An alcohol-based conductive formulation for printable photovoltaics

PEDOT:PSS is a water-dispersible hole-transport material commonly used in printed electronics, but its acidity, hygroscopicity and poor wetting properties can affect device performance. These issues can now be overcome by adopting an alcohol-dispersible formulation — PEDOT:F — that enables the production of efficient and stable fully printable organic solar cells.

This is a summary of:
Jiang, Y. et al. An alcohol-dispersed conducting polymer complex for fully printable organic solar cells with improved stability. *Nat. Energy* https://doi.org/10.1038/s41560-022-00997-9 (2022).

Published online:
14 April 2022

The problem

Solution processing of organic solar cells is desirable to realize the low-cost and scalable fabrication of devices. The introduction of the conductive and water-dispersible polymer composite poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) was a milestone for organic and printed electronics[1], and it has been broadly used in solid-state capacitors, antistatic coatings and organic electronic devices. In solution-processed organic photovoltaics, PEDOT:PSS facilitates efficient hole transport. However, PEDOT:PSS has the drawbacks of being acidic, hygroscopic (that is, absorbs water from its surroundings) and prone to dewetting, which causes the dispersion to bead when coated on hydrophobic surfaces, all of these drawbacks deteriorate the efficiency and stability of devices[2,3]. In particular, in emerging non-fullerene photovoltaic devices with an inverted configuration, in which the hole-transport layer is coated on the hydrophobic organic active layer, PEDOT:PSS delivers poor device performance owing to dewetting and poor electrical contact[4]. Thus, it is challenging to achieve efficient and stable fully printable non-fullerene organic solar cells.

The solution

The drawbacks of PEDOT:PSS must be overcome or avoided to enable the fabrication of efficient and stable fully printable organic photovoltaic devices. The properties of PEDOT:PSS are determined by its composition and structure. PEDOT:PSS is a blend of the positively charged PEDOT ionomer and negatively charged PSS ionomer, which are bound through electrostatic interactions, and is typically dispersed in water. PEDOT is electrically doped and is conductive, but has poor solubility. The PSS component acts as the counterion to balance the charge of PEDOT and also as a dispersing agent to enable solution processing. The drawbacks of PEDOT:PSS are associated with the PSS counterion and the use of water as the processing solvent: PSS is hygroscopic; the acidity is due to the high dissociation rate of protonated PSS in water; and the dewetting is caused by the high surface tension of water.

By replacing the PSS counterion and water processing solvent, it is possible to avoid these drawbacks. Ethanol is a good option to replace water because it has a lower surface tension, allowing good wetting, and the dissociation rate of acids is much lower in ethanol than in water, making it possible to suppress the acidity. However, most anionic polymers, including PSS, are not soluble in alcohols. We thus sought an alternative ionomer counterion and identified perfluorinated sulfonic acid (PFSA) as a good candidate because it has two solubility parameters[5], which enable it to disperse in both water and ethanol. PFSA has a hydrophobic polytetrafluoroethylene backbone and pendant perfluorinated vinyl ether side chains that are terminated by hydrophilic sulfonic acid groups; these structural features account for the two solubility parameters. With PFSA as the counterion, we synthesized an alcohol-dispersed formulation of PEDOT — PEDOT:F (Fig. 1). The perfluorinated chains of the PFSA counterion endow PEDOT:F films with high water resistance and a high work function.

The implications

Having synthesized PEDOT:F, we then applied our alcohol-dispersed formulation in multiple organic photovoltaic devices with various active layers, comprising different fullerene or non-fullerene acceptors and polymer donors with deep-lying or shallow-lying energy levels, and in conventional and inverted devices. PEDOT:F can efficiently extract holes from each of these organic active layers. Furthermore, we demonstrated fully printable non-fullerene cells and modules with PEDOT:F as the hole-transport layer, with power conversion efficiencies of 15% and 13% respectively (Fig. 1).

PEDOT:PSS is used in antistatic coatings, photovoltaics, light-emitting diodes, capacitors, rechargeable batteries, thermoelectrics and bioelectronics. The new formulation of alcohol-dispersed PEDOT:F could be widely applied in these fields owing to its superiority to PEDOT:PSS in terms of processing (good wettability), stability (lower hygroscopicity, lower acidity) and electrical properties (high work function).

The next challenge is to increase the conductivity of PEDOT:F. A conductivity of the order of 1,000 S cm^{-1} — a high value that is achievable with PH1000 (a PEDOT:PSS formulation) — is desirable to broaden the applications of PEDOT:F as a stable conductor or electrode. For fully printable organic photovoltaic cells to realize practical applications, mature coating methods, high device yield, affordable active layers and encapsulation will be needed.

Youyu Jiang and Yinhua Zhou, Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan, China.

