

## Stretchable, elastic materials and devices for solar energy conversion

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This Perspective reviews stretchable, elastic materials and devices of use for the conversion of solar energy. Stretchable and extremely flexible photovoltaic and photoelectrochemical cells would be useful as, for example, power sources for rugged and collapsible electronic and biomedical devices, foldable, weather-resistant solar roofs for applications in the field, and conformable solar panels for one-time bonding to the curved surfaces of buildings and vehicles. The review discusses elastic substrates, semiconductors, and electrodes. It then describes examples of whole devices comprising these elastic components. The Perspective tends to emphasize materials of interest for excitonic solar cells—*e.g.*, organic solar cells, those based on semiconductor nanocrystals, and dye sensitized solar cells—because of their potential for stretchability and extreme flexibility, but also discusses crystalline photovoltaic devices and nanostructured photoelectrochemical cells.

### 1. Introduction

Solar energy is, by far, the most abundant potential source of renewable energy in the world.<sup>1</sup> Perhaps the strongest argument in favor of the utilization of solar energy—through photovoltaic (PV),<sup>2</sup> photothermal,<sup>3</sup> and photoelectrochemical<sup>4</sup> mechanisms—is the well-known fact that more energy in the form of sunlight strikes the surface of the earth in one hour than human activity consumes in one year.<sup>5</sup> One to two percent of the area of the United States is required to convert enough solar energy to satisfy the needs of the entire country using typical commercial solar modules.<sup>1</sup> Converting even a fraction of the needed land

area, however, into utility-scale solar farms will produce significant and justified resistance on the basis of economics, politics, and potential harm to the environment. In addition to economic, political, and environmental hurdles, the widespread utilization of solar energy faces technical challenges of distribution,<sup>6</sup> inversion and transmission,<sup>7</sup> installation, and storage.<sup>8</sup> (Storage, in particular, is necessary for photovoltaic devices, but is solved in an integrated way in photoelectrochemical devices.<sup>4</sup>) Despite the challenges, realists agree that the pursuit of utility scale conversion of solar energy, wherever it is feasible, is one of the steps needed to avoid global climate change.<sup>9</sup>

Utility-scale, grid-connected generation of electricity is not the only logical implementation of solar energy, however, solar energy has characteristics not possessed by other renewables that render it uniquely suited for implementation off-grid. This Perspective focuses on developing solar materials and devices

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### Broader context

Electronic materials and methods of manufacturing that produce flexible, stretchable, collapsible, and fracture-proof devices would revolutionize consumer electronics, biomedical devices, and devices for fieldwork. While flexible electronics based on thin-film semiconductors are nearing commercialization, stretchable electronic materials and devices are in their infancy. This Perspective describes recent advances in the materials, methods of fabrication, and devices for the utilization of solar energy that have the potential for stretchability. Fully elastic solar panels could be used, for example, as “solar tarps”—weather resistant solar roofing for low-cost housing in resource-poor environments, disaster relief organizations, and military and intelligence services, and as sources of power for the exteriors of vehicles and buildings in a way that does not compromise aerodynamics or aesthetics. Achieving this goal presents a great challenge to materials science: essentially all components of solar panels—transparent substrates and conductors, semiconductors, and reflective electrodes—have strict requirements that are necessary for optimum electronic and optical performance but that seem to be incompatible with having mechanical properties that are rubber-like. This Perspective explores materials and methods of fabrication that combine to produce devices that are the first in a new generation of stretchable sources of power.

that will integrate with moving objects and non-planar substrates, and in applications that require portability and mechanical resilience.

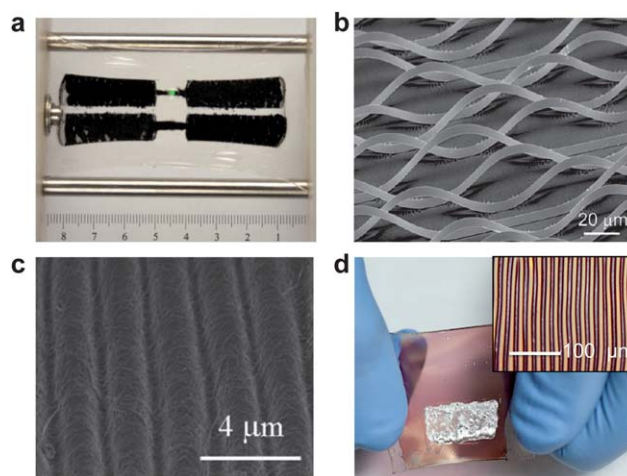
## 2. Motivation

### 2.1. Limitations of conventional solar materials

The installed capacity for PV grew 60% per year between 2004 and 2009, and stood at about 21 GW of grid-connected installations, and an additional 4 GW of off-grid power.<sup>10</sup> The technological and economic hurdles associated with conventional (polycrystalline silicon) and thin-film (especially cadmium telluride), solar modules are starting to erode. If current trends continue, worldwide conversion of solar energy on the TW scale is achievable in the next several years. The rapid growth of polycrystalline and inorganic thin-film technologies is so pronounced, and the scale of investment is so large, that they are likely to dominate utility-scale (>200 kW per installation) capacity for the foreseeable future. Researchers are right to focus on increasing efficiency and lowering the costs of modules and installation for utility scale implementation, but the point of this Perspective is to identify applications of solar devices and (primarily soft) materials that fill niches inaccessible to hard semiconductors. Introduction of elasticity—flexibility and stretchability—to solar devices would enable new off-grid applications, and would thus permit the generation of solar power more broadly than it now is.

### 2.2. Applications of elastic solar materials

Elastic solar materials are part of a larger class of mechanically compliant sources of power (Fig. 1).<sup>11–14</sup> The need to impart elasticity in response to bending, compressive, and tensile strains must be satisfied before solar power can be seamlessly integrated with moving parts of robots and machines, textiles,<sup>15</sup> collapsible displays, rugged equipment for fieldwork,<sup>16</sup> prostheses,<sup>17</sup> and non-



**Fig. 1** Examples of stretchable sources of power. (a) A stretchable dry-cell battery. Reproduced with permission from ref. 11. Copyright 2010, Wiley-VCH Verlag GmbH & Co. KGaA. (b) Stretchable piezoelectric nanoribbons. Reproduced with permission from ref. 19. Copyright 2011, American Chemical Society. (c) Buckled films of carbon nanotubes as electrodes in stretchable supercapacitors. Reproduced with permission from ref. 20. Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA. (d) Stretchable organic solar cells.

planar surfaces of vehicles and buildings.<sup>18</sup> We note that most of these applications require elasticity in response to tensile strain (stretchability), not just in response to bending strain (flexibility). Simple flexibility allows roll-to-roll production of some types of thin-film materials, but does not allow conformal bonding of these devices to non-planar substrates other than cylinders and cones. In general, we are interested in materials that have the potential to accommodate strains of  $\geq 10\%$ . Aside from the practical value of elastic materials for electronics, some of the most interesting and important scientific opportunities in materials science and chemistry arise from the combination of mechanical, electronic, and optical properties in a single material.



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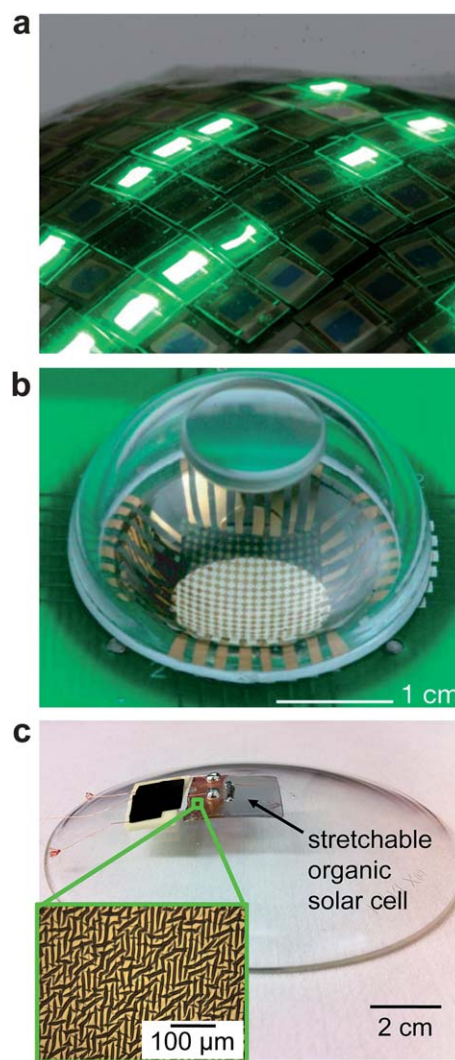
**2.2.1. Integration with moving parts.** The clearest application of elastic solar materials is perhaps integration with components that deform regularly as part of their operation, *e.g.*, robotic limbs,<sup>21</sup> or those that deform at random times in response to their environment, *e.g.*, sails. Integration of solar materials with textiles has long been a goal of the research community concerned with thin-film (particularly organic) technology.<sup>15</sup> Early demonstrations include integration of OPV devices with solar hats and umbrellas.<sup>22</sup> The integration of solar power into military uniforms could de-burden soldiers by reducing significantly the weight of batteries. Elastic solar materials also have obvious implications in space suits. Temporary base camps for the military and disaster relief organizations often have textile roofs that must be collapsible, and once deployed, must withstand harsh environments of regions prone to earthquakes and hurricanes. Housing in urban slums often comprise textile roofs, and thus inexpensive, elastic solar roofs—in addition to providing power for cooking and reading—could help offset the carbon emissions of kerosene and the particulate matter generated by unsustainably burned manure and trash.<sup>16</sup>

Soft robotics is an emerging area in which hydrostatic forces actuate devices composed of elastomeric materials.<sup>21</sup> Such devices could perform delicate tasks, such as assembling fragile components, performing surgery, or deactivating explosives, in ways that hard electronics cannot.<sup>21</sup> Electronic skin comprises a class of multifunctional, elastic devices that some day might be integrated to sense touch, tensile strain, temperature, and chemical and biological signals.<sup>23,24</sup> These devices could interface electronics with human touch, and could be used in prostheses, wound-healing, and a variety of consumer electronic devices, from collapsible displays, to devices that give biofeedback (*e.g.*, steering wheels that sense if the driver is falling asleep).<sup>25</sup>

**2.2.2. Integration with non-planar substrates.** Materials that offer only flexibility are unsuitable for applications that require bonding to or wrapping around non-planar substrates (Fig. 2).<sup>26</sup> One sector in which solar energy is underutilized is transportation, which consumes roughly 40% of distributed energy globally.<sup>6</sup> Some of the largest consumers of energy—automobiles, airplanes, trains, ships, and buildings—have nonplanar surfaces for reasons of aerodynamics as well as aesthetics. Conformable solar devices have the potential for seamless integration with the surfaces of these vehicles.

