

Water Soluble Amino Grafted Silicon Nanoparticles and Their Use in Polymer Solar Cells*

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Abstract Stable aqueous amino-grafted silicon nanoparticles (SiNPs-NH₂) were prepared *via* one-pot solution method. By grafting amino groups on the particle surface, the dispersion of SiNPs in water became very stable and clear aqueous solutions could be obtained. By incorporating SiNPs-NH₂ into the hole transport layer of poly(3,4-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT:PSS), the performance of polymer solar cells composed of poly[2-methoxy,5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as active layer can be improved. SiNPs-NH₂ are dispersed uniformly in the PEDOT:PSS solution and help form morphologies with small-sized domains in the PEDOT:PSS film. SiNPs-NH₂ serve as screens between conducting polymer PEDOT and ionomer PSS to improve the phase separation and charge transport of the hole transport layer. As a result, the sheet resistance of PEDOT:PSS thin films is decreased from $(93 \pm 5) \times 10^5$ to $(13 \pm 3) \times 10^5 \Omega/\square$. The power conversion efficiency (PCE) of polymer solar cells was thus improved by 9.8% for devices fabricated with PEDOT:PSS containing 1 wt% of SiNPs-NH₂, compared with the devices fabricated by original PEDOT:PSS.

Keywords: SiNPs-NH₂; Water-soluble; Phase separation; Polymer solar cells; Transport.

INTRODUCTION

Flexible electronics gain great interest for their flexibility characteristics and low processing costs. They have been widely used as carrier transport layer in organic light-emitting diodes (OLEDs)^[1–4], field-effect transistors^[5, 6], photodiodes^[7, 8] and organic photovoltaic devices (OPVs)^[9–18]. Among the numerous conductive polymers, poly(3,4-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT:PSS) is an important material in the creation of organic electronic devices because of its high conductivity and transparency. Commercial PEDOT:PSS is an aqueous dispersion, so many research groups have adopted a spin-casting process to fabricate thin films for investigation of its microstructure.

Many research groups found that incorporating an organic solvent^[19–21] or salt^[22] into the PEDOT:PSS aqueous solution could improve the conductivity of PEDOT:PSS thin films. They speculated that the organic solvents with large dipole moments or ions that exhibit high binding energies interact with the electropositive PEDOT chain and electronegative PSS chain, respectively. This would induce a strong screening effect between the positively charged PEDOT and negatively charged PSS dopant. Therefore, the localization length of the PEDOT:PSS domain in the complex could be extended. This lowers the effective energy barrier for the charge

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carriers to hop between individual PEDOT grains. Subsequently, functionalized silica nanodots were employed into nonemissive layer PEDOT:PSS to enhance luminance of OLEDs. The power efficiency could be increased by 100% by using amino-functionalized polymeric nanodots^[23, 24]. This method was also effective in enhancing power conversion efficiency (PCE) of organic/inorganic hybrid solar cells^[25]. Thus, such highly conductive PEDOT:PSS thin films help improve optoelectronic devices.

Silicon nanoparticles (SiNPs) are nontoxic^[26, 27] and have the inherent advantages of semiconductor nanocrystals, such as quantum confinement effects^[28–30] and band gap tunability^[31]. They have been widely investigated for their optoelectronic properties, surface functionalization and scale production^[32–34]. Several groups have utilize SiNPs as an electron acceptor^[35–37] or electron donor^[38] for organic/SiNPs solar cells. Recently, some reports show that the performance of solar cells can be improved by incorporating nanoparticles into the hole transport layer^[39–41], especially in the PEDOT:PSS layer^[42]. These reports have shown the potential use of SiNPs in solar cells.

This paper describes a simple synthesis of amino functionalized silicon nanoparticles (SiNPs-NH₂) which can be uniformly soluble in water. By incorporating different contents of SiNPs-NH₂ into the hole transport layer of PEDOT:PSS, the effects on the morphology and electrical properties of PEDOT:PSS thin films were studied. The effect of SiNPs-NH₂ in PEDOT:PSS on the performance of polymer solar cells composed of poly(2-methoxy,5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was also investigated.

