Facile Synthesis of FeS2 Quantum-Dots/Functionalized Graphene-Sheet Composites as Advanced Anode Material for Sodium-ion Batteries

Yiben Shao, a,b Jili Yue,* a,b Shuo Sun, a,b and Hui Xia* a,b

a School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China
b Herbert Gleiter Institute of Nanoscience, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China

FeS2 quantum-dots/functionalized graphene-sheet (QDs/FGS) composites are prepared by a facile and scalable method. The FeS2 QDs/FGS composites can be used as anode materials for sodium-ion batteries. The FeS2 QDs/FGS composites can achieve large specific discharge and charge capacities of 742 and 683 mAh•g⁻¹ (based on the total mass of the FeS2 QDs/FGS composites) at the current density of 0.5 A•g⁻¹ in the first cycle, respectively, and retain a reversible charge capacity of 552 mAh•g⁻¹ after 100 cycles. The FeS2 QDs/FGS composites can display high specific capacities of 452 and 315 mAh•g⁻¹ at the high current densities of 2 and 5 A•g⁻¹. These results indicate that the FeS2 QDs/FGS composites have good cycle performance and high rate capability, making them promising candidates as anode material for sodium-ion batteries.

Keywords quantum dots, FeS2, functionalized graphene-sheet, sodium-ion batteries

Introduction

Although rechargeable lithium-ion batteries (LIBs) have been widely used in commercial consumer electronics devices during the past two decades,[1-7] LIBs are too expensive to make them extensively apply in the fields of electrical vehicles (EVs), hybrid electrical vehicles (HEVs), and stationary electricity energy storage (EES). The high prices of LIBs are due to limited reserves and high extraction costs of lithium element used in battery materials. Sodium is widely distributed in the earth's crust and its cost is much lower compared to lithium. Therefore, in recent years, great efforts have been devoted to the research of sodium-ion batteries to obtain low cost, high capacity, and long cycling life batteries providing better performance to meet the demands of EVs, HEVs and EES.[8-10] Apart from the using of the cheap sodium, the electrode materials should be inexpensive, accessible, and abundant.

Pyrite (FeS2) is an earth abundant mineral and is an environmentally benign compound. Kitajou et al.[11] and Shadike et al.[12] studied the electrochemical reaction mechanism of FeS2 with Na during the discharge/charge processes in the carbonate-based electrolyte and found that the cycle performance of FeS2 electrode is poor in this electrolyte system. Suo et al.[13] demonstrated that the cyclability of FeS2 can be significantly enhanced by utilizing ether-based electrolyte, while, the rate performance of FeS2 is still poor and needs to be improved.

Moreover, nanostructured materials also have been widely used in energy storage and conversion electrodes to improve and optimize chemical storage processes (The typical systems are tabulated as shown in Table S1 (Supporting Information)).[14-24] The nanostructure can bring larger capacity because of the improvement of the utilization of active material, owing to the large specific surface area and short ion diffusion path. Some previous works reported the effect of using ultrafine materials on their electrochemical properties for sodium-ion batteries. Recent work by Douglas et al.[25] demonstrated that the ultrafine FeS2 nanoparticles possess many advantages for batteries that store charge through chemical conversion reactions. Compared to bulk FeS2 materials, ultrafine FeS2 NPs delivered higher capacity, better cycling performance, and enhanced rate capability.[11-13] The overall electrochemical performances of the pure FeS2 NPs, however, are still far from practical application. This is because the NPs tend to aggregate during charge/discharge processes, thus decreasing the effective surface area and deteriorating the electrochemical performance. Decorating certain NPs on carbon matrix (e.g. carbon nanotube and graphene) has been demon-
strated to be an effective strategy to circumvent this problem and further improve the electrochemical performance.[26]

In this work, we prepared FeS\textsubscript{2} quantum dots (QDs) on functionalized graphene sheets (FGS) by a facile and scalable method. For the composite, FGS with oxygen functional groups on the surface were used as the conductive matrix and the surface defective sites serve as the initial nucleation sites for the controllable growth of FeS\textsubscript{2} QDs[27-30] As expected, the FeS\textsubscript{2} QDs/FGS composites exhibited larger specific capacity, higher rate performance, as well as outstanding cycling stability compared to the pristine FeS\textsubscript{2} NPs.

