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Electrospray-assisted characterization and deposition of chlorosomes to fabricate a biomimetic light-harvesting device

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Photosynthesis is an efficient process by which solar energy is converted into chemical energy. Green photosynthetic bacteria such as *Chloroflexus aurantiacus* have supramolecular antenna complexes called chlorosomes attached to their cytoplasmic membrane that increase the cross section for light absorption even in low-light conditions. Self-assembled bacteriochlorophyll pigments in the chlorosome interior play a key role in the efficient transfer and funneling of the harvested energy. In this work it was demonstrated that chlorosomes can be rapidly and precisely size-characterized online in real time using an electrospray-assisted mobility-based technique. Chlorosomes were electrospray-deposited onto TiO_2 nanostructured films with columnar morphology to fabricate a novel biomimetic device to overcome the solvent compatibility issues associated with biological particles and synthetic dyes. The assembled unit retained the viability of the chlorosomes, and the harvesting of sunlight over a broader range of wavelengths was demonstrated. It was shown that the presence of chlorosomes in the biomimetic device had a 30-fold increase in photocurrent.

Introduction

Solar energy is a plentiful resource distributed over the surface of the earth and is already used to generate electricity trough photovoltaic devices. In recent years, dye-sensitized solar cells (DSSCs) based on a metal oxide film,[1] typically a titanium dioxide (TiO_2) nanostructured thin film, have been increasingly investigated to overcome the high-cost of fabrication of silicon-based photovoltaic devices. Key challenges for these DSSCs reside in increasing the photon collection efficiency over a broad spectrum of wavelengths in the visible regime, and in retarding the charge recombination process. In our previous studies, a TiO_2 nanostructured film with columnar morphology[2] was observed to be more efficient both in preventing the electron-hole recombination process and in enhancing the electron transport across the film than a granular morphology in a DSSC. A TiO_2 film made of vertically aligned nanostructured columns results in a higher interfacial area between the hole carrier (an electrolyte or a conductive polymer) and the electron acceptor (TiO_2) materials with highly-efficient electron transport properties.

When it comes to solar energy harvesting, nature provides valuable knowledge of the materials, of their functionality, and of the assembly mechanisms to produce efficient light-harvesting structures such as the ones found in plants and photosynthetic bacteria. A novel approach to develop light-harvesting devices to generate electricity, based on the concept of biomimetics, is to combine engineered nanostructured TiO_2 films having an efficient electron transport morphology, nano-columns or nano-wires, with robust natural light-harvesting supramolecular structures.

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Broader context

Dye-sensitized solar cells (DSSCs) have been touted as lower cost alternates to silicon-based photovoltaic devices. One of the challenges is to improve the energy conversion efficiency of DSSCs by extending the absorption at longer wavelengths. One approach is to extract the highly efficient natural photosynthetic components from green bacteria and incorporate them into robust nanostructured systems to fabricate engineered biomimetic hybrid devices. This paper reports a generalized fabrication methodology of a multilayered biomimetic light-harvesting device that combines a nanostructured TiO_2 film with columnar morphology with natural light-harvesting supramolecular structures, called chlorosomes, found in green bacteria. The key aspect was the use of an electrospray system to aerosolize the chlorosomes, and then deposit them using electric fields. The incompatibility issue of the dye (organic solvent) and biological components (aqueous solvents) was overcome by the sequential process: aerosolization, drying in flight, followed by deposition. An online, real time mobility-based technique was used to determine the size and charge characteristics of chlorosomes. The results of photocurrent as a function of wavelength show a thirty fold increase in photocurrent when the chlorosomes were incorporated into the solar cell. The approaches demonstrated in this work have broader applicability in the characterization and sequential deposition of components to fabricate biomimetic solar cell devices.

