Catalyzing n-doping

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The Innovation

Electrical doping, i.e., inducing p- or n-type conductivity by adding a dopant, is of fundamental importance for device physics of semiconductors and is used in about every commercially produced device. For organic semiconductors, the conductivity is intrinsically low (typically 10^{-4}–10^{-8} S/cm) due to the mostly amorphous nature, the weak coupling between molecules, and the low number of free charge carriers in the presence of large energy gaps.

Similar to their inorganic counterparts, organic semiconductors are electrically dopable if there is a suitable energy alignment, as shown in Figure 1A, although doping efficiency is often lower than in inorganics.[1] Electrical dopants for organic semiconductors are not limited to organic molecules, but also compounds like MoO_3 and WO_3 as p-dopants and elementary substances like Li and Cs as n-dopants can, which respectively stimulate the oxidation and reduction processes. Unlike the p-dopants with a deep lowest unoccupied molecular orbital (LUMO) (see Figure 1A), efficient n-dopants for organic semiconductors require a very shallow highest occupied molecular orbital (HOMO) in the vicinity of the LUMO of the matrix, which usually leads to instability in ambient air.[1] Alternatively, a precursor for triggering n-doping process, i.e., an n-precursor to ignite the reduction reaction, can be designed and synthesized to allow high air stability.[2] This frequently sacrifices the doping efficiency ascribed to the high activation energy of the reaction between the matrix and the n-precur-

sor when no external perturbations, e.g., high temperature and catalyst, are applied.

TRANSITION METAL CATALYSTS FOR N-DOPING

Recently, Guo et al. unraveled an efficient n-doping strategy of organic semiconductors by introducing transition-metal nanoparticles deposited via thermal evaporation at a minimal thickness (e.g., 0.1–1.5 nm), which resulted in a dramatic improvement in the electrical conductivity (Figure 1B).[3] Superior to the commonly used organometallic complexes, e.g., $Pd_2(dba)_3$ (E, E-dibenzylidene acetone [dba]), the novel metal-catalyzed n-doping offers faster reactions at mild conditions, e.g., annealing at 120°C for 10 s. As a proof of concept, Au nanoparticles, down to 1.4 ± 0.3 nm in size obtained and assembled after thermal evaporation on glass substrate at a nominal thickness as small as 0.1 nm, can efficiently trigger electron transfer from n-precursor/dopant to n-type organic semiconductors.

Most of the air-stable n-dopants for organic semiconductors, frequently regarded as n-precursors, feature low ionization potentials that sacrifice the doping efficiency. By simply spin coating the mixed solution of n-precursor and matrix atop the self-assembled novel metal nanoparticles, a significant change of the film color under ambient light after a quick baking indicates polaron- or charge-transfer-induced absorption in the visible region. This
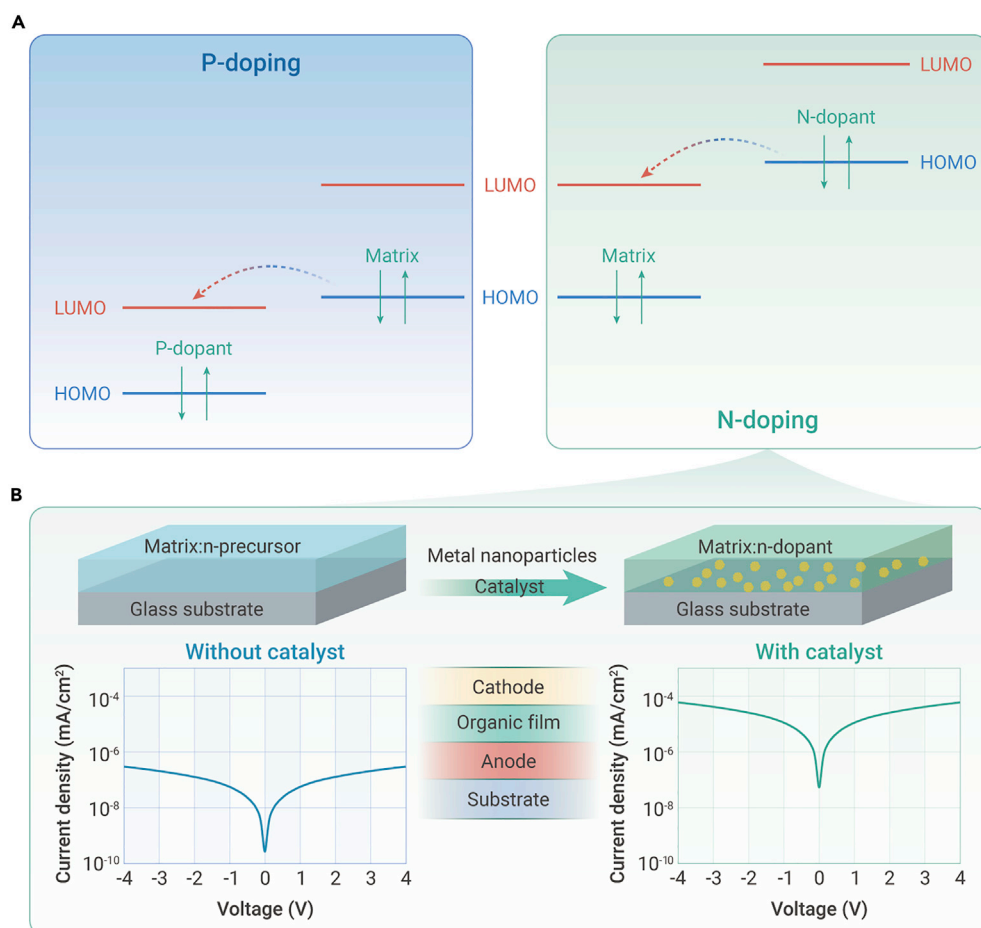

