Supporting Information

Demulsification-Induced Fast Solidification: A Novel Strategy for the Preparation of Polymer Films

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9th July 2019

Note added after first publication: This Supplementary Information file replaces that originally published on 4th July 2019.

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**Materials.** Polyvinyl alcohol (PVA; 1788) was purchased from Shanxi Sanwei Group Co., Ltd. (Shanxi, China). Potassium peroxydisulfate (KPS) and sodium dodecylsulfonate were purchased from XiLong Chemical Co., Ltd. (Guangdong, China). The emulsifiers octylphenol polyoxyethylene ether (OP-10) was purchased from Aladdin (Shanghai, China). Di-n-butyl phthalate (DBP) was purchased from Shenyang Xinhua Reagent Factory (Shenyang, China). The metal alloy wire (Al alloy; 750 μm diameter), Al sheet (1000 μm thickness), Al wire (1000 μm diameter), Cu wire (800 μm diameter), Cu sheet (100 μm thickness), Zn wire (500 μm diameter), and Zn sheets (100 μm thickness) were purchased from Changchun Metal Materials Corporation (Jilin, China). An electrode containing carbon and gold at each end was purchased from Shanghai Jingchong Electronic Technology Development Co., Ltd. (Shanghai, China). Ethanol (EtOH; EtOH≥99.7%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). RE-906 polyurethane acrylate emulsion (906; pH 4.0–7.0, 300–1000 cps, solid content 52.0±2.0) was purchased from Bondly Chemical Co., Ltd. (Guangdong, China). Vinyl acetate (VAc) and monomer potassium chloride (KCl) were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Sodium hydroxide (NaOH), hydrochloric acid (HCl), and sodium hydrogen carbonate (NaHCO₃) were purchased from Beijing Chemical Works (Beijing, China). Dialysis membranes (Mw 8000–14,000) were purchased from Beijing Dingguo Changsheng Biotechnology Co., Ltd. (Beijing, China). Cellulose acetate (CA) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Poly(ethylenimine) (PEI; Mw 750,000) and poly(acrylic acid) (PAA; Mw 100,000) were
purchased from Sigma-Aldrich (USA). All chemicals were used without further purification unless stated otherwise. Deionized water was used to prepare the aqueous solutions and for rinsing and washing operations in all experiments.

**Characterization.** The morphology of the samples was observed via scanning electron microscopy (SEM; XL-30 ESEM FEG, FEI/Phillips, Netherlands), and energy dispersive spectrometry (EDS; Oxford Instruments, X-Max) was employed for elemental identification. Cross-sectional SEM images were obtained for all film samples prepared by cutting with a blade, except that given in Fig. S15a, which was obtained by immersing the sample in liquid nitrogen to obtain a freeze-fractured surface. The thicknesses of the film samples were first measured with a Vernier caliper, and some of the material was then precisely measured via SEM results. The thickness of the film was measured from at least five different positions on the same film; the data are presented in terms of the mean ± standard deviation. The optical transmittance of the film samples was recorded on an ultraviolet/visible (UV-Vis) spectrophotometer (N4, INESA, China) with the spectrum of air (i.e., no sample) serving as the baseline. Tensile testing of the free-standing films was conducted in an ambient environment on a materials testing machine (INSTRON 1121, USA) with a constant tensile rate of 20 mm min$^{-1}$. The strain was defined as $\varepsilon = [(l - l_0)/l_0] \times 100\%$; here, $l$ is the instantaneous sample length during testing and $l_0$ is its initial length. The films used for tensile testing were rectangular (approximately 10 mm × 8 mm). The adhesion strength of the samples was tested on an electronic universal testing machine (PT14-014, 1 kN, China) with a load change rate of 50 N s$^{-1}$ and a displacement rate of 200 mm min$^{-1}$. At least five
samples were obtained under each condition and used for tensile testing and adhesion strength testing. The results are presented in terms of the mean ± standard deviation.

**Substrate treatment.** Glass substrates were cleaned with EtOH followed by drying with air flow. The dialysis membranes were immersed in ethanol (1:1 mixture of 50% deionized water and 50% EtOH) and heated at 80°C for 40 min in a water bath. The dialysis membranes were then rinsed with a large volume of deionized water. The thicknesses of dry and wet dialysis membranes were 22.86±2.67 and 43.33±2.50 μm, respectively.