**2.2.3. Applications requiring portable, rugged sources of power.** Conventional solar materials and devices fracture easily, and solar devices are usually fixed to rigid frames. Elastic solar cells would be less susceptible to mechanical failure than rigid cells, and could power devices in expeditionary applications for the military, intelligence services, and scientific community that require durability. For example, collapsible, interactive displays,<sup>27</sup> electronic notebooks, communication devices, and antennae<sup>30</sup> composed of stretchable materials would all benefit from mechanically and environmentally robust sources of power.<sup>31</sup>

Another application is for powering devices in resource-poor areas that are not connected to the grid.<sup>8</sup> Krebs and coworkers described a project as part of the Lighting Africa Initiative in which they produced integrated LED lanterns powered by



**Fig. 2** Photographs of optoelectronic devices bonded to hemispherical surfaces. (a) A stretchable array of organic light-emitting devices comprising interconnects of carbon nanotubes embedded in a fluoroelastomer. Reproduced with permission from ref. 27. Copyright 2009, Nature Publishing Group. (b) A hemispherical electronic eye camera composed of photodiodes embedded in an elastomeric matrix. Reproduced with permission from ref. 28. Copyright 2008, Nature Publishing Group. (c) A stretchable organic solar cell reversibly bonded conformally to a hemispherical watch glass. The inset is a micrograph of the surface of the photoactive layer of the device.<sup>29</sup>

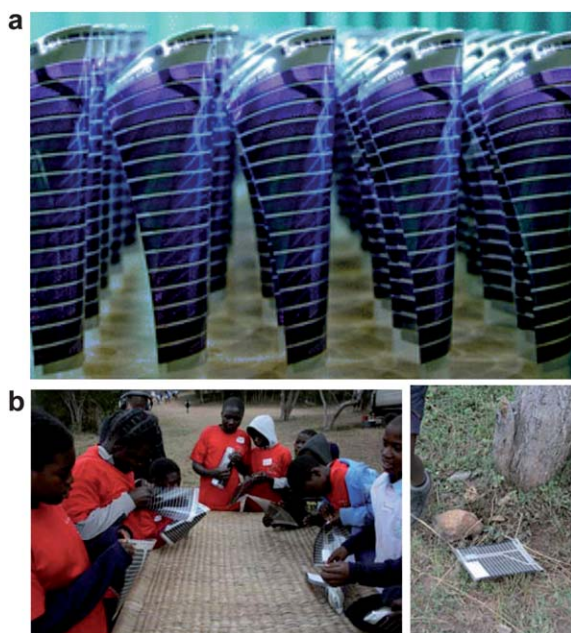
organic photovoltaic devices (Fig. 3).<sup>16</sup> The authors found that mechanical (as opposed to photochemical) degradation was the chief cause of device failure.<sup>16,32</sup> The use of mechanically compliant (“rubber” as opposed to “plastic”) photovoltaic cells devices might prevent cracking, delamination, and debonding of components within these devices.

### 3. Elastic materials

#### 3.1. Introduction and scope

The focus of this paper is on elastic solar photovoltaic materials and devices, but we will also include recent advances in elastic photoelectrochemical cells.<sup>4,33</sup> The selection of topics skews





**Fig. 3** (a) LED reading lamps charged by flexible organic photovoltaic modules. (b) Photograph of school children assembling the lamps (left), and image of the solar module charging (right). Reproduced with permission from ref. 16. Copyright 2010, Royal Society of Chemistry.

toward materials and processes applicable to excitonic<sup>34</sup>—particularly organic,<sup>35</sup> dye-sensitized,<sup>36</sup> and nanocrystal-based<sup>37</sup>—photovoltaic devices; this bias is idiosyncratic and reflects the expertise of the authors, and should not be taken as an endorsement of one area of research over another. In general, the challenge of designing materials that combine optical, electronic, and mechanical function is that properties usually cannot be added and subtracted independently. For example, free-flowing electrons of metallic bonds, which enable the high conductivity of metals, are also responsible for plastic flow when metals are strained, and thus preclude rubber-like values of Young's modulus ( $\leq 100$  MPa).<sup>38</sup> This section begins by describing the “tricks” used to produce elasticity in rigid electronic materials.

### 3.2. Methods used to generate elastic electronic materials

Many strategies for producing elastic electronic materials rely on converting stretching motions to microscopic bending strains. The peak strain experienced by a thin film under bending strain is directly related to the thickness of the substrate, and inversely related to the radius of curvature, as given by eqn (1)

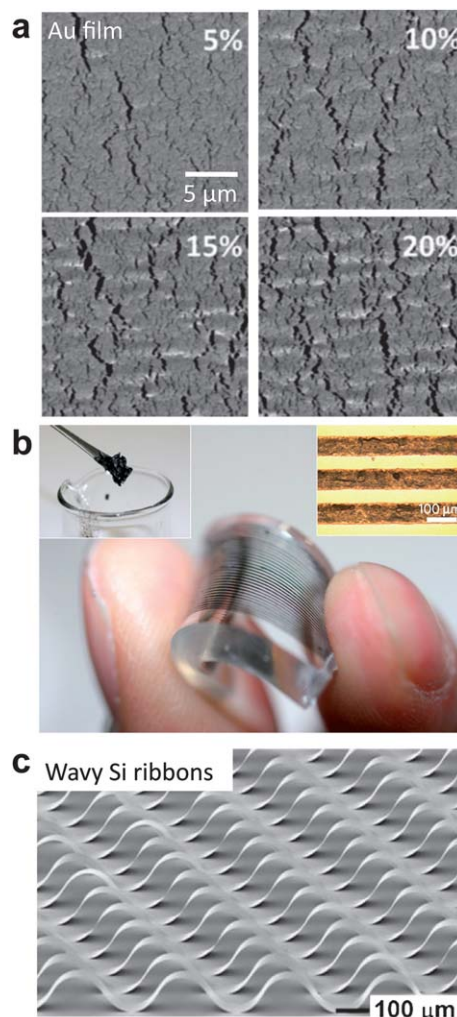
$$\varepsilon = \left( \frac{d_f + d_s}{2r} \right) \times 100\% \quad (1)$$

where  $\varepsilon$  is the peak strain,  $d_f$  is the thickness of the film,  $d_s$  is the thickness of the substrate, and  $r$  is the radius of curvature.<sup>39</sup> A film on a flexible substrate with 100  $\mu\text{m}$  thickness, bent to a radius of 5 mm, thus experiences a peak strain of 1%.<sup>40</sup> The smallest bending radii can be achieved when the most rigid device components are placed in the neutral mechanical plane, where the compressive and tensile strains produced by bending

counterbalance.<sup>39,41</sup> Flexibility can be exploited to form stretchable devices: buckling and coiling are strategies that convert bending strains into tensile strains.<sup>41</sup>

This section describes the different approaches to make elastic materials from inelastic constituents (Fig. 4). Most polymeric and metallic thin films are incidentally flexible, and can be bent to radii of curvature of a few millimetres or less, if supported by a sufficiently thin substrate. While there are rare exceptions of free-standing bulk materials or thin films with conducting or semiconducting properties that are likely to be intrinsically stretchable, such as carbon micro-coils,<sup>41,42</sup> most materials require dispersion in or coating on an elastomer, which supplies the restoring force when strained.

The existing literature on elastic conductors and semiconductors for photovoltaics tends to understate the levels to



**Fig. 4** Examples of the three general strategies used to render rigid materials stretchable. (a) Scanning electron microscope images of a gold film on a PDMS substrate under different levels of strain. Reproduced with permission from ref. 51. Copyright 2009, American Institute of Physics. (b) A conductive elastomer generated by dispersing carbon nanotubes in an elastomeric matrix. Reproduced with permission from ref. 27. Copyright 2009, Nature Publishing Group. (c) Stretchable, wavy silicon ribbons. Reproduced with permission from ref. 52. Copyright 2006, Nature Publishing Group.

which materials can be deformed reversibly. In much of the literature on elastic electronic materials, only flexibility is demonstrated. Often, materials are capable of reversible stretchability by buckling on an elastomeric substrate. In some reports, elasticity is limited not by the active material, but by the fragility of the interconnects, the strength of adhesion between the layers, the thickness of the substrate, and the rigidity of other materials in the device stack (especially the transparent conductive oxide).

The three primary strategies used to combine conductivity and elasticity are to stretch a rigid film to fracture it intentionally, or use micro- or nanostructured materials that form a percolated network when stretched (Fig. 4a), to impregnate elastic materials with a three-dimensional network of, for example, metallic particles,<sup>43</sup> or carbon nanotubes (CNTs) (Fig. 4b),<sup>27,44</sup> or to use mechanical buckling: thin films, deposited on pre-strained elastic substrates, form waves upon release of the pre-strain (Fig. 4c).<sup>45,46</sup> These buckles bend and unbend upon tensile strain of the film.<sup>28,47–50</sup>

**3.2.1. Percolated thin films.** One strategy of forming a stretchable thin film is to form an intentionally fractured metallic thin film on an elastomeric substrate.<sup>51</sup> Upon straining, the metallic film fractures into plates which form percolated pathways up to a certain strain.<sup>53</sup> Lacour and coworkers used this strategy to produce stretchable electrodes for capacitive touch sensors embedded in PDMS.<sup>54</sup> Thin films of carbon nanotubes and graphene can also maintain percolated pathways when strained, and will be covered more thoroughly in Section 3.5.

**3.2.2. Non-stretchable materials embedded in an elastic matrix.** The second general strategy to produce stretchable materials is to impregnate elastic materials with conductive particles, such as metals,<sup>43</sup> or carbon nanotubes (CNTs).<sup>44</sup> Such materials can withstand very high strains (>100%), but generally require a high volume fraction of conductive particles and are thus opaque.<sup>43,44</sup> This strategy is exemplified by the work of Someya and coworkers, who demonstrated a rubber-like bulk conductor of long CNTs embedded in a fluoroelastomer that accommodated strains—in one example—of 118% with a value of conductivity in the stretched state of  $9.7 \text{ S cm}^{-1}$ .<sup>27</sup> Baik and coworkers described a CNT–Ag composite material, with a value of conductivity  $20 \text{ S cm}^{-1}$  at 140% strain.<sup>43</sup>

**3.2.3. Rendered stretchable by buckling.** The third approach, which is applicable to thin films, is exploitation of the buckling instability.<sup>52</sup> Stretchable metallic, semiconducting, and polymeric films may be prepared by physical vapor deposition or lamination on pre-strained elastomeric substrates; release of the pre-strain compresses the films and produces topographic buckles that convert stretching motions into bending and unbending of the buckles.<sup>45</sup> This method of mechanical buckling, pioneered by Whitesides,<sup>47</sup> Suo and Wagner,<sup>48</sup> has since been a key component of many successful studies, especially by Rogers and coworkers, for applications in solar energy conversion,<sup>49</sup> imaging,<sup>28</sup> and biomedical engineering.<sup>50</sup>

The technique of mechanical buckling is not limited to metallic and polymeric films. Relatively thick (50 nm) macrofilms of carbon nanotubes, deposited on pre-strained elastomeric

substrates, can possess conductivities  $\leq 1000 \text{ S cm}^{-1}$  while accommodating strains of 40% when used as electrodes in stretchable supercapacitors.<sup>20</sup> A method related to buckling for preparing stretchable films of carbon nanotubes is by depositing a weakly adhered CNT film to an elastic substrate. A one-time application of strain and subsequent release produces topographic waves whose amplitudes lie in the plane of the substrate, and whose direction is aligned with the axis of stretching, produces films that can be strained up the value of the initial strain with minimal changes in resistance.<sup>55</sup>

