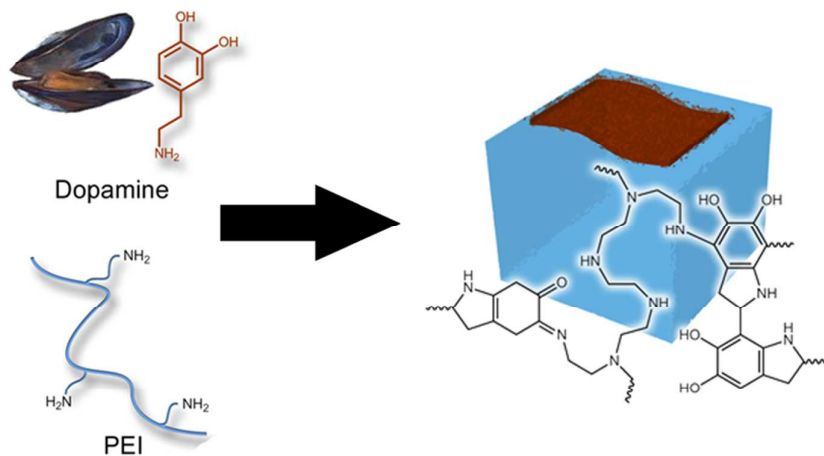# RSC Advances

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Graphic Abstract

Dopamine

PEI

A polydopamie/polyethyleneimine composite free-standing film is obtained via a facile oxidation and cross-linking process at the air/solution interface.

Journal Name

COMMUNICATION

Composite Free-Standing Films of Polydopamine/ Polyethyleneimine Grown at the Air/Water Interface

Hao-Cheng Yang[a], Wei Xu[b], Yong Du[a], Jian Wu[b] and Zhi-Kang Xu[a]*

Mussel-inspired free-standing composite films were formed by polymerization of dopamine in the presence of polyethyleneimine at the air/water interface. These films have controllable thickness and asymmetric structure. They can be potentially developed as templates for the fabrication of silver, hydroxyapatite, titania and silica hybrid films.

Mussel-inspired catecholamines have drawn increasing attention in recent years for their universality, simplicity and versatility.[1] As a remarkable representative, polydopamine (PDA) has been widely implemented to functionalize various substrates for a plethora of applications.[2-6] It generally acts as functional coating or "anchor", but barely as bulky materials except spheres, capsules and photonic crystals.[7-10] Ultrathin films were occasionally reported from typical polymers containing a small amount of PDA. For instance, Ball *et al.*[11] fabricated a free-standing membrane via dopamine polymerization in a polyelectrolyte multilayer film. Similar work was demonstrated by Zhao *et al.* to assemble PDA-conjugated poly(acrylic acid) and poly(allylamine hydrochloride) layer-by-layer into a robust free-standing multilayer film.[12] In these films, PDA is mostly regarded as "glue" without further functions, whose content is quite low. On the other hand, Kohri *et al.*[13] constructed free-standing brush films via surface-initiated atom transfer radical polymerization in which a PDA layer was used to chemically conjugate initiators. To the best of our knowledge, there is no report concerning the fabrication of free-standing films mainly composed of PDA, which may find applications in various fields such as nanofiltration,[14] photonics and electrics.[15-17].

Several methods have been employed to fabricate free-standing ultrathin films, including spin-coating,[18] layer-by-layer assembly,[19] and Langmuir-Blodgett deposition.[20] Nevertheless, most of them necessitate detachable underlying substrates, which may damage the ultrathin films during peeling or transfer. By contrast, interfacial polymerization is a common substrate-free approach. For example, free-standing polypyrrole films have been successfully polymerized at the liquid/liquid,[21] solid/liquid[22] and gas/liquid interfaces.[23,24] Recently, we reported a reaction gradient arising from oxygen

