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REVIEW

High efficiency dye-sensitized solar cell based on novel TiO_2 nanorod/nanoparticle bilayer electrode

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Abstract: High light-to-energy conversion efficiency was achieved by applying novel TiO_2 nanorod/nanoparticle (NR/NP) bilayer electrode in the N719 dye-sensitized solar cells. The short-circuit current density (J_{SC}), the open-circuit voltage (V_{OC}), the fill factor (FF), and the overall efficiency (η) were 14.45 mA/cm^2, 0.756 V, 0.65, and 7.1%, respectively. The single-crystalline TiO_2 NRs with length 200–500 nm and diameter 30–50 nm were prepared by simple hydrothermal methods. The dye-sensitized solar cells with pure TiO_2 NR and pure TiO_2 NP electrodes showed only a lower light-to-electricity conversion efficiency of 4.4% and 5.8%, respectively, compared with single-crystalline TiO_2 NRs. This can be attributed to the new NR/NP bilayer design that can possess the advantages of both building blocks, ie, the high surface area of NP aggregates and rapid electron transport rate and the light scattering effect of single-crystalline NRs.

Keywords: dye-sensitized solar cell, TiO_2 nanorod, bilayer electrode

Introduction

Since the first report of a dye-sensitized solar cell (DSSC) in 1991 by O'Regan and Gratzel,[1] this system has aroused a lot of interest over the last decade due to its high efficiency, low cost, and simple preparation procedure.[2–4] In general, a porous TiO_2 nanoparticle (NP) film is used as an electron transport medium in DSSC.[5] Electron transport in such porous film is by trap-mediated diffusion, which is a slow mechanism.[6] A novel approach is explored to improve the photovoltaic performance of DSSC by using one-dimensional (1D) TiO_2 nanomaterials,[7,8] such as nanorods (NRs), nanotubes, and nanowires because 1D materials can improve electron transport properties and reduce light scattering.[9]

In recent years, many 1D TiO_2 materials, such as nanowires,[10] nanotubes,[11] and NRs[12] have been successively synthesized and applied on the DSSCs because they could provide direct pathways for electrons from the injection points to the FTO substrate and have the potential to increase the charge collection efficiency. However, most of these studies only applied pure 1D TiO_2 nanomaterials on the DSSCs; few researches were reported for composite NR/NP electrode structured to complement the advantages of each other.[13,14]

In this article, we report a new promising bilayer design, a pure NP layer coated with pure single crystalline TiO_2 NRs that have been synthesized by simple hydrothermal methods, and apply this new bilayer film electrode in DSSCs. Up to our knowledge, this is the first time the TiO_2 NR/NP bilayer photoanode design has been applied in DSSCs. It is expected that the photovoltaic performance of DSSC can be improved by using this new TiO_2 NR/NP bilayer design.

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Experimental

Materials

Conducting glass plate (ITO glass, fluorine-doped SnO_2 overlayer, sheet resistance 8 Ω/cm^2, made by Beijing Building Material Factory, Beijing, China) was used as a substrate for precipitating TiO_2 porous film and was cut into 0.25 cm^2 sheets. Sensitizing dye *cis*-[$(dcbH_2)_2Ru(SCN)_2$] was purchased from SOLARONIX SA (Aubonne, Switzerland). All other reagents (from Xilong Chemicals, Shantou, China) were used without further purification.

