Enhanced hydrogen storage in sandwich-structured rGO/Co$_{1-x}$/S/rGO hybrid papers through hydrogen spillover

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Highlights

- A binder-free sandwich-structured rGO/Co$_{1-x}$/S/rGO hybrid paper was obtained.
- The Co$_{1-x}$/S was immobilized in between the rGO sheets by the chemical “bridges”.
- The hydrogen storage ability of rGO was enhanced by 10× through spillover effects.

Abstract

Reduced graphene oxide (rGO) based two-dimensional (2D) structures have been fabricated for electrochemical hydrogen storage. However, the effective transfer of atomic hydrogen to adjacent rGO surfaces is suppressed by binders, which are widely used in conventional electrochemical hydrogen storage electrodes, leading to a confining of the performance of rGO for hydrogen storage. As a proof of concept experiment, a novel strategy is developed to fabricate the binder-free sandwich-structured rGO/Co$_{1-x}$/S/rGO hybrid paper via facile ball milling and filtration process. Based on the structure investigation, Co$_{1-x}$/S is immobilized in the space between the individual rGO sheets by the creation of chemical “bridges” (C–S bonds). Through the C–S bonds, the atomic hydrogen is transferred from Co$_{1-x}$/S to rGO accompanying a C–H chemical bond formation. When used as an electrode, the hybrid paper exhibits an improved hydrogen storage capacity of 3.82 wt% and, most importantly, significant cycling stability for up to 50 cycles. Excluding the direct hydrogen storage contribution from the Co$_{1-x}$/S in the hybrid paper, the hydrogen storage ability of rGO is enhanced by 10× through the spillover effects caused by the Co$_{1-x}$/S modifier.

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1. Introduction

The ever-growing demand for hydrogen energy storage applications in electric vehicles and other energy storage devices has spurred significant researches in the development of high-capacity electrochemical hydrogen storage materials [1,2]. There is a consensus that a breakthrough in capacity could be achieved by combining transition metals with carbon-based materials [3]. Among the many candidates is graphene, a two-dimensional (2D), one-atom-thick carbon layer, which has been highly touted due to its excellent chemical stability, superior electrical conductivity, and high surface area. The key issue for utilizing the unique properties is in assembling transition metals and graphene into a layer by layer nanostructure. Compared to the three-dimensional (3D) bulk structure, the 2D nanostructure exhibits significant advantages, such as larger surface area and effective electron transport channels, which can further improve the electrochemical performance [4]. A series of transition metal (Ru, Pd, Pt, Ca, Ni and so on) modified rGO materials have been fabricated [5–9]. Though these materials have enhanced electrochemical properties, they lack direct interconnection, causing a decrease in cycling stability. The decrease in cycling stability is mainly caused by the rGO sheets cannot be effectively activated from nanosized Co9S8 particles within the hybrid due to their intrinsic geometrical characteristics [10,11]. To address this issue, there is a need to provide high activation energy to the reaction system and obtain stable chemical link (rather than weak “physical”) Van der Waals interactions). Moreover, it is noteworthy that such chemical “bridges” are favorable for atomic hydrogen transferred from transition metal atoms to adjacent carbon surfaces via spillover and surface diffusion [12], resulting in better hydrogen storage performance [13]. However, in reality, it is difficult to implement, because of the challenges in partly breaking the C–C bonds without distorting the entire structure of rGO. As a result, providing extremely high energy and introducing another nonmetal element to link them may be a possible way to avoid the distortion and breakage of the carbon supporter. Using inorganic compounds formed by the transition metal elements mentioned above would be the first choice to consider. Recently, we have used a novel high energy ball milling method to obtain a Co9S8–graphene electrode material, in which the addition of Co9S8 greatly increased the hydrogen storage capacity. However, due to the relatively large Co9S8 particle size, as well as when assembled into the electrode, we have to use binders, which cannot effectively con...
100 mA g\(^{-1}\) for 15 h, and then discharged to 0 V at current density of 200–1000 mA g\(^{-1}\). All of the electrochemical hydrogen storage experiments were carried out using the battery test system (LAND CT2001A) at room temperature and ambient pressure. The cyclic voltammetry (CV) curves were obtained via a three-electrode test cell on an electrochemical workstation (PRINCETON PARSTAT 4000).

