Graphical abstract

Plasmonic copper nanowire@TiO₂ nanostructures were prepared and applied for the application of dye-sensitized solar cells.

Plasmonic Copper Nanowire@TiO₂ Nanostructures for Improving the Performance of Dye-sensitized Solar Cells

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Abstract: Plasmonic copper nanowires@TiO₂ (Cu NWs@TiO₂) core-shell nanostructures are synthesized and applied for dye sensitized solar cells (DSSCs). Both experimental and theoretical studies (Finite Difference Time Domain Simulation) reveal that doping of the Cu NWs@TiO₂ nanostructures into the TiO₂ photoanodes can enhance the light absorption of dye molecules and the carrier's separation through the localized surface plasmon resonance (LSPR) and plasmonic waveguide (PW) effects, and thus significantly improve the light harvesting efficiency of the device. The optimized doped DSSCs show the best power conversion efficiency (PCE) of 9.44%, which is 23.40 % higher than that of undoped DSSCs (7.65%).

Keywords: Copper nanowires@TiO₂; Dye-sensitized solar cells; Localized surface plasmon resonance; Light harvesting efficiency

1. Introduction

Dye-sensitized solar cells (DSSCs), a typical sandwiched photovoltaic cells which composed of TiO_2 photoanode, electrolyte and a platinized counter electrode, have been considered as promising alternatives to harvest and convert solar energy.[1-7] Up to now, a photoelectric conversion efficiency (PCE) as high as 13% has been achieved, indicating the potential of commercial applications of the devices.[8] However, there are still some technological and scientific methods could be employed to further improve the performance before the widespread commercialization of DSSCs. For instance, extending the absorption coefficient of dye sensitizers to a broader range in the solar spectrum,[9] improving the light-harvesting efficiency (LHE)[10] and suppressing the process of carrier recombination[11] have been investigated to increase light utility in solar cells.

Recently, nanostructured metals (e.g., Au and Ag) have been employed to promote the DSSC performance because they can increase the light-harvesting efficiency of the dye via far-field scattering, near-field local surface plasmon, or as a sensitizer to induce charge separation.[12-21] In addition, the localized surface plasmon resonance (LSPR) of nanometals, which traps the light on the metal surface and induces a collective oscillation of metal free electrons, could increase the light absorption of dye molecules and boost the carriers separation.[22-27] However, LSPR effect of these plasmonic nanostructures could not effectively promote the light transmission and accelerate the

1 electronic transmission in the TiO_2 photoanode.[11, 28-30] Furthermore, the
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3 dye/nanometal/electrolyte interfaces usually lead to the recombination and back
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5 reaction of photo generated carriers. Core-shell metal@ SiO_2 nanostructures
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7 have also been applied to enhance the performance of cells.[17, 31] However, it
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9 is difficult for photo generated carriers (located on the SiO_2 surfaces) to inject
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11 into SiO_2 shell since SiO_2 is insulating.
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17 Inspired by these results, here, we report the synthesis and applications of
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19 plasmonic copper nanowires@ TiO_2 (Cu NWs@ TiO_2) core-shell nanostructures for
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21 improving the performance of DSSCs. The synthesized Cu NWs@ TiO_2
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23 nanostructures exhibit both the LSPR and plasmonic waveguide (PW) effects, as well
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25 as electric tunnel characteristics.[32] Compared with undoped TiO_2 photoanodes,
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27 doping of Cu NWs@ TiO_2 could promote light propagation with less loss, and thus
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29 effectively improve the light harvesting efficiency.[11], [33] In addition, Cu
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31 NWs@ TiO_2 doped TiO_2 can maintain a more negative Fermi level than the pure TiO_2 ,
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33 leading to the higher open voltage of DSSCs.
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44 **2. Experimental**

