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Enhanced the performance of dye-sensitized solar cells with a novel photoanode using TiO₂ nanoflower clusters and nanoparticles[☆]



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ABSTRACT

Titanium dioxide (TiO₂) nanoflower clusters (NFC) composed of anatase TiO₂ nanoflowers and TiO₂ nanobelts framework were prepared through a simple hydrothermal synthesis. Then a novel nanocomposite photoanode were fabricated by mixing NFC and P25 nanoparticles in different mass ratio. The highest conversion efficiency of 6.38% (16% higher than P25 based DSSC) is achieved for dye-sensitized solar cells (DSSCs) made by a 5:5 (wt/wt) mixture of NFC and P25. The higher efficiency using mixed photoanode derives from the high light harvesting and good transferring properties of NFC, as well as the sufficient dye absorption due to the high specific surface area of P25 nanoparticles.

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1. Introduction

Dye-sensitized solar cells (DSSCs) based on nano-structured titanium dioxide (TiO₂) electrodes have been attracting intense scientific and industrial attention for quite some time because of their unique hybrid architecture supporting interesting optoelectronic phenomena, potential for low cost scale up of the corresponding synthesis procedure and applicability for diffuse light harvesting [1]. In the past years, many efforts have been made to optimize the morphology of the nanostructured photoanode. In DSSCs, among various photoanode morphologies, 1D TiO₂ nanostructure is expected to be a promising substitute which can accelerate the movement of electrons in one direction and reduce their recombination [2–4]. Meanwhile hierarchical 3D architecture has attracted extensive attention that they may exhibit interesting properties because of the large numbers of active sites, unique multidimensional morphology, and the combination of micro-nanoscales [5]. Previous reports show that 3D hierarchical flower-like TiO₂ nanostructure shows a high efficiency result in

both high harvesting and good transferring properties [6]. Therefore, self-assembly of 3D architecture onto 1D nanostructure is very essential, and there are no reports on this kind of composite nanostructure for photoanodes.

In this work, a novel self-assembly composite nanostructure of mixed crystal TiO₂ nanoflower clusters (NFC) was prepared, then it was employed with P25 to construct a novel P25/NFC composite photoanode in DSSCs. When the mass ratio of P25 to NFC is 5:5, DSSC yields the highest conversion efficiency of 6.38%. The role of NFC played in DSSC has also been studied.

2. Experimental details

The typical experimental procedure of the NFC is represented in our previous works [7]. Then the P25 and NFC were uniformly mixed using a simple physical doping method. The mixture using different doping ratios (NFC:P25) of 0:10, 1:9, 3:7, 5:5, 7:3, 9:1 and 10:0 as photoanode materials. Dye-sensitized TiO₂ film was prepared by doctor-blading of TiO₂ slurry on a FTO glass and calcinated at 450 °C for 30 min [8]. After cooled to 80 °C, the TiO₂ film was immersed in 3 × 10⁻³ M ethanol solution of N719 dye for 24 h. Then the dye sensitized TiO₂ film was washed with anhydrous ethanol and dried in moisture-free air. Finally, the dye-covered TiO₂ electrode and Pt-covered FTO glass counter electrode were assembled into a sandwich type cell with 60 μm thick Surlyn. The I⁻/I₃⁻ liquid electrolyte with acetonitrile as the solvent was then injected between the two electrodes. The characteristic

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methods of NFC and DSSCs are represented in the Supporting information (see ESI†).

3. Results and discussion

The mixed crystal NFC was fabricated by assembling novel nanostructures on TiO₂ nanobelts through a simple hydrothermal synthesis. The FESEM images of TiO₂ nanobelts, NFC, P25 and NFC/P25 are shown in Fig. 1. Fig. 1a–a'' and b, shows the growth process of NFC, and Fig. 1b, shows the TiO₂ nanoflowers growing regularly on a nanobelt to form lots of banded structures. As can be seen from Fig. 1b', each flower is composed of a large number of nanorod petals with top square-shaped facets. The nanopetals are around 500 nm long, 250 nm wide and 100 nm thick, it can be seen clearly that each 3D nanoflower forms the interconnected electronic channel to accelerate electronic transmission. In addition, the SEM of P25 and NFC/P25 complex photoanode materials are shown in Fig. 1c and d. As can be seen from Fig. 1d, the P25 nano-particles filling the gap of the NFCs' petals uniformly after physical mixture process. Meanwhile, the thicknesses of these NFC/P25 films are roughly 9 μm (see Fig. S1 in ESI†). The XRD analysis was performed to investigate the NFC composed of two crystal phases, the anatase flowers and rutile nanobelts [7].