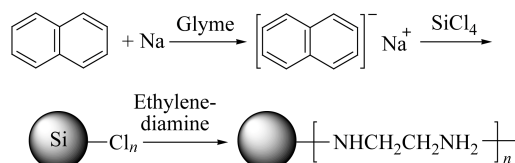
EXPERIMENTAL

Synthesis and Characterization of SiNPs-NH₂

Chemicals for synthesis were purchased from Aldrich without further purification. SiNPs-NH₂ were prepared by modifying the method according to the literatures^[43, 44]. Sodium naphthalide in 1,2-dimethoxyethane was prepared from 0.36 g of sodium and 1.48 g of naphthalene under stirring in 20 mL of 1,2-dimethoxyethane overnight, into which 0.52 g of SiCl₄ was added drop by drop. The color of the suspension turned from dark yellow to deep brown. After stirring for 2 h, excess ethylene diamine was added in the suspension to passivate SiNPs with amino group. After strong stirring overnight, distilled water was added to extract the water-soluble SiNPs-NH₂. The solvent was removed under reduced pressure and ethanol was added to extract SiNPs-NH₂ and remove salt. Repeating the method three times, the resulting red solid was resolved in distill water with 10 wt%. The sample was characterized by transmission electron microscopy (TEM, Phillips CM200 operating at 200 kV), photoluminescence spectroscopy (PL, F900 fluorescence spectrometer) and Fourier transform infrared spectroscopy (FTIR, Bruker Vector 33).

Fabrication and Characterization of PEDOT:PSS Thin Film

To fabricate PEDOT:PSS thin films that are incorporated with different weight ratios of SiNPs-NH₂, the following procedure was used: First, the PEDOT:PSS solution (Baytron P VP AI 4083, 1.3 wt%) was filtered through a 0.45 μm PVDF filter. 400 μL filtered solution was then blended with 0, 2.6 and 5.2 μL SiNPs-NH₂ solutions, respectively. A thin film of each PEDOT:PSS/SiNPs-NH₂ was prepared by spin coating upon Indium Tin Oxides (ITO) glass substrate and then baked at 140 °C for 10 min. The thickness of PEDOT:PSS films is *ca.* 50 nm, which is measured by an AMBIOS XP-1 high-resolution surface profiler. Atomic force microscopy (AFM, DI instrument Nanoscope 3D Multimode SPM, Tapping Mode) was used to study the thin film morphology. A four-point probe with a high-voltage source meter (Keithley model 2410) was used to measure the electrical properties of the different PEDOT:PSS/SiNPs-NH₂ thin films.



Scheme 1 Schematic diagram of synthesis and surface modification of silicon nanoparticle

Fabrication and Characterization of Solar Cell Device

The polymer solar cells were fabricated based on an interpenetrated network of conjugated polymer MEH-PPV and fullerene derivative PCBM. The MEH-PPV was purchased from Canton OLEDKING Optoelectronic Materials, and PCBM was bought from Aldrich, and used as received. 1,2-Dichlorobenzene solution of MEH-PPV and PCBM blend (stirred overnight) was spin-coated over the PEDOT:PSS layer as prepared, with the layer thickness of *ca.* 150 nm. Finally, 80 nm aluminum (99.999%) was deposited onto the active layer under high vacuum (about 10^{-4} Pa) as the top contact. The current-voltage (*J-V*) curves were obtained on a Keithley236 source-measuring unit under illumination of a Thermal Oriel solar simulator with AM1.5 solar irradiation ($100 \text{ mW} \cdot \text{cm}^{-2}$). The light intensity of the simulator was calibrated with a silicon diode. For measurements of external quantum efficiency (EQE) spectrum, light from a Xe arc lamp (Oriel 500 W) was coupled into a grating monochromator. The monochromatic light intensity was calibrated under normal incidence with a Si photodiode. The data were measured with Stanford lock-in amplifier 830 unit.