45 **2.1 Materials**

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48 CuCl₂·2H₂O, NaOH, ethylenediamine (EDA), ethylene glycol (EG), isopropyl
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50 alcohol (IPA), N₂H₄, polyvinylpyrrolidone (PVP, K-30), diethylhydroxylamine
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52 (DEHA), iodine (I₂), and tetrabutyl titanate (TBOT) were purchased from Aladdin
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Industrial Corporation (Shanghai). Lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) was supplied by Rhodia. Cis-bis(isothiocyanato) bis (2, 2'-bipyridyl-4, 4'-dicarboxylato) ruthenium (II) ([RuL₂(NCS)₂]) (dye N719) and 4-*tert*-butylpyridine (TBP) were purchased from Solaronix SA (Switzerland) without any further purification. TiCl₄ and H₂PtCl₆ were purchased from Sinopharm Chemical Reagent Co. Ltd. 1-Propyl-3-methylimidazolium iodide (PMII). Fluorine-doped tin oxide over layer (FTO) glass electrodes (7Ω/Sq), slurries containing 20 nm sized mesoporous and 200 nm light-scattering TiO₂ colloidal were purchased from Dalian Hepat Chroma Solar Tech. Co., Ltd.

2.2 Characterization and Photovoltaic Measurements

Tecnai G2 F30 field emission transmission electron microscope (TEM) was used to shot the photographs at an operating voltage of 300 kV. The collection of UV/VIS absorption spectra was acquired using a TU1800 SPC spectrometer. The solid UV/VIS absorption spectrum was obtained using a UV- 3150 UV-Vis-Nir spectrophotometer Shimadzu. The crystalline structure of the Cu NWs@TiO₂ doped TiO₂ films was tested by the X-ray diffraction (XRD) (D/MAX-2400, Japan). The electrochemical impedance spectra (EIS) of the DSSCs were carried out using a CHI660c electrochemical workstation through the AC impedance method at the forward bias voltage for the impedance measurement was -0.7 V. The photocurrent density-voltage (I-V) curves of the fabricated cells shielded by an aluminum foil mask

with an aperture area of 0.1 cm^{-2} were measured with a digital source meter (Keithley, model 2612) under simulated air mass (AM) 1.5 solar spectrum illumination at 100 mW cm^{-2} . Incident photo-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength was recorded on a Keithley 1612 source meter under the irradiation of a Xenon lamp with a monochromator (Oriel CornerstoneTM 260 1/4).

2.3 Synthesis of Cu NWs

The Cu NWs used in this work were synthesized follow the method reported.[34] A mixture containing 20 mL of 15 M NaOH, 1 mL of 0.1 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 3 mmol EDA was stirred at 70°C . Then, 0.12 mmol N_2H_4 was quickly added into the mixture and stirred for further two min. The reaction was stopped when the color of the solution changed to dark red. The obtained product was washed by the solution contain 3 wt % PVP and 5 wt % DEHA for several times.

2.4 Synthesis of Cu NWs@TiO₂ core-shell nanostructures

The synthesis process of Cu NWs@TiO₂ core-shell nanostructures is as following: 200 mg 0.5 mM TBOT, and 0.2 g Cu NWs were mixed with 20 mL EG. The mixed solution was loaded into a 50 mL Teflon thermal water kettle and maintained at 130°C for 2 to 10 h. Then the kettle was cooled to room temperature. The obtained precipitate was washed with acetone three times to remove the excess impurities, and

the product was dried at 80 °C in a vacuum oven over night.

2.5 Preparation of Cu NWs@TiO₂ doped photoanodes

The fabricated process was follow our earlier reports.[35, 36] The doping amount was defined by mixing the different weight of Cu NWs@TiO₂ with TiO₂ slurries used in this work. Fluorine-doped tin oxide (FTO) glass plates were cleaned with water, acetone, and ethanol for 10 min, respectively. Then the plates were soaked in 40 mM TiCl₄ solution for 30 min at 70 °C and washed with water and ethanol. Cu NWs@TiO₂ was mixed with 20 nm sized mesoporous TiO₂ paste in IPA, and then stirred at room temperature for 1 day. The TiO₂ paste was prepared by the doctor-blade to form a nanocrystalline layer. The photoanode was heated at 115 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min, respectively. The prepared photoanodes was treated again by TiCl₄ at 70 °C for 30 min and sintered at 500 °C for 30 min. After cooling to the room temperature, the photoanode was immersed in 0.5 mM N719 acetonitrile and tert-butyl alcohol solution over night to complete the sensitizer loading.

