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Hierarchical porous nanocomposite architectures from multi-wall carbon nanotube threaded mesoporous $NaTi_2(PO_4)_3$ nanocrystals for high-performance sodium electrodes

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HIGHLIGHTS

- Hierarchical porous nanocomposite from MWCNT-threaded MNTP NCs is prepared.
- The nanocomposite demonstrates superior Na storage performance.
- A general hetero-assembly approach for different nanocomposites is demonstrated.

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ABSTRACT

Rational design and self-assembly of nanostructured electrode materials for high-performance energy-storage devices is highly desirable but still challenging. Herein, we design and synthesize hierarchical porous nanocomposite architectures consisting of mesoporous $NaTi_2(PO_4)_3$ (MNTP) nanocrystals (NCs) with a pore size of about 10 nm and multi-wall carbon nanotube (MWCNT) networks for high-performance sodium ion batteries (SIBs). Our strategy is based on the hetero-assembly of MWCNTs and nanostructured building units by utilizing the screening effect of electrostatic repulsion in a solution engineered ionic strength using highly soluble ammonium salt to form three-dimensional hierarchical assemblies of MWCNT networks and packed MNTP NCs. Subsequent freeze-drying and calcination convert the assemblies into robust hierarchical porous MWCNTs-threaded particles. Calcination of residual ammonium salt introduces nitrogen into the MWCNTs. Such nanoarchitecture enhances electron/ion conductivity and structural stability as anode materials for SIBs. The nanocomposite has high initial Coulombic efficiency of 99%, high rate capability of 74.0 $mAhg^{-1}$ at 50C, as well as long-term cycling stability with capacity retention of 74.3 $mAhg^{-1}$ after 2000 cycles with only 0.012% loss per cycle at 10C. The results provide a general and scalable hetero-assembly approach to different types of nanocomposites for high-performance energy storage devices such as LIBs and SIBs.

1. Introduction

Li ion batteries (LIBs) have been the most common power sources in portable electronics and renewable energy integration because of high capacity, long cycle life, and environmental friendliness [1]. However, increasing demand by electrical vehicles and smart grid-scale energy storages has exposed high cost and limited natural resource of lithium. Hence, sodium ion batteries (SIBs) are receiving increasing attention as a good alternative in large-scale energy storage applications because of larger natural abundance and lower cost of sodium [2–4]. There have been a number of pioneering reports available on new electrode materials identified for SIBs including transition metal chalcogenides (MoS_2, SnS_2, FeS_2, $FeSe_2$, etc.) [3], Ti-based oxides (for instance,TiO_2 and $Li_4Ti_5O_{12}$) [5,6], phosphorus [7], 2D metal carbides [8], metallic alloy [9], sodium super ion conductor (NASICON) type compounds [10–12], renewable biomolecules (for example, Juglone) [13],

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although the reported electrochemical performances of these materials are inferior in terms of initial Coulombic efficiency, rate capability and cycle stability compared to LIBs. Among them, NASICON-type $NaTi_2(PO_4)_3$ (NTP) is an attractive SIB electrode because of high theoretical capacity of 133 $mAhg^{-1}$, small volume change during Na insertion and extraction, bi-functional properties as both anode and cathode, and intrinsically safety due to high voltage plateau of about 2.1 V vs Na/Na^+ [10–12]. As shown in the upper right of Fig. 1a, NTP has a three-dimensional (3D) structure consisting of PO_4 tetrahedra and TiO_6 octahedra with sharing corner oxygen atoms, resulting in roomy interstices. As a result, it possesses high Na^+ conductivity, which is an pivotal advantage in repetitive Na insertion/extraction reaction [3]. However, practical application of the NTP is hampered by low capacity release and poor high-rate capability as a result of its low electronic conductivity [11,12]. To overcome this hurdle, many strategies have been contrived to ameliorate electrochemical performance of the NTP, for example, by developing nano/microstructured architectures to shorten electron and ion transport paths [14], doping to improve transport properties and constructing highly robust conductive networks by combining NTP with carbon substance such as carbon nanotubes (CNTs) or graphene [11,12,15–17]. To fabricate hierarchical porous nanocomposites from CNTs (or graphene) and NTP is indeed effective to offer large specific surface areas, fast electron/ion transport kinetics and robust network structures. Among various nanoarchitectures, spherical mesoporous nanocrystals

