



SPECIAL ISSUE: Flexible and Stretchable Energy

# Plasmonic materials for flexible near-infrared photovoltaic devices

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There is no doubt that photovoltaic (PV) technologies represent a highly important approach to provide clean energy by directly converting sunlight into electricity. The high natural abundance of silicon together with its excellent reliability and good efficiency in PV cells envisage its bright future in the production of solar energy on massive scales. Yet the cost of silicon PV modules, based on the crystalline silicon wafers with thickness between 180 and 300  $\mu\text{m}$ , has to be significantly reduced to allow large-scale implementation. Currently a low-cost approach uses very thin layers of absorber materials in PV cells, referred to as “thin-film PVs”. Meanwhile, the development of these thin-film PVs would enable to achieve extreme mechanical properties in the devices (e.g., flexibility, stretchability, and foldability), opening up the possibility of inventing wearable PVs [1]. As amorphous silicon suffers from various problems such as doping difficulty and light-induced degradation, it tends to use polycrystalline silicon or ultrathin monocrystalline silicon. In terms of crystalline silicon, however, such reduction in absorber thickness greatly compromises the efficiency of the device due to relatively poor light absorption, in particular at 600–1200 nm for indirect-bandgap semiconductor silicon [2]. For this reason, it is crucial to develop solutions to efficiently harvest or trap light for the continued applications of low-cost, flexible PV modules.

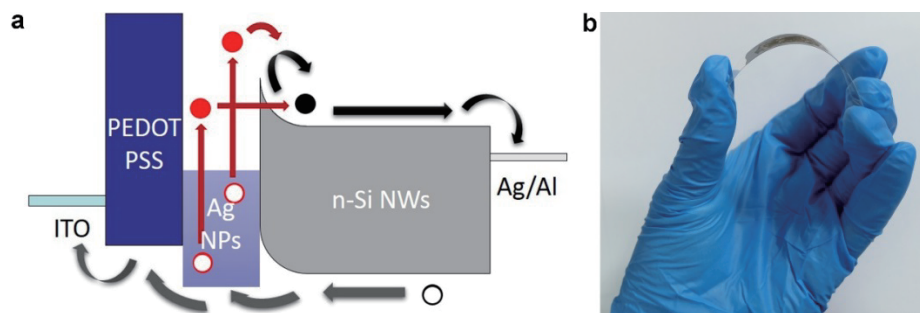
To enable light trapping, a variety of strategies have been developed by the research community. The first strategy is to tailor the silicon absorber into nanowires, which can induce multiple reflection to increase light traveling path lengths [3]. Another approach is the integration of plasmonics into PV technologies that uses nanostructured metal materials to guide and localize light at the nanoscale [4]. Plasmons are density waves of electrons, created when light hits the surface of a metal under precise circum-

stances. These density waves can couple light into a PV cell that would not otherwise be absorbed, increasing light absorption and therefore PV cell efficiency without the need to radically redesign devices. This technique could also avoid the problem of increased recombination that occurs in the conventional surface texture method. In the popularly used scheme, metallic nanoparticles serve as subwavelength scattering elements to couple and trap freely propagating plane waves from the sun into the absorber thin film [5]. Nevertheless, all these light-trapping techniques can mainly cope with the visible light spectrum where silicon materials can efficiently absorb photons and convert them into electrons.

Recently, the community for surface plasmon research has witnessed a growing interest on the utilization of plasmonic hot carriers [6]. Upon receiving photons, the electrons of a metal surface can be photoexcited to gain energy. Once the gained energy exceeds the Schottky barrier, the “hot” electrons would be injected into the conduction band of an n-type semiconductor when the metal and semiconductor are in intimate contact. Based on this mechanism, metal-semiconductor heterojunction devices have been invented for harvesting the hot electrons toward various applications such as the photodetector reported in 2011 [7]. Certainly this strategy can also be applied to the PV devices [8], and with the Schottky barrier well harnessed, near-infrared (NIR) light may be harvested to directly provide hot electrons for silicon semiconductor. Recent work by Liu *et al.* [9] has adopted such an approach to implement plasmonic silver nanostructures in two types of PV devices, inorganic-organic hybrid silicon-poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) PV cell (Fig. 1a) and Schottky-type silicon-graphene solar cell. In this design, they integrate silicon nanowires with the so-

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**Figure 1** Flexible NIR PV devices based on plasmonic hot electron injection. (a) The schematic illustrating the injection of plasmonic hot electrons from Ag nanoplates (NPs) to n-type Si nanowires (NWs) in a Si- PEDOT:PSS hybrid PV device. The plasmonic band of Ag NPs is located in NIR spectral region, allowing harvesting the NIR light for PV power conversion. (b) The photograph of a Ag nanoplates-mediated Si-PEDOT:PSS hybrid PV device with mechanical flexibility and NIR photo-response. Reprinted with permission from Ref. [9], Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA.

lution-processed plasmonic silver nanoplates that possess a plasmonic band in NIR. The silver nanoplates can directly harvest and convert NIR light into the plasmonic hot electrons that are injected into silicon for PV conversion, while the Si nanowire arrays offer light trapping. This combination has improved the external quantum efficiency at 550–1100 nm by more than 50%. Meanwhile, the silicon nanowires hosted in ultrathin monocrystalline silicon film offer excellent flexibility for the fabricated devices (Fig. 1b).

Corresponding author Prof. Yujie Xiong of the University of Science and Technology of China noted that if the long-wavelength light accounting for about 52% solar photons could be harvested through plasmonic hot electrons for electricity generation, the total power conversion efficiency for future PV modules would be substantially improved. Certainly the power conversion efficiency in this work is largely limited by the solution processing and is yet to be improved, so efforts should be made to engineer the interface of semiconductor absorbers with plasmonic nanostructures by refining nanofabrication techniques. Given the impact of infrared light on environmental heating, the implementation of this strategy in PV modules may enable the design of temperature-controllable devices

in the future. Meanwhile, this work provides an alternative route to flexible optoelectronic devices, leading to wearable applications.

Received 29 March 2016; accepted 1 April 2016;  
published online 20 April 2016

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