diffusion during dopamine oxypolymerization.[25] In this case, the oxygen concentration is higher at the interface than in the bulk solution. Therefore, it is possible for us to fabricate PDA film at the air/solution interface via the combination of interfacial reaction and assembly process. However, the fabricated PDA films are too fragile to transfer for further applications due to the inherent rigidity of melanin-like structures. To address this problem, low-molecular-weight polyethyleneimine (PEI, Mw=600) was introduced as a cross-linking agent,[26] which certainly enables the PDA/PEI composite films to be free-standing through Michael addition or Shiff base reaction between PDA and PEI (**Fig. 1a** and **Fig. S1** in Electronic Supplementary Information (ESI)). Moreover, these free-standing films formed by versatile PDA and PEI are able to be used as templates in metallization and mineralization.[27]
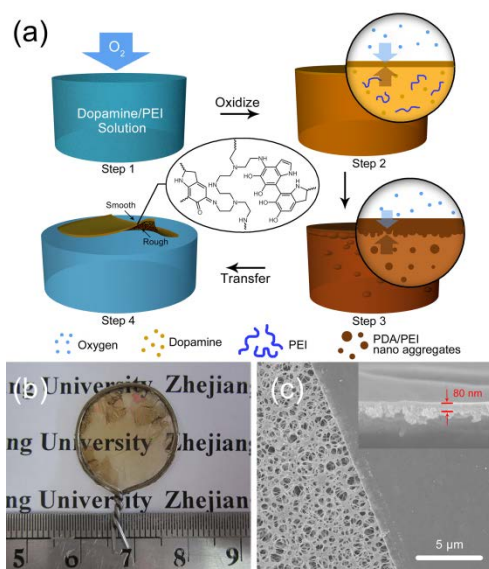
Fig. 1 (a) Schematic description of the formation process of PDA/PEI free-standing composite films; (b) A digital photo of a transparent and robust free-standing film supported by a wire loop with a diameter of about 1.5 cm; (c) FESEM images of the film on a cellulose microfiltration membrane.

The PDA/PEI free-standing films are transparent and can be supported by a wire loop with a diameter greater than 1 cm, as typically shown in **Fig. 1b**. There are no defects on the film surface as revealed by FESEM and AFM images (**Fig. 1c** and **Fig. S2** in ESI), which indicates PDA aggregates are homogenously connected by PEI through covalent bonding. The film size depends only on the calibre size of containers holding the dopamine/PEI solution. The film thickness is usually more than 80 nm, whereas it can be facilely tuned by changing the mass ratio of dopamine/PEI in solution or by controlling the reaction time. As can be seen from **Fig. 2a** (and **Fig. S3** in ESI), it decreases with the mass ratio of dopamine/PEI changing from 4:1 to 1:2 where the concentration of dopamine is fixed at 2 mg/mL. If we set the mass ratio of dopamine/PEI as 0.25, no film grew even after 24 hrs because PEI is excessive in this case and the polymerization of dopamine is easily terminated by PEI in solution. Additionally, the film thickness increases almost exponentially with the growing time, and reaches a value over 1 μm after 30 hrs at room temperature in the case of dopamine/PEI=2:1. Therefore, we can obtain a piece of brown composite paper with obviously asymmetric structure when the growing time is extended to 3 days (**Fig. S4** in ESI).
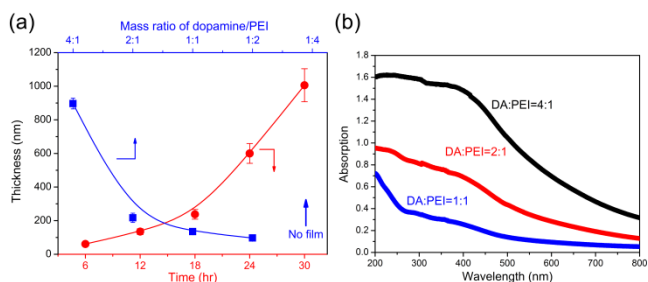
Fig. 2 (a) Dependence of the film thickness on the reaction time (red line, Dopamine/PEI concentration ratio = 0.5), and on the dopamine/PEI ratio (blue line, reaction time = 18 hrs); (b) UV-vis spectra of the composite films with different dopamine/PEI ratios. The reaction time is 12 hrs.