RESULTS AND DISCUSSION

Amino-grafted silicon nanoparticles (SiNPs-NH₂) in film coated on potassium bromide tablets were characterized by FTIR. In FTIR spectrum, strong peaks corresponding to alkyl C—H_x bonds at 2952 and 1463 cm^{-1} appear after treatment with ethylene diamine. The peak at 3363 cm^{-1} should be attributed to amino N—H_x bonds. The peak at 952 cm^{-1} responds to the Si—N bond, which confirms the existence of a surface-grafted amino^[45, 46].

The SiNPs-NH₂ solution in water was very clear and remained stable for several months. The above dispersion was dropped onto holey carbon-coated Cu TEM grids for TEM measurements. The TEM image revealed a good dispersibility for individual particles with an average diameter of about 2 nm (Fig. 1a).

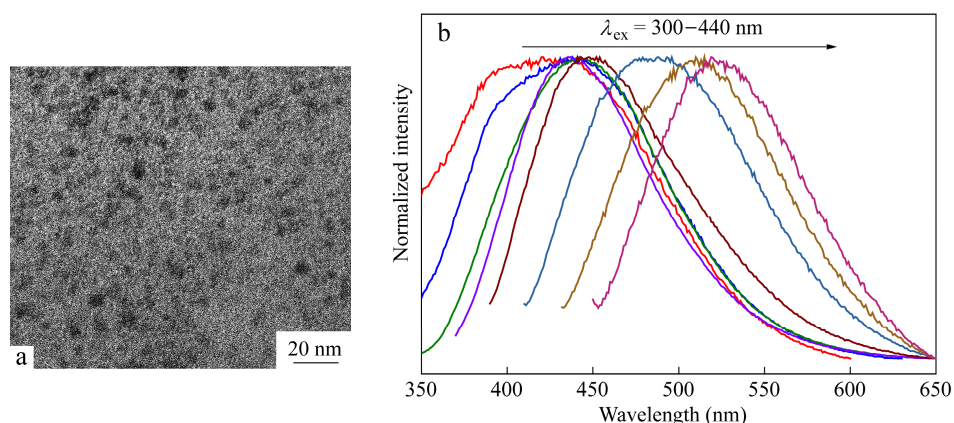


Fig. 1 (a) TEM image of amino-capped SiNPs-NH₂ on a holey carbon grid (Darker circular regions are SiNPs-NH₂) and (b) PL spectra of SiNPs-NH₂ under different excitation wavelengths

Because SiNPs synthesized from solution normally have a size distribution^[43, 44, 47–52], the size-dependent luminescence property is expected. The PL emission spectra (Fig. 1b) were collected with excitation

wavelengths from 300 nm to 400 nm (10 nm increments). The size-dependent luminescence property of the obtained SiNPs-NH₂ was indeed observed, and the emission peaks are red shifted by *ca.* 50 nm compared with the SiNPs coated with alkyl groups, which results from the conjugative effect of amine on the surface^[53].

We used the four-point probe method to evaluate the electrical properties of PEDOT:PSS thin films containing different amounts of SiNPs-NH₂. The sheet resistances are summarized in Table 1. PEDOT:PSS thin films containing SiNPs-NH₂ exhibit significant improvement in conductivity as compared with the pristine PEDOT:PSS. The extent of enhancement increases with increasing the amount of SiNPs-NH₂ in PEDOT:PSS. That is, the sheet resistance decreases from $93 \times 10^5 \Omega$ to $13 \times 10^5 \Omega$ after adding 1 wt% SiNPs-NH₂ into PEDOT:PSS film, which may arise from the aggregation changes in PEDOT:PSS films caused by surface groups of SiNPs-NH₂.

