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Nanostructured electrodes for organic bulk heterojunction solar cells: Model study using carbon nanotube dispersed polythiophene-fullerene blend devices

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We test the feasibility of using nanostructured electrodes in organic bulk heterojunction solar cells to improve their photovoltaic performance by enhancing their charge collection efficiency and thereby increasing the optimal active blend layer thickness. As a model system, small concentrations of single wall carbon nanotubes are added to blends of poly(3-hexylthiophene): [6,6]-phenyl-C₆₁-butyric acid methyl ester in order to create networks of efficient hole conduction pathways in the device active layer without affecting the light absorption. The nanotube addition leads to a 22% increase in the optimal blend layer thickness from 90 nm to 110 nm, enhancing the short circuit current density and photovoltaic device efficiency by as much as ~10%. The associated incident-photon-to-current conversion efficiency for the given thickness also increases by ~10% uniformly across the device optical absorption spectrum, corroborating the enhanced charge carrier collection by nanostructured electrodes. © 2011 American Institute of Physics. [doi:10.1063/1.3633236]

I. INTRODUCTION

Nanometer-scale phase separation in the bulk heterojunction solar cell architecture has increased the power conversion efficiency of organic-based solar devices from less than 1% to >5% by decoupling the length scale for light absorption from that of exciton diffusion,¹⁻⁶ thus enabling photogenerated excitons to readily reach junction interfaces.⁷ Even so, the active blend layer thicknesses of state-ofthe-art polymer-fullerene solar cells are usually limited to no more than ~100 nm,⁴⁻⁶ which is sufficient for only ~50% to 60% light absorption at the peak absorption wavelength.^{3,5,8} Further increasing the blend thickness for greater light absorption *decreases* the device efficiency because the poor mobility of dissociated free charge carriers results in excessive carrier recombination.^{9,10}

In this paper we describe a method for improving the photovoltaic performance of organic polymer-fullerene bulk heterojunction solar cells by increasing the active blend layer thickness *without* compromising the carrier collection efficiency. We incorporate nanostructured electrodes into bulk heterojunction solar cells composed of blended poly(3-hexylthiophene) (P3HT): [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and demonstrate improved photovoltaic performance from an associated increase in the carrier collection efficiency and optimal active blend layer thickness. The nanostructured electrodes protrude into the blend layer and shorten the travel distance for dissociated free charge carriers within the low mobility semiconductor blend (Fig. 1(a)), thereby reducing recombination loss in thicker active layers. This device architecture

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offers an alternative to other approaches targeting improved *intrinsic* charge transport within the blend layer, such as ordered bulk heterojunctions,^{11,12} the confining of semiconducting polymers to nanometer-scale pores,¹³ the cross-linking of active polymers,^{14,15} and the forming of semiconducting polymer nanowires,^{16–18} with which the change in the intrinsic charge mobility might also affect the associated Langevin-type bimolecular recombination.¹⁹ In principle, the nanostructured electrodes leave the active layer intrinsic charge mobility unchanged while enhancing the device's *effective mobility* for efficient charge carrier collection.

II. EXPERIMENTAL DETAILS

All device processing described here was performed in ambient air unless otherwise indicated. P3HT and PCBM powders (American Dye Source) were dissolved in monochlorobenzene with a 1:50 weight ratio to obtain a 2 wt. % solution. Functionalized single wall carbon nanotubes were added to P3HT solutions with a 1:100 weight ratio to P3HT. After ~ 10 to 30 s of bath sonication, the solution was filtered using a 0.4 μ m pore-size syringe filter. P3HT (with or without nanotubes) and PCBM solutions were mixed in a 1:1 ratio to form 2 wt. % blend solutions. A poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Sigma-Aldrich) solution was spin-coated at 5000 rpm for 45 s on a 140 nm thick indium tin oxide (ITO) coated glass substrate and baked at 140 °C in air for 10 min. The 2% blend solution (or P3HT solution, for bilayer devices) was then spin-cast at 500 to 1000 rpm for 45 s and dried in an enclosed sample carrier for \sim 15 to 20 min. The corresponding layer thickness was determined via ellipsometry. Top aluminum (Al) contacts \sim 80 nm thick (or 40 nm of C_{60} and 80 nm of Al on top for bilayer devices) were deposited via thermal evaporation through a shadow mask with an active device area of 0.0314 cm². The completed devices were thermally annealed in vacuum for 10 min (150 °C, \sim 100 mTorr).

