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Towards low cost materials and methods for transparent electrodes

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A transparent electrode is a key component of any optoelectronic or transparent device. With increasing number of large area applications, there is growing demand to replace the conventional oxide based transparent conducting films with nanomaterials, primarily to reduce the cost. This review deals with a range of materials and processes forming new generation transparent electrodes, while giving some insight into the cost.

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Introduction

In a scenario, where light photons have to traverse in or out of an active material, it is mandatory that the electrode(s) hosting the active material is kept transparent to light photons. Thus, optoelectronic devices such as display screens use transparent electrodes to carry electrical signals while making the display visible [1]. In a touchscreen on the other hand, the transparent electrode not only keeps the display visible, but also translates touch into electrical signals for further processing [2]. In new generation solar cells such as organic and dye sensitized cells, the transparent electrodes while allowing light photons to fall on the active layer, extract charge carriers generated due to the photovoltaic effect [3,4]. There are non-optoelectronic applications as well where transparent electrodes are required. In defogging or defrosting applications, a transparent electrode is joule heated to make the surface stand above the dew or frost point, respectively [5]. It is becoming fashionable to make conventional electronics transparent with the aid of transparent electrodes leading to transparent electronics, be it a gas sensor [6], H_2 catalyst [7], lithium ion battery [8], flexible capacitor [9], supercapacitor [10–11] or charge trap memory [12].

A transparent electrode typically consists of a transparent conducting material coated on a transparent substrate such as glass or PET. Conventionally, tin doped indium oxide (ITO) sputtered on the substrate such as glass is used practically in all currently existing devices. A well prepared film of ITO exhibits excellent optoelectronic properties, transmittance of over 90% and sheet resistance (R_s) of ~10 Ω/sq, which explains its widespread use [1]. The demand for transparent electrodes is becoming huge due to increasing production with newer and newer products being added to the consumer list. Parallely, the active user area within a product is also increasing. The limited abundance of indium and the process cost towards its extraction and deposition are indeed the stumble blocks in the progress of new industrial products based on transparent electrodes. In addition, high brittleness of ITO films makes it implausible to adapt to futuristic flexible electronics. The above issues have given rise to high impetus to alternate materials and methods to produce transparent conducting electrodes (TCE) with clear focus on making larger area electrodes at affordable cost [13].

The new generation materials that have emerged in the last few years can be classified broadly into ultra thin conducting materials and conducting networks. This article is essentially a mini-review covering topical developments of the above topics keeping the focus on low cost and environmentally benign TCEs for next generation flexible and low weight optoelectronic devices.

