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Original Research Paper

Design and development of electronic- and micro-structures for multi-functional working electrodes in dye-sensitized solar cells

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ABSTRACT

This paper outlines a new strategy to optimize the performance of electrodes in dye-sensitized solar cells (DSSCs), through the engineering of electronic structures in conjunction with the micro-structures of the devices. We propose a simple hydrolysis method for the fabrication of a family of quasi-core–shell TiO_2 (hydrolysis)/PbS composites for working electrodes. Measurements confirm a shift in absorption from the UV to visible range. We also measured cell performance, including short-circuit photocurrent, open-circuit photovoltage, and the power conversion efficiency (η) of DSSCs. The obtained η of DSSC (6.05%) with a TiO_2 (P-25)/TiO_2 (hydrolysis) + 0.005 M PbS electrode is substantially higher than that of the conventional DSSC (5.11%) with a TiO_2 (P-25) electrode, due to improved p–n junctions, light-scattering, and light absorption. Finally, the shell of TiO_2 (hydrolysis) protected the core of PbS from the corrosive effects of electrolytes, thereby prolonging the life span of the DSSC. This novel approach to electrode design could lead to advances in DSSC as well as other energy applications including photo-catalysis technology.

1. Introduction

The dye-sensitized solar cell (DSSC) proposed by O'Regan and Grätzel [1] provides many advantages over other solar cell technologies, including low production costs [2–4]. Unfortunately, current DSSC technology has a number of shortcomings, such as low power conversion efficiency (η) and a pronounced degradation in conversion rate. The conversion rate of DSSC is determined by two properties: short-circuit photocurrent density (J_{sc}) and open-circuit photovoltage (V_{oc}). The preferred method used to improve light absorption and attain a high J_{sc} is the application of a light-scattering layer [5–7]. Increasing the V_{oc} generally involves the application of two types of energy barrier between the electrode and dye, a wide band semiconductor [8,9] and/or a semiconductor p–n junction [10].

The addition of narrow-band semiconducting materials to the meso-porous TiO_2 electrode enables the absorption of light in the visible region, thereby increasing the light harvesting efficiency of DSSCs. For example, metal chalcogenide semiconductors such as cadmium sulfide (CdS) [11–15], cadmium selenide (CdSe) [16–19], lead sulfide (PbS) [20,21], and CdS/CdSe [22] have been used to produce quantum dot-sensitized solar cells. Luther et al. reported that lead chalcogenides quantum dots (PbX QDs) are easily synthesized and provide a band gap ranging from 0.5 to 2.0 eV with a small effective mass for electrons and holes, thereby increasing charge carrier mobility and conductivity [21]. Liu and Wang measured the incident photon to current efficiency (IPCE) of TiO_2/PbS films and observed that TiO_2 may play a role in the corrosion of PbS by the electrolyte [20]. No previous studies have reported the use of PbS to narrow the band gap of TiO_2 in working electrodes. Likewise, no previous study has reported the use of TiO_2 for the formation of a quasi-core shell microstructure to protect PbS from the corrosive effects of the electrolyte.

This study presents a simple method for the preparation of quasi-core–shell TiO_2 (hydrolysis) + PbS composite particles, in which smaller TiO_2 particles adhere to the surface of larger PbS particles. The colloid of these composite particles was prepared and deposited on a fluorine doped tin oxide (FTO) glass substrate (Fig. 1(a)). This colloid was also deposited on a meso-porous TiO_2 (P-25) electrode to enhance the light harvesting efficiency of a DSSC at wavelengths > 500 nm (Fig. 1(b)). The working electrodes were then applied to the DSSC. We also examined the effects of

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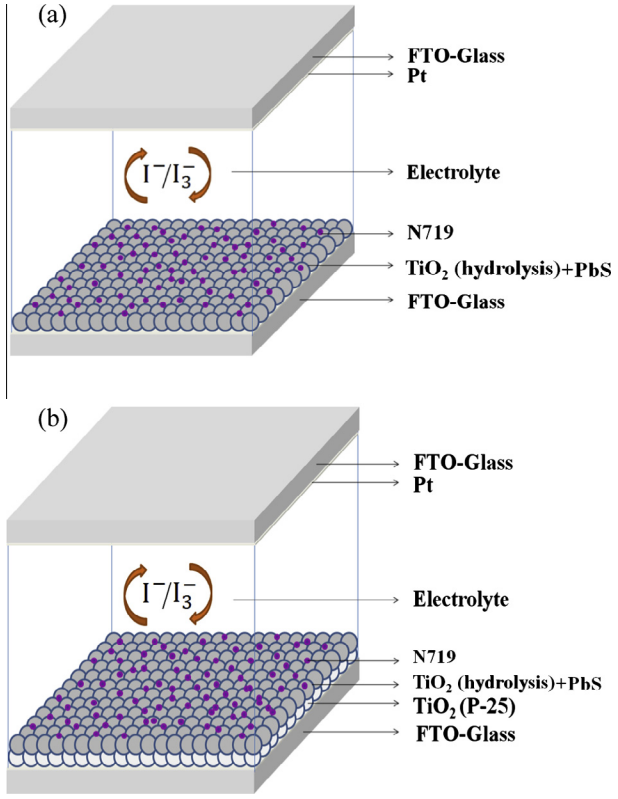