Preparation of TiO_2 NRs

TiO_2 NR was prepared according to the method reported in our previous work.[15] The preparation of the TiO_2 NRs was described as follows: 1 g of TiO_2 NPs prepared by sol-gel methods[16,17] was added into a 50 mL Teflon vessel containing an amount of hydroxides (NaOH/KOH = 1:1) as aqueous solution. The hydrothermal reaction was carried out at 200°C for 36 hours and then naturally cooled to room temperature, producing white $Na_2Ti_3O_7$-xH_2O and $K_2Ti_3O_7$-xH_2O precipitate. The white precipitate was isolated from the solution by centrifugating and washing with deionized water several times and dried at 70°C for 10 hours. For ion exchange, the sodium and potassium titanate NR was immersed into a 0.1M HNO_3 solution for 6 hours, washed with deionized water for several times until the pH value of the solution was approximately 7, and then dried at 70°C for 10 hours. The obtained H-titanate NR was added into a 100 mL Teflon vessel, then filled with dilute HNO_3 solution up to 80% of the total volume, and maintained at 180°C for 24 hours. The product was isolated from the solution by centrifugating and washing with deionized water for several times and dried at 70°C for 10 hours. The final step was to calcine the obtained sample at 450°C for 2 hours.

Measurement and characterization

The TiO_2 NRs were observed with a JEM-2000EX transmission electron microscope (JEOL, Tokyo, Japan). The crystal structure of the titania was identified by X-ray diffraction (XRD) on a Bruker D8-ADVANCE X-ray diffractometer (Cairo Scientific Corp, Cairo, Egypt) at 40 kV and 40 mA for monochromatized Cu Kα radiation at 0.154 nm.

The photovoltaic test of DSSC was carried out by measuring the J–V character curves under simulated AM 1.5 solar illumination at 100 mW·cm^{-2} from a xenon arc lamp (XQ-500W; Shanghai Photoelectricity Device Company, Shangai, China) in ambient atmosphere; the fill factor (FF) and the overall light-to-electrical energy conversion efficiency (η) of DSSC were calculated according to the following equations:[18]

$$FF = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}} \quad (1)$$

$$\eta(\%) = \frac{V_{max} \times J_{max}}{P_{in}} \times 100 = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}} \times 100, \quad (2)$$

where J_{SC} is the short-circuit current density (mA·cm^{-2}), V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} (mA·cm^{-2}) and V_{max} (V) are the current density and voltage at the point of maximum power output on the J–V curves, respectively.

All the measurements were performed in air. For each type of devices, a set of 5–8 devices was characterized to verify the reproducibility of the results.

The amount of chemisorbed dye was determined by a spectroscopic method by measuring the concentration of dye desorbed on the titania surface into a mixed solution of 0.1M NaOH and ethanol (1:1 in volume fraction). The absorption spectrum was analyzed by UV-vis spectrophotometer (UV 2450; Shimadzu, Kyoto, Japan).

Preparation of electrode and assembly of cell

The TiO_2 NR/NP electrode of DSSC was fabricated by layer assembly technique shown in Figure 1. The first layer

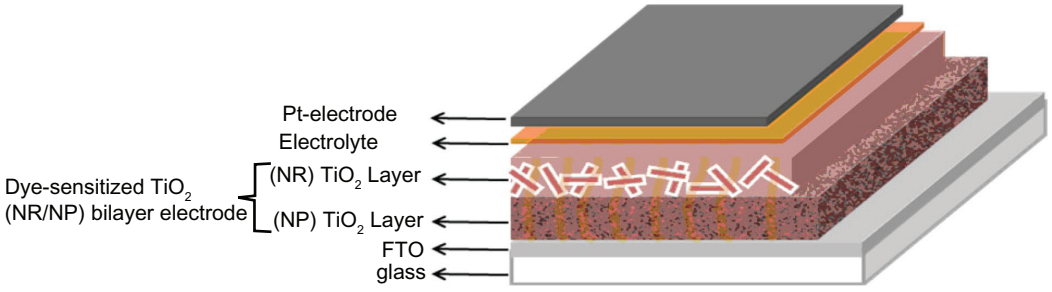

Figure 1 Schematic representation of the DSSC based on TiO_2 NR/NP bilayer photoanode.
Abbreviations: DSSC, dye-sensitized solar cell; NR, nanorod; NP, nanoparticle.