2.6 Preparation of the Pt counter electrode

0.1 mL of 5 mM H₂PtCl₆ in ethanol solution was dropped on the cleaned FTO glass, then the glass was dried and annealed at 400 °C for 15 min.

2.7 Fabrication of DSSCs

The devices were fabricated by sealing the photoanode and Pt electrode together with a hole of diameter 7 mm (Surlyn 1702, 25 mm, Solaronix) by using a thermal plastic spacer at 130 °C. The electrolyte was injected into the interspace between the photoelectrode and the Pt counter electrode. Then the devices were sealed with a Surlyn sheet and a thin glass by heating.

2.8 Dye desorption characterization

The N719-coated TiO₂ photoanodes were immersed in 2M NaOH aqueous solution for 2 h to remove the dye molecules at room temperature. Then the solutions were measured by the UV/Vis absorption spectrum using 2M NaOH solution as a reference.

3. Results and discussion

3.1 Properties of the Cu NW@TiO₂ nanostructures

Scheme 1 shows the flow diagram for the synthesis of Cu NWs@TiO₂ core-shell nanostructures, and their applications in DSSCs. The Cu NWs were prepared follow the methods reported.[34] The length and diameter of the copper nanowires are determined to be about 40 μm and 30-35 nm (**Scheme 1a, b**), respectively. The metal core oxide shells were synthesized through the hydrolysis–condensation reactions of TiO₂ precursor.[11] The thickness of the TiO₂ shell is controlled to be 15-20 nm, as

Scheme 1. Flow diagram for the synthesis of Cu NWs@TiO₂ core-shell nanostructures, and their applications in DSSCs. a) and b) the SEM images of synthesized Cu NWs; c) SEM image, and d) and e) TEM images of the synthesized Cu NWs@TiO₂; and f) The SEM image of the cross-section of the Cu NWs@TiO₂ doped TiO₂ photoanode. TBOT: tetrabutyl titanate.

shown in **Scheme 1d, e**. Then the prepared Cu NWs@TiO₂ nanostructures were doped into TiO₂ photoanodes.

The obtained Cu NWs@TiO₂ and analogous doped TiO₂ photoanodes (**Scheme 1f**) was further characterized by energy-dispersive X-ray spectroscopy (EDS) (**Fig. S1**), X-ray diffraction (EDX) and UV–vis absorption spectrum (**Fig. S2**). The observed Cu, Ti and O elements confirm the successful synthesis of Cu NWs@TiO₂ nanostructures (**Fig. S1**). The diffraction peaks of [110], [101], [111], [211] for TiO₂, and [111] and [220] peaks for Cu NWs are observed (**Fig. S2c**). The diffraction peaks appeared in the doped TiO₂ film indicate the dispersion of Cu NWs@TiO₂. In

addition, the pure Cu NWs show an absorption peak at about 585 nm,[37] while the Cu NWs@TiO₂ nanostructures present an absorption peak at about 593 nm (**Fig. S2d**). Such a red-shift may be caused by the change of the refractive index and dielectric constant surrounding the metal surface.[17, 26, 38] Compared with the pure TiO₂ film, the Cu NWs@TiO₂ doped TiO₂ film also shows a stronger absorption at 593 nm. Such a stronger absorption in the visible region could enhance the light-harvesting efficiency of the DSSCs.[5, 16, 39] Furthermore, the elemental mapping confirms the uniform distribution of Cu NWs@TiO₂ in the TiO₂ photoanodes (**Fig. S3**).

Fig. 1. UV/Vis absorption spectrum of a) Cu NWs@TiO₂ doped TiO₂ films; b) Relative enhancement in optical absorption ($\Delta OA/OA$) of doped TiO₂ films ($\Delta OA/OA = [Abs(doped\ films) - Abs(pure\ TiO_2\ film)] / Abs(pure\ TiO_2\ film)$); c) UV/Vis absorption spectrum of N719-coated TiO₂ films doped with various amounts of Cu NWs@TiO₂; and d) desorbed dye N719 from dye-coated TiO₂ photoanodes in 2M NaOH aqueous solution.

