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A high-performance flexible supercapacitor electrode material based on nano-flowers-like FeS_2/NSG hybrid nanocomposites

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ABSTRACT

Novel FeS_2/nitrogen-sulfur double doped graphene (NSG) flexible hybrids electrode materials have been successfully prepared via a rapid microwave method followed by tube furnace heating process. Small size nano-flower-like structure of FeS_2 uniformly supported on multi-fold NSG, which promote electron transport and electrochemical reaction. The material shows good electrochemical performance in a three-electrode system, such as high specific capacitance (528.7 F g^{-1} at the current density of 1 A g^{-1}), excellent charge/discharge stability and long-term cycling life (89% of capacitance retention after 10,000 cycles at 10 A g^{-1}). These results demonstrate great potential of FeS_2/NSG flexible hybrid nanocomposites for supercapacitor application.

1. Introduction

With advances in science and technology, there is a growing demand for flexible supercapacitor because of its lightweight performance, high power density and improved cycle stability [1]. Typically, the capacity of supercapacitor primarily depends on the electrode material [2], so researchers focus on developing flexible electrode materials with better performance. Graphene is often used as a flexible electrode material due to excellent flexibility and electrochemical performance [1]. Doping of N and S atoms in the lattice of graphene (NSG) can activate the surrounding C atoms, cause the redistribution of charge density and spin density, which led to the improved electrical conductivity and rate performance [3,4]. In addition, ferrous disulfide (FeS_2) has both mechanical stability [5] and relatively large capacity [6] compared with other transition metal sulfide, which are considered promising candidates as electrode materials for supercapacitors.

Up to now, although there have been many papers on the excellent electrochemical performance of FeS_2, the capacity stability is still the bottleneck of the preparation of sulfide [7]. Creatively, the simple microwave heating method to synthesize the regular nano-flower-like FeS_2 nanoparticles supported on the flexible materials NSG was the first time to try. In the preparation process, the microwave-assisted heating method plays a key role to facilitate the formation of better dispersed nanoparticles with more uniform size distribution [8]. The FeS_2/NSG hybrids materials have a capacitance of 401.2 F g^{-1} at the current density of 10 A g^{-1} with significant long-term cycle stability. The excellent properties can be attributed to the regular flower-like nanostructures with large specific surface area and the folds caused by double doping, which can form a multi-channel structure for electronic transmission and improve the stability of materials.

2. Experimental section

2.1. Materials preparation

Graphene oxide (GO) was prepared using the reported modified Hummers method [9]. During the FeS_2/NSG formation process, 3 mmol Ferric nitrate ninehydrate ($Fe(NO_3)_3{\cdot}9H_2O$) was dispersed in 70 mL ethylene glycol solution by vigorous stirring. Then, ammonia was added dropwise to the dispersion until pH was around 7.0. Subsequently, 6 mmol ammonium thiocyanate (NH_4SCN) and 30 mg GO were add to the above solution and followed by a microwave heating disperse for 3 min. Finally, FeS_2/NSG composites was obtained by subsequent tube furnace heating and maintained at 500 °C for 2 h under a protective gas atmosphere. In contrast, pure FeS_2 was synthesizedsynthetized by same procedure without adding GO.

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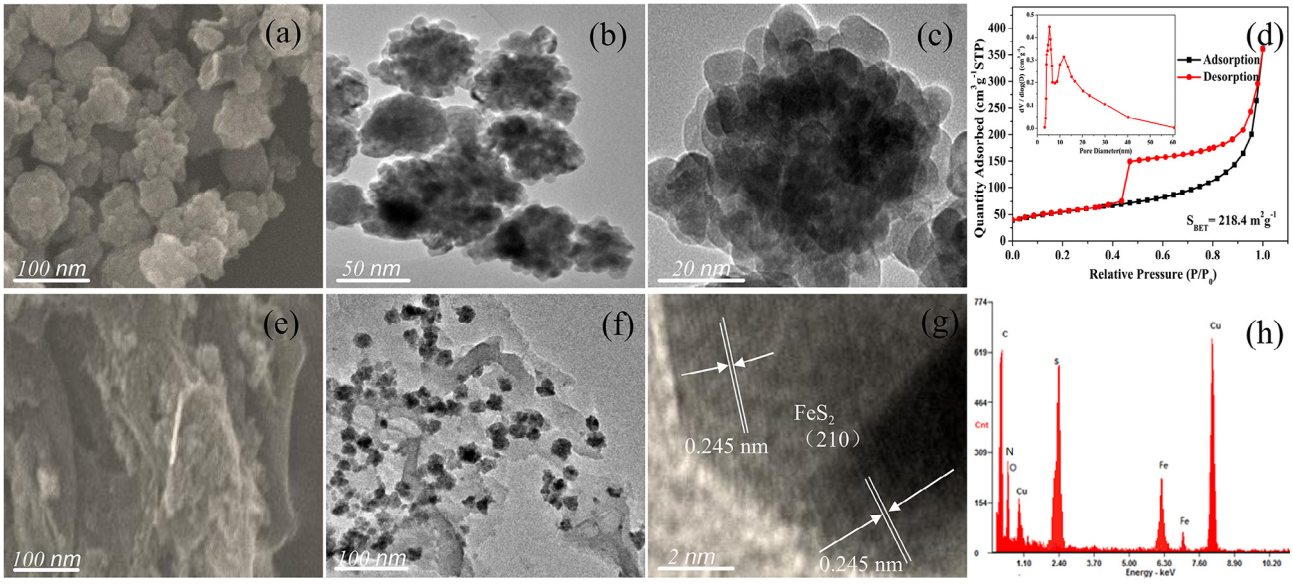

Fig. 1. SEM image (a) and TEM images (b, c) of FeS_2; BET surface analysis (d), SEM image (e), TEM images (f), HRTEM (g) and EDS spectra (h) of FeS_2/NSG.

