ULTRATHIN METAL NANOWIRES FOR PLASMON ENHANCED SOLAR CELLS

Technical Field

The present application relates to photovoltaic cells and in particular to surface plasmon enhanced photovoltaic cells with integrated solution deposited gold nanowire networks. The embodiments of the application comprise, among others, photovoltaic cells with a bulk heterojunction (BHJ) material as photoactive substance but also thin film and silicon photovoltaic cells.

Organic photovoltaic (OPV) devices have demonstrated a high potential due to their light weight, low cost, ease of fabrication and mechanical flexibility. One route towards low cost OPV is to fabricate thinner photovoltaic cells that can significantly reduce the amount of expensive OPV materials utilized. The advantage of a thin photoactive layer is a shorter carrier pathway that favors the effective charge carrier transport with a reduced charge carrier recombination loss. However, a drawback is a relatively weak light absorption in a thinner photoactive layer. So, an efficient light trapping mechanism is needed for an improved device performance without using a thicker photoactive layer. One promising approach is a utilization of surface plasmons to enhance the optical absorption of the photoactive layer.

Surface plasmons (SPs) can be optically excited in metallic nanostructures including nanoparticles, nanorods and nanowires. The surface plasmons in 1-D structures are also known as transverse plasmons since, unlike volume plasmons, surface plasmons comprise an oscillation component which is transverse to the propagation direction of the plasmons. The metallic

nanostructures provide a large surface to volume ratio which is advantageous for the excitation of the surface plasmons. Au and Ag nanostructures are of particular interest because of their surface plasmon resonances (SPR) in the visible region. At resonance condition, the local electromagnetic fields near the metal surface can be many orders of magnitude higher than the incident fields. The capture of these strong EM fields in nearby photoactive materials enhance absorption and photocurrent generation in photovoltaic devices.

The intensity, peak wavelength and spectral bandwidth of surface plasmon resonances strongly depend on the size, distribution and shape of the nanostructures and on the local dielectric environment. Metal nanostructures with a variety of geometrical forms produced by different fabrication techniques have been investigated both experimentally and theoretically for their SP resonance properties. However, to date there is only a limited number of quantitative studies on SP resonance properties of metal nanowires. Several OPV devices with SP active Au and Ag nanoparticles have been demonstrated in which the properties of plasmonic nanoparticles could be adapted for increased photocurrent in the device.

There are currently three main strategies for the assembly, patterning, and alignment of 1D nanostructures, such as nanowires, on surfaces. The first is by standard lithographic methods, where a material is etched or deposited into 1D structures on a surface through a patterned resist. Electron beam or scanning probe lithography is used for features below 100 nm. This method allows for excellent alignment with control of the pitch and the generation of complex patterns. On the other hand, extremely small diameter (<10 nm) nanostructures are difficult to fabricate and they are limited to

structures that are derived from films. A second approach involves solution- or vapor-phase synthesis of 1D nanostructures followed by dispersion in solutions and subsequent assembly/patterning on surfaces. For example, Si NWs can be grown by chemical vapor deposition followed by dispersion in organic solvents, assembly and alignment by the Langmuir-Blodgett technique, and patterning onto surfaces using photolithography. Crossed patterns can also be made and the NWs are electronically addressable. Other methods for the assembly, alignment and patterning of 1D nanostructures dispersed in solutions include the Langmuir-Blodgett method, liquid crystalline assemblies, microfluidics, chemical and biochemical assembly and electric-field alignment. Aggregation of 1D nanostructures often makes it challenging to assemble well-separated, individually addressable nanostructures on surfaces in this way. The third method involves direct growth of 1D nanostructures from catalysts, "seed" particles, or templates that are attached directly to surfaces. Patterning the catalyst or template on the surface leads to patterned 1D structures.

It is an object of the application to provide photovoltaic cells with an enhanced light absorption. Among others, the coverage of plasmonic nanoparticles and the mode of deposition is improved.

More specifically, the application provides improved metallic nanostructures which increase the light absorption of a photoactive material by harnessing surface plasmon excitations of the nanostructures. According to the application, the metallic nanostructures can be used to improve the efficiency of the most diverse types of photovoltaic cells. Further objects comprise an improved photovoltaic device and a production method of metallic nanostructures for an improved photovoltaic device.

To this end, the application discloses a photovoltaic device which comprises a first electrode layer and a second electrode layer and at least one photoactive layer which is arranged between the first electrode layer and the second electrode layer. According to the application, metal nanowires are provided in proximity to the at least one photoactive layer. Herein, "in proximity" means that the nanowires are provided in an adjacent layer or even within the photoactive layer. The nanowires may form bundles of nanowires, and the nanowires or the bundles of nanowires may be arranged in a network pattern or parallel to each other. The nanowires comprise a metal and are "plasmonically active" in the sense that surface plasmons can be excited on the surface of the nanowires by an incident radiation. For brevity, these nanowires are referred to as "nanowires" or "metal nanowires".

The photoactive layer is characterized by the ability of producing a voltage difference in response to incident light waves. It comprises a hole conducting organic and/or inorganic semiconductor and an electron conducting organic and/or inorganic semiconductor and the hole conducting semiconductor and the electron conducting semiconductor are in contact with each other.

