# Transparent electrodes based on conducting polymers for display applications

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## ARTICLE INFO

## ABSTRACT

The materials science and engineering related to the fabrication of conducting polymer thin films and the progress in the development of devices integrated with organic transparent electrodes based on conducting polymers for display applications are reviewed. Transparent electrodes are essential components for many display modules. With the evolution of display technologies, conducting polymers are recently emerging as important alternative materials for the fabrication of transparent electrodes. Conducting polymers offer some advantages, such as light weight, low cost, mechanical flexibility and excellent compatibility with plastic substrates for the development of next-generation display technologies and, in particular, are expected to play an important role in the development of flexible display technologies.

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## 1. Introduction

Conducting polymers are organic materials which exhibit optical, electrical, electronic and magnetic properties of metals, while mechanical properties and processability of conventional polymers [1–11]. The unique and intriguing properties of conducting polymers are widely explored for the development of functional materials/nanomaterials [12–28] and fabrication of advanced technological systems, such as sensors [29–36], transducers [37–43], fuel cells [44–48], organic solar cells [49–54], organic light-emitting diodes [55–71], field-effect transistors [72–77] and displays [78–81]. One of the most attractive applications of conducting polymers in display technologies is their use as transparent electrode materials [82–84]. Compared to other electrode materials, conducting polymers are advantageous because of their low cost, light weight, mechanical flexibility and excellent compatibility with plastic substrates [1,85–89].

Although the iodine-doped polyacetylene initially reported in 1977 could exhibit electrical conductivity comparable to that of silver or copper [1,90,91], this prototype conducting polymer was air-sensitive [92–94]. With the efforts of many researchers in the past three decades, different types of conducting polymers with improved air-stability have been developed [95–99]. Currently, polyaniline (PANI), polypyrrole (PPY) and poly(3,4-ethylenedioxythiophene) (PEDOT) are the three most important conducting polymers. The structures of those three conducting polymers are shown in Fig. 1.

In this article, the potential of conducting polymer thin films deposited on non-conductive substrates as transparent electrode materials for display applications is discussed. In particular, the issues related to the preparation, transparency, conductivity and adhesion of conducting polymer thin films are addressed. Devices integrated only with organic conducting polymer thin films as transparent electrodes for display applications are also reviewed.

## 2. Transparent conducting polymer thin films

### 2.1. Properties of conducting polymers

Conducting polymers can be synthesized by electrochemical polymerization or oxidative chemical polymerization methods [1,100]. To synthesize conducting polymers by electrochemical polymerization methods, conductive substrates are required. Electrochemical polymerization can take place when an electrical output from a power supply passes through the conductive substrate immersed in a solution containing the monomer for the synthesis of a conducting polymer. On the other hand, to synthesize conduct-

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**(A)**

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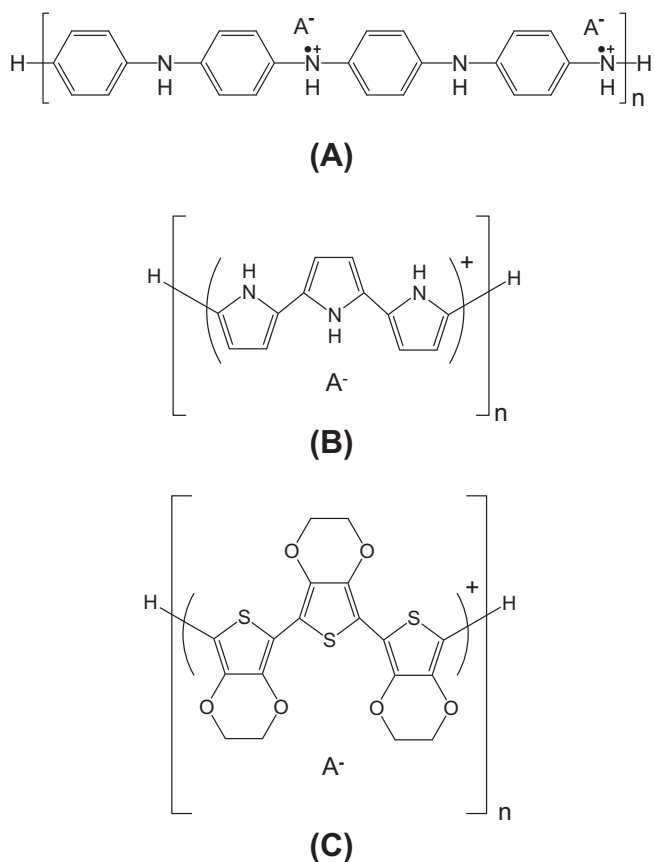
**Fig. 1.** Structure of (A) doped PANI, (B) doped PPY and (C) doped PEDOT (A⁻ is an arbitrary dopant species).



**Fig. 2.** Protonic doping of PANI (HA is an arbitrary protonic acid).

ing polymers by oxidative chemical polymerization methods, oxidizing agents are required. Oxidative chemical polymerization can be initiated when the oxidizing agent and the monomer used for the synthesis of a conducting polymer are brought into contact with each other [101–112].

Conducting polymers can undergo reversible doping to change their electrical conductivity [1]. There are two types of doping processes: redox doping and protonic doping [1]. Conductive PPY and PEDOT can be generated by redox doping. As non-conductive neutral PPY and PEDOT are not stable under ambient conditions, the backbones of PPY and PEDOT tend to be partially oxidized [112–114]. In the polymer backbones of PPY and PEDOT, approximately every 3–4 repeat monomer units would bear a unit positive charge [112,114]. As the polymer backbones are positively-charged, they can attract negatively-charged anions. Basically, the anions act as counter ions to balance the charges on the partially oxidized polymer backbones. As significant change in electrical properties of the polymers occurs upon partial oxidation and the concomitant incorporation of counter anions, together with the fact that the change in electrical conductivity can be anion-dependent, the counter anions are also treated as dopant anions of PPY and PEDOT. Conductive PPY and PEDOT can be dedoped to the non-condcutive neutral state by electrochemical reduction [79,113]. On the other hand, conductive PANI is generated by protonic doping (Fig. 2) [99]. When the non-conductive PANI is exposed to protonic acid (HA), the PANI becomes electrically conductive by protonic doping [115]. It should be noted that there is no change in the number of electrons on the polymer backbone when PANI undergoes protonic doping [1]. The HA-doped PANI can be dedoped by a basic solution, such as ammonium hydroxide solution, to its non-conductive state [116,117].
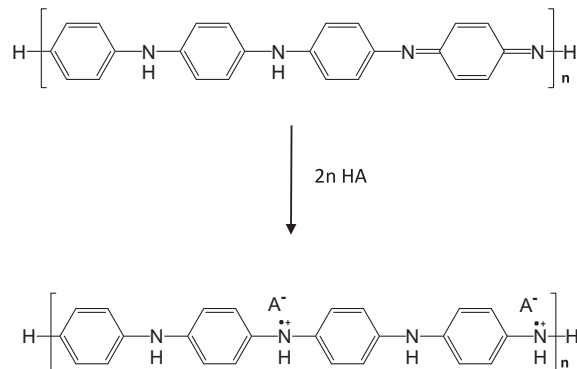
## 2.2. Preparation

Conducting polymer thin films can be prepared on non-conductive substrates by (i) coating treatment with a conducting-polymer solution/dispersion, (ii) deposition in a polymerizing solution and (iii) chemical vapor deposition.