For photovoltaic characterization, a 150 W solar simulator (Oriel) equipped with an AM1.5 G filter was used for solar illumination. The light intensity was calibrated for a 100 mW/cm² (1 SUN) condition by using a KG5 color filtered Si reference solar cell (Newport).²⁰ The current density versus voltage (J-V) characteristics of dark and illuminated solar cells or transport analysis devices were measured using a custom-modified probe station and an Agilent 4156 C precision semiconductor parameter analyzer. For each experimental condition, we fabricated 4 or 5 devices, and we report the average photovoltaic and electrical parameters, as well as their standard deviations. For the incident-photon-to-current conversion efficiency (IPCE) measurement, we used a 150 W xenon arc lamp (Newport) and a monochromator (Cornerstone 130, Newport). Monochromatic light (between 350 nm and 800 nm) was guided to a sample mounted on an electrical probe station through a liquid light guide (Newport), and the illuminated device's short circuit current was measured using a 4156 C parameter analyzer. We calculated the IPCE using the ratio of the short circuit current to the light intensity as measured by a calibrated Si detector (Newport).

Single wall carbon nanotubes were functionalized using the following method. Raw HiPCO single wall carbon nanotubes (Unidym) were further purified by heating in air at 300 °C for 4 h, followed by bath sonication in concentrated HCl to remove the remaining metal catalysts. A suspension of purified nanotubes (100 mg) in an acetone/water solution (20 ml/20 ml) was sonicated for 2 min using an ultrasonic probe. N-methylmorpholine-N-oxide (1 g) was added into the suspension, and the solution was stirred for 5 min. We then added 250 mg osmium tetroxide, after which the solution was stirred for 3 days at room temperature. The resulting mixture was filtered through a 0.45 μ m Nylon 66 membrane (Supelco Analytical) and washed with a copious amount of water and then acetone. The sample was dried under vacuum at room temperature overnight. We suspended 40 mg of dried sample in tetrahydrofuran, and 4-dimethylaminopyridine (24 mg) and pyridine (1 ml) were added. Then palmitoyl chloride was dripped in slowly under N2 gas. The solution was stirred at room temperature for 1.5 days, and then water was added. The solution was filtered through 0.45 μ m Nylon 66 membrane and washed with water thoroughly and then with acetone. The solid was dried under vacuum at room temperature overnight.

For transmission electron microscopy (TEM), P3HT:PCBM thin films containing carbon nanotubes were prepared on bare ITO coated glass substrates via spincoating. The fully dried composite film was released by removing the underlying ITO using a commercial ITO etchant (Transene Co., Inc.). The released film was rinsed in deionized water, transferred onto a 3 mm diameter Cu TEM grid, and observed using a 200 kV transmission electron microscope (JEOL-2100 F).

III. RESULTS AND DISCUSSION

A. P3HT:PCBM blend devices

In an effort to create a model system wherein the nanostructured electrode concept can be tested in a simplified manner, we have employed networks of functionalized single wall carbon nanotubes within a P3HT:PCBM blend layer as efficient conduction pathways for hole transport to the anode in a bulk heterojunction solar cell (Fig. 1(a)). Carbon nanotubes have excellent electrical properties along the longitudinal axis,^{21,22} and their previous successful application as efficient hole conductors in organic solar cells^{23–31} stems from their work functions' (~4.7-4.9 eV, regardless of tube species)^{32–34} being well aligned with the highest occupied molecular orbital of P3HT (~5.1 eV). Spontaneous helical wrapping of P3HT chains along the carbon nanotubes³⁵ might further improve



FIG. 1. (Color online) (a) Schematic of (left) an ordered nanostructured anode electrode in a P3HT:PCBM bulk heterojunction solar cell and (right) an equivalent model structure containing carbon nanotubes within the active blend layer. (b)-(d) Bright field TEM images of a P3HT:PCBM blend containing dispersed single wall nanotubes in the organic blend matrix. (b) A low magnification image with intentional over-focus, revealing the locations of nanotube bundles. (c) A high magnification image of an individual nanotube bundle. (d) Nanotube networks in the regions between bundles. (e) Optical absorbance of ~90 nm thick control (solid black line) and nanotubecontaining (red dashed line) P3HT:PCBM blend film spin coated on bare ITO substrates, showing that the addition of nanotubes does not affect the optical absorption.

