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The preparation of Co_9S_8 and CoS_2 nanoparticles by a high energy ball-milling method and their electrochemical hydrogen storage properties

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ABSTRACT

Two different Co–S compounds with enhanced hydrogen storage properties, Co_9S_8 and CoS_2 , were prepared by ball-milling mixtures of Co metal and S powder. X-ray diffraction, scanning electron microscopy and transmission electron microscopy were used to show that specific molar ratios of Co:S and ball-milling speeds and times result in pure Co_9S_8 and CoS_2 , thus overcoming a long-standing inability to obtain pure Co–S compounds via ball-milling. A galvanostatic charge–discharge process and cyclic voltammetry measurements showed that the as-obtained Co_9S_8 and CoS_2 nanoparticles have enhanced electrochemical hydrogen storage capacities of 1.79 and 1.57 wt% hydrogen, respectively, which are higher than those previously reported. In addition, based on the corresponding X-ray photoelectron spectroscopy and cyclic voltammetry measurements, a new electrochemical hydrogen storage mechanism for the two Co–S compounds was proposed and discussed.

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Introduction

As is acknowledged, hydrogen energy, a kind of clean energy characterised by low carbon or even zero carbon, is increasingly standing out in the energy field. Therefore, it is natural that high-performance hydrogen storage materials is needed urgently. However, hydrogen is difficult to store in an effective, safe and stable solid-state medium, restricting its practical application. Significant efforts have recently been devoted to search for suitable materials that can store

hydrogen with high capacity and good reversibility [1–3]. Carbon and its composites [4–6], metal-organic frameworks [7] and inorganic transition metal compounds [5,8,9] have become new research hotspots, following the exploration of metal alloys for hydrogen storage [10,11]. The hydrogen storage capacity of the present hydrogen storage materials still does not meet the ever increasing demands for practical applications, and materials with high capacities could only be made in the research laboratory. Therefore, it is necessary to develop new hydrogen storage materials with higher energy densities and more feasible manufacturing

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processes. Recently a series of Co-based materials (Co–B [12–14], Co–P [15–17], Co–Si [6,18,19], Co–S [20–22], Co–Si₃N₄ [23], Co–C [7], and Co–graphene [8,24,25]) were prepared and studied as hydrogen storage materials. As a new type hydrogen storage material, Co–S has attracted significant attention. Simple mixing, hydrothermal treatment, arc-melting and ball-milling methods were applied to prepare these materials. For example, amorphous Co–S products were synthesised through a hydrothermal method using Co(NO₃)₂·6H₂O and thiourea at 160 °C, and the products displayed a hydrogen storage capacity of 1.25 wt% hydrogen [26]. A Co–S alloy with spherical structure was prepared by a chemical reduction method and exhibited an electrochemical hydrogen storage ability of 1.45 wt% hydrogen [27]. CoS₂ nanowires with large specific surface areas obtained by a hydrothermal method exhibited greatly improved high-rate discharge ability (1.42 wt% hydrogen) and cyclability [28]. The above samples show that Co–S compounds are a candidate for hydrogen storage.

Although the mechanical ball-milling method has proven an effective physical–chemical technique for obtaining pure compounds and can be easily applied in industry production [18], few works about Co–S synthesis were performed through direct ball-milling, especially pure Co–S compounds. Table 1 summarises the synthesis and properties of the different Co–S materials. It was reported that Co–S obtained by a low-energy ball-milling with a speed of 400 revolutions per minute (rpm) had good cycling stability and a hydrogen storage capacity of 1.39 wt% hydrogen [29]. Compared with the theoretical hydrogen storage capacity of individual metal Co (3.39 wt% hydrogen) [30], the capacity obtained above is not satisfactory, which may be due to the deficient grain refinement and poor composite structures under a low activation energy provided by a low ball-milling speed. Therefore, a high-energy ball-milling method may overcome such shortcomings and has been successfully used to produce amorphous alloys [14], metastable metals [19] and inorganic compounds [20] and to induce the materials' phase transformations [31–33].

In this study, a high-energy ball-milling method is introduced to improve the electrochemical hydrogen storage properties of Co–S particles. The effects of different addition ratios of Co and S under high ball-milling speeds were studied. It was found that individual pure-phase Co₉S₈ and CoS₂, which present enhanced electrochemical hydrogen storage capacities, were produced under the current experimental conditions.

Experimental

Preparation and structural characterisation

The analytically pure Co and S reagents without further treatment were mixed at the selected mole ratios of 1:0.5, 1:1, 1:2 and 1:3, and the ball-to-powder weight ratio was 10. The mixtures were ball-milled using a planetary ball-mill under an Ar atmosphere at speeds of 600, 800, and 1000 rpm for 6 h. Finally, the powders were collected and analysed.

The crystalline phases of the products were identified first by X-ray diffractometry (XRD, Rigaku D/max IIIA, Cu Kα) with a 2θ range of 10–90°. The surface configurations of the products were with by a JSM-6700 F field emission scanning electron microscope (SEM, JEOL, Japan), whereby the resulting powders were mounted on a silicon slice. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS, TSC K-Alpha, AlKα) was adopted to measure the change of elements' relative contents before and after the charge process. AlKα radiation was used as the X-ray source, and the voltage and current for the excited state of AlKα were 12 kV and 6 mA, respectively. A binding energy of 284.6 eV for C 1s was chosen as an internal reference, and the samples for measurements were dried in vacuum at 60 °C for 5 h.

Electrochemical measurements

The electrochemical measurements were performed following the method reported in Ref. [36] with specific improvements. Briefly, the electrodes were prepared by mixing Co–S powders, acetylene black and polytetrafluoroethylene at the weight ratio of 7:2:1 and pressing the mixture onto a porous nickel mesh at 50 MPa. The Co–S negative electrodes were used as the working electrode, and Ni(OH)₂/NiOOH was used as the counter electrode. The Co–S negative electrode was charged for 8 h at a current density of 100 mA/g and discharged at 30 mA/g to 0 V. The electrolyte was 6 M KOH aqueous solution. The rest time between charge and discharge was 2 min. All of the electrochemical hydrogen storage experiments were conducted using the Land battery system (NEWARE) at room temperature.

A three-electrode test cell on a PARSTAT 4000 electrochemical workstation was used for cyclic voltammetry (scan

Table 1 – Hydrogen storage capacities of Co–S materials synthesised by different methods under atmospheric conditions (GP = gaseous phase, EC = electrochemistry).

Synthetic products	Synthetic methods and synthetic conditions	Hydrogen storage capacity (wt% hydrogen)
Co ₃ S ₄ (nanocrystal) [34]	Microwave radiation	1.25 (GP)
Co–S (non-crystal) [21]	Ball milling (mole ratio _{Co:S} = 1:1, 400 rpm, 10 h)	1.39 (EC)
CoS ₂ (nanocrystal) [35]	Direct heating (metal Co and S powder, 120 h, 400 °C)	1.42 (GP)
Co–S (non-crystal) [21]	Ball milling (mole ratio _{Co:S} = 1:3, 400 rpm, 4 h)	1.45 (EC)
CoS ₂ (this work, crystal)	Ball milling (mole ratio _{Co:S} = 1:2, 1000 rpm, 6 h)	1.57 (EC)
Co ₉ S ₈ (this work, crystal)	Ball milling (mole ratio _{Co:S} = 1:1, 600 rpm, 6 h)	1.79 (EC)

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