News & views

Materials chemistry

Charge-carrying films for solar cells made quickly

Jianfeng Lu & Fuzhi Huang

Organic semiconductors used in a promising class of solar cell are processed in a 'doping' step to improve the transport of charge carriers. A fast doping method has been developed that might enable mass production of these cells. **See p.51**

The next generation of solar cells could be based on materials called metal halide perovskites. Such devices are cheap, can be fabricated easily from solutions of the constituent materials and convert light into electricity with high efficiency (about 25.5% for cutting-edge devices[1]). Perovskite solar cells contain a film of an organic semiconductor, which is essential for achieving high power-conversion efficiency. But a key process in the preparation of these films, known as the doping step, typically takes many hours and generates by-products that seriously degrade solar-cell performance[2]. On page 51, Kong *et al.*[3] report a doping technique that might solve these problems, potentially overcoming a barrier to the commercialization of perovskite solar cells.

Doping — the deliberate addition of impurities — can modify the electronic properties of organic semiconductors. The discovery of this effect laid the foundation for the development of the multitude of electronic devices that pervade today's society[4]. In perovskite solar cells, doped organic semiconductors are used to facilitate the transport of holes — positively charged quasiparticles produced as part of the cells' power-generating mechanism. An organic semiconductor called 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamino)-9,9′-spirobifluorene (spiro-OMeTAD) is one of the most widely used hole-transporting layers (HTLs) in such devices.

The conventional approach for doping spiro-OMeTAD HTLs is to use a compound called lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) in combination with oxygen gas (O_2). In this process, a pre-prepared spiro-OMeTAD film is irradiated by ultraviolet light and oxidized by oxygen in ambient air, assisted by LiTFSI (Fig. 1a)[5]. The oxidized product acts as the dopant that enables hole transport. Lithium oxides are also left in the film as by-products. Many perovskite solar cells made using this doping technique have achieved record-breaking power-conversion efficiencies[6].

However, the process depends on the slow entry of oxygen into the film, and its subsequent diffusion through it — which usually takes between several hours and a day, depending on the ambient conditions. Furthermore, the lithium oxide by-products reduce the stability of the final solar cells[7], because the lithium ions in the oxide insert themselves into the device's perovskite layer (the 'active' layer of the device that absorbs light to produce charge carriers)[8]. Alternative doping strategies[9] and dopant-free HTL materials[10] have been developed to overcome these shortcomings, but none of the resulting solar cells has matched the power-conversion efficiency of the best perovskite solar cells. The conventional doping method therefore seemed to be a requirement for high power-conversion efficiencies.

Kong and colleagues' innovation is to dope the spiro-OMeTAD before it is made into a film, by bubbling carbon dioxide through a mixture of the semiconductor and LiTFSI in solution under UV light (Fig. 1b). The UV light excites the semiconductor, whereupon the CO_2 oxidizes it, forming a precipitate of lithium carbonate as a side product that can be removed by filtration. The filtered solution is then used to make an HTL that has a conductivity about 100 times higher than that of undoped spiro-OMeTAD, and approximately 3 times higher than that of HTLs made using the conventional doping method.

The authors found that perovskite solar cells made using CO_2-oxidized spiro-OMeTAD have higher power-conversion efficiencies than those of devices produced using

