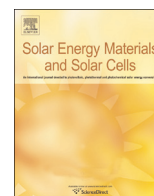




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## Enhanced efficiency of organic and perovskite photovoltaics from shape-dependent broadband plasmonic effects of silver nanoplates

Hsiang-Lin Hsu<sup>a</sup>, Tzong-Yuan Juang<sup>b</sup>, Chih-Ping Chen<sup>c,d,\*</sup>, Cheng-Ming Hsieh<sup>c</sup>, Chun-Chen Yang<sup>d,e</sup>, Cheng-Liang Huang<sup>b,\*</sup>, Ru-Jong Jeng<sup>a,\*</sup><sup>a</sup> Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan<sup>b</sup> Department of Applied Chemistry, National Chiayi University, Chiayi City, Taiwan<sup>c</sup> Department of Materials Engineering, Ming Chi University of Technology, New Taipei City 243, Taiwan<sup>d</sup> Battery Research Center of Green Energy, Ming Chi University of Technology, New Taipei City 243, Taiwan<sup>e</sup> Department of Chemical Engineering, Ming Chi University of Technology, New Taipei City 243, Taiwan

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## ABSTRACT

In this study, we systematically investigated the plasmonic effects of silver nanoplates (Ag NPLs) embedded in organic and perovskite (PVSK) photovoltaic (PV) cells. Optical properties of the Ag NPLs were manipulated by varying their sizes and shapes through controllable wet chemical processes. As the lengths of the edges of the Ag NPLs increased, their surface plasmon resonance bands broadened, with the maximum extinction wavelength extending to as far as 750 nm. After embedding various types of Ag NPLs into the PEDOT:PSS [poly(3,4-ethylenedioxythiophene)/polystyrenesulfonate] layer, the short-circuit photocurrent density increased by 7.6–17.5%, relative to that of the pre-optimized control PVs, with the power conversion efficiency (PCE) increasing by up to 13%. We obtained an optimized PCE of 8.5% for normal PVSK device under simulated AM 1.5G irradiation (100 mW cm<sup>-2</sup>). After the incorporation of Ag NPLs, a much higher PCE of 9.6% was obtained. External quantum efficiencies were increased significantly as a result of the increased plasmonic scattering effect of Ag NPLs.

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## 1. Introduction

Organic photovoltaics (OPVs) have great potential for use in harvesting renewable energy because these light-weight devices can be prepared at low cost through wet-processing techniques [1–7]. With advances in both device and material design, the power conversion efficiencies (PCEs) of OPVs have recently surpassed 10% [8–11]. The low carrier mobilities of conjugated organic materials result in the limitation of active layer thickness, and hence, restrict the enhancement of PCEs accordingly. This is because it is difficult for a relatively thin layer to absorb all of the solar photons that fall upon it. Consequently, the ultimate efficiency of an OPV is governed mainly by the limitations of its constituent materials.

A realistic approach toward ensuring both sufficient absorption and efficient charge extraction is to maximize the performance by optimizing the device architecture. Light trapping is an important phenomenon for an OPV to improve its light harvesting ability and its PCE when limited by a thin active layer [12–20]. The embedding

of solution-processed metallic nanomaterials is one of the most effective means to improve the light harvesting ability of the OPV devices by increasing optical scattering [12,21–25]. These metallic materials have been dispersed previously in the photoactive layer [14,25–27] in the hole transporting layer (HTL) [21,28,29] and between the interfacing layers [30] of OPVs, leading to significant enhancement in optical absorption as a result of (i) the formation of scattered waves for large (> 50 nm) metallic materials; (ii) the excitation of localized surface plasmon resonance modes for smaller (10–50 nm) metallic materials; and (iii) the excitation of surface plasmon polaritons at the interfaces, enabling the coupling of incident light to photonic modes and propagation in the active layer plane [31]. Various chemical routes have been demonstrated for the preparation of these metallic nanomaterials with controlled morphologies [31–35]. Indeed, the optical properties of these nanomaterials are readily manipulated by varying their shape and size as well as the nature of the surrounding matrix, thereby ensuring high compatibility as a means of optical engineering for optoelectronics applications [18,31].

To maximize effective broadband scattering, larger nanomaterials would be preferred over smaller ones. Because of limitations regarding the thicknesses of OPV films, restrictions in particle size have tended to act as a bottleneck. Indeed, the thicknesses of the

\* Corresponding authors.