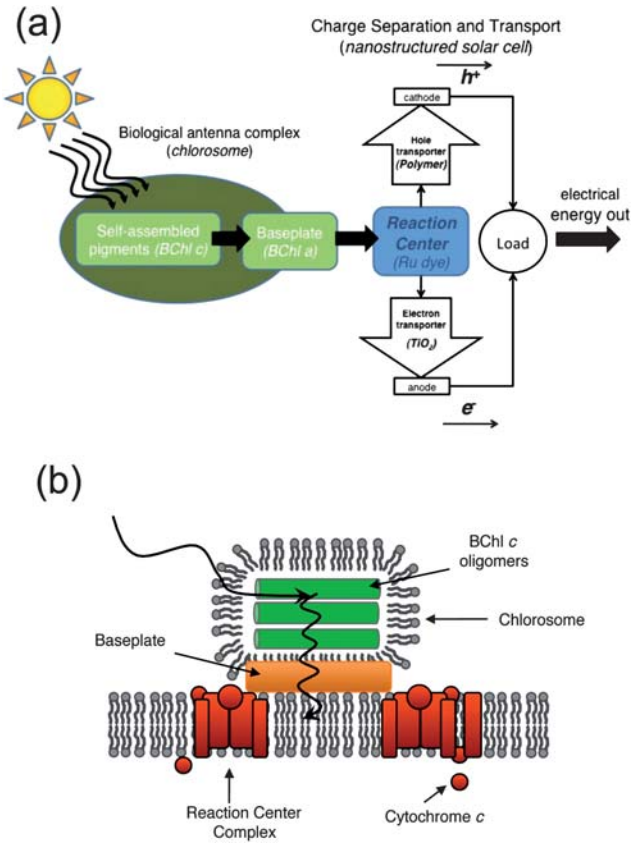

Fig. 1 (a) Illustration of the concept of a biomimetic hybrid device to harvest sunlight and structure of the chlorosome. (b) Cartoon showing the structure of chlorosomes in the green photosynthetic bacteria.

The concept for the fabrication of a biomimetic light-harvesting device, which uses chlorosomes extracted from the green photosynthetic bacterium *Chloroflexus aurantiacus* as light-harvesting supramolecular structures, is illustrated in Fig. 1(a). Chlorosomes are large ellipsoidal bodies made of an envelope of proteins and lipids that enclose both carotenoids and oligomers of self-assembled bacteriochlorophyll (BChl) *c* molecules (Fig. 1(b)). Chlorosomes are attached to the cytoplasmic cell membrane by the so-called baseplate complex, which contains BChl *a* pigments and it also serves as an intermediary in energy transfer between BChl *c* oligomers in the chlorosome and the membrane. Excitation absorbed by the chlorosome is ultimately used by a reaction center (RC) to facilitate electron transfer and generate a proton gradient across the membrane. Chlorosomes have drawn attention for applications in photovoltaics because of the effective natural organization of bacteriochlorophylls in the antenna, which provides optimal light collection and energy funneling.[3,4] When chlorosomes are extracted from the organism, however, the RC remains in the membrane.[5] A dye molecule that absorbs light in the same range as the BChl *a* in the natural RC (absorbance = 865 nm) could be used as a substitute to promote excitonic energy transfer and subsequent charge separation in the nanostructured solar cell. In the biomimetic light-harvesting device proposed in this work (see Fig. 1(a)) photons are absorbed by the chlorosomes, which are deposited onto a dye-chemisorbed TiO_2 film by a noninvasive method, and funneled by a fluorescence resonance energy transfer (FRET) mechanism to the dye molecule that serves as an artificial reaction center. When the excitonic energy reaches the dye, charge separation occurs that results in the injection of electrons into TiO_2 nanostructured columns and holes into a conductive polymer film, thereby resulting in the generation of electricity.

The diffusion length of the electron–hole pair, or exciton, in chlorosomes strongly depends on their size and on the amount of BChl *c* content.[6] Therefore, size characterization of chlorosomes is an important aspect for the effective application of these antenna complexes in photovoltaics. Current microscopy techniques for characterization often require complex protocols and the size distribution is generally obtained by visual inspection and direct count of the chlorosomes in several images. An attractive alternative for a rapid and precise size characterization of chlorosomes is the charge-reduced electrospray mobility analysis.[7–9] By electrospraying, a method of liquid atomization that generates multiply charged particles, single chlorosomes can be aerosolized and after adequate charge neutralization their size distribution can be precisely measured online, in real time, using an electrical mobility-based technique.[10] Furthermore, the electrospray is an elegant solvent-free deposition technique that allows for a one-step deposition method of chlorosomes (and other bio-particles), without modifying their structure or functionality[7,8] onto a grounded substrate with near 100% deposition efficiency.[11] For the fabrication of the biomimetic device the electrospray-deposition technique is highly preferred to avoid undesired contact of solvents with the components of the device. Since the presence of water in which the chlorosomes are dispersed may cause the dye to desorb from the surface of the TiO_2 columns, it is essential to deposit the chlorosomes by a method that allows the water to evaporate without making contact with the dye. Furthermore, because the electrosprayed chlorosomes are multiply charged, they can be deposited ballistically allowing penetration to the lower part of the TiO_2 columns by overcoming the hindrance effect caused by the columns themselves as in other aerosol deposition methods where Brownian motion and chlorosome–column interactions may dominate. Subsequently, a hole-carrier polymer must be deposited onto the chlorosomes to enhance charge separation and prevent electron–hole recombination, and this step must be solvent-free to prevent the BChl *c* oligomers from denaturing when they come into contact with the organic solvent.