EXPERT OPINION

"I consider this work to be a breakthrough for the development of organic solar cells, making fully printed cells possible. In addition, I believe that PEDOT:F can also be used for other solution-processed optoelectronic devices, especially where a high work-function is required."
An anonymous reviewer

FIGURE

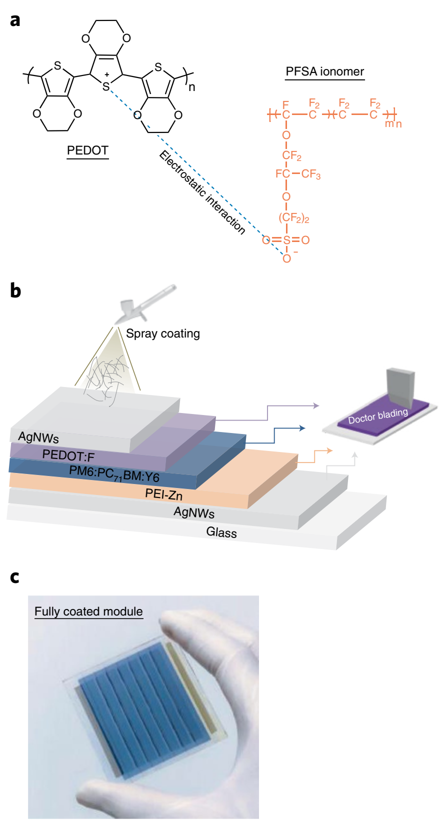

Fig. 1 | Structure of PEDOT:F and printed devices. a, The chemical structure of the PEDOT:F complex for alcohol-dispersed conductive formulations. **b**, The structure of a fully printed organic solar cell. Each layer of the cell is deposited by blade coating except for the top layer, which was deposited by spray coating. **c**, A photograph of a fabricated fully printed organic photovoltaic module with PEDOT:F as the hole-transport layer. AgNWs, silver nanowires; PEI-Zn, electron-transport layer; PM6:PC_{71}BM:Y6, active layer. © 2022, Jiang, Y. et al.

BEHIND THE PAPER

Our group has been working on tuning the properties of PEDOT:PSS to develop fully printable organic photovoltaics since 2013. In the early days (before 2017) when fullerene active layers were used, PEDOT:PSS was acceptable for hole collection in printable devices because the devices still achieve reasonable efficiencies despite the drawbacks of PEDOT:PSS.
After 2017, organic photovoltaics moved from fullerene to non-fullerene active layers. However, PEDOT:PSS does not work efficiently in printed photovoltaics with an inverted configuration. This forced us to develop a replacement for PEDOT:PSS. During the lockdown caused by the COVID-19 pandemic, we finalized a review paper on PEDOT:PSS that summarized our past work and other literature. This triggered an idea to prepare alcohol-based PEDOT formulations with PFSA ionomers. After the lab reopened, we synthesized PEDOT:F and found that it works even more efficiently in printed photovoltaics than we expected. **Y.Z.**

REFERENCES

1. Bayer AG. New polythiophene dispersions, their preparation and their use. EP0440957 (1997).
A patent that reports the invention of PEDOT:PSS.

2. de Jong, M. P., van Ijzendoorn, L. J. & de Voigt, M. J. A. Stability of the interface between indium-tin-oxide and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in polymer light-emitting diodes. *Appl. Phys. Lett.* **77**, 2255–2257 (2000).
This paper reports that the strong acidic nature of PEDOT:PSS degrades the interface between indium tin oxide and PEDOT:PSS.

3. Cameron, J. & Skabara, P. J. The damaging effects of the acidity in PEDOT:PSS on semiconductor device performance and solutions based on non-acidic alternatives. *Mater. Horiz.* **7**, 1759–1772 (2020).
This review article presents the damaging effects of the acidity of PEDOT:PSS on optoelectronic devices.

4. Sun, L. et al. Flexible all-solution-processed organic solar cells with high-performance nonfullerene active layers. *Adv. Mater.* **32**, 1907840 (2020).
This paper reports the problems of PEDOT:PSS in fully printable organic photovoltaics.

5. Kusoglu, A. & Weber, A. Z. New insights into perfluorinated sulfonic-acid ionomers. *Chem. Rev.* **117**, 987–1104 (2017).
This review article presents the structure, properties and applications of perfluorinated sulfonic-acid ionomers.

FROM THE EDITOR

"The ability to print organic solar cells is of great interest to industry and the consumer market. This work stands out because it accomplishes the challenging task of developing an alcohol-dispersible formulation of a charge-transport material commonly employed in organic photovoltaics. This innovation opens up the fabrication of fully printed solar cells that not only have high efficiency but also improved stability." **Giulia Tregnago, Senior Editor, *Nature Energy***