Ultra thin conducting electrodes

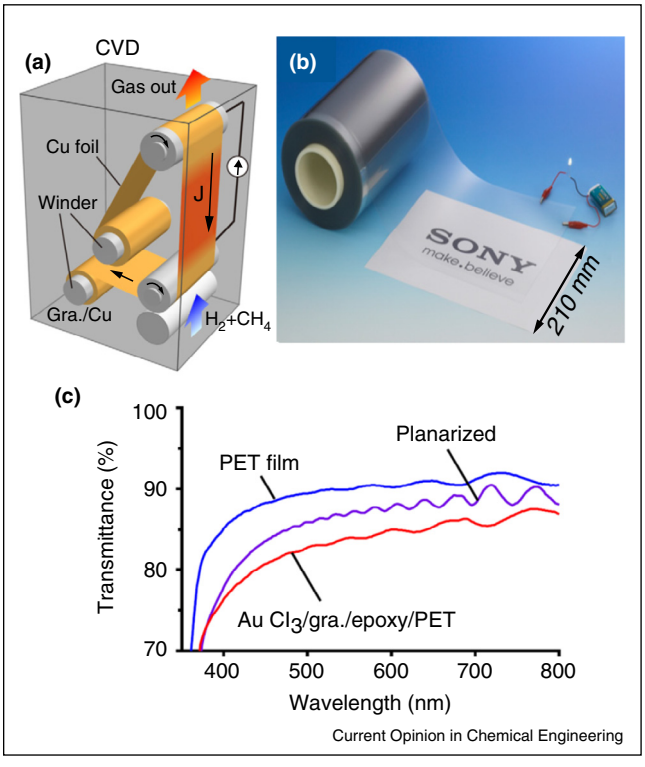
Graphene

Graphene is one carbon atom thick two dimensional sheet with sp^2-hybridization exhibiting extraordinary thermal, electrical and mechanical properties due to long range π-conjugation [14]. Novoselov *et al.* obtained single-layer graphene by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) [15]. Further, various physical and chemical routes have been established to fabricate graphene [16]. First ever application proposed for single layer graphene has been a transparent conductor as it can transmit about 97.7% of visible light while sheet resistance being reasonably low (~60 Ω/sq) [17]. The first demonstration of graphene based transparent electrodes was by Kang *et al.*, in which reduced graphene oxide film used as TCE was shown to exhibit 75% transmittance

with sheet resistance of 0.9 kΩ/sq. However, the performance of solar cells made out of this electrode was poorer compared to the standard ITO based devices [18].

The graphene based transparent electrodes find applications in several (flexible) lightweight optoelectronic devices [19]. However, fabricating them over large area is quite challenging. Iijima and coworkers have realized 30 in. graphene film by chemical vapor deposition method (CVD) [20]. Recently, Hobara and coworkers successfully prepared 100 m long high quality graphene using a roll-to-roll CVD technique (see Figure 1) [21••]. As the Cu foil was selectively annealed, there was very less heat load to the system. Thus, the CVD process was quite stable throughout the experiment (>16 hours). The photograph of thus formed roll of the TCE (graphene/epoxy/PET film) is shown in Figure 1b whose sheet resistance is reported to be 500 Ω/sq. The sheet resistance was brought down to ~250 Ω/sq by wet chemical doping of graphene with $AuCl_3$ solution but of course at the cost of transmittance (Figure 1c). Ni *et al.* have achieved R_s of 120 Ω/sq with 95% transmittance by doping graphene with non-volatile ferroelectric polymers [22]. The reliability of graphene based transparent electrodes for practical applications has been analyzed recently by Shi *et al.* [23]. Although high quality graphene with roll-to-roll CVD fabrication is a success, its large scale production at low cost is still at large.

Figure 1



Roll-to-roll synthesis of graphene. **(a)** Schematic illustration of roll-to-roll synthesis of graphene on Cu foil (Gra./Cu). Stainless steel vacuum chamber with current-feeding electrode rollers to joule heat Cu foil. The precursor gases (CH_4 and H_2) are introduced into a chamber (1000 Pa) where Cu foil (230 mm wide, >100 m long, 36 μm thick, >99.9% pure) is selectively joule heated to 1000 °C. The Cu foil moves with the velocity of 0.1 m/min. **(b)** The photograph of a roll of graphene/epoxy/PET film. The graphene/epoxy width is marked in the photograph. The film was later doped with $AuCl_3$. Optical transmittance of PET film (blue), $AuCl_3$/graphene/epoxy/PET (red) and planarized film, purple color (PET/Adhesive/$AuCl_3$/graphene/epoxy/PET) is shown in **(c)**. Reproduced with permission from Ref [21••].