**Experimental**

**Synthesis of FGS**

Graphene oxide (GO) was synthesized from purified natural graphite according to the method reported by Hummers and Offeman.[31-33] The dried GO was thermally exfoliated at 300 °C for 5 min under air atmosphere, and then treated at 900 °C in N\textsubscript{2} for 3 h with a heating rate of 2 °C·min\textsuperscript{-1} to obtain the functionalized graphene sheets.[34,35]

**Synthesis of pristine FeS\textsubscript{2} and FeS\textsubscript{2} QDs/FGS composites**

In a typical synthesis, 0.50 g Fe(NO\textsubscript{3})\textsubscript{3}•9H\textsubscript{2}O was first dissolved in ethanol (35 mL). 20 mg FGS was then added into the solution followed by 10 min ultrasonication to form a suspension. The suspension was magnetically stirred in a fume hood with slow evaporation of ethanol. After evaporation, the sample was collected and dried at 40 °C for 24 h in a blast drying oven. The dried Fe(NO\textsubscript{3})\textsubscript{3}•9H\textsubscript{2}O/FGS composite was then heated at 200 °C in an oven for 12 h to obtain the Fe\textsubscript{2}O\textsubscript{3} QDs/FGS composite. Finally, the powder and sulfur were put in two porcelain boats with sulfur at the upstream side of the tube furnace, and calcined at 300 °C for 1 h in flowing argon atmosphere. For comparison, FeS\textsubscript{2} nanoparticles were also prepared by the similar heat treatment mentioned above without adding FGS.

**Materials characterization**

The morphologies of the as-prepared materials were investigated by field-emission scanning electron microscopy (FESEM, Quant 250FEG) and TEM (HR-TEM, Tecnai G2 F30 S-TWIN). X-ray diffraction (XRD, Bruker-AXS D8 Advance with monochromatized Cu Kα radiation) and Raman spectroscopy (Jobin-Yvon T6400 Micro-Raman system) were used to characterize the phases and purity of the as-prepared materials.

**Electrochemical measurements**

The active materials, super-p, and polyvinilidene-fluoride binder with a weight ratio of 8 : 1 : 1 were mixed in N-methyl pyrrolidinone to form a homogeneous slurry. Then, the slurry was pasted on copper foil fol-

---

**Figure 1** The schematic diagram of the two-step synthesis of FeS\textsubscript{2} QDs/FGS composites.

---

**Figure 2(a)** shows the XRD patterns of the as-prepared pristine FGS, FeS\textsubscript{2}, and FeS\textsubscript{2} QDs/FGS composite (with an FGS content of 4 wt%). The standard XRD pattern of pyrite is also included at the bottom of Figure 2(a) for comparison. The XRD pattern of the pristine FGS shows a small hump at about 26°, which can be attributed to the low agglomeration degree of FGS.[20] The XRD pattern of the pristine FeS\textsubscript{2} is in good accordance with the standard pattern of cubic FeS\textsubscript{2} (red
sticks, standard JCPDS card no. 42-1340). The peak at about 26° for the (200) reflection of graphene is not obvious in the XRD pattern of the FeS₂ QDs/FGS composite, which can be attributed to the low content of FGS and further lowering the agglomeration degree of FGS. It is clearly confirmed that the cubic FeS₂ phase exists in the composite as all diffraction peaks from the composite can be assigned to the cubic FeS₂. The XRD patterns of the FeS₂ QDs/FGS composites with different FGS contents of 2 wt% and 10 wt% are depicted in Figure S2 (Supporting Information), showing tunability of the FGS content in the composites.

Figure 2  XRD patterns (a) and Raman spectra (b) of the FGS, FeS₂, and FeS₂ QDs FGS composite.

Figure 2(b) shows the Raman spectra of the pristine FGS, FeS₂, and FeS₂ QDs/FGS composite. The D-band located at 1325 cm⁻¹ and the G-band at 1598 cm⁻¹ are characteristic Raman bands of graphite, which can be observed in the Raman spectra of both FGS and FeS₂ QDs/FGS composite. Two prominent Raman peaks at 338 and 374 cm⁻¹ observed in the Raman spectra of both pure FeS₂ and FeS₂ QDs/FGS composite are due to the displacement of S atoms perpendicular to the S–S bond (E_g) and in-plane S–S stretching vibrations (A_g), respectively. A third peak appearing at 425 cm⁻¹ is attributed to the Tg symmetry mode. The XRD and Raman results confirm the successful synthesis of FeS₂ QDs/FGS composite without impurity phase.