### 2.2.1. Coating treatment with a conducting polymer solution/ dispersion

In this method, the conducting polymer thin film is prepared by applying an appropriate amount of conducting polymer solution/dispersion to the non-conductive substrate. It can be done by various coating techniques, such as spread-coating, bar-coating, cast-coating, spin-coating or dip-coating. A conducting polymer thin film can be formed on the non-conductive substrate surface when the solvent evaporates. There are commercial products, such as aqueous dispersions based on PEDOT doped with poly(styrenesulfonic acid-*random*-styrenesulfonate), available from chemical suppliers [118]. The conducting-polymer solutions/dispersions for coating treatment can also be obtained by dissolving custom-synthesized conducting polymers in appropriate solvents, such as dodecylbenzenesulfonate-doped PPY dissolved in *m*-cresol [119] and camphorsulfonic acid-doped PANI dissolved in chloroform or *m*-cresol [120].

### 2.2.2. Deposition in a polymerizing solution

A conducting polymer thin film can be prepared on a non-conductive substrate by immersing the substrate in a polymerizing solution in which oxidative chemical polymerization of a conducting polymer's monomer is taking place [101,121–123]. The most commonly used oxidizing agents include ferric chloride and ammonium peroxydisulfate, or $FeCl_3$ and $(NH_4)_2S_2O_8$. Depending on the polymerization conditions and the nature of the substrate surfaces, transparent conducting polymer thin films with different properties can be formed on the surfaces of the immersed substrates [123]. As the polymerization of aniline is pH-sensitive, the polymerizing solution must be maintained at pH < 2 for the deposition of conductive PANI thin films [124,125]. Preferably, an aqueous medium containing a strong acid, such as hydrochloric acid, with a sufficiently acidic concentration is used to ensure that the reaction will follow the desired polymerization mechanism and the obtained PANI thin films will be instantly doped by the strong acid in the polymerizing solution [101,124,126–130]. As PANI can undergo reversible protonic doping, conductive PANI dedoped by a basic solution, such as ammonium hydroxide solution, can be redoped by another acid of choice if desired [115,117]. To introduce a desired dopant anion to PPY or PEDOT, either the acid or salt containing the dopant anion can be added to the polymerizing solution (Fig. 3) [121,131–138]. The polymerization for the synthesis of

PANI and PPY can be easily initiated in aqueous media [121]. However, the polymerization kinetics for the synthesis of PEDOT is not favored in aqueous media. Alternatively, acetonitrile can be used for the synthesis of PEDOT [108].

### 2.2.3. Chemical vapor deposition

By adapting the work performed by Mohammadi et al. for the deposition of polypyrrole on conductive substrates [139], chemical vapor deposition can also be used to prepare transparent conducting polymer thin films on non-conductive substrates [140]. To prepare transparent conducting polymer thin films by this method, the surface of the non-conductive substrate can first be pre-coated with either the oxidant or the monomer. Subsequently, the substrate is placed in a deposition chamber in which the vapor of the other reactant can be generated. After initiating the deposition process, a transparent conducting polymer thin film can be formed on the non-conductive substrate. More recently, oxidative chemical vapor deposition which allows simultaneous supplies of the monomer and the oxidant for polymerization on the non-conductive substrate surface has also been developed [112].

### 2.3. Transparency

As conducting polymers absorb light in the visible range, distinctive colors can be added to the non-conductive substrates after the coating or deposition of conducting polymers. Basically, by controlling the deposition parameters, conducting polymer thin films with 70–90% light transmittance in the visible range can be obtained by the methods described in Section 2.2. The transparency of conducting polymer thin films deposited on transparent non-conductive substrates, such as glass or poly(ethylene terephthalate) (PET), is dependent on the thickness of deposited conducting polymer thin films. In other words, the transparency of conducting polymer thin films deposited on non-conductive substrates decreases with the thickness (or amount) of deposited conducting polymers. Although the transparency can be improved by the reduction in the amount of deposited conducting polymers, thinner conducting polymer thin films will result in greater sheet resistance. Therefore, the optimization between transparency and sheet resistance is very important for the preparation of conducting polymer thin films as transparent electrodes for display applications.

### 2.4. Conductivity

The conformation adopted by conducting polymers can affect the conductivity of conducting polymers. Conducting polymers adopting extended conformation tend to have higher conductivity. It has been shown that (i) the conductivity of stretched free-standing conducting polymer thin films were greater than that of the original unstretched films and (ii) the conductivity of the stretched films parallel to the stretching direction was higher than the conductivity of the stretched films perpendicular to the stretching direction [141–144]. Higher degree of crystallinity was found in stretched free-standing conducting polymer thin films with higher conductivity [144]. Feng et al. also showed that mechanical shaking could induce solid-state camphorsulfonic acid-doped PANI to adopt more extended conformation [145]. More recently, Lim et al. prepared PANI-based thin films with conductivity up to ~850 S/cm on plastic substrates using camphorsulfonic acid-doped PANI solutions mixed with crystallinity-promoting additives [146].

It has been shown that the conductivity of camphorsulfonic acid-doped PANI thin films was greater when the films were cast from the PANI's $m$-cresol solution than from the PANI's chloroform solution [147]. Further studies indicated that $m$-cresol (or the so-called "good solvent") could facilitate the extension of the dissolved PANI polymer chains, while chloroform (or the so-called "poor solvent") could cause the dissolved PANI polymer chains to coil [148]. When PANI adopts the extended conformation, the mobility of the charge carriers can be enhanced [149]. The solvent-induced increase in the conductivity of conducting polymer thin films is referred to as secondary doping [150]. The increase
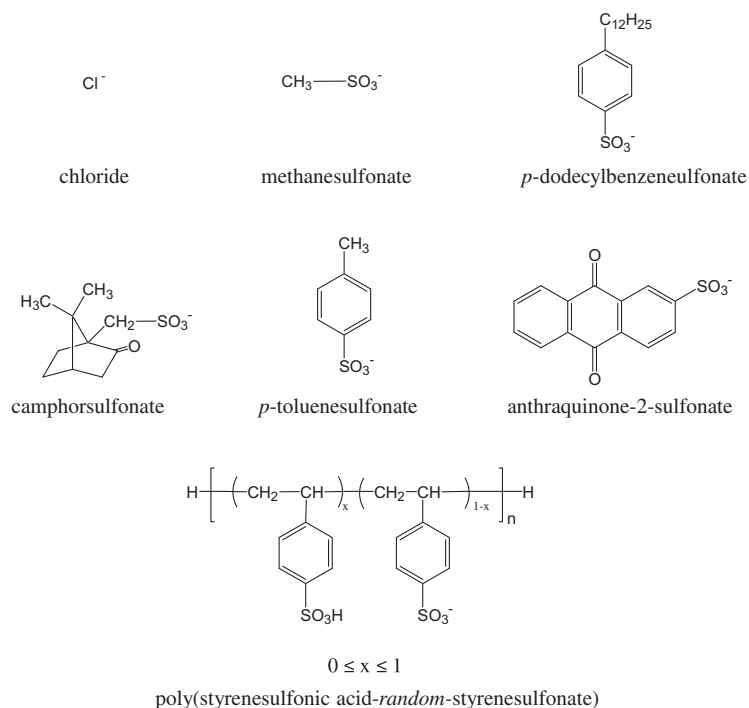