In addition, the nanowires may be covered by a buffer material such as a hole conductor, an electron conductor or a dielectric material. In one embodiment, the buffer layer is provided by the material of a layer which is adjacent to the photoactive layer and in which the nanowires are provided. In another embodiment in which the nanowires are placed within the photoactive layer, the buffer layer is provided in the form of an insulating spacer layer around the nanowires in order to

avoid recombination of charge carriers. The buffer layer is made thin, such that the field of surface plasmons on the surface of the nanowires can penetrate into the photoactive layer. Especially, the buffer layer may be in the form of a dielectric layer. The dielectric layer may be provided, for example, by a self-assembled monolayer, a polymeric coating or an inorganic insulator.

Advantageously, the first electrode layer is provided as transparent layer and the second electrode layer as reflective layer or, in the case of bifacial cells, as a semi-reflective layer. For example, the first electrode layer may be provided as ITO anode layer and the second electrode layer as aluminium cathode layer.

The lengths of the nanowires typically extend up to a few microns. The diameter of the nanowires can be made 50 nm or larger. This diameter range is particularly useful for inorganic solar cells whereas a diameter of 7-9 nm is particularly useful for organic solar cells. The diameters and spacings of the nanowire also depend on the production method as for example electrospinning, electrodeposition into templates etc. In particular, in one embodiment, the nanowires are arranged in bundles of nanowires which have a height of about 7 - 9 nm and a width of about 100 - 150 nm. The ultrathin nature of the nanowires allows for easy vertical integration, resulting in minimal perturbations on the layers deposited above.

In one embodiment, nanowires are provided in bundles of nanwires which are arranged essentially parallel to at least one layer of the photovoltaic device in a two dimensional network structure. This arrangement provides a flat layer of nanowires which can be placed close to the photoactive layer. However,

according to the application the nanowires need not be provided in the form of bundles.

The length to width ratio of nanowires according to the application is significantly greater than one, which is at least 5 - 10. According to a more narrow definition of a nanowire, the aspect ratio is at least 20. The length of the nanowires may be as long as several micrometers or even unconstrained. Absorption properties depend on the aspect ratio. For example, it has been observed that an absorption peak of silver nanoparticles with an initial diameter of 4 nm shifts from 500 to 700 nm wavelength when the aspect ratio varies from 1 to 10.

The application provides embodiments for thin solar cells with photoactive layers thinner than 200 nm in which case it is advantageous to choose the diameter of the nanowires in the range of 2-50 nm. This diameter specification takes into consideration the harnessing of the plasmonic near-field effect as well as to make sure that the integration of the nanowires will not disturb the existing layers within the photovoltaic device that comprises the photoactive layers, electron conducting layers etc. The length of the nanowires for thin solar cells may typically range from about 100 nm to several micrometers.

The application also provides embodiments for thicker solar cells with photoactive layers more than 200 nm in which case it is advantageous to choose the diameter of the nanowires in the range of 50-200 nm. In thicker solar cells, these diameters allow the utilization of a strong plasmonic scattering effect which is different from the near-field effect mentioned above. The length of the nanowires for thick solar cells may typically range from about 250 nm to several micrometers.

It has been found that surface plasmons can be generated effectively if the nanowires comprise a metal such as gold, silver, platinum, aluminium and copper or from alloys thereof. The nanowires may be entirely made of that metal, save for impurities, or the metal may be a coating on an inner structure such as a carbon nanowire. Gold Nanowires (AuNWs) may be used to harness lightwaves in the red spectral range. It is beneficial to provide a field increase in the low wavelength range where photons provide less energy to create excitons.

In one embodiment according to the application the metal nanowires are arranged in a nanowire network which is provided within a buffer layer of the buffer material. The buffer layer is provided between one of the electrode layers and the photoactive layer.

Furthermore, in one embodiment, a buffer layer in which the nanowires are arranged comprises a hole conducting material or mixtures of hole conducting materials and wherein the buffer layer is provided between an anode layer and the photoactive layer. This arrangement is beneficial if the hole conducting layer is at a side of incident light in which case the nanowires within hole conducting layer are also placed at a side of incident light.

In another embodiment, a buffer layer in which the nanowires are arranged comprises an electron conducting material or mixtures of electron conducting material. The buffer layer is provided between a cathode layer and the photoactive layer. In an arrangement in which the cathode layer is made of a reflective material, the nanowires can be used to enhance absorption of the reflected light. According to the application, a combi-

nation of the aforementioned arrangements in which a hole conducting buffer layer with nanowires is provided on one side of a photoactive layer and an electron condcting buffer layer is provided on an opposite side of the photoactive layer may be used to further enhance the light absorption in the photoactive layer.

In a further embodiment, the nanowires are integrated within the photoactive layer. In this way, the nanowires can be placed closer to the photoactive layer and provide a more effective light absorption enhancement. According to the application, the integration of nanowires may be achieved by forming a buffer layer of thin self assembled monolayers, for example monolayers with thiol or amine functional groups.

In a further embodiment, the nanowires are provided in a tandem configuration in which a first photoactive layer, a second photoactive layer and an intermediate layer is provided. The intermediate layer comprises a hole conducting layer and an electron conducting layer and the nanowire network is sandwiched between the hole conducting layer and the electron conducting layer. The tandem configuration allows to further enhance absorption, for example by choosing photoactive layer which are sensitive in different spectral ranges.

In a further embodiment, the nanowire network is embedded at the interface of a p-type semiconducting layer and an n-type semiconducting layer in which one or both semiconducting layers are photoactive. In this way, a photovoltaic device with inorganic semiconducting layers can provide a high efficiency even if the layers are made very thin. This in turn facilitates new improved applications such as semitransparent solar cells or others.

