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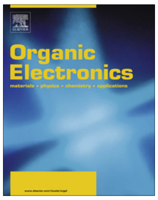

Gold nanorod enhanced organic photovoltaics: The importance of morphology effects

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ABSTRACT

Organic photovoltaic devices with a 30% improvement in power conversion efficiency are achieved when gold nanorods (Au NR) are incorporated into the active bulk heterojunction (BHJ) layer. Detailed analysis of the system is provided through microscopy, device characterization, and spectroscopy, demonstrating that the enhancement effects are predominantly caused by induced morphology changes in the BHJ film rather than plasmonic effects. Wide angle X-ray diffraction provides evidence that the nanorods loaded into the BHJ film have an effect on polymer crystal orientation, leading to a systematic performance increase in the devices as a result of both internal and external efficiency improvements.

1. Introduction

Solar energy is one of the most abundant sources of alternative energy available. More solar energy irradiates the earth in 1 h than human activity consumes in an entire year [1,2]. Therefore, investment in photovoltaic technology is currently undergoing significant growth, owing to the worldwide sensitivity to energy security and the importance of clean, renewable energy. Organic photovoltaic (OPV) systems represent one of the most promising photovoltaic technologies for light-to-electric conversion. The potential advantages of OPVs include low cost of fabrication, ease of processing, mechanical flexibility, and lightweight modules. Unfortunately, the efficiency of thin film OPVs has substantially lagged behind that of inorganic PV technologies, thereby limiting their marketability due to a poor price-to-power output ratio. At present, the record power conversion efficiencies for OPV devices are recorded near 12% [3].

The most representative high performance OPVs reported in the literature have been fabricated using bulk heterojunction (BHJ) architectures, which are formed by spin-casting a mixture of photosensitive electron donor and acceptor materials. This process creates a blended heterojunction of the donor and acceptor, with a high degree of interfacial surface area between each phase at which photo-induced charge transfer occurs [4]. While a variety of materials have been investigated in BHJ films, P3HT/PCBM blends (poly-3-hexyl thiophene/phenyl-C61-butyric acid methyl ester) represent the most well studied and reproducible system. The overall efficiency of an OPV device is highly dependent on the active layer film thickness [5]. A thinner active layer increases the excited state collection efficiency by lowering the probability of excited state recombination. However, light absorption, and subsequent exciton generation, is directly proportional to the

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film thickness. In other words, a thinner film has a lower absorption and thus limits the number of potential charge carriers through the reduction of photoactive material. Developing approaches to increase the effective absorption of light in thin films is a key challenge in the push to higher device efficiencies.

A recent approach towards improving light absorption within the polymer thin film is the incorporation of metal nanoparticles within the organic device architecture because of the potential for plasmonic enhancement effects [6–8]. The field of nanoparticle plasmonics has been incredibly active in the past two decades, leading to the discovery of some very interesting phenomena and the development of applications related to light manipulation and confinement [9–11]. The electric field component of incident electromagnetic radiation can excite the sea of conduction band electrons associated with the metal particle at a resonant mode which causes the electrons to oscillate coherently on the surface of the particle; this phenomenon is referred to as a localized surface plasmon resonance (LSPR). This resonant mode behaves much like an antenna, focusing the energy to a subwavelength dimension [11]. A portion of this energy is re-radiated to the environment in a range of directions, which is dictated in part by the shape of the particle, while the remaining energy is dissipated as heat. This ratio of scattered to absorbed energy, which is referred to as the particle's albedo, is dependent on several factors, such as the size of the particle and the dielectric environment [12].

The general set of phenomena categorized as plasmon enhancement in OPV devices involves several mechanisms that are related, but physically distinct. The most widely observed effect is the increase in beneficial far-field scattering [13–15] at the LSPR frequency from the nanoparticles, which have an extraordinary large scattering cross-section when compared with their geometric cross-section [11]. The far-field scattering is often multi-directional, and enhances the thin-film OPV device by redirecting normally incident light through the film, so that the light has a longer effective path-length, thereby leading to a higher probability of photon absorption within the film. This process is a linear effect (neglecting losses due to the nanoparticle absorption). A second enhancement mechanism from the localized plasmonic modes is surface enhanced absorption [16–18], which is a near-field effect involving spatial overlap of the concentrated evanescent field at the nanoparticle surface and a nearby organic chromophore. This effect has been proposed to be non-linear because it is related to the square of the concentrated field [19], E^2.

A variety of strategies have been used to incorporate plasmonic nanostructures into organic PV devices, such as placing nanoparticles at the electrode/polymer interface [13,14], incorporating particles within a charge blocking polymer layer [16–18], and mixing nanoparticles directly into the active BHJ film [15,20]. The majority of these studies utilize isotropic or nearly isotropic nanoparticles (spheres [21–24], octahedra [15]) of various sizes, with a few groups using anisotropic particles [20,21,25,26]. The nanoparticles have been reported to affect both the overall photo-conversion efficiency of a photovoltaic device [20,21,26–28] and some of the more specific photophysical properties of the organic layers [16,29,30]. In most cases, these effects are beneficial, with a few exceptions where the conversion efficiency is reported to degrade when metal nanoparticles are incorporated into the device [31]. In nearly every report, the effects are attributed to the induced LSPR modes of the nanoparticles, although these mechanisms are not always clearly differentiated between near-field and far-field effects. In addition to plasmonic effects, secondary effects of colloidal nanoparticle integration on the OPV performance are also likely, but are not readily discussed in the literature. Such effects are polymer morphology changes [20], conductivity improvements [32], electrode work function modification [33], changes to excited state lifetimes in the organic molecules [25], and improved long term performance durability [34]. These effects, induced by blending metal nanoparticles into the BHJ film, are only fleetingly addressed in the literature and are often proposed to play trivial roles in device performance enhancement.

In this work, we demonstrate how nanoparticle inclusion within the BHJ active layer can influence the polymer morphology to bring about significant photo-conversion efficiency enhancements via systematic integration of gold nanorods (Au NRs) into the active layer. The NRs are treated with a sophisticated ligand exchange protocol to render them soluble in organic solvents which are commonly used to cast BHJs, as well as allowing their dispersion within the aromatic BHJ active layer. The effects of NR concentration and aspect ratio (AR) on the device performance are investigated, and significant improvements in the photo-conversion efficiency (PCE) are observed. Using a combination of electron microscopy and device characterization, the different effects induced by the presence of the particles are discussed, including plasmonic mechanisms and morphological changes to the BHJ film. Based on these observations, the majority of the performance enhancement in the OPV devices studied here is primarily attributed to induced morphology changes in the BHJ film, which substantially increase the absorption of the P3HT, and some of the internal quantum efficiency processes, with negligible effects from plasmonic mechanisms observed.

2. Materials and methods

2.1. Materials

Cetyltrimethyl ammonium bromide (CTAB) and benzyldimethyl-hexadecyl-ammonium chloride (BDAC) were purchased from TCI America. Chloroauric acid, silver nitrate, sodium borohydride, and L-(+)-ascorbic acid) were purchased from Sigma–Aldrich. All chemicals were of analytical grade (purity > 98%) and were used without further purification. Deionized water (18 MΩ cm) was used in all the experiments.

2.2. Instrumentation

UV–Vis–NIR spectra were acquired with a Cary 5000 spectrophotometer at room temperature using a quartz