

RAPID COMMUNICATION

Optics-electrics highways: Plasmonic silver nanowires@TiO₂ core-shell nanocomposites for enhanced dye-sensitized solar cells performance



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Abstract

In this article, the unique bristled silver nanowires@TiO₂ core-shell nanostructure (AgNW@TiO₂) is introduced into the TiO₂ photoanode and applied to assemble dye-sensitized solar cells (DSSCs). The effects of the “optics-electrics highways” composites on the photovoltaic and photocatalytic behaviors of DSSCs are investigated in detail. Experiment research and FDTD simulation indicate that both the localized surface plasmon resonance (LSPR) and plasmonic waveguide effect could enhance light harvesting efficiency. By electrical properties and electrochemical analysis, it is demonstrated that the AgNW@TiO₂ significantly accelerates electron transport as well as reduces recombination, then the charge collection efficiency of DSSCs is improved. The composite-modified DSSC exhibits the best performance with the power conversion efficiency of 8.84% which is superior to that of the free-modified DSSC with the PCE of 6.16%.

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Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable interest and have been extensively studied since the discovery

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by Grätzel et al. [1]. For decades, the power conversion efficiency of DSSC has reached up to 12.3% [2]. Given their various advantages, such as relatively high photon-to-current conversion efficiency, simple fabrication processes, and low cost, DSSC have emerged to be one of the most potential alternatives to conventional silicon-based solar cells [3-6]. DSSC is composed of an inorganic semiconducting photoanode with a monolayer of adsorbed dye sensitizers and filled by electrolyte, and a platinized counter electrode in a sandwich structure. Extending the response of dye sensitizers to a broader range of the solar spectrum, improving the light-harvesting efficiency (LHE) and suppressing the carrier recombination process at the semiconductor/dye/electrolyte are the key factors to improve the performance of the DSSCs. A large number of strategies have been performed to improve the efficiency such as developed ordered nanostructures, [7] semiconductor nanorods and nanotubes, [8] co-sensitization dye [9] and surface chemical treatment technology [10]. Recently, metal nanostructures modified technology has been employed as a promising way to boost the performance of DSSCs via surface plasmon polariton (SPP) effect [11].

SPP effect is a light-induced collective oscillation of free electrons on the surface of metal nanostructures. It has been applied to significantly increase the light absorption of the dye and accelerate the carriers separation [12]. Hence, it is considered to be one of the most attractive technologies to improve the photoelectric conversion efficiency. A number of approaches are developed and introduced in photoanodes such as Ag nanoparticles (NPs), [13] Au NPs, [14] Ag@TiO₂ NPs, [15] Au@TiO₂ NPs and Au@SiO₂ NPs [11]. These spheroidal nanostructures take advantage of the localized surface plasmon (LSP) effect and light scattering to increase the light absorption of the dye, and provide the suppression of the recombination of electrons. However, the effects of these spheroidal nanostructures are in local area and do little to increase light path and electrons transport in the photoanode.

In order to further exploit the potentials of the plasmonic metal nanostructures, an "optics-electrics highways", bristled Ag nanowires@TiO₂ (AgNW@TiO₂), is introduced into photoanode and investigated in this article. Compared to the previously reported metal nanostructures, besides LSPR and electrons-separation effect of the spheroidal metal nanostructures, this one-dimensional metal nanostructure has the unique plasmonic waveguide effect [16] and electric antenna characteristics. The plasmonic waveguide effect could induce the effective light propagation as an excitation-plasmon-photon radiation process with low loss, [17] hence the optical path and light-harvesting efficiency is improved effectively.

The electric antenna characteristic shows that the carriers can move through the typical one-dimensional structure rapidly and reach the destination electrode with less paths, then it was expected as a promising architecture for accelerating electron transport as well as reducing recombination effectively. Meanwhile the dense and bristled TiO₂ shell of the composite avoids the contact between the AgNW core and electrolyte thus eliminating leakage, and the stability of the efficiency shows a good assessment. Moreover, AgNW@TiO₂ composite assists in maintaining a more negative Fermi level than the pristine TiO₂ to enhance the open voltage. Therefore, the novel optics-electrics double-channels nanostructures greatly contribute to the enhanced performance of DSSCs.

Results and discussion

Properties of the bristled AgNW@TiO₂ structures

Figure 1a and b shows the SEM images of the AgNW@TiO₂ core-shell composites. Figure 1c shows the TEM images of the composites. The composites have high aspect ratio with several micrometers length, the diameter of core is 60-80 nm and diameter of shell is near 300 nm. The EDX spectrum is used to analyze the ingredient of the composite and Ag, Ti and O peak were observed and shown in Figure S1†. Appropriate doping method is used to add various amounts of AgNW@TiO₂ composites to pure TiO₂ photoanode (0.00%, 0.45%, 1.05%, 1.58%, 2.04%, 2.52%). The XRD patterns of the metal-modified TiO₂ film and pure TiO₂ film are shown in Figure 2a. The diffraction peaks of (101), (004), (200), (105), (211), (204) for anatase TiO₂ and (110) for rutile TiO₂ were observed in these patterns. Additionally, diffraction peaks of Ag (111) were also found in the patterns of the AgNW doped films, indicating that the AgNW composite dispersed in TiO₂ films. With increasing doping concentration of the AgNW composite, the intensity of Ag diffraction peaks intensity increased. Figure 1d shows the cross-section SEM images of the composite-doped photoanode. Owing to the close contact between typical bristled TiO₂ shell of the composite and TiO₂ nanoparticles, the unique one-dimensional composites could blend in TiO₂ nanoparticles compactly and avoid defects and gaps.

UV-vis absorption spectrum of the AgNW@TiO₂ was shown in Figure 2b. The bristled AgNW@TiO₂ core-shell nanocomposites present a wide absorption spectrum in the visible region. As the metal nanostructure is covered with the media shell, the absorption peak red-shifts as the result of the change of the refractive index and dielectric constant surrounding the metal [18]. Compared with the pure Ag nanowire of the similar dimensions, significant broaden and red-shifted band with an absorption centered at about 467 nm was observed, which is the unique characteristic of this core-shell composite [19]. The strong absorption in the visible region of the composite could provide a more promising approach to enhance the light-harvesting efficiency of the photoanode.