Table 1. Properties of PEDOT:PSS thin films (50 nm) containing different content of SiNPs-NH₂

Thin film	SiNPs-NH ₂ (wt%)	Roughness (nm) ^a	Sheet resistance ($10^5 \Omega$)
S0	0	1.065	93 ± 5
S1	0.5	1.642	52 ± 2
S2	1.0	2.199	13 ± 3

^a Roughness was determined by the atomic force microscopy

To know the reason for the observed sheet resistance changes in PEDOT:PSS films containing SiNPs-NH₂, we employed AFM to study the film morphology. As shown in AFM images (Fig. 2), the roughness of the ITO glass (Fig. 2a) decreases from 1.938 nm to 1.065 nm after deposition of PEDOT:PSS upon the ITO glass (Fig. 2c). Thus, the presence of a PEDOT:PSS layer between the active layer and the ITO electrode can reduce possible charge recombination which results from the direct contact between active layer and ITO^[54, 55]. However, the surface roughness of the samples increases with increasing the amount of SiNPs-NH₂ in the PEDOT:PSS. To understand the differences in roughness among the different PEDOT:PSS/SiNPs-NH₂ films, phase images for the corresponding PEDOT:PSS/SiNPs-NH₂ films were also recorded. The phase images clearly show that the phase domain becomes more transparent and larger (from *ca.* 200 nm to *ca.* 300 nm) with increasing amount of SiNPs-NH₂ (Figs. 2d, 2f, 2g). These results indicate that SiNP-NH₂ can induce the phase separation between the conductive polymer PEDOT and the ionomer PSS.

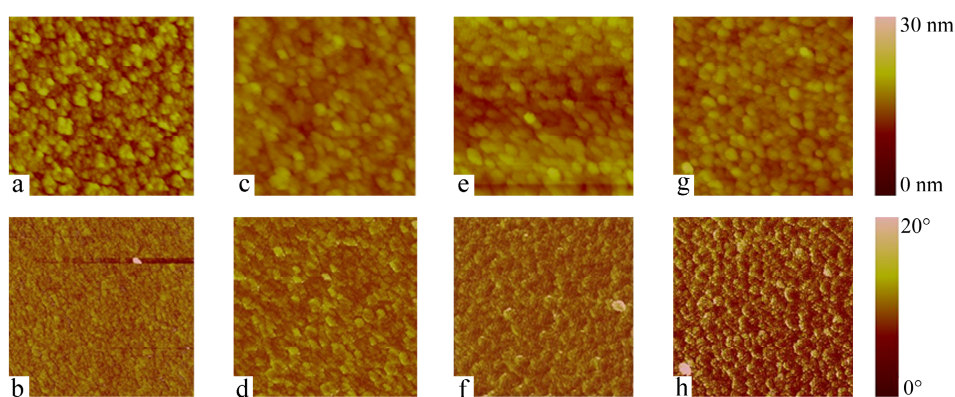


Fig. 2 AFM topographic images (top) and phase images (bottom) of (a, b) ITO substrate, (c, d) PEDOT:PSS/ITO substrate, (e, f) PEDOT:PSS containing 0.5 wt% SiNPs-NH₂ and (g, h) PEDOT:PSS containing 1.0 wt% SiNPs-NH₂ (The scale of each image is $5 \mu\text{m} \times 5 \mu\text{m}$.)

In the neat PEDOT:PSS aqueous solution, PEDOT and PSS associated with one another because of their opposite charges. The negatively charged PSS may help to enhance dispersion of PEDOT into the aqueous solution, thus improving the conductivity of the PEDOT polymer chain. Since SiNPs-NH₂ is well dispersed in water and the size (*ca.* 2 nm) is much smaller than the domain size of PEDOT:PSS, they can disperse well into

the PEDOT:PSS solution and induce a stronger phase separation between the conductive polymer of PEDOT and the ionomer of PSS. As a result, the phase separation induced by SiNPs-NH₂ forms a more continuous transport path that is composed of the conductive polymer PEDOT. It also reduces the probability of carrier trapping.

Finally, we compared the device performances of MEH-PPV/PCBM polymer solar cells with the hole transport layer of the PEDOT:PSS with different contents of SiNPs-NH₂. Figure 3 gives the device characteristics, and the photovoltaic performance is summarized in Table 2. We find that, under illumination (Fig. 3a), the J_{sc} increases from 5.63 mA/cm² to 6.46 mA/cm² as the content of SiNPs-NH₂ increases from 0% to 1.0% in the PEDOT:PSS layer. As a result, there is a 9.8% improvement in power conversion efficiency (PCE) for the device containing 1.0 wt% SiNPs-NH₂ when compared with the control device. Such improvement in performance for SiNPs-NH₂-containing devices mainly arises from the enhanced short circuit current density. As shown in Fig. 3(b), SiNPs-NH₂-containing devices exhibit an enhanced photon response. That is, EQE increases with increasing the content of SiNPs-NH₂.