In this work, the size distribution of chlorosomes from *C. aurantiacus* was investigated by electrospray-assisted mobility analysis. Furthermore, the use of electrospray to deposit intact chlorosomes and a conductive polymer onto a TiO_2 nanostructured film with columnar morphology was studied. Finally, a biomimetic light-harvesting device was fabricated by incorporating intact chlorosomes into a DSSC.

Experimental

Materials

Chlorosomes were extracted[12] from the green bacterium *Chloroflexus aurantiacus* and dispersed in pure water and in a buffer solution for size distribution and deposition experiments, respectively. A 0.33 mM solution of tris(isothiocyanato)-ruthenium(II)-2,2′:6′,2″-terpyridine-4,4′,4″-tricarboxylic acid,

tris-tertrabutylammonium salt (Black dye; 620-1H3TBA, Solaronix, Aubonne, Switzerland) was prepared in anhydrous ethanol. Conductive p-type polymer poly(3-octylthiophene-2,5-diyl) (P3OT) was obtained from Sigma-Aldrich (St. Louis, MO, USA) and dissolved in toluene to a concentration of 10 mg mL^{-1}. Indium tin oxide (ITO)-coated glass slides were purchased from Delta Technologies (Stillwater, MN, USA) and used after cleaning them with ethanol.

Electrospray-assisted characterization of chlorosomes

A syringe pump was used to feed a chlorosome suspension through a stainless steel capillary needle with id of 160 μm at a flow rate of 1 μL min^{-1}. A high-voltage power supply was connected to the capillary, and a positive potential of >4 kV was applied for cone-jet formation at the capillary outlet.[11] The needle was set inside a closed chamber, and particle-free CO_2 gas was introduced at a rate of 0.3 lpm. The CO_2 gas was used to prevent the formation of corona discharge at the tip of the capillary needle, due to the high surface tension of water, and to carry the aerosol particles to the sizing instrument. After the electrospray generation, the highly charged aerosol particles were passed through a bipolar neutralizer (Kr^{85}) to reduce the number of charges and bring them to an equilibrium charging state. The neutralizer was placed at the exit of the chamber to minimize loss of chlorosomes due to deposition onto system walls by the external electric field. Mobility-based real-time particle size distribution measurements were carried out using an electrostatic classifier (TSI Inc., Model 3080) and a long differential mobility analyzer (DMA, TSI Inc., Model 3081), which classifies particles according to their electrical mobility, coupled with an ultrafine condensation particle counter (UCPC, TSI Inc., Model 3025A), which gives the number concentration of particles classified by the DMA. The particle's electrical mobility is dictated by the particle size and charge; a more detailed description of the principle of functioning of the DMA can be found elsewhere.[10]

Biomimetic device fabrication

Columnar TiO_2 nanostructured film was deposited on an ITO-coated glass using a flame aerosol reactor in a single step process as described in previous publications from our group.[2] The columns were single crystals of approximately 2 μm height. A monolayer of black dye was chemisorbed on the surface of TiO_2 columnar films by immersing the films in the 0.33 mM dye solution overnight. After the chemisorption procedure the films were rinsed with anhydrous ethanol several times to remove any excess of dye. Following the dye chemisorption procedure, an aqueous suspension of chlorosomes containing a small amount of ammonium acetate, to increase the effective electrical conductivity of the suspension and facilitate the formation of the cone-jet, was electrosprayed in a similar setup as the one used to carry out the size distribution measurements. For these deposition experiments, however, the substrate (ITO/TiO_2/dye) was placed perpendicular to the capillary needle at a distance <5 mm from the chamber, to form an exit for the CO_2 gas. To enhance the hole transport and to prevent electron–hole recombination, hole-carrier P3OT conductive polymer solution was electrospray-deposited on an ITO/TiO_2/dye/chlorosomes substrate. For polymer deposition, no chamber and CO_2 gas were required, making the deposition procedure even simpler. A needle with id of 1 mm was used instead of the capillary needle to avoid clogging. The substrate was placed perpendicular to the needle at a distance of 1 cm.