Absorption spectroscopy and FDTD simulation

Compared to the general spherical metal nanostructures previously reported in DSSCs with LSPR effect alone, the one-dimensional AgNW@TiO₂ core-shell composite is supposed more expectation due to the dual behavior of both localized field enhancement and light propagation [20]. The former property is well-known and the latter is the unique and more attractive. As the material showing the lowest loss in visible spectrum, [21] Ag nanowire is a very effective waveguide for plasmon propagation and has the advantage of both localizing the electromagnetic energy in nanoscale regions and propagating light via surface plasmon polariton effect [22]. When the incident radiation acts on one facet end of AgNW, the SPP nanowire mode can be effectively excited owing to an additional wave vector provided by scatter effect to match that of the SPP mode [23]. SPP could propagate over distances exceeding tens of micrometers in AgNW beyond the diffraction limit. When referring to the

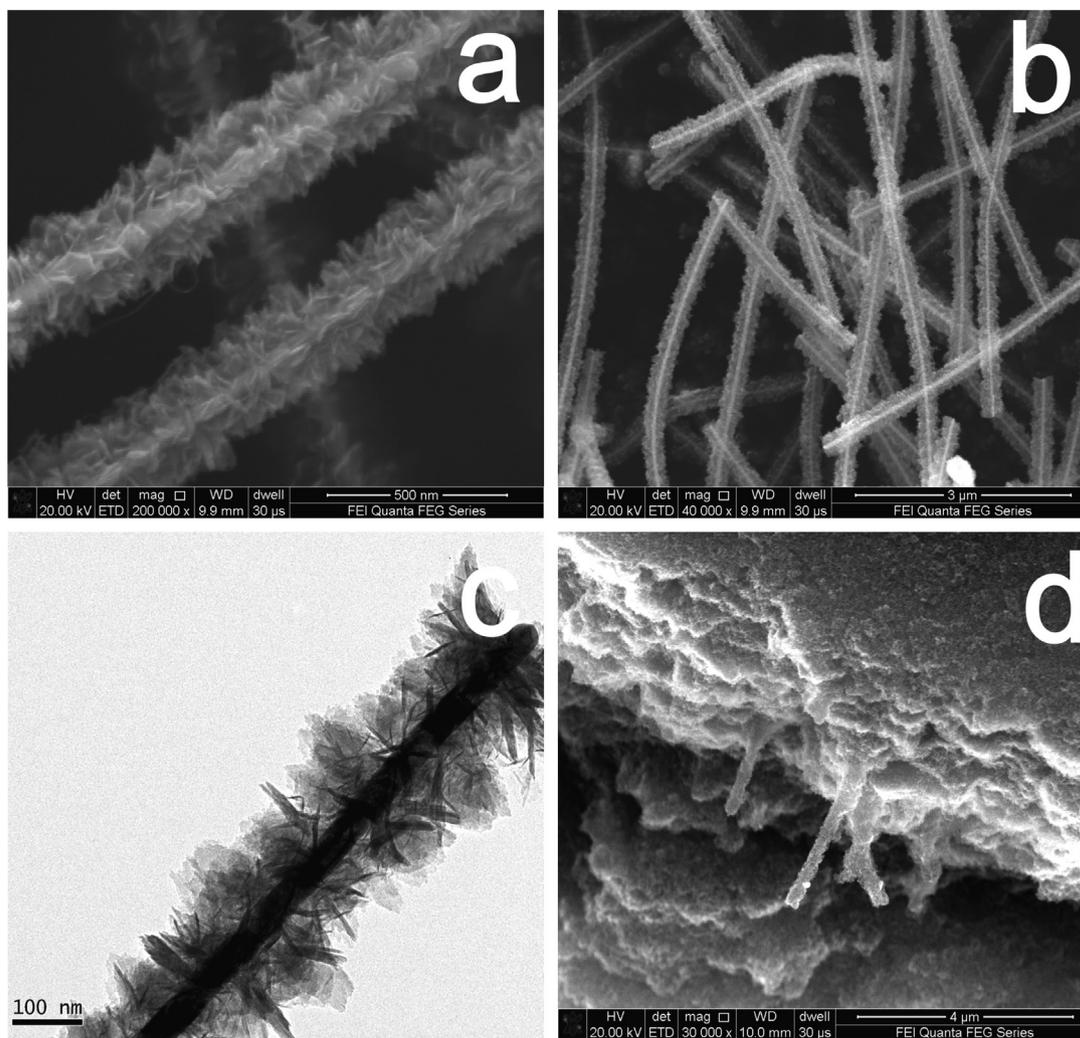


Figure 1 SEM images of the AgNW@TiO₂ nanocomposites (a and b) and nanocomposite-modified TiO₂ film (d), and TEM images of the AgNW@TiO₂ nanocomposites (c).

application of the AgNW@TiO₂ composites in DSSCs, both the direct incident light and scattered light from the neighboring TiO₂ nanoparticles could provide the excited source of the SPP of the AgNW, so the plasmonic effect can be effectively achieved and contribute to the enhancement of the light absorption in DSSCs.

In order to evaluate the contributions of the AgNW@TiO₂ core-shell composite on the light-harvesting effect, the UV-vis absorption spectrums of the dye-absence/adsorbed/desorption TiO₂ film incorporated different amounts of AgNW@TiO₂ composite were investigated and shown in Figure 3. As can be seen in Figure 3a, composite-modified films present the enhanced absorption compared to the pure TiO₂ film, and the intensity of SPR band increased with the increase of the composite concentrations. Figure 3b shows the dye-adsorbed spectrums. It was found that the absorption of the composite-modified films were both enhanced and broadened remarkably compared to that of the free-modified film. Here are two aspects benefiting in the utilization of the light. On one hand, localized surface plasmon resonance (LSPR) effect of the composite stimulated by illumination light leads to the collective excitation oscillations and creates a strong enhancement of the localized electromagnetic fields around the AgNW. This

enhanced electromagnetic field improves the interaction with the dye molecule dipoles and thus results in the enhanced light absorption of the dye and more charge carrier generation [24]. On the other hand, the unique plasmonic waveguide characteristic of this one-dimensional metal structure could promote the light propagation. As the excited SPP propagating mode reaches the far end of the nanowire, it scattered into free space and then radiates excited plasmons by wave vector compensation effect, which is known as the efficient exciton-plasmon-scattered photon conversion [25]. With the advantages with low propagation losses and long transmission length, [26] the plasmonic waveguide effect could effectively increasing the light path in photoanode, which could enhance the light harvesting efficiency of the dye molecules adsorbed on the back of the photoanode far away from the incident light.

