

Healable Layer-by-Layer Assembled WO₃-Polymeric Composite Films: Undergraduate Experiments for Nanomaterials

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Abstract Healable WO₃-polymeric composite films were fabricated by a simple method of layer-by-layer (LbL) assembly technique. The assembled films can heal damages such as scratches and cuts for multiple times on the same location by simply exposure to an acidic solution (pH 2.5). The healability was examined by UV-vis spectrophotometer. The surface morphology and composition of the films were characterized by atomic force microscopy (AFM), fourier transform infrared (FT-IR) spectrophotometer and X-ray powder diffraction (XRD).

Keywords Layer-by-layer assembly, Healing materials, Tungsten oxide, Electrochromics

1. Introduction

Self-healing materials can heal damages with inherent materials to prolong lifetimes and improve the stability. The healing mechanism can be categorized by the nature of the reversible bonds-covalent and non-covalent [1,2]. The healing process based on the covalent bonds can be realized by the Diels-Alder cycloaddition reaction, disulfide bridges, N-O bond, *et al.* The driving force for healing based on the non-covalently bounds include the hydrogen-bond [3], ionic interaction [4], π - π stacking [5], metal-ligand coordination [6] and host-guest interaction [7], hydrophobic interaction [8].

The compelling needs of next-generation electronics would require stretchable, foldable and even wearable electronic devices, including flexible electrochromic devices [9-11]. However, the reliability and lifespan of flexible electrochromic devices can be seriously decreased by the internal micro-cracks or partial injuries during the process of frequent stretching, folding, and screwing in practical applications. Motivated by this need, we propose to introduce the concept of self-healing into the electrochromic devices for realization of its self-healing to enhance operation

lifespan. In this research, inorganic/organic composite films are constructed based on the hydrogen-bond interactions by layer-by-layer (LbL) assembly technique. Tungsten oxide (WO₃) is selected as the inorganic electrochromic material, which originates from the peroxotungstic acid (PTA). Poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) are used as the film compositions. By alternatively assembling in PAA and (PTA&PEO) solutions, WO₃-polymeric composite films are prepared. The development of this project will provide a feasible method to build up a self-healing, flexible electrochromic film.

The goal of this experiment is to design a simple and practical procedure for preparing healable composite films. By doing this experiment, the undergraduate students understand the basic theoretical principles, the process of LbL assembly and the advanced knowledge in nanoscience. This experiment is suitable for undergraduate students in the study of general chemistry, inorganic chemistry and physical chemistry.

2. Experiment Description

2.1. Materials

Poly(ethylene oxide) (PEO, Mw ca. 100k) and H₂O₂ (30 wt.%) were purchased from Alfa Aesar. Tungsten powder was purchased from Aladdin. Poly(acrylic acid) (PAA, Mw ca. 250k) and poly(diallyldimethylammonium chloride) (PDDA, Mw 100k-200k) were purchased from Sigma-Aldrich. All chemical reagents were used as received

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without further purification. Distilled water was used in all the experiments.

2.2. Instruments and Characterization

The LbL deposition of composite films was conducted automatically by a programmable dipping machine (SYDC-100 M, SAN-YAN, Shanghai) at room temperature. The surface morphology was characterized by atomic force microscopy (AFM, Multimode 8, Bruker) under ambient conditions. AFM was operated in the ScanAsyst mode with an optical readout using Au-coated silicon cantilevers (SNL-10, Bruker). The film-thickness determination was carried out on a Quanta FEG 250 scanning electron microscope (SEM). The samples were coated with a thin layer of gold prior to imaging. The healing process of the composite film was tracked by a GAOPIN GP-650S optical microscopy. Optical transmittance spectra of the films were measured using a Varian Cary 500 UV-Vis-NIR Spectrophotometer. Infrared transmittance spectra were recorded with a Tensor 27 FT-IR spectrophotometer (Bruker). The crystal structure of tungsten oxide was characterized by a D/MAX-2500 X-ray powder diffractometer with Cu-K α radiation ($\lambda=1.5406$ Å) operated at 40 kV and 150 mA.

