

Research paper

Synthesis of ordered bowl-like polyaniline film with enhanced electrochromic performances



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ABSTRACT

A bowl-like polyaniline (PANI) film is synthesized by the combination of electrodeposition and monolayer colloidal crystal template (MCCT). The resulting film exhibits an ordered hexagonal close-packed bowl-like arrangement that is made up of macrobowls with a diameter of 450 nm. The unique bowl-like structure endows PANI film with enhanced electrochromic performances due to its increased accessible intercalation sites originating from larger surface areas and shortened diffusion distances of ions resulting from macroporous structure. It is found that the bowl-like PANI film possesses faster switching responses (1.45 s for coloration and 0.62 s for bleaching), larger optical transmittance modulation (52.1% at 740 nm) and higher coloration efficiency ($118.2 \text{ cm}^2\text{C}^{-1}$) than the dense PANI film prepared without the MCCT. Moreover, the bowl-like film also exhibits IR electrochromic performances in the wavelength range from 2.5–25 μm , which depicts a reflectance modulation $\sim 36.5\%$ at 10 μm . This work provides a promising strategy for constructing other bowl-like polymer electrochromic films.

1. Introduction

Electrochromic materials possess a capability of reversible color switch under applied voltages. The theory of electrochromism was proposed by Platt in 1961, and subsequently was first demonstrated by Deb in 1969 [5]. Electrochromism have been extensively studied for applying in optical display, smart windows, rear-view mirrors for automobiles due to low power consumption, high coloration efficiency, and stable memory effect under open circuit condition [1–4]. Among the wide variety of electrochromic materials, polyaniline (PANI) is particularly attractive because of its low cost, good environmental stability, ease of synthesis, as well as excellent controllability through an acid/base doping/dedoping chemistry [6–10]. It is well known that electrochromic process is essentially an electrochemical reaction associated with intercalation (de-intercalation) of ions to (from) the film [11–15]. For PANI film, its color change is due to the transition between different oxidation states accompanying intercalation (de-intercalation) of ions. The optical contrast is closely related with the amount of accessible intercalation sites. Usually, larger surface areas can provide more accessible intercalation sites, thus representing a higher

optical contrast. Switching time is restricted by the rate of ion transport into the EC film, which strongly depends on microstructures and morphology of films. In view of nanosized and porous processing of electrochromic film can obtain larger surface-to-volume ratio, the development of nano-porous structure is an ideal strategy for improving electrochromic performances of PANI.

Template assisted synthesis is one of the mostly used methods to fabricate nano-porous structure of PANI films owing to its controllability and versatility [16–18]. For example, vertically oriented nanorod arrays were prepared using supramolecular assemblies of block copolymer as scaffold material [16], and ordered nanotubes were synthesized via the introduction of anodic aluminum oxide as template [17]. Recently, three-dimensional ordered macroporous (3DOM) structure of PANI film obtained by the replication of colloidal crystal template was also demonstrated to possess enhanced electrochromic performance compared with dense film owing to the interconnected pores [19]. These interconnected pores provide inter-continuous pore spaces for good electrolyte penetration, while the continuous walls give effective transport pathways for ions. Generally, a smaller porous size implies better electrochromic performances in 3DOM structure because

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it possesses larger surface areas [13]. The colloidal crystal template is an ordered and multilayer colloidal microsphere (typically polystyrene (PS) or silica spheres) array with a hexagonal close-packed alignment [20,21]. Actually, the synthesis of the colloidal crystal template is quite tedious, which usually requires three days or more. However, the monolayer colloidal crystal template (MCCT) can be easily self-assembled in a short time, and the resulting two-dimensional ordered macroporous (2DOM) structure exhibits similar properties with 3DOM structure [22–24].

Motivated by above efforts, we herein fabricated a bowl-like PANI film with 2DOM structure by the MCCT assisted electrodeposition for the first time. Compared with dense PANI film prepared without MCCT, such bowl-like structure possesses larger surface-to-volume ratio, and thus improves electrochromic performances in the spectral range of 400–1100 nm. Moreover, IR electrochromic performance of the bowl-like PANI film in the spectral range of 2.5–25 μm was also investigated.