3. Results and discussion

Fig. 1 illustrates the fabrication steps of the sandwich-structured rGO/Co\(_{1}\)S/rGO hybrid paper, wherein the most critical step is to ensure homogeneous, tight coating of Co\(_{1}\)S on the surface of rGO sheets. Typically, the Co\(_{1}\)S and rGO were first blended together, then ball milled in a ZrO\(_2\) vessel at the speed of 700 rpm for 10 h under an Ar atmosphere. In the process, large rGO sheets were crushed into smaller pieces with much more structural defects. Meanwhile, the activated Co\(_{1}\)S by ball-milling was readily dispersed on the surface of the rGO, and then partly combined with the activated C atoms especially on the surface and defects of rGO. During the later composition process, the bounded and activated Co\(_{1}\)S particles aggregate and grow rapidly, homogeneously, and tightly coat on the surface of rGO sheets. As a result, Co\(_{1}\)S was incorporated into the space between the individual rGO sheets, and the sandwich structure was formed. As shown in Fig. 51, the Raman spectra for rGO and the rGO/Co\(_{1}\)S/rGO hybrid paper display both D band (sp\(^3\) defects induced disordering) and G band (sp\(^2\) bonded pairs) peaks [21]. The negative shift and the slight increasing of D band (sp\(^3\) defects induced disordering) and G band (sp\(^2\) bonded pairs) peaks before 1000 cm\(^{-1}\) could be freely rolled, showing high mechanical flexibility.

The high-energy ball milling formation is a cost efficient process for producing various interesting, solid-state composites with finely controlled microstructures. The high pressure can perturb surface-bonded species, leading to enhanced kinetic and thermodynamic reactions between solids [19,20,23]. In order to study the effect of this process, X-ray photoelectron spectroscopy (XPS) was conducted for the as-filtered rGO paper (Fig. S3a), Co\(_{1}\)S (Fig. S3b) and the rGO/Co\(_{1}\)S/rGO hybrid paper (Fig. S3c). The spectrum of the rGO/Co\(_{1}\)S/rGO hybrid paper shows only the peaks assigned to S, C, O, and Co, without any other impurity. The high-resolution C 1s spectrum of rGO in Fig. 2a can be fitted to two peaks of C–C (284.6 eV) and C–O (286.4 eV) [24,25]. After the composition has taken place, the C 1s spectrum shows an overlap of the C–C, C–O, and another peak, revealing the appearance of a new C–S peak (285.6 eV) [26]. The difference between the two samples suggests the ball milling process could produce more defects and bond the activated S and C atoms. In addition, the S 2p spectrum of Co\(_{1}\)S in Fig. 2b indicates the presence of two main peaks at 162.8 eV and 161.4 eV respectively, which are assigned to cobalt sulfide [27]. In the case of the rGO/Co\(_{1}\)S/rGO hybrid paper, a small shoulder related to the S–C bond appears at 163.6 eV, which is in accordance with the previous result [28]. The Co 2p spectra (Fig. S3d) in the samples reveal the Co2p 1/2 and Co2p 3/2 spin-orbit peaks, which can be assigned to its sulfide [29,30]. The slight changes in morphology and location of the main peaks and the shake-up satellites between the two samples suggest different valence states and ion distribution between different S surroundings of Co [29,31]. These results together indicate the successful establishment of chemical “bridges” between rGO and Co\(_{1}\)S through a simple high energy ball milling method.