Fig. 3. Examples of dopant anions.

in conductivity can also be observed when the PANI thin films cast from the chloroform solution were exposed to vapor-phase secondary dopants, such as m-cresol and o-chlorophenol [151]. The effect of vapor-phase secondary doping by o-chlorophenol on PANI thin films prepared by oxidative chemical polymerization could be observed in camphorsulfonic acid-doped PANI thin films, but not hydrochloric acid-doped PANI thin films [152]. Similar effects were observed when camphorsulfonic acid-doped PANI was exposed to N-2-methyl-pyrolidinone (NMP) vapor, but not when exposed to chloroform vapor, indicating that some organic vapors could relax the coiled conformation of doped PANI [153]. When an exhaustive bending test was performed on PPY deposited on PET by a flexible-characteristics inspection system (FCIS) [154,155], it was found that the relative sheet resistance of the sample decreased after continuous mechanical bending for 11000 times (Fig. 4), suggesting that the conformation of the PPY on the PET substrate might have been relaxed to adopt more extended conformation by the mechanical bending.

It has been shown by Avlyanov et al. that the conductivity of PPY thin films could be increased by three orders of magnitude when the dopant anion was varied from chloride (or the so-called "poor dopant") to anthraquinone-2-sulfonate (or the so-called "good dopant") [131]. The above study showed that PPY thin films doped with dopant anions containing fused aromatic rings would have higher conductivity than PPY doped with smaller or bulky dopant anions. Wang et al. also showed that hydrophobic surface could enhance the conductivity of deposited PPY thin films even when a "poor" chloride dopant anion was used [156]. Jang et al. prepared di(2-ethylhexyl) sulfosuccinate-doped PPY thin films cast from various alcohol solutions and showed that the PPY thin films cast from PPY dissolved in bulkier alcohol (e.g. oleyl alcohol) had higher conductivity than cast from PPY dissolved in simple alcohol (e.g. methanol) [157]. Oh et al. showed that di(2-ethylhexyl) sulfosuccinate-doped PPY thin films cast from PPY dissolved in oxygen-containing solvents had higher conductivity [158], while Song et al. showed that dodecylbenzenesulfonate-doped PPY thin films cast from PPY dissolved in oxygen-containing solvents had lower conductivity [159].

Commercially available PEDOT solutions/dispersions are commonly used to prepare PEDOT thin films [160]. Basically, the major ingredients in commercially available aqueous PEDOT solutions/dispersions are PEDOT and poly(styrenesulfonic acid-random-styrenesulfonate) [161]. The conductivity of PEDOT thin films prepared from commercially available aqueous PEDOT solutions/dispersions by various coating methods typically range from 0.05 S/cm to 10 S/cm [118,162,163]. The conductivity of PEDOT



**Fig. 4.** Relative sheet resistance vs. bending cycle curve of a PET substrate coated with PPY characterized by FCIS.

thin films can be further increased when the aqueous PEDOT solutions/dispersions used for the preparation of PEDOT thin films are mixed with one or more additives [164]. Most of the additives are common polar organic compounds, including methanol, ethanol, isopropanol (IPA), ethylene glycol (EG), glycerol, diethylene glycol (DEG), sorbitol, dimethyl sufoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF), N,N-dimethylacetamide, etc. [54,164–172]. Other specialty compounds, such as zwitterions [173] and ionic liquids [174], have also been used.

Some processes for preparing PEDOT thin films with enhanced conductivity have recently been developed. Kim et al. showed that oxygen-plasma could enhance the conductivity of PEDOT thin films prepared by vapor phase deposition using ferric p-toluenesulfonate (or ferric tosylate) as the oxidizing agent [175]. Ha et al. synthesized methanol-substituted 3,4-ethylenedioxythiophene for the preparation of PEDOT-based thin films with enhanced conductivity of 900 S/cm [176]. Kim et al. prepared PEDOT-based thin films with conductivity up to 735 S/cm on glass or plastic substrates using a commercial PEDOT product mixed with ethylene glycol by spin-coating [177]. The conductivity of the PEDOT-based thin films was further increased to 1418 S/cm when the thin films were subject to post-fabrication immersion treatment in ethylene glycol [177]. Winther-Jensen et al. employed base-inhibited vapor-phase polymerization, in which a surface covered with a mixture containing ferric p-toluenesulfonate (the oxidizing agent) and pyridine (a volatile base) was exposed to 3,4-ethylenedioxythiophene, to prepare PEDOT thin films with conductivity exceeding 1000 S/cm [178]. Alemu et al. prepared PEDOT-based thin films with conductivity up to 1362 S/cm on glass substrates using a commercial PEDOT product by spin-coating, followed by post-fabrication immersion treatment in methanol [179]. Badre et al. prepared PEDOT-based thin films with conductivity up to 2084 S/cm on glass or plastic substrates using a commercial PEDOT product mixed with an ionic liquid, 1-ethyl-3-methylimidazolium tetracyanoborate, by spin-coating [174]. Xia et al. prepared PEDOT-based thin films with conductivity up to 1325 S/cm on glass substrates using commercial PEDOT products by spin-coating, followed by post-fabrication treatment with hexafluoroacetone [180], and also found that this method was more effective when the commercial product containing PEDOT with higher molecular weight was used [181]. More recently, Xia et al. prepared PEDOT-based thin films with conductivity up to 3065 S/cm on plastic substrates using a commercial PEDOT product by spin-coating, followed by post-fabrication treatment with sulfuric acid [182]. Fabretto et al. also fabricated PEDOT-based thin films with enhanced conductivity (3400 S/cm) comparable to that of ITO using ferric tosylate as the oxidizing agent and poly(ethylene glycol–propylene glycol–ethylene glycol), or PEG–PPG–PEG, as the additive, by vacuum vapor phase polymerization [183].