2. Experimental section

2.1. Assembly of the MCCT

The fabrication process of the bowl-like PANI film involves three steps, which is depicted in Fig. 1. The first step was to prepare MCCT by self-assembly. Monodispersed PS latex spheres with a diameter of 510 nm were obtained by an emulsifier-free emulsion polymerization method [25,26]. The resulting PS spheres were washed several times with deionized water and ethanol, collected by centrifugation, and dried at 50 °C for 6 h in a vacuum oven. Then the precipitate was redispersed at 1 wt% in a 1:1 by volume mixture of deionized water:ethanol to obtain PS spheres suspension. ITO glass was ultrasonically cleaned in NaOH solution (0.5 M), ethanol, and distilled water for 15 min, respectively. The hydrophilic ITO glass was placed at the middle of a Petri dish to which deionized water was added slowly to a level of slightly higher than the upper glass surface without submersion. Subsequently, the PS spheres suspension was dropped carefully onto the upper surface of ITO glass to form a floating monolayer of PS spheres. With a few drops of sodium dodecylsulfate solution (2 wt%) added into the deionized water, the floating PS spheres were pushed aside and became tight because of the change of surface tension. The monolayer of close-packed PS spheres was easily picked up by the hydrophilic ITO glass. After naturally dried in air, the MCCT was obtained finally and

stored in a desiccator for further use.

2.2. Synthesis of the bowl-like PANI film

The bowl-like PANI film was prepared in an aqueous solution of 0.1 M H_2SO_4 and 0.1 M aniline monomer by potentiostatic method at 0.8 V for 300 s. The above MCCT, Ag/AgCl and Pt foil were used as the working electrode, reference electrode and counter electrode, respectively. After electro-polymerization, the resulting PANI/PS composite film was washed carefully using deionized water, and then naturally dried in air. Subsequently, the composite film was immersed in toluene for 24 h to remove the MCCT. Finally, the bowl-like PANI film was obtained after dried at 50 °C. The dense PANI film was synthesized under the same conditions in the absence of MCCT.

2.3. Characterizations

Scanning electron microscope (SEM) images were obtained using a FEI Helios Nanolab600i. Fourier transform infrared (FT-IR) spectra were performed on a Bruker VERTEX-70 spectrophotometer using the standard KBr disk method. Cyclic voltammetry (CV) and chronoamperometry (CA) tests were carried out using a CHI760D electrochemical workstation in a three-compartment system with an aqueous solution of 0.5 M H_2SO_4 as the electrolyte, Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The optical transmission spectra (400–1000 nm) and IR reflectance spectra (2.5–25 μm) of electrochromic films in the fully colored and fully bleached states were recorded respectively using a MAYA 2000-Pro (Ocean Optics) and a VERTEX 70 (Bruker) FT-IR spectrometer with an A562 integrating sphere after the films were subjected to CA tests with a potential step 0.55 V (10 s) and -0.25 V (10 s).

3. Results and discuss

3.1. Morphology and structure

The surface profiles of films were investigated by electron microscopic studies. Fig. 2a–c presents SEM images of the MCCT, the bowl-like PANI film and the dense PANI film. The MCCT shows a typically close-packed array with long-range order perpendicular to the ITO glass (Fig. 2a). After removing the MCCT by toluene etching, the obtained