About the dye-adsorbed spectrums shown in Figure 3b, the maximum was obtained at 1.58 wt% and then there is a slight decrease trend with the increase of the doping concentration. To investigate the phenomenon, the Absorption spectra of the dyes C106 desorbed from various photoanodes measured in NaOH solution are shown in Figure 3c. It was found that the adsorbed dye amount is lowered by the presence of AgNW@TiO₂ and the dye adsorption decreases with the increase of the

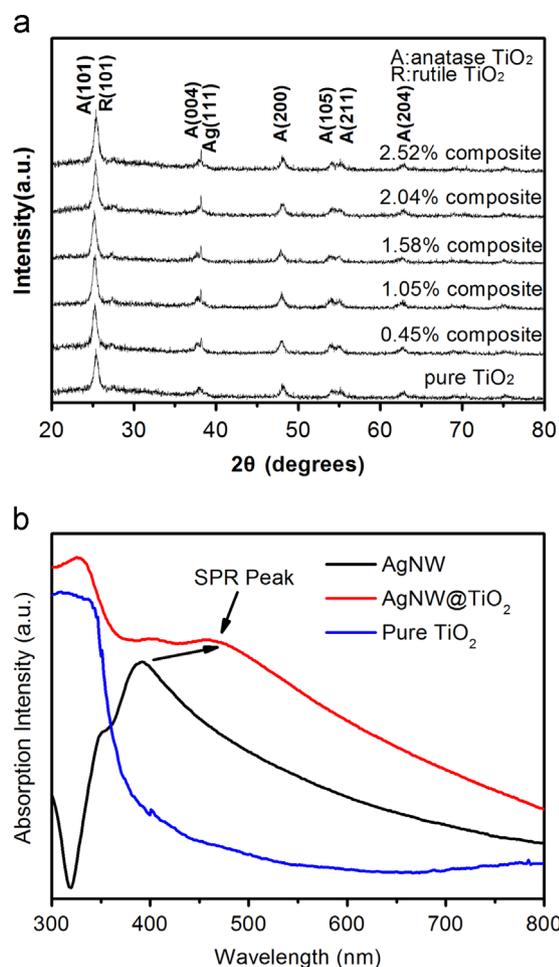


Figure 2 (a) X-ray diffraction (XRD) patterns of pure and metal modified TiO_2 films and (b) absorption spectrum of the AgNW@- TiO_2 dispersion in ethanol.

doping concentration of the composites. The results confirm the above inference that the enhanced absorption of the composited-modified photoanode is attributed to the dual plasmonic effect of the AgNW@ TiO_2 . With the increase of the doping concentration, the plasmonic effect of the AgNW@ TiO_2 is enhanced at the expense of the lower adsorbed dye amounts, so there is an optimal concentration for keeping the balance of the two aspects.

To further clarify the effects of plasmonic behaviors of the composite, theoretical investigation on spatial properties of light trapping by plasmonic effect is developed. Finite Difference Time Domain method (FDTD) is applied to calculate the electric field intensity distributions and the results are shown in Figure 4 (Lumerical FDTD solutions). The geometry of the AgNW is modeled as a cylinder in the air with the diameter of 80 nm and the length 5 μm , respectively. An incident plane-wave at $\lambda_0=450$ nm stimulates one near cusp of the AgNW to obtain the LSPR effect. Figure 4a shows the intensity of electrical field of AgNW on the cross section. It was found that the local field surrounding the AgNW is strongly enhanced, hence dye molecules located to the plasmonic nanostructures can be sufficiently affected by LSPR effect.

Figure 4b shows the field distribution of electrical field intensity along the radial direction when plasmonic

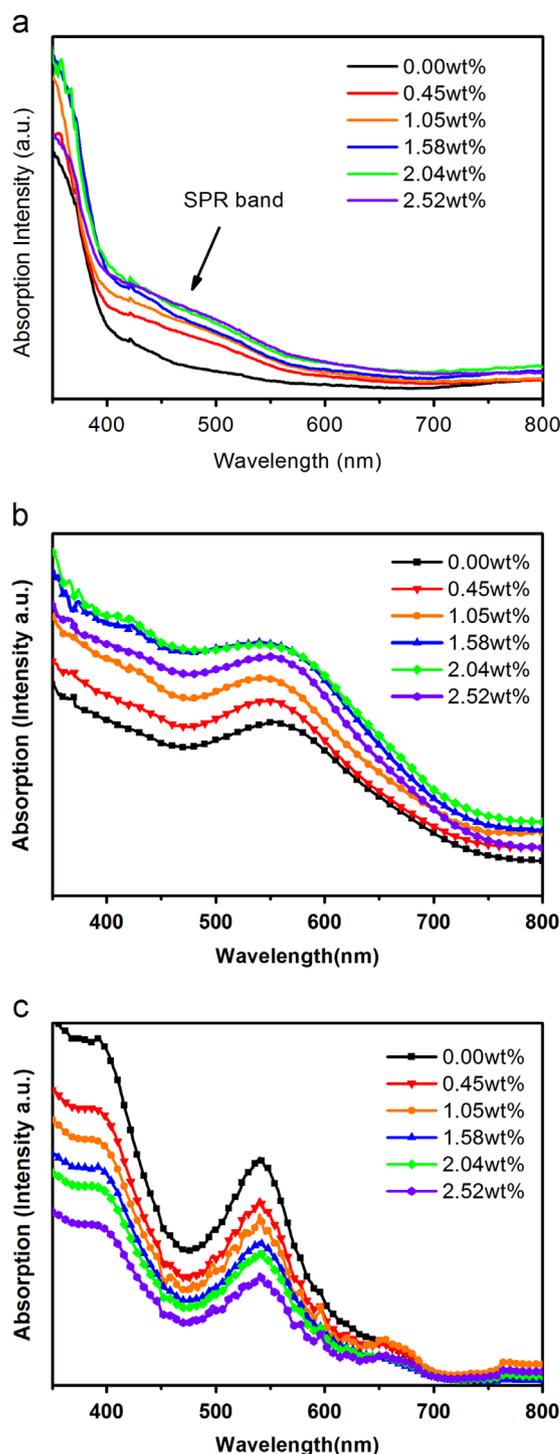


Figure 3 (a) Absorption spectra of pure TiO_2 film and composite-modified TiO_2 films. (b) Absorption spectrum of the different TiO_2 photoanodes adsorbed dyes. (c) Absorption spectra of the desorbed C106 from dye-loaded TiO_2 film in NaOH solution.