UV-visible absorption measurements

Light absorption measurements of films deposited on ITO-coated glass were carried out with a Varian Cary UV-Visible spectrophotometer (Series II). A certified reflectance standard (Labsphere) provided by the spectrophotometer manufacturer was used during the measurement of the films. These measurements were done under ambient conditions.

Fluorescence measurements

All fluorescence measurements were made on a fluorometer (Photon Technology International, Inc.) equipped with a Xe light source under ambient conditions. For measurements of nano-structured films, a 45° geometry between excitation and detection was used. The fluorescence spectra of chlorosomes shown in Fig. 3(b) were recorded with 440 nm excitation.

Photon-to-current quantum efficiency measurements

The photocurrent action spectra were acquired using a modified spectrofluorimeter (Spex Tau 2). The active area of the devices was approximately 0.2 cm^2. The short-circuit photocurrent was measured as a function of wavelength using an electrometer (Keithley 6514). The raw photocurrent spectrum per active area of device was divided by the relative photon flux spectrum, obtained from the measured lamp profile; and this is the corrected photocurrent action spectrum of each sample reported in Fig. 5(b). Note that the reported photocurrent action spectra are not actual incident photon to current conversion efficiency (IPCE) measurements.

Results and discussion

Electrospray-assisted online real time characterization of chlorosomes

Chlorosomes from the green bacterium *C. aurantiacus* suspended in water were electrosprayed to generate single chlorosome particles. As shown in Fig. 2(a), the size distribution is bimodal with a sharp mode mobility diameter (D_m) at 24 nm and a smaller peak at 80 nm. The first peak represents the width of the chlorosomes, which is in good agreement with the reported value of 30 nm from microscopy images for chlorosomes from *C. aurantiacus*.[4,12,13] The second peak most probably represents chlorosome agglomerates and impurities of cell fragments left over from the isolation procedure. The chlorosomes are known to have an aspect ratio (β) of approximately 3.0,[4,12,14] and thus D_m represents a diameter equivalent to a spherical particle with the same electrical mobility as the chlorosomes. Nevertheless, because the β of the chlorosomes is relatively low and the electric field in the DMA was less than 1000 V cm^{-1} the chlorosomes, which are ellipsoidal particles, were thought to be randomly oriented in the DMA.[9] Therefore the measured D_m most probably

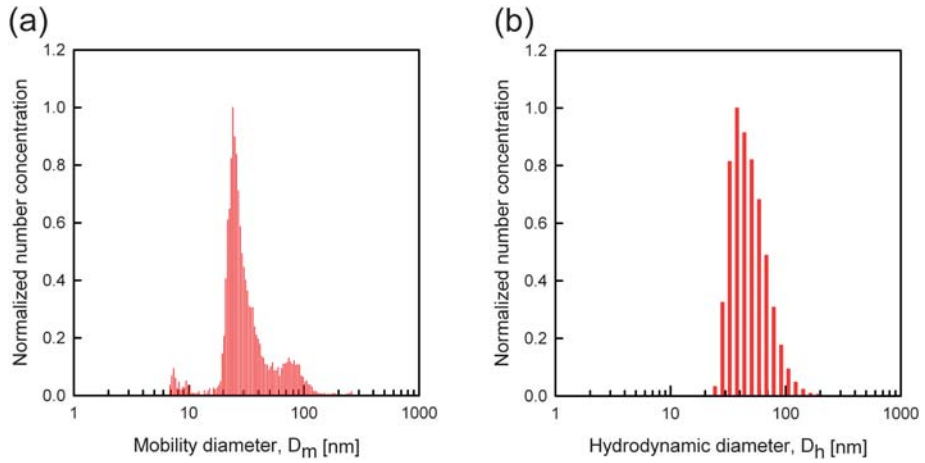

Fig. 2 (a) Normalized particle size distribution of single chlorosomes aerosolized with an electrospray and classified with a differential mobility analyzer. (b) Normalized particle size distribution of chlorosomes suspended in deionized water measured with a dynamic light scattering (DLS) instrument.

