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### **Regular Article**

# Laser generated nanoparticles based photovoltaics

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### G R A P H I C A L A B S T R A C T



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### 1. Introduction

The realization of the importance of renewable energy sources to satisfy the continuously increasing global energy needs [1] has

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### ABSTRACT

The exploitation of nanoparticles (NP), synthesized via laser ablation in liquids, in photovoltaic devices is reviewed. In particular, the impact of NPs' incorporation into various building blocks within the solar cell architecture on the photovoltaic performance and stability is presented and analysed for the current state of the art photovoltaic technologies.

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boosted the development of environmentally friendly, low cost, energy technologies. Solar energy, including photovoltaic devices, has the highest potential. However, several challenges, such as the solar cell's cost competitiveness with fossil fuel technologies, must be addressed in order to commercially capitalize its potential. Since the cost of materials used in solar cells is a major issue, R&D has focused on fabricating devices that use less and more abundant materials. However, as solar cells become thinner, the absorption is lower and thus the number of photo-generated excitons is reduced. In this context, photon management, i.e. control over photon propagation and light distribution in photovoltaic devices, has emerged as powerful strategy to address this issue. The traditional photon management techniques involve the use of antireflection coatings, as well as doping or surface texturing to maximize trapping of incident light into the solar cell active layer [2,3]. However, these techniques are not appropriate for thin film solar cells whose thickness is only few hundreds of microns. Recently, a new nano-photonic management approach utilizing plasmonic effects was introduced [4-8]. Plasmons are collective, non-propagating excitations of electrons that occur more prominently in materials with high conduction electron densities such as metals. These strategies propose the use of nanoparticles (NPs) of different sizes and shapes dispersed into or deposited onto the various layers and interfaces of a photovoltaic device in order to trap more efficiently the incident solar light. Plasmonic structures offer three alternative mechanisms to reduce the physical thickness of the active layer and at the same time to improve solar light harvesting (Fig. 1). Firstly, small-sized NPs, with diameters in the range of 5-20 nm, operate as nano-antennas, giving rise to incident light field enhancement, due to excitation of the collective electron oscillations. Localized Surface Plasmon Resonance (LSPR) is attained when such collective oscillations reach resonance. Secondly the large diameter NPs (>50 nm) operate as subwavelength scattering centers. Finally, the NPs can be periodically arranged within the solar cell architecture, providing in-plane momentum for scattered light to be coupled into waveguide modes.

At conditions leading to LSPR, a significant enhancement of the NP's absorption and scattering cross section takes place [9] (Fig. 2). The plasmon wave is efficiently coupled into the active layer when (a) the LSPR frequency is matched with the active layer's absorption spectrum and (b) the absorption rate of the photoactive material is larger than the reciprocal of the typical plasmon decay rate (lifetime ~10–50 fs), otherwise the absorbed energy is dissipated into ohmic damping in the NP.

The LSPR frequency is determined by NPs' (a) size, (b) shape, (c) material and (d) the optical constants of the surroundings where

NPs are incorporated [10,11]. On the other hand, relatively larger diameter NPs (>50 nm) made by low loss material (e.g. silver) behave as effective sub-wavelength scattering centers [12,13] that couple and trap freely propagating plane waves of the incident light into the active layer. Besides this, it was proposed that large metallic nanoparticles facilitate the transport of holes, offering an additional contribution to the improved current density and PCE [14]. Finally, when the NPs are periodically arranged and interface the active layer, incident solar radiation excites resonant scattering modes coined as surface plasmon polaritons (SPP) at each NP – active layer interface [15]. In this case, the periodicity of the NPs arrangement dictates the SPP's frequency. While, NPs should be within few tens of nanometers from the active layer considering that the plasmon enhanced fields decay evanescently away from their surface [16,5].

Based on the above light management principles, improved efficiencies have been demonstrated in plasmonic solar cells [17–21] to date. For this purpose, it is found to be critical to fine-tune the concentration, dispersion, size of metal NPs, especially upon incorporation into the active layer. Furthermore various strategies have been proposed to avoid loss mechanisms including non-radiative decay, charge carrier recombination, local shunts and excitons quenching [22].

In this article we present a promising plasmonic-based photon management strategy, which relies on the incorporation of laser ablated NPs in liquids into various types of photovoltaic devices, including inorganic, organic, dye and hybrid solar cells. Laser ablation in liquids (LAL) is a simple physical synthesis technique and has the advantage of producing a large variety of NPs that are free of both surface-active substances and counter-ions [23–28]. Indeed, the absence of unnecessary reagents including stabilizers and byproducts that are usually generated in chemical syntheses becomes useful when NPs are used for potential applications. Particularly for plasmonic photovoltaic applications, the presence of a ligand coating on the NPs may promote undesirable exciton quenching, via nonradiative energy transfer between the NPs and the active layer [29,30]. On the other hand, and contrary to chemical synthesis methods, LAL provides NPs exhibiting a rather wide



**Fig. 1.** (Top) Schematic of the plasmon oscillation of a sphere, showing the displacement of the conduction electrons relative to the nuclei [14]. (Bottom) Different geometries for plasmonic light trapping in OPVs: (a) scattering from large diameter (>50 nm) metal NPs into high angles inside the photoactive layer, causing increased optical path lengths in the device; (b) LSPRs induced by small diameter (5–20 nm) metal particles and (c) excitation of SPPs at the NPs/photoactive layer interfaces ensures the coupling of incident light to photonic modes propagating in the semiconductor layer plane. The 2D periodic array of NPs scatterers could also provide in-plane momentum for scattered light to be coupled into waveguide modes (see text) [3].

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