**Preparation of PVAc emulsion via radical polymerization.** The KPS initiator was prepared by dissolving KPS (0.24 g) in deionized water (24 mL) at room temperature. A protective colloid of PVA (90 mL, 10 wt% PVA solution in water) and deionized water (36 mL) were added into a three-necked flask equipped with a reflux condenser and a mechanical agitator. This was followed by the addition of OP-10 (2.4 mL) as a non-ionic emulsifier, sodium dodecylsulfonate (0.75 g) as an anionic emulsifier, KPS initiator (6 mL), and VAc monomer (15 mL). The pre-polymerization reaction was performed at 70°C for 1 h in a water bath with stirring. Then, VAc (81 mL) and KPS initiator (18 mL) were alternately added into the above reaction. The reaction was continued at 70°C for 2 h with stirring. The temperature was adjusted to 90°C until no reflux was observed followed by cooling to 50°C. The pH of the obtained emulsion was adjusted to 5–6 using 5% NaHCO₃. Finally, DBP (11.9 g, 10 wt%) as a plasticizer was added with stirring for 15 min at 50°C. The solid content obtained from the above
process was determined as \[ S = \left( \frac{m}{M} \right) \times 100\% = 42.37\% \] after drying the emulsion of initial weight \( M \) in an oven at 115°C until the final weight \( m \) remained constant.

**Preparation of ethylene diamine tetraacetic acid (EDTA) solution.** EDTA (0.025 g) was added to the deionized water (50 mL), and the mixture was heated at 100 °C until the EDTA dissolved.

**Fabrication of a free-standing film via mechanical exfoliation.** The glass substrate was dipped in emulsion followed by dipping in a 1 M KCl solution (1 min) for fast solidification and then water washing. Finally, the free-standing film was prepared via mechanical exfoliation in water with a blade (Fig. S1, ESI†).

**Fabrication of films via electrochemical deposition.** A metal wire or sheet working electrode was dipped in a 906 or PVAc emulsion at room temperature, and a specific voltage \( U \) was applied to the working electrode for a specific period (Fig. 1b). After deposition, the working electrode was rinsed in deionized water to remove the uncured emulsion.

**Thickness of the film fabricated via electrochemical deposition.** The thickness of films obtained from the electrochemical deposition process was calculated using 
\[ T = \frac{T_W - T_M}{2}, \]
where \( T_W \) is the total thickness of the film and metal substrate, and \( T_M \) is the thickness of the metal substrate.

**Fabrication of 906/PVAc films on metal substrates by casting.** The 906/PVAc emulsion was poured on the surface of a metal substrate and then used for the adhesion
of metal substrates without drying.

**Adhesion of films deposited on Zn sheets.** Films were deposited on Zn sheets via electrochemical deposition (8 V, 5 min) or simple casting emulsion on one end of the two Zn sheets. The Zn sheets were then bonded manually with a contact area of 5 mm × 5 mm by applying a pressure of approximately 0.15 MPa for 1 min (Fig. 2a). This was then held under ambient conditions with relative humidity values of 30–70% prior to tensile testing and underwater adhesion strength testing. The average thicknesses of the films were equivalent for both deposition methods.

**Fabrication of free-standing films with hollow tube shapes by dissolving the substrate.** Polymer films electrochemically deposited on a wire or sheet working electrode were immersed in 1 M NaOH, and the fresh film was directly removed after sufficiently dissolving the metal substrate.

**Deposition of (PEI/PAA)*7 coatings on Cu wires.** We prepared (PEI/PAA)*7 coatings according to literature.[1] Generally, a Cu wire was alternately immersed in PEI (1 mg mL⁻¹; pH 9.5) and PAA (1 mg mL⁻¹; pH 4.0) for 20 min. These were rinsed twice in water for 1 min after deposition in polyelectrolytes and then dried in air. This process was repeated n times to obtain (PEI/PAA)*n coatings on Cu wires. The Cu wires deposited with (PEI/PAA)*7 coatings were first wetted with water to make them conductive.

**Fabrication of free-standing films with hollow tube shapes via sacrificial layers.**
We deposited (PEI/PAA)*7 on a wire anode as a sacrificial layer for deposition of a 906 film via electrochemical deposition. The composite was then immersed in 2 M HCl to dissolve the (PEI/PAA)*7 coating, and transparent and hollow tubular free-standing 906 films with an average thickness of 52.56±17.41 μm were removed by mechanical exfoliation using tweezers.

Fabrication of 906 free-standing films with a cast 906 film layer. The 906 emulsion was poured on the outer surface of a free-standing 906 film prepared by electrochemical deposition.

