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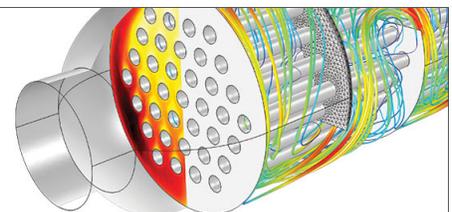
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Results of optical spectroscopy reveal strong influence of plasmon excitations in silver nanowires on the fluorescence properties of poly(3-hexylthiophene) (P3HT), which is one of the building blocks of organic solar cells. For the structure where a conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) was used as a spacer in order to minimize effects associated with non-radiative energy transfer from P3HT to metallic nanoparticles, we demonstrate over two-fold increase of the fluorescence intensity. Results of time-resolved fluorescence indicate that the enhancement of emission intensity can be attributed to increased absorption of P3HT. Our findings are a step towards improving the efficiency of organic solar cells through incorporation of plasmonic nanostructures. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4829623]

Optically induced plasmon excitations make metallic nanoparticles promising structures for enhancing the efficiency or sensitivity of various devices including optical emitters,[1] biosensors,[2] and medical imaging agents.[3] It has also been postulated and demonstrated that incorporating properly selected metallic nanostructures into photovoltaic and water-splitting assemblies can lead to measurable improvement of their performance. It has been shown that the combination of strongly catalytic TiO_2 nanoparticles with strongly plasmonic Au nanoparticles yields significant improvement of the efficiency of catalytic water splitting upon visible light illumination. This effect is attributed to plasmonically induced increase of absorption of the electromagnetic radiation in such a hybrid system.[4,5] Similar conclusions have also been derived for structures involving silver (Ag) nanoparticles.[6] Appropriately chosen metallic nanoparticles have also been used to increase the absorption of naturally evolved photosynthetic complexes and it was found that enhancement can be obtained for silver island films[7] as well as for spherically shaped Au and Ag nanoparticles. Recently, strong modifications of the optical properties of photosynthetic complexes were demonstrated upon coupling them to silver nanowires (AgNWs).[8] All these results provide solid evidence that incorporation of metallic nanoparticles can be used with a wide range of architectures and materials.[9]

In this paper, we focus on semiconducting polymers because of their promise for low-cost, lightweight solar cells. Several approaches have been reported and in most cases the incorporation of silver nanoparticles indeed results in an improvement of the overall efficiency of a solar cell based upon P3HT:PCBM (Poly(3-hexylthiophene):Phenyl-C61-butyric acid methyl ester) bulk heterojunction device. Theoretical studies[6] focused on spherical nanoparticles embedded in the active layer of the solar cell suggest that the absorption can be increased by a factor of 1.6 for a structure with optimal spacing between the nanoparticles of a well-defined size. The effect of a dielectric coating of metallic nanoparticles upon the absorption increase in organic solar cells was investigated in this work. Experimental attempts concern incorporation of silver spherical nanoparticles as well as nanowires into the active layer.[10] The plasmon-induced increase of the absorption of 50% in the spectral range around 500 nm resulted in approximately 4% efficiency of the solar cell.[10] Incorporation of metallic nanoparticles directly into the active layer places them essentially in direct contact with absorbing molecules. In this case, part of the absorbed energy is lost via non-radiative energy transfer from the absorber to the metallic nanostructures.[11] There have also been several attempts to fabricate structures incorporating metallic grids or nanowires into the back electrode of a device, mainly in order to replace ITO as the electrode material.[12–15] In all these cases, the correlation between plasmon excitations in metallic nanostructures and improvement of the efficiency of the solar cell was to some degree speculative, as no fluorescence imaging experiments aimed at proving such a correlation were carried out.

In this Letter, we show that plasmon excitations in silver nanowires strongly enhance the absorption of the polymer P3HT in a structure, in which the nanowires are embedded in a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer. In such a hybrid nanostructure, we reduce the influence of the non-radiative energy transfer by introducing a separation layer between absorbing molecules and metallic nanoparticles. The results of time-resolved fluorescence show that the fluorescence lifetime of the P3HT emission is unaffected by the interaction with plasmonic excitations in silver nanowires. We conclude that the dominant mechanism responsible for the observed increase of the P3HT fluorescence is an increase of the absorption rate. This result can be considered important for devising plasmonic organic solar cells.

