



Efficient ternary cobalt spinel counter electrodes for quantum-dot sensitized solar cells



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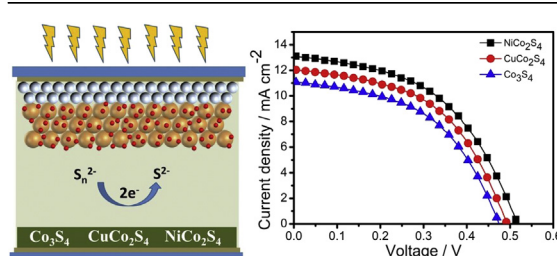
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HIGHLIGHTS

- CuCo_2S_4 and NiCo_2S_4 are synthesized by a low-temperature coprecipitation method.
- The catalytic activities of CuCo_2S_4 and NiCo_2S_4 are enhanced as compared with Co_3S_4 .
- The QDSC using NiCo_2S_4 achieves a promising power conversion efficiency of 3.3%.

GRAPHICAL ABSTRACT



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ABSTRACT

Cobalt-based spinel binary and ternary sulfides (Co_3S_4 , CuCo_2S_4 and NiCo_2S_4) are prepared via an economical, facile and versatile synthesis strategy and used as counter electrodes for quantum-dot sensitized solar cells (QDSCs) in conjunction with the aqueous polysulfide electrolyte. The spinel sulfides exhibit superior catalytic activities toward the polysulfide electrolyte reduction than that of the Cu_2S . Both electrochemical impedance spectroscopic and Tafel polarization measurements imply that the incorporation of Cu or Ni cation into the spinel lattices induces a significantly faster electrocatalytic rate towards the polysulfide reduction than that of the binary Co_3S_4 . Using ternary NiCo_2S_4 as counter electrode, the QDSC achieves a power conversion efficiency of 3.3%; which is increased by 26% compared with the QDSC fabricated with binary Co_3S_4 counter electrode (2.61%). The excellent electrochemical performance of the ternary cobalt spinel sulfides suggests their promising application as counter electrodes for efficient QDSCs.

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1. Introduction

The ever worsening energy depletion and increasing global environmental concerns have greatly stimulated the worldwide

research interests in inexpensive renewable energies [1]. Dye-sensitized solar cells (DSCs) have been considered as one of the most promising energy conversion devices due to their superior advantages, including cheap raw materials, ease of fabrication and energy-saving device processing compared with that of the dominant silicon-based photovoltaic devices [2–4]. Recently, a power conversion efficiency (PCE) up to 13% under AM 1.5G illumination (100 mW cm^{-2}) has been achieved in conjunction with a donor- π -bridge-acceptor zinc porphyrin dye and a $\text{Co}^{\text{(II/III)}}$ tris(bipyridyl)-based redox mediator [5]. As an alternative to conventional organic

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sensitizers, inorganic semiconductor quantum dots (QDs) such as CdS, CdSe, CdTe, PbS, Ag₂S, InAs and InP have been drawing widespread attention as reliable alternative light absorbers [6–8], due to their tunable band gap energy [9], high absorption coefficient [10], and multiple excitation generation effect by impact ionization [11]. These intrinsic properties in colloidal QDs could promote the thermodynamic efficiency limit of the devices up to 44% in comparison to 31% of the Shockley-Queisser limit [12,13], which make them more attractive and competitive for photovoltaic applications. Due to the recent development of the nanotechnology on the preparation and characterization of QDs, the PCEs of quantum dot-sensitized solar cells (QDSCs) have reached over 5% using metallic chalcogenides [14–17]. However, most QDs suffer from photodegradation in conjunction with the conventional I⁻/I₃⁻ redox mediator due to its corrosive nature on the QDs. Consequently, QDSCs commonly use the aqueous polysulfide electrolyte as redox mediator. However, in conjunction with such polysulfide electrolyte, noble platinum catalyst exhibits poor catalytic activity and stability, thus generate considerable overpotential for the polysulfide electrolyte regeneration. An effective electrocatalyst could reduce the regeneration overpotential and thus enhance the PCE of the QDSCs. Therefore extensive research efforts have been invested in exploring alternative inexpensive and efficient electrocatalysts for QDSCs. Recent works have shown that some low-cost transition metal sulfides (TMS) such as FeS₂, CoS, CoS₂, Co₃S₄, NiS, NiS₂, Cu₂S, CuInS₂ and Cu₂ZnSnS₄, carbon materials as well as TMS/reduced graphene oxide composite exhibit attractive catalytic behaviors for the polysulfide electrolyte reduction [18–28]. Nevertheless, Cu₂S and CoS may contaminate the polysulfide electrolyte and subsequently the photoanode in QDSCs [18]. Therefore, it would be of high importance to identify alternative highly catalytic counter electrode for the polysulfide electrolyte utilized in QDSCs.

