

An in-depth understanding of photophysics in organic photocatalysts

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The urgent need to replace conventional fossil fuels with clean energy has stimulated a large number of research efforts on photocatalytic hydrogen evolution^[1–4]. Alternatively, organic semiconductors with tunable light absorption, well-positioned band edges, and excellent charge separation are highly expected^[5–8]. Conventionally, a semiconductor material with a wide band gap has a larger exciton binding energy, while a semiconductor material with a narrow band gap has a smaller exciton binding energy^[9]. Since smaller exciton binding energies are favorable for exciton separation, choosing a semiconductor with a suitable bandgap seems to be the first step toward high solar-to-hydrogen efficiency. The tunable light-harvesting ability determines the advantage and potential of organic semiconductors as photocatalysts. However, the insufficient external quantum efficiency (EQE) and the underlying photophysical mechanism remain restricting the orientation toward industrialization^[10].

To address the challenge in EQE, one strategy is to configure donor/acceptor (D/A) organic heterojunction to obtain excellent charge separation. In a recent article (*Nat. Energy*, 2022, 7, 340)^[11], Kosco and colleagues constructed two kinds of D/A organic heterojunction for hydrogen evolution reaction (HER) containing a typical donor polymer PBDB-T2F (PM6) and two common acceptors named non-fullerene BTP-4F (Y6) and fullerene PCBM with the optimized D/A ratios. As shown in Figs. 1(a) and 1(b), the authors developed blends with different morphologies of intermixed and phase-separated states due to the different miscibility via the mini-emulsion method. There is an energy level matching reflecting not only in the energy levels of the donor and acceptor but also in the alignment relationship with the reduction potential of water and the oxidation potential of the sacrificial agent (Fig. 1(c)). Impressively, photophysics is also given adequate attention in this work. A variety of characterization methods containing ultrafast transient absorption spectroscopy (uf-TAS) and photoinduced absorption spectroscopy (PIAS) were carried out to explore photophysical steps closely related to semiconductor photocatalysis (Fig. 2), such as charge generation, exciton dissociation, and charge transfer^[12]. It is revealed that the second-scale long-life charges are induced only by photo-

excitation in the nanoparticle-formed D/A heterojunction whether in the presence or absence of Pt and sacrificial agent. It was found that no measurable long-lived charge accumulation was observed from the spin-coated PM6:PCBM films. This is noteworthy and highlights the unique advantage of nanoscale D/A heterojunctions. Their results showed that organic D/A heterojunction NPs can inherently generate long-lived reactive charges, thereby allowing them to exhibit efficient photocatalytic HER performance.

There is no doubt that these results are charming and encouraging. The innovation and breakthroughs of this work are reflected in the HER performance and photophysical mechanism. This work announces the broadest wavelength range up to 900 nm and comparable EQEs to plasmonic photocatalyst systems for an organic photocatalyst to date, which highlights the potential of D/A organic heterojunction NPs for broad-spectrum HER, making these organic photocatalysts more ready for use in real applications. Careful consideration and ingenious comparisons are carried out throughout the whole photophysical exploring process, and the results fill the gap in the field of organic photocatalysis. In conclusion, this work provides an in-depth understanding of the photophysics in organic D/A heterojunction photocatalysts. Particularly, this thinking is conducive to further directing the research focus to the intrinsic mechanisms of the photocatalytic processes, which may be the key to the current breakthrough in solar energy conversion efficiency.

Since the long-lived charge has been demonstrated to be excited by light irradiation in the absence of the sacrificial reagent, the great promise can be articulated in two ways. On the one hand, it takes a significant step towards non-sacrificial reagent organic NPs photocatalysis. On the other hand, the long-lived charge opens up available applications for driving kinetically slow catalysis processes such as water oxidation. From a long-term perspective, the stability of organic semiconductor photocatalysts and the firmness of their binding will also be the research focus. Organic semiconductors present weak chemical bonds, which is detrimental for long-term photocatalysis, and the construction of heterostructures (for example, the D/A heterojunction of this work) or nano-assembly will be feasible strategies^[13]. The weak non-covalent interactions between molecules, such as hydrogen bonding, dipolarization, π - π stacking, van der Waals forces, hydrophobic interactions, electrostatic interactions, and metal-ligand interactions, will be converted from inferiority for