was TiO_2 NP (approximately 9 μm in thickness) prepared by sol-gel method according to the method by Wang et al.[19] Then the second layer was TiO_2 NR (approximately 3 μm in thickness), coated by using a doctor-blading technique. After air drying, the electrode was sintered at 450°C for 30 minutes and cooled down to 80°C. Then the calcined TiO_2 electrode was immersed in ethanol solution of 2.5×10^{-4} M *cis*-$[(dcbH_2)_2Ru(SCN)_2]$ for 24 hours. After the substrate was adequately washed with anhydrous alcohol and dried in moisture-free air, the dye-sensitized TiO_2 electrode was obtained. A DSSC was assembled by filling an electrolyte solution (0.6M tetrapropylammonium iodide, 0.1M iodine, 0.1M lithium iodide, 0.5M 4-tertbutylpyridine in acetonitrile) between the dye-sensitized TiO_2 electrode and a platinized conducting glass electrode. The two electrodes were clipped together, and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte solution from leaking.

Results and discussion

Characterization of the TiO_2 NRs

The detailed morphology of the TiO_2 NRs was characterized with transmission electron microscopy (TEM) images, as shown in Figures 2A, 2B. It can be seen that the synthesized titania has NR structure with length ranging from 200 to 500 nm and diameter 30–50 nm. The single crystallinity of the NRs was confirmed by the selected area electron diffraction pattern (inset in Figure 2B) and the high-resolution TEM (Figure 2C). Energy dispersive X-ray analysis of the prepared TiO_2 NRs (Figure 2D) confirmed the purity of the prepared TiO_2 NRs and the absence of residuals of Na or K ions.[20]

The XRD pattern of the TiO_2 NRs is shown in Figure 3. All diffraction peaks were assigned to pure anatase phase (JCPDS no. 21-1272)[21] without other crystalline byproducts. Moreover, the peaks are rather sharp, which indicates that the obtained TiO_2 has relatively high crystallinity.

Photovoltaic characteristics and performance

Figure 4 shows the photocurrent density vs voltage (J–V) characteristics of a DSSC based on the hybrid NR/NP bilayer titania electrode (approximately 12 μm in total thickness). The performance of the DSSCs based on this bilayer film was measured under 1 Sun AM 1.5 simulated sunlight. The J_{SC},