To further demonstrate the structure of the rGO/Co\(_{1}\)S/rGO hybrid, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed. As shown in Fig. 3a, the hybrid paper is considered to be the layer by layer structure. Homogeneously distribute Co\(_{1}\)S is embedded in the space of interconnected and overlapped rGO sheets. As shown by the TEM image (Fig. 3b and S4), Co\(_{1}\)S is evenly and uniformly coated on the surface of rGO sheets. Fig. 3b inset depicts the corresponding selected area electron-diffraction (SAED) patterns. There are two sets of diffraction patterns which belong to the indexed (100), (101), (102), and (110) planes of hexagonal Co\(_{1}\)S, and rGO, respectively. A high resolution TEM image (Fig. 3c) was taken at the edge of the nanosheets, which presents Co\(_{1}\)S sandwiched between two rGO sheets. The inter-planar d spacing of 1.935 Å corresponds to the (102) plane of hexagonal Co\(_{1}\)S crystal, which was confirmed by the later XRD test. In the central position of the sample, it can be observed that the inter-planar d spacing of 1.935 Å and 2.537 Å corresponds to the (102) and (101) planes of hexagonal Co\(_{1}\)S crystal (Fig. 54). This further demonstrates the Co\(_{1}\)S not only grew on the edge defects but also between the middle of the rGO sheets. Furthermore, the distribution of Co\(_{1}\)S in the hybrid was analyzed by EDS elemental mappings (Fig. 3d,e, and...
hybrid paper for (a) C 1s and (b) S 2p. The (102) diffraction peak position of rGO/Co1xS/rGO sheets are observed, suggesting tight interaction between the individual rGO sheets, is uniform. It should be emphasized that even after 1 h of ultrasonication during the preparation of the sample, very few uncoated rGO sheets could be isolated from the Co1xS/rGO hybrid. The strong diffraction peaks at 30.6°, 35.1° and 46.9° correspond to (002) spacing of the Co1xS/rGO hybrid paper, the FT-IR spectra remain almost unchanged except for the S–H stretching vibrations at 530 cm⁻¹. These characteristic features indicate the fact that the process of hydrogen adsorption, hydrogen dissociation, and subsequent spillover from the Co1xS to the rGO are due to the C–S chemical “bridges.” It is noted that these observations are also in agreement with the above studies.

To further confirm the electrochemical hydrogen adsorption/
desorption behavior of the rGO/Co_{1-x}S/rGO hybrid paper, the cyclic voltammogram (CV) curve for the charge/discharge cycle was recorded as shown in Fig. 4c. In the cycle, one broad reduction peak of hydrogen is clearly observed at the potential of $-1.10\ V$, corresponding to the insertion of H atoms into the layers and the formation of rGO/Co_{1-x}S/rGO-H_x. During the following anodic polarization, three anodic peaks appear, which are attributed to a multistep desorption of hydrogen on the rGO/Co_{1-x}S/rGO hybrid paper. Interestingly, the three current peaks suggest the three-step adsorption phenomenon of hydrogen. The first current peak at $-0.96\ V$ is attributed to the electrochemical oxidation of the rGO/Co_{1-x}S/rGO hybrid, which is consistent with previous observation.

Fig. 3. (a) SEM images of the rGO/Co_{1-x}S/rGO hybrid paper from cross-sectional view; TEM images of (b) rGO/Co_{1-x}S/rGO hybrid and (c) high magnification of rGO/Co_{1-x}S/rGO; (d) and (e) EDS elemental mapping images of Co and S; (f) and (g) XRD patterns of the rGO paper, Co1-xS, and rGO/Co_{1-x}S/rGO hybrid paper; (h) the best fit schematic model for (c); (i) Stress–strain curve of rGO and the rGO/Co_{1-x}S/rGO hybrid paper.
Fig. 4. (a) Charge-discharge curves of the rGO/C01−xS/rGO electrode and the rGO/C01−xS/rGO-Hx hybrid paper electrode compared with those with PTFE. Fig. 5b demonstrates the rate capabilities of the binder-free rGO/C01−xS/rGO hybrid paper electrode shows much better capacity retention relative to the rGO/C01−xS/rGO hybrid paper electrode. Fig. 5b demonstrates the rate capabilities of the three electrodes under different current densities: 200 mA g−1, 400 mA g−1, 600 mA g−1, 800 mA g−1, and 1000 mA g−1. It can be found that the high rate discharge capacities of the three electrodes steeply decline with an increase in the current density. It is obvious that high discharge capacity has negative impact on electrodes, such as accelerating the corrosion speed of the composites, so the phenomenon is consistent with the previous findings [37–39]. In addition, the binder-free rGO/C01−xS/rGO hybrid paper electrode shows much better rate capability than those with PTFE binder under every investigated current density. For instance, at the discharge current density 200 mA g−1, the rate discharge characteristic of the binder-free rGO/C01−xS/rGO electrode (90%) is nearly 10% and 20% greater than that of electrode with 25% (81%) and 50% (73%) PTFE. Unexpectedly, even at a very high current density of 1000 mA g−1, binder-free electrode is still able to deliver high rate discharge characteristic of 74%, which is 27% higher than that of electrode with 25% PTFE binder (58%). The results above imply that the unique sandwiched structure of the binder-free rGO/C01−xS/rGO hybrid paper electrode can efficiently buffer volume changes and be maintained well even under high current density tests.