Fig. 2 shows the photocurrent density–voltage (J – V) curves for the DSSCs of NFC/P25 with different mixture proportions (0:10, 1:9, 3:7, 5:5, 7:3, 9:1 and 10:0). As noted in Table 1, The DSSC with 5:5 photoanode demonstrates the highest conversion efficiency of 6.38% (the short current (J_{sc})=13.57 cm⁻², open-circuit voltage

(V_{oc})=0.78 V and fill factor (FF)=0.60) among these TiO₂ films DSSCs. Compared with P25–DSSC, J_{sc} , V_{oc} and FF are all enhanced. This is mainly due to the directed electron pathway along the axis of the 1D nanostructure (nanorod and nanobelt) and the strong light absorption capacity of the 3D nanoflower in NFC [9,10].

Generally, the J_{sc} in DSSCs is depended on the light harvesting efficiency, charge injection yield, and charge transport properties. In the NFC, hierarchical 3D nanorod flowers can offer a lot of merits which are beneficial for the improvement of the conversation efficiency, such as (1) the enhanced light absorption capability

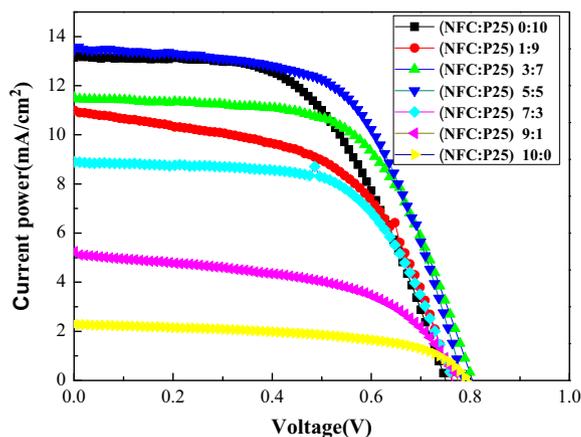


Fig. 2. Current–voltage (J – V) characteristics of the as prepared DSSCs based on different photoanodes (NFC:P25/ 0:10, 1:9, 3:7, 5:5, 7:3, 9:1 and 10:0).