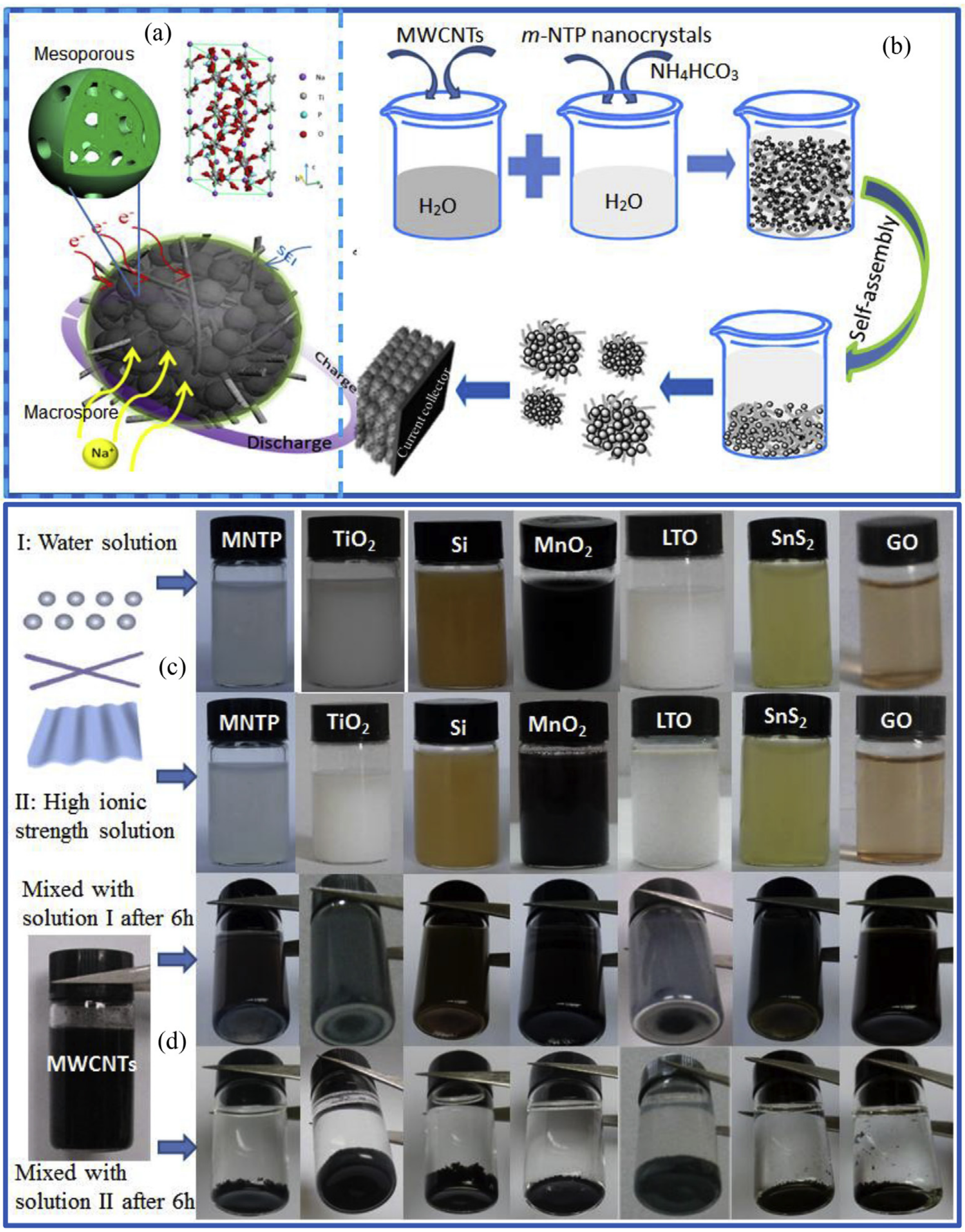

Fig. 1. (a) Schematic of hierarchical mesoporous and macroporous h-MNTP/MWCNTs electrode with pathways for both electrons and sodium ions as well as formation of the SEI layer on the nanocomposites during charging/discharging. The crystal structure of the NASICON-type NTP is shown in the upper right corner; (b) Schematic showing how the h-MNTP/MWCNTs electrode is formed; (c) Optical images of the MNTP NCs, TiO_2 NCs, Si NCs, MnO_2 nanowires, LTO nanosheets, SnS_2 nanosheets, and GO in pure water and 1 M NH_4HCO_3 solution; (d) Optical images of the MWCNTs aqueous suspension mixed with MNTP NCs, TiO_2 NCs, Si NCs, MnO_2 nanowires, LTO nanosheets, SnS_2 nanosheets, and GO dispersed in water and 1 M NH_3HCO_3 solution after 6 h.