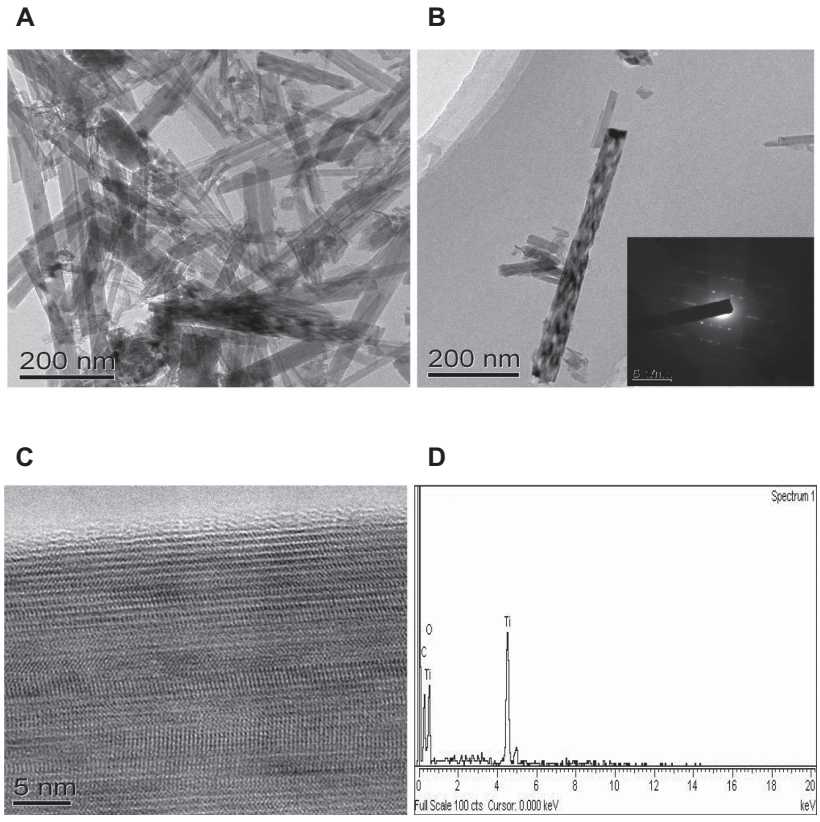

Figure 2 A – B) TEM images of the TiO_2 nanorod sample; inset in **B**) the corresponding SAED patterns of the nanorod. **C**) The HRTEM image of the nanorod. **D**) SEM-EDS element analysis of the nanorod.

Abbreviations: SAED, selected area electron diffraction pattern; HRTEM, high-resolution transmission electron miscroscopy; SEM, scanning electron microscopy; EDS, energy dispersive X-ray analysis.

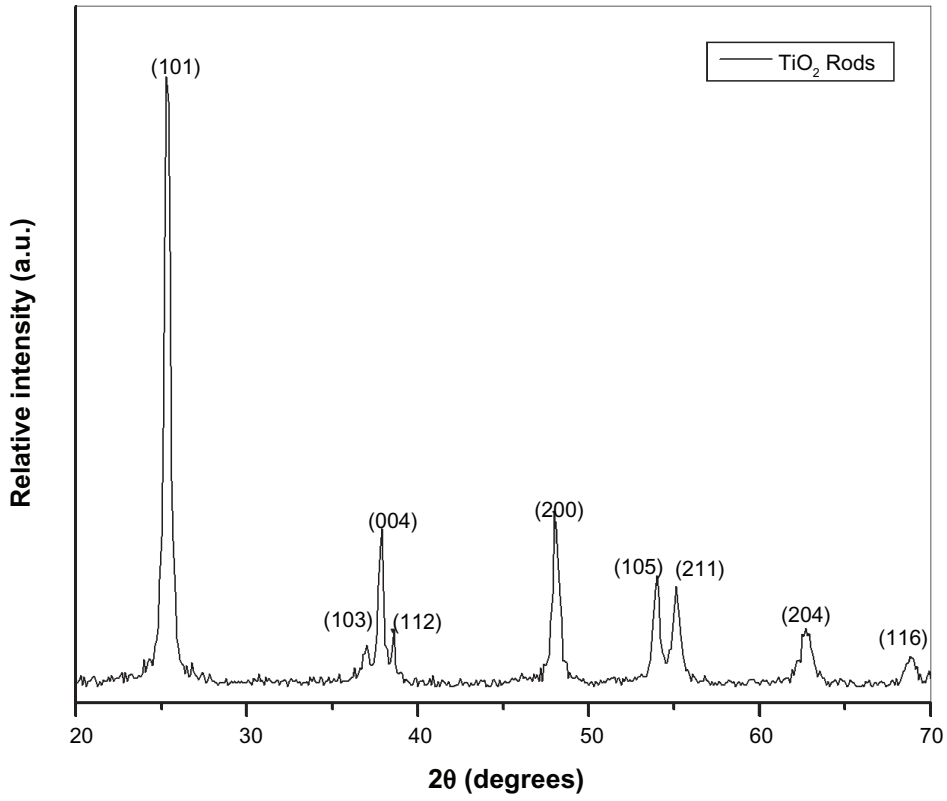

Figure 3 X-ray diffraction pattern of the as-synthesized TiO_2 nanorods.