the selective collection of hole carriers from P3HT. Previous measurements of P3HT:PCBM solar cells have shown an increase in the device photocurrent upon replacing the planar PEDOT:PSS hole contact with a more three-dimensional carbon nanotube network coated with PEDOT:PSS,³¹ providing initial evidence of performance benefits. Importantly, in our experiments we have dispersed the nanotube network electrode within the P3HT:PCBM active blend layer in a manner that permits precise control of the active layer thickness and which does not influence the blend optical absorption. In this way, we have created a well-controlled model system for testing the efficacy of nanostructured electrodes through a systematic variation of the blend layer thickness, and we have confirmed the improvements in charge collection by correlating the device optical absorption, photovoltaic performance, and IPCE.

We form nanotube networks by dispersing single wall carbon nanotubes functionalized with C15H3 alkane chains into a P3HT:PCBM blend solution in chlorobenzene (2 wt. %, 50:50 weight ratio), with a nominal P3HT to nanotube weight ratio of 100:1 (~0.01 wt. % nanotube concentration in solution). The low magnification TEM image of blend films spincast from solution (1000 rpm) shows that the nanotube bundles have diameters of \sim 200 nm with lateral inter-spacings of ~ 5 to 10 μ m (Figs. 1(b) and 1(c)). Careful examination at high magnification reveals that nanotubes also form networklike structures within the film regions between bundles (Fig. 1(d)). The small nanotube loading percentage changes neither the measured ellipsometric film thickness nor the optical absorption of the P3HT:PCBM blend layers (Fig. 1(e)). This allows us to clearly distinguish the effects of the nanotube network on the charge carrier collection. Higher nanotube loading percentages might further optimize the device and result in improved performance, but that is beyond the scope of the current study.

We observed improved photovoltaic performance in P3HT:PCBM bulk heterojunction solar cells upon the addition of the nanotube network to the blend. Our solar cells consist of P3HT:PCBM blend layers (with or without nanotubes) sandwiched between bottom PEDOT:PSS/ITO and top Al electrical contacts. The active blend layer was spin-cast from solution in ambient air at speeds ranging from 500 to 1000 rpm in order to form layers with different thicknesses, and this was followed by a post-fabrication vacuum thermal anneal (150 °C for 10 min) to promote blend phase separation and reduce oxygen charge traps resulting from the ambient device processing.³⁶ A comparison of the J-V characteristics of the best-performing P3HT:PCBM devices with and without nanotubes shows a $\sim 10\%$ enhancement in the power conversion efficiency (PCE) upon addition of the nanotube network (Fig. 2(a)), from 3.4% to 3.8% under 100 mW/cm² AM1.5 G illumination-a significant increase given the small amount of added nanotubes. Nanotube addition to the blend leaves the device open circuit voltage ($V_{oc} \sim 0.63$ V) and fill factor $(FF \sim 0.63)$ essentially unchanged, with efficiency improvements coming mainly from a $\sim 9\%$ increase in the short circuit current (J_{sc} , from 8.7 mA/cm² to 9.5 mA/cm²), which is associated with the increase in the blend layer thickness for optimal device performance. Our enhanced J_{sc} is consistent with previous photocurrent improvements in P3HT:PCBM solar cells having three-dimensional nanotube:PEDOT:PSS hole contacts,³¹ but those suffered concomitant reductions in V_{oc} and FF due to the non-optimized active layer thickness and morphology.