UV-vis spectra are shown in **Fig. 2b** for the films developed from different mass ratios of dopamine/PEI in solution. PDA has a similar absorption spectrum to melanin covering the whole visible and ultraviolet region. The absorbance decreases with the increase of PEI in the free-standing film, especially in the visible light region. This is caused by both the thinning of the composite film and the decreasing of PDA content in the film. It is very interesting that the free-standing PDA/PEI films have asymmetric structure as demonstrated by surface roughness and wettability from AFM images and water contact angle measurements. The AFM images indicate that the film surface facing to air is smooth with Rms = 0.6 nm while the other surface facing to solution is relatively rough with a high roughness value (Rms = 7.6 nm) (**Fig. 3a**). The phenomena are similar to the reported polypyrrole free-standing films fabricated at the air/ionic liquid interface, and the authors attributed these to the increasing reaction rate of the film surface towards solution.[28] In our cases, the asymmetric structure is due to the assembly of PDA/PEI aggregates growing in the solution. A dense skin layer is firstly formed at the beginning of film formation without the existence of large particles in the solution. Then, PDA nano aggregates start to form and grow onto the film surface facing to the solution as the oxidation reaction

occurs both at the interface and in the solution. This can be corroborated by the cross-section images of the freeze-fractured films (**Fig. S5** in ESI). XPS data show that the N/O ratio of the film surface facing to solution (N/O = 0.862) is higher than that of the surface facing to air (N/O = 0.614, **Fig. 3b** and **Table S1** in ESI). It denotes the higher PEI and less PDA of the former surface than that of the later one. Furthermore, the film surface facing to solution is quinone-rich as determined from narrow scan spectra (**Fig. S6** in ESI), whose detailed mechanism is still elusive. Anyway, the asymmetry in both chemical composition and morphology brings remarkable disparity in the surface properties such as wettability, which will bring significant distinction in underwater adhesion behaviours. For instance, if we drag the film from the surface towards water by up-stroke method, as described by case 1 in **Fig. 3c**, it can be easily peeled off when re-soaking the sample in water. However, it will attach on the glass slide tightly when the other surface is contacted to the substrate. The situation is totally reversed when the films are kept in air after fully-dried treatment. The film surface facing to air keeps unwetted and even envelopes the tweezers when the free-standing film is forced into water.
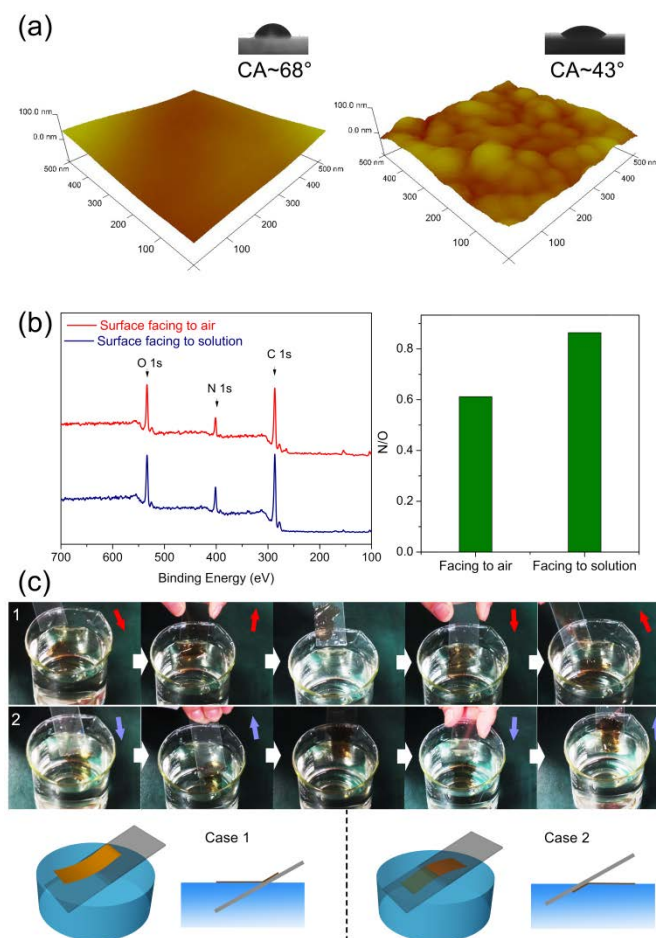
Fig. 3 (a) AFM images, water contact angle measurements and (b) XPS spectra and N/O ratio of both surfaces of free-standing films; (c) transferring floating films onto glass slides by up-stroke (case 1) and down-stroke (case 2) method.

