Layer-by-Layer Deposition of Polyelectrolyte Complexes for Electrochemical Device Applications

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Polymer electrochromic (EC) devices are primary electrochemical devices that hold great promise for futuristic applications such as flexible screens and wearable displays. In order to attain satisfactory electrochemical properties for electrochromic application, thick electroactive films with fast ionic intercalations are desired. Layer-by-layer (LbL) self-assembling is one of the most efficient and powerful methods to fabricate films with ordered nanoscale structures with excellent functionalities and electrochemical activities. Compared with traditional EC film fabrication methods, such as thermal evaporation deposition and electrochemical deposition which require complex set-ups and operating conditions, LbL deposition is a facile, energy efficient, and environmentally friendly wet chemical deposition technique with high compatibility for large scale production on arbitrary substrates. However, polymer films made by traditional LbL deposition usually suffer from very slow process.

Polyelectrolyte complexes, formed by electrostatic interactions between oppositely charged polymers, possess versatile and easily tailored compositions and structures in solution, which is helpful to obtain polymeric films with well-designed structures as well as functionalities. Their large dimensions compared with simplex linear polymers also enable the rapid fabrication of LbL films.

In this work, we used two linear polymers, poly(acrylic acid) (PAA) and polyethylenimine (PEI), to make stable complexes under certain pH, and fabricated polyaniline (PANI)/PAA-PEI multilayer films via LbL deposition. Compared with [PANI/PAA]30 films, [PANI/PAA-PEI]30 films grew much faster under the same condition. The fast film growth is resulted from the large dimensions of the PAA-PEI complexes and relatively large amount of charges carried by the complexes. The high mobility of linear PEI also contributed to the exponential growth of the film. The contrast of [PANI/PAA-PEI]30 films was around 30% at 630nm compared with 11% of [PANI/PAA]30 films. The switching time of [PANI/PAA-PEI]30 films was only half of that of [PANI/PAA]30 films which indicated a faster redox process. We also studied other polyelectrolyte complexes, such as PEDOT-PSS and PAA-PSS, and the EC devices made by these kinds of polyelectrolyte complexes LbL films. Improved electrochromic performance was also observed on the films deposited with polyelectrolyte complexes compared to the films fabricating by individual polyelectrolytes.
We conclude that the using polyelectrolyte complex enables a very effective method to prepare fast growing LbL films for high performance electrochromic applications.