Deposition of CA films on Cu wires. A Cu wire was immersed in a 10 wt% CA solution in acetone for 5 s at room temperature and then dried in air. The CA films on the Cu wire were treated according to the treatment process and applied to the dialysis membranes discussed above for substrate treatment.
A mechanism for the film building is suggested in Fig. S3a (ESI†) based on the experimental results described in Fig. 1. The metal substrate used $U$ to produce metal ions; the metal ions or $H^+$ were put into contact with the emulsion leading to demulsification to form a film. Finally, the ions diffused to the film surface and then constantly induced demulsification to form the film. The diffusion process of the ions from the metal surface to the film surface is illustrated schematically in Fig. S3b (ESI†).

Fick’s second law was used to study the build-up mechanism of the film.[2] We assumed the following: (a) The solidification process is instantaneous, i.e., the demulsification occurs immediately when the ions contact the emulsion; (b) the film thickness is the transmission rate of ions or is the velocity from emulsion to solid; (c) the ion content is constant on the surface of the metal substrate, the transmission content of the ions decreases with increasing film thickness, and the film surface has no ions; (d) the demulsification efficiency of various ions is equivalent; (e) the thickness of the anodes and cathodes is thick enough versus the required diffusion ions; thus, it do not affect the production and transmission of ions; and (f) the film is homogeneous in three dimensional space, and thus a planar schematic drawing was applied to study the diffusion of the ions. Therefore, we analyzed the film-building process following Fick’s second law for a semi-infinite diffusion couple in Fig. S3b and 3c (ESI†). Here:

$$C(x,t) = C_0 \text{erfc} \frac{x}{2\sqrt{Dt}}$$

(1)

This can also be expressed as:

$$x = D_f \sqrt{t}$$

(2)

where $C_0$ is the initial concentration of the diffusion ions on the surface of metal.
substrate, D is the diffusion coefficient of ions from the metal surface to the film surface, x is the thickness of the film, and t is the conduction time. The diffusion coefficients of the ions were calculated by fitting Fick’s law of diffusion to the film thickness:

$$D_f = \frac{T}{\sqrt{t}},$$  \hspace{1cm} (3)

where T is the experimental thickness. The calculated diffusion coefficients ($D_f$) (Table S2) of the ions approached a maximum and then decreased after initially increasing with increasing conduction time in the emulsion for up to 30 s. This supports the hypothesis that the transmission content of ions decreases with increasing film thickness. Importantly, the predictions from the Fick’s second law matched our experiments.
According to Fig. 1, S5, and S6, ESI† this can be formalized by the anodic reaction equation for metal alloy-metal alloy pairs:

\[
M(s) + 2H_2O(l) - ne^- \rightarrow M^{n+} + O_2(g) + 4H^+ + 4e^- \tag{4}
\]

and the cathodic reaction equation:

\[
H^+ + e^- \rightarrow \frac{1}{2}H_2(g) \tag{5}
\]

This represents the overall reaction equation

\[
M(s) + 2H_2O(l) + nH^+ \rightarrow M^{n+} + \frac{n+4}{2}H_2(g) + O_2(g) \tag{6}
\]

For the CE-CE electrode pair, demulsification is expected to be due to H\(^+\) ions. Thus, the anodic reaction equation in this case is:

\[
2H_2O(l) - 4e^- \rightarrow O_2(g) + 4H^+ \tag{7}
\]

the cathodic reaction equation is:

\[
4H^+ + 4e^- \rightarrow 2H_2(g) \tag{8}
\]

and the overall reaction equation is:

\[
2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \tag{9}
\]
Fig. S1. Schematic illustrating the preparation process of a free-standing film via mechanical exfoliation. The thickness of the free-standing film as a function of dipping time in the 906 emulsion.

Fig. S2. a) Thickness of the 906 film electrochemically deposited using a metal alloy-metal alloy electrode pair that wires placed in the 906 emulsion with a 1 cm, 2 cm, and 3 cm separation distance as a function of applied $U$ ($t = 1$ min). Thickness of the 906 film electrochemically deposited using a metal alloy-metal alloy electrode pair as a function of b) applied $U$ ($t = 1$ min) and c) deposition time ($U = 1, 1.5$ V).
Fig. S3. a) Schematic drawing of the build-up mechanism of the film based on the DIFS method. b) Cross-section from metal to film. c) The natural logarithm of thickness is plotted versus square root of time for film-building.

Fig. S4. Thickness of PVAc film electrochemically deposited using a metal alloy-metal alloy electrode pair as a function of a) applied $U$ (t = 1 min) and b) deposition time ($U = 8$ V).
Fig. S5. SEM images of 906 film formation on the metal alloy working electrode (1 V, 3 h). a) Cross-sectional image of a 906 film; b) metal alloy working electrode cross section after deposition; and c) surface of the 906 film.