In a further embodiment, a nanowire network is embedded within a photoactive layer which is sandwiched by a p-type semiconducting layer and an n-type semiconducting layer. Herein, a similar method as above can be used to embed the nanowires. This embodiment can have an advantage in a production step of providing an insulating buffer layer around the nanowires.

The application furthermore discloses an electricity generator, which comprises one or more of the abovementioned photovoltaic devices which are connected in series or parallel to an input and an output connection of the electricity generator. Moreover, the application also discloses a light sensor which comprises one or more of the abovementioned photovoltaic devices which are connected in series or in parallel to an indicating means of the light sensor.

In addition, the application discloses a method for producing a photovoltaic cell. A nanowire network is provided on a substrate and the nanowire network on the substrate is coverd with a buffer layer. A photoactive layer is provided on top of or around the buffer layer. An electrode layer is provided on top of the photoactive layer. In a more specific embodiment, the step of providing a nanowire network on the substrate comprises deposting a nanowire solution on the substrate by a solution based technique. The solution based technique may be one of several methods such as spin coating, dip coating, spray coating, screen printing and Langmuir-Blodgett methods.

The application also discloses a method of providing a nanowire network on a substrate. Oleylamine and triisopropylsilane are added to a solution of metal ions, which are dissolved in hexane. A nanowire solution is obtained by letting

the solution of metal ions, oleylamine and triisopropylsilan react until a color change is observed. The nanowire solution is washed with ethanol and redispersed with hexane. The nanowire solution is deposited on a substrate by a solution based technique as mentioned above. The deposition causes a self assembly of a nanowire network. In particular, the deposition may be effected by dipping the substrate into the nanowire solution. Possible substrates comprise, among others, glass or quartz with an electrode layer and flexible polymers.

The application will now be explained in further detail with reference to the following figures in which

Fig. 1 illustrates a synthesis method for gold nanowires (Au-NWs),

Fig. 2 shows transmission electron microscopy (TEM) images of the synthesized ultrathin Au-NWs in two different resolutions,

Fig. 3 shows a 2-D self assembly of Au-NWs on a substrate,

Fig. 4 shows the assembled Au-NWs on the silicon substrate,

Fig. 5 shows light absorption spectra of Au-NWs on quartz, Au-NWs on an ITO layer and Au-NWs on an ITO layer which is coated with a PEDOT:PSS layer, wherein the inset shows the coupling of the electrons in the nanowires with the incoming light,

Fig. 6 shows an absorption enhancement for a PEDOT:PSS/P3HT/Al system with incorporated Au-NWs,

Fig. 7 shows a schematic view of an OPV device with integrated Au-NWs according to the application,

Fig. 8 shows current density to voltage characteristics of a photovoltaic cell with an active layer thickness of 80 nm with and without Au-NWs and with and without illumination of 100 mW/cm^2,

Fig. 9 shows current density to voltage characteristics of a photovoltaic cell with an active layer thickness of 60 nm under the experimental conditions of Fig. 8,

Fig. 10 shows the relative enhancement % of the incident photon to current efficiency (IPCE) in the 400-700 nm spectral range for an OPV with integrated Au-NWs with respect to the control device (active layer thickness of 80nm), wherein the inset shows the absolute IPCE spectra for control device and an OPV with integrated Au-NWs,

Fig. 11 shows a steady-state photoluminescence of P3HT with and without incorporated Au-NWs,

Fig. 12 shows a photocurrent J_ph versus effective applied voltage V_eff for a control P3HT-PCBM device and for an Au-NWs incorporated device, both having an active layer thickness of about 60 nm,

Fig. 13 shows an OPV device configuration in which Au-NWs are integrated on the cathode side,

Fig. 14 shows an OPV device configuration in which Au-NWs are integrated on the cathode and on the anode side,

Fig. 15 shows an OPV device configuration in which Au-NWs are embedded within the photoactive layer,

Fig. 16 shows a tandem solar cell configuration with Au-NWs in an interlayer,

Fig. 17 shows a cross sectional view of a p-n junction solar cell with Au-NWs at the interface,

Fig. 18 shows a cross sectional view of extremely thin absorber (ETA) type solar cells with Au-NWs in an interlayer,

Fig. 19 shows IPCE characteristics in the 400-700 nm spectral range for an OPV with and without integrated Au-NWs for an active layer thickness of 60nm, and

Fig. 20 shows surface morphologies for a thin PEDTO:PSS layer on ITO with and without AuNWs.

Here and in the following, ITO refers to indium tin oxide, PEDOT refers to poly(3,4-ethylendioxythiophene), PSS refers to poly(styrenesulfonate), P3HT refers to poly(3-hexylthiophene) and PCBM refers to the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester.

The application provides a method for the synthesis of gold nanowires and for depositing the gold nanowires on a substrate. The method is based on a simple and rapid wet-chemistry and is employed at room temperature. The steps of the synthesis are illustrated in Fig. 1.

In a first step, 3mg of $HAuCl_4 \cdot 3H_20$ is dissolved in 2.5 ml of hexane to obtain a gold-hexane solution. In a next step, 100 µl of Oleylamine are added to the gold-hexane solution. According to the application, the Oleylamine is used as a stabilizer and as a one-dimensional growth template.

