Supplementary Information

Hydrothermal synthesis of Ni₃S₂/graphene electrode and its application in supercapacitor

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Calculations:

Since the Ni in Ni₃S₂ comes from Ni foam, so the weight increment (*x* mg) of Ni foam could not be considered as the mass of the active materials. The mass of pure Ni₃S₂ grown on Ni foam is calculated as following: $m_{Ni3S2} = x \text{ mg} \times (M_{Ni3S2}/2M_S) = x \text{ mg} \times$ (240/64) = 3.75*x* mg, where M is the molecular weight of atomic weight.^{1, 2} For Ni₃S₂/GNS electrode, the $m_{\text{composite}} = m_{\text{GNS}} + m_{\text{Ni3S2}}$. Because the Ni₃S₂/GNS composites were synthesized by one-step, at the moment it is difficult to define the true mass ratio of Ni₃S₂ and graphene nanosheets in the composite, so we assume the composite is pure Ni₃S₂, $m_{\text{composite}} = x \text{ mg} \times (M_{\text{Ni3S2}}/2M_S) = x \text{ mg} \times (240/64) = 3.75x$ mg. The specific capacitance (C) of the electrode can be evaluated according to the following equation: $C = (I \times \Delta t)/(m \times \Delta V)$, where C (Fg⁻¹) is the specific capacitance of the electrode based on the mass of active materials, I(A) is the current during discharge process, $\Delta t(s)$ is the discharge time, $\Delta V(V)$ is the potential window. Therefore, the actual capacitance value of Ni₃S₂/GNS electrode is higher than the presented value in the paper.



Figure S1. SEM images of plain nickel foam.

The SEM images of plain nickel foam are shown in Figure S1. The nickel template with crosslink structure presents numerous pores, and their sizes range from 200 to 500 μ m. The special network porous structure may not only increase the contact area between the collector and active material, but also shorten the diffusion and migration paths of electrolyte ions, consequently resulting in an enhanced electrochemical performance.



Figure S2. SEM images of pure GNS deposited on nickel foam.

After the hydrothermal treatment, pristine graphene nanosheets have been successfully deposited on the surface of nickel foam to form individual threedimensional interpenetrating porous structure, which can act as a platform to anchor the Ni_3S_2 nanoparticle and benefit the transport of electrolyte ions.



Figure S3. SEM images of pure Ni₃S₂ deposited on nickel foam.

The morphologies of pure Ni_3S_2 are exhibited in Figure S3. Without the addition of graphene oxide, the sole Ni_3S_2 may agglomerate to form a dense layer covering the surface of nickel substrate, thus restraining the redox reaction of inner active material and impacting the electrochemical properties.



Figure S4. EDS image of Ni₃S₂/GNS composite.

Except for the Ni element stemming from both nickel foam and Ni_3S_2 , as well as sulfur peaks, which originate from only Ni_3S_2 , the C element is observed, indicating the addition of graphene.



Figure S5. CV curves of pure GNS (a) and Ni_3S_2 (b).

The CV curves of pure GNS with various scan rates are in typical rectangular shape, which is indicative of double layer capacitor behavior. Differently, according to the CV curves for pure Ni_3S_2 in Figure S5(b), a pair of redox peaks are observed, which is consistent with the reaction process mentioned in this paper.



Figure S6. Charge-discharge curves of pure GNS (a) and sole Ni_3S_2 (b).

The charge/discharge plots of GNS electrode exhibit the near linear and symmetric triangles, indicating the obvious double layer capacitor behavior. However, the well-defined plateaus during discharge process are observed at various current densities in Figure S6(b), suggesting that the pure Ni_3S_2 have pseudocapacitive behaviors, which is in agreement with the result of above CV test.

Reference:

- S1. W. Zhou, X. Cao, Z. Zeng, W. Shi, Y. Zhu, Q. Yan, H. Liu, J. Wang and H. Zhang, *Energy & Environmental Science*, 2013, 6, 2216.
- S2. W. Zhou, X.-J. Wu, X. Cao, X. Huang, C. Tan, J. Tian, H. Liu, J. Wang and H. Zhang, *Energy & Environmental Science*, 2013, 6, 2921-2924.