waveguide is stimulated. The plasmonic waveguide propagates along the AgNW and the intensity of electrical field has cyclical changes, and finally the propagating plasmons are coupled into photons at the output end by scattered effect (Figure 4c). A schematic diagram describes the light propagating process (Figure 5). When incident illumination propagates through the pure TiO_2 film (Figure 5a), due to the

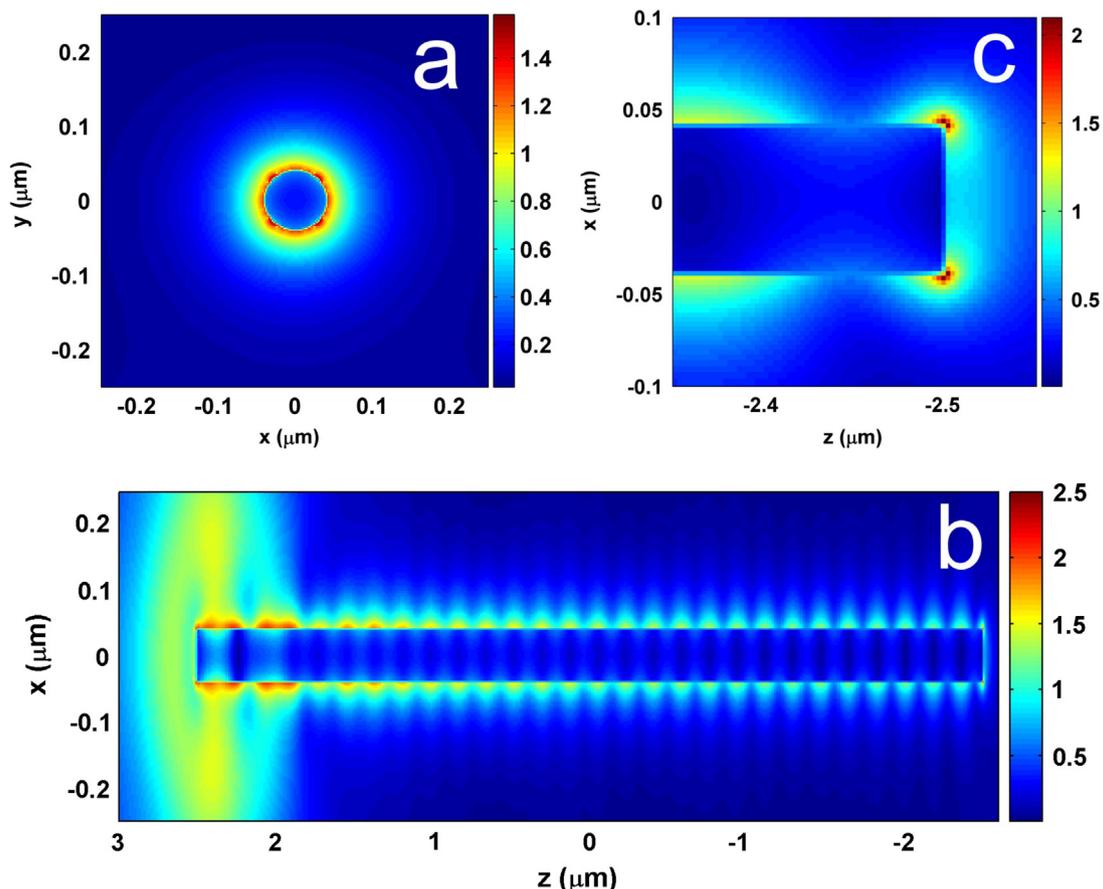


Figure 4 The calculated distribution of electric field amplitude intensity around a AgNW. (a) The localized electric field distribution around AgNW on the cross section, (b) the electric field distribution of plasmonic waveguide along the radial and (c) the electric field distribution at the output end of AgNW.

scattering effect of the TiO_2 NPs and the absorption of the dyes, the intensity of the light decreased gradually along with the propagation distance. So the layer far away from the incident illumination may not harvest enough light, which would affect the light harvesting efficiency of the whole film. As to the composite-modified film (Figure 5b), the plasmonic waveguide effect of the AgNW could propagate the light from one cusp to the other cusp with less loss. These extra optical pathways ensured the layer far away from the illumination could obtain the sufficient light for a higher performance.

Therefore, the localized field enhancement and plasmonic waveguide effect significantly improved the absorption of dye molecules and the optical propagation path in the whole TiO_2 photoanode, respectively. Hence, these unique characteristics are beneficial to boost the J_{sc} and the power conversion efficiency of DSSCs.