In a next step, 150 µl of Triisopropylsilane (TIPS) are added. According to the application, TIPS is used as an effective reduction agent in the synthesis.

According to the application, the yellow solution of the previous step is allowed to react under slow stirring until it transforms into a dark-red solution. Preferentially, a reaction time of 9 hrs at room temperature is employed. The change of color indicates the excitation of surface plasmons in the optical range. A similar dark red color can also be observed in stained glass windows with gold particles, for example. If a metal other than gold is used which exhibits surface plasmon

excitations in the visual range, the color change may be different.

In a next step, the dark-red solution is washed with ethanol by centrifuging at 2500 rpm for 10 min followed by a redispersion in 2.5 ml of hexane.

For an investigation of the Au-NWs, the solution is dropped on copper grid and a TEM image is recorded. In the TEM images depicted in Fig. 2, the Au-NWs are long and ultra-thin with a diameter of 2 nm. They are structured as parallel and closely packed Au-NWs which form stacked bundles. The bundles can be best seen in the first image of Fig. 2 whilst the individual nanowires can be best seen in the second image of Fig. 2. In a production process, the investigation steps may be omitted or used for quality control.

Fig. 3 illustrates a step 9of self assembly of AuNWs on a substrate such as Si, ITO or quartz. The Au-NW solution is diluted with hexane to a ratio of 1:15 ml/ml. For the abovementioned data, the substrate is dipped in the solution for 15 min to allow for the self-assembly of a two dimensional network of Au-NWs on the substrate. For other substance amounts, the self-assembly time may be longer or shorter.

For an investigation of the Au-NWs on the substrate, the resulting Au-NW decorated substrate is scanned by an atomic force microscope (AFM). The AFM topography image of Fig. 4 shows that the packing structure of the Au-NWs grids in the TEM image of Fig. 2 is preserved. Due to a lower resolution of the AFM, the fine parallel wires of Fig. 2 are not resolved in Fig. 2. A closer investigation reveals that the bundles of Au-NWs have a dimension of 7-9 nm height and 100-150 nm width.

The investigation steps may be left out in a production process or they may be used for quality control.

Figs. 5 and 6 show light absorption characteristics of materials which comprise the Au-NWs.

For obtaining the three absorption curves of Fig. 5, the Au-NWs, which are synthesized according to the abovementioned method, and are respectively deposited onto a quartz substrate, onto an ITO substrates and onto an ITO substrate that is coated with a PEDOT:PSS layer. The nanowires on the substrates are irradiated with ultraviolet to visible (UV-vis) light and the absorption is measured. Figs. 5 and 6 show the absorption in arbitrary units (a.u.). For comparison, the inset of Fig. 5 shows the excitation of electrons in non-embedded gold nanowires which exhibit surface plasmon resonances that are not influenced by the embedding material. The inset is not drawn to scale. The spectral absorption curve for the electron excitation may be obtained by reflection measurements on sputtered gold layers, for example.

A first UV-vis absorption spectrum of Fig. 5 indicates that the absorption maximum of Au-NWs on a quartz substrate is located at 516 nm. This absorption maximum is caused by a transverse plasmon resonance of the Au-NWs.

A second absorption spectrum of Fig. 5 shows that the resonance of Au-NWs on ITO broadens and is red-shifted to 575 nm. The broadening and red shift is caused by the sensitivity of the position and bandwidth of the surface plasmon resonance to the dielectric environment.

A third absorption spectrum of Fig. 5 which is obtained for an Au-NW decorated ITO substrate that is coated with an PEDOT:PSS spacer layer of thickness 15 nm shows an additional red-shift in the surface plasmon resonance peak position. The peak is positioned at around 620 nm.

The application also discloses production methods for a solar cell with incorporated gold nanowires. Preferentially, the Au-NWs which are synthesized according to the abovementioned method are deposited on an ITO substrate and spin coated with a PEDOT:PSS spacer layer.

In a further step, a photovoltaic polymer P3HT layer of thickness 40 nm is spun on the PEDOT: PSS coated ITO with the Au-NWs sandwiched in between. In the present application, the photovoltaic polymer P3HT is also referred to as a kind of "(photo)active substance" and the corresponding layer as a kind of "(photo)active layer".

In order to simulate the conditions in organic photovoltaic cells, the reflective Al (100 nm) is vacuum-evaporated on top of the photoactive layer in a first step. In a next step, UV-vis absorption spectra are recorded on these systems. An SP induced absorption enhancement is observed in the Au-NW integrated system.

According to the application, the absorption enhancement in the P3HT molecules is generated by an increased local electric field in the photoactive P3HT which in turn is generated by the SP resonance of the Au-NWs. The interaction between localized surface plasmons in the metal nanostructures and incident photons creates a high density of photons at the near-field distance and a strong local electromagnetic field builds up.

When this resonant frequency matches the absorption band of photoactive molecules, the absorption in the photoactive molecules is enhanced which leads to an increased photogeneration of charge carriers. Thereby, a higher efficiency of the photovoltaic cell can be achieved.

