The Race To Replace Tin-Doped Indium Oxide: Which Material Will Win?

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ABSTRACT The search for materials that can replace tin-doped indium oxide (ITO) as the leading transparent conductive electrode (TCE) has intensified significantly in the past few years, motivated by the ever-increasing price of indium. Materials such as carbon nanotube (CNT) films, graphene films, metal nanowire gratings, and random networks have been at the forefront of research in this direction. A paper by Wu *et al.* in this issue discusses the use of solution-processed graphene as the TCE in organic light-emitting devices. Advantages such as large-scale fabrication at relatively less expense, compatibility with flexible substrates, and improving performance have significantly contributed to their case as potential candidates for TCEs. Demonstrations of various display and photovoltaic devices using TCEs made of these materials, with performances rivaling those employing ITO, have provided the research community with encouragement to explore new materials and to address the associated scientific and technological challenges.

See the accompanying Article by Wu *et al.* on p 43.

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Materials with a remarkable combination of high electrical conductivity and optical transparency are important components of various optoelectronic devices such as organic light emitting diodes (OLEDs) and solar cells.[1,2] In the case of solar cells, these components work as anodes to extract separated charge carriers from the absorbing region, while in the case of OLEDs, they inject charge carriers without affecting the light out-coupling efficiency. Doped metal oxide films such as tin-doped indium oxide (ITO) and fluorine-doped tin oxide have single-handedly dominated the field for almost four decades.[3] The ability to deposit these materials with controlled thickness and controlled doping concentration has significantly contributed to their widespread application. However, the next generation of optoelectronic devices requires transparent conductive electrodes (TCEs) to be lightweight, flexible, cheap, and compatible with large-scale manufacturing methods, in addition to being conductive and transparent. These requirements severely limit the use of ITO as transparent conductors because ITO films fail under bending, restricting their use in flexible optoelectronic devices.[4] In addition, the limited availability of indium sources resulting in ever-increasing prices of indium creates an urgent need to find other materials that can work as transparent conductors for future optoelectronic devices.

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The question arises: what materials can fulfill these requirements? Having realized the need to replace ITO, the research community has made significant advances in this direction, with identification and evaluation of potential candidate materials. The most significant materials among these are carbon nanotube (CNT) films,[5−7] graphene films,[8−10] metal gratings,[11] and random networks of metallic nanowires.[12,13] Figure 1 represents these different materials used for various optoelectronic applications.

Leading the Pack: Nanotube and Nanowire Networks. Great efforts by many research groups have led to significant improvements in the performance of CNT films and their subsequent applications in display[14,15] and photovoltaic devices.[16] Figure 1a shows a typical scanning electron micrograph (SEM) of well-interconnected nanotube films, obtained using vacuum filtration and a poly(dimethyl siloxane) (PDMS)-assisted transfer technique and subsequently used for an OLED.[14] One of the critical requirements for CNT films is that the density of nanotubes must be above the threshold for the formation of a percolation network.[17] Although the conductivity of individual nanotubes is high, the high resistance at the nanotube−nanotube junction limits the conductivity of these films.[18] Researchers have devised many approaches to enhance the conductivity of these films by manipulating surfactant molecules, using various acid treatments, and so on.[19] In general, CNT films are comparatively inexpensive and can be fabricated over large areas in various thicknesses and patterns; however, their performance still lags behind those of ITO films. For example, to achieve a sheet resistance of 10 ohms/sq, CNT films need to be >100 nm thick, severely