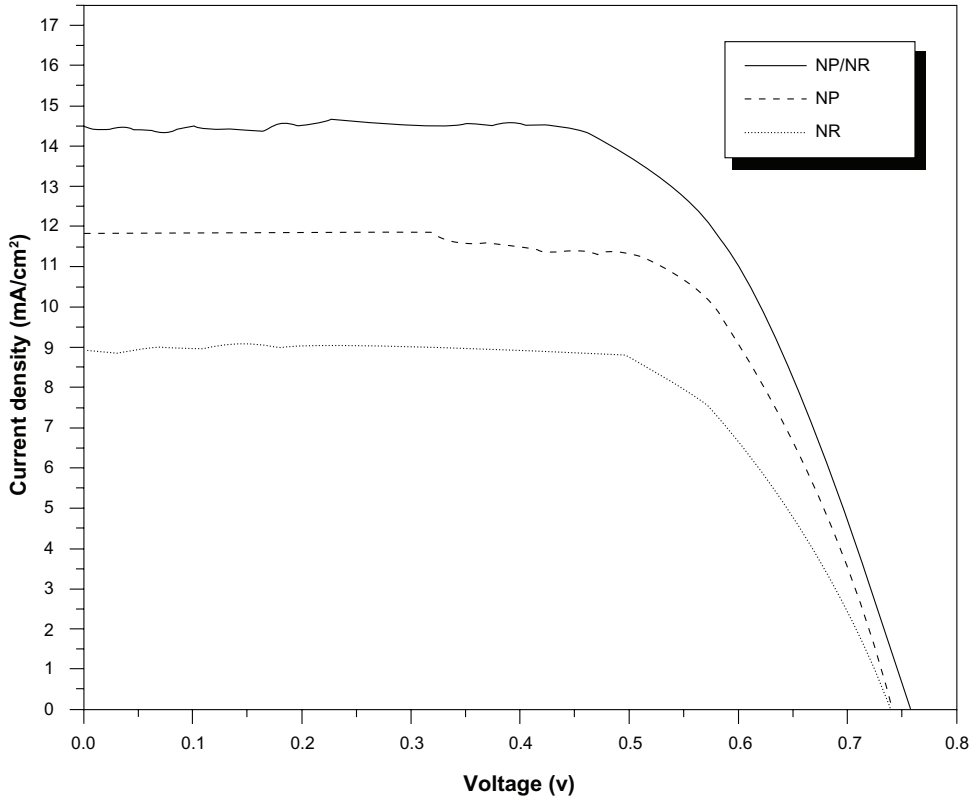

Figure 4 Photocurrent density–voltage (J–V) curves of DSSCs constructed with TiO_2 pure (NP); pure (NR) and bilayer (NR/NP) photoanodes.
Abbreviations: DSSCs, dye-sensitized solar cells; NP, nanoparticle; NR, nanorod.

V_{OC}, FF, and η of the bilayer electrode were found to be 14.45 mA/cm^2, 0.756 V, 0.65, and 7.1%, respectively.

The comparison between photocurrent–voltage characteristics of the DSSC using the TiO_2 NR/NP bilayer electrode with those of cells using pure TiO_2 NR and NP electrodes (with the same film thickness) are shown in Figure 4. The photoelectrical data of the DSSCs are summarized in Table 1. From the results in Figure 4 and the data in Table 1, it can be seen that high short photocurrent density, as well as high photovoltaic performance, has been obtained by applying the hybrid design TiO_2 NR/NP bilayer electrode in the DSSC than that of pure NR and NP devices.

The adsorption of the dye molecules in the three TiO_2 films is compared using UV–vis absorption spectra, which is shown in Figure 5. The results clearly indicate that the absorption intensity of the adsorbed dye on the hybrid TiO_2 NR/NP bilayer electrode is larger than the pure NP and pure NR electrodes with the same thickness. The amount of chemisorbed ruthenium dye onto the NR, NP, and NR/NP film electrodes are listed in Table 1 and are determined as 2.1, 3.6, and 6.2×10^{-5} mol·cm^{-2}, respectively. It means that hybrid NR/NP bilayer electrode can absorb more ruthenium dye than pure NR and pure NP do, which is ready for the enhancement of incident light harvest and improvement of light-to-electricity conversion efficiency of the DSSC.