3. Experimental Procedure

3.1. Preparation of Peroxotungstic Acid (PTA) Precursor

Peroxotungstic acid (PTA) was used as a precursor for tungsten oxides. The PTA solution was synthesized by oxidative dissolution of tungsten powder in H₂O₂ according to the literature [12,13]. Tungsten powder was added into 30 wt.% H₂O₂ solution and stirred for 2 days at room temperature. A yellowish solution of PTA solution was obtained, which was filtered to remove non-reacted tungsten powder. A transparent and stable mixture of PTA and PEO (2 mg·mL⁻¹, pH 2.5) was obtained, before deposition the composite films, and the mixture was noted as (PTA&PEO).

3.2. Preparation of WO₃ Composite Films

The (PAA/PTA&PEO) multilayer films were assembled on the substrates of silicon wafer or glass microscope slide by the layer-by-layer (LbL) assembly technique [14,15]. The driving force for the film assembly is the hydrogen-bonding interaction between carboxylic acid groups in PAA and ether oxygens (-C-O-C-) in PEO polymer. A newly cleaned substrate was immersed in an aqueous solution of 1 mg·mL⁻¹ PDDA for 20 min to obtain a positive charged layer of PDDA. The (PAA/PTA&PEO) multilayer films were prepared by alternating immersion of the PDDA-modified substrates into the PAA polymer solution (2 mg·mL⁻¹, pH 2.5) and the mixture solution of PTA and PEO for 5 min each. After each deposition, the substrates were rinsed for 1 min in acidic solution (pH 2.5)

for two times. By repeating the above deposition and rinsing steps in a cyclic fashion, (PAA/PTA&PEO)ⁿ films with desired number of deposition cycles were fabricated. The above assembly process can also be manually operated, as shown in Figure 1. The drying step with N₂ flow was only conducted after depositing the last layer.

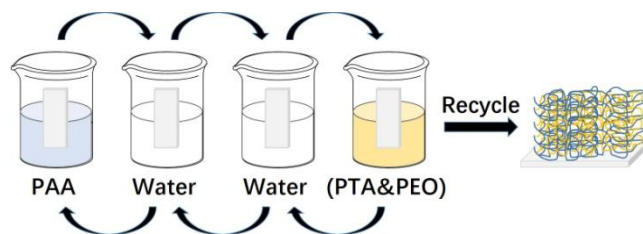


Figure 1. Schematic illustration for the preparation of (PAA/PTA & PEO)ⁿ multilayer films by LbL assembly technique

4. Result and Discussion

4.1. Characterization of Synthesized PTA Precursor

The typical XRD patterns of the as-synthesized PTA precursor and the mixture of PEO and PTA are shown in Figure 2. According to the figure, the wide peaks at $2\theta \approx 26^\circ$ represent the amorphous phase formation of WO₃, which are in good agreement with the literature values [12,16]. Even after mixing with PEO polymer, the amorphous phase of WO₃ is not changed.

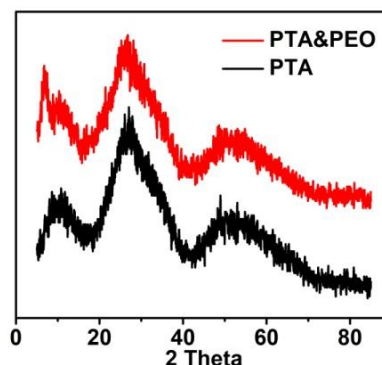


Figure 2. XRD patterns of the powdered PTA precursor and the mixture of PEO and PTA

