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Improved performance of dye-sensitized solar cells using gallium nitride–titanium dioxide composite photoelectrodes

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ABSTRACT

Dye-sensitized solar cells (DSSCs) are fabricated with gallium nitride–titanium dioxide (GaN–TiO_2) composite photoelectrodes to enhance the power conversion efficiency. The value of power conversion efficiency increases with the incorporation of GaN in TiO_2 matrix and reaches a maximum at 0.05 wt% GaN. Internal resistance in the DSSC is characterized by electrochemical impedance spectroscopy (EIS). From the EIS of electrolyte/dye/GaN–TiO_2 interface resistances under illumination and in the dark, a decrease in the charge transfer resistance and an increase in the charge recombination resistance of the DSSCs are obtained after the inclusion of GaN (0.01–0.05 wt%) in the TiO_2 matrix. The power conversion efficiency of the DSSC based on the GaN (0.05 wt%)-TiO_2 composite photoelectrode is enhanced by ~61% in comparison with a pristine TiO_2 photoelectrode.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been intensively studied because they offer an alternative method for the fabrication of low-cost solar cells [1]. They are composed of a dye-immobilized wide bandgap semiconductor photoelectrode, a redox active electrolyte, and a counter electrode. Some porous photoelectrodes such as TiO_2 [2–6], ZnO [7,8], Nb_2O_5 [9,10], and Zn_2SnO_4 [11] have been reported in DSSCs. A nanocrystalline TiO_2 film was combined with ruthenium–polypyridine complex dye and an overall conversion efficiency of ~10% was achieved on this system [12]. In a DSSC, sunlight is absorbed by dye molecules, in which photoexcited electrons are injected to the conduction band of the nanocrystallite and transport across the nanoparticle network. There are many factors limiting the performance of a DSSC, among which charge recombination between the photoexcited electrons and the oxidized dye or redox couple in the electrolyte is very important. There have been many strategies addressing the suppression of charge recombination at the electrode/electrolyte interface. Effects have been made to improve the power conversion efficiency (η) of DSSCs by using of composite photoelectrodes [13–18], coupled semiconductor photoelectrodes [19], and highly oriented TiO_2 nanotube arrays photoelectrodes [20–25]. Therefore, searching for a new photoelectrode for the reduction of charge recombination in a DSSC is of great significance.

Composite materials have been applied in many fields of technology. In DSSCs fabricated with composite photoelectrodes, different semiconductors contribute some of their physical and chemical properties to provide a better overall performance. Reports over the past decade have shown that the uses of composite photoelectrodes in DSSCs improved the η. A better charge separation in the composite photoelectrode can be obtained by using a mixture of SnO_2 and ZnO with different energy levels [13]. Furthermore, the incorporation of ZrO_2 nanofibers to a TiO_2 photoelectrode was reported to enhance the efficiency of DSSCs [14]. Gallium nitride (GaN), a wide bandgap semiconductor (~3.4 eV), has attracted great attention in improving photocatalytic activity because of its high chemical stability and strong heat impact resistance [26–28]. Its natural structure under standard conditions is the hexagonal wurtzite structure. In this study, we demonstrate the inclusion of GaN into TiO_2 matrix to form GaN–TiO_2 composites for use as photoelectrodes in DSSCs in an attempt to reduce the charge recombination. The DSSC fabricated using the GaN–TiO_2 photoelectrode was compared with that of pristine nanocrystalline TiO_2 photoelectrode. The parameters that could affect the photovoltaic performance of the DSSCs were evaluated and the photoelectrochemical characteristics were described and discussed.

2. Experimental

2.1. Reagents

TiO_2 was purchased from Degussa (P25, 80% anatase). GaN (99.99%) with a diameter of 40 nm and 4-tert-butylppridine

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(TBP) were obtained from Sigma–Aldrich. I_2 was purchased from Merck. H_2PtCl_6 and LiI were purchased from Alfa Aesar. Polyethylene glycol (PEG, Mw = 16,000–24,000) and 3-methoxypropionitril (MPN) were obtained from Fluka. *Cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) dye (N719) and 1-propyl-2,3-dimethylimidazolium iodide (DMPII) were purchased from Solaronix. The reagents were used as purchased without any further pretreatment.

2.2. Apparatus

Field emission scanning electron microscopy (FESEM) images were obtained using a JSM-6700F (JEOL, Japan). Photocurrent–voltage (*J–V*) characteristics were measured with a Keithley 2400 source meter under illumination from a solar simulator composed of a 500 W Xe lamp and an AM 1.5 filter (Oriel). Light intensity was calibrated with a silicon photodiode. Amount of adsorbed dyes was estimated with a Lamda-25 (Perkin Elmer, USA). Electrochemical impedance measurement was performed with an Autolab PGSTAT30 Electrochemical Analyzer with FRA2 module (Eco Chemie, Netherlands) under AM 1.5 (100 mW cm^{-2}) illumination and in the dark. The frequency range explored was from 0.01–65,000 Hz.

2.3. Preparation of the GaN–TiO_2 composite photoelectrode

GaN–TiO_2 pastes were prepared with addition of appropriate amounts of GaN in 2 ml of 5 wt% TiO_2 and mixed with PEG at a 0.3 of PEG/TiO_2 ratio with the aid of ultrasonic agitation for 1 h. The paste was coated by using the doctor blade technique onto fluorine-doped SnO_2 glass substrates (FTO, Solaronix) and annealed at 450 °C for 30 min in the air to form a GaN–TiO_2 composite film. The thickness of the GaN–TiO_2 composite was varied from 2.7 to 10.3 μm which was determined by FESEM (not shown).