Organic thin films

Another promising transparent electrode material for flexible and stretchable devices which can be coated as a thin film, is poly(3,4 ethylenedioxythiophene) (PEDOT), discovered by Heywang *et al.* [24]. Upon polymerization with poly-(styrenesulfonate) (PSS), a polyanion, it forms an intrinsically conducting polymer (PEDOT:PSS), highly preferred as its work function (5–5.2 eV) is electronically suited for optoelectronic applications. Among other organic conducting polymers such as polyaniline (PANI), polypyrrole (PPY) and polythiophenes (PT), PEDOT:PSS is more promising. However, its low intrinsic conductivity ($\sim 10^{-3}$–10^{-4} S cm^{-1}) is a matter of concern. The conductivity can be enhanced further by doping with high boiling polar solvents termed as 'secondary dopants', though the exact mechanism of the enhancement is yet to be understood [25]. In the literature, dimethyl sulfoxide (DMSO), ethylene glycol (EG), diethylene glycol, sorbitol, sulphuric acid (H_2SO_4), zonyl, etc. have been used to improve PEDOT:PSS conductivity [26–28]. For example, the sheet resistance of zonyl doped PEDOT:PSS on poly(-dimethylsiloxane) substrate was 42 Ω/sq with 82% transmittance. Zonyl besides improving conductivity, also enhances wettability even on hydrophobic surfaces [28]. In another report, non-ionic surfactant (Triton X-100) was used to produce conformal coating on hydrophobic substrates by reducing the surface tension of the polymer solution. Also, it induces the formation of nanofibrils of PEDOT which increases the mechanical stability of the polymer and thereby, of the devices [29]. Extending the electrode formation over large area by simple roll-to-roll process has also been already realized and commercialized [30]. The reduction in electrical conductivity of polymers upon exposure to humidity, high temperature and UV-light are vital issues inhibiting practical implementation of conducting polymers [31].

Ultra thin metal films (UTMF)

Highly conducting noble metal films of 1–5 nm thickness on mica were reported as early as 1970s. At such small thicknesses, metal films tend to be optically quite transparent, but are exceptionally fragile ending up with high sheet resistances. Depositing a bimetal layer on a transparent substrate such as glass is shown to improve the mechanical stability of the TCE. For instance, a sub-nm thick Ag layer yielded a well conducting Au overlayer with total thickness of only 3.2 nm. Later, Pt was used as

nucleating layer for better adhesion and stability [32]. Briggs and coworkers demonstrated that depositing gold (7 nm) over pre-treated (3-mercaptopropyl(methyl)dimethoxysilane) substrate led to less surface roughness. Besides improving adhesion, it provides better average transmittance (75%) and low sheet resistance of 20 Ω/sq [33]. Such thin metal films possess great advantage of being compatible with flexible devices as metals by nature are malleable and ductile. While UTMF can be potential substitute for ITO, corrosion and oxidation of the metal (like Ag) in ambient atmosphere tend to deteriorate transmittance and conductivity. Among many proposed permeation blocking layers, thin Ni layer is shown to serve well as a stable, flexible barrier layer [34]. In another report, 7 nm Cu with Al shell of 0.8 nm served as low work function window electrodes for OPV with ~65% transmittance at 550 nm with sheet resistance of 15.7 Ω/sq [35]. UTMF were even sandwiched between metal oxide thin films to fabricate better performing TCEs. This method of fabricating TCE is highly cost effective since it can be extended for large scale roll-to-roll processes as well.

Conducting networks

Unlike thin conducting electrodes in network structures, only designated paths conduct electricity while the rest of the regions transmit light. These can be classified into non-template based networks and template based networks. Naturally in template based methods, the formation of conducting paths is guided by lithography processes and the paths tend to remain in a plane with seamless junctions, but suffer from diffraction effects due to the orderliness of the patterns. In contrast, the non-template based networks are usually formed by brute-force and therefore, the conducting paths are usually random in nature forming cross-bar junctions and therefore, the electrical conduction takes place mainly through the perculative paths. There are many theoretical studies to relate their behavior to bulk-like systems such as continuous thin films. For networks with $T > 90\%$, the expected the bulk-like behavior does not occur. The main reason is that below a critical density termed percolation threshold, the network conductivity decreases drastically with decrease in the density of the wires and therefore, the conduction can only be described by percolation theory. By increasing the wire lengths or the number of wire junctions, the conductivity is seen to increase due to increasing conduction paths, following a percolation scaling law [36]. Such theoretical treatments have helped researchers to optimize conditions for nanowire deposition.