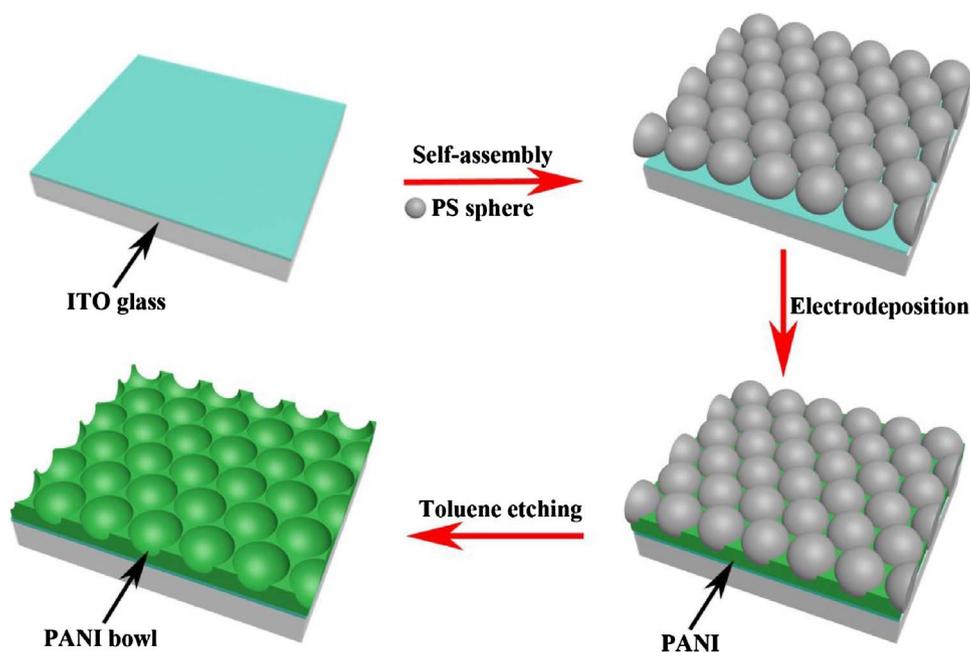


Fig. 1. Schematic illustration for the formation of the bowl-like PANI film.

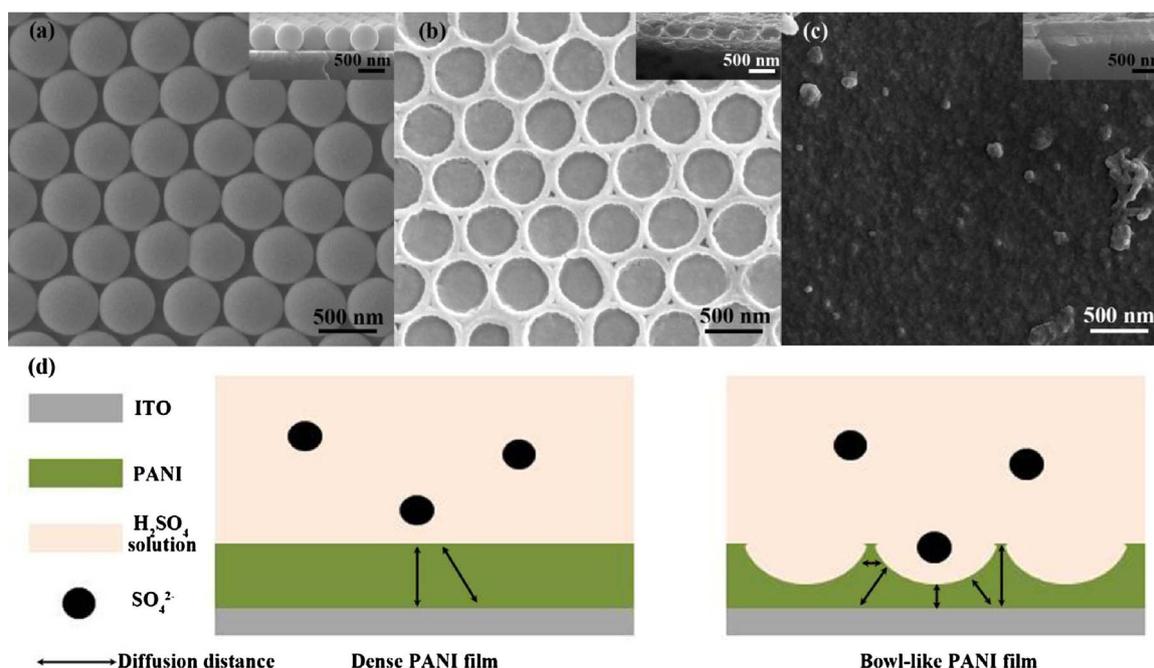


Fig. 2. SEM images of (a) the MCCT, (b) bowl-like PANI film, and (c) dense PANI film; (d) Schematics illustrating the differences of diffusion distance in dense PANI film and bowl-like PANI film. The upper-right insets in (a), (b) and (c) correspond to the side views of films.

PANI film forms a highly ordered bowl-like arrangement (Fig. 2b). For comparison, the dense PANI film without MCCT exhibits double morphologies, namely, underlying homogeneously compact structure and overlying sparse nanoclusters (Fig. 2c). With respect to the diameter of macrobowls (about 450 nm) slightly less than that of hemispheric pore (510 nm), this is because it is too difficult to prepare perfect hemispheric bowl. This 2DOM structure can shorten the diffusion distance of ions and increase surface areas, and thereby effectively improves electrochromic performance of materials. Fig. 2d illustrates the influence of the 2DOM structure on the behavior of ions diffusion. For dense PANI film, the diffusion distance of ions throughout whole PANI layer in the axial direction is the shortest. After introducing 2DOM structure, diffusion paths possess more options because of the electrolyte solution infiltrated into ordered macro-pores. In this case, the distances of most diffusion paths are shorter than axial thickness of PANI layer. The surface areas were also roughly estimated using formulas of circular area and spherical cap area. The calculated results suggest that the surface area of the bowl-like PANI film is nearly 1.4 times larger than that of dense PANI film.

