

CAGING NONCARBONS IN A PRECISELY SHRUNKEN GRAPHENE NETWORK TOWARDS HIGH VOLUMETRIC LITHIUM STORAGE

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Introduction

Considering the continuing demand for the miniaturization of electrochemical energy storage devices, volumetric energy density has become a critical parameter, but rarely emphasized in earlier studies of lithium-ion batteries. The replacement of graphitic anodes by noncarbon anodes (e.g. tin and silicon-based materials) holds promise to improve the energy density of a lithium ion battery. However, the imprecise design of carbon cages to buffer noncarbon volume changes during cycling, which is the biggest obstacle to be overcome before the real applications, results in insufficient void space or much that cannot be used, greatly lowering the volumetric capacity. Here, we demonstrate a well-designed method to introduce an accurate amount of void space in three-dimensional graphene networks using sulfur as Transformers-like template. In a typical synthesis using the capillary shrinkage of networked graphene hydrogels, flowable sulfur is used with the tin oxide nanoparticles inside the shrinking hydrogels, and the void space around tin oxide particles is precisely controlled by tuning the content of the surrounding and removable sulfur. Our materials design fulfills the most stringent requirements for balancing the complete expansion of tin oxide and the high density of the graphene-caged tin oxide hybrids, and an ultrahigh high volumetric capacity (over 2100 mAh cm⁻³) with good cyclic stability is achieved. This strategy also demonstrates its versatility to silicon anodes and has been an ideal remedy for low volumetric energy density in current energy storage devices.

Materials and Methods

Fabrication of SnO₂@GC. Tin chloride pentahydrate (SnCl₄·5H₂O) as the precursor of tin oxide (SnO₂) was added to the graphene oxide and sulfur suspension with a subsequent hydrothermal treatment to obtain a cylindrical SnO₂@graphene@sulfur hybrid hydrogel. This hydrogel was then subjected to capillary drying for 48 h, followed by thermal treatment at 400°C for removing all original sulfur.

Results and Discussion

In the capillary drying of networked graphene hydrogels, flowable, deformable and removable sulfur is a template leaving exact voids for the expansion of the noncarbon nanoparticles (**Figure 1a**). In contrast to the common hard templates, soft sulfur can encapsulate noncarbon particles even of nanometer size (< 10 nm) without any gap between them. In hydrothermal process, sulfur, like *Transformers* presented in a famous film, possessing both fluidity and viscosity, covers every single noncarbon particle and therefore prevents noncarbon particles from aggregation, and the strong interaction between the sulfur and the noncarbon components ensures the tight contact between them (**Figure 1b**). The sulfur is used as a void space precursor around noncarbons in a shrinking 3D graphene cage, and a precisely tuned and well distributed void space at the nanoscale is guaranteed after sulfur removal (**Figure 1c**). As a typical example, a nanosized tin oxide@graphene cage hybrid (SnO_2 @GC) with 67 wt% SnO_2 is prepared, which is characterized by a high specific capacity (974 mAh g^{-1}) and an ultrahigh volumetric capacity of 2123 mAh cm^{-3} due to the well-designed void ($\sim 260\%$) in a graphene cage for expansion of SnO_2 upon lithiation (**Figure. 1d**).

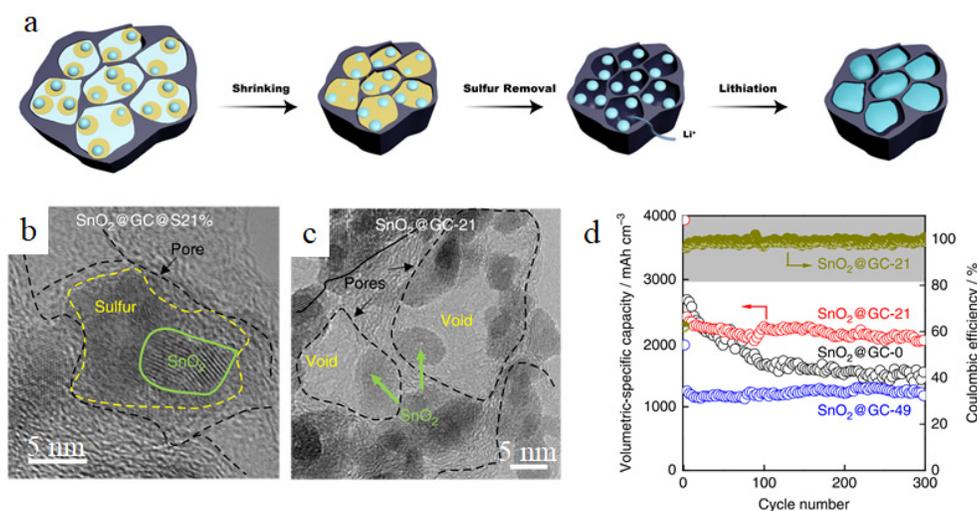


Figure 1. (a) Illustration of the strategy of sulfur template control of incorporated void space. HRTEM image of (b) SnO_2 @GC with sulfur and (c) SnO_2 @GC with all original sulfur removed. (d) Cycling performance of SnO_2 @GCs with various sulfur template usage.

Conclusions

Flowable, deformable and removable sulfur as a template to precisely control the void space around SnO_2 nanoparticles, including both its size and location in a shrinking 3D graphene cage. Our materials design fulfills the most stringent requirements for balancing the complete expansion of SnO_2 and the high density of the SnO_2 @GC hybrids. Also, this strategy has proved its generalization to other noncarbon anodes for lithium-ion batteries to buffer large volume expansions during electrochemical reactions and is absolutely an ideal remedy for low volumetric energy density in energy storage devices with carbon cages as electrochemical reaction frameworks, not just limited to lithium-ion batteries.

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