In order to investigate the doping effects of Cu NWs@TiO₂ on the performance of DSSCs, TiO₂ photoanodes doped with various amount of Cu NWs@TiO₂ (1.00 wt%, 2.50 wt%, 3.90 wt%, 4.70 wt%) were prepared. **Fig. 1a** shows the UV/Vis absorption spectrum of the TiO₂ photoanodes prepared. A broad LSPR band absorption at around 580 nm was observed for Cu NWs@TiO₂ doped TiO₂ photoanodes, while no absorption peaks appeared for undoped photoanodes. In addition, the absorption intensity increased with the increasing of the Cu NWs@TiO₂ content. The relative enhancement in optical absorption ($\Delta OA/OA$) of doped TiO₂ films is shown in **Fig. 1b**. Similarly, the absorption intensity is improved with the increase of the Cu NWs@TiO₂ content. It can be seen that the $\Delta OA/OA$ increased during the LSPR band which is consist with the previous reports, indicating that the Cu NWs@TiO₂ nanostructures could efficiently scatter the light.[3, 5, 11]

Fig. 1c shows the UV/Vis absorption spectrum of N719 coated TiO₂ photoanodes. It is not surprising that the light absorption intensities of the Cu NWs@TiO₂ doped TiO₂ photoanodes are enhanced and significantly broadened. The enhanced light absorption is mainly due to the LSPR effects,[16, 40-42] which create a strong localized electromagnetic fields around the Cu NWs@TiO₂, and therefore boost the interaction with the dye molecules and generate more contributions of resonant energy transfer between the surface plasmon and the dye excited state.[43, 44] In addition, Cu NWs@TiO₂ nanostructures show the unique plasmonic waveguide characteristic, which is better for light propagation. Here, the maximum absorption

peak was observed for 3.90 wt% Cu NWs@TiO₂ doped TiO₂ photoanodes.

The adsorbed dye molecules on TiO₂ photoanodes was desorbed in NaOH aqueous solution, and further characterized by UV/Vis absorption spectrum (**Fig. 1d**). It can be seen that the dye desorbed from the undoped TiO₂ photoanode shows the strongest absorption density, while decreases with the increasing of Cu NWs@TiO₂ doping content. The result indicates that doping of Cu NWs@TiO₂ could effectively decrease the dye absorption amount. Therefore, it can be concluded that the enhanced UV/Vis absorption is mainly due to the doping of Cu NWs@TiO₂. [11, 26] Based on these results, the optimal doping amount to keep the balance of adsorbed dyes and the advantages of Cu NWs@TiO₂ is 3.90 wt%.

To further prove the superior effects of Cu NWs@TiO₂ in DSSCs, models of the Cu NWs (diameter in 30 nm, length in 20 μ m) and the Cu NWs@TiO₂ (with a shell of 20 nm) are built and the theoretical investigation on the spatial properties of the light trapping is introduced. Here, Finite Difference Time Domain method (FDTD) is carried out to calculate the electric field intensity distributions. The results were calculated according to the Maxwell equations (shown in Supporting Information). **Fig. S4** shows the calculated excitation wavelength of the models. Consider the absorption region of N719, the excitation wavelength at $\lambda=585$ and 593 nm was investigated emphatically. **Fig. 2a, b** shows the electrical field intensity of Cu NWs and Cu NWs@TiO₂ at the xz plane when the plasmonic waveguide is stimulated. It was found that local

field surrounded the Cu NWs@TiO₂ was strongly enhanced. Therefore, the dyes located near the plasmonic nanostructures can be affected by the LSPR effects. **Fig. 2c, d** shows the intensity of electrical field of Cu NWs and Cu NWs@TiO₂ at the *xy* plane. The electrical field intensity of the Cu NWs@TiO₂ is stronger if compared with that of Cu NWs, mainly due to the fact that surface-coating plasmonic metal nanostructures with TiO₂ could boost the localized electric field intensity.[45] It has already been demonstrated that there are defect states within the band gap of TiO₂. [46, 47] The low density of these defect states limits the visible-light absorption and thus the photoactivity of TiO₂ in visible region will be decreased.[48] Meanwhile, with metal nanostructures inside, the optical absorption of TiO₂ will be increased due to the plasmon resonance energy transfer effects, leading to a strong electric field in the visible region substantially. In addition, energetic hot electrons may be generated in the metals. When the hot electrons possess sufficient energy, they can inject into the TiO₂ conduction band, and the energetic positive charges will be left in the metal.[41] The FDTD study indicates that the TiO₂ shell enhances the electric field, further supports the superior of Cu NWs@TiO₂. **Fig. S5** shows the distribution of localized electric field intensity around nanowires at the excitation peaks of 332, 345 and 348 nm, respectively.

