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FULL PAPER

Biochemistry-derived porous carbon-encapsulated metal oxide nanocrystals for enhanced sodium storage

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Abstract
Transitional metal oxides are promising anode materials for sodium ion batteries (SIBs) due to their high theoretical capacities and material abundance; however, their sodium storage capability is significantly hindered by the sluggish sodiation/desodiation reaction kinetics. Herein, towards achieving fast and durable sodiation/desodiation reaction, Fe_3O_4 and Co_3O_4 nanocrystals encapsulated in carbon micro-spheres are synthesized via a biochemistry approach using recombinant elastin-like polypeptides containing hexahistidine tag (ELP16-His) followed by annealing. Fe_3O_4 and Co_3O_4 nanocrystals of approximately 5 nm in size, which are uniformly dispersed in a carbon matrix, are obtained. The carbon-encapsulated metal oxides exhibit encouraging sodium storage capacities (657 and 246 mA h g^{-1} at 0.1 and 2 A g^{-1}, respectively, for carbon-encapsulated Fe_3O_4; 583 and 183 mA h g^{-1} at 0.1 and 2 A g^{-1}, respectively, for carbon-encapsulated Co_3O_4), and have a high capacity retention after 100 cycles at 0.5 A g^{-1}. The superior electrochemical properties of the

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carbon-encapsulated metal oxide nanocrystals demonstrate their potential for use as anode materials for high-capacity, high-rate and durable sodium storage.

1. Introduction

Lithium ion batteries (LIBs) have dominated the market as power sources for portable electronic devices. However, depleting lithium resources and their high costs limit the application of LIBs in several emerging areas, such as electronic vehicles (EVs), hybrid electronic vehicles (HEVs), and particularly, large-scale grid energy storage. Sodium, also a Group I element, shares similar chemical properties to lithium, and thus is a promising alternative to lithium. More importantly, sodium is much more abundant compared to lithium. As such, sodium ion batteries (SIBs) have gained considerable interests in the past few years [1].

Nonetheless, the development of SIBs is significantly hindered by the unsatisfactory electrochemical performance of electrode materials. Some cathode materials explored for SIBs showed promising performance such as P2-$Na_{2/3}MnO_2$ [2,3] and $Na_3V_2(PO_4)_3$ [4-7]. As the state-of-the-art anode material for LIBs, graphite is nearly electrochemically inactive with sodium due to the large ionic radius of Na^+. Though many carbonaceous materials with various nanostructures have been investigated as anodes for SIBs, their sodium storage capabilities in terms of specific capacitance or rate capability cannot meet the demands of practical applications [8,9]. Recently, reports on the potential application of transitional metal oxides as anodes for SIBs have emerged [10-14]. Transitional metal oxides such as iron oxides and cobalt oxides possess high theoretical capacities for lithium storage by means of conversion reaction mechanism (e.g., 1005 mA h g^{-1} for Fe_2O_3, much higher as compared to 372 mA h g^{-1} for graphite) [15]. Theoretically, such metal oxides are also able to store sodium via similar conversion reaction mechanisms to achieve similar theoretical capacities as lithium storage. However, due to the sluggish sodiation/desodiation reaction kinetics induced by the large ionic radius of Na^+, the reported metal oxides materials exhibit much inferior capacity for sodium storage compared to that for lithium storage [16]. In order to increase the deliverable capacity for sodium storage, engineering robust nanostructured electrode materials is urgently needed. It is expected that the ion transportation pathway would be significantly decreased and more reactive sites would be created for nanostructured electrodes, thereby resulting in fast sodiation/desodiation reactions. In addition, hierarchically porous 3D architectures are highly desired for batteries from practical viewpoint [17-19]. The presence of micro-pores can act as a transport system while the meso-pores provide high surface areas to facilitate high-rate transportation of ions and electrons. To date, much effort has been put to prepare 3D metal oxides architectures, including post-template oxidation [20], template-free hydrothermal synthetic route [21], ethylene glycol-mediated self-assembly process [22], ionic liquid-assisted synthesis [23] and so on. However, despite these recent progresses, assembly of low-dimensional building blocks into 3D hierarchically porous superstructures still remains a challenge.

Biological molecules and organisms have received much attention for the fabrication of advanced functional materials due to their mild and environmentally friendly synthesis conditions, and the ability to tailor their structures and compositions [24-29]. In particular, recombinant proteins can be designed to contain self-assembling domains and motifs to guide the self-assembly of metallic precursors [26]. Examples include Au nanowires formed from the interaction of gold ions with histidine-rich peptides [27], metal phosphates nanofibers mineralized by self-assembled hydrophobic peptides [28], mono-dispersed silver nano-particles grown inside

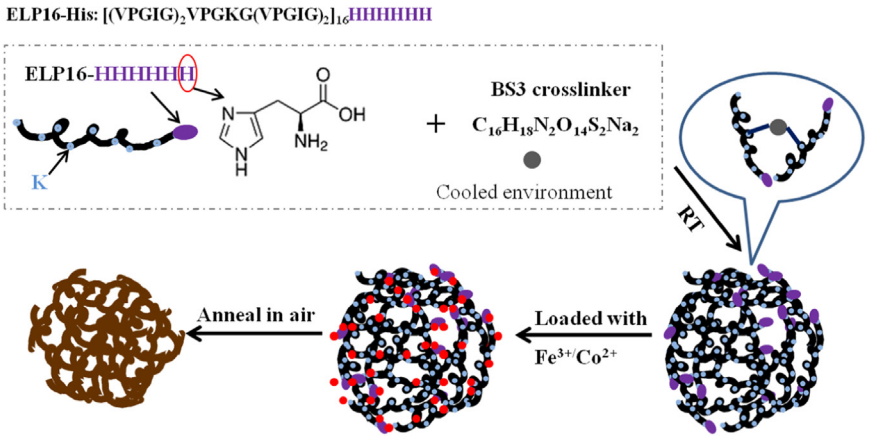

Figure 1 Scheme illustrating the synthesis of carbon-encapsulated metal oxides using recombinant elastin-like polypeptides (ELP16-His). The amino acid sequence of ELP16-His is also shown.