Fig. S6. a) Cross-sectional SEM image and corresponding b) EDS line scanning data for a 906 film electrochemically deposited using a metal alloy-metal alloy electrode pair (0.5 V, 1 min).
Fig. S7. SEM images of 906 films electrochemically deposited using a metal alloy-metal alloy electrode pair (12 V, 1 h): a) and b) outer surfaces; c) wire cross section; d) cross-sectional SEM image; and e) corresponding EDS line scanning data. f) SEM and EDS elemental mapping images of the wire cross-section shown in Fig. S7c: g)–k) C, O, Fe, Zn, and Ca elemental maps.
Fig. S8. Image of a transparent 906 film deposited on wire netting (wire netting-metal alloy; 8 V, 5 min).

Fig. S9. Lap shear strengths of Zn sheets bonded using 906 films electrochemically deposited on Zn anodes with a metal alloy cathode (8 V, 5 min) or by simple casting as a function of bonding time.
Fig. S10. Image of branched hollow 906 tube with an α shape deposited on Al (Al-metal alloy; 12 V, 18.5 min).

Fig. S11. SEM images of a hollow 906 tube fabricated by deposition on the surface of a Cu wire anode (8 V, 20 s) coated with a sacrificial (PEI/PAA)*7 layer: a) inner surface and b) outer surface.

The DIFS approach proposed above offers films with controllable thicknesses and compositions. However, the films could only be prepared on a conductive substrate surface, and it is difficult to transfer to other surfaces. A spacer with a penetrable ion could be used in DIFS for double- or multi-layer structures with diverse function design. This is because the ion can penetrate from the metal to film directly. Therefore, in addition to direct deposition on the metal anode, the anode can also be wrapped in a dialysis membrane as a spacer to allow the metal ions from the working electrode to pass through the dialysis membrane during the electrolysis process. A film is electrochemically deposited directly on the dialysis membrane (Fig. S12a, ESI†) after which a 3D hollow tubular free-standing film is obtained by mechanical exfoliation with tweezers in water (Fig. S12b, ESI†, Video S4, ESI†). The average minimum film thickness obtained with a Cu anode wrapped with a dialysis membrane, a metal alloy cathode, and the 906 emulsion (8 V, 20 s) was 13.33±5.16 μm. The film was easily
separated from the dialysis membrane after immersion in water for 3 d. This is due to
two reasons: (a) water breaks the weaker interactions between the film and the dialysis
membrane, and (b) water causes the film to swell and soften. The transparent 906 film
tube has a blue cast demonstrating that Cu\textsuperscript{2+} was present in the film. SEM images (Fig.
S13a and b, ESI†) show that the prepared transparent 906 free-standing film had a flat
inner surface and a rough outer surface that detracts from the transparency of the film,
as the rough outer surface randomly alters the path of light propagation through the
film.\textsuperscript{[17]} Therefore, a flat film was obtained on both the inner and outer surfaces by
casting 906 on the outer surface of the free-standing film prepared \textit{via} electrochemical
deposition. The flatness of the casted outer surface was verified by SEM analysis (Fig.
S13c, ESI†). Moreover, UV-Vis results verify that the transmittance of the 906 free-
standing film with the cast outer surface was greater than that obtained without casting
(Fig. S14, ESI†). This is clearly observable from the images of the two films (inset of
Fig. S14, ESI†).

The use of a dialysis membrane in conjunction with electrochemical deposition
can also be employed to fabricate a composite 906 free-standing film by changing the
metal of the anode at some midpoint of the overall deposition process. To demonstrate
this phenomenon, a film was first deposited on a working electrode made from a Zn
sheet wrapped in a dialysis membrane (8 V, 10 min). This was then dried in air for 2 h,
and then the dialysis membrane with the initially deposited film was slipped off the Zn
anode and then slipped onto the Cu anode for continued deposition (8 V, 10 min). The
SEM images and EDS data indicate that the cross-section of the resulting free-standing
film has no interface at the point in the deposition process where the anode metal changed (Fig. S15a, ESI†); both Zn and Cu are evenly distributed throughout the film’s cross section (Fig. S15b–i, ESI†).

The metal ions can be removed from the films when the transparent 906 free-standing film prepared by electrochemical deposition on combined with dialysis using Cu as substrates was immersion in the EDTA solution for 20 h at room temperature. We noted that the colour of film changed from blue to colourless (Fig. S16, ESI†), indicating that the Cu$^{2+}$ was coordinated with EDTA and removed from the 906 free-standing film. The tensile testing data indicated that the transparent 906 free-standing film prepared by electrochemical deposition combined with dialysis had excellent mechanical performance (Fig. S17, ESI†). And the tensile strength of the transparent 906 free-standing film is related to the demulsifier. It is probably that the metal ion and the group in the film generated coordination and crosslinking, which inducing the difference in mechanical performance. After metal ions coordinated with EDTA solution, crosslinking degree of films decreased, thus the tensile strength decreased.