The chemical structure of films was determined by FT-IR spectroscopy in the range of 400–4000 cm^{-1} . As displayed in Fig. 3, the pure dense PANI film presents a pronounced absorption bands at 3433 cm^{-1} , which is ascribed to the N–H stretching mode [27]. The

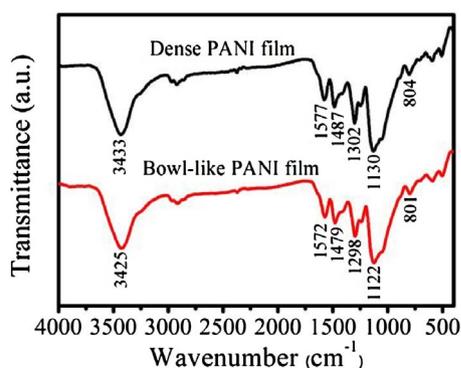


Fig. 3. FT-IR spectra of the bowl-like PANI film and dense PANI film.

bands at 804 cm^{-1} and 1130 cm^{-1} are assignable as the C–H in and out of plane bending vibration [28]. The band at 1577 cm^{-1} , 1487 cm^{-1} and 1302 cm^{-1} originate from the quinonoid structure, benzenoid structure and aromatic amine (C_6H_4)–N, respectively [29]. After introducing ordered architecture, the FT-IR spectra of the bowl-like PANI film and dense PANI film show very close characteristic peaks, suggesting that the bowl-like PANI has been formed.

3.2. Electrochemical and electrochromic properties of the bowl-like PANI film

The reversible electrochemical reaction during ion insertion/extraction is the basis for electrochromism. The CV test is a mostly common analysis method for the reversible electrochemical properties study. The CV curves of the bowl-like PANI film and the dense PANI film are compared in the potential region of -0.25 to 0.8 V at a scan rate of 50 mV s^{-1} (Fig. 4). The dense PANI film exhibits an oxidation peak at 0.321 V and a reduction peak at 0.002 V, which correspond to the transformation between leucoemeraldine and emeraldine [30,31]. The involved oxide/redox reactions were briefly proposed as follows [32]:

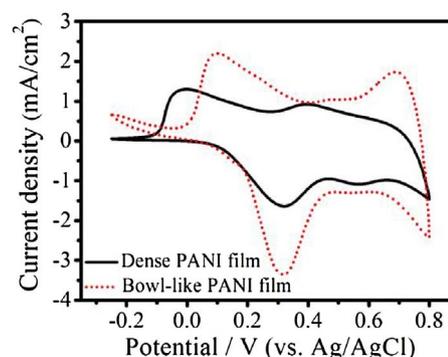
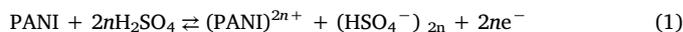


Fig. 4. CV curves with a scan rate of 50 mV s^{-1} between -0.25 and 0.8 V of the bowl-like PANI film and dense PANI film.

A pair of humps in the region of 0.35–0.6 V originates from defects in the linear polymer structure (cross-linking) [33]. The cross-linking reaction results in an interruption in the delocalization of both the charge and electrons along the polymer chain [34]. Thus, the humps can be linked to a decrease of the conductivity and an increase in the number of residual spin in the polymer upon potential cycling [35]. For the bowl-like PANI film, this pair of humps becomes particularly weak and almost disappeared. This observation suggests that the spatial restraint in the gaps between PS spheres is sufficient to induce the formation of more ordered PANI chains in the MCCT [36,37]. Generally, ordered PANI chains are favourable to inter-chain charge transfer. Therefore, the bowl-like PANI film should possess better conductivity compared with the dense PANI film. As expected, the position of oxidation peak shifts to 0.318 V and that of reduction peak shifts to 0.097 V for the bowl-like PANI film because a smaller potential separation between the oxidation and the reduction peak represents lower resistance of electrode [10]. The anodic and cathodic peak currents of the bowl-like PANI film are much higher than those of the dense PANI film. This improvement of the currents suggests that the bowl-like PANI film has a higher surface area exposed to the electrolyte solution. Moreover, the integral area based on CV curve of the bowl-like PANI film is much larger than that of the dense PANI film, indicating that the bowl-like PANI film can store more ions. These observations clearly imply that the bowl-like PANI film should possess a higher optical contrast and a faster switching speed in comparison with the dense PANI film.