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AgNWs were synthesized using the polyol process, in which ethylene glycol (EG) served as the reducing and solvent reagent.[16] The product was purified by centrifugation process, and the mixture was diluted with isopropyl alcohol and centrifuged. The supernatant containing silver particles and unreacted substrates was removed. Finally, the product was redispersed in 2 ml of pure water. Scanning electron microscopy yields diameters of the nanowires in the range from 50 to 150 nm, while their lengths range from 4 to 30 μm.[8]

P3HT is a semiconducting polymer commonly used in organic solar cells and was purchased from Rieke Metals. In this work, 7 mg of P3HT of molecular weight of 50 000 g/mol were dissolved in 1 ml of toluene and then stirred and heated at 60 °C for complete dilution. An aqueous solution of the conductive polymer PEDOT:PSS (1:6) from Heraeus was used either as a spacer between the AgNWs and P3HT or as an embedding medium for the AgNWs. In this way, we test the impact of a particular geometry upon the enhancement effect. Also, changing the geometry of the nanostructure allows for assessing possible influence of light scattering by metallic nanoparticles on the observed effects.

Absorption spectra of AgNWs, P3HT solution, and P3HT films were measured using a Cary 50 UV-VIS spectrophotometer in the spectral range from 250 to 800 nm. The fluorescence spectrum of P3HT solution and a spin-coated layer was acquired using a Fluorolog 3 spectrofluorometer with a Xenon lamp as an illumination source. Slits were set to assure spectral resolution better than 1 nm.

Hybrid assemblies studied in this work were obtained in two ways. In the first case, we spin-coated a mixture containing PEDOT:PSS and AgNWs solutions with 1:1 volume ratio on a glass coverslip and then P3HT solution was spin-coated on top of it. In the second case, we first spin-coated the AgNWs solution on a glass coverslip and then covered it with PEDOT:PSS and finally P3HT was deposited on the PEDOT:PSS surface. All the solutions were spin-coated for 10 s at 3600 rpm giving a film thickness of undiluted PEDOT:PSS of about 40 nm and P3HT of about 30 nm.

Fluorescence intensity maps were measured on a Nikon Eclipse Ti inverted wide-field microscope equipped with an oil immersion objective (Plan Apo, 100×, Nikon) and coupled with Andor iXon Du-888 EMCCD camera. Due to the plasmon excitation of AgNWs near 400 nm and the P3HT absorption maximum near 530 nm, we used 405 nm and 485 nm LED illuminators as excitation sources, at excitation power of 120 μW and 70 μW, respectively. The sample was illuminated from the AgNW side, next exciting the P3HT layer. In order to directly compare fluorescence intensities, images were acquired for the same area of the sample for both excitation wavelengths. For spectral selection, we used a dichroic beam splitter (Chroma 505DCXR) coupled with a narrow band-pass filter (Chroma HQ675-20).

Fluorescence spectra and transients were measured using a home-built scanning confocal microscope based on the Olympus microscope objective LMPlan 50×.[17] The sample was placed on a XYZ piezoelectric stage (Physik Instrumente), which enabled us to position a laser beam on or off a nanowire. Fluorescence was excited with a 485 nm laser at an excitation power of 5 μW. For spectrally resolved detection, we used an Amici prism coupled with a CCD detector (Andor iDus DV

420A-BV). Fluorescence lifetimes were measured using a time-correlated single photon counting module (Becker & Hickl) equipped with a fast photodiode (idQuantique id100-50) triggered by a 50 ps laser pulse at 20 MHz repetition rate and temporal resolution of about 100 ps.

The optical spectra of P3HT and AgNWs are shown in Fig. 1. The absorption of the AgNWs is similar to that published previously.[8] The plasmon resonance of AgNWs appears at around 430 nm and extends towards the near-infra-red. The optical spectra of P3HT depend on the sample preparation, and for toluene solution, the P3HT absorption reaches a maximum at 450 nm, while the emission peak appears at 570 nm. These values are typical.[18] In contrast, for thin films, the absorption of P3HT exhibits a redshift by approximately 80 nm. At the same time, the maximum emission of the P3HT layer appears at 660 nm. Such huge shifts of the electronic transitions are of key importance when considering coupling of organic polymers with other nanostructures, for instance, metallic nanoparticles.

