



In-situ synthesis of metal nanoparticle-polymer composites and their application as efficient interfacial materials for both polymer and planar heterojunction perovskite solar cells

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ABSTRACT

A new approach for the synthesis of gold nanoparticles (Au NPs) via a simple and fast in-situ generation method using an amine-containing polymer (PN4N) as both stabilizer and reducing agent is reported. The application of the Au NPs-PN4N hybrid material as efficient interfacial layer in different types of solar cells was also explored. The synthesized Au NPs show good uniformity in size and shape and the Au NPs doped PN4N hybrid composites exhibit high stability. Amine-containing polymers are good cathode interfacial materials (CIMs) in polymer solar cells (PSCs) and planar heterojunction perovskite solar cells (PVKSCs). The performance of the PSCs with Au NPs doped PN4N CIMs is largely improved when compares to devices with pristine PN4N CIM due to the enhanced electronic properties of the doped PN4N. Furthermore, by incorporating larger Au NPs into PEDOT:PSS to enhance absorption of the light harvesting layer, power conversion efficiencies (PCEs) of 6.82% and 13.7% are achieved for PSC with PCDTBT/PC₇₁BM as the light harvesting materials and PVKSC with a ~280 nm-thick CH₃NH₃PbI_{3-x}Cl_x perovskite layer, respectively. These results indicate that Au NPs doped into both PEDOT:PSS and PN4N interlayers exhibited a synergistic effect in performance improvement of PSCs and PVKSCs.

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1. Introduction

Solar cell technologies provide an effective approach to supply clean and inexhaustible energy. Polymer solar cells (PSCs) have been studied for two decades due to their advantages of being low cost, light weight and mechanically flexible, and power conversion efficiencies (PCE) over 10% have been reached [1–5]. Recently, organometallic halide perovskite solar cells (PVKSCs) have also attracted intensive attention and their performance rapidly improved from 4% to ~20% in just couple years [6,7], making them a promising candidate for the future solar market, although several issues such as stability and toxicity still remained to be solved [8,9]. The perovskite material can be introduced in different device architectures to fabricate the PVKSCs [10–14]. The p-i-n planar

heterojunction PVKSC [12,14] is a promising type of cell architecture due to its simplicity in structure and also its low temperature processing properties, making it suitable for high-throughput manufacturing on flexible substrates. The structure of the planar heterojunction PVKSC also closely resembles that of the PSCs, with the light harvesting layer sandwiched between the hole and electron selective interlayers. So it will be important if a common strategy can be developed and applied to both PSC and PVKSC to improve their performance.

Several strategies have been explored to improve the performance of both PSCs [15,16] and PVKSCs [17,18], including new material design, device configuration optimization, morphology control and light trapping strategy. In addition, interface engineering is also considered as a critical strategy to improve the device characteristics of both types of solar cells. The insertion of appropriate charge selection layers between the light harvesting layer and the electrodes is important to achieve ohmic contact at the electrodes, which maximizes the open circuit voltage (V_{oc}), charge collection efficiency as well as device performance [14,19–22]. It has been proven that conjugated polymers with pendant polar groups (such as amine groups, phosphonate groups

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and ionic groups *etc.*) are excellent cathode interfacial materials (CIMs) in PSCs [23–29] and PVKSCs [30–32]. Among these CIMs, amine-functionalized water/alcohol soluble CIMs are considered to be the most promising one and had been widely adopted to improve the efficiency of PSCs and PVKSCs [27–32]. It was reported that those CIMs can effectively reduce the work function of the cathode to provide more efficient electrode extraction property and also possess good hole blocking property to reduce charge recombination at the electrode interface, making them a good electrode selective layer [33–36].

Introduction of metal nanoparticles (Au NPs or Ag NPs) into PSCs is another important strategy to improve the device performance by enhancing light absorption through plasmonic effect [37–41] and also charge transport properties through metal NP doping [42–45]. The most widely adopted method is directly mixing metal NPs into poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonic acid) (PEDOT:PSS) [38–40], active layer [37] or even CIMs [38,42]. From a chemical point of view, the synthetic methods of Au NPs with different sizes and shapes are well developed. Typically some molecules such as sodium citrate were introduced as a stabilizer and reducing agent to control the growth of the metal NPs [46–49]. It was also found that amine containing small molecules can be a good reducing agent for the synthesis of Au NPs [47]. Considering that amine-containing polymer is an important class of CIMs in PSCs and PVKSCs, it will be interesting to explore the possibility to simultaneously use the amine-containing polymer as a template to guide to grow the Au NPs and also the resulting hybrid polymer-Au NPs composite as interfacial material for solar cells. This approach is simpler than the traditionally used direct mixing method and can circumvent the potential problems of inhomogeneous mixing and leftover of inactive surfactants that are used to synthesize the metal NPs, which may introduce adverse effect to the device performance. In this article, we developed a method to in-situ synthesize Au NPs in a solution containing a chemically tailored amine-containing polymer (PN4N). It was found that PN4N which possesses a hard–soft structure can act as an excellent stabilizer for the formation of Au NPs, and effectively avoid the aggregation of Au NPs. Thus, the synthesized Au NPs showed good uniformity in size and shape and the resulting Au NPs doped PN4N hybrid composites showed very good stability. The Au NPs doped PN4N hybrid materials were then successfully applied to PSCs and PVKSCs as CIMs. The performances of the resulting devices were largely improved compared to those with undoped CIMs, with major enhancement in both photocurrent and fill factor. To take one step further, Au NPs were also doped in the PEDOT:PSS layer to improve the property of the anode interface. With these dual metal NPs doped interlayers, PSCs composed of a PCDTBT/PC₇₁BM bulk heterojunction layer and PVKSCs composed of a 280 nm-thick CH₃NH₃PbI_{3-x}Cl_x perovskite layer showed PCEs of 6.82% and 13.7%, respectively, which corresponded to a 25% and 9% increase in performance when compared to undoped devices. These results indicate that Au NPs doping in both PEDOT:PSS and PN4N exhibit a synergistic effect on performance improvement of PSC and PVKSC devices.