The electrochromic properties of the bowl-like PANI film and the dense PANI film were performed by recording their optical transmittance curves and IR reflectance curves under different potentials, and the summarized results are listed in Table 1. For polarized at -0.25 V, a characteristic absorbance band can be observed around 850–900 nm in the optical transmittance spectra (Fig. 5a), which is related to π -polaron transition [38]. This absorbance band is blue shifted to the visible region with the increasing of the potentials from -0.25 to 0.55 V, in accordance with previous literature [39]. Typically, the optical transmittance modulation of the bowl-like PANI film is up to 52.1% at 740 nm, higher than that of the dense PANI film (42.8%). The transmittance modulation of 52.1% is comparable to those obtained from 3DOM PANI film (47%) and ultraporous PANI nanofibers (54.1%) [19,40]. Actually, both the bowl-like PANI film and the dense PANI film also possess IR electrochromic performance (Fig. 5b). As shown in Table 1, the reflectance modulations are 27.7% and 36.5% at $10\ \mu\text{m}$ for the dense PANI film and the bowl-like PANI film, respectively. This enhanced electrochromic modulation is because compared with the dense PANI film, the bowl-like PANI film possesses a 2DOM morphology, which can provide more accessible intercalation sites, and therefore more PANI units can be effectively switched.

The switching time from one state to another state is a very key parameter for electrochromic materials. CA tests of the bowl-like PANI film and the dense PANI film with voltage step between -0.25 V (10 s) and 0.55 V (10 s) was carried out in 0.5 M H_2SO_4 electrolyte. The switching times are defined as the times required for achieving 90% of full transmittance modulation [41]. Fig. 6a and b show the current-time curves and corresponding *in situ* transmittance variation with time. It is apparent that the slopes of transmittance variation curves are different for these two films, suggesting their different switching speed. The

calculated switching times of the bowl-like PANI film for the coloration and bleaching are 1.45 and 0.62 s, respectively, which are faster than those of the dense PANI film (1.79 and 0.76 s). The improvement of switching speeds is due to the ordered macroporous structure that facilitates ion intercalation/deintercalation by reducing their diffusion path lengths. These switching times of the bowl-like PANI film are also faster than those of micropatterned PANI film prepared by electrostatic field-assisted potentiostatic deposition (2.13 and 0.75 s), PANI film covalently bonded to ITO substrate (20.8 and 19.5 s) and 3DOM PANI film (2.85 and 2.07 s) [5,19,42].

The coloration efficiency (CE), another key parameter for electrochromic material, is defined as the change in optical density (OD) per unit charge (Q) inserted to the films. A high CE means that a large optical modulation can be obtained by a small charge insertion or extraction. It can be estimated according to following equation [43]:

$$CE = \frac{\Delta OD}{\Delta Q} = \frac{\log(T_b/T_c)}{\Delta Q} \quad (2)$$

where T_b and T_c are the transmittance in the bleached and colored states, respectively. The calculated CE value of the bowl-like PANI film is $118.2\ \text{cm}^2\text{C}^{-1}$, which is nearly 2.4 times larger than that of the dense PANI film ($48.5\ \text{cm}^2\text{C}^{-1}$). The improved CE of the bowl-like PANI film is attributed to its bowl-like macroporous structure that provides more surface area for ion intercalation, resulting in a higher utilization of charge. Meanwhile, this value is much higher than those of 3DOM PANI film and micropatterned PANI film.

The durability of electrochromic material is also extremely important for practical applications. The durability of the bowl-like PANI film and the dense PANI film was evaluated by CA measurements and corresponding *in-situ* transmittance at 740 nm. Fig. 7 displays the transmittance discrepancies of the bowl-like PANI film and the dense PANI film during a 1000-cycle test. The transmittance modulation of the bowl-like PANI film maintains 68.1% of the highest value after 1000 cycles, much more stable than 57.2% of the dense PANI film, indicating the bowl-like PANI film would be a very stable and efficient electrochromic film. The improved stability of the bowl-like PANI film should be attributed to its more ordered chains, which are more stable compared with disorderly chains in the electrochromic reactions.