corresponds to the width of the chlorosomes. These findings are supported by the results of Allmaier *et al.*[7] and Kim *et al.*[9] who, using a similar electrospray-assisted mobility-based technique and electron microscopy, demonstrated that the D_m of cylindrical-shaped virus fragments ($\beta = 4.2$) corresponded directly to the diameter of the viruses and that of cylindrical nanowires ($\beta < 8.0$) corresponded to their projected area diameter, respectively. In an ancillary experiment the same suspension used in the electrospray-assisted size distribution measurement was analyzed with dynamic light scattering (DLS), and the resulting size distribution measurement is shown in Fig. 2(b). The mode hydrodynamic diameter (D_h) was 40 nm. For prolate spheroids, Perrin's formula, which introduces a correction factor for non-spherical particles and end effects, should be used to calculate the size. However, for spheroids with small aspect ratios (<3) Perrin's formula approaches the Stokes–Einstein expression. Defining an effective spherical diameter as $D_h = (ab^2)^{1/3}$ as done by Wang *et al.*,[15] where a and b are the short and long axes of the spheroid, and taking $b = 24$ nm (from the electrical mobility measurement), gives a chlorosome length of 111 nm. The dimensions of the chlorosomes obtained with the electrospray-assisted and DLS techniques, without the implementation of microscopy images, are in very good agreement with previous literature reports.[4,6,13,14,16] Both methods, which complement other techniques, can be coupled in the size characterization of non-spherical biological particles. Furthermore, the average number of elementary charges carried by electrosprayed spherical particles is known to scale with the square of the particle size,[17] which is proportional to the particle surface area. The chlorosomes electrosprayed in this study, having a mean surface area of 5725 nm^2 were found to carry 334 elementary charges before the charge neutralization and one elementary charge after they were passed through the bipolar neutralizer for the size distribution measurements. This charging of chlorosomes by electrospray enhances their effective deposition onto films with complex morphology as will be discussed later. The implementation of

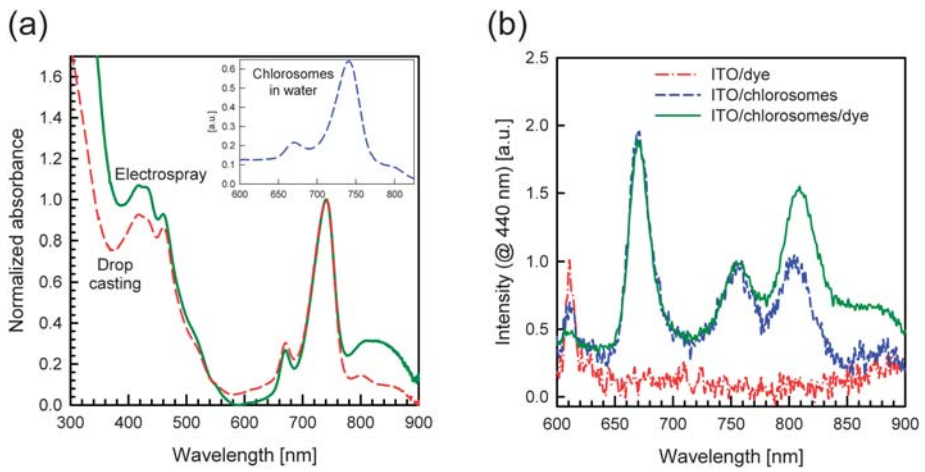

Fig. 3 (a) UV-visible absorption spectra of chlorosomes deposited on ITO-coated glass by drop-casting and by electrospray, normalized at the peak of the BChl *c* oligomers (740 nm). The inset shows the UV-visible absorption spectra of chlorosomes dispersed in water; the presence of a small amount of monomeric BChl *c* in the original suspension can be observed at 660 nm. (b) Fluorescence spectra of chlorosomes, dye, and dye/chlorosomes deposited onto an ITO-coated glass. The spectra were normalized at the 760 nm peak.

electrospray-deposition facilitates the fabrication of such devices because it simplifies the deposition step as compared to a layer-by-layer deposition technique,[14] a multiple step procedure that uses surfactants to generate electrostatic interactions to attach the chlorosomes to the substrate, and which would require further steps to remove undesired surfactant.