Photovoltaic performance of DSSCs

To investigate the optics-electrics properties of Bristled AgNW@TiO_2 on the performance of DSSCs, the current-voltage (I - V) and incident photon-to-current conversion efficiency (IPCE) characteristics of DSSCs with pure and composite-modified TiO_2 photoanodes are discussed in this section. Figure 6a shows the I - V curves of devices with different Ag amount. The short-circuit current density (J_{sc}), the open voltage (V_{oc}) and the

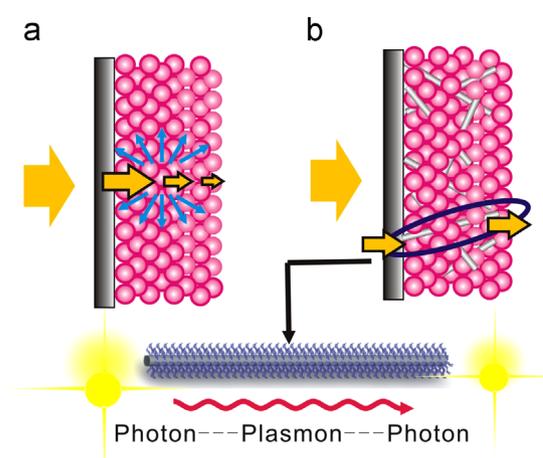


Figure 5 Schematic diagram of the light propagating process in different photoanodes: (a) scattering and absorption in pure TiO_2 film, and (b) extra optical pathways in composite-modified film.

power conversion efficiency (η) can be significant modified with different Bristled AgNW@TiO_2 concentration, ranging from 0.00% to 2.52 wt% (results displayed in Table 1). J_{sc} , V_{oc} and η increased firstly and then dropped with the increase of Bristled AgNW@TiO_2 concentration. The maximum of optimized J_{sc} (16.83 mA cm^{-2}) and V_{oc} (756 mV) are obtained at 1.58 wt%.

In Table 1, the increasing of J_{sc} mainly benefits from the enhanced light-harvesting efficiency and superior electrical highway characteristic. The interaction between the LSPR effect of Bristled AgNW@TiO₂ and the dye molecular dipole could enhance the photoelectron quantum yield, meanwhile the plasmonic waveguide effect would significantly increase the optical pathway. Consequently, both light harvesting effect and charge generation effect are enhanced. The Schottky barrier at the Ag/TiO₂ interface [11,27] will form electron-hole separation centers, and this steady state of semiconductor-metal nanostructure contact could be beneficial in improving the movement of photo-generated electrons transporting from excited dye to TiO₂ nanoparticles, then it reduces the recombination of carriers [28]. Moreover, the AgNW core of the composite could play a role as

the electrons transport highway. Due to the excellent electrical conductivity and the typical structural feature of the one-dimensional metal nanostructures, the separated charges transport rapidly in photoanode with less trapping and pathway, then it effectively enhanced the charge collection efficiency and increases the J_{sc} .

It is noted that when the concentration of the composite is more than 1.58 wt% the J_{sc} of the devices has a decrease trend, and this case is associated with the change of the photoanode structure and adsorbed dye amount. Excess concentration of composite would probably induce the aggregation and the flaw of TiO₂ film, which increases charge carrier recombination. The advantage of the increased light harvesting effect is offset by the suppressive. Also the composite with a higher percentage in photoanode is at the expense of decreasing the amounts of TiO₂ nanoparticles, which result in the reduction of the surface area of the photoanode relatively. Hence the less amount of dye molecules can be adsorbed [29]. The IPCE of DSSCs is shown in Figure 6b. As the consequence of both improved light-harvesting efficiency and electron collection efficiency, the tendency of IPCE is consistent with the trend of J_{sc} , which indicated the improvement of the LHE, electron injection and collection efficiency.

In addition to the enhancement of J_{sc} in Table 1, the introduction of bristled AgNW@TiO₂ composite into TiO₂ film can improve the V_{oc} of the DSSCs by participation in Fermi level equilibration [30]. The electrons rapidly transport from the neighboring TiO₂/dye/nanoparticles to AgNW and then the electrons-storage within the AgNW is formed. This process is beneficial to the photoelectrochemical performance of the Ag-TiO₂ films. This property makes the quasi-Fermi energy of the Ag-TiO₂ composite system shift to a more negative level compared to that of a pure TiO₂ photoanode which is reflected as a higher V_{oc} [12].

The stability of the efficiency is an important indicator for the DSSCs, Original metal-modified DSSCs have notable advantages in enhancing the performance of the DSSC. Whereas, considering the thermal stability, corrosion resistance, antioxidant quality and the charge recombination ability, these typical DSSCs did not have a good performance on the stability of the efficiency. Here in our study, the unique “bristled” core-shell structure solved this problem. Bristled TiO₂ shell of the composite formed close contact with neighboring TiO₂ nanoparticles, which is benefit in electron transport. Moreover, the shell could prevent AgNW core from electrolyte leakage and corrosion, and the deformation can be avoided when annealing. To investigate the chemical stability of the bristled TiO₂ shell to the electrolyte containing iodide/triiodide redox couple, a preliminary

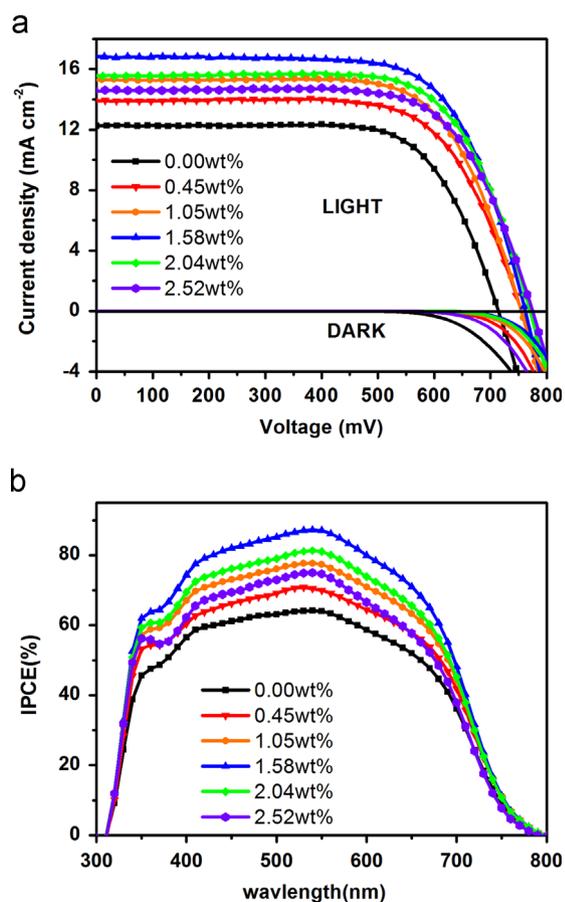


Figure 6 (a) I - V and (b) IPCE characteristic of DSSCs with various TiO₂ photoanodes.