A recent review by Khang, Rogers, and Lee will provide the interested reader with enough background to appreciate the literature in which mechanical buckling is used to achieve elasticity.<sup>56</sup> The authors describe three regimes of buckling, in which thin films are bonded to substrates under small and large compressive strains, and systems in which the substrate, bearing patterns of activated and inactivated regions, produces buckled films adhered only in activated regions and delaminated elsewhere.<sup>56</sup> For small strains, the buckling wavelength ( $\lambda$ ) is dependent on the Young's modulus of the film ( $E_f$ ) ( $\lambda$  increases with increasing  $E_f$ ) and substrate ( $E_s$ ) ( $\lambda$  decreases with decreasing  $E_s$ ), the thickness of the film ( $d_f$ ) ( $\lambda$  increases with increasing  $d_f$ ), and is independent of the value of the compressive strains less than  $\sim 5\%$ . For large strains, the buckling wavelength exhibits dependence on strain, because the stress-strain relationship is non-linear at large strain for elastomeric substrates.<sup>56</sup> The relationship between Young's modulus and thickness of the film, and the buckling wavelength, is described by eqn (2),

$$E_f = 3E_s \left( \frac{1 - \nu_f^2}{1 - \nu_s^2} \right) \left( \frac{\lambda}{2\pi d_f} \right)^3 \quad (2)$$

where  $\nu_f$  and  $\nu_s$  are the values of Poisson ratio of the film and substrate. Stafford and coworkers developed a simple buckling-based metrology around this relationship, and were able to determine the moduli of polymeric films simply by measuring the buckling wavelength of films with different thicknesses.<sup>57</sup> Khang *et al.* recently used this methodology to determine the elastic moduli of organic semiconductors of interest in photovoltaic devices, including a blend of poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM).<sup>46</sup> The simplicity of the buckling-based metrology also allows one to correlate mechanical properties with electronic properties of organic semiconductors. O'Connor *et al.* combined buckling-based measurements of Young's modulus with measurements of field-effect hole mobility for two conjugated polymers, P3HT and poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-*b*]thiophene) (PBTTT).<sup>58</sup> The authors found that the structural order of annealed PBTTT, which is consistent with good mobility of charge carriers (a factor of 5 higher than that of P3HT in their materials), was also responsible for PBTTT films that were stiffer and more brittle than P3HT films. The modulus of PBTTT was about  $10\times$  larger than that of P3HT, and the strain at which cracks appeared was  $<2.5\%$  for PBTTT and  $150\%$  for P3HT.<sup>58</sup> A rigorous analysis that relates chemical structure and solid-state packing to both electronic and mechanical properties is crucial in organic electronics—a field whose implementations in biomedicine and compliant devices require resistance to fracture and electronic properties that are affected minimally by strain.

### 3.3. Elastic substrates

The composition and thickness of the substrate are limiting factors in the amount of bending and tensile strain a photovoltaic device can accommodate.<sup>40</sup> Poly(ethylene terephthalate) (PET) substrates coated with ITO are available commercially. Materials such as PET—while sufficient for flexible applications—will be unsuitable for applications requiring stretchability.<sup>59</sup>

Poly(dimethylsiloxane) (PDMS, specifically Dow Corning Sylgard 184) is often used in elastic electronic devices. When mixed in its prescribed ratio of base-to-crosslinker of 10 : 1, PDMS has a Young's modulus of 1.8 MPa,<sup>60</sup> elongation at a failure of 160%, a shore hardness of A-48.<sup>30</sup> The native surface energy of 21.6 dynes cm<sup>-1</sup> is too low to permit wetting of materials processed from aqueous solutions (*e.g.*, PEDOT:PSS),<sup>60</sup> but there are many ways to alter the surface chemistry of PDMS to render it compatible with the formation of thin films.<sup>61</sup> Methods to increase the surface energy include treatment with UV/ozone, oxygen or air plasma, and aqueous hydrochloric acid.<sup>46</sup> Fluorosilanization, typically with tridecafluorotetrahydrooctyltrichlorosilane, can render the surface of PDMS Teflon-like,  $\sim 12$  dynes cm<sup>-1</sup>.<sup>60</sup>

### 3.4. Elastic semiconductors

The literature on elastic bulk semiconductors is limited to PDMS membranes embedded with silicon nanowires that are electrically contiguous through the thickness of the membrane, but not across it.<sup>62</sup> Single-crystalline wavy nanomembranes,<sup>63</sup> flexible films of semiconductor nanocrystals,<sup>37</sup> and stretchable films of buckled conjugated polymers are the most prominent examples of intrinsically elastic semiconductor materials.<sup>18,46</sup> Areas for opportunity include stretchable films of semiconducting CNTs, which offer the possibility of stretchability without mechanical buckling, as has been shown in films of CNTs, when used as conductors.<sup>55,64</sup>

**3.4.1. Wavy crystalline materials.** The rapid, recent development of stretchable, wavy films of single-crystalline semiconductors is largely due to the efforts of Rogers, Nuzzo, Lagally, and others.<sup>45,65–67</sup> Crystalline semiconductors are ordinarily brittle and are characterized by small strains of failure (<1%).<sup>40</sup> In the first demonstration of wavy single-crystalline silicon, p–n photodiodes and field-effect transistors were demonstrated.<sup>68</sup> This demonstration provided the proof of principle for stretchable photovoltaics in which the semiconductor itself was elastic. In the most sophisticated applications of stretchable photovoltaic devices based on single-crystalline materials, however, the substrates are engineered in such a way to localize the strain to the parts of the circuits most insensitive to strain, *e.g.*, the interconnects.<sup>26</sup>

**3.4.2. Semiconductor nanoparticles.** Semiconductor nanoparticles, including quantum dots and other single crystals,<sup>69</sup> wires and other 1D structures,<sup>70</sup> and particles of different shapes such as tripods,<sup>71</sup> are flexible when cast into thin films.<sup>37</sup> Gur *et al.* reported a solution-processed, all-inorganic, flexible solar cell from CdTe (electron donor) and CdSe (electron acceptor) semiconductor nanocrystals with efficiencies of  $\sim 3\%$ , but the effect of bending on electronic characteristics was not reported.<sup>37</sup>

In 2008, the group reported the synthesis of environmentally benign Cu<sub>2</sub>S nanocrystals, which behaved as an electron-donor when paired with CdS nanocrystals in a photovoltaic device.<sup>72</sup> Bending to 105° decreased the efficiency by 8%, but the decrease could have been due to the damage to the ITO transparent electrode, rather than to the nanocrystal films.<sup>72</sup>

**3.4.3. Organic semiconductors.** Conjugated organic semiconductors have the potential to be the active materials in flexible and stretchable photovoltaic devices. Recently, our laboratory reported the first stretchable organic solar cell, which comprised an active layer of P3HT:PCBM, a transparent electrode composed of PEDOT:PSS, and a liquid metal top electrode, eutectic gallium–indium (EGaIn).<sup>18</sup> These layers were deposited on a pre-strained PDMS membrane. Release of the pre-strain produced buckles in the layers; the buckles planarized upon the application of tensile strain, and thus rendered the device elastic.<sup>18</sup> The details of this approach will be discussed in Section 4.4. The buckling mechanism is most likely to be successful for conjugated polymers, or blends of conjugated polymers and molecular semiconductors, as opposed to neat films of molecular semiconductors: Tahk *et al.* observed that thin films of pentacene cracked extensively when compressed by 10% on PDMS.<sup>46</sup> The development of conjugated elastomers would enable the fabrication of all-organic, stretchable devices without the need for mechanical buckling.

**3.4.4. Carbon nanomaterials.** Since the work of Tomblor *et al.* on the electromechanical characteristics of individual single-walled carbon nanotubes suspended over gaps and deflected by the tip of an atomic force microscope,<sup>73</sup> the use of carbon nanotubes (CNTs) as electronic materials in elastic devices has been the focus of many important studies.<sup>74,75</sup> The use of elastic films of carbon nanotubes as conductors, however, is significantly more advanced than the use of these films as elastic semiconductors. For example, recent research has shown that films cast from unsorted suspensions containing conducting and semiconducting single- and multiwalled carbon nanotubes<sup>20,25,55,75,76</sup> and graphene<sup>43,77,78</sup> can be stretched with small changes in resistance. While individual carbon nanotubes have shown impressive electrical characteristics as photodiodes, including the generation of multiple electron–hole pairs,<sup>79</sup> and thin films of semiconducting nanotubes can form flexible networks of field-effect transistors,<sup>80</sup> pure films of semiconducting carbon nanotubes have thus far not been used as the sole active material in thin-film photovoltaic devices. Carbon nanotubes have been used as additives in bulk heterojunction organic photovoltaic devices, however, when blended with, for example, poly(3-octylthiophene) in Schottky photodiodes,<sup>81</sup> or as complexes with C<sub>60</sub> in bulk heterojunction devices to improve the transport of charge carriers.<sup>82</sup> One expects that the lessons learned in generating elastic conductive films of carbon nanotubes and graphene will be applicable to semiconducting films, once issues of selective synthesis of only semiconducting tubes, or sorting in solution<sup>83,84</sup> or on chemically modified surfaces,<sup>85,86</sup> are solved.

### 3.5. Elastic transparent electrodes

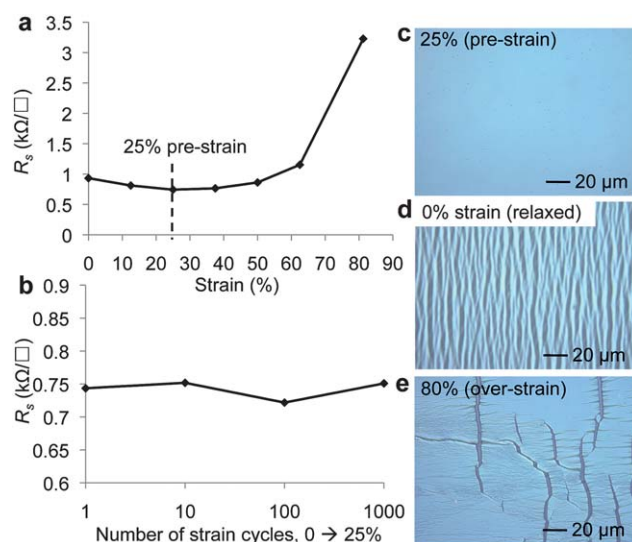
Tin-doped indium oxide (ITO) exhibits the benchmark combination of sheet resistance and transparency ( $10 \Omega \text{ sq}^{-1}$  at 90%



transmittance). It is a ubiquitous component of liquid crystal displays and thin-film photovoltaic devices. Large-scale implementation of thin-film solar photovoltaic technology will probably require a transparent electrode that does not rely on indium, which is scarce and increasingly expensive (natural abundance 0.05 ppm).<sup>87</sup> In elastic systems, ITO is essentially inapplicable: Hu *et al.* and Rowell *et al.* demonstrated that the properties of ITO films degrade rapidly when bending to radii of only 5 mm.<sup>88,89</sup>

The generation of elastic thin films with combinations of sheet resistance and transparency comparable to ITO is a coveted goal of the science of electronic materials.<sup>90</sup> Transparency and conductivity are seemingly mutually exclusive properties; the addition of elasticity eliminates all but a few possible materials as candidates for elastic transparent conductors. Conductive polymers<sup>46</sup> and carbon-based nanomaterials (*e.g.*, CNTs and graphene<sup>78</sup>), however, have many of the right characteristics for elasticity intrinsically or by buckling.<sup>78,90,91</sup>