Silver nanowires, due to their length reaching frequently tens of μm, are one of the few metallic nanoparticles, the positions of which can be directly determined using optical microscopy. In Fig. 2, we show wide-field microscopy images of the P3HT/AgNWs structure obtained using the mixture of PEDOT:PSS and AgNWs. The images were acquired for the same area of the sample for two excitation wavelengths of (a) 405 nm and (b) 485 nm. For both cases, we find elongated shapes with increased fluorescence intensity, and their positions and overall distribution on the surface are identical for the two excitation energies.[16] By correlating the fluorescence image with transmission image measured using a halogen lamp, the stripes of increased intensity occur at positions where silver nanowires are present onto the surface. This observation indicates that the optical properties of P3HT are strongly affected by the presence of the AgNWs. Namely, the interaction leads to increase of the fluorescence intensity of P3HT. In the case of the sample prepared by spin-coating a layer of P3HT on a PEDOT:PSS spacer covering the nanowires, the results were qualitatively similar.

In order to quantify the effect of plasmon excitations upon the fluorescence of P3HT, we calculated intensities of
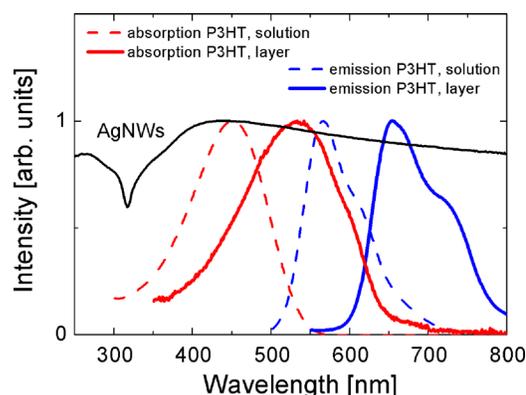

FIG. 1. Absorption and emission spectra of P3HT dissolved in toluene (red and blue dashed lines) compared with absorption and emission spectra of P3HT layers (red and blue solid lines). Emission spectra were excited at 485 nm. For comparison, we also show the extinction spectrum of the silver nanowires in aqueous solution (black).
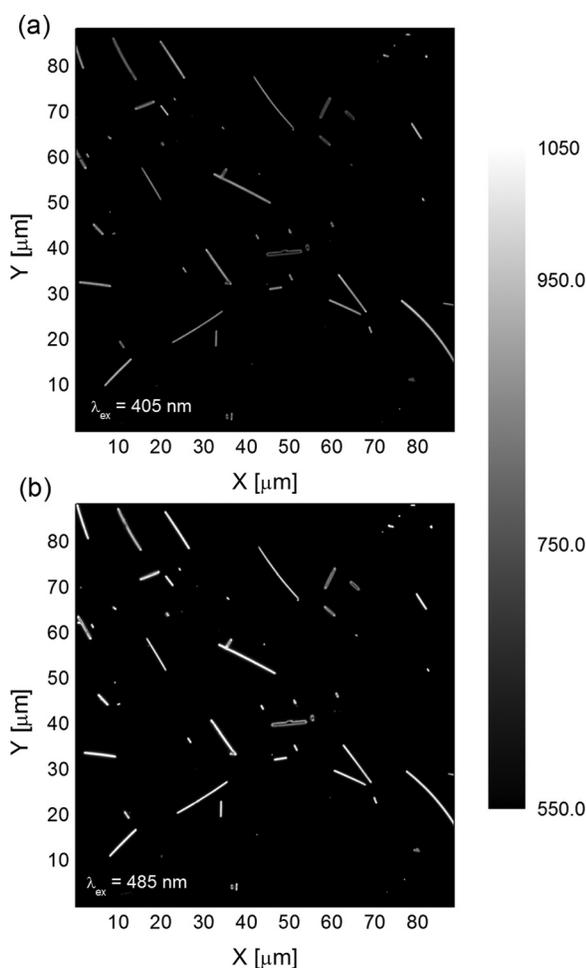
FIG. 2. Fluorescence intensity maps of hybrid nanostructures containing AgNWs mixed with a PEDOT:PSS layer, on top of which a layer of P3HT was deposited. Excitation wavelength was (a) 405 nm and (b) 485 nm. In both cases, the same region of the sample was imaged.
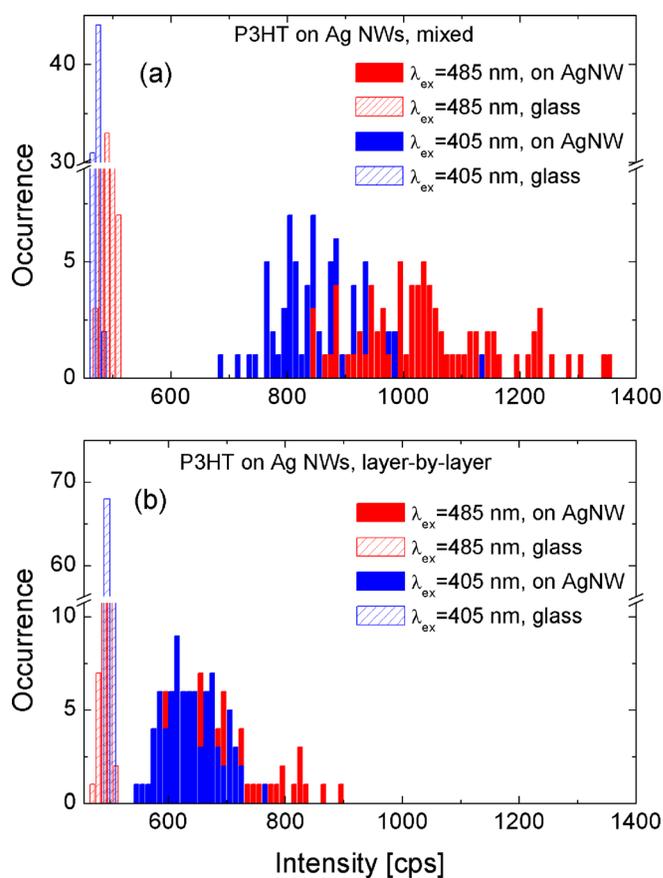