In the embodiments of a photovoltaic cell which are shown in Fig. 7 and Figs. 13 - 16, the Au-NWs are integrated into organic photovoltaic cells comprising a P3HT:PCBM bulk heterojunction material. More specifically, the photoactive layer is provided by a bulk heterojunction (BHJ) blend of poly (3-hexylthiophene) (P3HT) and acceptor [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM) in this embodiment. According to the application, a blend solution of P3HT and the PCBM with a weight ratio of (10:8) is prepared in 1,2 dicholorobenzene to obtain a final concentration of 18 mg/ml. The Figs. 7 and 13 - 16 show a so called "normal configuration" of electrodes in which an anode layer is provided in contact with a substrate while a cathode layer is provided on an opposite side of a photoactive layer. However, an inverse configuration in which the anode material is provided on the substrate and a cathode layer is provided on the opposite side of the photoactive layer is also possible. In the inverse configuration, the arrangement of the hole- and electron conducting layer is swapped with respect to the normal configuration.

An optically active material in the sense of the current application comprises a donor component and an acceptor component. The donor component of a bulk heterojunction (BHJ) material forms paths which lead to an anode of a photovoltaic device and the acceptor component forms paths which lead to a cathode of the photovoltaic device. By analogy, these paths or junctions are also referred to as percolation paths. After

creation of an electron-hole pair through incident light, the electron travels from the acceptor component to the cathode and the hole travels from the donor component to the anode, respectively, and generate a photoelectric voltage. More specifically, the electron-hole pair is generated in the donor component as a localized exciton. The electron is then transferred to the acceptor component, whereby the exciton is split up. By an alternative mechanism, an exciton is generated in the acceptor and a hole is transferred to the donor. The bulk heterojunctions of the BHJ material are advantageous in providing a close distance between donor and acceptor material such that a charge separation occurs before the exciton decays again, for example by a fluorescence of the donor. For P3HT:PCBM, the P3HT provides the donor component while the PCBM provides the acceptor component.

For the P3HT:PCBM BHJ material, the fullerene component of the PCBM material provides acceptance of electrons. The chain of the PCBM material provides solubility for easier processing. The polymer chain of the P3HT material, on the other hand, provides a hole conduction path. P3HT can be regarded as an organic p-semiconductor and PCBM as an organic n-semiconductor. The lowest unoccupied molecular orbital of PCBM is lower than that of P3HT to provide an effective separation of the exciton's electron. Other materials with similar properties may be used for the photoactive material, such as polymers or dyes for the electron donor component and other fullerene derivatives for the electron acceptor component.

The electrodes of an organic photovoltaic cell are often provided by a transparent conducting oxide (TCO) and by a metal, respectively. In the embodiments of Fig. 7 and Figs. 13 to 16, the TCO is provided by ITO and the metal is provided by alu-

minium. Other TCOs may be used such as flourine doped tin oxide and also other metals, but it is essential that the electrodes have a different Fermi level to provide a charge separation. Instead of the glass layer 11, other transparent materials such as plastic may be used as a transparent front layer 11.

In order to provide a directed current, in the embodiments of Fig. 7, and 13 to 16 a hole conducting layer is provided between the photoactive material and the anode. In the embodiments of Fig. 13 to 16 an electron conducting layer is provided between the photoactive material and the cathode. Furthermore, in the tandem configuration of Fig. 16, an Au-NW layer is sandwiched between an electron conducting layer and a hole conducting layer.

An electron conducting layer may be provided by all n-type semiconducting layers including C60 and other fullerene derivatives, metal oxides, metal sulfides and nitrides, specifically, but not exclusively, comprising the materials TiO_2, ZnO and Cs_2CO_3. A hole conducting layer may be provided by all p-type semiconducting layers including thiophene derivatives, carbazole derivatives and other semiconductors, specifically, but not exclusively, comprising the materials P3HT, PCDTBT, carbon nanotubes, graphenes, PEDOT:PSS, SPDPA, PTFE, MoO_3, WO_3, V_2O_5, NiO, AgO_x.

According an embodiment of the application, the PEDOT:PSS layer is used not only as a hole conducting layer but also as an effective buffer layer between the Au-NWs and active layer to prevent the quenching of excitons in the metal nanostructures by recombination of charge carriers. Since the SP resonance is an evanescent wave, the PEDOT:PSS layer should be as thin as

possible in order to provide a maximum coupling between the SP resonance and the photoactive material. According to the application, it is advantageous to provide a layer thickness of about 15 nm which is, on the one hand, sufficient to cover the Au-NWs of diameter 7-9 nm and which, on the other hand, does not increase the RMS roughness (2.4-2.6 nm) of the layer significantly.

In a next step, a deposition of a P3HT-PCBM photoactive layer with a thickness between 60 nm and 80 nm onto the ITO anode layer and the PEDOT:PSS buffer layer is performed in a nitrogen glovebox. In a production process the layer deposition is realized by an automated process such as spin coating in a spin coater, chemical vapor deposition or physical vapor deposition. A functional photovoltaic cell 10, which is shown in Fig. 7, is obtained by a step of depositing a cathode layer of aluminium with a thickness of 100 nm by evaporation deposition followed by a step of low temperature annealing at 60 °C for 2.5 hours. According to the application, a high temperature annealing is avoided in order to keep the fabrication process compatible to plastic substrates. High temperature annealing may be used, though, if the use of a plastic substrates is not intended in order to achieve a faster annealing process. In one particular embodiment, the effective cell area defined by the geometrical overlap between ITO and Al is 0.071 cm^2. The aluminium layer serves as a cathode and, at the same time, as a mirror which reflects light which has not been absorbed back into the photoactive layer.

In general, it is advantageous to provide one transparent electrode layer and one reflective electrode layer in a photovoltaic device. For the embodiment of Fig. 7, the transparent

electrode layer is provided by the ITO layer and the reflective electrode layer by the aluminium layer.