The morphologies of the pristine FGS, FeS₂, and FeS₂ QDs/FGS composite were investigated by FESEM. Figures 3(a) and 3(b) show the low and high magnification FESEM images of the pristine FGS, respectively, revealing a two-dimensional morphology comprised of crumpled nanosheets with numerous wrinkles and folds. Numerous macropores are observed between the nanosheets, which results from the thermal exfoliation of FGS. Figures 3(c) and 3(d) show the FESEM images of the pristine FeS₂ nanoparticles, showing the average particle size is about several tens of nanometers. Figures 3(e) and 3(f) show the FESEM images of the FeS₂ QDs/FGS composite. It can be seen that the morphology of the FGS was perfectly retained after anchoring the FeS₂ QDs. The FeS₂ QDs on the FGS cannot be detected from the FESEM images due to the very fine particle size.

Figure 3  (a, b) FESEM images of the as-prepared pristine FGS. (c, d) FESEM images of the as-prepared pristine FeS₂. (e, f) FESEM images of the as-prepared FeS₂ QDs/FGS composite.

Figures 4(a) and 4(b) show TEM images of the as-prepared FeS₂ QDs/FGS composite with low and high magnifications, respectively, revealing uniform dispersion of FeS₂ QDs on the transparent FGS without severe aggregation. The square area in Figure 4(a) is enlarged in Figure 4(b), where the light contrast can be assigned to the graphene nanosheets while the dark contrast suggests the FeS₂ QDs with higher projected mass density. Figure 4(c) shows the HRTEM image of a square area marked in Figure 4(b). The FeS₂ QDs in Figure 4(c) show clear lattice fringes with interplanar spacings of 0.24 nm, which can be attributed to the (210) plane of cubic FeS₂. The particle size of the FeS₂ QDs lies in the range between 2 and 5 nm (Supporting Information, Figure S3) with an average diameter of about 3 nm. Figure 4(d) shows the selected area electron diffraction (SAED) pattern of the composite. Several diffraction rings can be observed, corresponding to the (210), (220), (311), (200), and (111) planes of FeS₂, respectively.
Figure 4 (a, b) TEM and (c) HRTEM images of the as-prepared FeS$_2$ QDs/FGS composite in different magnifications. (d) The SEAD pattern of the FeS$_2$ QDs/FGS composite. (e) STEM and corresponding element distribution images of C, Fe, and S elements.

Figure 4(e) shows the scanning tunneling electron microscopy (STEM) image and the corresponding element mapping images of C, Fe, and S elements for the FeS$_2$ QDs anchored FGS. It can be observed that the Fe and S element distributions are uniform on the FGS, indicating uniform dispersion of FeS$_2$ QDs on the transparent FGS.

