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The effects of the solvent ratio on the electron transport for non-sintering flexible TiO_2 photoanodes

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ABSTRACT

Chemically modified TiO_2 colloidal paste with a mixed solvent of water and *t*-butanol are developed for preparation of dye-sensitised photoanodes on plastic indium-tin oxide (ITO)-coated polyethylene-naphthalate (PEN) substrates. The effects of the solvent ratio on the rheological behaviour of the binder-free paste and the contact angle between the paste and the substrate for TiO_2 photoanodes are scrutinised. First, tests of the rheological behaviour revealed that the increasing content of water leads to a decrease in the viscosity of the paste. Second, the dependence of the contact angle on the content of *t*-butanol is attributed to the trends of surface tension. Third, both the rheological properties and the contact angle influence the microstructure and morphology of the TiO_2 coating on the ITO-PEN surface. Finally, the EIS results confirm that electron transport and recombination are significantly influenced for the mixed case. All of these results enable the optimisation of the connection in the photoanodes, achieving the highest energy conversion efficiency of 5.30%.

1. Introduction

Flexible dye-sensitised solar cells (DSCs) with conductive plastic substrate of ITO-PEN have received widespread attention because of their unique advantages of low cost, portability, light weight and flexibility [1,2]. However, the conversion efficiency of flexible devices is not very high to date. This relatively poor efficiency of flexible DSCs is mainly due to the poor connection between the TiO_2 nanoparticles and the conductive polymer substrates. The heat treatment temperature for these polymer substrates of ITO-PEN is generally limited to a temperature lower than 150 °C. Due to the lack of a high-temperature heat treatment, the interparticle connections in the TiO_2 film remain at a poor level, which inhibits the transport of photo-induced electrons in the film and gives rise to electron recombination [3–6]. Many attempts were made to modify the interparticle connections of flexible TiO_2 photoanodes at low temperature, such as $TiCl_4$ post-treatment, acid treatment [7,8], the use of hierarchical structure [9,10] and the transfer of composite porous layers [11,12]. Although significant improvements were achieved, these methods still have not met the demand for large-scale production of flexible DSCs via a simple process [13].

Low-temperature chemically modified TiO_2 colloidal paste both effectively improves the interparticle connections and is also suitable for industrial applications of flexible DSCs [14]. Both the mechanical strength of the film and the photovoltaic performance of flexible DSCs are significantly improved. Arakawa et al. have developed a compression method for preparation of plastic-substrate TiO_2 photoanodes at low temperature without heat treatment [15,16]. The results revealed that the organic solvent in the TiO_2 paste can decrease the photovoltaic performance of flexible DSCs. Miyasaka et al. have also indicated that ITO surface of PEN without particular treatments exhibits hydrophobicity; the wet paste should develop high adhesion to the hydrophobic surface of the plastic substrate. Therefore, *t*-butanol was used to reduce the surface tension of the liquid paste and to improve its adhesion to the ITO-PEN surface [17]. Nevertheless, the effects of *t*-butanol on the paste and the microstructure of the photoanodes remain unclear. Although no further systemic study and theoretical explanations are given, these results provide the evidence that solvent plays an important role in the microstructure of flexible TiO_2 films, such as the connection from the TiO_2 nanoparticles to substrate, the uniformity of TiO_2 film, the cracks in the film, and so on. All of those factors affect the electron-harvesting efficiency and the photovoltaic performance of flexible TiO_2 photoanodes. Therefore, the effects of solvent on the paste should be studied to enable higher electron-harvesting efficiency.

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In the present paper, we studied the rheological behaviour of binder-free paste and the contact angle between the paste and substrate for TiO_2 photoanodes by optimising the solvent ratio of water and *t*-butanol. Electron harvesting within the TiO_2 film is enhanced by optimising the microstructure and the connection between TiO_2 nanoparticles and substrate, which is demonstrated by electrochemical impedance spectroscopy (EIS) measurements. Finally, the optimisation of the solvent ratio of water and *t*-butanol on the photovoltaic performance improvement is performed.

2. Experimental

2.1. Preparation of binder-free paste with different solvent ratios

The preparation of binder-free paste consisting of three sizes of nanoparticles essentially followed our previous method [8]. The optimum mass ratio of the smaller TiO_2 particles (with an average diameter of 9 nm via hydrothermal synthesis with tetrabutyl titanate as a precursor [18]), commercial P25 particles (with an average diameter of 23 nm, anatase: rutile = 7:3, Degussa, Germany) and larger scattering particles (with an average diameter of 60 nm, anatase: rutile = 23:77, Showa Denko Kabushiki Kaisha, Japan) was 2:5:2. Three types of nanoparticles were dispersed at various solvent ratios of water and *t*-butanol following continuous stirring for 24 h to form a homogeneous viscous paste. Next, 0.025 M nitric acid was added to the paste. The resulting paste was dispersed further through a de-aggregation treatment (Thinky Mixer, Are-310, Japan) at a speed of 2000 rps for 5 min to obtain a uniform paste with high viscosity and good stability during long-term preservation at room temperature. The concentration of TiO_2 nanoparticles was 22 wt%.