**3.5.1. PEDOT:PSS.** Progress has been made on ITO-free devices comprising only poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) as the transparent electrode. The greatest value of conductivity for PEDOT:PSS films reported thus far has been  $1418 \text{ S cm}^{-1}$ ; the ranges of  $R_s$  and  $T$  achieved were  $65\text{--}176 \text{ } \Omega \text{ sq}^{-1}$  and  $80\text{--}88\%$ .<sup>92</sup> Organic solar cells incorporating these films instead of ITO achieved efficiencies of 2.55%.<sup>92</sup> Polar additives, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), and sorbitol, are frequently employed to increase the conductivity of PEDOT:PSS.<sup>93</sup> The mechanism that leads to increased conductivity is believed to involve coalescence of the PEDOT grains; by excluding the insulating PSS from the conductive pathways, the overall conductivity of the film increases.<sup>92</sup> Because PEDOT:PSS is processed from an aqueous suspension, it does not form thin films on the native surface of PDMS. Exposure to oxygen plasma or aqueous hydrochloric acid is required to form films on PDMS,<sup>46</sup> though we note that trace acid present in the PDMS layer will destroy the performance of devices that incorporate polymers—*e.g.*, polythiophenes—whose properties are degraded by acid.<sup>29</sup> Treatment of PDMS surfaces with UV/ozone will permit the formation of films of PEDOT:PSS mixed with 5% DMSO and 1% Zonyl FS-300 fluorosurfactant by buckling (Fig. 5).<sup>18</sup> A combination of Zonyl and isopropanol, in concentrations of 0.4% and 10%, has also been used to wet hydrophobic active layers of P3HT:PCBM in the inverted geometry of polymer-based solar cells.<sup>94</sup> Isopropanol alone, in a concentration of 37.5% in aqueous PEDOT:PSS, is sufficient to form films of the transparent conductor on a P3HT:PCBM active layer;<sup>95</sup> in a slot-die coating process, the authors additionally found it helpful to pre-wet the active layer with isopropanol.<sup>96</sup> ITO-free devices, comprising PEDOT:PSS alone as the transparent electrode, exhibit photovoltaic properties comparable to ITO for small device areas ( $<20 \text{ mm}^2$ ),<sup>92</sup> but the most conductive films of PEDOT:PSS are still significantly less conductive than ITO, and thus the electrical properties of ITO-free devices exhibit high series resistance, and therefore lower values of fill factor (FF).<sup>97</sup> It seems likely, however, that advancements in the technology of conductive polymers will eventually produce elastic transparent conductors with figures of merit comparable to those of ITO.

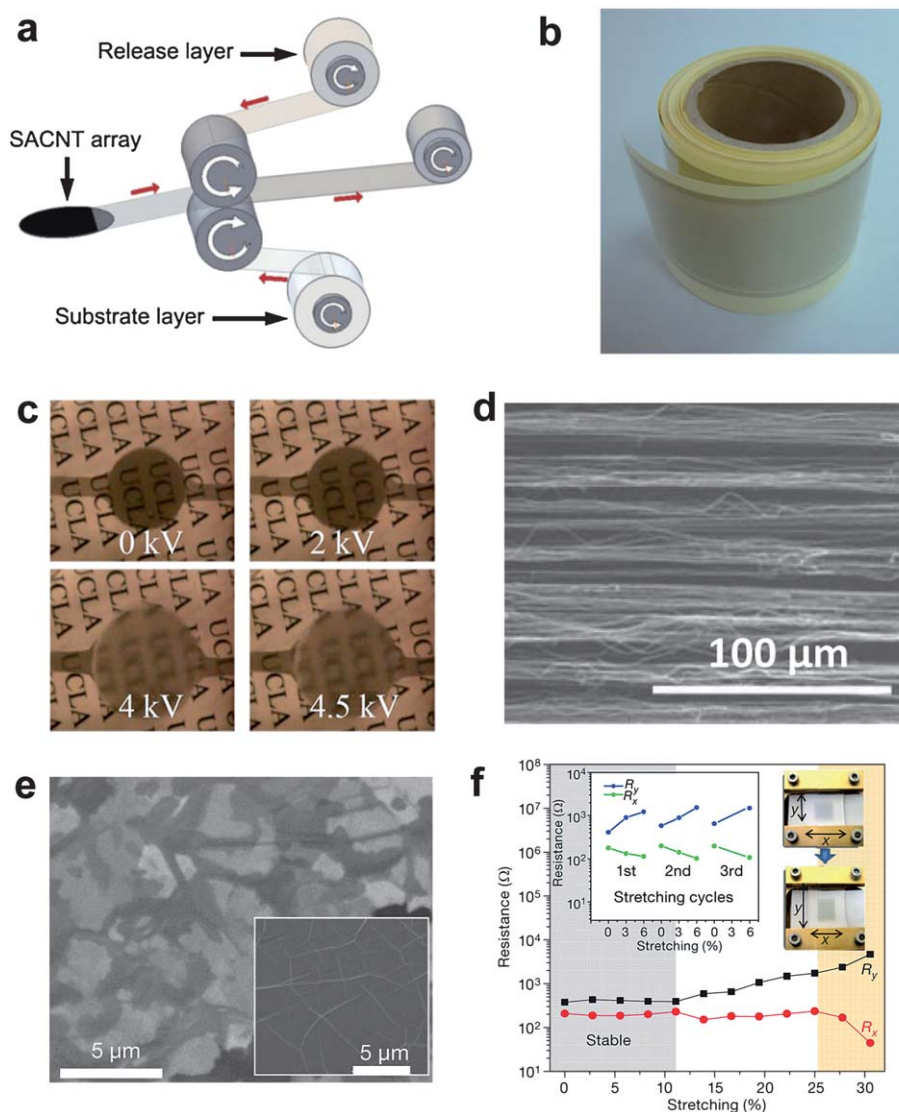


**Fig. 5** (a) Sheet resistance vs. strain for a buckled film of PEDOT:PSS, doped with DMSO and Zonyl fluorosurfactant, on a PDMS membrane pre-strained by 25%. (b) The sheet resistance of the film remained constant after 1000 cycles of manually applied strain. Optical micrographs of the film of PEDOT:PSS at different points in its strain history: (c) pre-strained to 25%, (d) relaxed to 0%, and (e) over-strained to 80%.

**3.5.2. CNTs.** Thin films of carbon nanotubes are attractive candidates as potential replacements for ITO (Fig. 6).<sup>75,90,91</sup> In an early example of CNTs in a flexible, OPV device, Rowell *et al.* demonstrated devices that could be bent to a radius of 5 mm.<sup>89</sup> Carbon nanotubes<sup>64</sup> and graphene<sup>78</sup> have two characteristics that could allow a combination of conductivity, transparency, and elasticity. First, the long mean-free path of electrons in defect-free graphene and CNTs contributes to high conductivity, but does not decrease transparency.<sup>98</sup> Second, two-dimensional, percolated networks of carbon nanomaterials on elastomeric substrates might permit reversible elastic deformation of the film. Zhang *et al.* fabricated ribbons of uniaxially aligned multi-walled CNTs that withstood strain reversibly up to 100% along the aligned axis, but neither stretching perpendicular to the aligned nanotubes, nor a way to pattern the films, was demonstrated.<sup>64,99</sup>

**3.5.3. Graphene.** Graphene has properties as a stretchable transparent conductor similar to those of carbon nanotubes. For example, Bae *et al.* developed a roll-to-roll method of processing graphene sheets with an exceptional combination of sheet resistance ( $125 \text{ } \Omega \text{ sq}^{-1}$ ) and transparency (97.4%), and could accommodate strains of up to 6%.<sup>78</sup> In other examples, Kim *et al.* produced a remarkably conductive transparent electrode composed of graphene, but the resistance increased by about an order of magnitude after only 30% strain (Fig. 6e and f).<sup>78</sup> Bao and Peumans *et al.* used solution-processed graphene and electrodes in organic solar cells,<sup>100</sup> while Becerril *et al.* explored the use of solution processed, reduced graphene oxide films that had  $R_s$  in the range of  $10^2$  to  $10^3 \text{ } \Omega \text{ sq}^{-1}$  at 80% transmittance.<sup>101</sup>

**3.5.4. Metallic nanowires.** One of the most promising materials with the potential to replace ITO in thin film optoelectronic devices is solution-deposited nanowires.<sup>90</sup> Nanowires lend themselves well to elasticity, because in principle, it should be

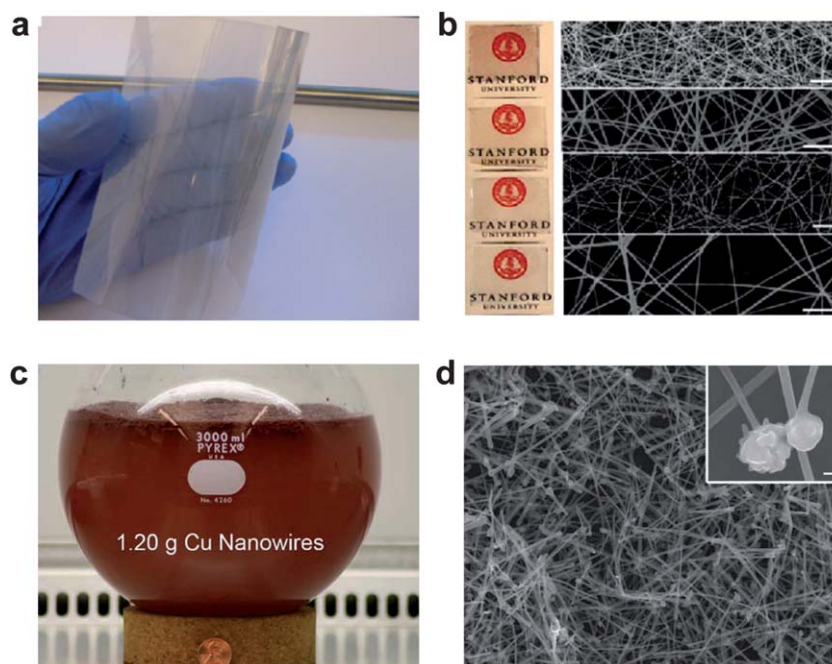


**Fig. 6** Images of stretchable transparent electrodes based on carbon nanomaterials. (a) The roll-to-roll processing method for generating uniaxially aligned, stretchable films (b) from forests of carbon nanotubes on silicon. Reproduced with permission from ref. 99. Copyright 2010, Wiley-VCH Verlag, GmbH & Co. KGaA. (c) Isotropically stretched CNT films when subjected to different voltages. Reproduced with permission from ref. 76. Copyright 2009, American Institute of Physics. (d) The uniaxially aligned CNT film drawn from wafer-bound CNT forest. Reproduced with permission from ref. 64. Copyright 2010, Wiley-VCH Verlag, GmbH & Co. KGaA. (e) SEM image of a stretchable graphene film and (f) resistance vs. strain of the film under tension and compression. Reproduced with permission from ref. 78. Copyright 2009, Nature Publishing Group.