It has been widely reported to use PDA and PEI as templates for constructing inorganic coatings or generating metal nanoparticles on various substrates.[1,27,29-33] Here, the free-standing films were explored as in-situ templates for the growth of silver, hydroxyapatite, titania and silica (**Fig. 4** and **Fig. S7** in ESI). The films turn dark brown after being immersed into silver nitrate solution for 12 hrs (**Fig. S8** in ESI). Judging from FESEM images, both sides of the film are coated with Ag nanoparticles, but in different morphologies (**Fig. 4a**). A peak ascribed to the (111) lattice plane of Ag appears in the XRD spectrum (**Fig. S9** in ESI). These Ag nanoparticles can significantly enhance the Raman shift of PDA by SERS (**Fig. S10** in ESI).[33] On the other hand, PDA-assisted hydroxyapatite formation was studied for potential biomedical applications.[35, 36] The suggested mechanism is related to the Ca^{2+} chelation by catechol.[26] We also prepared hydroxyapatite films via transferring the free-standing films to a modified simulated body fluid (mSBF) solution at 37 °C. **Fig. 4b** shows that the formed hydroxyapatite can transform from granule-like to lath-like as the mineralization time increases from 24 h to 48 h. Furthermore, both titania and silica coatings can be prepared on the basis of the sol-gel process by immersing the free-standing films into sol solution containing corresponding precursor (**Fig. 4c** and **d**). The amino groups play a crucial role during these processes. All these results demonstrate the free-standing films show great potential for the fabrication of inorganic-organic hybrid composites, which depends on the strong coordination ability of the amino and catechol groups.
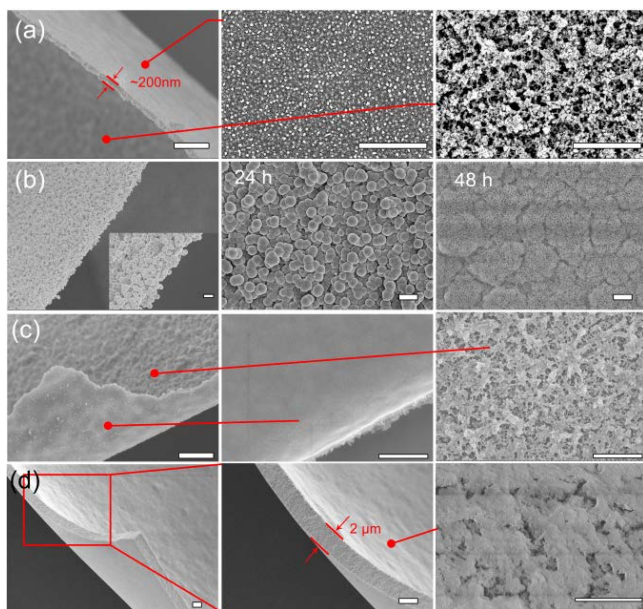
Fig. 4 FESEM images of the free-standing films coated by (a) Ag nanoparticles on both surfaces, (b) hydroxyapatite with different growth time, (c) titania and (d) silica via sol-gel method. The scale bars in this figure is 1 μm.

As a summary, we report the ultrathin PDA/PEI composite films prepared by both the oxypolymerization of dopamine and the cross-linking between PDA and PEI via a simple and controllable process at the air/water interface. They are robust and free-standing owing to the cross-link reaction between PEI and PDA. Besides, the composite films exhibit a Janus-like geometry with different morphologies, components and surface properties. They can be regarded as a kind of universal template to fabricate silver, hydroxyapatite, titania and silica films, and it can be extended to other minerals with special functions via the coordination or electrostatic interactions between PDA/PEI and precursors.

Acknowledgements

Notes and references

[a]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China. E-mail: xuzk@zju.edu.cn
[b]Department of Chemistry, Zhejiang University, Hangzhou 310027, China.
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