2.2. Preparation of the flexible photoanodes and fabrication of the DSCs

The resulting binder-free paste of different solvent ratios described above were coated onto conductive ITO-PEN substrates (thickness 200 μm, sheet resistance 13–15 Ω/□, transmittance 79.2–81.3%, Tobi, Japan) via a simple doctor-blade method using polyimide tape (thickness 50 μm) as the frame and spacer. After air-drying at room temperature, theTiO_2 film was cut into the desired shapes and then pressed under 125 MPa for 2 minutes at room temperature (MiniTestPress-10, Toyo Seiki). The thickness of the film after compression was approximately 8 μm. The pressed film was then sensitised by immersion in a 5×10^{-4} mol·L^{-1} ethanol solution of Ruthenium (2,2′-bipyridyl-4,4′-dicarboxilate)$_2$(NCS)$_2$ (N719, Solaronix SA, Switzerland) overnight at room temperature.

The flexible Pt counter electrode was prepared by an ion sputtering method onto the ITO-PEN substrate. The sensitised photoanode and the Pt-based counter electrode were assembled into a flexible cell and sealed with a 25-μm-thick hot-melt type Surlyn (R) film (DuPont, USA). The electrolyte was composed of 50 mM iodine (I_2), 500 mM lithium iodide (LiI), and 500 mM *tert*-butyl pyridine dissolved in acetonitrile. The active area of plastic DSCs was 0.16 cm^2.

2.3. Characterisation

The viscosity η of the binder-free paste after dispersion was measured at temperature of 25 °C using a Modular Compact Rheometer (MCR300, Physica, Germany). The contact angle of mixed solvent on the substrate was characterised by the Optical Contact Angle Measuring Device (DSA100, Krüss GmbH, Hamburg, Germany). The microstructure and morphology of the TiO_2 films prepared with different mass ratio of water and *t*-butanol were observed using a scanning electron microscope (SEM, LEO 1530; Germany). The photovoltaic properties were measured by a computer-controlled digital source meter (Keithley 2400) under simulated AM1.5G irradiation from a solar simulator (91192, Oriel, USA) with a black mask. The incident monochromatic photon-to-current conversion efficiency (IPCE) was measured as an action spectrum in the UV–vis range (400–800 nm) (PEC-S20, Peccell, Japan). EIS scans over the frequency range of 1 Hz to 100 kHz were recorded under AM1.5 illumination of 100 mW·cm^{-2} by using a CHI650C electrochemical analyser (CH Instrument Corp., USA) with an amplitude of the alternative signal of 10 mV. The measuring temperature was maintained at 25 °C. The obtained spectra were fitted using Z-View software (v2.1b, Scribner Associate, Inc. USA).

3. Results and discussion

3.1. The rheological behaviour of paste with different solvent ratios of water and t-butanol

Both the internal connections among the TiO_2 particles and the stability of TiO_2 film required to enable roll-to-roll manufacturing are largely influenced by the rheological behaviour of TiO_2 paste. The rheological behaviour of the paste is found to be highly dependent on the water-to-organic ratio of the solvent. The rheological property usually corresponds to a viscous fluid. The viscosity of the paste is related to the electrical double layer repulsion and van der Waals attraction. Repulsive forces due to the electrical double layer result in well-dispersed low viscosity suspensions, whilst attractive van der Waals forces result in aggregated suspensions and exhibit shear thinning viscosity behaviour [19,20]. Cheng and co-workers investigated the effects of the viscosity of the ethanol-based TiO_2 paste at different shear rates and proved that the low viscosity paste have strong, long-range repulsive interactions and short-range attractive interactions [21]. The long-range repulsive interactions are beneficial for the long-term stability of the well-dispersed colloid paste, while the short-range attractive interactions are beneficial for interparticle connections among different sizes of nanoparticles.

Here, we used a Modular Compact Rheometer to study the rheological property systematically. The shear viscosity as a function of the shear rate for the binder-free paste with different ratios of water and *t*-butanol is shown in Fig. 1. The TiO_2 paste

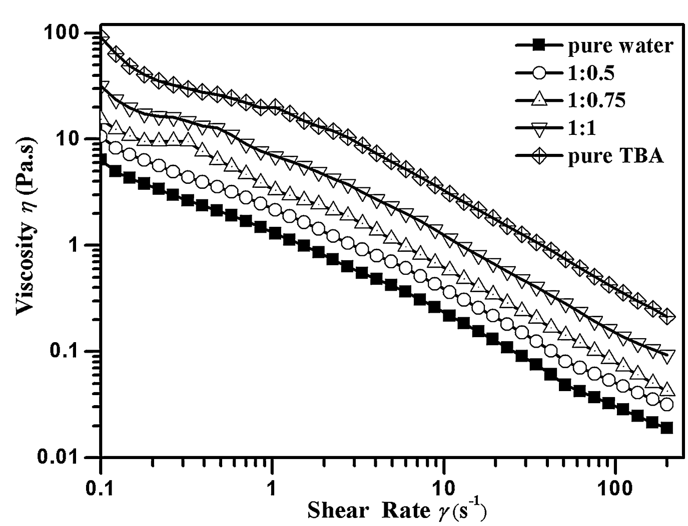

Fig. 1. Dependence of the viscosity on the shear rate for the binder-free paste with different mass ratios of water and *t*-butanol