A typical photo of the rGO/C01−xS/rGO electrode before and after 50 cycles in 6.0 M KOH aqueous solution is given in Fig. 5c. After 50 cycles, only a small amount of precipitation can be observed and the hybrid paper maintained its integrity and flexibility, which indicates a stable formation. To further confirm the structure stability of the rGO/C01−xS/rGO hybrid paper electrode upon cycle, we then investigated the morphology of the rGO/C01−xS/rGO hybrid by TEM. As shown in Fig. 5d–g, the 2D sheet-like morphology of the rGO/C01−xS/rGO hybrid still remains and the C, Co, and S elements are uniformly dispersed over the entire range without aggregation. These results indicate that the sandwich-structured rGO/C01−xS/rGO hybrid electrode is stable during the charge/discharge cycles. The excellent electrochemical performance of the binder-free rGO/C01−xS/rGO hybrid paper electrode is attributed to the following reasons: (1) The high energy ball mill process strongly promotes the formation of an intimate relationship, and results in the steady formation of chemical “bridges” (C–S bonds) through which the hydrogen confined by C01−xS could subsequently spillover to the rGO surface. (2) The Co1−xS layer is very thin, which is beneficial for providing more tunnels for the spillover of hydrogen in the alkaline solution and acts as a buffer zone for releasing the stress formed in the hydrogen absorb/dis- absorb process [40]. (3) The absence of non-conducting PTFE binder could also improve the electrode's electronic conductivity. These unique characteristics lead to the competitive advantages of the binder-free rGO/C01−xS/rGO hybrid paper electrode.
4. Conclusions

In summary, Co$_1$S was incorporated into the space between the individual rGO sheets by high energy ball milling and the rGO/Co$_1$S/rGO hybrid paper was prepared by vacuum filtration. The unique structure and hydrogen storage capacities of the obtained hybrid paper were studied in detail. The Co$_1$S was highly crystallized and homogenously and tightly coated on the surface of rGO sheets through chemical “bridges” (CeS bonds). When used as a cathode, chemical “bridges” (CeS bonds) have been shown to be effective for facilitating hydrogen spillover and, hence, hydrogen storage. Through the CeS bond, the atomic hydrogen can be transferred from Co$_1$S to rGO accompanying a CeH chemical bond formation, and an increased hydrogen storage capacity of 3.82 wt % was achieved at the current density of 30 mA g$^{-1}$.

Excluding the direct hydrogen storage contribution from the Co$_1$S in the hybrid paper, the hydrogen storage ability of rGO was enhanced by 10% through the spillover effects caused by the combination of the strong interaction between the Co$_1$S and rGO. The results show that the fabrication method and the hydrogen storage capacity of the rGO/Co$_1$S/rGO hybrid paper deserve further exploration for creating versatile hybrid hydrogen storage materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.05.026.

References


Fig. 5. (a) Cycle performances and (b) Rate capabilities of the binder-free rGO/Co$_1$S/rGO electrode and electrodes with PTFE as binder; (c) Digital photo of: 1 rGO/Co$_1$S/rGO hybrid paper and 2 rGO/Co$_1$S/rGO hybrid paper after 50 cycles; (d) TEM image of the binder-free rGO/Co$_1$S/rGO hybrid after 50 charge/discharge cycles and corresponding elemental mapping images of (e) C, (f) Co, and (g) S.