Non-template based networks

Metal nanowire networks

Metal nanowires prepared by simple solution processes are deposited onto large area transparent substrates by various coating techniques (rod, spray, drop, etc.). The density and length of nanowires decide the trade-off between optical transmittance and sheet resistance. Thus, longer nanowires even with low wire density provide well conducting network with high transmittance [37•]. The key merits of metal nanowires are simple solution processing, large area amenability, stability towards flexing and highly tunable opto-electronic properties.

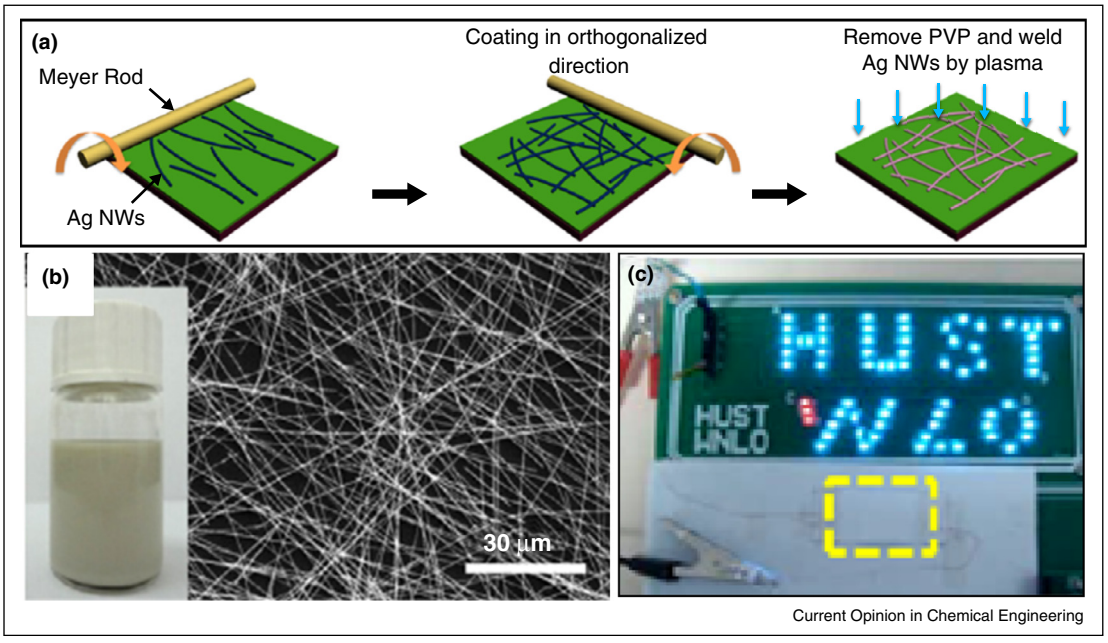
Among metals, Ag is highly conducting with the lowest resistivity (1.67 nΩ m). Coleman and coworkers were the first to use Ag nanowire networks as transparent electrodes and achieved 85% transmittance with sheet resistance of 13 Ω/sq [36]. Many researches have attempted to minimize junction resistances of nanowire networks (Figure 2) [38–40] by decreasing the density of the junctions or by post annealing or plasmonic welding. Flexible organic solar cells, fabricated with Ag nanowires were highly stable even to a bending radius of 200 μm [41]. As process costs involved are minimal in case of solution processed Ag nanowires, roll-to-roll processing can be easily realized.