possible to deform a film of nanowires without destroying the electronically percolated network. Cui, Peumans, and coworkers demonstrated silver nanowire meshes as electrodes in OPV devices; the electrodes could be bent to a radius of curvature of 4 mm without changing the sheet resistance.<sup>102</sup> In later work, the authors described improvements to the process, including the use of longer nanowires, a route to roll-to-roll processing, a decrease in junction resistance by galvanic displacement of silver with gold, and demonstrated a minimal increase in sheet resistance after 100 cycles of bending to a 5 mm radius of curvature.<sup>88</sup> Yu *et al.* developed a composite electrode based on silver nanowires on a crosslinked polyacrylate substrate that could be deformed and locked into different curvilinear shapes with small change in resistance, and used these electrodes in deformable polymer light-emitting devices.<sup>103</sup>

The use of silver and gold is hampered potentially by low natural abundance; copper is 1000 times more abundant than that of indium or silver, and copper is 1% the cost of silver.<sup>87</sup> Copper nanowires can be deposited in a multitude of ways (Fig. 7). For example, Kang *et al.* demonstrated a top-down printing technique that produced nanowire meshes that could be bent into radii of curvature of 3 nm, and had performance comparable to ITO in OPV devices.<sup>104</sup> Wiley and coworkers developed a solution-phase synthesis of copper nanowires, and used them as flexible transparent electrodes that—in the first report—were only 25% less transmissive than ITO films with the same sheet resistance.<sup>87</sup> An interesting approach—and the only report of copper nanowire films demonstrating significant tensile strain—was described by Cui and coworkers, in which electrospun copper nanofibers yielded  $R_s = 50 \Omega \text{ sq}^{-1}$  at  $T = 90\%$ . These





**Fig. 7** The use of metallic nanowires as elastic transparent electrodes. (a) Film of silver nanowires coated on a flexible polymeric sheet. Reproduced with permission from ref. 88. Copyright 2010, American Chemical Society. (b) Electrospun copper nanowire webs. Reproduced with permission from ref. 105. Copyright 2010, American Chemical Society. (c) Photograph of a reaction vessel containing a large-scale synthesis of inexpensive copper nanowires. (d) SEM image of copper nanowires. Reproduced with permission from ref. 87. Copyright 2010, Wiley-VCH Verlag, GmbH & Co. KGaA.

electrodes could be bent and stretched by 10% with substantially smaller increases in resistance than experienced by a copper thin film when bent.<sup>105</sup>

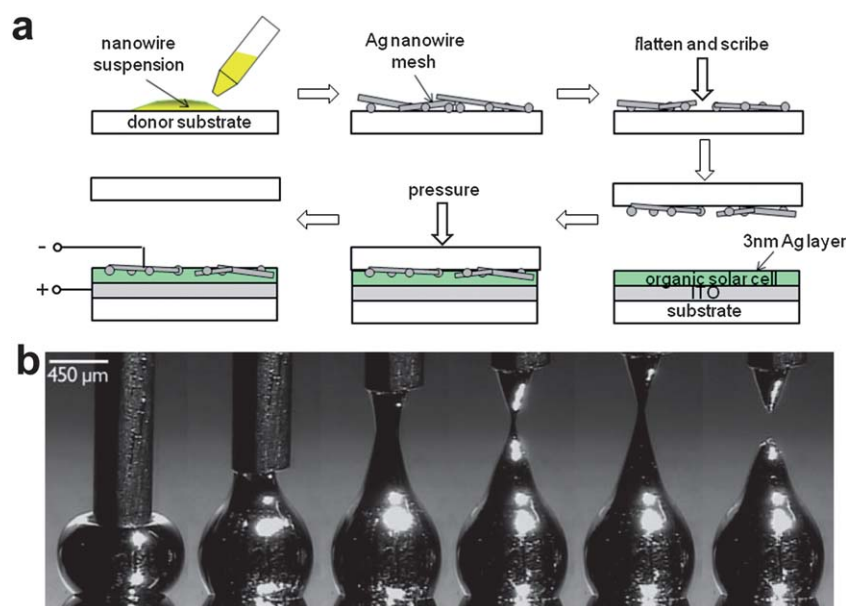
**3.5.5. Metallic grids.** Metallic grids in OPV devices can be used in addition to PEDOT:PSS. These grids lower the series resistance for large-area devices, and thus increase FF and power conversion efficiency (PCE).<sup>92</sup> Unbuckled grids are subject to cracking at the same low levels of strain as unpatterned thin films,<sup>106</sup> but a potentially useful approach is to deposit a metallic grid and a PEDOT:PSS film on a pre-strained elastomeric membrane to form buckled for large-area, elastic solar cells.<sup>18</sup>

### 3.6. Non-transparent (or top) electrodes

The name for the non-transparent electrode depends on its role in the device: the top electrode, reflective electrode, or cathode. In semitransparent devices (*e.g.*, for windows and tandem solar cells), both electrodes must be transparent.<sup>107</sup> Vapor-deposited films of low-work-function metals such as aluminium, which has high natural abundance, is inexpensive to deposit, and readily adopts radii of curvature of 5 mm or less on thin polymeric substrates, are the standard top contact materials used in thin-film photovoltaic cells such as those based on organic semiconductors or semiconductor nanocrystals. Our attempts to form stretchable thin-film devices bearing metallic cathodes have thus far failed: we found that significant compressive strains, imposed by the relaxation of a pre-strained PDMS substrate (*e.g.*, >20%), are sufficient to crack films of aluminium evaporated on films of conjugated polymers.<sup>18</sup>

**3.6.1. Metallic nanoparticles.** A mesh of silver nanowires has been demonstrated as a semitransparent top electrode for tandem organic solar cells (Fig. 8a).<sup>108</sup> The advantage of this procedure is that all layers are processed from solution.<sup>109</sup> It is likely that films of metallic nanowires are just as accommodating of bending strain when coated above and below the active layer, but thus far, significant tensile strain has not been demonstrated. Metallic nanoparticles in suspension have the ability to be deposited by spray-coating, as Girotto *et al.* demonstrated that sintered, spray-coated films of silver nanoparticles gave similar photovoltaic properties to control devices in which the top electrodes were deposited by evaporation.<sup>110</sup>

**3.6.2. PEDOT:PSS.** The use of conjugated polymers as the top electrode is significantly less common than their use as the bottom electrode. Materials such as PEDOT:PSS as a top electrode, however, have the advantage of being processable from solution, as well as having greater mechanical compliance than metals. The most common use of PEDOT:PSS as a top electrode is in the “inverted” geometry of organic photovoltaic devices.<sup>94,107,109,112</sup> In this configuration, the first electrode deposited is the low-work-function electrode, such as ITO modified with zinc oxide nanocrystals.<sup>107</sup> The active layer is then deposited, followed by PEDOT:PSS, whose role is to collect the holes as in the conventional geometry. In organic photovoltaic devices, additives are necessary to induce PEDOT:PSS to form a thin film on the surface of the hydrophobic organic semiconductor. For example, the fluorosurfactant, Zonyl, or a combination of Zonyl and isopropanol was required to wet the hydrophobic active layer of P3HT:PCBM in a technique of gravure printing.<sup>94</sup> PEDOT:PSS has been used as both the top



**Fig. 8** Images of elastic top electrodes used in organic and hybrid solar cells. (a) A schematic drawing of the process used to deposit and flatten a mesh of silver nanowires as a top electrode in an “inverted” organic solar cell. Reproduced with permission from ref. 108. Copyright 2010, American Chemical Society. (b) Images of eutectic gallium–indium (EGaIn), which is a conformable liquid metal top contact for stretchable organic solar cells. The images highlight the extent to which EGaIn retains its shape. Reproduced with permission from ref. 111. Copyright 2008, Wiley-VCH, GmbH & Co. KGaA.

and bottom contacts simultaneously in the inverted geometry; bending tests (radius  $\approx 7.4$  mm) confirm that the device architecture supports greater strains than those incorporating ITO.<sup>107</sup>

The use of PEDOT:PSS as the top electrode in the conventional geometry (where PEDOT:PSS takes the place of evaporated aluminium) is limited by the high work function of the conducting polymer, which is poorly suited to extracting electrons. Strategies to induce PEDOT:PSS to accept electrons include incorporating an n-type dopant, such as lithium-doped bathophenanthroline, on top of a standard polymer–fullerene active layer blend;<sup>113</sup> this device achieved an efficiency of 0.6%. Another potential strategy is to change the work function of a derivative of PEDOT directly, using a strong electron donor, such as tetrakis(diamino)ethylene (TDAE).<sup>114</sup> Lindell *et al.* used this strategy to produce a PEDOT-tosylate film with a work function of 3.8 eV,<sup>114</sup> while Jakobsson *et al.* used TDAE to reduce the work function of PEDOT from 4.8 to 3.9 eV, in an all-polymer light-emitting device.<sup>115</sup> A PEDOT:PSS top electrode has also been used opposite to a graphene transparent cathode in an organic light-emitting electrochemical cell.<sup>116</sup>

**3.6.3. Eutectic gallium–indium (EGaIn).** Liquids—while not elastic themselves—can be compatible with stretchable systems when encapsulated. Dye-sensitized solar cells, and cells exploiting a semiconductor–liquid interface, use liquids because of the molecular-scale contact between the liquid redox couple and the semiconductor interface.<sup>117</sup> Eutectic gallium–indium (EGaIn, Fig. 8b)<sup>118</sup> combines metallic conductivity with conformal coverage of microstructured surfaces by extrusion through a syringe without the need for physical vapor deposition.<sup>111</sup> It forms a “skin” in the ambient air that comprises oxides of gallium.<sup>118</sup> The skin allows EGaIn to resist flow when tilted or even inverted, but is compatible with microfluidics,<sup>119</sup> and is

useful as a soft top contact for metal–insulator–metal junctions useful under ambient conditions.<sup>111</sup> The work function of EGaIn is 4.3 eV, which is close to that of aluminium (4.2 eV), and is thus a suitable material for screening solar cells.<sup>120,121</sup> EGaIn has recently been employed in a variety of demonstrations of stretchable electronic devices, including as the stretchable, self-healing element in mechanically tunable radiofrequency antennae,<sup>30,122</sup> stretchable Schottky diodes comprising silicon nanowires embedded in PDMS,<sup>123</sup> and conforms to the wavy surface of buckled, stretchable organic photovoltaic devices.<sup>18</sup> It is also recyclable in a research setting.

### 3.7. Practical issues: delamination and stretchable encapsulants

Devices in which every component exhibits elasticity independently can be compromised by weak interfaces: those that fail at strains smaller than the strains at which the components fail.<sup>39</sup> For example, Suo and coworkers found that delamination between a spin-on glass planarization layer and the steel substrate was a source of failure of thin-film transistors under either tensile or compressive strain.<sup>39</sup> Krebs *et al.*, at the conclusion of the “Lighting Africa” study, found the loss of function at the corners of all the devices, where delamination occurred, and identified delamination of the master button contact from the printed silver electrode as the principal source of total device failure.<sup>16</sup> Delamination and cracking of rigid electrodes can be a problem even when evaluating the electro-mechanical properties of stretchable materials, as Bae *et al.* were unable to evaluate transparent graphene films beyond 6% strain because of cracking of the printed silver electrode.<sup>77</sup> Methods that have been successfully employed to reduce delamination are localizing strain at the interconnects,<sup>49,124</sup> placing the least elastic components at the neutral mechanical plane,<sup>39,125</sup> buckling all

components of a multilayer film,<sup>18</sup> and use of liquid electrodes.<sup>18,123</sup> Encapsulation of stretchable devices poses a particular challenge for organic photovoltaic devices, where common elastomers such as PDMS are highly permeable to oxygen. While buckled encapsulants might be compatible with some systems, optical effects could be deleterious. Transparent, gas-impermeable elastomers as encapsulants for stretchable solar cells will be required.