### 2.5. Adhesion

Surface modification for improving and manipulating interfacial adhesion is important for technological applications involving interactions of heterogeneous substances/materials [184–197]. Organosilanes are frequently used to modify surface properties of silica-based substrates, such as glass, quartz or silicon dioxide on silicon chips [186,198–200]. For the preparation of conducting polymer thin films on silica-based substrates, organosilane-modified surfaces can provide tailored surfaces for the deposition of conducting polymer thin films with different properties [156,201,202]. Examples of some organosilanes relevant to surface treatment for the deposition of conducting polymer thin films are shown in Fig. 5. The general reaction schemes for the immobilization of trifunctional organosilanes on silica-based substrates are shown in Fig. 6. As is shown in Fig. 6, hydrolysis of organosilanes
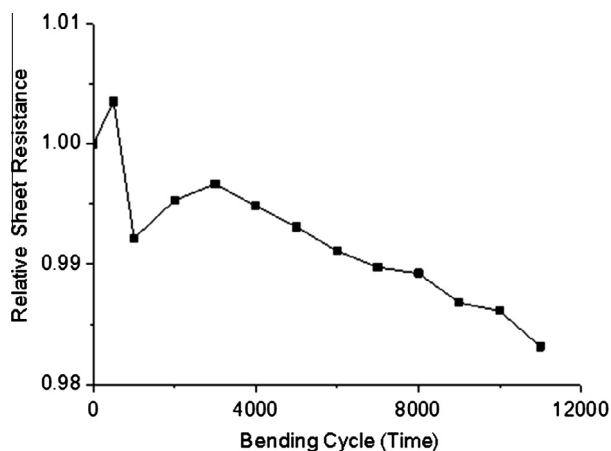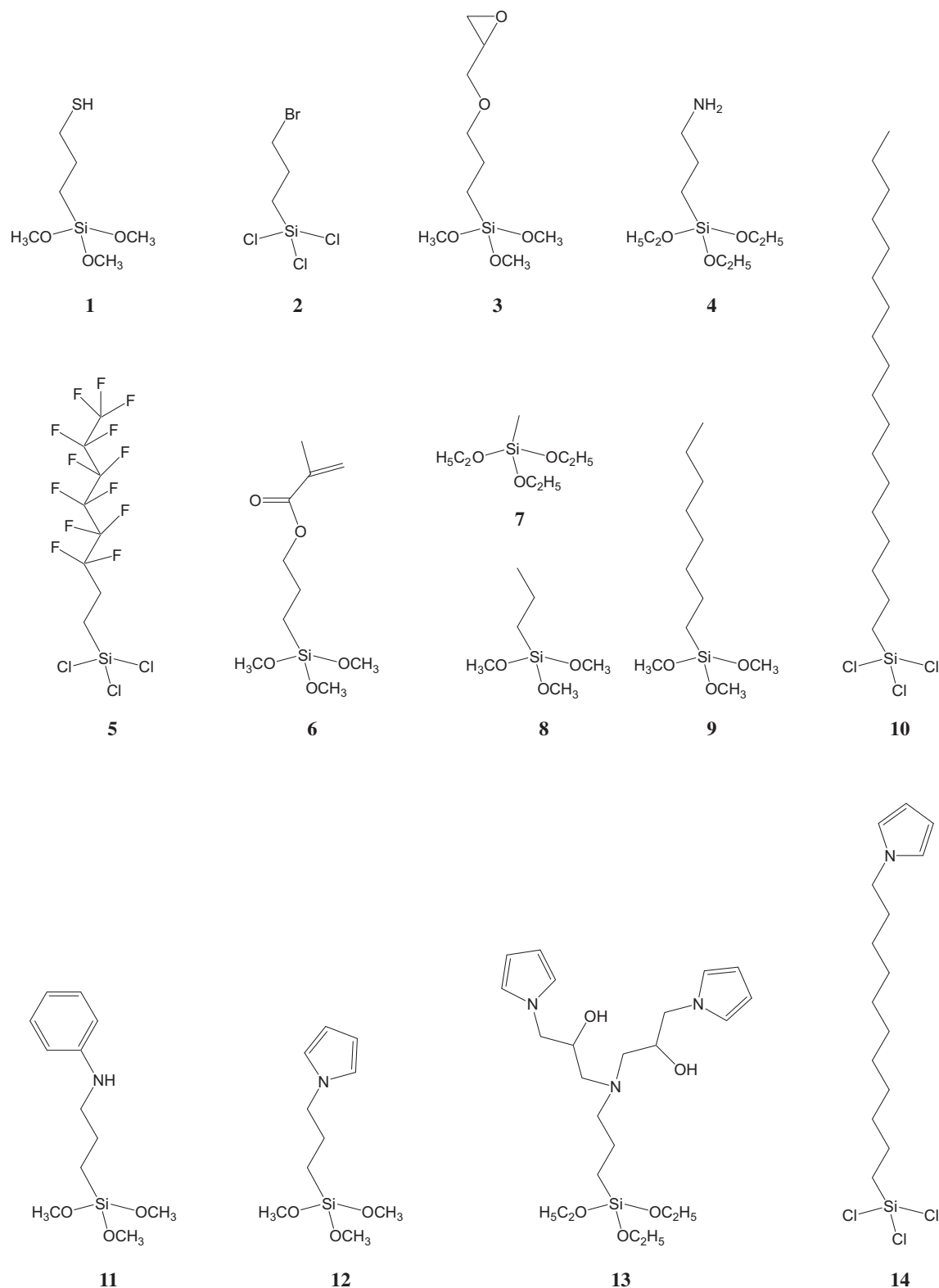
Fig. 5. Examples of organosilanes.

is required for the surface modification reaction to proceed [199,200,203]. The hydrolysis of organosilanes applied for surface modification can be initiated by the water molecules adsorbed on the hydrophilic silica-based substrates [199,203].