Table 1 Photovoltaic characteristics of DSSCs with various TiO₂ photoanodes.

Group	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF	η (%)
Pure TiO ₂	710 ± 7	12.25 ± 0.14	0.704 ± 0.03	6.15 ± 0.11
0.45%-AgNW@TiO ₂	750 ± 9	13.91 ± 0.21	0.698 ± 0.02	7.22 ± 0.14
1.05%-AgNW@TiO ₂	751 ± 11	15.29 ± 0.22	0.699 ± 0.04	7.99 ± 0.17
1.58%-AgNW@TiO ₂	756 ± 10	16.83 ± 0.17	0.701 ± 0.03	8.84 ± 0.15
2.04%-AgNW@TiO ₂	760 ± 9	15.55 ± 0.19	0.705 ± 0.02	8.39 ± 0.16
2.52%-AgNW@TiO ₂	763 ± 8	14.60 ± 0.18	0.698 ± 0.03	7.85 ± 0.13

experiment was designed. Same amounts of electrolyte were injected into AgNW@TiO₂ and bare AgNW respectively, and the absorption spectrums of the two mixtures were measured at different time. As shown in Figure S2†, absorption peak of the pure AgNW quickly disappear after mixed with electrolyte, and absorption curve of AgNW@TiO₂ mixed with electrolyte remains almost unchanging in intensity after 15 days. This result demonstrates the excellent chemical stability of bristled TiO₂ shell to electrolyte containing iodide/triiodide redox couple. As a result, both high performance and good stability of DSSCs are achieved. When it comes to the photoanodes with AgNW@TiO₂ and bare AgNW, absorption spectrums of two photoanodes before and after annealing at 500 °C are measured and shown in Figure S3†. It was found that the peak and intensity of absorption with Ag NW@TiO₂ are almost unchanged, which indicated the excellent thermal stability of core-shell nanostructures. Whereas, the decrease of the absorption intensity and slight red-shift of the SPR peak are observed in the photoanode with bare Ag NW, which clarified that deformation and melt of Ag NW occurred and some Ag nanoparticles are formed. The weak performance of bare Ag NW limit the light harvesting efficiency of the DSSCs. That is, only LSPR effect can be developed, and plasmonic waveguide effect is not utilized due to the deformation of the bare AgNW. Figure S4† shows the evolution of the power efficiency about two types of DSSCs (1.58 wt% AgNW@TiO₂ and 1.20 wt% bare AgNW). It was found the decrease of the efficiency about DSSC 1 (with AgNW@TiO₂) is almost non-obvious for 500 h, which indicates that this metal modified system is stable and high-efficiency. To the contrary, improvement of DSSC 2 (with bare AgNW) is related weak and short-term (Dozens of hours). It can be interpreted that bare AgNW is corrosive and oxidized, then the improvement of the performance almost disappeared after a period of time. The comparison further confirmed that the AgNW@TiO₂ is stable and high-efficiency, and it is expected as a potential modified technology for the enhancement of the DSSCs.

Electrical properties of bristled AgNW@TiO₂ composite applied in DSSCs

The introduction of bristled AgNW@TiO₂ composite into TiO₂ photoanode also significantly impact on the separation, recombination and transporting process of the photoelectrons. Traditional DSSCs using pure metal oxide nanoparticles are usually a random network of crystallites [31] with uncontrolled electron scattering and electron trap. The typical composite-modified cells could transport charges rapidly with less recombination probability which are expected to deliver much higher conversion efficiency. As the effective charge separation center and high-speed electrical tunnel, the electrical properties of the bristled AgNW@TiO₂ influenced on the performance of the DSSCs exhibit in two aspects: firstly, it accelerates the production-separation of charges and suppresses the charge recombination with triiodide ion and excited dye effectively, then improve the charge injection efficiency; secondly, it provides direct transmission path and fast transport rate for charges, and thus the charge collection efficiency is improved. Schematic diagram of the photoelectrons transporting process in different photoanodes is shown in Figure 7.

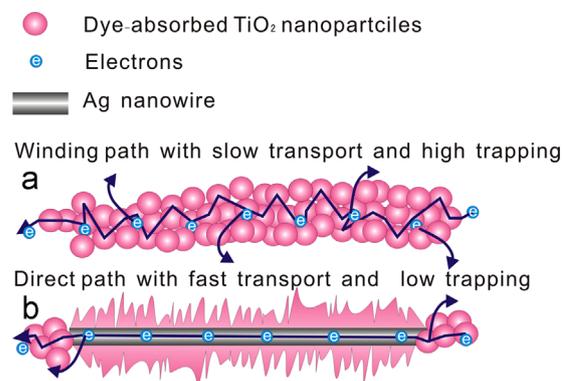


Figure 7 Schematic diagram of photoelectrons transporting process in photoanodes of (a) pure TiO₂ DSSCs and (b) nanocomposite-modified DSSCs.

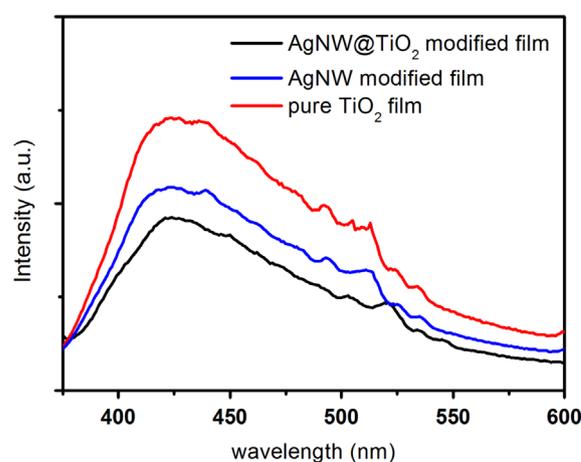


Figure 8 Photoluminescence (PL) spectra of pure TiO₂ film, AgNW-modified TiO₂ film and AgNW@TiO₂-modified TiO₂ film.