Fig. 3 shows a visual schematic diagram described the light propagating process within the Cu NWs@TiO₂ doped TiO₂ photoanodes. The red arrows

Fig. 2. The calculated distribution of localized electric field intensity around nanowires at plasmon wavelengths. Cu NWs: (a) 585 nm at the xz plane and c) 585 nm at the xy plane; Cu NWs@TiO₂: b) 593 nm at the xz plane and d) 593 nm at the xy plane.

Fig. 3. Schematic diagram of the light propagating process in Cu NWs@TiO₂ doped photoanode.

indicate the scattering effect of the undoped TiO₂ nanoparticles. With the incident illumination propagated through the photoanode, the intensity of the light will decrease along with the propagation pathway. As a result, less light will be harvested.

However, doping of Cu NWs@TiO₂ may optimize the light pathways. The PW effect of the Cu NWs can propagate the light with less loss due to the formed unique electronic tunnels which can accelerate electron transport as well as suppresses recombination.

Fig. 4. Photoelectrons transporting process in dye-coated TiO₂ photoanodes: a) dye-coated undoped TiO₂ photoanode (the electron transmission is random); and b) Cu NWs@TiO₂ doped dye-coated TiO₂ photoanode (Cu NWs serve as a tunnel for electron transfer, leading to less surface trapping and recombination).

Fig. 4a shows the transport process of the electrons in dye-coated TiO₂ photoanode. As it can be seen that the electron scattering and traps are randomly distributed in the photoanode. Doping of Cu NWs@TiO₂ (**Fig. 4b**) may promote the production-separation of the charges and inhibit the charge recombination induced by excited dyes and triiodide ion, and thus increase the charge injection efficiency.^[11] In addition, the formed electron transfer tunnels

can accelerate the transport rate of charges. Therefore, the charge collection efficiency can be effectively improved.

3.2 Photoelectrochemical performance of Cu NWs @TiO₂ doped DSSCs

To gain a further investigation into the effects of Cu NWs@TiO₂ on the photovoltaic properties of the DSSCs, Cu NWs@TiO₂ doped DSSCs were fabricated and studied. **Fig. 5** shows the dependence of DSSCs parameters (short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall conversion efficiency (η)) on the doping amount of Cu NWs@TiO₂. The obtained data are summarized and listed in **Table 1**. It can be seen that doping of Cu NWs@TiO₂ increased the photocurrent and the open-circuit voltage and thus improve the PCE of the devices. The LSPR effect of Cu NWs@TiO₂ and the dye molecules dipole interaction could enhance the light-harvesting. In addition, the PW effect would shorten the light path in TiO₂ photoanode significantly. The electron-hole separation centers will be formed at the Cu NWs/TiO₂ interface. Such a steady state of semiconductor/nanometal contact could accelerate the movement of photo-generated electrons from excited dye to TiO₂ layers, resulting in the lowered carriers recombination.[49] Meanwhile, the separated charges can transport rapidly through the provided electronic tunnels in photoanode with less trapping and pathway due to the high electrical conductivity of the Cu NWs. The charge efficiency can be effectively improved and thus increase the J_{sc} . The dark-current curve reflects the

recombination of charges in the mesoporous TiO_2 conduction band with triiodide (Fig. S6). We can see that the dark current of the doped DSSCs was significantly decreased as compared to the undoped DSSC. The higher the amount of Cu NWs@ TiO_2 , the lower the dark-current of the DSSCs. These results can also be attributed to the suppression of the recombination in the TiO_2 layer.[3, 5]

Fig. 5. Dependence of DSSCs parameters on the doping content of Cu NWs@ TiO_2 : a) short-circuit current (the optimal J_{sc} is 18.26 mA cm^{-2}); b) fill factor (the FF almost unchanged); c) open-circuit voltage (the optimal V_{oc} is 0.76V , about 40 mV higher than that of the undoped DSSCs); and d) overall power conversion efficiency (η) under AM 1.5 illumination. All the photoanodes were sensitized with dye N719.