## 4. Devices

### 4.1. Introduction

This section describes the effort to combine stretchable components into whole devices. There are three general classes of demonstrated stretchable devices for the conversion of solar energy: stretchable crystalline inorganic solar cells,<sup>49,68,124</sup> stretchable photoelectrochemical cells,<sup>62,123</sup> and stretchable organic solar cells.<sup>18</sup>

### 4.2. Stretchable inorganic and crystalline solar cells

The first example of an intrinsically stretchable photovoltaic device based on single-crystalline semiconductors was the photodiode comprising a wavy p–n junction; this device showed a clear photovoltaic effect when exposed to ambient light.<sup>68</sup> A disadvantage of deforming single-crystalline semiconductors as a route to stretchability is that mechanical effects can change the optoelectronic properties of the semiconductor.<sup>68</sup> Thus, the most sophisticated stretchable PV devices based on crystalline materials employ rigid semiconductor elements connected using buckled interconnects; the circuits are embedded in elastomeric substrates, which often bear relief structures whose geometry is designed to localize strain at the interconnects.<sup>45</sup>

Ahn *et al.* described a method of omnidirectional printing silver electrodes from nanoparticle inks that was used to form connections between individual silicon devices, including PV cells, for stretchable applications.<sup>124</sup> Recently, another procedure, in which high-performance gallium–arsenide cells were embedded in a PDMS matrix, produced photovoltaic properties (and efficiencies of 13%) that were independent of strain (Fig. 9a and b).<sup>49</sup> Silicon solar cells can be made in semitransparent, flexible, concentrator module designs.<sup>125</sup> Baca *et al.* used ultra-thin strips of silicon solar cells to achieve efficiencies of 8% per cell and voltage outputs of 200 V.<sup>126</sup> The *I*–*V* characteristics of arrays of these devices remained constant when bent to a radius of 4 mm, twisted by 45°, and survived fatigue testing of 1000 bending cycles.<sup>126</sup>

### 4.3. Stretchable photoelectrochemical cells

The problem with PV, in general, is of storage.<sup>1</sup> A research effort that seeks to solve the problem of storage is developing materials and devices to convert sunlight and water into hydrogen fuel in an integrated, single device.<sup>4</sup> To this end, a number of systems of nanowire-forest based devices<sup>127</sup> (such forests can be quite efficient—7.9%—as PV devices<sup>128</sup>) have been developed for the use as photoelectrodes in devices that split water at a semiconductor–liquid interface using solar energy as the input of energy.<sup>129</sup> Such nanowires can be embedded in PDMS to produce elastic

electrodes,<sup>62</sup> which have already been successfully employed in photoelectrochemical cells (Fig. 9c and d).<sup>123</sup>

### 4.4. Stretchable organic solar cells

Solar cells comprising organic materials are potentially low-cost alternatives to crystalline silicon and even other thin-film materials. In principle, the inferior performance and environmental stability of organic semiconductors can be offset by the low intrinsic cost of organic materials, the relaxed requirements of purity, the minute thicknesses of material required ( $\leq 100$  nm), and the relative ease with which they can be processed from solution<sup>130</sup> (and in a roll-to-roll manner<sup>131</sup>). While important work is being carried out on increasing the performance, lowering the cost, and prolonging the lifetime of devices, another research strategy is to focus on areas where OPV can run away with part of the market by exploiting characteristics of OPV that inorganic materials do not possess. Organic PV devices, for example, are an order of magnitude thinner and less massive than inorganic thin film devices because the active materials are more strongly absorbing. The materials are also soft, less dense, and potentially biodegradable and biocompatible.<sup>132</sup> One characteristic that could be built into OPV devices is stretchability.

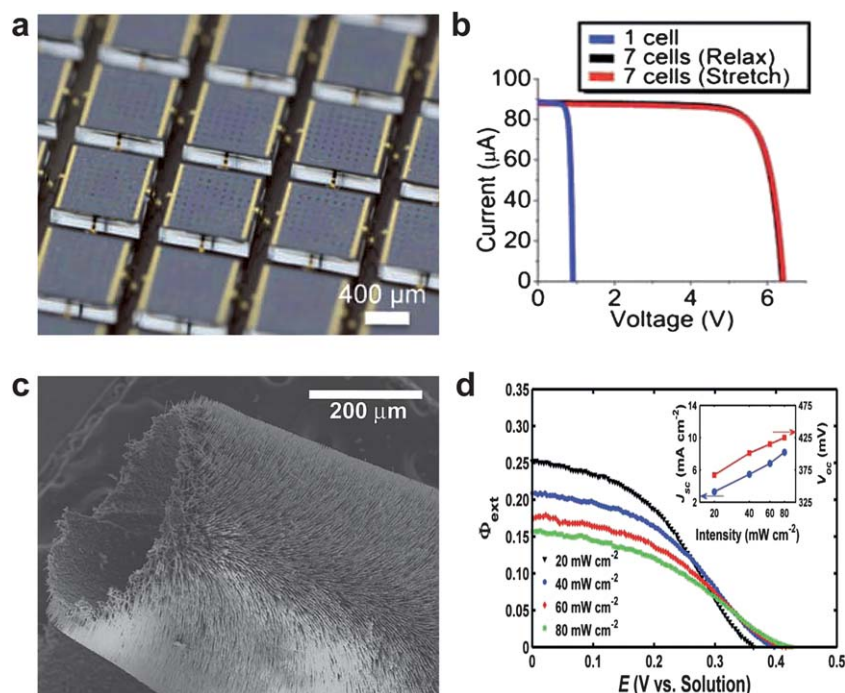
In a previous report from our laboratory, we fabricated a stretchable OPV device by depositing the transparent conductor, the active layer, and a conformal top electrode on a pre-strained elastomeric membrane (Fig. 10). We reasoned that release of the pre-strain would produce buckles in the thin film that could be “unbuckled” by straining up to the value of the pre-strain. Our goal was to produce a reversibly stretchable solar cell that could accommodate strains of at least 30% along at least one axis with minimal degradation in PCE.

Fig. 10c shows two plots of current density (that is, the current adjusted for the change in area produced by stretching) vs. voltage from a stretchable solar cell at 0% and 18.5% strain, after the first and tenth full cycles of strain up to 18.5%. An initial pre-strain (not shown) was required to stabilize the photovoltaic properties of the device. When stretched to 18.5% after ten full cycles, the device exhibited the following figures of merit under a flux of 95 mW cm<sup>-2</sup>: short-circuit current density = 7.4 mA cm<sup>-2</sup>; open-circuit voltage = 415 mV; FF = 0.38; and PCE = 1.2%. Stretching beyond 22.2% produced cracks in the active layer (visible by a naked eye), and concomitant reductions in figures of merit. We expect that rigorous optimization would improve the devices. Additionally, the topographic features produced by buckling could potentially be used as a mechanism of light trapping.<sup>133</sup> Lessons learned could be applied to other photovoltaic systems, and might lead to more efficient, elastic, and ultimately more useful devices.

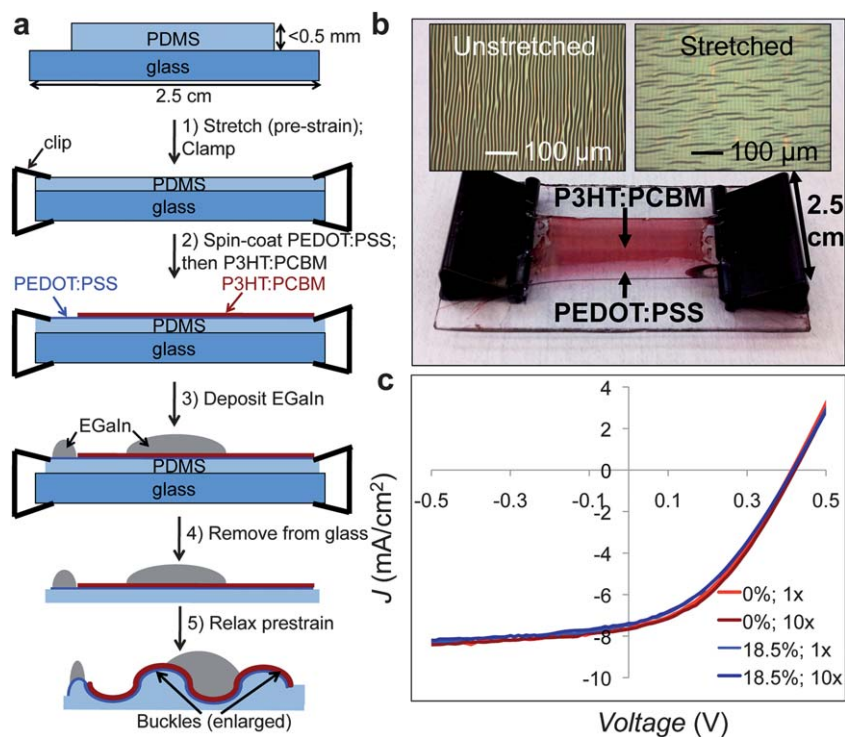
## 5. Summary and outlook

This review described the motivation for pursuing elastic materials and devices for the conversion of solar energy, as well as many promising examples of transparent conductors, semiconductors, reflective electrodes, and whole devices from the literature. We found that demonstrations of elasticity for most materials have been limited to simple bending tests. The ability to accommodate small radii of curvature, however, implies some





**Fig. 9** Images of stretchable solar and photoelectrochemical materials. (a) Photograph of high-efficiency GaAs photovoltaic cells, separated by buckled gold interconnects, embedded in an elastomeric PDMS matrix and (b) photovoltaic properties of the devices. Stretching has no effect on the photovoltaic properties of the device. Reproduced with permission from ref. 49. Copyright 2011, Wiley-VCH, GmbH & Co. KGaA. (c) Silicon nanowires embedded in a stretchable PDMS membrane and photoelectrochemical properties (d). Reproduced with permission from ref. 123. Copyright 2010, Wiley-VCH, GmbH & Co. KGaA.



**Fig. 10** (a) Summary of the processes used to fabricate stretchable organic solar cells. (b) Photograph of an organic solar cell stretched between two clips. The insets are micrographs of the surface of the P3HT:PCBM film in the unstretched (left) and stretched (right) states. (c) The photovoltaic properties of the devices change minimally when stretched up to the value of the pre-strain, and when stretched multiple times. Reproduced with permission from ref. 18. Copyright 2011, Wiley-VCH, GmbH & Co. KGaA.

degree of tensile elasticity, and suggests that the material might be rendered stretchable by exploiting mechanical buckling. We found few examples of thin films that can withstand significant strains without intentional, out-of-plane buckling, but thin films of carbon nanotubes and graphene are promising examples. Dispersing conductive particles in elastomeric matrices produces materials that can typically accommodate greater strains than can buckled thin films, but the bulk properties tend to be diluted by the presence of the matrix. Embedding semiconducting components in elastic membranes—in which only the interconnecting wires are stretchable—already produces devices with photovoltaic performances that rival those of their inelastic counterparts. Producing solar devices in which every component is intrinsically stretchable is a significant challenge, but might provide some advantages to embedded devices. (For example, rigid devices that are embedded in an elastic matrix permit light to pass through the interstitial area, which increases when stretched.) Another opportunity is to use chemical synthesis to produce stretchable materials (e.g., stretchable semiconducting polymers). It is our hope that this Perspective stimulates excitement and research efforts in this field, which we regard as both an extension and new direction of the interesting and important work of approximately the last decade on flexible electronics and optoelectronics.