It has been reported by Wang et al. that when a glass slide treated with piranha solution to become highly hydrophilic (water contact angle <2°) and then part of the same surface of the same glass slide treated by **10**, or octadecyltrichlorosilane, to become hydrophobic (water contact angle ∼110°) was immersed in a polymerizing solution of pyrrole for PPY thin film deposition, the polypyrrole deposited on the hydrophilic region formed discrete nanoparticles, while the polypyrrole deposited on the hydrophobic
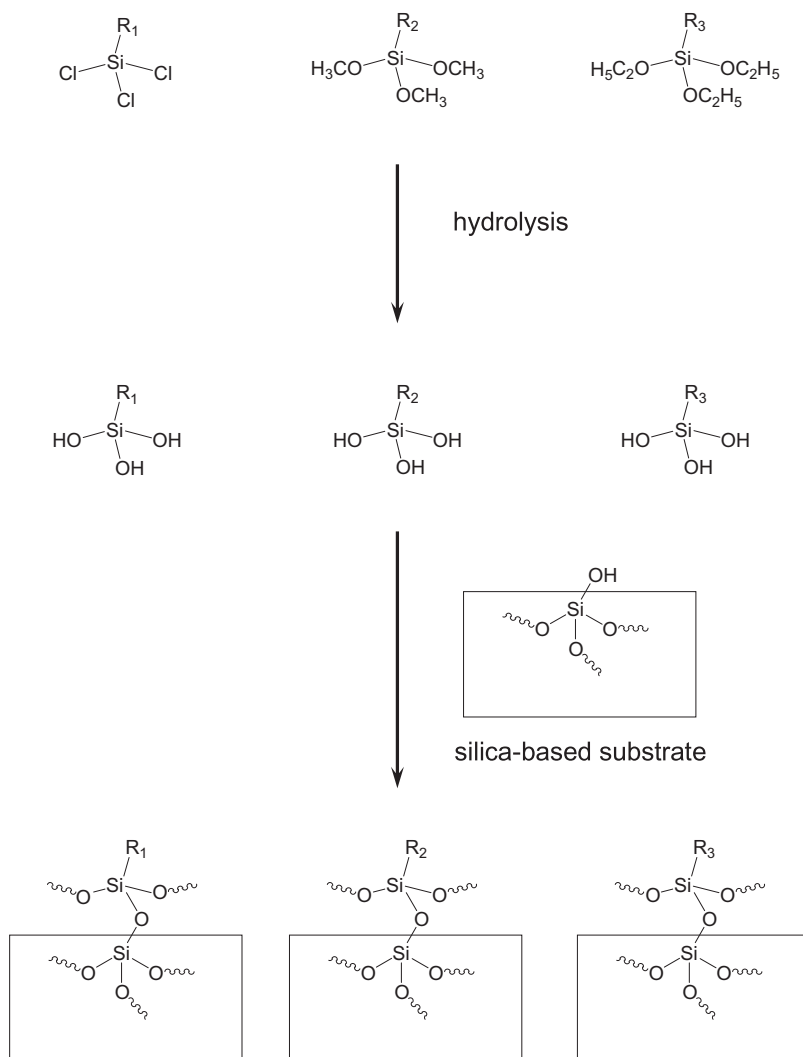
**Fig. 6.** Immobilization of trifunctional organosilanes on silica-based surfaces.

region formed a cohesive thin film covering the hydrophobic octadecyltrichlorosilane-treated surface (Fig. 7). Macroscopically, the above results indicate that the PPY deposited on a hydrophobic surface forms an electrically conductive thin film, while the PPY deposited on a highly hydrophilic surface forms an electrically insulating thin film [204]. When the effects of surface nature (piranha-solution-treated hydrophilic surface and octadecyltrichlorosilane-treated hydrophobic surface) vs. dopant anion (chloride, methansulfonate and anthraquinone-2-sulfonate) were compared, Wang et al. showed that the effect of hydrophobic surface dominated over the effect of dopant anion to determine the conductivity of the obtained PPY thin films. In other words, the conductivity of anthraquinone-2-sulfonate-doped PPY thin film was three orders of magnitude greater than chloride-doped PPY thin film when deposited on glass slides cleaned with acetone, isopropyl alcohol and deionized water [205]. However, the conductivity of anthraquinone-2-sulfonate-doped PPY thin film was only 1.6 times greater than chloride-doped PPY thin film when deposited on hydrophobic octadecyltrichlorosilane-treated glass slides [156]. While there was no significant change in the magnitude of anthraquinone-2-sulfonate-doped PPY thin film's conductivity, the conductivity of chloride-doped PPY thin film could be increased by two orders of magnitude from 0.64 S/cm to 67 S/cm. Perruchot et al. compared the adhesion of chloride-doped PPY deposited on
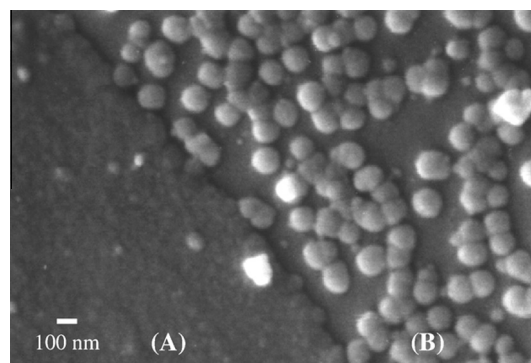


**Fig. 7.** PPY deposited on a (A) hydrophobic vs. (B) hydrophilic surface (reproduced from [204] with permission. Copyright 2008 Elsevier).

glass slides pre-treated with amino organosilane (3-aminopropyltriethoxysliane, or **4**) vs. alkyl organosilanes of various alkyl chains (methyltriethoxysilane, propyltrimethoxysilane and octyltrimethoxysilane, or **7**, **8** and **9**) and found that only PPY thin films deposited on the glass surface pre-treated with 3-aminopropyltriethoxysilane survived the 90° Scotch-tape peeling test [202]. Similar to the results reported by Perruchot et al., Huang et al. also

found that patterned PPY thin films deposited on glass surface pre-treated with **10**, or octadecyltrichlorosilane, could be easily transferred to the sticky surface of Scotch tape [126]. Cho et al. demonstrated that PPY deposited on the glass surface pretreated with **6**, or 3-(trimethoxysilyl)-propyl methacrylate, could survive the Scotch-tape peeling test [206]. By the immobilization of a designer peptide (**THRTSTLDYFVI**) on aminosilanized silica-substrates via glutaraldehyde as the crosslinker, Choi et al. prepared a peptide-presenting substrate for the deposition of chloride-doped PPY thin films with enhanced adhesion [207].

Organosilane chemistry can also be used to covalently introduce the monomeric units of conducting polymers, such as aniline or pyrrole, to silica-based substrates. Wu et. al. used **11** and **12** to treat silica-based substrates for the preparation of PANI and PPY thin films [65,208–210]. Faverolle et. al. synthesized **13** [211] and Intelmann et. al. synthesized **14** [212] to modify silica-based substrate surfaces for the deposition of polypyrrole thin films. Alternatively, the monomeric units of conducting polymers can be covalently derivatized on silica-based substrates pre-treated with some functional organosilanes. Li. et al. derivatized aniline monomers onto glass surface pre-treated with **2**, or 3-bromopropyltrichlorosilane, via a substitution reaction to replace the bromo group with aniline [213]. Chen et al. grafted aniline onto glass substrate surface pre-treated with **3**, or (3-glycidoxypropyl)trimethoxysilane, via the ring-opening reaction of the epoxy group with the amino group of aniline [214].

