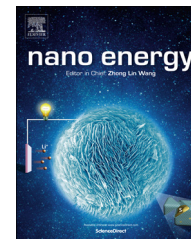


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## COMMUNICATION

# Multi-yolk-shell copper oxide@carbon octahedra as high-stability anodes for lithium-ion batteries

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**Abstract**

Although transition metal oxides have attracted considerable attention for their high energy density as anode materials of lithium-ion batteries, they suffer from large volume expansion during lithiation process, which usually causes fast capacity degradation. Herein, we report a rational design and facile preparation strategy of copper oxide encapsulated mesoporous carbon multi-yolk-shell octahedra, in which multiple CuO nanoparticles are well-confined in the compartments of micro-scale octahedral carbon scaffolds. The advantages of the novel multi-yolk-shell design are that the three-dimensional carbon scaffolds can buffer the volume change and prevent aggregation of CuO nanoparticles during the charge/discharge cycles, provide pathways for electron transport and Li<sup>+</sup> diffusion, and restrict the thin solid-electrolyte interphase layer to the outer surface of carbon shells. The results demonstrate how the electrochemical properties of anodes can be significantly improved by the multi-yolk-shell nanostructures with greatly enhanced structural stability and electrochemical actuation. Moreover, the micrometer-size CuO@C octahedra reduce the relative quality of SEI, resulting in high Coulombic efficiency and long cycling stability. In Li-ion cells, the CuO@C multi-yolk-shell octahedra anodes deliver a highly-reversible capacity of 598 mA h g<sup>-1</sup> at 250 mA g<sup>-1</sup>, excellent rate capacity of 365 mA h g<sup>-1</sup> at 3000 mA g<sup>-1</sup> and exhibit long-term cyclability with a capacity of 512 mA h g<sup>-1</sup> after 300 cycles at 500 mA g<sup>-1</sup>.

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## Introduction

Owing to the high energy density and long cycle life, lithium-ion batteries (LIBs) have been intensively used in portable electronics, electric vehicles, renewable energy systems and smart grids [1-3]. To satisfy the enormous demands of wearable consumer electronics, a new generation of electrode materials with higher capacity, cyclability and rate performance is required. Compared with conventional graphite anodes, transition metal oxides (TMOs) such as copper oxide (CuO), iron oxide, cobalt oxide, manganese oxide, etc., have been viewed as promising anode materials for next generation LIBs owing to their high theoretical capacity [4-7]. Among them, CuO is noteworthy due to its high earth abundance, cost effectiveness, low toxicity and high theoretical capacity of  $674 \text{ mA h g}^{-1}$  [8]. However, CuO nanomaterials usually suffer from capacity fading and poor cycling life during lithiation/delithiation processes. These disadvantages are caused by low electrical conductivity and large volume expansion. To circumvent these issues, great efforts have been made to enhance the performance of CuO anode electrodes [9-13].

Motivated by their high specific surface areas and tunable pore structures, metal-organic frameworks (MOFs) have been used as sacrificial templates or precursors to form unique porous nanostructures for the applications in energy storage field [14-17]. For examples,  $\text{Fe}_2\text{O}_3$  [18], CuO [19], CuO/Cu<sub>2</sub>O [20],  $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$  [21], and ZnO/ZnFe<sub>2</sub>O<sub>4</sub>/C [22] porous nano-architectures have been prepared by using suitable MOF precursors, exhibiting good electrochemical performance as anode materials for LIBs. It is well known that the morphology and architecture of nanostructured materials originated from the synthesis process have significant impacts on the electrochemical performance. An ideal nanostructured electrode should have a three-dimensional (3D) porous architecture encapsulated with nanosized electrochemically-active building blocks, which can reduce the formation of the SEI layer and shorten the distance of Li<sup>+</sup> diffusion [22]. Coincidentally, the multi-yolk-shell not only possesses nanometer-sized subunits that can provide high specific capacity and outstanding rate capability, but also has a stable 3D porous octahedral micro-structure for excellent cycling stability. Therefore, rationally designed yolk-shell nanostructures with conductive carbon shells can solve some crucial issues of anode materials, such as large volume variation and low electric conductivity, attributed to their enhanced structural integrity, high stability of solid-electrolyte interphase (SEI) films and electrochemical actuation. Recently, the synthesis of MnO<sub>2</sub>@C [23], Fe<sub>3</sub>O<sub>4</sub>@Fe<sub>3</sub>C [24] and FeO<sub>x</sub>@C [25] yolk-shell nanostructures has been reported to improve the cycle life of LIBs. Moreover, Si@C yolk-shell architectures also have been studied to accommodate the large volume expansion of Si-based anode materials during cycling [26-29]. Nevertheless, it still remains a great challenge to design delicate multi-yolk-shell nanostructures with numerous electrochemical-active nanoparticles encapsulated in 3D porous conductive nano-scaffolds to remarkably improve the electrochemical performance of TMO anodes.