To assess any structural damage of chlorosomes during their electrospraying the UV-visible absorption spectra of drop-casted and electrospray-deposited chlorosomes on ITO-coated glasses were measured and plotted in Fig. 3(a). The spectra were normalized at the 740 nm peak to compare the key features of the absorption spectra of chlorosomes. The inset depicts the UV-visible absorption spectra of the chlorosome suspension used for the film fabrication. The characteristic peak at 740 nm in the spectra of both films indicates the presence of oligomers of BChl *c*, suggesting that the electrospray-deposited chlorosomes maintained their integrity and that no significant physical transformation nor degradation occurred during the electrospray-deposition. Fig. 3(b) also indicates that the observed monomeric BChl *c* peak at about 666 nm is not due to the electrospray-deposition, since it appears in the spectra of both films and in the spectrum of chlorosomes in water, but it may arise from partially damaged chlorosomes during the isolation from the bacterium, as shown in the inset where a small amount of monomeric BChl *c* can be observed in the absorption spectra of chlorosomes in water. Other authors[18] artificially assembled porphyrins films, to mimic the naturally self-assembled BChl *c* rods of chlorosomes, onto TiO_2 electrodes. The films were fabricated by spin-coating from a porphyrin solution onto the TiO_2 electrode, followed by heat treatment.[18] However, the authors reported that monomers of BChl were formed on the surface of the porphyrin stacks upon annealing. Furthermore, they concluded that although a more efficient charge separation occurs in the monomeric BChl, the exciton transfer from a oligomer to a monomer is energetically unfavorable, thus decreasing the electron injection rate into the TiO_2.[18] The difficulty in linking the BChl *c* oligomers to the surface of the semiconductor material demonstrates that the electrospray of whole chlorosomes represents a potential approach to avoid both the formation of large amount of monomeric BChl *c* during deposition and the additional steps for surfactant removal.[14,19]

Characteristics of chlorosome–dye interactions

The first step for the fabrication of a biomimetic light-harvesting device is to study the chlorosomes-dye energy transfer, because ultimately an interaction between those two components is critical for the functioning of the device. To study the chlorosome–dye interaction, an anhydrous ethanol solution of black dye was electrospray-deposited onto chlorosomes that were drop-casted onto an ITO-coated glass. The dye was electrosprayed to avoid contact of ethanol with the chlorosomes and thus, prevent. Fig. 3(b) shows the fluorescence spectra, with 440 nm excitation, of chlorosomes, of black dye, and of black dye/chlorosomes deposited onto ITO-coated glasses. The characteristic peaks of monomeric and polymeric BChl *c*, and the BChl *a* (baseplate) in the ITO/chlorosomes film appeared at 660, 760, and 805 nm, respectively as observed earlier by us and other authors.[4,20] Note that the film with black dye/chlorosomes showed higher

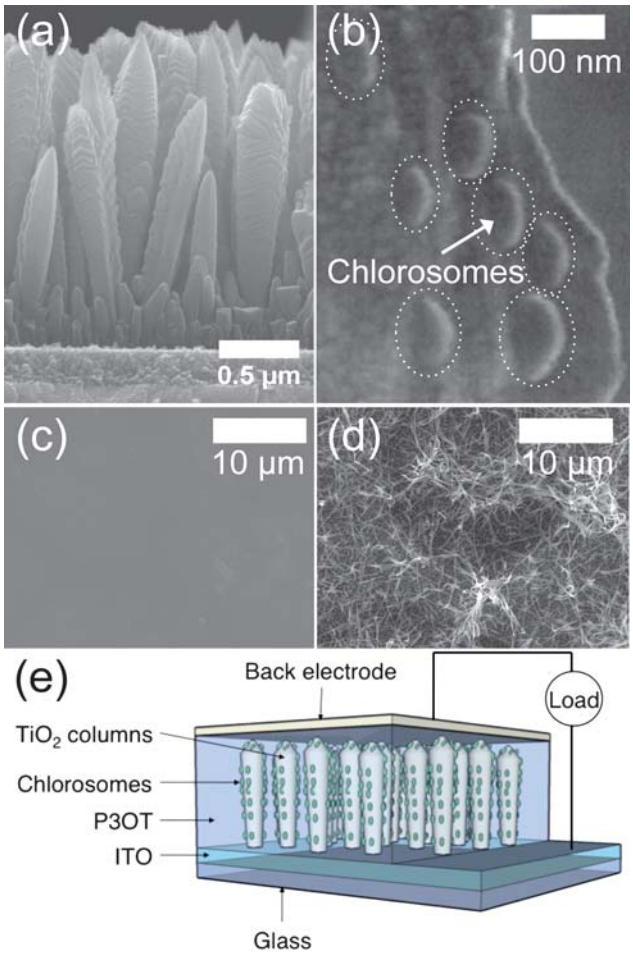

Fig. 4 (a) A TiO_2 nanostructured film with columnar morphology deposited onto an ITO-coated glass by a flame aerosol reactor. (b) Microscopy image of chlorosomes electrospray-deposited onto a columnar TiO_2 nanostructured film. Images of P3OT polymer film at spray distances of (c) 1.0 cm and (d) 1.7 cm. (e) Schematic cartoon of a novel biomimetic light-harvesting hybrid device that incorporates whole chlorosomes (without a natural RC) and nanostructured TiO_2 columns.