FIG. 3. (a) Fluorescence intensities of P3HT on and off AgNW for the sample where AgNWs were mixed with PEDOT:PSS prior deposition of P3HT. (b) Fluorescence intensities of P3HT on and off AgNW for the sample where PEDOT:PSS was deposited on AgNWs prior deposition of P3HT. In both cases, the results obtained for lasers excitations of 405 nm (blue bars) and 485 nm (red bars) are displayed.

P3HT emission on and off the nanowires for both excitation wavelengths. Since the intensity along the nanowires is quite homogeneous, we estimated the fluorescence intensity of a given nanowire by taking a cross-section along a single, well-separated nanowire and determining the average intensity per pixel. Next, reference values were extracted using the same procedure for an identical shape as the nanowire, but in the area free of nanowires. The fluorescence intensities of P3HT obtained in such a way are summarized in Fig. 3 for both excitation wavelengths for the sample with AgNWs mixed with PEDOT:PSS prior deposition on a substrate. In each case, we analyzed approximately 80 individual AgNWs.

In agreement with the qualitative result shown in Fig. 2, the intensities of P3HT fluorescence measured at the nanowires are considerably higher than for the reference P3HT. In the case of 405 nm excitation, the average value of emission intensity for the mixed sample was 470 cps and 880 cps for P3HT off and on the nanowires, respectively. Analogously, for the 485 nm excitation, the average values of 500 cps and 1050 cps were extracted. Evaluation of the data indicates that for P3HT coupled to the AgNWs mixed with PEDOT:PSS we obtain robust enhancement of the emission intensity that amounts to enhancement factors of 1.9 and 2.1 for 405 nm and 485 nm excitation wavelengths, respectively. For the sample, where the nanowires were