2. Results and discussion

2.1. Preparation and characterization of Au NPs doped PN4N

Several reducing agents and stabilizers have been investigated to prepare Au NPs with different sizes and shapes [46–49]. Amines, including primary amines, amino acid and poly(amines), are widely explored as both reducing agents and stabilizers for the synthesis of Au NPs [47–49]. The oxidation potential of amine group (1.079 V vs SHE, taking triethylamine as example) is within the range of

reduction potential (0.888 V vs SHE) of HAuCl₄ to Au⁰ and the oxidation potential (1.555 V vs SHE) of Au⁰ to Au¹⁺ [47], indicating that the reduction of HAuCl₄ to Au NPs should be thermodynamically favorable if tertiary amines (or secondary amines) are acted as a reducing agent [47]. PN4N (Fig. 1(b)) is an amine-rich polymer with secondary amines in its main chain and tertiary amines in its side chain. Undoubtedly, PN4N can be a good reducing agent for the synthesis of Au NPs facilitated by the efficient electron transfer from the high density amine groups to HAuCl₄. (Fig. 1(a) Besides, the high density amine groups endow PN4N good solubility in alcohol solvents, unlike other amine-containing conjugated polymer which can only be dissolved with the existence of organic acid [50]. The excellent solubility of PN4N can provide an uniform environment for the growth of Au NPs with good homogeneity, it also allows the Au NPs doped PN4N composite dispersible in alcohol solvents. Moreover, PN4N with the conjugated–nonconjugated (hard–soft) structure may also exhibit better ability to prevent the aggregation of Au NPs than traditional small molecular stabilizers, which is evidenced by the formation of clear solution even at high Au NP concentrations as shown in Fig. 1(c). The solution of PN4N coated Au NPs is also highly stable and can be stored over months without aggregation while Au NPs protected by citrate sodium slowly precipitate out over time. (see Fig. S1).

Since PN4N is highly soluble in alcohols, the synthesis of Au NPs doped PN4N hybrid composite can therefore be conducted in either methanol or isopropanol instead of the commonly used aqueous solvent [49,51]. The advantage of using alcohol as the solvent is that it can provide good wetting property on non-polar surface so that the PN4N–Au NPs composite layer can be homogeneously coated on the bulk-heterojunction (BHJ) film, while aqueous based solutions will dewet the BHJ surface and prevent the formation of good quality film. The PN4N concentration in methanol used in this work is 0.5 mg/mL, which is targeted to deposit a thin film without any dilution procedure. The concentration of Au NPs can be tuned by adjusting the feeding ratio of HAuCl₄ precursor. Various weight ratios of Au NPs to PN4N from 5% to 20% were prepared and the absorption spectrum of the resulted solutions is shown in Fig. 2. The Au NPs doped PN4N solutions all showed two absorption peaks at ~340 nm and ~530 nm. The former one is attributed to the absorption from PN4N and the weaker absorption peak at 530 nm is attributed to the surface plasmon resonance (SPR) band positions of Au NPs [49]. When the weight ratio of Au NPs to PN4N increased from 5% to 20%, the absorption peak intensity at ~530 nm also increased with an approximately linear relationship. The SPR band position also showed a slightly red-shift from 530 nm to 534 nm when the weight ratio of Au NPs increased. This observation indicates that the size of Au NPs was increased according to the classic quantum size confinement theory of metal NPs [49]. For Au NPs using sodium citrate or CTAB as stabilizers, a SPR peak of 530–534 nm corresponds to a NP size of 40–50 nm [49,51]. However, transmission electron microscope (TEM) study revealed that the sizes of the Au NPs in our case were much smaller, which diameters were only around or less than 10 nm (Fig. 3). The difference can be attributed to the different dielectric environment around the Au NPs created by both the alcohol solvent and polymers, which is known to affect the plasmonic absorption properties of metal NPs [52].

The TEM images of PN4N–Au NPs composites are shown in Fig. 3. The size of the Au NPs was found to be increased with Au NP weight ratio. At low weight ratios of 5%, 10% and 15%, the Au NPs present as spherical particles with diameters of less than 10 nm, some Au NPs with sizes even down to 2 nm were also observed. When the weight ratio of Au NPs to PN4N increased to 20%, the Au NPs became larger and also some Au NPs with cubic structure were formed. The

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