Although resistivity of Cu (1.59 nΩ m) is about the same as that of Ag, in terms of abundance and cost, it outdoes Ag. In the last half-decade, Cu nanowires have emerged as potential candidate for next generation TCEs for the realization of low cost and flexible optoelectronic devices [42]. Wiley and coworkers have developed a simple solution route to prepare large quantity of Cu nanowires and shown that thus fabricated TCE has transmittance and sheet resistance of 67% and 61 Ω/sq, respectively [43]. The aggregation problem of nanowires along with its shorter lengths (10 ± 3 μm) and larger diameters (90 ± 10 nm) have been the main reasons for its poor performances. Modified processes have been reported to synthesize longer (>20 μm) and thinner (<60 nm) Cu nanowires and transmittance of 85% with sheet resistance of 30 Ω/sq have been achieved [44,45]. However, highly oxidizing nature of the Cu surface and its reddish orange haze hinder its practical implications in display devices. Alloying Ni with Cu does provide solution to above-mentioned problems, however, with some loss in transmittance due to the increase in diameter of nanowires [46]. Ferromagnetic Ni shell is shown to assist in self-assembling Cu nanowires with the aid of a guiding magnetic field [47]. A more effective solution to improve the stability towards oxidation was offered by forming transparent oxide shell over Cu nanowires, without affecting the transmittance [48]. Im *et al.* demonstrated that embedding Cu nanowires in polymers provides smoother surface with high thermal/dimensional stability and also improved adhesion to the substrate [49]. On the other hand, other metal nanowires such as Au has been tried out as TCEs [50], but those are quite expensive.

Carbon nanotube networks

Carbon nanotubes (CNTs) are known to exhibit excellent electrical, optical and mechanical properties. Synthesis

Figure 2



Meyer rod coating method to fabricate Ag nanowire based TCE. **(a)** Schematic of the process and SEM image of silver nanowire network **(b)**. Inset in (b) is photograph of their suspensions in alcohol. **(c)** A OLED device fabricated using Ag nanowire TCE.

procedures yield CNTs with variety of tube number, diameter, length and chiralities along with mixture of amorphous or non-tubular carbon and catalyst particles. Obtaining well-defined CNTs in large scale is the major challenge for real applications [51]. CNT based transparent electrodes have been fabricated by dry transfer as well as solution based methods. The dry or solvent-less method to fabricate CNT electrodes using vertically grown MWNT was pioneered by Baughman's group [52]. The electrodes fabricated using solution method are more promising for industrial scale process. Falco *et al.* have fabricated SWCNT based TCE with low surface roughness by a spray coating process, and achieved sheet resistance of 160 Ω/sq with 84% transmittance [53]. The high sheet resistances resulting from poor electrical contact between nanotube network were resolved by exfoliation/doping by the superacid (60 Ω/sq and 90.9%) [54]. Limited environmental stability of CNT networks has prevented its practical applications.

Template based networks

Lithography processes

In these methods, the conducting feature in the network is produced by various printing and lithography processes. Using a maskless direct laser writing on a film of Ag nanoparticles, Ag grid patterns were produced which showed high transmittance (>85%) and low sheet resistance (30 Ω/sq) [55]. Lewis and coworkers developed a concentrated Ag nanoparticle ink for direct writing. Thus formed electrodes have shown optical transmittance of ~94% [56]. The overlapping ring pattern of Ag nanoparticles was obtained by inkjet printing [57] for making a TCE. Interconnected Cu mesh structure realized through polystyrene microsphere lithography has shown excellent robustness towards thermal, bending and abrasion tests [58]. Grayscale xerographic lithography was adopted to fabricate Ag TCE by spreading Ag ink over toner patterned region. After thermal curing of Ag ink and removal of the toner, thus obtained electrodes have shown 72% transmittance [59]. Krebs and coworkers have fabricated a promising hybrid TCE with printed silver grids on polymer substrates interlaced with PEDOT:PSS and ZnO layers, termed as flextrode [60•]. These electrodes exhibit low sheet resistance (10 Ω/sq) with transmittance of ~60%. Importantly, the TCE can be processed at high speed of 10 m/min. Another possible technique to realize metallic patterns over rigid glass/flexible PET is nanoimprint lithography (NIL) which makes use of a hard mold [61]. Such lithography techniques involve multistep processes and the instrumentation is usually expensive. However, few attempts have been made to realize fabrication using continuous roll-to-roll nanoimprint lithography (R2RNIL) [62].