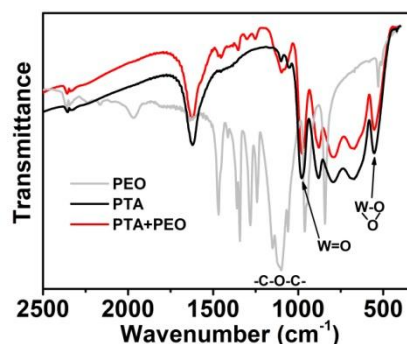


Figure 3. FT-IR spectra of the powdered PTA, PEO and the mixture of PTA and PEO (KBr pellet)

The results of FT-IR for the amorphous PTA precursor and PEO polymer are shown in Fig. 3. Two strong bonds at 980 cm^{-1} and 553 cm^{-1} are observed, which can be attributed to stretching vibrations of $\text{W}=\text{O}$ double bond and $\text{W}(\text{O}_2)$ bond of the amorphous WO_3 network, respectively [12]. In case of the PEO mixed with KBr and pressed into pellet, the three $-\text{C}-\text{O}-\text{C}-$ peaks appear at 1150 cm^{-1} , 1099 cm^{-1} and 1059 cm^{-1} , which are in good agreement with the literature values [17]. After mixing PTA with PEO, all the characteristic peaks are not shifted, which means there is no interaction between PTA and PEO polymer.

4.2. Surface Morphology and Thickness of Composite Films

The surface morphology of the assembled $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ multilayers was examined by AFM, as shown in Figure 4a. The surface roughness is 0.56 nm with scan size of $8\times 8\text{ }\mu\text{m}$. The WO_3 particles are uniformly distributed on the film surface and the particle size is range from 120 nm to 250 nm . The thickness of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ multilayers was determined by the cross-sectional SEM, as shown in Figure 4b. The LbL-assembled $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ film is uniform, and the thickness is about $4.2\text{ }\mu\text{m}$.

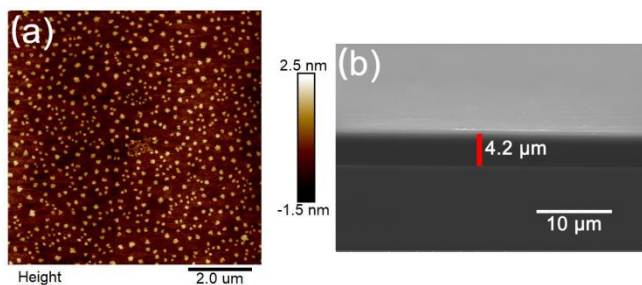


Figure 4. (a) AFM image for the assembled $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ multilayers on the silicon wafer. Scan size is $8\times 8\text{ }\mu\text{m}$; (b) Cross-sectional SEM image of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ film

4.3. Healing Properties of $(\text{PAA}/\text{PTA}\&\text{PEO})$ Films

The $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ multilayer film is colorless and transparent. As shown in Fig. 5, in the whole visible light region and near-infrared region, the multilayer film assembled on the glass slide is highly transparent, with its transmittance at 550 nm being $\sim 80\%$. The transparency of the film significantly decreased to $\sim 46\%$ at 550 nm when the film was repeatedly scratched with a 800-grit sandpaper. After immersing the scratched composite film in acidic solution ($\text{pH } 2.5$) for 30 min , the transparency of the film is almost restored to $\sim 75\%$, as indicated in Fig. 5. In the near-infrared region, the transparency of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ film decreased from $\sim 83\%$ to $\sim 47\%$ at 1800 nm after scratching with the sandpaper. While the transparency of the film restores to $\sim 77\%$ at 1800 nm after healing in $\text{pH } 2.5$ water for 30 min . It is found that the further elongation of the healing time in $\text{pH } 2.5$ water does not improve the transparency of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ film.