Cohesive PPY thin films deposited on PET substrates can be easily peeled off by sticky Scotch tape [215]. To improve the interfacial adhesion between PPY and PET, Mehmood et al. applied gaseous plasma to treat PET substrates prior to PPY deposition and showed that PPY thin film exhibited better adhesion when deposited on plasma-treated PET substrates [216]. Im et al. found that PEDOT deposited on plastic substrates containing aromatic rings, such as PET, by oxidative vapor chemical deposition using $FeCl_3$ as the oxidizing agent showed better adhesion than plastic substrates without aromatic rings, such as polycarbonate (PC), and proposed that the presence of aromatic rings in PET could favor the $FeCl_3$-induced covalent linkage between PEDOT and the substrate surface [217]. To promote the uptake of aniline to the substrate surface for polymerization, Wang et al. pre-treated PET substrates with Ar plasma to initiate the polymerization of acrylic acid [218]. The carboxylic groups of the grafted poly(acrylic acid) then could attract more aniline monomers to promote the growth kinetics of PANI on the PET surface when the PET substrates were immersed in the polymerizing solution of aniline [218].

### 2.6. Stability

Although PANI, PPY and PEDOT are more stable than the prototype conducting polymer (i.e. polyacetylene) under ambient conditions, ageing of materials still inevitably occurs over time [219,220]. The degradation can be further accelerated when conducting polymers are exposed to harsh weathering conditions and/or elevated thermal environment [221–223]. Therefore, improving the stability of conducting polymers is still an important issue in dealing with technological applications of conducting polymers.

It has been shown by Kaynak et al. and Kuhn et al. that anthraquinone-2-sulfonate-doped PPY had better thermal stability than chloride-doped PPY [222,224]. With the addition of 2,4-dihydroxybenzophenone (DHBP), Child and Kuhn showed that the thermal stability of anthraquinone-2-sulfonate-doped PPY could be further improved [225]. As many commercially available PEDOT dispersion products contain poly(stryenesulfonic acid-*random*-styrenesulfonate), PEDOT thin films prepared from those aqueous dispersions tend to be acidic. Moreover, water moisture has high affinity for poly(stryenesulfonic acid-*random*-styrenesulfonate). To reduce the acidity and hygroscopy of PEDOT thin films, PEDOT thin films can be prepared by oxidative chemical polymerization of 3,4-ethylenedioxythiophene using ferric tosylate as the oxidizing agent, meanwhile with the addition of a weak base, such as pyridine or imidazole, in the oxidant solution or other singly-charged anions as the counter (or dopant) anions [50,176,226,227]. Hydrochloric acid is a common dopant for PANI [99]. However, hydrochloric acid is a volatile strong acid. To avoid the elimination of hydrochloric acid from doped PANI and the concomitant dedoping of PANI [228], a non-volatile dopant acid, such as camphorsulfonic acid, can be used to replace hydrochloric acid [229]. It has also been shown by Motheo et al. that the electrochemical stability of hydrochloric acid-doped PANI was poorer than camphorsulfonic acid-doped PANI [230].

## 3. Display devices integrated with organic transparent electrodes based on conducting polymers

### 3.1. Polymer-dispersed liquid crystal (PDLC) devices

Fig. 8 shows the structure of a PDLC device. The PDLC layer is composed of liquid crystal microdroplets dispersed in a porous polymer-based matrix [231–233]. When an electric field is applied across the PDLC layer, the liquid crystal molecules in the microdro-
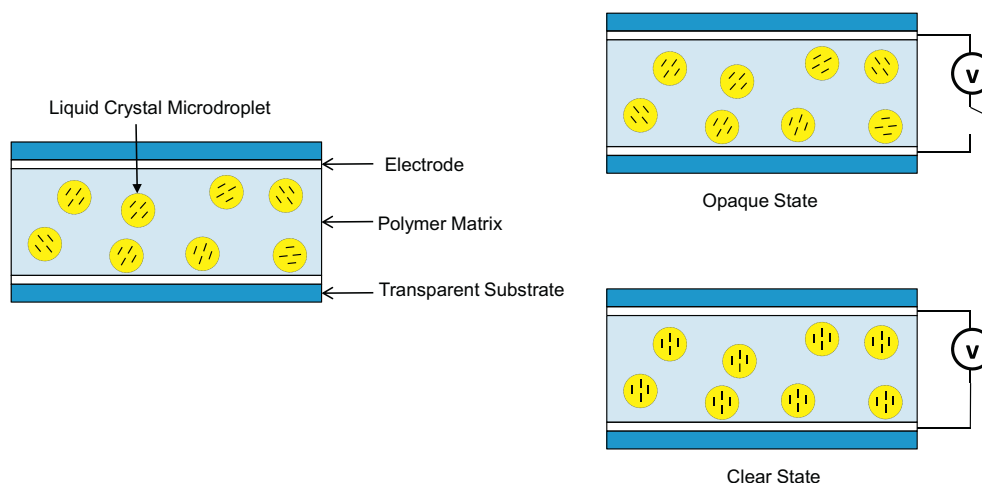


Opaque State

Clear State

**Fig. 8.** Structure of a PDLC device.

plets will be aligned (Fig. 8). Electro-optically, the PDLC device can be turned from the opaque state to the clear state upon the application of a sufficiently effective electric field.

PDLC devices integrated with conducting polymer thin films as the driving electrodes have been reported by several research groups. Harlev et al. used PET substrates coated with PANI synthesized in pyruvic acid solution as the driving electrodes to fabricate flexible PDLC devices showing 80% clear-state transmittance [234]. Roussel et al. prepared transparent electrodes by casting conducting polymer solutions (non-doped PANI dissolved in N-methyl-2-pyrolidinone followed by HCl vapor exposure after cast-coating, camphorsulfonic acid-doped PANI dissolved in α,α,α-trifluoro-methyl-m-cresol, camphorsulfonic acid-doped PANI dissolved in chloroform, dodecylbenzenesulfonate-doped PPY dissolved in chloroform and poly(styrenesulfonic acid-random-styrenesulfonate)-doped PEDOT in water) on glass or plastic substrates for PDLC device fabrication and showed that (i) the electro-optical performance of PDLC devices integrated with conducting polymer electrodes was not determined only by the conductivity of the transparent polymeric electrodes, and (ii) the resulting applied electric field and its ability to align the nematic director inside the microdroplets were affected by the conducting process, the nature, the number, and the mobility of the charge carriers of the various driving electrodes based on conducting polymers [235]. Kim et al. prepared p-toluenesulfonate-doped PEDOT on PET substrates by chemical vapor deposition to fabricate PDLC devices with 60% clear-state transmittance [236]. Wang et al. prepared anthraquinone-2-sulfonate-doped PPY on PET substrates in a polymerizing solution of pyrrole to fabricate PDLC devices showing 50% clear-state transmittance [215]. Kim et al. prepared PEDOT-based transparent electrodes on PET substrates by casting a commercially available aqueous poly(styrenesulfonic acid-random-styrenesulfonate)-doped PEDOT mixed with N-mehtyl-2-pyrolidinone, 3-trimethoxysilylpropyl acrylate, isopropyl alcohol, Daynol 604 (a wetting agent) and 2-hydroxy-2-methyl-1-phenyl propanone (a photo-initiator) followed by UV exposure to fabricate PDLC devices showing 60% clear-state transmittance [175]. Boussoualem et al. prepared PEDOT-based transparent electrodes on glass substrates
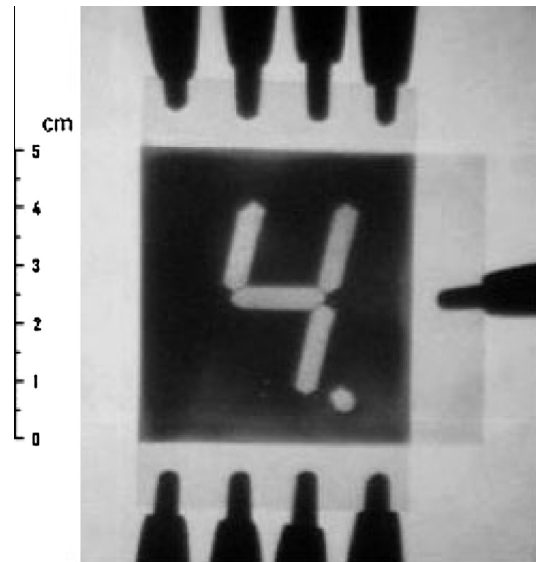


