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Iron diselenide combined with hollow graphitic carbon nanospheres as a high-performance anode material for sodium-ion batteries

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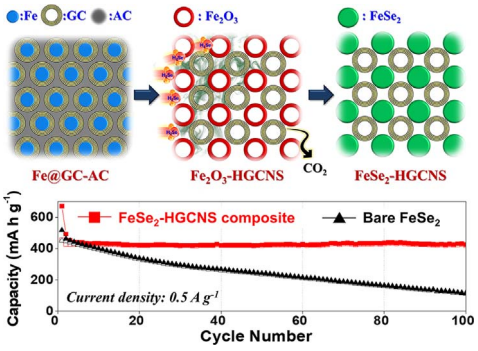
HIGHLIGHTS

- Scalable synthesis of iron diselenide nanoparticles composited with hollow graphitic carbon nanospheres is presented.
- $FeSe_2$-graphitic carbon composite shows discharge capacity of 425 mA h g^{-1} after 100 cycles.
- Excellent electrochemical performances of composite are attributed to both ultrafine $FeSe_2$ and graphitic carbon.

GRAPHICAL ABSTRACT



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ABSTRACT

A scalable method for the synthesis of iron diselenide ($FeSe_2$) nanoparticles composited with hollow graphitic-carbon nanospheres (HGCNS) is presented. The resultant composite exhibits high sodium-ion-storage performance. A solution of iron acetylacetonate, polystyrene, and polyacrylonitrile dissolved in dimethylformamide is subjected to three continuous heat treatment steps. During this process, the amorphous carbon formed around the Fe species in the composite is selectively transformed into graphitic carbon by the catalytic action of the Fe. Residual amorphous carbon was selectively removed. Subsequent selenization of this carbonaceous material affords $FeSe_2$-HGCNS composite. The discharge capacity of this composite is 425 mA h g^{-1} after 100 cycles at a current density of 0.5 A g^{-1}, and its capacity retention compared to that in the third cycle is 94%. The excellent sodium-ion-storage performance of the composite is attributed to both ultrafine $FeSe_2$ and HGCNS, which decrease Na^+ ion diffusion length, increase electrical conductivity and allow easy penetration of the electrolyte.

1. Introduction

Na-ion batteries (NIBs) present a feasible alternative to Li-ion batteries as efficient energy-storage devices for application in electric vehicles and energy storage systems owing to their low cost and resource abundance [1–5]. Transition metal dichalcogenides (TMDs), which take the form MY_2 (where M=Fe, Sn, Co, or Mo, and Y=S or Se) have been studied for application as anode materials in NIBs because they exhibit higher initial electrochemical decomposition plateau values compared to those of transition metal oxides [6–10]. Among the TMDs, $FeSe_2$, which is resource abundant, chemically stable, and non-toxic, has been reported as an anode material for NIBs [11–18]. Zhang et al. prepared $FeSe_2$ microspheres for the first time by a hydrothermal method and applied them as an anode material. This material delivered a discharge

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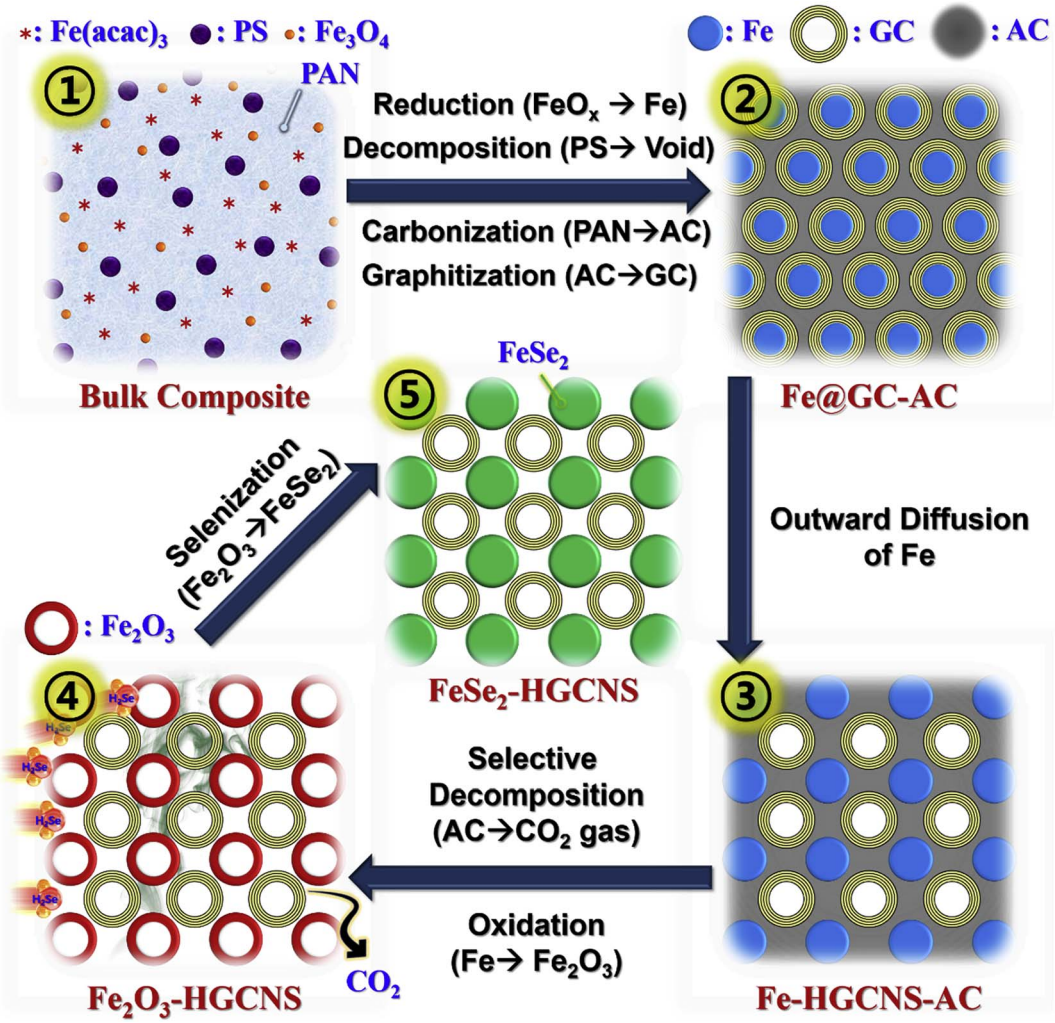