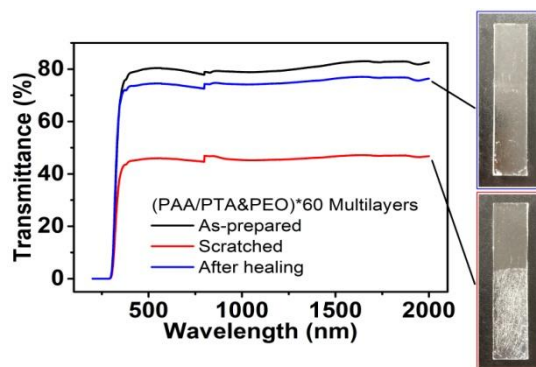


Figure 5. UV-vis transmission spectra of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ film prepared on a glass substrate before and after healing in $\text{pH } 2.5$ water. The corresponding digital images for the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ film are shown on the right

The optical microscopy was used to track the healing process. As shown in Figure 6a, there are some particles on the surface of $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ composite film, which may be the aggregates of the incorporated WO_3 particles and bubbles. The surface of the composite film becomes rough and is all scratched up after scratched with a 800-grit sandpaper. After immersing the scratched composite film in acidic solution ($\text{pH } 2.5$) for 5 min , the number of scratches are obviously decreased, indicating that the healing of scratches takes place (Figure 6c). The scratches are totally disappeared after immersing for 30 min (Figure 6d). The healing process of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ composite film is dependent on the immersion time in acidic water. The complete healing of the scratches takes about 30 min . The assembled films can heal scratches for at least 3 times on the same location.

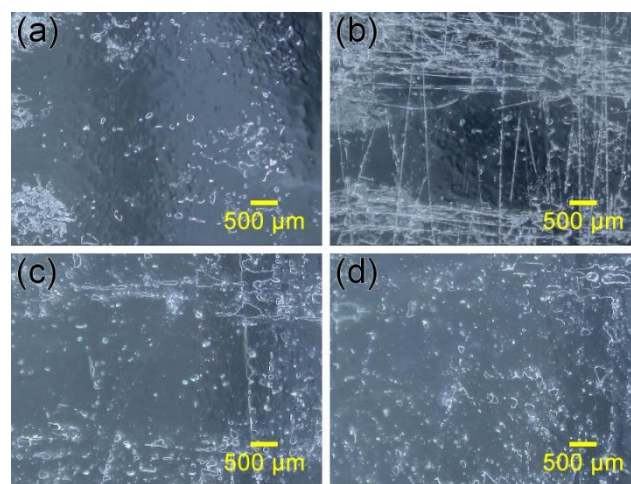


Figure 6. Healing process of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ film prepared on the glass slide. (a) original film surface; (b) film surface scratched with a 800-grit sandpaper; (c) and (d) film surface after healing in acidic solution ($\text{pH } 2.5$) for 5 min and 30 min , respectively

The healability of the $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ films originates from the reversibility of the hydrogen-bond interaction between PAA and PEO polymers. When the scratched $(\text{PAA}/\text{PTA}\&\text{PEO})^*60$ films are immersed in an acidic water, the polymer chains of the PAA and PEO

become flowable [18]. The adsorbed water in films can act as plasticizers to facilitate the migration of PAA and PEO polymers to fill the scratches, where hydrogen bonding interactions between PAA and PEO are reformed [15].

4.4. Application of the Healable Composite Films

These healable (PAA/PTA&PEO) composite films can be further used as an electrochromic film for preparing healable and stretchable electrochromic device, due to the existence of WO₃ [19]. All the experiments are performed at room temperature and atmospheric pressure, which making them suitable for physical chemistry and materials chemistry laboratories.

5. Conclusions

Layer-by-layer assembled (PAA/PTA&PEO) composite films based on hydrogen-bond interaction between PAA and PEO are successfully prepared. The (PAA/PTA&PEO)*60 composite film behave good healing property in acid water (pH 2.5), due to the fluidity of the polymers and reformation of the hydrogen-bonding interactions in the films. The healing process is dependent on the immersion time in acidic water and the complete healing of the scratches takes about 30 min. The incorporation of WO₃ makes this healable composite films have potential applications in the field of stretchable electrochromic devices.

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