Fig. 7 shows an embodiment of a photovoltaic cell 10 which is obtained by the abovementioned production method. The photovoltaic cell comprises, from the side of the incident light, a glass layer 11, an anode ITO layer 12, a AuNW network 13, a PEDOT:PSS hole conducting layer 14, a P3HT:PCBM layer 15, in which the heterostructure is indicated, and a cathode aluminium layer 16. In the embodiment of Fig. 7, the hole transporting layer 14 serves as buffer layer for the AuNWs. The thicknesses of the PEDOT:PSS layer 14, the P3HT:PCBM layer 15 and the aluminium layer 16 are 15nm, 60nm and 100nm, respectively. In Fig. 7 and in the following embodiments of photovoltaic cells, connections to the anode and to the cathode are not shown.

In an analysis step, an incident photon to current efficiency (IPCE) measurement is carried out using a 150 W Newport-Oriel Xenon light source, a Cornerstone 260 1/4M monochromator, an optical chopper set at 60 Hz and a Merlin radiometry system. The light power-density is calibrated with Hamamatsu silicon photodiode. A measured IPCE enhancement is shown in the inset of Fig. 10.

The wavelength dependence of the photocurrent enhancement was recorded for the 80 nm and 60 nm thick devices. The IPCE characteristics are shown in the inset of Fig. 10 and in Fig. 19. It is found that the IPCE of both devices were enhanced in the spectral region from 400 nm to 650 nm.

In a further analysis step, current density to voltage (J-V) curves of the photovoltaic devices are recorded with an HP

4155 semiconductor analyzer under illumination by a solar simulator (San-Ei XES-300, AAA rating). The J-V curves are shown in Figs. 8 and 9.

Figs. 8 and 9, respectively, display the current density to voltage characteristics of 80 nm and 60 nm thick devices in the dark and under illumination. Further device parameters are tabulated in the Table 1 below and are the mean values from ten cells. Upon integrating the Au-NW structure according to the application, the short circuit current density (J_sc) increased from 7.87 to 9.02 mA/cm^2 in the 80 nm devices and from 6.38 to 7.86 mA/cm2 in the 60 nm devices. The photocurrent is thus enhanced by 14.6% and by 23.2% in the 80 nm and 60 nm devices, respectively.

Table 1. Power conversion efficiency increase PCE, short circuit current density J_sc, open current voltage V_oc, fill factor FF and series resistance Rs of the control and Au-NWs incorporated devices under AM 1.5 solar illumination with intensity of 100 mW/cm^2.

	PCE (%)	J_sc (mA/cm^2)	V_oc (V)	FF	Rs (Ω cm^2)
Control (80nm)	2.44	-7.87	0.65	0.48	19.75
With Au-NWs (80nm)	2.72	-9.02	0.65	0.46	20.73
Control (60nm)	2.31	-6.38	0.65	0.56	19.45
With Au-NWs (60nm)	2.45	-7.86	0.65	0.48	23.65

In all devices, the open circuit voltage (V_oc) remained constant at 0.65V suggesting that the PEDOT: PSS completely covers the Au-NWs and does not act as a recombination center for the light induced charge carriers. The modification of contact properties such as injection barriers can lead to changes in the series resistance Rs of the device. The examination of the current density to voltage curve in the dark reveals that Rs is not changed in Au-NW incorporated device. The Rs values listed in Table 1 are obtained by linearly fitting the charge density-voltage (J-V) curve under illumination around the point (J = 0).

AFM topography images show that the morphology of the P3HT-PCBM layer is essentially unchanged in the devices with and without Au-NWs indicating that the Au-NWs below the PEDOT:PSS results in a minimal perturbation to the active layer morphology. This can be seen in Fig. 20. The left side of Fig. 20 shows a surface morphology of a PEDOT:PSS layer on ITO without integrated Au-NWs and the right side of Fig. 20 shows a surface morphology of a PEDOT:PSS layer on ITO with integrated Au-NWs. A statistical evaluation yields an RMS roughness of 2.4 nm for the PEDOT:PSS layer without integrated Au-NWs and of 2.7 nm for the PEDOT:PSS layer with integrated Au-NWs. This difference shows up in the slightly different range of the greyscales.

Fig. 10 shows a calculated relative enhancement (%) of the power conversion efficiency against wavelength. This relative enhancement is obtained according to the formula Enhancement in %= 100 X (IPCE Au-NW- IPCE Standard)/IPCE Standard, where IPCE Standard is the IPCE value for a photovoltaic value of the photovoltaic cell with integrated Au-NWs. The IPCE is significantly enhanced around 620 nm coinciding with

the SP resonance band of Au-NWs in the ITO-PEDOT:PSS environment which can be seen in Fig. 5. In both the current density to voltage and in the IPCE measurements, the current enhancement is more pronounced in thinner photovoltaic cells.

The photocurrent enhancements of Fig. 10, that were determined in the device are linked to the increased photoabsorption on the integration of the nanowires shown in Fig. 6. Fig. 11 shows a photoluminescence intensity of the photoactive material versus the wavelength of the incident light in arbitrary units (a.u.). The P3HT molecules in direct proximity to Au-NWs produce a 2.5 fold enhancement in the steady-state photoluminescence intensity indicating that a larger number of excitons are generated within the photoactive P3HT film. The increase in the number of excitons is ascribed to a coupling between the excited P3HT molecules and the electron vibration energy in Au-NWs at surface plasmon resonance. The increased number of excitons generated by increased absorption of light in the photoactive layer leads to an enhancement of photocurrent in the solar cells.