Table 2. Photovoltaic properties of MEH-PPV/PCBM solar cells containing different hole transport layers (HTLs)

HTLs	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
PEDOT:PSS	5.63 ± 0.07	0.842 ± 0.011	47.3 ± 0.6	2.24 ± 0.05
0.5% SiNPs-NH ₂	6.30 ± 0.05	0.835 ± 0.012	45.6 ± 0.8	2.40 ± 0.06
1.0% SiNPs-NH ₂	6.46 ± 0.06	0.832 ± 0.009	45.5 ± 0.9	2.46 ± 0.06

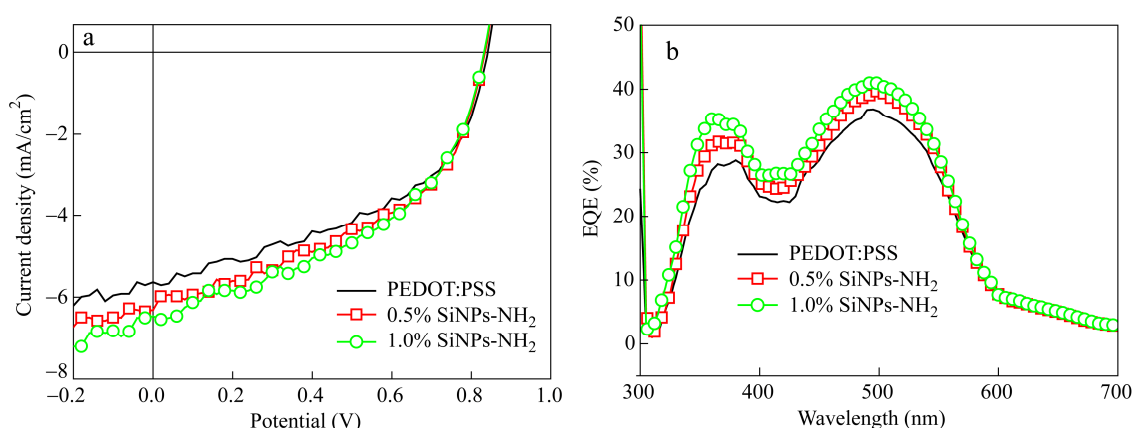


Fig. 3 J - V curves and EQE spectra of MEH-PPV/PCBM photovoltaic devices with different PEDOT:PSS hole transport layers.

As mentioned above, SiNPs-NH₂ in the PEDOT:PSS not only induce phase separation between PEDOT and PSS but also increase the film roughness. The phase separation improves the conductivity of PEDOT:PSS thin films and thus enhances charge injection efficiency in MEH-PPV/PCBM solar cells. The proper roughness gives more interface connection between PEDOT:PSS and active layer, leading to better charge collection efficiency^[56], and thus an increases of EQE with increasing the content of SiNPs-NH₂. These factors are responsible for the improvement of the J_{sc} and in turn the power conversion efficiency. Hence, SiNPs-NH₂ are suitable for use in the hole transport layer of polymer photovoltaic devices.

CONCLUSIONS

In summary, we offer a novel approach for improving the performance of MEH-PPV/PCBM polymer photovoltaic devices by incorporating water soluble SiNPs-NH₂ into the hole transport layer of PEDOT:PSS. Increasing the amount of SiNPs-NH₂ can increase the extent of phase separation and improve the conductivity of PEDOT:PSS films. When adding 1 wt% SiNPs-NH₂ in PEDOT:PSS thin film, the PCE increases from 2.24% to 2.46%. The improvement mainly arises from the increased short circuit current density, which makes us believe

that the incorporation of SiNPs-NH₂ enhances the carrier transport of the PEDOT:PSS layer in polymer photovoltaic devices.

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