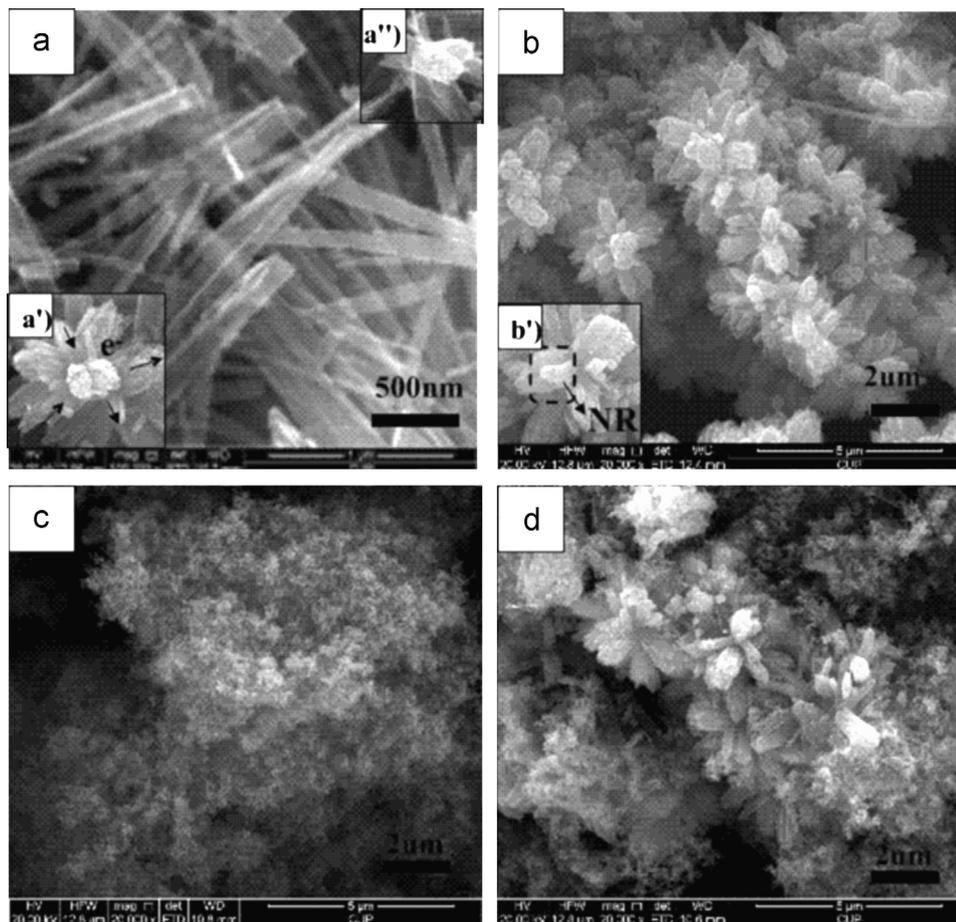


Fig. 1. FESEM images of photoanodes (a) nanobelt; (a') the nanorods petals form the conductive channel; (a'') nanoflowers began to grow on the junction of nanobelts; (b) nanoflower-belts; (b'), top view of a flower on nanobelt, and the nanoflower composed of a large amount of nanorods petals; (c) commercial P25 and (d) the commercial P25 and NFC composite anode after the physical doping.

by permitting more lights reflection and multiple-scattering inside its interior [11]; (2) enhanced charge transfer facilitated by 1D TiO₂ nanorod structure thus retarding the recombination of photogenerated electrons and holes [12,13]. Based on the analysis above, NFC offers high light harvesting efficiency and good charge transport properties which are contributed to the DSSCs; Nevertheless, charge injection yield lies on the relative energy levels of the dye adsorption of TiO₂, so the 5:5-DSSC with an appropriate doping ratio presents the highest J_{sc} among these DSSCs. Better than that, all the complex photoanode materials–DSSCs exhibit higher V_{oc} and FF compared with P25–DSSC. As we know, nanorods and nanobelts have fewer interparticle connections, which decrease the recombination sites, and in the novel structure, with the 3D nanoflowers composed of closely linked 1D nanorod petals (Fig. 1a'), similarly, the NFC composed of closely 3D nanoflowers, for this, an electronic conducting path was easily formed by nanobelt and nanorod so as to improve the electronic transmission efficiency [14–16]. Thus, the added NFC can help to increase the open circuit voltage. Therefore, with increased addition of NFC, 5:5-DSSC presented higher conversation efficiency, but when the amount of P25 was too little, the specific surface area of the mixed material was too small, making it difficult to absorb enough dye for DSSC, which is a main reason that lead to the low conversion efficiency of NFC–DSSC.

To understand the different photovoltaic performance of two-treated DSSCs (i.e., 0:10 and 5:5 based DSSCs), the incident-photon-to-current efficiency (IPCE) spectra were measured as shown in Fig. 3a. The IPCE is defined as the number of electrons in the external circuit under short circuit conditions per incident photon at a given wavelength [17–21]. And it is determined by the light absorption efficiency of the dye, the quantum yield of electron injection, and the efficiency of collecting the injected electrons at the conducting glass substrate [22]. Compared with P25 film, the NFC film had a higher IPCE from 400 nm to 700 nm wavelength ranges. At the maximum value of the IPCE spectra at

approximately 535 nm, the IPCE of the 5:5-DSSC was 66% higher than the P25–DSSC, which is in good agreement with the increased photocurrent density for the former. The enhanced IPCE is mainly resulted of the NFC built from TiO₂ nanobelts and nanoflowers, whose large size can effectively minimize the grain interface effect and thus reduce the electron loss, which is beneficial to the improvement of the efficiency of the DSSCs.