To evaluate the electrochemical properties of different samples, the galvanostatic charge-discharge measurements were carried out on the pristine FGS, FeS$_2$, and FeS$_2$ QDs/FGS composite electrodes. Figures 5(a) and 5(b) show the 1$^{st}$ and 2$^{nd}$ cycle charge-discharge curves of the pristine FeS$_2$ and FeS$_2$ QDs/FGS composite electrodes at the current density of 0.5 A$\cdot$g$^{-1}$, respectively. The pristine FeS$_2$ electrode can deliver discharge and charge capacities of 534 and 478 mAh$\cdot$g$^{-1}$, respectively, for the first cycle, with a coulombic efficiency of about 89.51%. The pristine FGS electrode can show only a reversible capacity of about 250 mAh$\cdot$g$^{-1}$ at the same current density (Figure S4, Supporting Information). Interestingly, the FeS$_2$ QDs/FGS composite electrode can deliver discharge and charge capacities of 742 and 683 mAh$\cdot$g$^{-1}$ (based on the total mass of the FeS$_2$ QDs/FGS composite) at the first cycle with a coulombic efficiency of about 92.04%. It can be seen that the reversible capacity of the FeS$_2$ QDs/FGS composite electrode is much larger than those of the pristine FeS$_2$ electrode and FGS electrode. Figure 5(c) shows the discharge specific capacities of the pristine FGS, FeS$_2$, and FeS$_2$ QDs/FGS composite electrodes as a function of cycle number at a current density of 0.5 A$\cdot$g$^{-1}$. The FGS electrode delivers a stable capacity of 250 mAh$\cdot$g$^{-1}$ with excellent cycle performance. The pristine FeS$_2$ electrode, however, exhibits fast capacity fading and
only 284 mAh g\(^{-1}\) is retained after 100 cycles. Great improvement in cycle performance has been achieved when graphene was introduced into FeS\(_2\). The FeS\(_2\) QDs/FGS composite electrode delivered a charge capacity of about 552 mAh g\(^{-1}\) after 100 cycles, corresponding to 81% capacity retention. The cycle performances of the QDs/FGS composite electrodes with other FGS contents are compared in Figure S5 (Supporting Information), indicating the FeS\(_2\) QDs/FGS composite electrode with 4 wt% FGS possesses the best electrochemical performance, the picture of the areal capacity for the FeS\(_2\) QDs/FGS composite electrode with 4 wt% FGS versus cycle number is depicted in Figure S6 (Supporting Information). Except for the first cycle, the cycling efficiencies of the FeS\(_2\) QDs/FGS composite are all nearly 100%. The superior electrochemical performance of the present FeS\(_2\) QDs/FGS composite electrode can be explained by its unique hybrid structure. The high specific capacity can be attributed to the small particle size of the FeS\(_2\) QDs and the uniform distribution of FeS\(_2\) QDs on the FGS, enabling short ion diffusion path and fast electron transfer. This unique hybrid electrode design is also beneficial to fast charge and discharge capabilities. The rate capabilities of the pristine FGS, FeS\(_2\), and FeS\(_2\) QDs/FGS composite electrodes were further investigated at various current densities. Figure 5(d) compares the rate capabilities of the pristine FGS, FeS\(_2\), and FeS\(_2\) QDs/FGS composite electrode at various current densities ranging from 0.1 to 5 A g\(^{-1}\). The FeS\(_2\) electrode shows low specific capacity but high rate performance due to its good electrical conductivity. It is noteworthy that the pristine FeS\(_2\) electrode can deliver very low specific capacity of 50 mAh g\(^{-1}\) at the high current density of 5 A g\(^{-1}\), indicating poor rate capability. In contrast, the FeS\(_2\) QDs/FGS composite electrode can still deliver a large specific capacity of 315 mAh g\(^{-1}\) at the current density of 5 A g\(^{-1}\), demonstrating significantly enhanced rate capability. When the current density was abruptly decreased from 5 to 0.1 A g\(^{-1}\), the FeS\(_2\) QDs/FGS composite electrode can recover its high capacity of about 650 mAh g\(^{-1}\), indicating excellent electrode kinetics and reversibility.

Conclusions

In conclusion, we developed a facile method to synthesize FeS\(_2\) QDs/FGS composites with 3–5 nm FeS\(_2\) QDs uniformly anchored on the FGS. The FeS\(_2\) QDs/FGS composite electrode exhibits superior electrochemical performance to the pristine FeS\(_2\) electrode when used as anodes for sodium-ion batteries. Specifically, the FeS\(_2\) QDs/FGS composite electrode can deliver a large reversible capacity up to 748 mAh g\(^{-1}\) as well as good cycling stability (81% capacity retention after 100 cycles) and excellent rate performance (315 mAh g\(^{-1}\) at a current density of 5 A g\(^{-1}\)). The greatly enhanced sodium storage capability of the FeS\(_2\) QDs/FGS composite electrode can be attributed to its unique hybrid structure, favoring fast electrode kinetics and structural stability.

Acknowledgement

This work was supported by National Natural Science Foundation of China (Nos. 51572129, U1407106), Natural Science Foundation of Jiangsu Province (No. BK20131349), Qinglan Project of Jiangsu Province, a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), the Fundamental Research Funds for the Central Universities (No. 30915011204).

References


(Zhao, X.)