Scheme 1. Formation mechanism of $FeSe_2$-HGCNS composite by three sequential heat treatment steps and a subsequent selenization process.

capacity of 372 mA h g^{-1} with a capacity retention of 89.0% after 2000 cycles at 1.0 A g^{-1} [11]. Furthermore, Cho et al. synthesized nanofibers comprising reduced graphene oxide decorated with graphitic-carbon (GC)-coated hollow $FeSe_2$ nanospheres. The product delivered a discharge capacity of 412 mA h g^{-1} after 150 cycles at 1.0 A g^{-1} [12]. Moreover, Park et al. used a two-step method involving a spray drying process to synthesize $FeSe_2$-amorphous carbon composite powders. The discharge capacity of the powders for the 150th cycle at 0.5 A g^{-1} was 379 mA h g^{-1} [13].

Recently, porous GC materials have received increasing research attention as they can act as reservoirs for Na^+-ion storage and have channels for facile electrolyte permeation along with high electrical conductivity [19–24]. Therefore, the development of a highly efficient and cost-effective processes for the scalable production of TMD-combined porous GC structures is desired [22–24].

In this study, a simple and easily scalable process for the fabrication of $FeSe_2$ composited with hollow GC nanospheres (HGCNS) is introduced. The preparation of $FeSe_2$-HGCNS composite is performed by heating iron acetylacetonate, polystyrene, and polyacrylonitrile in a quartz beaker using a static furnace, followed by a subsequent simple selenization process. Unlike the general case where the polymers totally decompose into amorphous carbon (AC), the AC around the Fe is transformed into GC owing to the catalytic effect of the Fe. Initially, Fe metal crystals grow, and then the iron diffuses outward as the temperature increases, resulting in HGCNS. The highly conductive HGCNS are effective as a support material for active $FeSe_2$ nanocrystals because they can accommodate the strain arising from the volumetric changes of the $FeSe_2$ during sodiation/desodiation cycles. Furthermore, HGCNS that are well dispersed throughout the structure provide a three-dimensional (3D) network for the fast transfer of Na^+ ions and electrons so that very good rate capabilities can be achieved. Moreover, the porous GC matrix allows for the storage of Na^+ ions and easy penetration of the electrolyte. These synergetic effects result in excellent electrochemical properties, making $FeSe_2$-HGCNS composite a highly promising anode material for NIBs.

2. Experimental

2.1. Sample preparation

$FeSe_2$-hollow GC nanospheres (HGCNS) composite was synthesized using a quartz beaker placed in a static furnace with a subsequent simple selenization process. The precursor solution was prepared in the quartz beaker by dissolving 5 g of $Fe(acac)_3$, 5 g of polyacrylonitrile (PAN, M_w: 150,000), and 5 g of polystyrene (PS, M_w: 192,000) in 100 mL of *N,N*-dimethylformamide (DMF) with vigorous stirring overnight. The quartz beaker containing the solution was then transferred to a static furnace and subjected to a three-step post-treatment process. First, the solution was dried for 1 h at 150 °C in air to evaporate the solvent. Then, the dried solution was carbonized at 700 °C for 3 h at a heating rate of 5 °C min^{-1} under a 10% H_2/Ar gas mixture. Finally, the powders were treated at 300 °C for 3 h at a heating rate of 5 °C min^{-1} in