Electrons transporting in pure TiO₂ photoanode is a tortuous process with certain trapping rates. In comparison, the presence of the one-dimensional composite could provide the direct high-speed pathways for electrons, and the rate of the surface trapping and recombination of charges transport in photoanode can be reduced. The PL spectra, electron residence time, electron collection time and electron collection efficiency are discussed to study the electrical properties of bristled AgNW@TiO₂ applied in DSSCs in detail.

To confirm the capability of charge separation by the composite, the PL spectra of pure TiO₂, AgNW-modified TiO₂ and composited-modified TiO₂ are discussed and shown in Figure 8. PL spectra are often employed to study the surface processes involving electron-hole recombination of semiconductors [32]. The observed emission around 425 nm can be assigned to the recombination of photoexcited holes with electrons occupying the singly ionized oxygen vacancies in TiO₂. The PL spectra shows that both of the pure AgNW and AgNW@TiO₂ has the lower PL intensity compared to the pure TiO₂ film, and it indicated that the recombination of electron-hole pairs has been reduced effectively. In addition this, the lowest intensity was observed in AgNW@TiO₂-modified TiO₂ film. This result explained the effect of the bristled shell on

reducing the recombination. As the bristled shell of the AgNW@TiO₂ could ensure the close contact with neighboring TiO₂ nanoparticles, which was beneficial for reducing the traps and accelerating the charge separation-transport. Consequently, it indicated that the recombination of electron-hole pairs has been reduced effectively by both the bristled TiO₂ shell and the AgNW core of the composite.

To further investigate the effect of the bristled AgNW@TiO₂ composite on the device performance, electrochemical impedance spectroscopy (EIS) is carried out for devices based on TiO₂ photoanodes with and without AgNW@TiO₂ composite doping. An equivalent circuit model is illustrated in Figure 9a [33]. From left to right: R_s is the sheet resistance of FTO and the contact resistance between the FTO and TiO₂; R_{pt} and C_{pt} are the charge transfer resistance and interfacial capacitance at the Pt/electrolyte interface; R_w is the charge transfer resistance in TiO₂ film, and R_{ct} and C_{μ} are the charge transfer resistance and interfacial capacitance related to the recombination/transfer of electrons at the TiO₂/electrolyte interface. The first small semicircle at high frequency is assigned to the R_{pt} and C_{pt} , the second semicircle at low frequency is related to the R_{ct} and C_{μ} , and the short linear section between the two semicircles (at middle frequency) reflects the R_w [34].

In dark condition, the electron process is only the recombination between electrons and I^-/I_3^- in the electrolyte. The larger the value of R_{ct} was, the slighter the electron recombination at the TiO₂/dye/electrolyte interface was. Figure 9b showed the Nyquist plots of different DSSCs at -700 mV bias voltage in dark condition. Compared to the DSSCs with pure TiO₂, the interface resistance of DSSCs with AgNW@TiO₂ was much bigger, which indicated that the charge re-combination was obviously retarded. The decrease of recombination was mainly due to the effective charge separation ability of the AgNW@TiO₂.

Under illumination condition, the process of electron injection from dyes to conductive dominated the dynamic behavior of electrons. So resistance at the TiO₂/dye/electrolyte interface was also presented by the middle frequency semicircle in the Nyquist plots. The smaller the value of R_{ct} was, the faster the electron transfer at the TiO₂/dye/electrolyte interface was. Figure 9c showed the Nyquist plots of different DSSCs under illumination condition. Compared to the DSSCs with pure TiO₂, the interface resistance of DSSCs with AgNW@TiO₂ was smaller, which indicated that the charge injection was obviously improved. The acceleration of charge injection was mainly due to high-speed electrical tunnel role of the AgNW core.

Electron residence time τ_n and electron collection time τ_d can be derived from the EIS measurements under dark condition with different bias voltage, which reflect the charge recombination and transporting characteristic in charge dynamics process of the DSSCs respectively [35]. τ_n and τ_d can be estimated as $\tau_n = R_{ct}C_{\mu}$ and $\tau_d = R_wC_{\mu}$ [36]. Figure 10a and b exhibits the linear description of τ_n and τ_d under different bias voltage. τ_n of composite-modified DSSCs is longer than that of pure TiO₂ DSSCs, this indicates that the recombination rate of the electrons is suppressed by composites doping. But a falling-rising trend of the τ_n value was observed with the increasing composite amounts and the maximum value presents at the concentration of 1.58 wt%, which reflects the appropriate doping concentration is needed to ensure the optimal performance of DSSCs. Electrons transport from the semiconductor to the neighboring

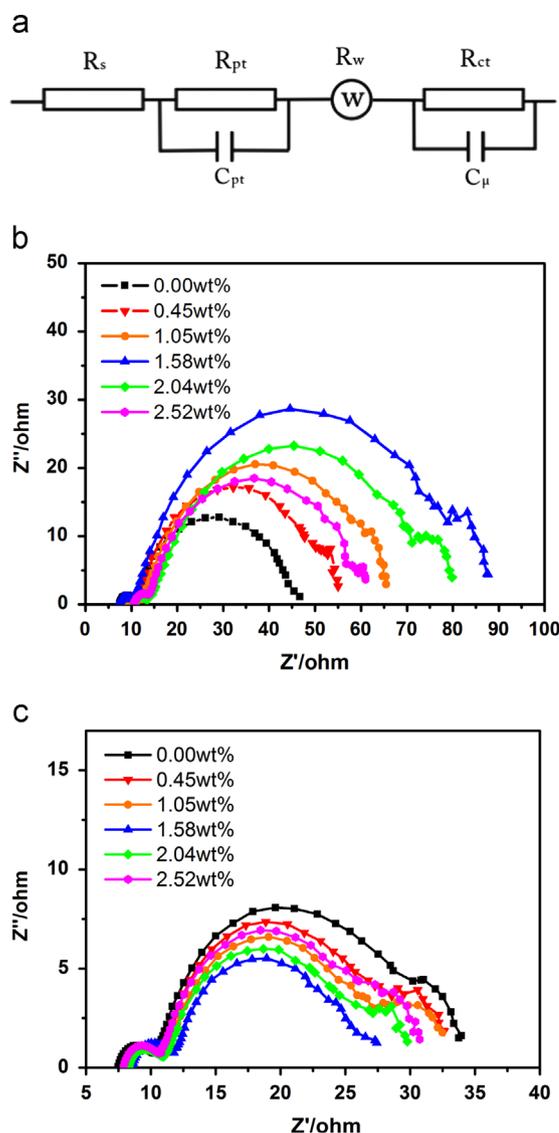


Figure 9 Electrochemical impedance spectra of DSSCs. (a) Equivalent circuit model, (b) Nyquist plots of electrochemical impedance spectra of pure and composites-modified DSSCs at -700 mV forward bias under the dark condition and (c) Nyquist plots of electrochemical impedance spectra of pure and composites-modified DSSCs under the illumination condition.