Fig. 10. Operation of an all-polymer PDLC device with a seven-segment digit pattern (adapted from [239] with permission. Copyright 2005 Wiley-VCH).



Fig. 11. Structure of an OLED device.



Fig. 9. Operation of a PDLC device with an interdigitated pattern with (A) no voltage applied, (B) voltage applied on the left hand, (C) voltage applied on the right hand and (D) voltage applied on both hands (reproduced from [204] with permission. Copyright 2008 Elsevier).

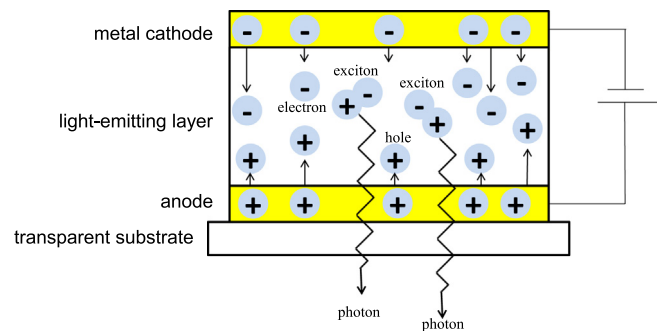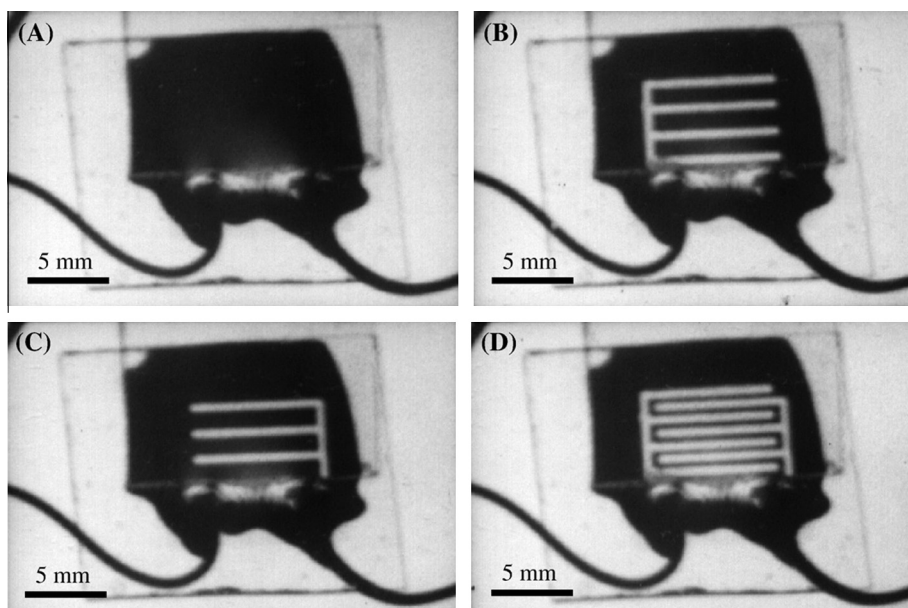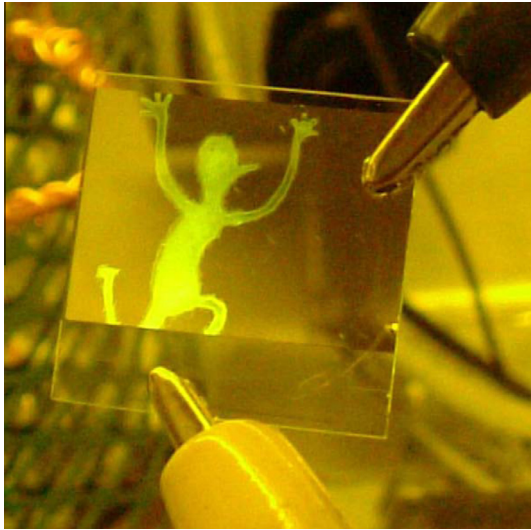**Fig. 12.** Operation of a patterned OLED device (reproduced from [243] with permission. Copyright 2006 Elsevier).

by bar-coating a commercially available aqueous poly(styrenesulfonic acid-*random*-styrenesulfonate)-doped PEDOT mixed with ethylene glycol and sodium dodecylbenzenesulfonate to fabricate PDLC devices capable of modulating transmittance by varying the frequency of the applied electric field [237].

PDLC devices with patterned driving electrodes based on conducting polymers have also been reported. Wang et al. prepared patterned anthraquinone-2-sulfonate-doped PPY on glass substrates by soft lithography and fabricate PDLC devices with addressable interdigitated circuitry (Fig. 9) [204]. Hohnholz et al.

prepared seven-segment digit patterns based on poly(styrenesulfonic acid-*random*-styrenesulfonate)-doped PEDOT on PET substrates by line-patterning [238] and fabricated addressable PDLC devices for numeric display (Fig. 10) [239].

### 3.2. Organic light-emitting diode (OLED) devices

Fig. 11 shows the structure of an OLED device. When a current is applied through the device, the hole-electron recombination in the emissive layer will result in electroluminescence [55].

