. (b) Thünemann, A.F.; Müller, M.; Dautzenberg, h.; Joanny, J. F.; Löwen, H. *Adv. Polym. Sci.* **2004**, *166*,113-171.