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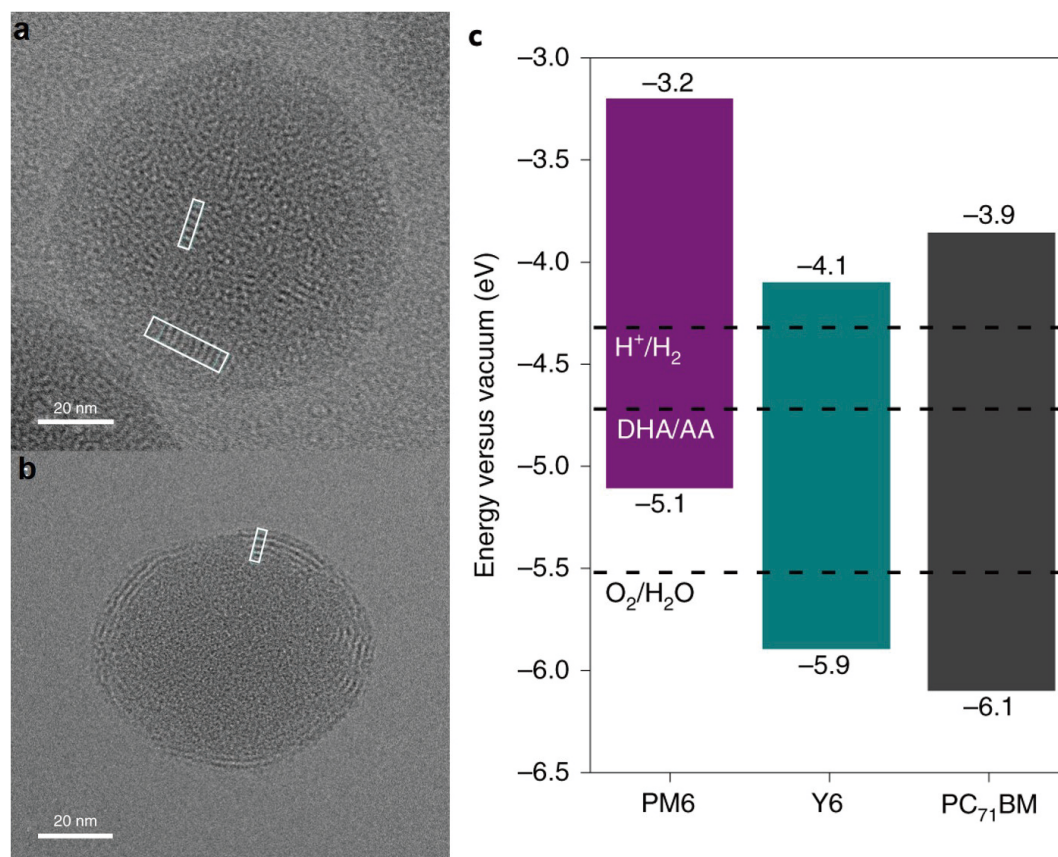


Fig. 1. (Color online) (a) Bright-field cryo-TEM images of intermixed PM6:Y6 7 : 3 NPs and (b) phase-separated core-shell PM6:PCBM 2 : 8 NPs. (c) Energy level diagram of PM6, Y6, and PCBM measured by UPS and IPES. The dashed lines correspond to the proton reduction potential (H^+/H_2), water oxidation potential ($\text{O}_2/\text{H}_2\text{O}$), and the calculated potential of the two-hole oxidation of ascorbic acid to dehydroascorbic acid in solution (DHA/AA) at pH 2 (the experimentally measured pH of 0.2 mol/L ascorbic acid).

the advantages during the self-assembly process^[14, 15]. The challenge lies in achieving regular crystallization and smooth charge transport through perfect molecular packing. Furthermore, positioning catalytic active sites is increasingly attracting broad interest. Particularly, the complex molecular architectures and the ubiquitous bonds caused by diverse positions of the bonding molecules make it challenging to investigate the active sites for organic photocatalysts^[16–18]. Ingenious design to embed synergistic Brønsted acid/base sites or active metal atoms into organic frameworks seems to reduce the difficulty of exploring active sites while remarkably enhancing catalysis^[19].