fluorescence intensity than the films with only chlorosomes at the baseplate peak (805 nm), while the intensities of the 660 nm and the 760 nm peaks remained unchanged. Furthermore, a slight shift was observed in the baseplate peak from 805 nm in the ITO/chlorosomes film to 809 nm in the ITO/chlorosomes/dye film. It is important to highlight that similar results were obtained from fluorescence measurements of black dye/chlorosomes in water (data not shown), implying that the increase in the fluorescence of the baseplate peak was neither a product of the electrospray deposition nor an artifact of the measurements. Although a precise reason could not be elucidated and further studies are needed to understand an excitation energy transfer mechanism from the chlorosome to the dye.

Fabrication and performance of a biomimetic light-harvesting device

As the second step in the device fabrication, chlorosomes were electrosprayed onto columnar TiO_2 nanostructures, which had chemisorbed dye on the surface. The TiO_2 nanostructured

columns synthesized by a flame aerosol reactor are shown in the image in Fig. 4(a), and the chlorosomes electrospray-deposited onto the TiO_2 film are shown in Fig. 4(b). The image in Fig. 4(b) corresponds to the lower part of a column, confirming the effective deposition of chlorosomes over the entire film, even in parts difficult to reach by other aerosol techniques such as atomization or nebulization. The deposition at the bottom of the columns along their long axis is a result of the multiple charging of chlorosomes during electrospray. The established electric field between the capillary needle and the grounded substrate forced the highly charged chlorosomes (having about 330 elementary charges) to penetrate deeper into the columns, by ballistic deposition, overcoming the effect of Brownian motion. Note that the values of 24 nm and 111 nm for the width and length of the chlorosomes, respectively, obtained with the electrospray-assisted mobility-based technique agree well with the dimensions of the chlorosomes observed in Fig. 4(b).

For the third step of device fabrication, P3OT polymer was electrosprayed onto an ITO-coated glass and the film morphology was analyzed with electron microscopy. The polymer film morphology, which plays a role in the hole transport and in preventing charge recombination, can be controlled by simply adjusting the spray distance[21] (the distance between the tip of the capillary needle and the substrate). A smooth film (Fig. 4(c)) was obtained at a spray distance of 1.0 cm while a ribbon-like morphology was obtained at 1.7 cm (Fig. 4(d)). At a longer spray distance, the toluene evaporated completely, leaving small particles of P3OT that grew on the substrate in a ribbon-like morphology. Conversely, at a shorter spray distance toluene evaporated only partially, but presumably its volume was small enough not to damage the integrity of the BChl *c* aggregates in the chlorosomes, as indicated by the spectra in Fig. 5(a), and upon collision of the toluene-P3OT droplet with the substrate, the polymer extended and reorganized on the substrate into a smooth layer.[21] In the following deposition experiments, the smooth morphology was preferred because it allowed a unidirectional hole transport and suppressed short circuiting during back contact formation.