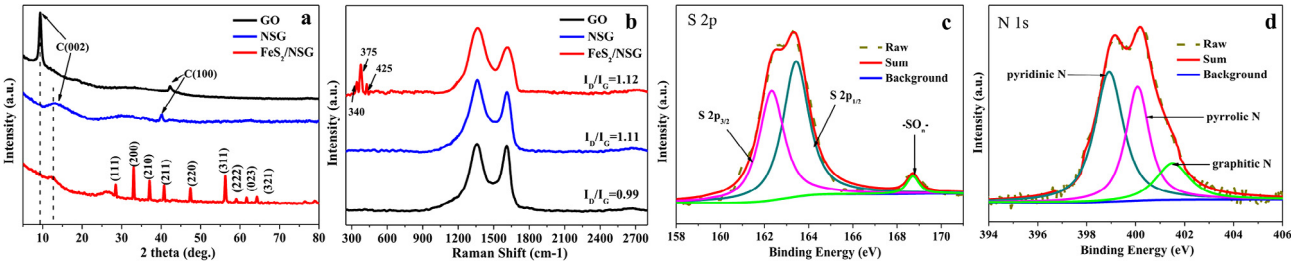

Fig. 2. XRD pattern (a) and Raman spectrum (b) of GO, NSG and FeS_2/NSG; High-resolution S 2p core level (c) and N 1 s core level (d) XPS spectrum in FeS_2/NSG.

2.2. Electrochemical measurement

A CHI660D Autolab with a three-electrode cell was applied to electrochemical measurement in 6 M KOH solution. The electrode was made of active materials, acetylene carbon black and polyvinylidene fluoride (PVDF) (at a mass fraction ratio of 8: 1: 1). The above-mentioned substances were mixed and stirred for 48 h. Subsequently, the mixture was coated on a foamed Ni (1×1 cm^2) substrate and dried. Finally, the prepared electrode was pressed at 10 MPa, followed by drying for 24 h.

3. Results and discussion

As can be seen from Fig. 1(a, b, c), the images shows that FeS_2 has a nano-flower-like structure, and the petals are superimposed on each other, resulting in a fluffy porous structure. In Fig. 1(e, f), FeS_2 are uniformly supported on the surface of NSG sheets and the size of nanoflower is significantly smaller than that of pure FeS_2, because nitrogen and sulfur double doping graphene limits the growth of petals so that the overall size of nanoflower remains about 20 nm. The high-resolution TEM image of FeS_2/NSG hybrids is shown in Fig. 1g, where the lattice fringes of 0.245 nm correspond well to the (2 1 0) plane spacing of FeS_2. Fig. 1h indicates the presence of Fe and S, and the Fe/S ratios is about 1:2. Fig. 1d is the nitrogen adsorption-desorption isotherm of hybrids, the embedded is the pore-size distribution diagram, from which the specific surface area can be calculated. The FeS_2/NSG hybrids exhibit a relatively high Brunauer-Emmett-Teller (BET) surface area of 218.4 m^2/g. Most of pores have a size of less than 20 nm, which is due to the existence of nano-flower-like structure from FeS_2. Additionally, this special morphology is conducive to the formation of an interconnected network structure, which could increase the contact area between electrode and electrolyte and improve the rate of electrochemical reaction.

Fig. 2a shows the XRD patterns of GO, NSG, FeS_2/NSG hybrids. Due to the introduction of N and S, the 001 peak of graphene become not obvious and a clear shift to the right. The diffraction peaks for hybrids can be assigned to the (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (3 1 1), (2 2 2), (0 2 3) and (3 2 1) planes consistent with standard pyrite FeS_2 (PDF No.71-0053). As presented in Fig. 2b, the spectra of FeS_2/NSG show not only the FeS_2 related peak (340, 375 and 425 cm^{-1}) [10], but also the characterized peak of NSG. Moreover, the intensity ratio of D band to G band (I_D/I_G) for NSG is higher than GO, which can be attributed to the defects caused by N and S. High-resolution S 2p core level XPS spectrum in Fig. 2c, confirms the formation of FeS_2 by exhibiting spin-orbit coupled S $2p_{1/2}$ and S $2p_{3/2}$ peaks at 163.5 and 162.2 eV, respectively [11]. Besides these two obvious peaks, another weak peak at 160.9 eV is also detected, corresponding to the -SO_n- functional group in NSG [12]. The high resolution N1s XPS spectrum of FeS_2/NSG in Fig. 2d can be fitted to three main peaks (at 398.2, 400.2 and 401.3 eV), corresponding to pyridinic N, pyrrolic N and graphitic N, respectively.[13] All of these characterization results provide sufficient evidence for the successful synthesis of FeS_2 /NSG hybrids.