covered with a PEDOT:PSS layer, the enhancement factors are less, amounting to approximately 1.4, and they feature little dependence upon the excitation wavelength. The histograms displayed in Fig. 3 indicate also that the distributions of fluorescence intensity for areas off the nanowires for both geometries are extremely narrow, indicating high homogeneity of the P3HT layer thickness and reproducibility of sample fabrication. On the other hand, the distribution of the fluorescence intensities of P3HT coupled to the AgNWs exhibits significant broadening. This broadening is attributed to inherent inhomogeneity of the fabricated structure associated, for instance, with distribution of distances between P3HT and the nanowires. As the distance plays the key role in determining the strength of the interaction and thus the increase of the emission intensity, a much broader range of fluorescence intensities for P3HT coupled to the silver nanowires is expected. In the case of the structure, where the nanowires were covered with PEDOT:PSS layer, the disorder was less pronounced. Therefore, it is necessary to optimize the structure geometry with respect to both the strength and homogeneity of the plasmonic interactions. Although there is need for future efforts aimed at optimizing the plasmonic interactions in such structures, the effect of increased fluorescence intensity is highly promising for possible improvement of solar cell efficiency, in particular, in the case where the increase of the emission is associated
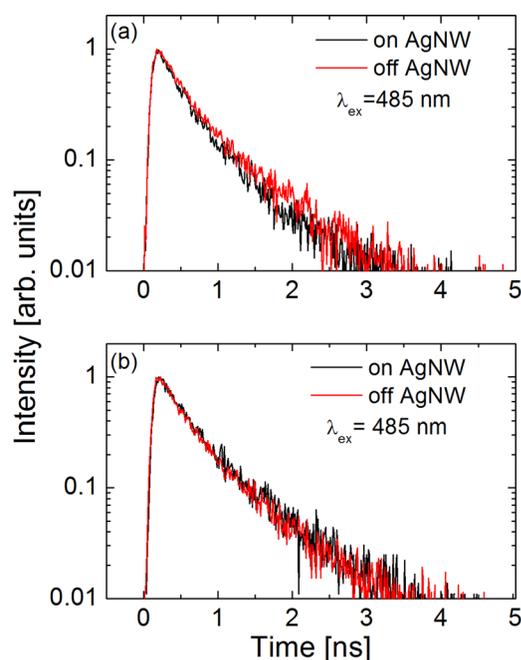
FIG. 4. Normalized fluorescence transients for samples where AgNWs were (a) mixed with PEDOT:PSS and (b) covered with PEDOT:PSS prior to deposition of the P3HT layer. Red curves correspond to data measured off the nanowires, while black curves represent data obtained with a laser spot placed at the nanowire. The excitation energy of 485 nm was used.

primarily with improved absorption of the P3HT layer in the vicinity of the silver nanowires. The difference in observed fluorescence intensities for the two sample geometries points towards plasmonic character of the measured enhancement. Should the increase of the emission intensity be associated with scattering of light by the NWs only, the enhancement factors measured for the two geometries should be the same. Therefore, we attribute the result displayed in Figs. 2 and 3 predominantly to plasmonic interactions between silver nanowires and P3HT polymer.

The origin of the fluorescence enhancement can be determined using time-resolved fluorescence spectroscopy.[19] In the case of the hybrid nanostructure containing AgNWs in PEDOT:PSS layer and P3HT emitter, the observed increase of P3HT emission intensity can be attributed to either increase of radiative rate or increase of absorption rate or a combination of these two processes. For a structure, in which radiative rate is enhanced through plasmonic interactions, a shortening of the fluorescence lifetime is expected.[19] In contrast, should the absorption rate get enhanced, it induces no modifications to the fluorescence lifetime. Such a behavior has been recently observed in the case of photosynthetic complexes coupled to a silver island film.[20] In Fig. 4, we compare P3HT fluorescence transients measured for both geometries excited at 485 nm. The decay curves were measured with laser spot placed either on (black curve) or off (red curve) the nanowire. As can be seen in Fig. 4, all the transients are identical. The emission of P3HT on and off the nanowires decays biexponentially with decay constants of approximately 0.30 ns and 1 ns. The absence of any measurable change in the fluorescence decay times of P3HT deposited on and off the AgNWs suggests that the enhancement of emission is a result of increase of the absorption rate of P3HT. We note

that prior to acquiring fluorescence decays we measured emission spectra of P3HT. In all cases, the spectral shape of the emission with the laser spot placed on the nanowires was unchanged as compared to the reference measurements.

The results of optical spectroscopy and microscopy demonstrate two-fold enhancement of fluorescence of P3HT upon coupling with plasmon excitations in silver nanowires. The enhancement factors measured for excitations at 405 nm and 480 nm are comparable. Appearance of a robust enhancement of emission indicates that by placing silver nanowires in a PEDOT:PSS layer we diminish the influence of non-radiative energy transfer between the emitter and the metallic nanoparticles. The absence of any changes in fluorescence decay times for P3HT interacting with AgNWs as compared to the reference indicates that the dominant, and perhaps only process responsible for the increase of fluorescence intensity is the increase of absorption rate. The result can be applied in designing organic solar cells with plasmonically improved efficiency.

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