We measured the photovoltaic characteristics of devices with different P3HT:PCBM blend layer thicknesses (ranging



FIG. 2. (Color online) Measured photovoltaic device characteristics of control (black solid square) and nanotube-containing (red solid circle) P3HT:PCBM blend solar cells. Error bars denote the standard deviations from 4 or 5 measured devices. (a) *J*-*V* characteristics of the highest performing P3HT:PCBM blend solar cells with and without nanotubes, illuminated under 100 mW/cm² AM1.5 G conditions. (b)-(d) Plots of average device photovoltaic PCE, J_{sc} , V_{oc} , and FF vs the device active blend layer thickness.

from \sim 74 nm to \sim 126 nm) and found that the bestperforming devices with nanotube networks had a $\sim 22\%$ thicker active layer than control devices without nanotubes (\sim 110 nm versus \sim 90 nm; Figs. 2(b) and 2(c)). The presented data set is taken from one representative batch of experiments consisting of the fabrication and measurement of 4 or 5 devices for each active layer thickness. The nanotube network electrodes *increase* the average J_{sc} and PCE of the highest performing devices (with 110 nm thick active layers) by 9% and 11%, respectively, compared to the best performing control devices without nanotube networks (with 90 nm thick active layers). Increasing the blend thickness from 90 to 110 nm without adding the nanotube networks reduces the average J_{sc} and PCE by ~1% to 2%. A further increase of the thickness beyond 110 nm degrades the J_{sc} of both nanotubecontaining and control devices (Fig. 2(c)), decreasing the PCE. Voc and FF remain constant in the tested blend thickness range for both nanotube-containing and control devices (Fig. 2(d)). We note that the identical thickness-dependent trends in the photovoltaic characteristics were consistently reproduced throughout 3 independent batches of experiments, with fluctuations in the baseline device performance, likely due to uncontrolled factors such as ambient air exposure. The optimal blend layer thickness in a bulk heterojunction solar cell is generally decided by the interplay between the optical absorption and the free charge carrier recombination, both of which increase overall with increasing blend layer thickness, although the former does so in a more complex oscillating manner due to optical interference effects.³⁷ The tested blend thickness range in this study falls into the first maximum region in such an oscillation.

Measurements of the device IPCE for a 110 nm thick active layer device show that the effect of the nanotubes is to uniformly increase the photo-conversion efficiency by 14% across the spectral absorption range as compared to the control device without nanotubes (Fig. 3). Because the blend layer optical absorption is unaffected by the incorporation of the nanotube networks and control P3HT:nanotube devices (without PCBM) display no photovoltaic response, these measurements strongly suggest the nanotube network's primary role in improving charge carrier collection. The observed commensurate increase in the average J_{sc} in the 110 nm thick blend devices (by ~13%, from 7.9 mA/cm² to 8.9 mA/cm²; Fig. 2(c)) correlates well with the measured IPCE improvement.

B. P3HT-C₆₀ bilayer devices

We more clearly demonstrate the role of the carbon nanotube network electrode on solar cell performance by studying its effect on the photovoltaic characteristics of model P3HT-C₆₀ *bilayer planar* solar cells. In these devices, exciton dissociation and free carrier recombination occur only at the planar P3HT-C₆₀ interface, unlike in the bulk heterojunction in which these processes occur throughout the entire active layer thickness. We therefore expect lower overall performance of these planar devices as compared to the bulk heterojunction architecture described above. Our model devices consist of bilayers of different thicknesses of



FIG. 3. (Color online) Measured representative IPCE of control (black solid square) and nanotube-containing (red solid circle) P3HT:PCBM blend solar cells having 110 nm active blend layers.

solution-processed P3HT and thermally deposited C_{60} (40 nm thick) sandwiched between ITO/PEDOT:PSS and Al electrical contacts. We include nanotube networks only in the P3HT layer by mixing 0.01 wt. % concentrations of nanotubes into a P3HT solution in chlorobenzene. Control P3HT:nanotube devices without a C_{60} layer exhibit a negligible photovoltaic response.

The average PCE of nanotube-containing P3HT-C₆₀ bilayer solar cells also increases for all measured P3HT thicknesses as compared to the PCE of control devices without nanotube electrodes (Fig. 4(a)). Similar to that measured for bulk heterojunction devices, the performance improvement primarily stems from a significant increase in J_{sc} (Fig. 4(b)). V_{oc} and FF also increase for all P3HT thicknesses (Fig. 4(c)), coinciding with a reduction in the device leakage current,³⁸ possibly due to the presence of insulating alkane chains within the P3HT layer. Unlike the bulk heterojunction device, the nanotube network electrode does not measurably increase the optimal P3HT layer thickness for device performance beyond 49 nm. Nanotube networks provide an average J_{sc} increase of ~29% for devices having a 49 nm thick P3HT layer (from 1.7 mA/cm² to 2.2 mA/cm²), along with $\sim 22\%$ and $\sim 4\%$ increases in V_{oc} and FF, respectively. The combined improvements result in an average PCE enhancement of $\sim 80\%$ (from 0.20% to 0.36%).