4. Conclusion

The bowl-like PANI film is deposited on ITO glass using an electrodeposition method with MCCT as template. The film shows a macroporous morphology with ordered hexagonal close-packed bowl-like arrangement. Compared to the dense PANI film prepared without the MCCT, the bowl-like PANI film has enhanced electrochromic performances with a larger optical modulation, faster switching responses and higher CE due to its large surface areas and shortened diffusion distances of ions. The transmittance modulation at 740 nm and the reflectance modulation at $10\ \mu\text{m}$ reach 52.1% and 36.5%, respectively. The response time is only 1.45 s for coloration and 0.62 s for bleaching. Moreover, the bowl-like film depicts a high stability and durability after 1000 cycles. However, the diameter of current macrobowls is very single. On the basis of such a starting point, our future research would hammer at researching the effect of different diameters on the electrochromic performances of PANI bowl-like films.

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Table 1
Electrochromic performances of the bowl-like PANI film and dense PANI film at 740 nm.

Sample	Optical modulation (%)		Switching speed (s)	
	740 nm	$10\ \mu\text{m}$	Coloration time	Bleaching time
Dense PANI film	42.8	27.7	1.79	0.76
Bowl-like PANI film	52.1	36.5	1.45	0.62

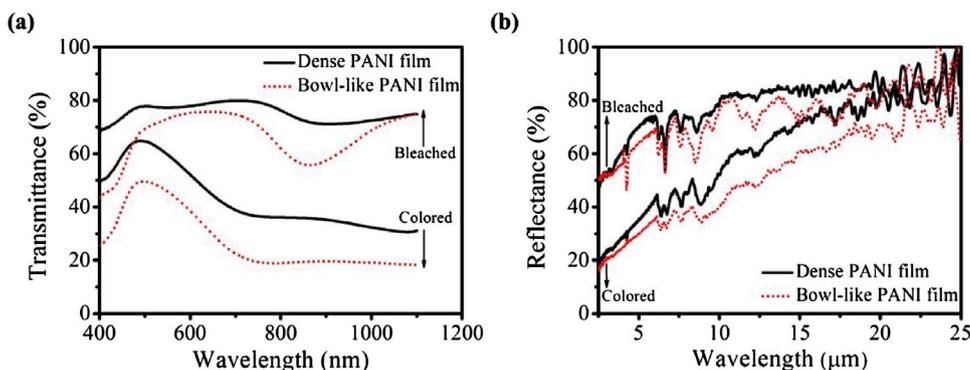


Fig. 5. (a) Optical transmittance spectra and (b) IR reflectance spectra of the bowl-like PANI film and dense PANI film under different potentials.

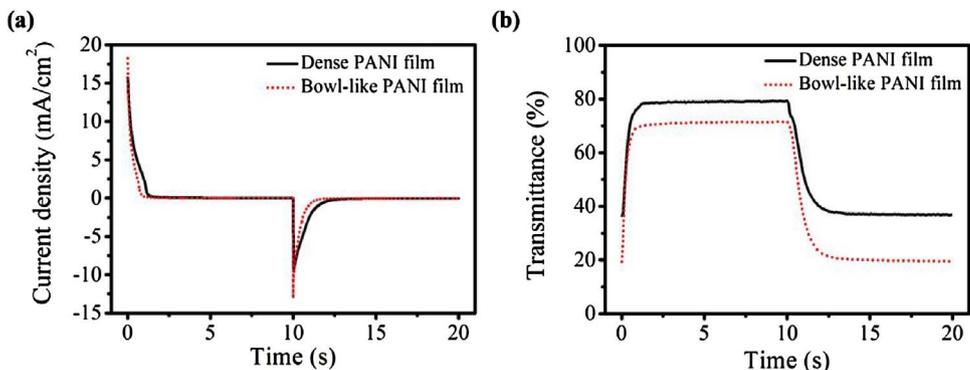


Fig. 6. (a) Chronoamperometric curves and (b) corresponding transmittance variations at 740 nm with time of the bowl-like PANI film and dense PANI film.

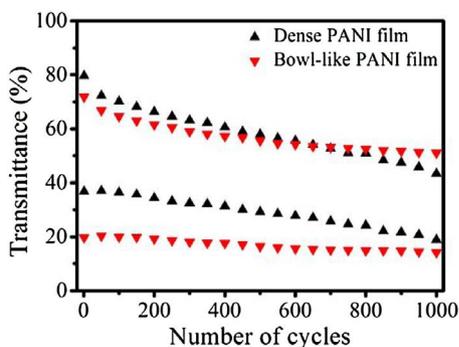


Fig. 7. Durability tests of the bowl-like PANI film and dense PANI film.

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