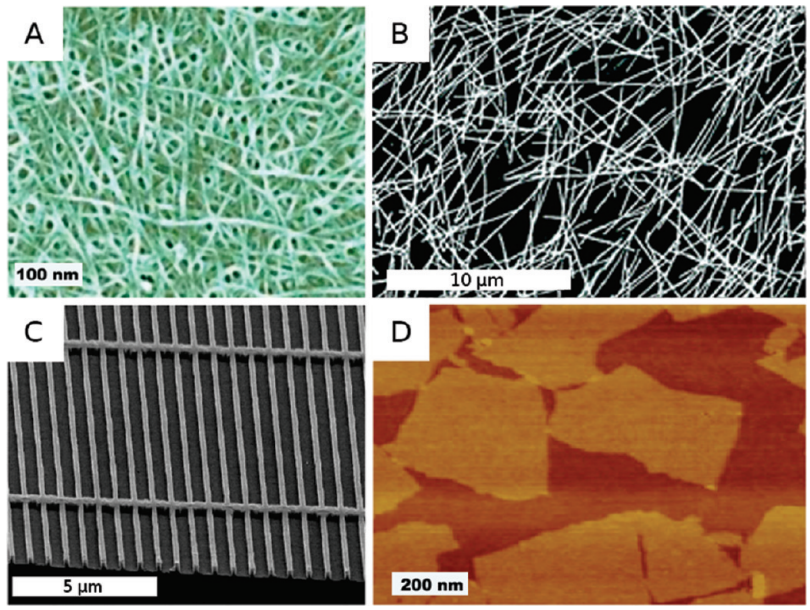

Figure 1. Various candidate materials for transparent and conductive electrodes. (a) Scanning electron micrograph (SEM) of a carbon nanotube (CNT) film, (b) SEM of a silver nanowire network film with high optical-to-electrical-conductivity ratio, (c) SEM of a Au nanowire grating fabricated using the nanoimprinting technique, and (d) atomic force microscopy (AFM) image of solution-processed graphene flakes. Panel A reproduced from ref 14. Copyright 2006 American Chemical Society. Panel B reproduced from ref 13. Copyright 2009 American Chemical Society. Panel C reproduced with permission from ref 11. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KgaA. Panel D reproduced with permission from ref 23. Copyright 2008 Nature Publishing Group.

affecting their transparency. New approaches are being explored to enhance the performance of CNT films.

Along the same lines, a random network of metal nanowires and ordered arrays of metallic nanostructures have recently been put forward as leading candidate materials. Initial results show that films of metal nanowires exhibit performances that rival those of ITO, with sheet resistances approaching ~16 ohms/sq at a transparency of ~86%.[12] Recently, small-molecule photovoltaic cells were fabricated on silver nanowire networks and were shown to compete well with cells fabricated on traditional ITO films.[12] Figure 1b shows a SEM of a silver nanowire film obtained using a cellulose-assisted transfer method with σ_{DC}/σ_{OP} values approaching ~500.[13]

Use of surfactant-free silver nanowires eliminates the need for high-temperature annealing, thus enabling their deposition on flexible substrates[13] for subsequent application in flexible optoelectronic devices. Similarly, a nanowire grating structure with well-defined dimensions represents an ideal configuration for device applications (Figure 1c). This approach enables manipulation and optimization of parameters such as line-width, thickness, pitch, and also different metals, to obtain electrodes with low sheet resistance and high transparency. For instance, using 40-nm-thick Au gratings, an electrode with 13 ohms/sq sheet resistance was demonstrated for OLED applications.[11] Although this is a good start for metal nanowire networks, research in this direction is still in its infancy and would require scalable approaches to fabricate these films.

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A New Contender: Graphene. Another promising candidate for this purpose is graphene films. Graphene is a single sheet of sp^2-bonded carbon atoms. As a zero band gap semiconductor, its electronic structure is unique in the sense that charge carriers are delocalized over large areas, making it a scattering-free platform for carrier transport.[20] High Fermi-velocity and the ability to dope the graphene films externally result in extremely high in-plane conductivities.[21] In their article in this issue, Wu *et al.* have demonstrated the application of solution-processed graphene films as transparent conductors in OLEDs.[22] Using such films, they achieve OLED performance similar to a control device on ITO transparent anodes. The graphene used by the authors is prepared using Hummers' method followed by vacuum annealing to reduce the graphene oxide. Previously, Kaner's group[23] demonstrated that graphene sheets produced in this manner can be uniform and can have extremely small thicknesses (Figure 1d). Small molecules such as *N,N'*-di-1-naphthyl-*N,N'*-diphenyl-1,1'-biphenyl-4,4'diamine/tris(8-hydroxyquinoline) aluminum (NPD/Alq_3) were vacuum-deposited followed by top cathode deposition to complete the OLED fabrication. These devices resulted in current drive and light emission intensity comparable to those prepared on ITO electrodes. In addition, the turn-on voltage for the devices was 4.8 V, as compared to 3.8 V for ITO devices. The most significant result comes from the external quantum efficiency (EQE) measurements, which show that EQE and power efficiency for the graphene devices nearly matches the ITO-based devices, despite having a sheet resistance of ~800 ohms/sq, nearly 2 orders of magnitude higher than the ITO sheet resistance.