Self-forming process

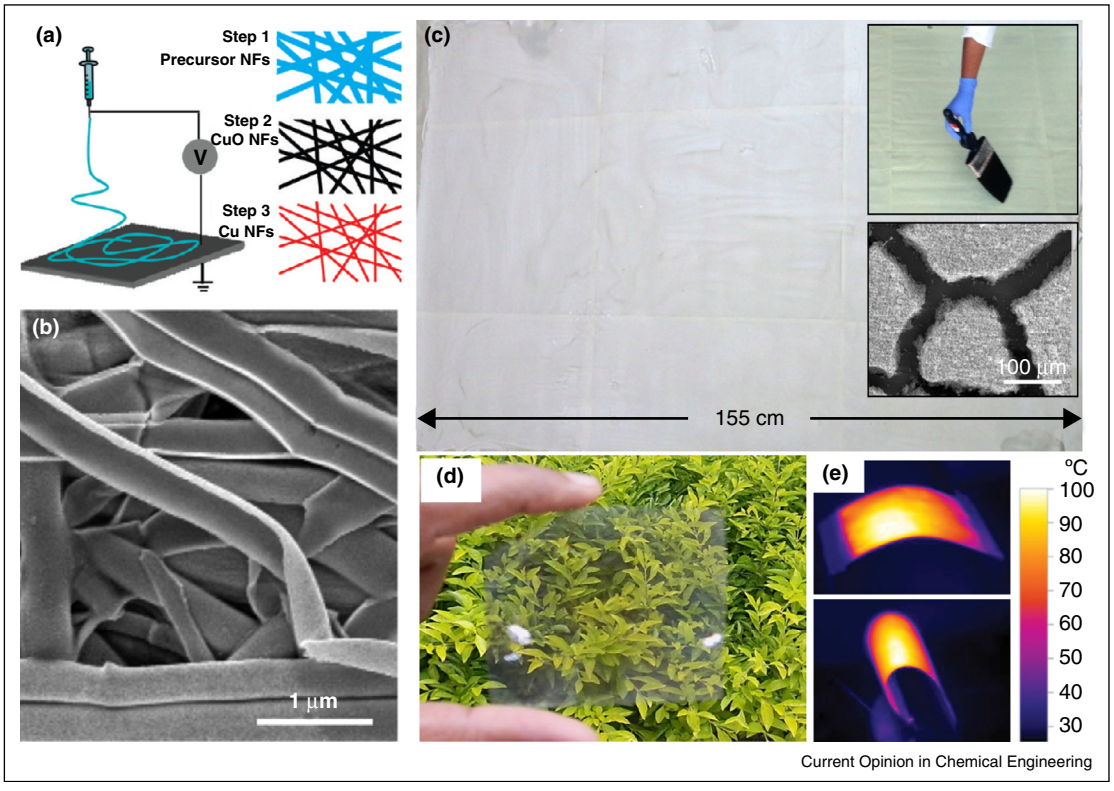
Different innovative techniques have recently evolved under this category of transparent conducting electrodes. This involves formation of uncontrolled junctionless

metal wire network in a random process. For example, bubble template method [63], inorganic crystal growth template [64], colloidal TiO_2 crack template [65,66], interconnected coffee rings [57] have been observed to form itself resulting in patterns that are utilized for TCE fabrication. However, these are limited to small areas with limited success. Using low-cost and scalable electrospinning process, ultralong polymeric fibers with nanoscale dimension can be synthesized (see Figure 3a). By successive calcination steps, Cu fiber networks have been obtained [67,68]. In another work, fiber networks were electrospun and metals of choice were deposited onto fibers depending on the application. The dissolution of fiber material resulted in the formation of metal nanotroughs (see Figure 3b) with excellent optoelectronic properties and mechanical stability [69••]. Combination of electrospun process and simple electroless deposition technique was employed to obtain metal wire network over large area [70].

Using inexpensive commercial dispersions to form fine crack templates over ultra-large areas (see Figure 3c), Kulkarni and coworkers have achieved metal mesh TCEs [71••] with excellent optoelectronic properties (~90% transmittance with sheet resistance of ~few Ω/sq). Large area Cu TCE by a complete solution process was realized (Figure 3d) which showed better stability than Cu nanowire based networks [72••]. Using such TCEs, ITO-free solar cells have been demonstrated [73]. Uniformity of metal mesh distribution is evident from IR camera images of flexible heater fabricated on PET substrates (Figure 3e) [71••]. Low power consuming large area defrosting window panel was demonstrated [74] in addition to curved surface applications [75]. An unusual transparent heater fabricated on a quartz substrate was shown to have high thermal stability and extraordinary thermal response [76•]. This crack template based method is quite appealing for large scale fabrication.