Fig. 1. (a) and (b) Schematic of a DSSC with a film of TiO_2 (hydrolysis) + PbS composite particles (a), and schematic of a DSSC with a film of TiO_2 (P-25) particles and a film of TiO_2 (hydrolysis) + PbS composite particles (b).

the relative molar ratio of Pb to S on the η of a DSSC. Moreover, a DSSC [with TiO_2 (P-25)/PbS electrode] was fabricated with PbS deposited atop the TiO_2 (P-25) electrode via chemical bath deposition (CBD). We compared a DSSC with the proposed working electrode to a conventional DSSC [with a TiO_2 (P-25) electrode] as well as a DSSC with a TiO_2 (P-25)/PbS (CBD) electrode.

This study selected TiO_2 (P-25) (20% rutile and 80% anatase) for the fabrication of working electrodes. To increase the J_{sc}, we introduced a narrow band semiconductor (PbS) into the electrode to enhance the intensity of solar absorption and narrow the band gap of TiO_2 (hydrolysis) using cationic as well as anionic doping. To reduce the population of electron recombination centers, we used a PbS (p-type semiconductor) to form a p–n junction between TiO_2 (hydrolysis) and the dye. During the formation of the TiO_2 + -PbS composite, Pb and S were used as dopants for TiO_2 to narrow its band gap and move the light absorption peak towards visible wavelengths.

2. Experimental details

2.1. Preparation and characterization of TiO_2 + PbS composite particles

The procedure used to obtain TiO_2 (hydrolysis) + PbS composite particles was as follows. (1) A solution of PbS was prepared by mixing solutions of sodium sulfide ($Na_2S{\cdot}9H_2O$) and lead (II) nitrate [$Pb(NO_3)_2$] (Table 1); (2) 100 ml PbS solution was added dropwise into the precursor of 50 ml titanium isopropoxide ($C_{12}H_{28}O_4Ti$), which was held at room temperature until it fully reacted; (3) the mixture was dehydrated in an oven at 80 °C for 1 day and then calcined in a high-temperature furnace (Thermolyne, 46100) to obtain the TiO_2 + PbS composite particles (Table 2).

Photographic images, micrographs, and energy dispersive spectroscopy analysis of TiO_2 (hydrolysis) particles, PbS particles, and TiO_2 (hydrolysis) + PbS composite particles were obtained using a digital camera (Panasonic DMC-LZ2), a scanning electron microscope (SEM) (HITACHI, 600-S), and an energy dispersive spectrometer (EDS) (Horiba EX-200), respectively. Further, a powder X-ray diffractometer (Shimadzu, XRD-6000) was used to obtain the X-ray diffraction (XRD) patterns of the particles obtained using the hydrolysis method.

Table 2
Test conditions of preparing TiO_2/PbS composite particles.

	Precursor	Additive	Calcining time (h)	Calcining temperature (°C)
B1	Titanium isopropoxide	DI water		
B2		A1		
B3		A2	0.5	450
B4		A3		
B5		A4		

2.2. Preparation and characterization of the working electrode

The procedure used for fabricating the working electrode comprised two stages. The first-stage involved fabrication of an active layer including the preparation of a colloid of TiO_2 particles (Table 3), the deposition of the colloid on an FTO-glass substrate using $TiCl_4$ treatment, and the sintering of this substrate in a high-temperature furnace (Table 4). The procedures used in the preparation of this active layer were outlined in our previous work [5].

The second-stage of fabrication included the following steps: (1) the colloid in Table 3 was deposited as a film on the TiO_2 (P-25) particles prepared in the first stage (Fig. 1(b)); (2) $TiCl_4$ treatment was repeated to modify the surface of the film prepared in step (1), which was then sintered in a high-temperature furnace (Table 5); and (3) the electrode was immersed in a solution of

Table 3
Test conditions of preparing colloids.

	Solute		Solution		
	Particle	Mass (g)	Ethanol (mL)	Acetylacetone (mL)	Triton X-100 (mL)
C1	TiO_2 (P-25)	2	8	0.8	0.1
C2	B1				
C3	B2				
C4	B3				
C5	B4				
C6	B5				

Table 1
Test conditions of preparing PbS solutions.

	$Na_2S{\cdot}9H_2O$ solution			$Pb(NO_3)_2$ solution		
	Mass (g)	DI water (mL)	M (mole L^{-1})	Mass (g)	DI water (mL)	M (mole L^{-1})
A1	0.6127	50	0.05	0.8364	50	0.05
A2	0.0613	50	0.005	0.08364	50	0.005
A3	0.6127	50	0.05	0.08364	50	0.005
A4	0.0613	50	0.005	0.8364	50	0.05