The hole conductivity (σ) of a P3HT film increases on average by ~27% (~10⁻⁶ S/cm range) upon addition of the nanotube network electrode.³⁸ Model ITO/PEDOT:PSS/P3HT/Au devices showed a linear *J-V* behavior over the measured voltage bias range (0-2 V), indicating a dominance of Ohmic current from bulk free carriers in the P3HT,

$$J = \sigma V/d = q n_h \mu_h V/L, \tag{1}$$

over the space charge limited current injected from the contacts,³⁹

$$J = \frac{9}{8} \varepsilon_o \varepsilon_r \mu_h \frac{V^2}{L^3},\tag{2}$$

where q is the electron charge, n_h is the free hole concentration, μ_h is the free hole mobility, ε_o is the vacuum



FIG. 4. (Color online) (a)-(c) Measured photovoltaic device characteristics of control (black solid square) and nanotube-containing (red solid circle) P3HT-C₆₀ bilayer solar cells. The plots show the average PCE, J_{sc} , V_{oc} , and FF with respect to different device P3HT layer thicknesses, measured under 100 mW/cm² AM1.5 G illumination. Error bars denote the standard deviations from 4 or 5 measured devices. (d) Plots of simulated IPCE for bilayer solar cells vs the P3HT layer thickness (*L*) with two different effective hole mobilities in the P3HT layer (solid black (bottom) and red (top) lines, each corresponding to control and nanotube-containing devices; mobility values are indicated), obtained from Eq. (7) using $\beta_{re} = 2$ cm/s and $\Lambda = 23$ nm.

permittivity, ε_r is the relative dielectric constant (~3 for P3HT), and *L* is the P3HT thickness. By equating Eqs. (1) and (2) at V = 2 V, we estimate a lower bound $n_h \sim 2 \times 10^{17}$ cm⁻³ with corresponding $\mu_h \sim 10^{-5}$ cm²/V s. The relatively high free hole concentration and somewhat low hole mobility are consistent with oxygen-induced doping and charge trap formation during ambient device processing^{36,40} and likely occur equally in P3HT films with and without nanotube networks. Although the film conductivity alone cannot independently determine n_h and μ_h , we expect that most of the observed σ increase following nanotube addition is due to an enhancement in the *effective* hole mobility ($\mu_{h,eff}$) by the nanotube network electrodes.

A simplified planar bilayer solar cell model illustrates the effect of $\mu_{h,eff}$ on the device free carrier collection and shows that the experimentally observed enhanced photocurrent output (J_{sc}) is consistent with an increased $\mu_{h,eff}$. Under the simplifying assumption that the device J_{sc} is limited by the transport of dissociated free holes in P3HT, and considering that free carrier loss occurs only via surface recombination at the P3HT-C₆₀ interface, we can write J_{sc} as

$$J_{sc} = J_{ex} - J_{re}, \tag{3}$$

where J_{ex} is the steady-state exciton flux reaching the P3HT-C₆₀ interface (i.e., the total available hole carrier flux, assuming 100% exciton dissociation), and J_{re} is the surface carrier recombination loss. Here, such loss can be parameterized in terms of a surface recombination velocity (β_{re}) as $J_{re} = \beta_{re} n_{h,photo}$, with $n_{h,photo}$ being the photogenerated free hole concentration. If dissociated free holes are collected by drift transport— $J_{sc} = q n_{h,photo} \mu_{h,eff} E$, with electric field E then Eq. (3) becomes

