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RAPID COMMUNICATION

An "all-in-one" mesh-typed integrated energy unit for both photoelectric conversion and energy storage in uniform electrochemical system

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Abstract
An "all-in-one" mesh typed integrated energy unit is developed which converts solar energy to electric energy and stores it simultaneously. The entire integrated device operates in uniform electrolyte system which contains 0.8 M Na_2S, 0.8 M S, and 2 M KCl. A double-sided mesh electrode coated with Cu_2S film and carbon nanoparticles is shared by both energy conversion and storage sections. The device we fabricated can realize the co-operation of the energy conversion and storage sections effectively by taking advantages of the mono electrolyte system and the shared double-sided mesh-typed electrode. These properties are beneficial to assembly, miniaturization, and integration of a self-powered system for portable microelectronic devices.

Introduction

Renewable energy resource has attracted great scientific and technological attention due to the sustainable development in the future. Among the variety of energy generation devices

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[1-7], solar cell has a history over 60 years since the invention of the silicon-based solar cell in 1954 [8]. Extensive study has been implemented in this field and this solar energy harvesting technology has a thriving progress with time [3,6-15]. However, one issue in common solar cells is that the power output varies with the solar irradiation intensity which depends on the changing climate environment and the incident angle of the sun [16]. Therefore, it is as important as promoting the photoelectric conversion efficiency that makes the generated power stable under a changeable light irradiation condition. Connecting solar cells with energy storage devices could solve this problem. The energy storage devices, like Li-ion battery [17,18] and supercapacitors [19-22], can not only store the surplus energy for later utilization but also serve as a buffer to reduce the impact of the outputs fluctuation of the solar cells to the rear electric system as possible.

The simple and direct external wire connecting solar cells and energy storage devices together may realize co-work of the two devices but cause problems in internal resistance [23] and cannot meet the demands of miniaturization, integration and multi-functionalization [24,25]. Recently, attempts have been made to integrate the solar cell and energy storage device into a single device which can convert the solar irradiation into electric energy and store them simultaneously. For example, a novel design of planar structure has a promising potential for flexible semi-transparent energy generation/storage applications [26]. Single-fiber-based hybridization of energy converters and storage units have been demonstrated using ZnO nanowires and graphene [27]. Dye sensitized solar cells (DSSCs) and Li-ion batteries have been integrated into a power pack using double-sided TiO_2 nanotube arrays [28]. A series of researches around wire-shaped “energy fiber” have demonstrated good photoelectric conversion and energy storage efficiencies and the outstanding flexibility and stability make it very promising for the wearable and self-powered applications [29-31]. However, one common issue of the present researches is that the energy conversion and storage parts are still sealed separately and operated independently. In addition, the two parts use two different electrolytes for each part, resulting in a complex and difficult sealing method to prevent the leaking of electrolytes which may cause the integrated device fail and influence the promising large scale applications.

Herein, a novel three-layer planar structured integrated energy unit has been designed and manufactured for both photoelectric conversion and energy storage. The entire integrated device is in mono electrolyte with a shared double-sided middle mesh electrode. A CdS/CdSe quantum dots (QDs) co-sensitized solar cell is selected to serve as energy conversion section while a mesh-based carbon supercapacitor is utilized for energy storage unit. The unique mesh structure makes a connected and continuous internal space of the integrated energy unit and allows the free flow of mono electrolyte to make both energy conversion and storage sections work well. The double-sided middle mesh electrode is shared by the two sections. The special asymmetrical design of this electrode containing Cu_2S and carbon films on the opposite two sides realizes the co-operation of energy conversion and storage sections in mono electrolyte. Taking advantages of the specially designed mono electrolyte and the shared double-sided middle electrode, we have simplified the sealing problem compared to previous research and promoted the performances of both energy conversion and storage sections compared with the un-optimized structure.

Experimental section

CdS/CdSe quantum dots (QDs) co-sensitized mesoscopic TiO_2 photoanode preparation

First, the FTO/glass was covered by a layer of nanosized TiO_2 using a 40 mM $TiCl_4$ aqueous solution in 70 °C for 30 min. The homemade TiO_2 paste was prepared by adding commercial P25 TiO_2 nanoparticles (Degussa) into 10 wt% hydroxypropyl cellulose (Aldrich) in diethylene glycol solution with continuous stirring. The semitransparent mesoporous TiO_2 layer was fabricated by the doctor blading method. Then, the as-made TiO_2 electrode was immersed into CdS QD deposition solution containing 20 mM $CdCl_2$, 66 mM NH_4Cl, 140 mM thiourea, and 0.23 mM ammonia for 35 min and into CdSe QD solution containing 26 mM $CdSO_4$, 40 mM $N(CH_2COONa)_3$, and 26 mM Na_2SeSO_3 for 5.5 h, respectively. The whole deposition process was proceeded at 10 °C under dark. Finally, the photoanodes were passivated with ZnS by twice dipping into 0.1 M $Zn(CH_3COO)_2$ and Na_2S aqueous solution for 1 min alternately. The active area of the photoanodes used in this work was about 0.09 cm^2 measured by a vernier caliper [32,33].

Mesh-typed electrode and mono electrolyte preparation

The fabrication process of the mesh electrode is similar to the previous work of our group [34]. The commercial mesh-typed stainless steel substrate was cut into small pieces (1×2 cm^2) first and then ultrasonically cleaned in dilute hydrochloric acid, acetone, ethanol, and deionized water for 15 min, respectively. 50 nm Ni film was deposited on the two sides of the mesh by magnetron sputtering. The mesh with Ni film was immersed into commercial pen ink (from Hero, Shanghai Ink Factory in China) in an ultrasonic cleaner for 1 min, taken out, annealed on the hot plate in air at 300 °C for 1 h. Then the mesh-typed carbon electrode was obtained. For the multifunctional double-sided middle electrode, 50 nm Cu was deposited on the single side of the carbon electrode via electronic beam evaporation. Then the electrode was immersed into an aqueous solution containing 1 M Na_2S and 1 M S for 5 s to get Cu_2S, followed by cleaning and drying. To obtain the mono electrolyte, an aqueous solution containing 0.8 M Na_2S and 0.8 M S was stirred continuously more than 5 h, and subsequently, 2 M KCl was added and stirred uniformly.

Device assembly and characterization

The integrated energy unit was assembled by stacking up the carbon electrode, double-sided mesh electrode, and photoanode with double-sided adhesive (3M Company, America) for encapsulation. To prevent short circuit, a porous polymer spacer, 10 μm of thickness, was sandwiched between the two mesh-typed electrodes. Then the energy unit was filled with the aqueous mono electrolyte for the following characterization.