It is worth noting that there is a decrease tendency of the J_{sc} and PCE values when the Cu NWs@ TiO_2 doping content is higher than $3.9 \text{ wt}\%$. This result can be attributed to the defects formed in the TiO_2 films and the less amount of adsorbed dye (Fig. 1d). With the increasing doping amount of Cu NWs@ TiO_2 (for example, $4.70 \text{ wt}\%$ in this

work), both the less dye adsorbing and the flaws formed in the TiO_2 film decreased the suppression of charge carrier recombination.[3]

Table 1. Performance parameters of the DSSCs based on the Cu NWs@ TiO_2 doped DSSCs. Cells were tested under simulated AM 1.5 solar spectrum irradiation at 100 mW cm^{-2} by using an aluminum foil mask with an aperture area of 0.1 cm^{-2} (average of three cells).

Cu NWs@ TiO_2 (wt%)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
Pure TiO_2	15.92 (± 0.13)	0.72 (± 0.01)	0.67 (± 0.01)	7.65 (± 0.13)
1.00 wt%	16.44 (± 0.15)	0.75 (± 0.01)	0.68 (± 0.01)	8.39 (± 0.15)
2.20 wt%	17.34 (± 0.16)	0.76 (± 0.01)	0.68 (± 0.01)	8.94 (± 0.12)
3.90 wt%	18.26 (± 0.16)	0.75 (± 0.01)	0.68 (± 0.01)	9.44 (± 0.18)
4.70 wt%	17.70 (± 0.14)	0.76 (± 0.01)	0.67 (± 0.01)	9.01 (± 0.14)

Fig. 6. Schematic illustration of the electron equilibration and the influence on Fermi level of a) undoped DSSCs; b) Cu NWs@ TiO_2 doped DSSCs. It is worth noting that a shift in Fermi level can be seen in b) because of the LSPR effect, which enhances the V_{oc} of the devices.

Apart from the incensement of J_{sc} , we can also see the enhancement of V_{oc} by undergoing the Fermi level equilibration. Fig. 6 illustrates the electron equilibration and the influence on the Fermi level. For the undoped DSSCs (**Fig. 6a**), the charge of excited dye injects to the neighbouring TiO_2 nanoparticles, and the electrons will transport to the collecting electrode surface. The V_{oc} of the DSSCs is determined by the potential difference between the Fermi level of the electrons in the TiO_2 layer and the redox potential of the I^-/I_3^- electrolyte. According to the previous reports, the work function of copper is 4.1~4.5 eV.[50, 51] The Fermi level of pure TiO_2 is calculated to be -0.54 (V VS NHE) and the conduction band (CB) is 3.96 eV.[52] The Fermi level of copper lies below the CB of TiO_2 . The Fermi level is related to the electron steady-state concentration which depends on the energy offset between the Fermi level and the CB potential.[53] When the DSSCs are under illumination, electrons can be released from TiO_2 and excited dyes. The Cu NWs@ TiO_2 nanostructures can accept the electrons from the neighbouring TiO_2 /dye particles, and form a Fermi level equilibration (**Fig. 6b**). Such a Fermi level equilibration is beneficial to the photo electrochemical performance of the Cu NWs@ TiO_2 doped TiO_2 photoanodes. After the electron equilibration, the stored electrons assist in shifting the apparent Fermi level to more negative potential than the pristine TiO_2 , leading to an increase in the V_{oc} value. Similar results have also been reported by other groups.[3, 11, 54-56]

Fig. 7. a) IPCE curves of DSSCs doped with various amount of Cu NWs@TiO₂ nanostructures; b) Spectral responses of TiO₂ only and plasmon enhanced the relative change of the IPCE ($\Delta\text{IPCE}/\text{IPCE}$) caused by the incorporation of Cu NWs@TiO₂. (The maximum IPCE and $\Delta\text{IPCE}/\text{IPCE}$ are achieved at the doping amount of 3.90 wt%) ($\Delta\text{IPCE}/\text{IPCE} = [\text{Abs}(\text{doped DSSCs}) - \text{Abs}(\text{pure TiO}_2 \text{ DSSC})] / \text{Abs}(\text{pure TiO}_2 \text{ DSSC})$).