Incident photon-to-current conversion efficiency

The incident photon-to-current conversion efficiency (IPCE) is defined as the ratio of the number of electrons in the external circuit produced by an incident photon at a given wavelength. Using Equation (3), the IPCE values of the DSSCs with the NR/NP bilayer, NR and NP electrodes as a function of the illumination wavelength are shown in Figure 6.

$$\mathrm{IPCE}(\%) = 100 \times 1240 \times I_{SC}/(W_{in} \times \lambda), \quad (3)$$

where I_{sc} is the short-circuit photocurrent (mA/cm^2), W_{in} is the incident light intensity (W/cm^2), and λ is the wavelength (nm).

As expected, the DSSC with the NR/NP bilayer film showed higher conversion efficiency in the wavelength range 300–700 nm than that with pure NR and NP electrodes. The TiO_2 NR/NP bilayer electrode shows a maximum IPCE of 88.9% at a wavelength of 575 nm, whereas the NR and NP electrodes show an IPCE of 63.5% and 70%, respectively. This resulted in a 22% improvement in the conversion efficiency and 27% in IPCE of the DSSC with NR/NP electrode than with NP electrode.

This large improvement in the photovoltaic performance of the new DSSC-based NR/NP bilayer design can be explained as, although the high surface area of TiO_2 NP meets the requirement of adsorbing dye, it brings about, at the same time, many opportunities for the recombination of photoinjected electrons and the oxidized dye and/or the electron acceptors in the electrolyte.[21] The 1D TiO_2 electrodes such as NRs can enhance the light harvesting,[22] straight pathway electron transport,[23] and also have no serious light loss due to back scattering. Therefore, the design of the TiO_2 NR/NP bilayer film balances the surface area and the light scattering; thus, the performance of DSSC with TiO_2 NR/NP bilayer electrode is higher than those with NP or NR electrode.

Conclusion

In summary, anatase TiO_2 NR was successfully synthesized by hydrothermal method. High light-to-electricity conversion efficiency of 7.1% was achieved by applying high-efficient TiO_2 NR/NP bilayer photoanode in DSSC compared with pure TiO_2 NP as electrode, which shows the conversion efficiency of only 5.8%. This 22% enhancement is attributed to the balance between less light scattering for TiO_2 NR and the more light harvesting for TiO_2 NP.

Acknowledgments

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Table 1 The parameters of the dye-sensitized solar cells with the different TiO_2 electrodes

Electrode	Adsorbed dye (10^{-5}mol·cm^{-2})	IPCE (at 575 nm), %	J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF	η,%
Pure NR	2.1	63.5	8.88	0.739	0.67	4.4
Pure NP	3.6	70.0	11.89	0.738	0.67	5.8
NR/NP	6.2	88.9	14.45	0.756	0.65	7.1

Abbreviations: IPCE, incident photon-to-current conversion efficiency; NP, nanoparticle; NR, nanorod.