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## References

- 1 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 20142.
- 2 L. M. Peter, *Philos. Trans. R. Soc. London, Ser. A*, 2011, **369**, 1840.
- 3 S. A. Kalogriou, *Prog. Energy Combust. Sci.*, 2004, **30**, 231.
- 4 M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. X. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446.
- 5 N. S. Lewis, *Science*, 2007, **315**, 798.
- 6 G. M. Whitesides and G. W. Crabtree, *Science*, 2007, **315**, 796.
- 7 E. Olias and V. Salas, *Renewable Sustainable Energy Rev.*, 2009, **13**, 1541.
- 8 T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets and D. G. Nocera, *Chem. Rev.*, 2010, **110**, 6474.
- 9 J. Baxter, Z. Bian, G. Chen, D. Danielson, M. S. Dresselhaus, A. G. Fedorov, T. S. Fisher, C. W. Jones, E. Maginn, U. Kortshagen, A. Manthiram, A. Nozik, D. R. Rolison, T. Sands, L. Shi, D. Sholl and Y. Wu, *Energy Environ. Sci.*, 2009, **2**, 559.
- 10 REN 21: Renewables 2010 Global Status Report, 2010.
- 11 M. Kaltenbrunner, G. Kettlgruber, C. Siket, R. Schwodiauer and S. Bauer, *Adv. Mater.*, 2010, **22**, 2065.
- 12 S. Tominaka, H. Nishizeko, J. Mizuno and T. Osaka, *Energy Environ. Sci.*, 2009, **2**, 1074.
- 13 H. Gwon, H.-S. Kim, K. U. Lee, D.-H. Seo, Y. C. Park, Y.-S. Lee, B. T. Ahn and K. Kang, *Energy Environ. Sci.*, 2011, **4**, 1277.
- 14 M. Peckerar, Z. Dilli, M. Dornajafi, N. Goldsman, Y. Ngu, R. B. Proctor, B. J. Krupshaw and D. A. Lowy, *Energy Environ. Sci.*, 2011, **4**, 1807.
- 15 F. C. Krebs, M. Biancardo, B. Winther-Jensen, H. Spanggaard and J. Alstrup, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 1058.
- 16 F. C. Krebs, T. D. Nielsen, J. Fyenbo, M. Wadstrom and M. S. Pedersen, *Energy Environ. Sci.*, 2010, **3**, 512.
- 17 Y. Qi and M. C. McAlpine, *Energy Environ. Sci.*, 2010, **3**, 1275.
- 18 D. J. Lipomi, B. C.-K. Tee, M. Vosgueritchian and Z. N. Bao, *Adv. Mater.*, 2011, **23**, 1771.
- 19 Y. Qi, J. Kim, T. D. Nguyen, B. Lisko, P. K. Purohit and M. C. McAlpine, *Nano Lett.*, 2011, **11**, 1331.
- 20 C. J. Yu, C. Masarapu, J. P. Rong, B. Q. Wei and H. Q. Jiang, *Adv. Mater.*, 2009, **21**, 4793.
- 21 F. Ilievski, A. D. Mazzeo, R. F. Shepherd, X. Chen and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2011, **50**, 1890.
- 22 F. C. Krebs, M. Jorgensen, K. Norrman, O. Hagemann, J. Alstrup, T. D. Nielsen, J. Fyenbo, K. Larsen and J. Kristensen, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 422.
- 23 S. C. B. Mannsfeld, B. C. K. Tee, R. M. Stoltenberg, C. V. H. H. Chen, S. Barman, B. V. O. Muir, A. N. Sokolov, C. Reese and Z. N. Bao, *Nat. Mater.*, 2010, **9**, 859.
- 24 A. N. Sokolov and Z. N. Bao, submitted.
- 25 T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-Jajafabadi, D. N. Futaba and K. Hata, *Nat. Nanotechnol.*, 2011, **6**, 296.
- 26 D. H. Kim, J. L. Xiao, J. Z. Song, Y. G. Huang and J. A. Rogers, *Adv. Mater.*, 2010, **22**, 2108.
- 27 T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata and T. Someya, *Nat. Mater.*, 2009, **8**, 494.
- 28 H. C. Ko, M. P. Stoykovich, J. Z. Song, V. Malyarchuk, W. M. Choi, C. J. Yu, J. B. Geddes, J. L. Xiao, S. D. Wang, Y. G. Huang and J. A. Rogers, *Nature*, 2008, **454**, 748.
- 29 D. J. Lipomi, B. C.-K. Tee, M. Vosgueritchian and Z. N. Bao, unpublished result.
- 30 M. Kubo, X. F. Li, C. Kim, M. Hashimoto, B. J. Wiley, D. Ham and G. M. Whitesides, *Adv. Mater.*, 2010, **22**, 2749.
- 31 T. Sekitani and T. Someya, *Adv. Mater.*, 2010, **22**, 2228.
- 32 H. Gleskova, I. C. Cheng, S. Wagner, J. C. Sturm and Z. G. Suo, *Sol. Energy*, 2006, **80**, 687.
- 33 M. W. Kanan and D. G. Nocera, *Science*, 2008, **321**, 1072.
- 34 B. A. Gregg, *J. Phys. Chem. B*, 2003, **107**, 4688.
- 35 B. Kippelen and J. L. Bredas, *Energy Environ. Sci.*, 2009, **2**, 251.
- 36 F. Huang, D. Chen, L. Cao, R. A. Caruso and Y. B. Cheng, *Energy Environ. Sci.*, 2011, DOI: 10.1039/C1EE01269J.
- 37 I. Gur, N. A. Fromer, M. L. Geier and A. P. Alivisatos, *Science*, 2005, **310**, 462.
- 38 M. Ohring, *Materials Science of Thin Films, Deposition and Structure*, Academic Press, San Diego, CA, 2nd edn, 2002.
- 39 Z. Suo, E. Y. Ma, H. Gleskova and S. Wagner, *Appl. Phys. Lett.*, 1999, **74**, 1177.
- 40 A. J. Baca, J. H. Ahn, Y. G. Sun, M. A. Meitl, E. Menard, H. S. Kim, W. M. Choi, D. H. Kim, Y. Huang and J. A. Rogers, *Angew. Chem., Int. Ed.*, 2008, **47**, 5524.
- 41 T. Sekitani, U. Zschieschang, H. Klauk and T. Someya, *Nat. Mater.*, 2010, **9**, 1015.
- 42 S. M. Yang, X. Chen, S. Motojima and M. Ichihara, *Carbon*, 2005, **43**, 827.
- 43 K. Y. Chun, Y. Oh, J. Rho, J. H. Ahn, Y. J. Kim, H. R. Choi and S. Baik, *Nat. Nanotechnol.*, 2010, **5**, 853.
- 44 T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida and T. Someya, *Science*, 2008, **321**, 1468.
- 45 J. A. Rogers, T. Someya and Y. G. Huang, *Science*, 2010, **327**, 1603.
- 46 D. Tahk, H. H. Lee and D. Y. Khang, *Macromolecules*, 2009, **42**, 7079.
- 47 N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson and G. M. Whitesides, *Nature*, 1998, **393**, 146.
- 48 S. P. Lacour, S. Wagner, Z. Y. Huang and Z. Suo, *Appl. Phys. Lett.*, 2003, **82**, 2404.
- 49 J. Lee, J. A. Wu, M. X. Shi, J. Yoon, S. I. Park, M. Li, Z. J. Liu, Y. G. Huang and J. A. Rogers, *Adv. Mater.*, 2011, **23**, 986.
- 50 D. H. Kim, J. Venti, J. J. Amsden, J. L. Xiao, L. Vigeland, Y. S. Kim, J. A. Blanco, B. Panilaitis, E. S. Frechette, D. Contreras, D. L. Kaplan, F. G. Omenetto, Y. G. Huang, K. C. Hwang, M. R. Zakin, B. Litt and J. A. Rogers, *Nat. Mater.*, 2010, **9**, 511.
- 51 I. M. Graz, D. P. J. Cotton and S. P. Lacour, *Appl. Phys. Lett.*, 2009, **98**, 071902.
- 52 Y. G. Sun, W. M. Choi, H. Q. Jiang, Y. G. Y. Huang and J. A. Rogers, *Nat. Nanotechnol.*, 2006, **1**, 201.
- 53 S. P. Lacour, J. Jones, S. Wagner, T. Li and Z. G. Suo, *Proc. IEEE*, 2005, **93**, 1459.

