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Full Length Article

# Hierarchically assembled 3D nanoflowers and 0D nanoparticles of nickel sulfides on reduced graphene oxide with excellent lithium storage performances

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ABSTRACT

Constructing heterostructure can endow composites with many novel physical and electrochemical properties due to the built-in specific charge transfer dynamics. However, controllable fabrication route to heterostructures is still a great challenge up to now. In this work, a $SiO_2$-assisted hydrothermal method is developed to fabricate heterostructured nickel sulfides/reduced graphene oxide ($NiS_x$/rGO) composite. The $SiO_2$ particles hydrolyzed from tetraethyl orthosilicate could assist the surface controllable co-growth of 3D nanoflowers and 0D nanoparticles of $Ni_3S_2$/NiS decorated on reduced graphene oxide, and the possible co-growth mechanism is discussed in detail. In this composite, the heterostructured nanocomposite with different morphologies, chemical compositions and crystal structures, along with varied electronic states and band structure, can promote the interface charge transfer kinetics and lead to excellent lithium storage performances. Electrochemical measurements reveal that the $NiS_x$/rGO composite presents 1187.0 mA h $g^{-1}$ at 100 mA $g^{-1}$ and achieves a highly stable capacity of 561.2 mA h $g^{-1}$ even when the current density is up to 5 A $g^{-1}$.



## 1. Introduction

Considering the merits with high power density, high operating voltage, low self-discharge and environmental friendliness, lithium ion batteries (LIBs) have been generally accepted as one of the important sources in the application of portable electronic equipments. Furthermore, they are used as the mainly energy sources of electric vehicles (EV) and hybrid electric vehicles (HEV) [1–3]. As we all known, LIBs performance depends on mainly the electrochemical performances of the active materials [4]. For a long time, graphite was used as anode material in commercialized LIBs because of its low cost, high columbic efficiency, excellent structural stability and cycle performance. However, the theoretical capacity of graphitic material is just as low as 372 mA h $g^{-1}$, which cannot fully achieve the further demands of LIBs in EVs or HEV. Therefore, it is necessary to develop some alternative anode materials for traditional graphite to improve the performance of LIBs [5–8].

Nowadays, metal sulfides have attracted the most intensive attention due to their interesting intrinsic properties and high lithium storage capacities [9–12]. As a typical type of transition metal dichalcogenides, nickel sulfides have been widely investigated because of their heazlewoodite exists in nature, excellent catalytic and electrochemical properties [13–16]. In the recent years, nickel sulfides with different phases have been synthesized, which are diversity nanostructures including NiS submicrometer-sized hollow spheres [17], $Ni_3S_2$ thin films, NiS nanowhiskers [18], $Ni_3S_2$ nanowires arrays [15], rhombohedral NiS nanorods and triangular nanoprisms [19], and nickel sulfides ($Ni_3S_4$/$NiS_{1.03}$) nanoparticles/N-doped graphene composites [20], etc. Among them, $Ni_3S_2$ has become one of the most important phase of nickel sulfides, which has attracted considerable attention in the last few years since of their important applications in photocatalysis [21], oxygen evolution reaction [22], lithium ion batteries and electrochemical capacitors [13]. As an anode material in LIBs with many different advantages, $Ni_3S_2$ has attracted much attention because of its alternative application in energy storage [23,24]. However, $Ni_3S_2$ is not good enough at electrical conductivity and faces the problem of serious pulverization during the lithiation and

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