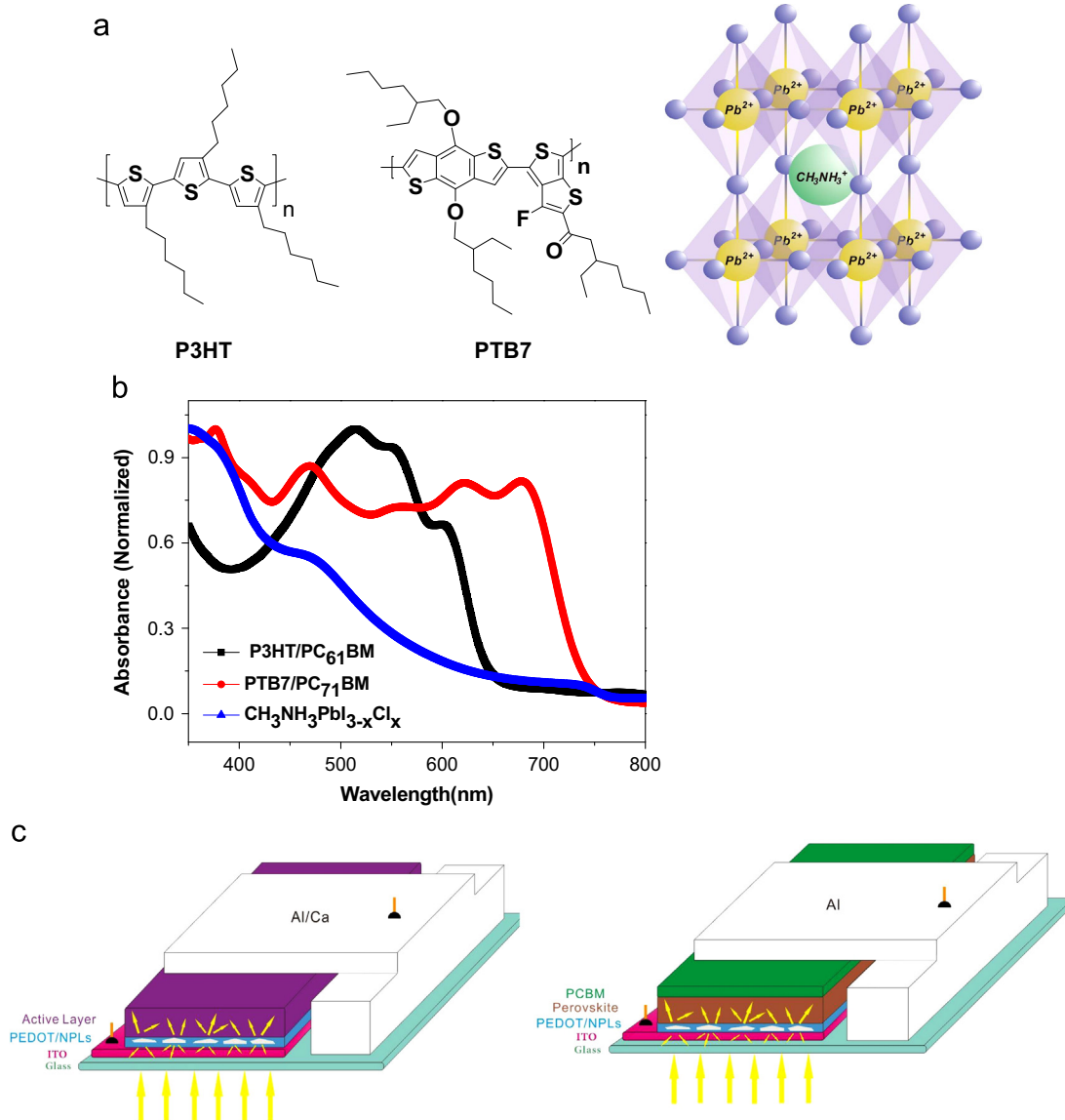
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HTLs and active layers of efficient OPVs are generally limited to 50 and 200 nm, respectively [31]. Therefore, the reproducibility and performance of OPVs are constrained when using relatively large nanomaterials. One way to overcome this restriction is to prepare plasmonic OPV devices via the incorporation of two-dimensional (2D) nanostructures [nanoprisms [14,22,36] and nanoplates (NPLs) [25]] with high aspect ratios [34]. Such 2D nanomaterials prefer lying flatly along the film, rather than stand up, after spin-casting from solution. For example, when Choy et al. embedded mixed Ag nanoparticles and nanoprisms (diameter: 60 nm) in the active layer for a device based on poly(3-hexylthiophene) (P3HT), a 19% enhancement in PCE was observed [14]. Only a few reports [14,25] have described the shape effects of embedded nanomaterials on the performance of OPV devices; we are unaware, however, of any previous paper discussing both the shape and size effects of embedded NPLs, especially in HTL.

In this study, we synthesized shape- and size-controlled Ag NPLs [33,34] and embedded these nanoparticles into the HTLs, comprising poly(3,4-ethylenedioxythiophene)/polystyrenesulfonate (PEDOT:PSS), of OPV devices. These NPLs, prepared through a simple, inexpensive,

readily scalable wet chemical synthesis method, exhibited various shapes and diameters ranging between 40 and 100 nm, thereby resulting in a variety of absorption spectra and reflectance levels. Because Ag NPLs tend to favor orientation parallel to the surface of a substrate [37], it is likely that the incorporation of Ag NPLs into the PEDOT:PSS layers would not significantly change the dimensions of the film. We have studied the size and shape effects of these plasmonic NPLs on the PCEs and external quantum efficiencies (EQEs) of OPVs based on P3HT and poly{(4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)(3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3]thiophenediyl)} (PTB7). Fig. 1a displays the chemical structures of P3HT and PTB7 as well as the UV-vis spectra of their blend films (P3HT/[6-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM); PTB7/PC<sub>71</sub>BM). For OPV devices incorporated with various NPLs and active layers, we observed 7.6–17.5% enhancements in the short-circuit photocurrent density ( $J_{sc}$ ), relative to those of pre-optimized control OPVs prepared without Ag NPLs, and thereby, an increase in PCE up to 10.5%.

Organometal halide perovskite(PVSK) PV devices became popular after their PCEs skyrocketed from 3.8% to greater than



**Fig. 1.** (a) Chemical structures of P3HT, PTB7 and the typical PVSK structure adopted by ABX<sub>3</sub> compounds (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> ions occupy position A (green) whereas Pb<sup>2+</sup> and halides occupy the B (yellow) and halide occupy position X (blue) positions (b) UV-vis spectra of P3HT/PC<sub>61</sub>BM, PTB7/PC<sub>71</sub>BM and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> thin films (c) device architectures of OPV and PVSK cells. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

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