Journal of Power Sources 404 (2018) 118–125

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Integration of solar cells with hierarchical CoS_x nanonets hybrid supercapacitors for self-powered photodetection systems

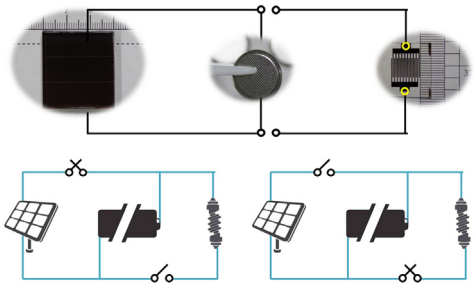
Yuliang Yuan[a], Yuhao Wu[a], Tian Zhang[a], Haichao Tang[a], Lu Meng[a], Yu-Jia Zeng[b], Qinghua Zhang[c], Zhizhen Ye[a], Jianguo Lu[a,*]

[a] State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China
[b] Shenzhen Key Laboratory of Laser Engineering, College of Optoelectronic Engineering, Shenzhen University, Shenzhen, 518060, China
[c] Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China

HIGHLIGHTS

- Integration system was developed with solar cells, HSCs and photodetectors.
- CoS_x hybrid supercapacitors demonstrated high electrochemical performances.
- CoS_x HSCs are charged by *a*-Si:H solar cells for stably driving ZnO photodetectors.
- Integration system is self-powered with acceptable operation behaviors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Self-powered integration system
Solar cells
Hybrid supercapacitors
Photodetectors
Cobalt sulfide

ABSTRACT

We have developed a self-powered integration system consisting of *a*-Si:H solar cells as the energy generation device, CoS_x hybrid supercapacitors (HSCs) as the energy storage device and ZnO photodetectors as the energy consumption device. The CoS_x HSC plays a crucial role in determining the system performances. By elaborately designing hierachical 3D CoS_x nanonets as the faradic electrode, the specific capacity reaches 225 mAh g^{-1} at a current density of 0.6 A g^{-1}. The HSCs assembled with the CoS_x faradic electrode and active carbon capacitive electrode have a high energy density of 32 Wh kg^{-1}, high power density of 6.61 kW kg^{-1} and long-term cycling lifetime. The CoS_x HSC can be charged to 0.85 V by the *a*-Si:H solar cell under AM 1.5 G illumination and serves as a stable power supply for driving ZnO photodetector. The CoS_x HSC not only acts as a buffer to diminish the solar energy fluctuations, but also provides a strategy for designing self-powered detector systems. The integration system exhibits a stable photoelectric conversion, excellent storage characteristic and sensitive photoelectric response, verifying the feasibility and potential applications. This study is expected to offer a basic guideline for designing self-powered and environment-friendly systems.

1. Introduction

The issues of exhausting energy crisis and greenhouse gas pollution derived from fossil fuels demand for not only the development of clean energies but also efficient energy storage [1,2]. The integration of energy generation, storage, and consumption devices has been explored in recent years because of the diversified functions for practical applications [3–7]. Among the generation devices, solar cells have long been

* Corresponding author.
E-mail address: lujianguo@zju.edu.cn (J. Lu).

https://doi.org/10.1016/j.jpowsour.2018.09.101
Received 24 May 2018; Received in revised form 2 September 2018; Accepted 30 September 2018
0378-7753/

investigated for the aim of mitigating today's overreliance on fossil fuels such as petroleum, coal and natural gas. Over six decades, the research on solar cell's materials has passed from crystalline silicon, vacuum vapor deposition derived inorganic compounds (*a*-Si:H, CdTe and CIGS) thin films and solution process derived (organic, dye-sensitized) thin films to perovskite solar cells [8,9]. Especially, with the low cost processable technology and continuously improved efficiency approaching commercialized polycrystalline silicon, the industrialization of perovskite solar cells is put on the agenda [10]. Together with traditional polycrystalline silicon, CdTe and $CuIn_{(1-x)}Ga_xSe_2$ solar cells, photovotaic devices are becoming more and more prominent in the acquisition of energies where we can only acquire from fossil fuels in the past. In an integration system, however, the energy storage devices play a crucial role in the integration system. As is known, most of the clean energies, such as solar, wind and tidal energy sources, are intermittent and thus unsuitable for round-the-clock power generation. For example, as the solar cells can merely work under sunlight illumination, the energy storage devices are ultimately required to store the generated energy for a commercial power [11–13]. The energy storage devices can mitigate the electric output swing of solar cells, serving as a buffer to alleviate the imbalance between the power output and energy requirement.

The energy storage devices mainly include rechargeable batteries and supercapacitors [1,14–16]. Although the secondary batteries have high energy density, they are unsuitable for storing intermittent and unstable energy due to their short cycling life time and unsafety [17,18]. The supercapacitors are potential candidates considering the high power density, fast charge capability, and long cycling stability [19–21]. However, the low energy density of supercapacitors based on carbon materials has been the main constraint on the storage of clean energies [18,22]. Recently, hybrid supercapacitors (HSCs), also named battery-supercapacitor hybrid devices, have been attracted more and more attention as the new energy storage devices [23]. The hybrid supercapacitors are constituted by a battery-type electrode and a capacitive electrode, are expected to have higher power density, faster charging time and longer cycle life than secondary batteries and higher energy density than conventional supercapacitors [23]. The typical HSCs are Li- and Na-ion capacitors [24–29], as well as those using transition metal oxides and hydroxides as the faradic electrodes and active carbon (AC) as the capacitive electrodes [23,30–33]. The latter contains neither Li nor Na in the matrix, which results in several evident advantages including good rate capability, long cycle life, considerable safety, and high energy density as well. The hybrid supercapacitors may be ideal candidates for storage of clean energies such as solar energy.