Finally, a complete biomimetic light-harvesting hybrid device was constructed as shown in the cartoon in Fig. 4(e). The device consisted of the following layers of materials from the bottom to the top, glass/ITO/nano-columnar TiO_2/black dye monolayer/chlorosomes/P3OT polymer/Pt back electrode. The UV-visible absorption spectra of the device at each fabrication step are shown in Fig. 5(a) where the contribution of the individual components to the spectra can be deciphered. The characteristic peaks of monomers and oligomers of BChl *c* in the ITO/TiO_2/dye/chlorosomes film were in good agreement with the spectra in Fig. 3(a), implying again that the chlorosome deposition process did not damage the structure of the BChl *c* oligomers to any significant extent. Furthermore, a small peak of the BChl *c* oligomers can be observed in the spectra after the P3OT deposition that implies the presence of the efficient light-harvesting structures in the complete device. The photocurrent action spectra of devices with and without chlorosomes, and the photocurrent increase in a device with chlorosomes are shown in Fig. 5(b) top and bottom, respectively. The photocurrent increase was calculated from $\%P$ increase $= 100 \times (P_{\text{chlorosomes}} - P_{\text{dye only}})/P_{\text{dye only}}$, where P denotes photocurrent. Clearly, an interaction between the dye and chlorosomes enhanced the current generation in the nanostructured solar cell by several times over the entire range of wavelengths measured. In the device containing chlorosomes there is a remarkable photocurrent increase, particularly at longer wavelengths, from 640 nm to the near-infrared regime where BChl *c* oligomers and BChl *a* in the baseplate have their absorption maxima (Fig. 5(b) bottom). Indeed, it appears as though the ratio of the peak at 680 nm to the peak at 430 nm increases from 0.67 in the dye-only case, to 1.13 in the dye–chlorosome case, a 168% increase. Chlorosome-containing bacteria are able to survive under extreme low light conditions. Success of these organisms is due, in part, to the large cross-sectional area of the chlorosome as well as its high energy transfer efficiency, and to its ability of harvesting near-infrared radiation that does not originate from the sun, even at more than 2300 m oceanic depth near a volcanic vent.[22]

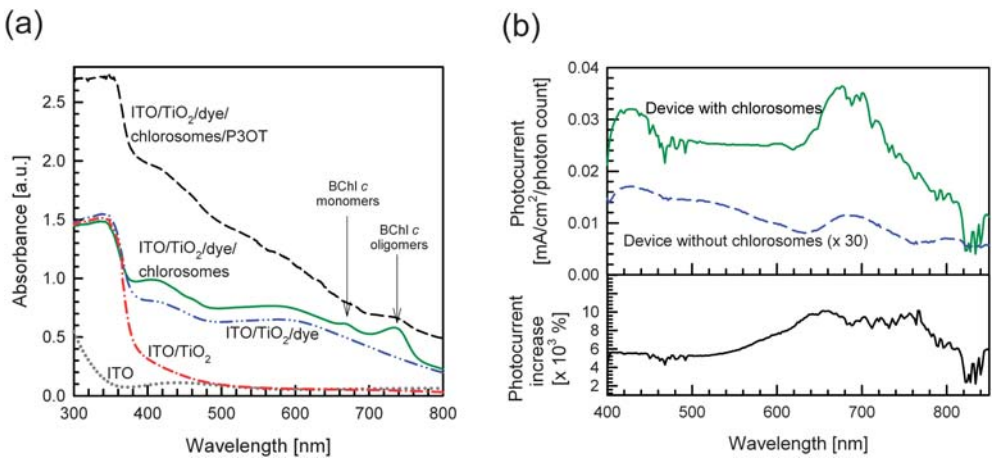

Fig. 5 (a) UV-visible absorption spectra of the biomimetic device at different steps of the fabrication; ITO-coated glass; ITO/TiO_2 nanocolumns, ITO/TiO_2 nanocolumns/dye, and ITO/TiO_2 nanocolumns/dye/chlorosomes/P3OT. (b) Measured photocurrent in biomimetic devices with and without chlorosomes. The photocurrent of the device without chlorosomes was increased 30 times for plotting purposes. The bottom figure shows the percentage increase in the photocurrent.

Conclusions

This study represents the first attempt to build a complete biomimetic light-harvesting device that incorporates intact whole chlorosomes from green bacteria. The electrospray technique was successfully applied to aerosolize intact chlorosomes to measure their particle size distribution online in real-time, and to deposit them onto a TiO_2 nanostructured film. The use of chlorosomes with naturally self-assembled pigments rather than artificially self-assembled bacteriochlorophyll pigments[18] takes advantage of the efficient organization of the pigments in the antenna and prevents the formation of large amounts of undesired monomeric BChl *c* on the surface of the oligomers that hinder the electron transport to the TiO_2 film as occurred in artificially assembled rods of BChl *c*.[18] Some BChl *c* monomers may form during the chlorosomes isolation procedure, however, the electrospray-deposition did not seem to affect the structure of the rods. The presence of the chlorosomes in the device increased the photocurrent over thirty times. The results presented here are encouraging, nevertheless, additional studies must be carried out to elucidate the interactions of chlorosomes with the black dye, and perhaps with other dyes, and to assess the stability of the components in the long term with the aim of improving the efficiency of such devices.

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