Among a variety of TMS, of particular note ternary cobalt spinel sulfides formulated as ACo₂S₄, are a family of important functional materials that could find widespread applications, such as electrocatalysts for oxygen reduction reaction, and electroactive materials for high-rate pseudocapacitors due to their superior chemical and physical properties [29,30]. This category of material generally possesses versatile structure, which is able to accommodate various transition metal cations including Fe, Co, Ni, Cu, etc. Therefore, the manageable chemical composition in the TMS may provide vast opportunities to manipulate their physico-chemical properties. However, there is little report on the use of cobalt spinel sulfides as counter electrodes for QDSCs [31,32]. In particular, the incorporation of the second transition metal elements such as Cu or Ni cation into the spinel lattices could change their electric and composition properties, and consequently influence their electrochemical behavior toward the polysulfide electrolyte reduction, which, however, is never reported up to date.

In addition, to present a more straightforward comparison and understand of the catalytic trends of the cobalt spinel catalysts, a versatile synthesis approach is highly desirable since the electrocatalytic activity of the catalyst strongly depends on the preparation method. Several different synthetic methods of cobalt spinel sulfides have been proposed [29–39]. For example, Chen and co-workers fabricated polycrystalline Co₃S₄ nanotubes using a two-step hydrothermal method based on the Kirkendall effect [33]. Liu and Zhang reported a solvothermal approach to prepare hierarchical Co₃S₄ microflowers [29]. In addition, self-standing hollow NiCo₂S₄ single crystalline nanorod arrays was prepared via vulcanization and subsequent etching process and urchin-like NiCo₂S₄ was obtained through a precursor transformation method [30,32]. Porous NiCo₂S₄ nanotubes was also hydrothermally synthesized by sacrificial template method [34]. However, to the best of our knowledge, there has not been any report on the facile and versatile

low-temperature synthesis of the cobalt spinel binary and ternary sulfides.

In this work, we demonstrated, for the first time, a simple and low temperature method to prepare cobalt spinel binary and ternary sulfides (Co₃S₄, CuCo₂S₄ and NiCo₂S₄) and exploited their electrocatalytic utilization as inexpensive counter electrodes for QDSCs in conjunction with the polysulfide electrolyte. The compositions and morphologies of as-prepared spinel sulfides were well characterized by means of power X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The electrocatalytic activity of the as-prepared spinel sulfides was investigated by electrochemical impedance spectroscopic (EIS) and Tafel polarization measurements. The cobalt spinel sulfides obtained are highly catalytic when used as counter electrodes for QDSCs in conjunction with the polysulfide electrolyte, rivalling the performance of the Cu₂S counter electrode. More importantly, the ternary spinel sulfides shown improved catalytic activity toward the polysulfide electrolyte in comparison with that of the binary Co₃S₄. The current work presents the systematic study on cobalt spinel sulfide counter electrodes for QDSCs in conjunction with the polysulfide electrolyte and is expected to provide new insights in designing efficient counter electrode for QDSCs applications.

2. Experimental section

2.1. Source materials

Cu(NO₃)₂ (Aladdin, 99%), Ni(NO₃)₂ (Aladdin, 99.999%), Co(NO₃)₂ (Aladdin, 99.99%), Na₂S·9H₂O (Alfa Aesar, 98%), CuCl (Aladdin, 99.95%), CH₄N₂S (Alfa Aesar, 99%), polyvinylpyrrolidone (Alfa Aesar, M.W. 1300000), polyvinylidene fluoride (Alfa Aesar, 44080), *N*-methylpyrrolidinone (Aladdin, 99.9%).

2.2. Synthesis of spinel Co₃S₄, CuCo₂S₄ and NiCo₂S₄

In a typical synthesis, 26.7 mmol Co(NO₃)₂·6H₂O and 13.3 mmol nitrate hydrated salt of the second metal (Cu, Co) were firstly dissolved in 60 ml deionized water under stirring, then a 8 mmol NaOH water solution (10 mL) was added to the mixture solution. After vigorous stirring for 30 min, the as-obtained mixture was heated to 80 °C, followed by addition of Na₂S·9H₂O aqueous solution (0.106 mol). The reaction was kept at 80 °C for 6 h. After cooling down naturally to ambient temperature the resulting samples were washed with deionized water and ethanol several times by centrifugation, and then dried at 50 °C in a vacuum drying cabinet for 12 h before use and characterization.

To obtain NiCo₂S₄, 13.3 mmol Ni(NO₃)₂·6H₂O and 26.7 mmol Co(NO₃)₂·6H₂O were firstly dissolved in 60 ml deionized water under stirring before Na₂S·9H₂O (0.106 mol) was added. After vigorous stirring for 30 min, the as-obtained mixture was heated to 80 °C and kept for 8 h at this temperature. After cooling down naturally to ambient temperature the resulting precipitate was collected by centrifugation, and washed thoroughly with deionized water and ethanol several times, and then dried at 50 °C in a vacuum drying cabinet for 12 h.

For comparison, we also prepared Cu₂S via a solvothermal procedure according previous report [20]. 2 mmol CuCl and 3.9 mmol CH₄N₂S were firstly dissolved in 40 ml deionized water and ethanol mixed solution (volume ratio of 1:1) under stirring, then a 0.3 g polyvinylpyrrolidone (PVP) was added to the mixture solution. After vigorous stirring for 30 min, the as-obtained mixture was placed in a Teflon-lined autoclave (50 ml), followed by heating at 150 °C for 12 h in an electrical oven. The autoclave was then

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