Most recently, transition metal sulfides such as SnS, CoS, NiS, ZnS, MoS, CuS and CdS have received considerable attention due to their excellent electrochemical properties. Among all the sulfides, CoS is probably most promising due to its merit of high conductivity and high specific capacity. Several reports have been focused on the application of hybrid supercapacitors based on CoS electrode. CoS electrodes with nanowire [34], nanosheet [35], nanotube [36], nanocage [37] and flower-like [38] morphologies have been reported. The morphology of electrode materials plays a vital impact on the overall performance of the hybrid supercapacitors. Herein, we report the hierachical CoS_x nanonets with large specific area and hierachical pore structure as the electrode material. Combined with active carbon, the HSC was also assembled using CoS_x electrodes and the corresponding performances were investigated comprehensively.

In this work, we have designed an integration system, consisting of *a*-Si:H solar cells, CoS_x hybrid supercapacitors and ZnO photodetectors, for simultaneous energy generation, storage and consumption (optoelectronic detection). For improved performances of HSCs, we present a new kind of three-dimensional (3D) hierarchical CoS_x nanostructures as the faradic electrode. Benefited from the unique hierarchitectures, the CoS_x electrode displays a high specific capacity of 225 mAh g^{-1} at a current density of 0.6 A g^{-1} with a high mass loading of 3.3 mg cm^{-2}. The aqueous hybrid supercapacitors, based on CoS_x nanonets as the binder-free cathode and AC as the anode, display acceptable performances such as high energy density of 32 Wh kg^{-1}, high power density of 6.61 kW kg^{-1} and long cycling stability. Using the CoS_x HSCs as the energy storage device, the integration system is self-powered and very steady. The CoS_x HSCs are charged by the *a*-Si:H solar cells and drive the ZnO photodetectors for operation. The performances of the integration system, as well as the behaviors of the respective devices, are evaluated in detail. The integration system realized the clean energy utilization with solar cells providing power source for photodetectors, and HSCs as the energy storage station to ensure a steady power output no matter what the weather is. We hope our study can open the door for practical applications of CoS_x HSCs and the self-powered, environment-friendly system.

2. Experiments

2.1. Assembly of CoS_x nanonets hybrid supercapacitors

The hierarchical 3D CoS_x nanonets were synthesized by an elaborately designed two-step hydrothermal process. For the first step, the precursor nanostructures were synthesized on the nickel foam. Specifically, $Co(NO_3)_2{\cdot}6H_2O$ (2 mmol), NH_4Cl (2 mmol) and $CO(NH_2)_2$ (2.5 mmol) were dissolved into deionized water (36 ml) and stirred magnetically to obtain homogeneous solution. The claret-red solution was transferred to a Teflon-lined stainless-steel autoclave (100 ml) with a piece of nickel foam in it. The reaction proceeded at 100 °C for 6 h. As being cooled down to room temperature (RT), the nickel foam coated with precursor nanostructures was washed with deionized water and dried at 60 °C for 4 h. For the second step, the nickel foam with precursor nanostructures was immersed in 600 mg/30 ml $Na_2S{\cdot}9H_2O$ aqueous solution and maintained at 120 °C for 15 h. After being cooled down to RT, the nickel foam was taken out, washed with deionized water, and dried to remove residual water. The products were formed on the nickel foam. The mass loading of active materials was calculated by the increased mass on the substrate.

The HSCs were assembled with 3D CoS_x nanonets as the binder-free cathode and AC as the anode. The AC electrode was prepared by a widely adopted method, as displayed in our previous report [39]. A piece of filter paper was adopted as membrane. The 6 M KOH aqueous solution was used as the electrolyte. At last, the cathode, anode and membrane were packed in a button cell with 20 mm in diameter and 1.6 mm in thickness. The capacity matching principle was adopted to determine the mass ratio between cathode and anode materials [39].

2.2. Fabrication of single-junction *a*-Si:H solar cells

In the integration system, the *a*-Si:H solar cells were used as the energy generation devices. The structure of single junction solar cells is of glass/textured AZO/*p*-type *a*-Si:H (~20 nm)/intrinsic a-Si:H (~300 nm)/*n*-type *a*-Si:H (~30 nm)Al, as fabricated in our group [40]. In the design of *a*-Si:H solar cells, the principle that the enhanced light trapping in the active layers will be in favor of higher quantum efficiency was chiefly taken into consideration. Therefore, we adopt textured AZO films as the front contact layer due to the increased path length of sunlight. The detailed process for fabrication of *a*-Si:H solar cells could be found in our previously reported work [40].

2.3. Fabrication of flexible ZnO photodetectors

Semiconductor photodetectors have received tremendous attention due to their various applications such as environmental and biological monitoring, flame detection, and missile launch detection. ZnO has been regarded as one of the most important materials for UV photodetectors [41]. In this work, the flexible ZnO UV photodetectors were