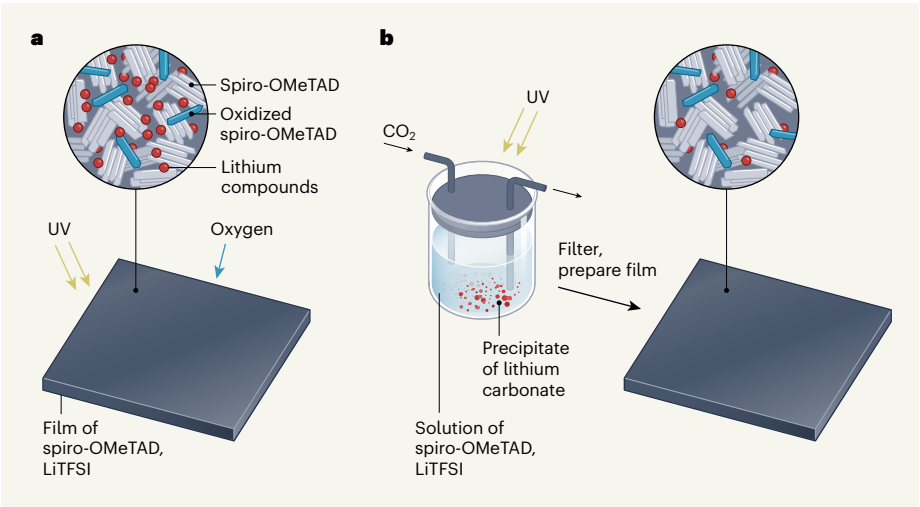

Figure 1 | Doping strategies for organic semiconductors. For use in perovskite solar cells, organic semiconductors such as spiro-OMeTAD must be 'doped' to improve their charge-carrying properties. **a**, In the conventional doping process, a film of spiro-OMeTAD containing the lithium compound LiTFSI is irradiated with ultraviolet light and exposed to air. Oxygen enters the film and, assisted by LiTFSI, oxidizes some of the spiro-OMeTAD molecules. The process takes many hours, and the resulting doped film contains lithium compounds, which degrade the performance of solar cells over time. **b**, Kong *et al.*[3] instead bubble carbon dioxide through a solution of spiro-OMeTAD and LiTFSI, under UV light, for one minute to oxidize some of the spiro-OMeTAD molecules. The by-product, lithium carbonate, precipitates from the solution and is filtered off. The solution is then used to make the doped film, which contains smaller quantities of lithium compounds than do the films produced in **a**, and is therefore more stable.

either non-doped or conventionally doped spiro-OMeTAD. More importantly, CO_2 bubbling decreases the doping time to just one minute. Having such a short doping time will be essential for the commercial production of perovskite solar cells.

Because the lithium carbonate by-product is removed by filtration, the density of lithium ions in the resulting HTL is lower than that in HTLs made using conventional doping. Kong *et al.* show that solar cells prepared using their method are much more stable than are control devices prepared using conventional doping, consistent with the smaller amount of lithium in the HTL. The authors' solar cells retain about 80% of their initial power-conversion efficiency after 500 hours of continuous operation, whereas the efficiency of the control devices rapidly drops to less than 75% after just 6 hours.

Even more excitingly, Kong and colleagues report that their CO_2-bubbling method is not limited to small-molecule organic semiconductors such as spiro-OMeTAD — the conductivity of a broad range of polymeric organic semiconductors (mixed with LiTFSI) is between 2 and 100 times greater than that of polymer–LiTFSI films not treated with CO_2. The power-conversion efficiency of perovskite solar cells made using the resulting doped polymeric HTLs is also substantially increased.

Perovskite solar cells show great promise, and have the potential to find industrial applications in the next few years. However, mass-manufacturing methods must first be developed that produce devices with long-term stability. This means that any compounds that reduce performance must be rigorously removed from HTLs during manufacturing. Kong and colleagues' work is important because it shows the feasibility of removing stability-lowering compounds using potentially scalable doping methods. So, although the power-conversion efficiency and stability of the authors' devices are not the best in the field, the new findings will inspire the development of other advanced doping strategies for rapidly producing clean films of organic semiconductors — thereby accelerating the pace of commercialization of perovskite solar cells.