Figure 1. Transition metal nanoparticles catalysis maximizing n-doping efficiency (A) Schematic of electrical p/n-doping in organic semiconductors. (B) Schematic of n-doping catalyzed by transition metal nanoparticles and the corresponding current density—voltage characteristics of organic semiconducting devices with and without the catalyst.

phenomenon tends to be universal, although the influence of the dopant diffusivity on the doping efficiency remains unclear. Nevertheless, considering the experiments and chemical reaction theory, the generality of such a catalyst-induced n-doping effect is sound.

MECHANISMS

To figure out the n-doping mechanisms in the presence of novel metal nanoparticles, conductivity and electron spin resonance measurements were used to confirm the generation of free charge carriers. Furthermore, the selection of transition metal is found to be crucial for catalyzing an efficient n-doping. Changes in absorbance of the doped films are good indicators of possible catalysts based on the ultrathin transition-metal nanoparticles. However, it is challenging to exactly quantify the catalytic efficiencies of different transition metals. Alternatively, the solid- and solution-state chemical reactions, proven by density functional theory calculations with and without transition-metal nanoparticles, reveal the vital difference of Gibbs free energy in heterolytic cleavage of the

chemical bond (C−H → C$^+$ + H$^-$), taking (4-(1,3-dimethyl-2,3-dihydro-1*H*-benzoimidazol-2-yl)phenyl)dimethylamine (N-DMBI-H) as the n-dopant, for example. Therefore, electron transfer from n-dopant to matrix is energetically favorable and spontaneous in the presence of Au nanoparticles via a drastic reduction of the activation barriers from precursors to *in-situ*-generated, active-doping species.[3]

APPLICATIONS

As shown in Figure 1B, the catalyzed n-doping is technologically feasible when the *in situ* n-doped film is deposited, either via solution processes or thermal evaporation, directly on the transition-metal nanoparticles. For example, organic thermoelectric devices, organic thin-film transistors, and laterally conductive organic photodiodes possessing in-plane contacts/channels can be fabricated directly with the catalyzed n-doped layers based on the ternary system, reducing the ohmic loss and thus maximizing device performance.[3] For the vertical stack-based devices, e.g., organic/perovskite solar cells and organic light-emitting devices, unintentional catalysis induced by metal-contact evaporation provides another possible strategy to implement the transition-metal-nanoparticle-based catalyst, although it might depend on the diffusivity to trigger the n-doping.

CONCLUDING REMARKS

Air-stable and efficient n-doping in organic semiconductors for optoelectronic applications is a key technique for device engineering, typically requiring complicated molecular design for n-dopants to release free electrons.[4] Although commercialized in consumer electronics, e.g., smart phones based on organic light-emitting devices as screens, the electrical doping of organic semiconductors are still complicated and ruled by many factors, e.g., single-electron transfer, ground-state charge transfer, Coulomb barrier, and energetic disorder.[5]

N-doping induced by transition-metal-nanoparticles-based catalysts provides a very creative solution with more freedom in designing efficient n-precursors/dopants and more ease of handling.[3] However, only limited candidates of n-precursors/dopants are available for practical applications. In terms of fundamental research, it is essential to explore more versatile dopant and catalyst systems and to also quantify the catalytic activity and doping efficiency for screening a good pair of dopant and matrix. For instance, the energy levels of the dopants should be easily tunable for universal applications. There may be many more transition-metal-based catalysts available for ternary n-doped systems, e.g. Au nanoclusters with size-dependent catalytic activity. Ideally, the residual catalyst should have no side effects for long-term operation. In addition, it is necessary to reconsider the effect of unintentional doping when employing high work-function metal contacts for multi-layered organic devices, e.g., Au and Ag. To overcome the issue of residual catalysts, transfer printing might be favorable since the catalyzed n-doped layer could be transferred to any other seeding films if adhesion between the catalyst and the n-doped layer is small enough. This also allows for the design of device architectures. Importantly, for non-inverted and vertical device stacks, the n-doped electron injecting/transporting layers adjacent to the top contact typically require minimal post-treatments. Therefore, new catalyzed ternary n-doped systems without activation barriers at room temperature are urgently needed.

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DECLARATION OF INTERESTS

The authors declare no competing interests.