- 54 S. P. Lacour, J. Jones, Z. Suo and S. Wagner, *IEEE Electron Device Lett.*, 2004, **25**, 179.
- 55 D. J. Lipomi; M. Vosgueritchian; B. C.-K. Tee; C. H. Fox; J. A. Lee; Z. N. Bao 2011, submitted.
- 56 D. Y. Khang, J. A. Rogers and H. H. Lee, *Adv. Funct. Mater.*, 2009, **19**, 1526.
- 57 C. M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. Vanlandingham, H. C. Kim, W. Volksen, R. D. Miller and E. E. Simonyi, *Nat. Mater.*, 2004, **3**, 545.
- 58 B. O'Connor, E. P. Chan, C. Chan, B. R. Conrad, L. J. Richter, R. J. Kline, M. Heeney, I. McCulloch, C. L. Soles and D. M. DeLongchamp, *ACS Nano*, 2010, **4**, 7538.
- 59 M. Toivola, J. Halme, K. Miettinen, K. Aitola and P. D. Lund, *Int. J. Energy Res.*, 2009, **33**, 1145.
- 60 B. D. Gates, Q. B. Xu, M. Stewart, D. Ryan, C. G. Willson and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1171.
- 61 D. J. Lipomi, R. V. Martinez, L. Cademartiri and G. M. Whitesides, in *Comprehensive Polymer Science*, ed. E. Kumachera and T. P. Russell, in press.
- 62 K. E. Plass, M. A. Filler, J. M. Spurgeon, B. M. Kayes, S. Maldonado, B. S. Brunschwig, H. A. Atwater and N. S. Lewis, *Adv. Mater.*, 2009, **21**, 325.
- 63 D. H. Kim and J. A. Rogers, *Adv. Mater.*, 2008, **20**, 4887.
- 64 Y. Y. Zhang, C. J. Sheehan, J. Y. Zhai, G. F. Zou, H. M. Luo, J. Xiong, Y. T. Zhu and Q. X. Jia, *Adv. Mater.*, 2010, **22**, 3027.
- 65 R. H. Kim, D. H. Kim, J. L. Xiao, B. H. Kim, S. I. Park, B. Panilaitis, R. Ghaffari, J. M. Yao, M. Li, Z. J. Liu, V. Malyarchuk, D. G. Kim, A. P. Le, R. G. Nuzzo, D. L. Kaplan, F. G. Omenetto, Y. G. Huang, Z. Kang and J. A. Rogers, *Nat. Mater.*, 2010, **9**, 929.
- 66 S. A. Scott and M. G. Lagally, *J. Phys. D: Appl. Phys.*, 2007, **40**, R75.
- 67 H. C. Yuan, J. H. Shin, G. X. Qin, L. Sun, P. Bhattacharya, M. G. Lagally, G. K. Celler and Z. Q. Ma, *Appl. Phys. Lett.*, 2009, **94**, 013102.
- 68 D. Y. Khang, H. Q. Jiang, Y. Huang and J. A. Rogers, *Science*, 2006, **311**, 208.
- 69 C. Burda, X. B. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025.
- 70 Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim and Y. Q. Yan, *Adv. Mater.*, 2003, **15**, 353.
- 71 I. Gur, N. A. Fromer and A. P. Alivisatos, *J. Phys. Chem. B*, 2006, **110**, 25543.
- 72 Y. Wu, C. Wadia, W. L. Ma, B. Sadtler and A. P. Alivisatos, *Nano Lett.*, 2008, **8**, 2551.
- 73 T. W. Tomblor, C. W. Zhou, L. Alexseyev, J. Kong, H. J. Dai, C. S. Jayanthi, M. J. Tang and S. Y. Wu, *Nature*, 2000, **405**, 769.
- 74 D. Y. Khang, J. L. Xiao, C. Kocabas, S. MacLaren, T. Banks, H. Q. Jiang, Y. Y. G. Huang and J. A. Rogers, *Nano Lett.*, 2008, **8**, 124.
- 75 Q. Cao and J. A. Rogers, *Adv. Mater.*, 2009, **21**, 29.
- 76 L. B. Hu, W. Yuan, P. Brochu, G. Gruner and Q. B. Pei, *Appl. Phys. Lett.*, 2009, **94**, 161108.
- 77 S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong and S. Iijima, *Nat. Nanotechnol.*, 2010, **5**, 574.
- 78 K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi and B. H. Hong, *Nature*, 2009, **457**, 706.
- 79 N. M. Gabor, Z. Zhong, K. Bosnick, J. Park and P. L. McEuen, *Science*, 2009, **325**, 1367.
- 80 S. J. Kang, C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M. A. Alam, S. V. Rotkin and J. A. Rogers, *Nat. Nanotechnol.*, 2007, **2**, 230.
- 81 E. Kymakis, I. Alexandrou and G. A. J. Amaratunga, *J. Appl. Phys.*, 2003, **93**, 1764.
- 82 C. Li, Y. H. Chen, Y. B. Wang, Z. Iqbal, M. Chhowalla and S. Mitra, *J. Mater. Chem.*, 2007, **17**, 2406.
- 83 A. Nish, J. Y. Hwang, J. Doig and R. J. Nicholas, *Nat. Nanotechnol.*, 2007, **2**, 640.
- 84 S. N. Barman, M. C. LeMieux, J. Baek, R. Rivera and Z. N. Bao, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2672.
- 85 M. C. LeMieux, M. Roberts, S. Barman, Y. W. Jin, J. M. Kim and Z. N. Bao, *Science*, 2008, **321**, 101.
- 86 M. Vosgueritchian, M. C. LeMieux, D. Dodge and Z. N. Bao, *ACS Nano*, 2010, **4**, 6137.
- 87 A. R. Rathmell, S. M. Bergin, Y. L. Hua, Z. Y. Li and B. J. Wiley, *Adv. Mater.*, 2010, **22**, 3558.
- 88 L. B. Hu, H. S. Kim, J. Y. Lee, P. Peumans and Y. Cui, *ACS Nano*, 2010, **4**, 2955.
- 89 M. W. Rowell, M. A. Topinka, M. D. McGehee, H. J. Prall, G. Dennler, N. S. Sariciftci, L. B. Hu and G. Gruner, *Appl. Phys. Lett.*, 2006, **88**, 233506.
- 90 D. S. Hecht, L. B. Hu and G. Irvin, *Adv. Mater.*, 2010, **23**, 1482.
- 91 L. B. Hu, D. S. Hecht and G. Gruner, *Chem. Rev.*, 2010, **110**, 5790.
- 92 Y. H. Kim, C. Sachse, M. L. Machala, C. May, L. Muller-Meskamp and K. Leo, *Adv. Funct. Mater.*, 2011, **21**, 1076.
- 93 X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andersson, A. Volodin, C. van Haesendonck, M. Van der Auweras, W. R. Salaneck and M. Berggren, *Chem. Mater.*, 2006, **18**, 4354.
- 94 M. M. Voigt, R. C. I. Mackenzie, C. P. Yau, P. Atienzar, J. Dane, P. E. Keivanidis, D. D. C. Bradley and J. Nelson, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 731.
- 95 F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 465.
- 96 F. C. Krebs, S. A. Gevorgyan and J. Alstrup, *J. Mater. Chem.*, 2009, **19**, 5442.
- 97 J. S. Yeo, J. M. Yun, S. S. Kim, D. Y. Kim, J. Kim and S. I. Na, *Semicond. Sci. Technol.*, 2011, **26**, 034010.
- 98 P. Avouris, *Phys. Today*, 2009, **62**, 34.
- 99 C. Feng, K. Liu, J. S. Wu, L. Liu, J. S. Cheng, Y. Y. Zhang, Y. H. Sun, Q. Q. Li, S. S. Fan and K. L. Jiang, *Adv. Funct. Mater.*, 2010, **20**, 885.
- 100 J. B. Wu, H. A. Becerril, Z. N. Bao, Z. F. Liu, Y. S. Chen and P. Peumans, *Appl. Phys. Lett.*, 2008, **92**, 163302.
- 101 H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao and Y. Chen, *ACS Nano*, 2008, **2**, 463.
- 102 J. Y. Lee, S. T. Connor, Y. Cui and P. Peumans, *Nano Lett.*, 2008, **8**, 689.
- 103 Z. B. Yu, Q. W. Zhang, L. Li, Q. Chen, X. F. Niu, J. Liu and Q. B. Pei, *Adv. Mater.*, 2011, **23**, 664.
- 104 M. G. Kang, H. J. Park, S. H. Ahn and L. J. Guo, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1179.
- 105 H. Wu, L. B. Hu, M. W. Rowell, D. S. Kong, J. J. Cha, J. R. McDonough, J. Zhu, Y. A. Yang, M. D. McGehee and Y. Cui, *Nano Lett.*, 2010, **10**, 4242.
- 106 D. P. J. Cotton, I. M. Graz and S. P. Lacour, *IEEE Sens. J.*, 2009, **9**, 2008.
- 107 S. K. Hau, H. L. Yip, J. Y. Zou and A. K. Y. Jen, *Org. Electron.*, 2009, **10**, 1401.
- 108 J. Y. Lee, S. T. Connor, Y. Cui and P. Peumans, *Nano Lett.*, 2010, **10**, 1276.
- 109 W. Gaynor, J. Y. Lee and P. Peumans, *ACS Nano*, 2010, **4**, 30.
- 110 C. Girotto, B. P. Rand, S. Steudel, J. Genoe and P. Heremans, *Org. Electron.*, 2009, **10**, 735.
- 111 R. C. Chiechi, E. A. Weiss, M. D. Dickey and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2008, **47**, 142.
- 112 F. C. Krebs, *Org. Electron.*, 2009, **10**, 761.
- 113 F. Nickel, A. Puetz, M. Reinhard, H. Do, C. Kayser, A. Colmann and U. Lemmer, *Org. Electron.*, 2010, **11**, 535.
- 114 L. Lindell, A. Burquel, F. L. E. Jakobsson, V. Lemaire, M. Berggren, R. Lazzaroni, J. Cornil, W. R. Salaneck and X. Crispin, *Chem. Mater.*, 2006, **18**, 4246.
- 115 F. L. E. Jakobsson, X. Crispin, L. Lindell, A. Kancierzewska, M. Fahlman, W. R. Salaneck and M. Berggren, *Chem. Phys. Lett.*, 2006, **433**, 110.
- 116 P. Matyba, H. Yamaguchi, G. Eda, M. Chhowalla, L. Edman and N. D. Robinson, *ACS Nano*, 2010, **4**, 637.
- 117 M. Gratzel, *Nature*, 2001, **414**, 338.
- 118 M. D. Dickey, R. C. Chiechi, R. J. Larsen, E. A. Weiss, D. A. Weitz and G. M. Whitesides, *Adv. Funct. Mater.*, 2008, **18**, 1097.
- 119 C. A. Nijhuis, W. F. Reus, J. R. Barber, M. D. Dickey and G. M. Whitesides, *Nano Lett.*, 2010, **10**, 3611.
- 120 A. Du Pasquier, S. Miller and M. Chhowalla, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 1828.
- 121 D. J. Lipomi, R. C. Chiechi, W. F. Reus and G. M. Whitesides, *Adv. Funct. Mater.*, 2008, **18**, 3469.
- 122 J. H. So, J. Thelen, A. Qusba, G. J. Hayes, G. Lazzi and M. D. Dickey, *Adv. Funct. Mater.*, 2009, **19**, 3632.



- 123 J. M. Spurgeon, S. W. Boettcher, M. D. Kelzenberg, B. S. Brunschwig, H. A. Atwater and N. S. Lewis, *Adv. Mater.*, 2010, **22**, 3277.
- 124 B. Y. Ahn, E. B. Duoss, M. J. Motala, X. Y. Guo, S. I. Park, Y. J. Xiong, J. Yoon, R. G. Nuzzo, J. A. Rogers and J. A. Lewis, *Science*, 2009, **323**, 1590.
- 125 J. Yoon, A. J. Baca, S. I. Park, P. Elvikis, J. B. Geddes, L. F. Li, R. H. Kim, J. L. Xiao, S. D. Wang, T. H. Kim, M. J. Motala, B. Y. Ahn, E. B. Duoss, J. A. Lewis, R. G. Nuzzo, P. M. Ferreira, Y. G. Huang, A. Rockett and J. A. Rogers, *Nat. Mater.*, 2008, **7**, 907.
- 126 A. J. Baca, K. J. Yu, J. L. Xiao, S. D. Wang, J. Yoon, J. H. Ryu, D. Stevenson, R. G. Nuzzo, A. A. Rockett, Y. G. Huang and J. A. Rogers, *Energy Environ. Sci.*, 2010, **3**, 208.
- 127 A. I. Hochbaum and P. D. Yang, *Chem. Rev.*, 2010, **110**, 527.
- 128 M. C. Putnam, S. W. Boettcher, M. D. Kelzenberg, D. B. Turner-Evans, J. M. Spurgeon, E. L. Warren, R. M. Briggs, N. S. Lewis and H. A. Atwater, *Energy Environ. Sci.*, 2010, **3**, 1037.
- 129 M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, *Nat. Mater.*, 2010, **9**, 239.
- 130 Y. Li, Q. Guo, Z. Li, J. Pei and W. Tian, *Energy Environ. Sci.*, 2010, **3**, 1427.
- 131 F. C. Krebs, T. Tromholt and M. Jorgensen, *Nanoscale*, 2010, **2**, 873.
- 132 C. J. Bettinger and Z. N. Bao, *Adv. Mater.*, 2010, **22**, 651.
- 133 S. I. Na, S. S. Kim, J. Jo, S. H. Oh, J. Kim and D. Y. Kim, *Adv. Funct. Mater.*, 2008, **18**, 3956.