These conclusions are also supported by calculations of the maximum exciton generation rate (Gmax) and exciton dissociation probability from measurements shown in Fig. 12. According to Fig. 12, the photocurrent Jph is plotted as a function of effective voltage (Vo-V) for the 80 nm-thick device. Jph is the difference between the dark current (JD) and the current under illumination (JL) while Vo is defined as the compensation voltage applied when JL equals JD. At higher effective voltages, all free charge carriers are extracted (zero recombination) and Jph saturates to q*G*L, wherein G is the maximum exciton generation rate, q is the elementary charge and L is the thickness of photoactive layer. In this regime, all bound

electron-hole pairs are separated into free carriers and consequently the maximum exciton generation rate Gmax is determined only by the amount of absorbed photons. For the devices reported in this study, the maximum exciton generation rates increased by 10-17% after incorporating Au-NWs, with 60 nm devices showing a higher increment than 80 nm thick ones. This correlates well with increased absorption in the Au-NWs integrated devices.

The light scattering and concentration utilizing the plasmonic nanostructures enhances light trapping in photoactive layer that allows the reduced thickness of photoactive layer maintaining the constant optical absorption. In the embodiment of Fig. 7, the Au-NW network structure is integrated at the anode side between an anode and a hole transporting layer. In a similar embodiment of a photovoltaic cell 10' shown in Fig. 13, the Au-NW networks are placed at cathode side between a cathode and an electron conducting layer. A hole conducting layer 17 is provided which also serves as buffer layer for the Au-NW network layer 13. Fig. 14 shows an embodiment of a photovoltaic cell 10'' in which Au-NW networks 13, 13' are integrated at the cathode and at the anode, respectively. An electron conducting layer 17 is provided as buffer layer at the cathode and a hole conducting layer 14 is provided as buffer layer at the anode. According to the application, the additional layer 13' of nanowires further enhance the absorption of the reflected light in the photoactive layer.

According to the application, the metal nanostructures are provided close to photoactive materials where photoexcitation occurs as the electromagnetic field has an evanescent nature. Furthermore, in order to avoid exciton quenching by non-radiative energy transfer due to the close placement of the

metal nanostructures to the active layer, a thin spacer layer that can insulate the nanostructures from the polymer blend is provided. The spacer layer can be formed by attaching thin self assembled monolayers chemically to the metal nanostructures. These self assembled monolayers can have thiol or amine functional groups which can bind on to metal nanostructures. This will also allow the nanowires to be suspended in the solution of the active layer and allows fabrication of the solar cell in the conventional way. This procedure allows the formation of another embodiment 10''', which is shown in Fig. 15. The solution processable nanowires are embedded into a bulk heterojunction material. In the case of organic solar cells, the nanowires are blended with organic molecules. A further embodiment, which is shown in Figure 16 comprises a tandem architecture in order to enhance the spectral sensitivity of solar cells and for realizing a higher efficiency. In the tandem structure, thin photoactive layers 15, 15' with complementary absorption characteristics are stacked via a light transparent and electrically conductive recombination layer. The complementary absorption characteristics may be realized by providing photoactive layers 15, 15' with sensitivities in different spectral ranges.

An interlayer 20 is provided which acts as a recombination site for oppositely charged carriers from the top and bottom cells. The interlayer 20 comprises a hole conducting layer 18 at the side of the cathode and an electron conducting layer 19 at the side of the cathode. The interlayer 20 ensures that the subcells of the tandem solar cell 10'''' are in a series configuration and the photovoltages add up. In a typical configuration in which the light is incident from one side only, the subcell closer to the light permeable electrode is referred to

as front cell and the other subcell is referred to as back cell.

In an exemplary embodiment for an organic solar cell 10'''' according to Fig. 16, the photoactive layers 15, 15' of the front and back cells are PCPDTBT:PCBM composites and P3HT:PCBM composites which are respectively separated by an interlayer system 19, 18 of TiOx-PEDOT:PSS. An Au-NW network 13 is sandwiched between the TiOx layer 19 and the PEDOT:PSS layer 18 in the interlayer 20, such that the enhanced light scattering and charge carrier concentration which is caused by the Au-NWs 13 in the interlayer 20 is beneficial to both subcells.

Figs. 17 and 18 illustrate cross sectional views of more generalized embodiments 30, 30' of photovoltaic cells which can be implemented in thin film solar cells as well as in silicon solar cells. In the embodiments of Fig. 17 and 18, the anode layer 12' is transparent, as indicated by incident lightbeams. Alternatively, the cathode layer 16' or both electrode layers may be provided as transparent layers. In silicon solar cells, a nanowire layer 13 is embedded at the p-n junction interface between an n-semiconductor layer 21 and a p-semiconductor layer 22, as shown in Fig. 17. In a silicon solar cell, the p and n type layers are made of appropriately doped Si layers. In a thin film solar cell according to Fig. 17, for example a CIGS cell, the n type layer can be made of CdS while the p-type layer is made of $CuInGaSe_2$. CIGS stands for the components copper, indium, gallium and selenium in the composition $CuIn_xGa_{(1-x)}Se_2$ wherein x can vary from 0 to 1.