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1. Jeong, J. *et al. Nature* **592**, 381–385 (2021).
2. Schloemer, T. H., Christians, J. A., Luther, J. M. & Sellinger, A. *Chem. Sci.* **10**, 1904–1935 (2019).
3. Kong, J. *et al. Nature* **594**, 51–56 (2021).
4. Salzmann, I., Heimel, G., Oehzelt, M., Winkler, S. & Koch, N. *Acc. Chem. Res.* **49**, 370–378 (2016).
5. Forward, R. L. *et al. ACS Energy Lett.* **4**, 2547–2551 (2019).
6. Ren, G. *et al. J. Mater. Chem. A* **9**, 4589–4625 (2021).
7. Tan, B. *et al. Adv. Energy Mater.* **9**, 1901519 (2019).
8. Li, Z. *et al. Energy Environ. Sci.* **10**, 1234–1242 (2017).
9. Hu, M. *et al. ACS Appl. Mater. Interfaces* **12**, 8260–8270 (2020).
10. Yin, X., Song, Z., Li, Z. & Tang, W. *Energy Environ. Sci.* **13**, 4057–4086 (2020).

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Cell biology

Host ubiquitin protein tags lipid to fight bacteria

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Host cells battle invading bacteria using a degradation process facilitated by the protein ubiquitin. The discovery of the host enzyme responsible and its bacterial target reveals that this process defies convention. **See p.111**

Intracellular bacteria such as *Salmonella* are a major threat to human health. These disease-causing microorganisms enter human cells cloaked in a host-derived membrane, which forms a structure termed a vacuole. To proliferate, *Salmonella* then need to access the cytoplasm, a feat that they typically manage through vacuole rupture. On page 111, Otten *et al.*[1] reveal the host's front-line mode of attack against invading *Salmonella* — a previously unknown mechanism and machinery that marks *Salmonella* with the host protein ubiquitin. This tagging sets in motion events that lead to the degradation of the microbial invader.

It was already known that this destruction process involves coating *Salmonella* with ubiquitin[2]. The presence of ubiquitin-tagged *Salmonella* in the cytoplasm launches a defence response when signalling proteins bind to the tagged microbe. This triggers the formation of a double-membraned organelle called an autophagosome, which envelops the bacterium[3,4]. The autophagosome then fuses with the destruction machinery — an organelle called the lysosome[5,6]. Many of the steps in this process are understood, but the contributors to the initial step, the bacterial molecule modified by ubiquitin and the enzyme that directly marks *Salmonella*, were previously unknown.

Ubiquitin is typically joined to target proteins through covalent links to amino (and, in rare cases, hydroxyl) groups on proteins. These ubiquitylation reactions are catalysed by what are termed E3 ligase enzymes. Indeed, many bacterial and host proteins are ubiquitylated during infection by *Salmonella*[7]. Various E3 ligases have been proposed as having a role in combating *Salmonella*[5]. Unexpectedly, however, Otten and colleagues reveal not only that the ubiquitylation of *Salmonella* is catalysed by a different mechanism from that used by a classic E3 ligase, but also that the ubiquitylation target itself is not even a protein.

From microscopy and biochemical studies, the authors gathered evidence pointing to the bacterial target for ubiquitylation as a lipid component of the surface of the bacterial membrane — the molecule lipopolysaccharide (LPS). LPS consists of lipid A in the bacterial outer membrane, sugars and what are termed O-antigen molecules (Fig. 1). Armed with *Salmonella* mutants that had altered versions of LPS, and using super-resolution imaging to track distinct stages of ubiquitylation, the authors analysed the ubiquitylation of *Salmonella* purified from host human cells. They found that these ubiquitylation targets were soluble after boiling. This result is consistent with a ubiquitylation target that is not a protein.

To confirm unequivocally that LPS is the target of ubiquitin tagging, Otten *et al.* used chemical and genetic methods that ruled out amino groups of proteins or other macromolecules as being sites of modification by ubiquitin. Next, using extracts from human host cells as the source of ubiquitylation enzymes, and bacteria from strains with either lipid A alone or shortened forms of LPS on the bacterial surface, the authors reconstituted the ubiquitylation event *in vitro*. This identified lipid A as the minimal form of LPS subject to ubiquitylation, potentially on its hydroxyl groups, its phosphate groups, or both.

This reconstitution of LPS ubiquitylation provided the authors with a way to identify the E3 ligase enzyme. Through skilful biochemical purification, Otten and colleagues identified