OLED devices integrated with conducting polymer thin films as the organic transparent anode electrodes have been reported by several research groups. After Cao et al. developed PANI solutions based on camphorsulofinic acid-doped PANI [120,240,241], Gustafsson et al. [56,57] and Yang et al. [242] employed the PANI solutions to prepare transparent conducting polymer thin films for the fabrication of OLED based on poly[methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] as the electroluminescent layer on PET substrates and glass substrates, respectively. Yoshioka et al. prepared PEDOT-based thin films as the anode on glass substrates by ink-jet printing for the fabrication of patterned OLED devices (Fig. 12) [243]. Fehse et al. prepared conducting polymer thin films on glass substrates using a commercial aqueous PANI solution by spin-coating and fabricated white OLED devices containing fluorescent and phosphorescent emitting layers [244]. Kim et al. prepared conducting polymer thin films based on a solution of *p*-toluenesulfonate-doped PEDOT on polyethersulfone (PES) substrates by spin-coating and fabricated flexible OLED devices with maximum luminance of 4500 cd/m$^2$ [69]. Cai et al. prepared conducting polymer thin films on glass substrates using a commercial aqueous PEDOT product by spin-coating and fabricated green OLED devices with peak luminous efficiency of 127 cd/A [245]. De Girolamo Del Mauro et al. prepared conducting polymer thin films on glass substrates

**Table 1**
Conductivity data of various conducting polymer thin films prepared by the methods described in Section 2.2.

| Material | Preparation and processing | Conductivity (S/cm) | Ref. |
|---|---|---|---|
| PEDOT | Coating of a commercial aqueous PEDOT/PSSA-*random*-PSS product on PET substrates | 0.01–0.06 | [239] |
| PPY | Deposition in a polymerizing solution of pyrrole using FeCl$_3$ as the oxidizing agent on PET substrates | 0.1 | [131] |
| PEDOT | Coating of a commercial aqueous PEDOT/PSSA-*random*-PSS product mixed with EG as the additive on PET substrates | 0.6–1.8 | [239] |
| PANI | Deposition in a 4 M H$_3$PO$_4$ polymerizing solution of aniline using NH$_4$VO$_3$ as the oxidizing agent on glass substrates, followed by washing with 1 M HCl | 2–6 | [102] |
| PPY | Deposition in a polymerizing solution of pyrrole using FeCl$_3$ as the oxidizing agent, with sodium anthraquinone-2-sulfonate and 5-sulfosalicylic acid as the additives, on PET substrates | 200 | [131] |
| PANI | Casting of camphorsulfonic acid-doped PANI solutions mixed with crystallinity-promoting additives on PET substrates | 850 | [146] |
| PEDOT | Casting of polymerizing solution of methanol-substituted 3,4-ethylenedioxythiophene using ferric tosylate as the oxidizing agent and various alcohol solvents containing a weak base, imidazole, on glass substrates | 900 | [176] |
| PEDOT | Vapor phase polymerization using ferric tosylate as the oxidizing agent with the addition of a weak base, pyridine, in the oxidant solutions on PET substrates | 1000 | [178] |
| PEDOT | Coating of a commercial aqueous PEDOT/PSSA-*random*-PSS product on glass substrates, followed by post-fabrication treatment with hexafluoroacetone | 1325 | [181] |
| PEDOT | Coating of a commercial aqueous PEDOT/PSSA-*random*-PSS product on glass substrates, followed by post-fabrication immersion treatment in methanol | 1362 | [179] |
| PEDOT | Coating of a commercial aqueous PEDOT/PSSA-*random*-PSS product mixed with EG as the additive on glass and PET substrates, followed by post-fabrication immersion treatment in EG | 1418 | [177] |
| PEDOT | Coating of a commercial aqueous PEDOT/PSSA-*random*-PSS product mixed with an ionic liquid, 1-ethyl-3-methylimidazolium tetracyanoborate, as the additive on plastic and glass substrates | 2084 | [174] |
| PEDOT | Coating of a commercial aqueous PEDOT/PSSA-*random*-PSS product on glass substrates, followed by post-fabrication treatment with H$_2$SO$_4$ | 3065 | [182] |
| PEDOT | Vacuum vapor phase polymerization using ferric tosylate as the oxidizing agent with the addition of block copolymers based on poly(ethylene glycol–propylene glycol–ethylene glycol), or PEG–PPG–PEG, in the oxidant solutions on glass substrates | 3400 | [183] |
| ITO | Commercial products | 3300–6740 | [50,183,253] |

using a commercial aqueous PEDOT product by spin-coating and fabricated OLED devices based on N,N′-di-1-naphthalenyl-N,N′-di-phenyl-1,1′-biphenyl-4,4′-diamine and tris-8-hydroxyquinoline aluminum (Alq3) [246]. Wang et al. prepared conducting polymer thin films on PET substrates using a commercial aqueous PEDOT product by screen-printing and fabricated flexible white OLED devices with power efficiency of 10.8 lm/W at 1000 cd/m$^2$ [88]. Lee et al. prepared conducting polymer thin films using a commercial aqueous PEDOT product by negative mold transfer printing and fabricated flexible OLED devices with luminance of 1800 cd/m$^2$ at 10 V [89].

## 4. Outlook

Table 1 summarizes the conductivity data of various conducting polymer thin films prepared by the methods described in Section 2.2. With proper control in the amounts of deposited conducting polymers on the non-conductive substrates, transparent electrodes with transparency ranging from 70% to 90% can be obtained. Conventionally, ITO thin films are commonly used as the transparent electrodes in many display modules. As ITO is a rigid and brittle material, it is not suitable for the development of many next-generation display technologies. Therefore, the quest for alternative electrode materials is necessary.

Recently, conducting polymers are emerging as a class of promising materials for the fabrication of transparent electrodes. In general, the conductivity of most air-stable conducting polymers is still relatively low when compared to that of ITO. However, with the efforts of many researchers, conducting polymers with enhanced conductivity have been developed. Most importantly, PEDOT-based conducting polymer thin films with enhanced conductivity approaching that of ITO (3300 S/cm) have recently been fabricated by Xia et al. [182] and Fabretto et al. [183]. Indeed, those researchers' achievements are significant milestones on the roadmap for promoting the applications of conducting polymer thin films as alternative electrodes. Not only in display technologies, it is worth noting that the expertise developed for enhancing the conductivity of conducting polymer thin films can also be readily applied to other technologies, such as smart windows [247] and organic solar cells [49], and some other mutually indispensable modules, such as field-effect transistors, transducers, sensors and actuators based on conjugated polymers [248–252], to be used in sophisticated and multi-functional display technologies.

## 5. Conclusion

Light weight, low cost, mechanical flexibility and excellent interfacial compatibility with various non-conductive substrates make conducting polymers ideal for applications as transparent electrodes in display technologies. Many prototype devices integrated with conducting polymer thin films as transparent electrodes for display applications have been demonstrated. With further improvement in the properties desired for transparent electrodes, such as enhanced conductivity, interfacial adhesion and long-term environmental stability, it is expected that conducting polymers will become important materials for the development of next-generation display technologies.

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