

Caging noncarbons in a precisely shrinked graphene network towards high volumetric lithium storage

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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.

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2. **Han, J.**; Kong, D.; Yang, Q.-H. et al, *Nat. Commun.* **9**, 402 (2018)