Summary

In the present study, thin functional conducting polyaniline (PANI) films, either doped or undoped, patterned or unpatterned, were prepared by different approaches. The properties of the obtained PANI films were investigated in detail by a combination of electrochemistry with several other techniques, such as SPR, QCM, SPFS, diffraction, etc. The sensing applications (especially biosensing applications) of the prepared PANI films were explored.

Firstly, the pure PANI films were prepared by the electropolymerisation method and their doping/dedoping properties in acidic conditions were investigated in detail by a combination of electrochemistry with SPR and QCM. Dielectric constants of PANI at different oxidation states were obtained quantitatively. The results obtained here laid a good foundation for the following investigations of PANI films in neutral pH conditions.

Next, PANI multilayer films doped by a variety of materials were prepared by the layer-by-layer method in order to explore their biosensing applications, because of the loss of redox activity of pure PANI in neutral pH conditions. The dopants used include not only the traditionally used linear polyelectrolytes, but also, for the first tim, some other novel materials, like modified gold nanoparticles or modified carbon nanotubes. Our results showed that all the used dopants could form stable multilayer films with PANI. All the obtained PANI multilayer films showed good redox activity in a neutral pH environment, which makes them feasible for bioassays. We found that all the prepared PANI multilayer films can electrocatalyze the oxidation of NADH in neutral conditions at a low potential, although their catalytic efficiencies are different. Among them, PANI/carbon nanotube system showed the highest catalytic efficiency toward the oxidation of NADH, which makes it a good candidate as a NADH sensor. Besides, because some of the prepared PANI multilayer systems were end-terminated with –COOH groups (like PANI/Au nanoparticles system), which can be utilized to easily link biomolecules for biosensing applications. Here, we demonstrated, for the first time, to use the prepared PANI multilayer films for the DNA hybridisation detection. The detection event was monitored either by direct electrochemical method, or by enzyme-amplified electrochemical method, or by surface plasmon enhanced fluorescence spectroscopic method. All the methods can effectively differentiate non-complementary DNA from the complementary ones, even at the single-base mismatch level.

It should also be noted that, our success in fabricating PANI multilayer films with modified Au nanoparticles or carbon nanotubes also offered another novel method for incorporating such novel materials into (conducting) polymers. Because of the unique electrochemical and optical properties of each component of the obtained PANI multilayer films, they should also find potential applications in many other fields such as microelectronics, or for electrochromic and photovoltaic devices.

Finally, patterned PANI films were fabricated by the combination of several patterning techniques, such as the combination of electrocopolymerization with micromolding in capillaries (EP-MIMIC), the combination of microcontact printing with the layer-by-layer technique (μCP-LBL), and the polystyrene (PS) template induced electropolymerisation method.

Using the obtained stripe-shaped PANI/PSS film, a redox-switchable polymer grating based on the surface-plasmon-enhanced mode was constructed and its application in the field of biosensing was explored. It was found that the diffraction efficiency (DE) of the grating was very sensitive to the applied potential (i.e. redox state of the film) as well as the pH environment of the dielectric medium. Moreover, the DE could also be effectively tuned by an electrocatalytic event, such as the electrocatalytic oxidation of NADH by the grating film.

By using PS colloidal crystal assemblies as templates, well-ordered 3D interconnected macroporous PANI arrays (PANI inverse opals) were fabricated via electropolymerisation method. The quality of the obtained inverse opals was much higher than those reported by chemical synthesis method. By electrochemical method, the structures of the prepared inverse opals can be easily controlled. To explore the possible biosensing applications of PANI inverse opals, efforts were also done toward the fabrication of PANI composite inverse opals. By selecting proper dopants, high quality inverse opals of PANI composites were fabricated for the first time. And the obtained opaline films remained redox-active in neutral pH conditions, pointing to their possible applications for electrobioassays.