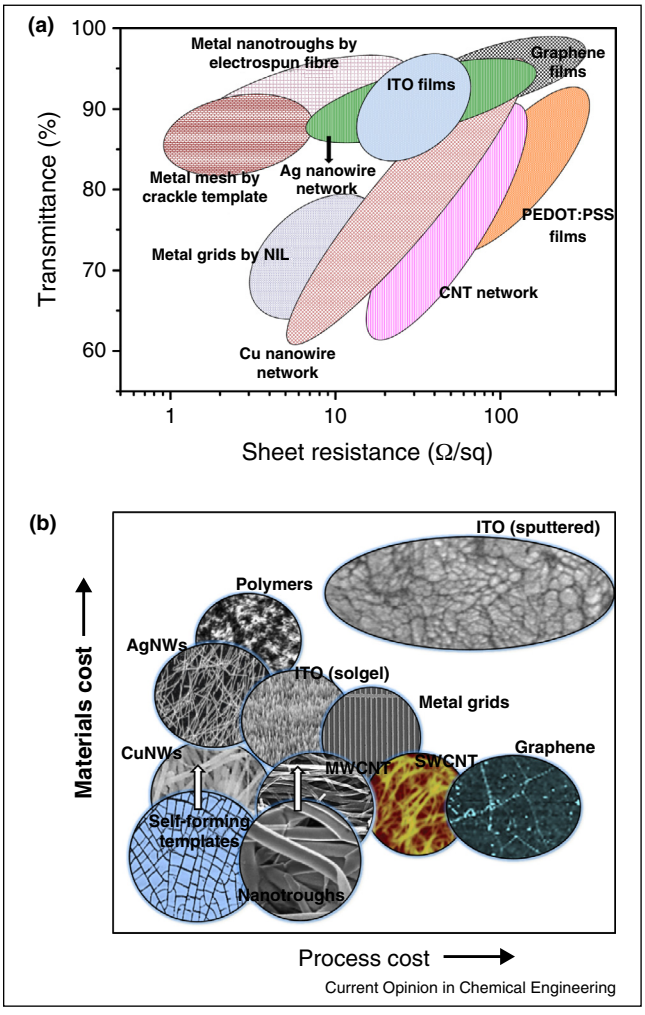
Figure 4a contains a plot showing schematic trends in transmittance against sheet resistance for various families of TCEs. Metal networks fabricated through self-forming crackles and electrospun nanotroughs, ultralong Ag nanowires and graphene thin films usually show a minimal

Figure 3



Fabrication of TCE using electrospun and crackle template process. **(a)** Schematic of an electrospinning process with syringe pump is shown in left side whereas systematic process steps are shown in right. Reprinted with permission from [67] *Nano Lett.* 2010 **10**:4242-4248. Copyright (2010) American Chemical Society. SEM image of Ag nanotroughs clearly showing its concave shape **(b)** Reproduced with permission from [69••]. **(c)** Photograph showing the formed crackle network on about 1.5 m length PET substrate. Top inset shows the spreading of crackle precursor using paint brush and bottom inset is SEM image of thus formed crackle network. **(d)** Photograph of Cu TCE/PET fabricated using electroless deposition process. Reproduced with permission from Ref [72••] **(e)** IR images clearly illustrate the stability of heater while bent to different curvatures. Reproduced with permission from Ref [71••].