Fig. 7a shows the incident photon-to-electron conversion efficiency (IPCE) curve of the DSSCs. The IPCE of devices exhibits the same tendency of J_{sc} values. As shown in Fig. 7a that the IPCE of Cu NWs@TiO₂ doped DSSCs improved significantly in the visible region, indicating that the dyes around Cu NWs@TiO₂ can harvest more photons. Moreover, the enhancement is most significant at a peak around 590 nm, which is consistent with the absorption peak of Cu NWs@TiO₂ (Fig. 7b), suggesting that the photocurrent generation can be improved. The similar IPCE trend and the relative enhancement both suggest that the LSPR and PW effects from Cu NWs@TiO₂ can improve the DSSCs performance through the increased LHE, electron injection and collection efficiency.[49, 54]

For comparison, the J - V and the IPCE curves of undoped, doped with Cu NWs@TiO₂ or Cu NWs DSSCs were studied. The results are shown in **Fig. S7**, and the data are summarized in **Table S1**. Compared to the efficiency of undoped DSSC (7.65%), the efficiency of Cu NWs and Cu NWs@TiO₂ are determined to be 8.78% and 9.44%, respectively. It is not surprising that the Cu NWs doped cell shows a lower PCE than that of Cu NWs@TiO₂. Without the oxide shell, the electrolyte contacts Cu NWs surface directly.[57] The Cu NWs surface provided a site for recombination and the photo generated electrons and I₃⁻. While the TiO₂ shell of Cu NWs@TiO₂ can provide an energy barrier between Cu, dye molecules and electrolyte, which may suppress the recombination and back reaction of electrons on the surface of Cu NWs.[54] **Table 2** exhibits the performances of the nanostructured metal doped DSSCs reported in the representative literature. It can be seen that the CuNWs@TiO₂

Table 2. The performances of the nanostructured metal doped DSSCs reported in the representative literature.

	J_{sc} (mA cm ⁻²)	V_{oc} (V)	η (%)	Enhancement of PCE (%)	Ref.
Reference	13.90	0.75	7.34		
AuNPs@SiO ₂	17.58	0.76	9.22	25.61	[58]
Reference	11.55	0.73	6.38		
AuNPs@TiO ₂	14.73	0.72	7.28	14.11	[59]
Reference	11.20	0.65	5.60		
AgNPs@SiO ₂	14.40	0.70	7.40	32.14	[60]
Reference			7.80		
AgNPs@TiO ₂			9.00	15.38	[61]
Reference	12.54	0.75	5.58		
CuNPs	13.11	0.74	6.12	9.68	[62]
Reference	15.79	0.71	7.52		This
CuNWs@TiO ₂	18.42	0.76	9.44	23.40	work

doped DSSCs showed relatively higher enhancement of PCE as compared with the nanostructured metal doped DSSCs reported. Meanwhile, copper is cheaper than Au or Ag which could further reduce the cost of DSSCs.

3.3 Electrochemical impedance spectroscopy of DSSCs

Electrical impedance spectroscopy (EIS) measurements were further performed to understand the influence of the Cu NWs@TiO₂ on the dye-coated TiO₂ photoelectrode/electrolyte interfacial properties. **Fig. 8a** shows the EIS spectra carried out at -0.7 V bias in the dark environment. From left to right frequency, three semicircles of the EIS spectra can be found: R_1 , R_2 , and R_3 , which represent the resistance at the Pt counter electrode/electrolyte interface, TiO₂ film/electrolyte interface, and the Nernst diffusion in electrolyte, respectively.[35] The obtained data of the cells are summarized in **Table 3**. It can be seen that the doping of Cu NWs@TiO₂ mainly affects the resistance of TiO₂/FTO and TiO₂/electrolyte interface. There is only the recombination between electrons and I^-/I_3^- in the electrolyte in the dark. The larger the diameter of the middle-frequency semicircle, the slighter the charge recombination happened at the dye-coated photoanode-electrolyte interface. Compared to the undoped DSSCs, the doping of Cu NWs@TiO₂ increases the resistance of the charge-transfer elements and the charge recombination will be suppressed efficiently.