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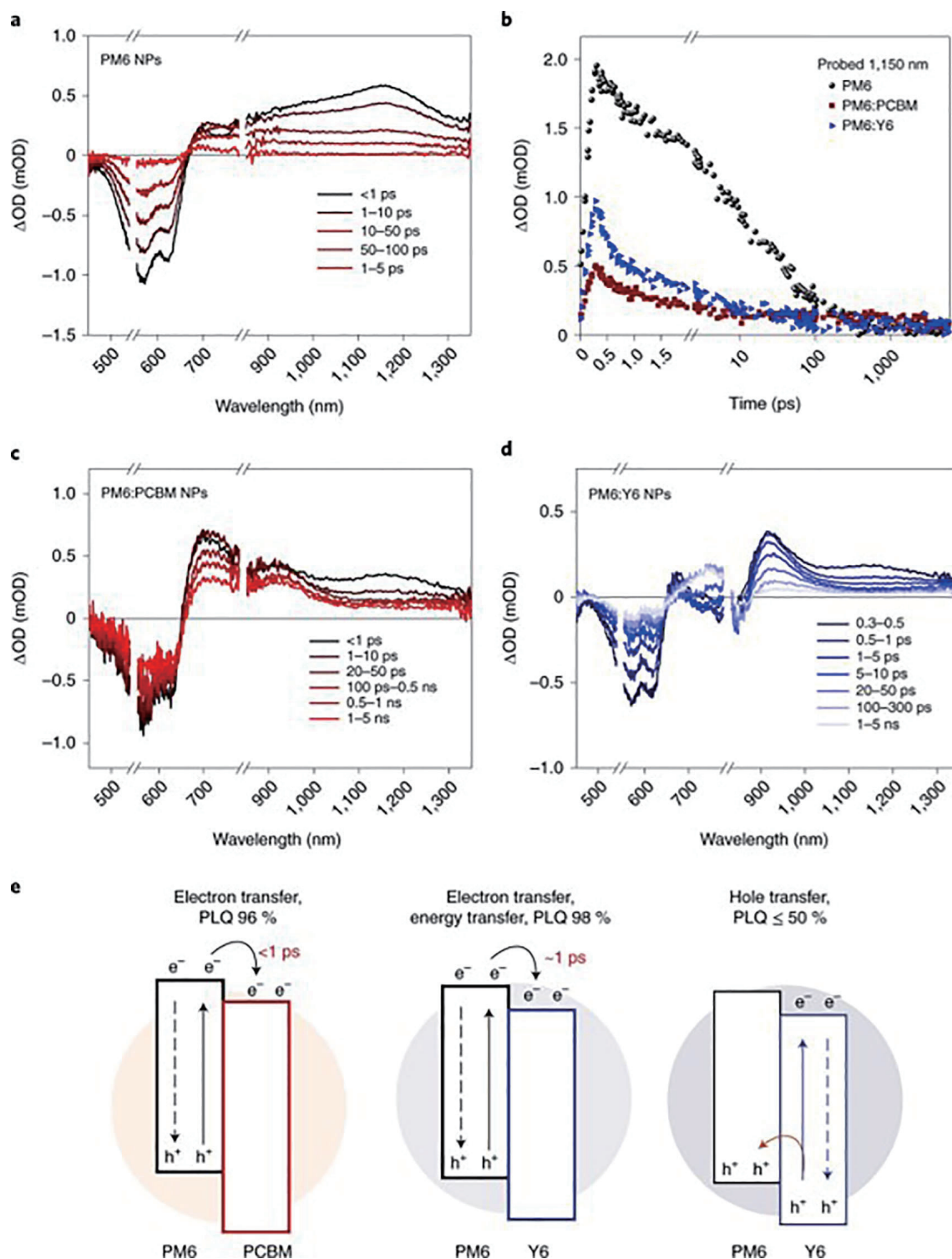


Fig. 2. (Color online) Ultrafast TAS characterization for neat PM6, PM6:Y6 7 : 3, and PM6:PCBM 2 : 8 nanoparticles in aqueous suspensions. (a) Transient absorption spectra of PM6 NPs at different time delays following excitation at 550 nm (fluence: $7.5 \mu\text{J}/\text{cm}^2$). (b) Comparison of transient absorption decay dynamics for neat PM6, PM6:PCBM 2 : 8, and PM6:Y6 7 : 3 NPs excited at 550 nm and probed at 1150 nm, assigned to PM6 exciton decay, with the long-lived residual signal assigned to PM6 polaron decay in the heterojunction NPs. (c, d) Transient absorption spectra of PM6:PCBM 2 : 8 NPs (c) and PM6:Y6 7 : 3 NPs (d) at different time delays, also excited at 550 nm (fluence: $7.5 \mu\text{J}/\text{cm}^2$). The disconnect in the transient absorption spectra axis corresponds to the pump laser scattering (550 nm) and the switch from visible to NIR detector (800–850 nm). (e) Schematic representation of exciton decay and electron/energy transfer processes in these NPs.

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