Fig. 18 shows another type of thin solar cells which comprise an absorber layer 23 between an electron conducting layer 21' and a hole conducting layer 22'. A nanowire layer 13 is placed

between the hole conducting layer 22' and the electron conducting layer 21'. Coated nanowires may also be provided in the embodiments of Figs. 17 and 18. Advantageously, the gold nanowires are placed close to the absorber layer 23 to improve the photocurrent generation within these devices. In the embodiment of Fig. 18, extremely thin absorber cells (ETA) as well as dye sensitized solar cell (DSC) such as Grätzel cells may be used.

According to the application, metal nanowire networks improve the performance of solar cells through increasing the coupling between the incident light and the absorber layer. These nanowire networks are synthesized and deposited through solution processable means. The synthesis strategy described above can be used to form nanostructures out of other plasmonically active materials such as Al, Cu, Ag and Pt. Herein, "Plasmonically active" refers to the capability of exhibiting surface plasmon resonances in the optical to ultraviolet frequency range.

According to the application, the ultrathin nature and also the orientation of the nanowires which is essentially parallel to the substrate surface allows for easy vertical integration, resulting in minimum perturbations on the layers deposited above. Moreover, in contrast to nanoparticles, nanowires do not easily agglomerate. This facilitates the production of a nanostructure with a large surface area. According to the application it is furthermore advantageous to provide nanowires with long lengths as nanostructures. The long lengths of the nanowires allow for plasmonic structure integration over large areas. An arrangement of nanowires according to the application provides a geometric advantage by which a long, plasmonically active nanowire achieves a similar effect a row of nano-

particles that are assembled at close proximity. A network of nanowires according to the application provides an easier way of making a substrate plasmonically active. The nanoparticle approach in contrast requires careful assembly over a large area at high densities to give plasmonic advantages.

Claims

1. A photovoltaic device comprising:
- a first electrode layer,
- a second electrode layer,
- at least one photoactive layer which is arranged between the first electrode layer and the second electrode layer, wherein a plurality of nanowires is provided in proximity to the at least one photoactive layer.

2. Photovoltaic device according to claim 1, wherein the nanowires are covered by a buffer material.

3. Photovoltaic device according to claim 1 or claim 2, wherein the photoactive layer is thinner than 200 nm and a diameter of the nanowires is between 2 and 50 nm.

4. Photovoltaic device according to claim 3, wherein an average length of the nanowires is at least 100 nm.

5. Photovoltaic device according to claim 1 or claim 2, wherein the photoactive layer is thicker than 200 nm and a diameter of the nanowires is between 50 and 200 nm.

6. Photovoltaic device according to claim 5, wherein an average length of the nanowires is at least 250 nm.

7. Photovoltaic device according to one of the preceding claims, wherein the nanowires are arranged essentially parallel to at least one layer of the photovoltaic device.

8. Photovoltaic device according to one of the preceding claims, wherein the nanowires comprise a material which

is selected from gold, silver, platinum, aluminium and copper or from alloys thereof.

9. Photovoltaic device according to one of the preceding claims, wherein the nanowires are provided within a buffer layer of the buffer material and wherein the buffer layer is provided between one of the electrode layers and the photoactive layer.

10. Photovoltaic device according to claim 9, wherein the buffer layer comprises a hole conducting material or mixtures of hole conducting materials and wherein the buffer layer is provided between an anode layer and the photoactive layer.

11. Photovoltaic device according to claim 10, wherein the buffer layer comprises an electron conducting material or mixtures of electron conducting material and wherein the buffer layer is provided between a cathode layer and the photoactive layer.

12. Photovoltaic device according to one of the preceding claims, wherein the nanowire is coated by a dielectric layer.

13. Photovoltaic device according to claim 12, wherein the dielectric layer is provided by a monolayer, polymeric coating or an inorganic insulator.

14. Photovoltaic device according to one of the preceding claims, wherein the nanowires are integrated within the photoactive layer.

15. Photovoltaic device according to one of the preceding claims, the photovoltaic device comprising a first photoactive layer, a second photoactive layer and an intermediate layer, wherein the intermediate layer comprises a hole conducting layer and an electron conducting layer and wherein the nanowires are sandwiched between the hole conducting layer and the electron conducting layer.

16. Photovoltaic device according to one of the preceding claims, wherein the nanowires are embedded at the interface of a p-type semiconducting layer and an n-type semiconducting layer in which one or both semiconducting layers are photoactive.

17. Photovoltaic device according to one of the preceding claims, wherein the nanowires are embedded within a photoactive layer which is sandwiched by a p-type semiconducting layer and an n-type semiconducting layer.

18. Electricity generator, the electricity generator comprising one or more of the photovoltaic devices according to one of the previous claims, the photovoltaic devices being connected to an input and an output connection of the electricity generator.

19. Light sensor, the light sensor comprising one or more of the photovoltaic devices according to one of the previous claims, the photovoltaic devices being connected to an indicating means of the light sensor.

20. Method for producing a photovoltaic cell, the method comprising steps of
- providing a nanowire network on a substrate;

- covering the nanowire network on the substrate with a buffer layer;
- providing a photoactive layer on top of the buffer layer;
- providing an electrode layer on top of the photoactive layer.

21. The method of claim 20, wherein the step of providing a nanowire network on the substrate comprises
- depositing a nanowire solution on the substrate by a solution based technique, wherein the solution based technique is selected from the group of spin coating, dip coating, spray coating, screen printing, Langmuir-Blodgett and electrodeposition methods.