The dialysis membrane in this process can be replaced by a layer of cellulose acetate (CA) cast on the anode, and mechanical exfoliation was completed using tweezers. This process was used to fabricate a 3D hollow tubular film with a double-layer structure (Fig. S18, ESI†). These double-layer films have a structure that offers amazing and tuned functionality. This highlights its potential applications for smart devices such as bilayer actuators.
Fig. S12. a) Schematic illustrating the DIFS method in conjunction with electrochemical deposition conducted by wrapping the anode in a dialysis membrane and depositing the film directly on the dialysis membrane via electrochemical deposition. b) Image of a hollow transparent 906 tubular free-standing film fabricated by electrochemical deposition directly on the surface of a dialysis membrane wrapping a Zn sheet anode with a metal alloy cathode (8 V, 20 min).

Fig. S13. SEM images of the hollow transparent 906 tubular free-standing film: a) inner surface; b) outer surface; and c) outer surface with a subsequently cast 906 transparent film.
Fig. S14. Transmittances of the transparent 906 free-standing film prepared via electrochemical deposition (black) and the 906 free-standing film with the outer cast 906 surface (red). This inset presents images of the films without (left) and with (right) the outer casted 906 surface. Here, the background was 2 cm behind the film.
Fig. S15. Composite 906 free-standing film fabricated with a dialysis membrane by changing the metal of the anode at the midpoint of the overall electrochemical deposition process: a) cross-sectional SEM image; b)–g) EDS elemental mappings; h) and i) EDS line scanning of the resulting free-standing film.

Fig. S16. Images of the transparent 906 free-standing films prepared by electrochemical deposition combined with dialysis using Cu as substrates without (left) and with (right) the immersion in EDTA solution.

Fig. S17. Typical stress/strain curves of the transparent 906 free-standing film prepared by electrochemical deposition combined with dialysis using Cu and Zn as substrates, respectively. And the transparent 906 free-standing film prepared by electrochemical deposition on combined with dialysis using Cu as substrates was immersion in the EDTA solution for 20 h.
Fig. S18. Cross-sectional SEM image of a hollow 906 tube fabricated by deposition on the surface of CA (8 V, 20 s).
Table S1. Electrode pairs employed for electrochemical deposition analysis.

<table>
<thead>
<tr>
<th>Anode-cathode</th>
<th>Types of electrodes</th>
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<td>Active metal-active metal</td>
<td>Al-Zn, Al-metal alloy, Zn-metal alloy, Al-Al, Zn-Zn, metal alloy-metal alloy</td>
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<tr>
<td>Inactive metal-inactive metal</td>
<td>Cu-Cu, Au-Au</td>
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<tr>
<td>Active metal-inactive metal</td>
<td>Zn-Cu, Al-Cu, metal alloy-Cu</td>
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<tr>
<td>Inactive metal-active metal</td>
<td>Cu-Zn, Cu-Al, Cu-metal alloy</td>
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<tr>
<td>Carbon electrode (CE)</td>
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<tr>
<td>Inactive metal-CE</td>
<td>Au-CE</td>
</tr>
<tr>
<td>CE-active metal</td>
<td>CE-metal alloy</td>
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<tr>
<td>CE-inactive metal</td>
<td>CE-Au</td>
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Table S2. Calculated diffusion coefficients of ions from the metal surface to the film surface.

<table>
<thead>
<tr>
<th>Number</th>
<th>Time ($\times 10^3$ s)</th>
<th>Experimental thickness (μm)</th>
<th>Calculated diffusion coefficients</th>
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<tr>
<td>1</td>
<td>0.01</td>
<td>22</td>
<td>220</td>
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<td>39</td>
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<td>3</td>
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<td>48</td>
<td>88</td>
</tr>
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<td>4</td>
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<td>97</td>
<td>125</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>140</td>
<td>128</td>
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<td>139</td>
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Video S1. Preparation of a 906 film on wire netting via electrochemical deposition.

Video S2. Preparation of a 906 branched hollow tube with an α shape via electrochemical deposition.

Video S3. Preparation of a 906 hollow tubular free-standing film by electrochemical deposition directly on the surface of a sacrificial layer of (PEI/PAA)*7 formed on the working electrode surface.

Video S4. Preparation of a 906 hollow tubular free-standing film by electrochemical deposition directly on the surface of a dialysis membrane wrapping a working electrode.
References