Figure 4



(a) Schematic shows the clear trade off between T and R_s for different categories of TCEs. Lowering R_s compromises transmittance, in general. **(b)** Comparison plot of materials cost versus process cost for different categories of TCE materials. Microscopy images were reproduced with copyright from references mentioned in bracket. Sputtering process to deposit ITO is a cost-expensive process. The process cost is widely spread denoting its dependency on the quality of end-product [77]. On the other side, ITO synthesized by sol–gel process is cost effective [81]. The process cost is minimal for Cu nanowires (Reprinted with permission from [45] *J Am Chem Soc* 2012 **134**:14283–14286. Copyright (2012) American Chemical Society.), Ag nanowires (Reprinted with permission from [36] *ACS Nano* 2009 **3**:1767–1774. Copyright (2009) American Chemical Society.), PEDOT:PSS (Reprinted with permission from [80] *Chem Mater* 2011 **24**:373–382. Copyright (2011) American Chemical Society.), nanotroughs [69••] and self-forming processes (Reproduced by permission of the PCCP Owner Societies [73]) whereas their materials cost has huge variation. Upward arrows shown on nanotroughs and self-forming processes indicate that material cost may fluctuate with the choice of metal. Metal grid patterns realized by NIL [64] is middling. SWNT (Reprinted with permission from [79] *Nano Lett* 2006 **6**:2472–2477. Copyright (2006) American Chemical Society.), MWNT [78] and graphene [20] are also compared.

decrease in transmittance while sheet resistances were reduced drastically. This may be related to highly probable percolation paths with less or no junction resistance. Cu nanowires and CNT based electrodes belong to another category whose sheet resistances are generally high for higher transparency regime due to sparse density of shorter conducting paths. Organic TCE shows moderate transmission with relatively high sheet resistance as compared to metal based TCEs.

The cost of a TCE is determined mainly by the material and process costs (Figure 4b); the cost towards the substrate is relatively much less. With ITO, the material is usually deposited by ion sputtering under tightly monitored conditions. Solution methods for ITO produce electrodes with compromised optoelectronic properties [81]. This explains the wide range of pricing for the ITO plates on the market. In the case of carbon nanostructures, carbon as a source may be trivial, but the synthesis of nanostructures, be it CNTs or graphene, is usually cost intensive, more so if the high purity is the requirement. Graphene and CNTs are prepared with thermal and plasma CVD based methods that increase the fabrication cost. The conventional lithography methods used for fabrication TCEs are process intensive, laborious and based on expensive materials and equipment, thus increasing acquisition cost in terms of material and facility besides the manufacturing cost. In new template based methods, the fabrication cost is reduced due to use of simpler equipment. The material cost can be reduced as one need not rely on expensive metals. However, the processing is subtractive and multiple steps are required to obtain a TCE. The most successful TCE is based on metal nanowires grown using solution routes which keep the process cost at bay since the coating of nanowires can be done by single step roll-to-roll processing thus decreasing the manufacturing cost. Post deposition processing with encapsulants and additive layers may also increase the cost of nanowire based TCEs. More importantly, the cost of Ag is increasing at alarming rate. This issue is addressed by using less expensive Cu and other metals. Nevertheless, the metal nanowire based TCEs are now available at competing rates as substitute for ITO. Like in any type of TCE, ensuring large area uniformity [82] may enhance the cost non-linearly. In all above cases, amenability of the synthesis and deposition recipes for roll-to-roll conditions remains a determining factor for large scale production. New materials and processes need to be developed in the near future to overcome this trade-off between the optoelectronic properties and the cost.

Conclusions

This topical review on transparent electrodes has brought out important examples pertaining to different classes of new generation transparent conductors, while mentioning salient features of currently used material, ITO. Besides

graphene and ultra-thin metal films, networked structures involving Ag nanowires, Cu nanowires, carbon nanotubes have been dealt with. Periodic metal grids as well as mesh-like structures derived from template based methods have also been discussed. Besides providing the details of the optoelectronic properties, due attention has been paid to the cost in all these examples. The latter involving material and process components is however difficult to assess from an academic stand-point. Nonetheless, the attempt made in Figure 4b should be quite informative if not exact.

Acknowledgements

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- • of special interest
- •• of outstanding interest

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