Here we demonstrate that a novel CuO@C multi-yolk-shell octahedral nanostructure can be obtained by using Cu-based MOFs as template. To the best of our knowledge, this is the first report on the preparation of TMO-based multi-yolk-shell octahedra for improving lithium storage performance. The synthesis process involves a simple solvothermal process to

obtain MOF precursors followed by thermal treatment in N<sub>2</sub> and then in air. Multiple CuO nanoparticles were encapsulated in the compartments of micro-scale carbon nano-octahedra. Compared with the reported porous CuO and CuO/Cu<sub>2</sub>O polyhedrons [19,20,30], the architecture of CuO@C multi-yolk-shell octahedra have the following advantages: (1) the conductive carbon octahedral scaffold can restrict the formation of the SEI layer; (2) the stable multi-yolk-shell structure strongly confines the CuO nanoparticles in the carbon octahedra, resulting in a high utilization efficiency of active material CuO; (3) the porous carbon layer between CuO nanoparticles can buffer the volume change, prevent aggregation of CuO nanoparticles, and also provide unobstructed pathways for electron transport and Li<sup>+</sup> diffusion during charge/discharge processes. As a consequence, the novel CuO@C multi-yolk-shell electrodes can deliver very high reversible capacity, rate capacity and long cycling life for lithium storage.

## Experimental

### Chemicals

Polyvinylpyrrolidone (PVP, M.W. 40,000), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (99.5%), and 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>btc, 98%) were purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.

### Synthesis of the CuO@C multi-yolk-shell octahedra

Typically, 17.2 mmol of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in 30 mL of deionized water. A solution of 1,3,5-benzenetricarboxylic acid (9.6 mmol) in a co-solvent of DMF and ethanol (60 mL, 1:1 by volume) was mixed with 4.0 g of PVP under continuous stirring. After complete dispersion of the reactants, the two solutions were mixed directly. Subsequently, the mixed solution was stirred for 15 min and transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated at 100 °C for 10 h. The product was collected and washed with 100 mL ethanol for 3 times. The as-obtained product was called as Cu<sub>3</sub>(btc)<sub>2</sub> MOF/PVP-4. Similarly, for the preparation of Cu<sub>3</sub>(btc)<sub>2</sub> MOF/PVP-2 and pristine Cu<sub>3</sub>(btc)<sub>2</sub> MOFs without PVP, the same procedures were conducted except that the weights of added PVP were 2.0 g and 0 g, respectively. The as-prepared Cu<sub>3</sub>(btc)<sub>2</sub> MOF/PVP-4 was carbonized at 700 °C at a heating rate of 2 °C min<sup>-1</sup> for 4 h in N<sub>2</sub> (99.999%), and then annealed in air at 350 °C for 1 h. To obtain bare CuO octahedra, the Cu<sub>3</sub>(btc)<sub>2</sub> MOF/PVP-4 precursor was directly calcined at 500 °C in air for 1 h instead.

### Material characterizations

The morphology of samples was characterized by scanning electron microscopy (SEM, HITACH S-4800) and transmission electron microscopy (TEM, JEM-2100). Elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDX) equipped in the SEM. Nitrogen sorption isotherms were obtained through Brunauer-Emmett-Teller (BET) analysis at

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