

ABSTRACT:

Nanoconfined Crystallization of PEDOT:PSS for Organic Thermoelectric Energy Harvesting

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Organic thermoelectric materials are attractive for energy harvesting from low-temperature heat gradients because they combine low weight, mechanical flexibility, and compatibility with scalable solution-based fabrication. As in all thermoelectric materials, their performance is governed by the interplay among electrical conductivity, Seebeck coefficient, and thermal conductivity. In organic systems, however, the relatively low electrical conductivity is often the main limitation, while strategies aimed at increasing σ may also reduce the Seebeck coefficient and increase thermal conductivity, which is often assumed to remain intrinsically low. Given its widespread use in organic thermoelectrics, PEDOT:PSS is adopted as a benchmark material. We exploit lithographically controlled wetting to induce confinement both vertically, through ultrathin film thickness, and laterally, through sub-micrometric patterned features. To consistently assess thermoelectric performance, the films were deposited onto an in-house developed microfabricated chip that enables the measurement of the main thermoelectric transport parameters on the same sample. Compared with spin-coated films, confined crystallization promotes a more ordered chain arrangement and improved packing, leading to higher electrical conductivity; when combined with DMSO secondary doping, conductivity exceeds 5000 S cm^{-1} . By progressively reducing the lateral size from about 850 nm to about 160 nm, the in-plane thermal conductivity decreases because of enhanced phonon-boundary scattering. Under the strongest confinement, the Seebeck coefficient also increases, leading to a maximum power factor of $265 \mu\text{W m}^{-1} \text{ K}^{-2}$, about 3.1 times higher than in identically treated spin-coated references. These results show that nanoconfined crystallization is an effective and additive processing strategy to tailor charge and heat transport in conducting polymer thin films for organic thermoelectric energy harvesting.