 $J_{sc} = \frac{J_{ex}}{1 + \beta_{re}/(\mu_{h,eff}E)} = \frac{J_{ex}}{1 + \gamma_{h,eff}},$ (4)

where $E = V_{bi}/(L + t_{C_{60}})$, $\gamma_{h,eff}$ is the ratio of surface recombination and hole drift velocities, V_{bi} is the difference in the work functions of PEDOT:PSS and Al (0.9 eV), and $t_{C_{60}}$ is the C_{60} thickness (40 nm; see the inset of Fig. 4(d)). The enhanced photocurrent after the addition of the nanotube network electrodes ($J_{sc,NT}$) is then

$$\frac{J_{sc,NT}}{J_{sc}} = \frac{\mu_{h,eff,NT}}{\mu_{h,eff}} \left(\frac{1 + 1/\gamma_{h,eff}}{1 + 1/\gamma_{h,eff,NT}} \right),\tag{5}$$

with $\mu_{h,eff,NT}$ being the effective carrier mobility in the P3HT/nanotube network. For $\beta_{re} \gg \mu_{h,eff}E$ (i.e., a recombination velocity higher than the carrier drift velocity), Eq. (5) simplifies to $J_{sc,NT}/J_{sc} \approx \mu_{h,eff,NT}/\mu_{h,eff}$ which is roughly consistent with our observations of a ~29% increase in J_{sc} from a comparable increase in σ (i.e., $\mu_{h,eff}$) upon introduction of the nanotube network into the P3HT layer.

A plot of simulated IPCE as a function of P3HT layer thickness (*L*) reproduces the experimentally observed optimal *L* for the maximum J_{sc} (Fig. 4(d)). Using a onedimensional exciton diffusion model, the steady-state exciton flux reaching the P3HT-C₆₀ interface, J_{ex} , can be expressed as⁴¹

$$J_{ex}(L) = I_o \left(\frac{\alpha^2 \Lambda^2}{\alpha^2 \Lambda^2 - 1}\right) \left(\frac{\operatorname{csch}(L/\Lambda) - e^{-\alpha L} \operatorname{coth}(L/\Lambda)}{\alpha \Lambda} - e^{-\alpha L}\right)$$

$$\equiv I_o \zeta(\alpha, \Lambda, L), \tag{6}$$

where Λ is the exciton diffusion length (~5 to 20 nm)⁴⁰⁻⁴⁴ and I_o is the input light flux. By combining Eqs. (4) and (6), the IPCE can be given as

$$IPCE(L,\mu_{h,eff}) \equiv J_{sc}/I_o = \frac{\zeta(\alpha,\Lambda,L)}{1 + \beta_{re}/\left[\mu_{h,eff}V_{bi}/(L + t_{C_{60}})\right]}.$$
 (7)

A plot of Eq. (7) (with $\beta_{re} = 2 \text{ cm/s}$ and $\Lambda = 23 \text{ nm}$) illustrates a peak device performance at a ~50 nm thick P3HT layer thickness (Fig. 4(d)), independent of the P3HT layer effective mobility ($\mu_{h,eff}$) and consistent with our experimental observations. The P3HT exciton diffusion length best describing our data (23 nm) falls at the upper bound of the reported values (>20 nm),⁴² possibly because the molecular structure of pure P3HT in a bilayer device is unaffected by the presence of fullerene as in a P3HT:PCBM blend. A previous study shows the influence of the blend on the polymer molecular ordering and the resulting exciton diffusion length.⁴⁵

IV. CONCLUSION

In summary, using model carbon-nanotube-dispersed P3HT:PCBM blend devices, we confirmed that the nanostructured electrodes extending into the bulk heterojunction blend active layer could allow an increase in the optimal active blend layer thickness by increasing the collection efficiency for dissociated free carriers. Carbon nanotube networks provided a straightforward implementation of nanostructured hole collectors in P3HT:PCBM blend devices and resulted in as much as a 10% increase in the device power conversion efficiency from a 20% increase in the associated optimal active layer thickness, which was caused by improved J_{sc} in the tested blend thickness range. For larger thicknesses, we expect that the effects of nanostructured electrodes will be manifested mainly by the enhanced FF over planar electrical contacts, because the FF is more strongly affected by charge recombination. We note that nanostructured electrodes are generally applicable to solar cells relying on transport in lowmobility semiconductors. The presented device implementation, having randomly dispersed nanotube network electrodes and a low nanotube loading percentage, is far from an ideal structure, and we expect further enhancements from more ordered versions of this concept.

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