metal nanoparticles is an ultrafast process. The interaction between TiO₂ nanoparticles and AgNW@TiO₂ composite is beneficial to the electrons separation and the suppression of the recombination. In addition, the unique core-shell structure could avoid the contact between AgNW core and electrolyte then eliminating the leakage phenomenon. However, excess composite impairs the capability of electrons separation and structural integrity of photoanode and thus the recombination ratio increases. This noticeable variation is consistent with the dark current curves of the DSSCs.

About the electron collection time τ_d related to the transfer property of conduction band electrons, the value of τ_d increased with increasing the ratio of composites. Due to the excellent electrical conductivity and one-dimensional feature of the composites, the “antenna-like” bristled AgNW@TiO₂ composites provide transfer highways for the

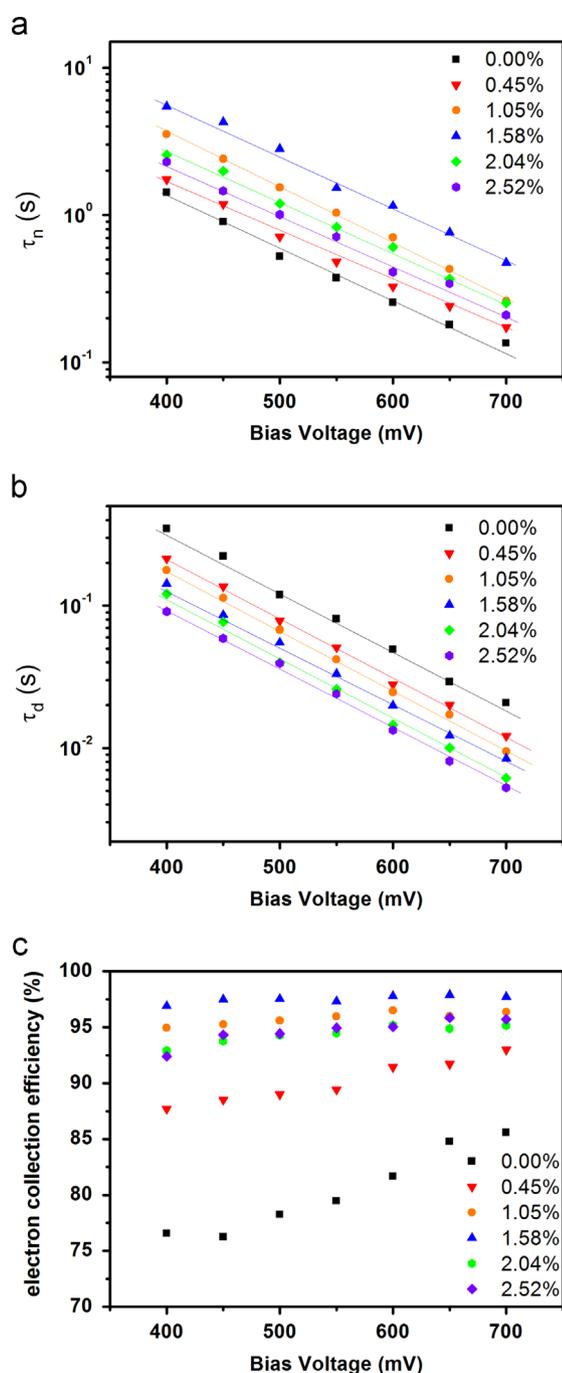


Figure 10 (a) Electron residence time (τ_n) and (b) Electron collection time (τ_d) in different DSSCs. (c) Charge collection efficiency (η_c) at different bias voltage for DSSCs.

electrons with shorter collecting distance. Then the transfer of electrons in is in composite-modified DSSCs faster than that in pure TiO₂ DSSCs.

The efficiency of charge collection efficiency η_c can be defined as $\eta_c = 1 - \tau_d/\tau_n$ [35,36]. For higher collection efficiency, the cell should render better transport of charges and with lesser recombination. Figure 10c shows the result of the η_c in different DSSCs, and it exhibits that the presence of the composite is benefit in the improvement of charge collection efficiency, Whereas the trend of η_c increased from 0% to 1.58% and decreased $\geq 1.58\%$, it

suggested that only the appropriate doping concentration can provide the optimal competition of both restraining the trapping and accelerating the transfer, then the highest efficiency is obtained. This trend of η_c is also consistent with the I - V curves of the DSSCs. The “electrical highways” property of the composite effectively promoted the electrons collection with its dual transfer-recombination features superior to the previous metal modified technology.

Conclusion

In this article, the typical bristled core-shell AgNW@TiO₂ composites are prepared and applied in DSSCs. The influence of the composite on the performance of DSSCs was systematically investigated with experimental and theoretical methods. The plasmonic composite effectively enhanced the light absorption and optical path of the photoanodes. Meanwhile, the recombination at the TiO₂/dye/electrolyte interface is suppressed and the charge transport-collection efficiency is improved. The optimal properties of the composite-modified DSSC was obtained with power conversion efficiency of 8.84%, which is significantly superior to that of the DSSC with pure TiO₂ photoanode of 6.16%. Compared to the previous spherical metal nanostructures, the unique “optics-electrics expressways”, the bristled core-shell AgNW@TiO₂ composites, fully exploits the plasmonic waveguide effect, localized surface plasmon effect and electron collection characteristic in DSSCs. It is expected to be a potential metal-modified technology for improving the performance of DSSCs.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2014.09.011>.

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