2.4. Preparation of the DSSCs

The above prepared photoelectrode had a 0.25 cm^2 active area which was immersed in ethanol containing 0.5 mM N719 for 24 h. The counter electrode was prepared by drop casting of H_2PtCl_6 solution (7 mM in ethanol solution) onto FTO and heated at 400 °C for 15 min. The DSSCs were sealed with sealing material, SX1170 (Solaronix). The electrolyte consisted of 0.1 M LiI, 0.05 M I_2, 0.6 M DMPII, and 0.5 M TBP in MPN.

3. Results and discussion

3.1. Photovoltaic performance of DSSCs based on the GaN–TiO_2 composite photoelectrodes

J–V characteristics were carried out with a pristine nanocrystalline P25 TiO_2 film photoelectrode and GaN–TiO_2 composite photoelectrodes in order to investigate the function of GaN on the performance of DSSCs based on the GaN–TiO_2 composite. The *J–V* curves of DSSCs for a nanocrystalline P25 TiO_2 film photoelectrode and GaN–TiO_2 composite photoelectrodes are shown in Fig. 1. It is clear that the short-circuit current density (J_{sc}) in DSSCs with GaN–TiO_2 composite photoelectrodes was higher than that of pristine nanocrystalline P25 TiO_2 film photoelectrode, resulting in improved η. The higher J_{sc} obtained in the GaN–TiO_2 composite photoelectrodes is probably related to either the amount of adsorbed dye or the nature of GaN–TiO_2 composite or both. In order to investigate the causes of the enhancement of J_{sc} in a DSSC with a GaN–TiO_2 composite photoelectrode, the amount of adsorbed dyes was estimated by an UV/visible absorption spectra.

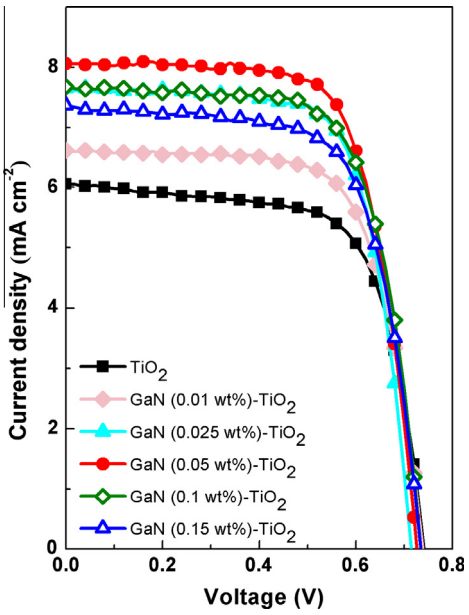

Fig. 1. *J–V* characteristics of DSSCs using nanocrystalline P25 TiO_2 film photoelectrode and GaN–TiO_2 composite photoelectrodes.

The amount of adsorbed dyes for the pristine nanocrystalline P25 TiO_2 film photoelectrode and GaN (0.05 wt%)-TiO_2 composite photoelectrode were 7.2×10^{-8} and 7.8×10^{-8} mol cm^{-2}, respectively. The similar value for the pristine nanocrystalline P25 TiO_2 film photoelectrode and GaN (0.05 wt%)-TiO_2 composite photoelectrode suggested that the effect of amount of adsorbed dyes on the performance of the DSSCs is insignificant. This phenomenon was further confirmed by the surface morphology of pristine nanocrystalline P25 TiO_2 film and GaN (0.05 wt%)-TiO_2 composite as shown in Fig. 2a and b, respectively. It can be observed that no obvious morphology difference between the TiO_2 film and GaN (0.05 wt%)-TiO_2 composite film. Therefore, the enhanced performance of DSSCs with GaN–TiO_2 composite photoelectrodes might be attributed to the nature of the GaN–TiO_2 composite photoelectrode. The conduction band of GaN is more negative than TiO_2 and matches the lowest unoccupied molecular orbital of N719 [28]. Therefore, it can be expected electrons transfer from excited state of dyes to the conduction bands of GaN and TiO_2 and from conduction band of GaN to conduction band of TiO_2. A GaN–TiO_2 composite photoelectrode thus offers more pathways for electrons transfer, which results in an opportunity to facilitate photoexcited electron transport and increase photovoltaic performance of DSSCs. The enhanced values of J_{sc} may be resulted from the high probability of transfer of electrons by excited dye molecules throughout GaN–TiO_2 composite film to underlying FTO substrate. This process leads to a suppression of charge recombination and a better charge separation with the GaN–TiO_2 composite photoelectrode. This result indicates that the performance of DSSC can be successfully improved by the incorporation of GaN in TiO_2 matrix.

3.2. Effect of GaN content in the GaN–TiO_2 composite photoelectrode on the photovoltaic performance

The *J–V* characteristics of DSSCs based on the GaN–TiO_2 composite photoelectrodes with different GaN contents are shown in Fig. 1. These results indicate that the inclusion of GaN in TiO_2 matrix is able to enhance the efficiency of charge transport. Open-circuit voltage (V_{oc}), J_{sc}, fill factor (FF), and η for all photoelectrodes are listed in Table 1. The J_{sc} increased from 6.50 to 8.06 mA cm^{-2} (from 0.01 to 0.05 wt% GaN), and then decreased from 8.06 to 7.37 mA cm^{-2} (from 0.05 to 0.15 wt% GaN). The values