Impedance spectroscopy (EIS) has been regarded as a powerful technique to characterize the interfacial charge transfer, charge recombination and charge transport in the photoanode. Generally, three characteristics semicircles can be obtained from EIS spectra in the frequency range between 100 K Hz and 0.1 Hz. Fig. 3b shows two well-defined semicircles in the Nyquist plots, which can represent the charge transfer for redox reaction of I^- and I_3^- at the counter Pt electrode/electrolyte interface (over 1000 Hz) and the electron transfer/charge recombination at the photoanode oxide/dye/electrolyte interface (1–100 Hz), respectively. The obtained spectra were fitted with Z-View software in terms of the equivalent circuit containing constant phase elements (CPE) and charge transfer resistance (R_{CT}) at interface contract. In the absence of a change in the other elements of impedance, here we only concerned the larger semicircles of the middle frequency. Compared with P25–DSSC, the semicircle size of 5:5-DSSC has reduced in the middle frequency region, and the fitting values of R_{CT} corresponding to 5:5-DSSC and P25–DSSC are 31 Ω and 38 Ω , respectively. That is owing to the increased acceleration of electron transfer process in the photoanode of 5:5-DSSC. The 5:5-electrode has a much longer electron lifetime than that of the P25-electrode, indicating a much weaker charge recombination [14]. The low transfer resistance could be an important factor for the improvement of the photovoltaic performance of the 5:5-DSSC.

4. Conclusion

In conclusion we have successfully fabricated a composite nanostructure of TiO₂ nanoflowers grown on the TiO₂ nanobelts, using different proportions (0:10, 1:9, 3:7, 5:5 7:3, 9:1 and 10:0) of NFC/P25 mixed film as photoanodes. The results demonstrate that the highest energy-conversion efficiency of 6.38% was obtained in DSSC using NFC/P25 photoanode with 5:5 mass ratio, presenting J_{sc} and V_{oc} of 13.57 mA and 0.78 V, respectively. The high efficiency DSSC is mainly attributed to two aspects: one is that NFC enhances light harvesting by light scattering and provides direct electrical transport pathways for photogenerated electrons; the other one is that the P25 with large surface area boost dye absorption. Hence, the composite architecture improves the power conversion efficiency of DSSCs.

Table 1
Performance characteristics of DSSCs based on photoanodes of different mixture proportions on NFC and P25.

Sample (NFC:P25)	V_{oc} [V]	ISC [mA cm ⁻²]	FF	PCE [%]
0:10	0.75	13.05	0.55	5.50
1:9	0.77	10.94	0.56	4.66
3:7	0.78	11.51	0.61	5.51
5:5	0.78	13.57	0.60	6.38
7:3	0.79	8.90	0.60	4.25
9:1	0.78	5.14	0.56	2.24
10:0	0.79	2.24	0.55	0.98

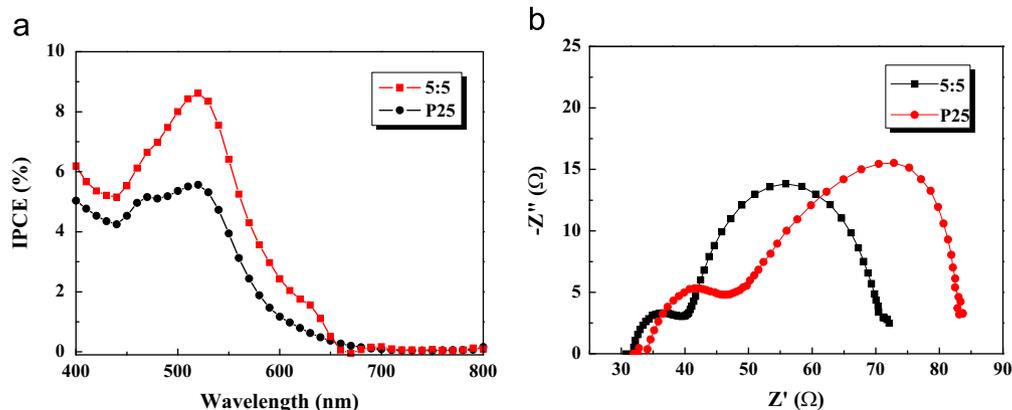


Fig. 3. (a) Incident-photo-to-current conversion efficiency (IPCE) spectra for the as-prepared DSSCs and (b) electrochemical impedance spectra of 5:5 DSSC and P25–DSSC.

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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.matlet.2013.06.009>.

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