The same group led by Peter Peumans has previously demon-

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strated the use of solution-processed graphene in photovoltaic devices.[24] The current report by Wu *et al*. puts forward a strong case for graphene as a transparent conductor given its competitive performance, even with significantly high sheet resistance. In principle, a 7-nm-thick graphene film would have a sheet resistance of 1−10 ohms/sq,[22] which would enhance the charge injection process and thus lead to a many-fold improvement in performance. This would still require further development of synthesis protocols to fabricate high-quality graphene films.

It is important to point out that the main factor contributing to the high sheet resistance of solution-processed graphene sheets arises from innumerable grain boundaries present because of rather small grain sizes (roughly a few micrometers) of graphene flakes, and because of the presence of many defects in each flake. Recently, a high temperature chemical vapor deposition (CVD) approach has been adapted by many groups[25−30] to synthesize single- or few-layer graphene sheets over entire wafers (Figure 2a,b). Single-crystalline or polycrystalline metal films (*e.g.,* Cu, Ni) serve as nucleating templates for the incoming carbon source gases, which decompose on the surface of these metals and initiate formation of graphene. Although there is still a need to understand the growth mechanism, to control the grain size of graphene flakes, and to develop methods to characterize these sheets, application of the CVD technique is a significant advance in this field and may ultimately be the method to produce high-quality graphene sheets for optoelectronic applications. While solution methods have advantages in large-scale production and scalability, the CVD method still faces challenges in large-scale production at low cost. Toward this end, researchers have developed transfer techniques that enable transfer of CVD-grown graphene to various rigid and flexible substrates,[26−28] increasing their usability as reported recently in the case of photovoltaics.[31]

CONCLUSION AND OUTLOOK

The questions remain: which material holds the key to these problems? Which material can combine high electrical conductivity with optical transparency, while simultaneously being low-cost, scalable, and compatible with flexible substrates? We do not yet know. The solution may include all or a combination of the above-mentioned materials. Initial results on these materials have been encouraging, although issues remain with large-scale production, technological improvements in material quality, and in the cost to fabricate and to implement these materials. The key to success is to continue to explore new materials and to strive to develop and to optimize methods to produce these materials on large scales. If we continue to do so, we may find the "holy grail" that combines all of these desirable

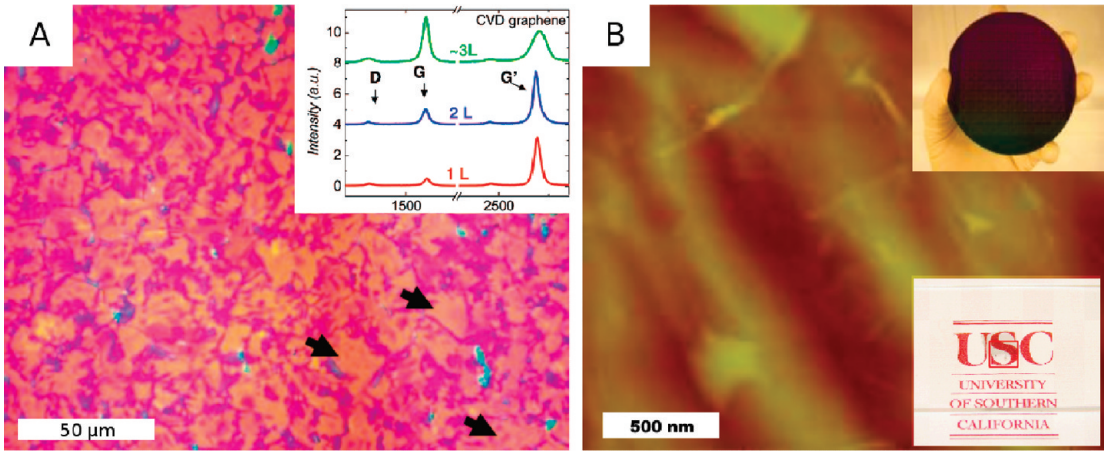

Figure 2. Chemical vapor deposition (CVD) synthesis of single- or few-layer graphene. (A) Optical microscopy image of graphene grown on Ni film and transferred to a Si/SiO_2 substrate. Black arrows show flakes of graphene. Inset shows typical Raman spectra of one-, two-, and three-layer graphene obtained using this method. Reproduced from ref 26. Copyright 2009 American Chemical Society. (B) AFM image of a graphene film grown on a single-crystalline Ni film. Top inset shows full wafer transfer of this graphene to a Si/SiO_2 substrate with photolithographically patterned electrodes. Bottom inset shows a graphene film transferred to a glass substrate, demonstrating its transparency. Panel B insets reproduced with permission from ref 27. Copyright 2009 IEEE.

properties for optoelectronic devices.

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