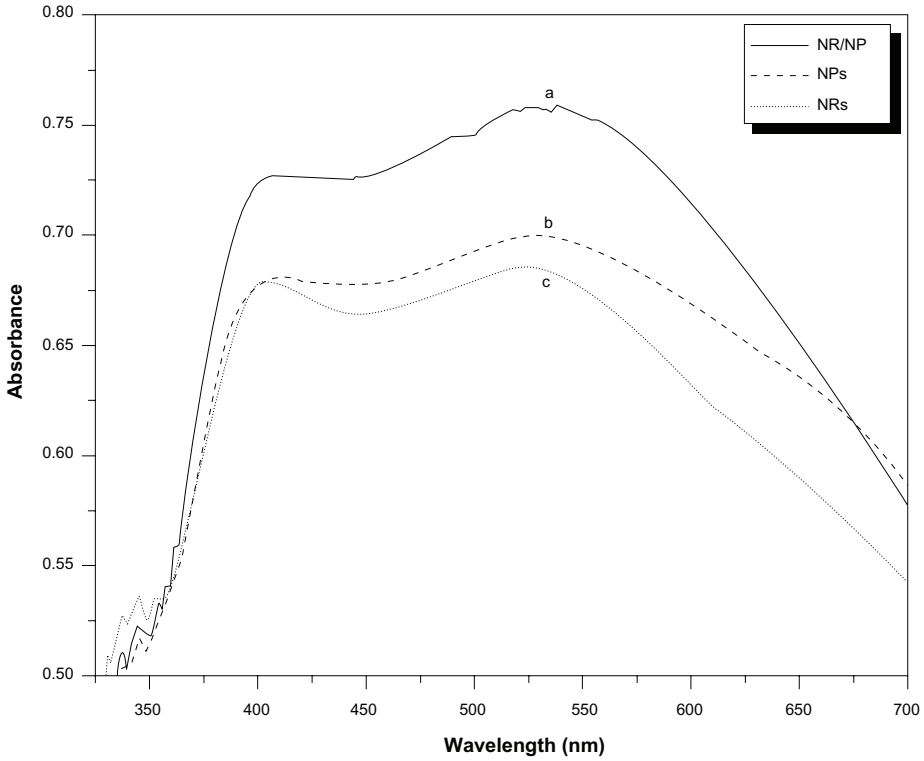

Figure 5 UV–vis absorption spectra of the adsorbed (N719) dye sensitized onto (a) bilayer NR/NP, (b) NP, and (c) NR TiO_2 electrodes.
Abbreviations: NP, nanoparticle; NR, nanorod.

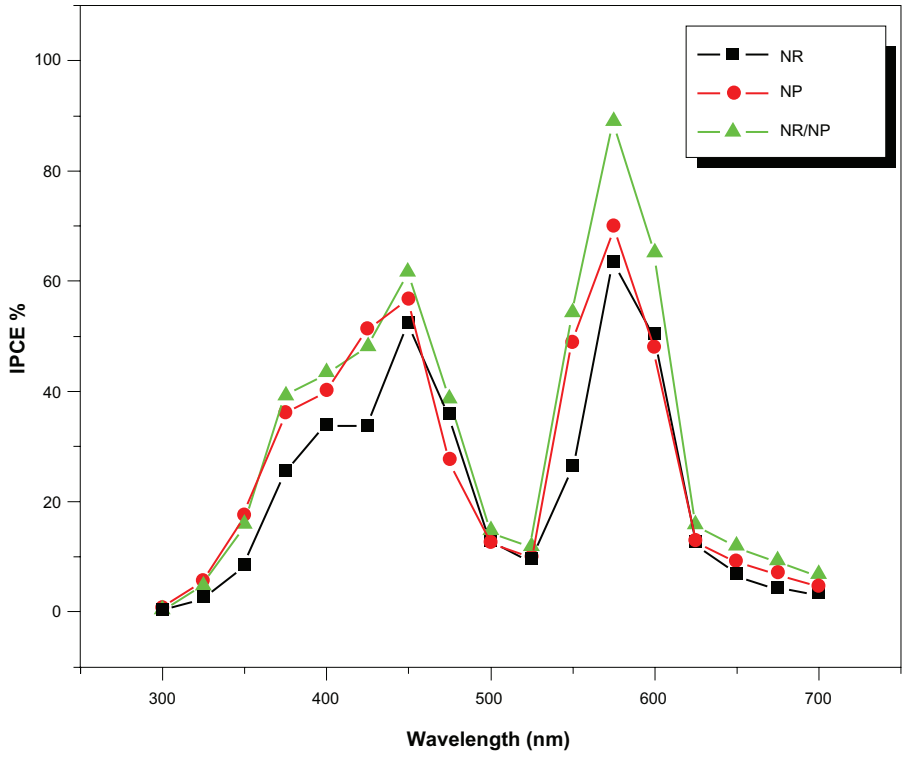

Figure 6 IPCE curves of the DSSCs based on pure NP, pure NR, and the NP/NR bilayer photoanodes.
Abbreviations: IPCE, incident photon-to-current conversion efficiency; DSSCs, dye-sensitized solar cells; NP, nanoparticle; NR, nanorod.

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Disclosure

The authors report no conflicts of interest in this work.

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