Fig. 8. (a) EIS Nyquist plots. (carried out at -0.7 V bias in the dark environment. R_1 , R_2 , and R_3 represent the resistance at the Pt counter electrode/electrolyte interface, TiO_2 film/electrolyte interface, and the Nernst diffusion in electrolyte, respectively); (b) Bode phase plots in the dark for different DSSCs.

Table 3. Parameters obtained by fitting the EIS of the DSSCs doped with different amounts of Cu NWs@ TiO_2 .

Cu NWs@ TiO_2 amount	R_1 [Ω]	R_2 [Ω]	R_3 [Ω]	τ_e [ms]
Pure TiO_2	2.63	29.13	14.26	3.92
1.00 wt%	2.31	36.90	11.24	4.53
2.20 wt%	2.11	41.76	10.40	5.34
3.90 wt%	1.87	48.71	7.72	7.89
4.70 wt%	2.02	46.21	9.06	6.45

The increased R_2 values of the doped cells suggest that the charge-transfer process can be promoted, leading to a lower recombination and higher PCE. The maximum value of R_2 is obtained at the amount of 3.90 wt%, indicating that an appropriate doping amount is important for the recombination-reduced ability. From **Table 3**, we can see that the value of R_3 increases with the increasing amount of Cu NWs@TiO₂, indicating an increase in the conductivity.[3, 5] These results further support the J - V results of the cells.

Fig. 8b shows the Bode phase plots of the EIS spectra which display the characteristic frequency peaks of the charge-transfer process in DSSCs. The effective lifetime of electrons (τ_e) before recombination in the TiO₂ photoanode can be related to the inverse of the characteristic frequency and estimated by Equation 1 below:[36]

$$\tau_e = \frac{1}{\omega_{max}} = \frac{1}{2\pi f_{max}}$$

where f_{max} is the maximum frequency of the low-frequency peak. The lifetime of electrons is summarized in **Table 3**. It can be seen that doping of the Cu NWs@TiO₂ increase the electron recombination lifetime, favouring the electron transport through a longer distance with less diffusive hindrance due to the LSPR and PW effects and the special electronic tunnels (direct transmission optical pathways).

3.4 Long-term stability test

The stability of the efficiency is also an important indicator for the DSSCs. A preliminary long-term stability experiment of the DSSCs fabricated with pure TiO₂,

Cu NWs and Cu NWs@TiO₂ was designed, and all the cells are stored under the ambient conditions without further sealing (**Fig. S8**). The PCE of the cells is measured every 5 days and the total efficiencies are normalized to the values measured on the first day. During the first several days, the efficiency of Cu NWs and Cu NWs@TiO₂ doped DSSCs showed an enhancement due to the increase of the dye re-generation rate and the effects of Cu NWs and Cu NWs@TiO₂. It is worth noting that the cell containing Cu NWs@TiO₂ maintains a high efficiency over 90% after 40-day test due to the LSPR and PW effects of Cu NWs@TiO₂ and the protection of TiO₂ shell. This comparison can further prove that the cells based on Cu NWs@TiO₂ is relatively stable and is expected to be a potential doped technology for the enhancement of the DSSCs.

4. Conclusions

In summary, the Cu NWs@TiO₂ nanostructures were synthesized and introduced into DSSCs. Both experimental and theoretical studies were carried out to investigate the influence of Cu NWs@TiO₂ on the DSSCs. Doping of the Cu NWs@TiO₂ nanostructures can enhance the light absorption of dye molecules and the carriers separation through the LSPR and PW effects. Meanwhile, the formed electrical tunnel (optical pathways) can accelerate the electronic transmission and the light propagation which can suppress the recombination and improve the charge transport-collection efficiency. The optimal power conversion efficiency of the Cu NWs@TiO₂ doped

DSSC was 9.44% which is 23.40% higher than that of the undoped DSSCs.

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