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An interlayer defect promoting the doping of the phosphate group into TiO_2(B) nanowires with unusual structure properties towards ultra-fast and ultra-stable sodium storage†

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Heteroatom doping is an effective way to modulate the local structure of TiO_2-based materials, enabling enhanced electrochemical performance. However, current studies generally adopt a single atom doping strategy, and ionic group doping has rarely been achieved and is a distinctly bigger challenge. Herein, doping of the phosphate group at high concentrations into blue TiO_2(B) nanowires is proposed and realized for the first time by skillfully utilizing the defects induced during the dehydration and topology transformation process of the H-titanate precursor; based on experimental characterization and first-principles calculations, it has been demonstrated that this material possesses exceptional electrical properties, a remarkably reduced band gap, magnetic characteristic from the extra electrons outside the Ti atomic nucleus and remarkable phase stability. Benefiting from the unusual structure properties, phosphate-doped TiO_2(B) exhibits the ultra-fast sodium storage capability of 124 mA h g^{-1} at the extremely high rate of 50 A g^{-1} and excellent long cycling stability even at 10 A g^{-1} after 5000 cycles. Moreover, this electrode material was tested at low temperatures and exhibited comparable reversible capacity and outstanding cycling stability to those at normal temperatures. We also assembled a B–TiO_2(B)–P//(NVPF) full cell, which delivered the maximum energy density of 170 Wh kg^{-1} and the maximum power density of 5000 W kg^{-1}.

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1. Introduction

Sodium-ion batteries (SIBs) were initially deemed to be an alternative energy storage device to innovate lithium-ion batteries primarily due to the abundance of sodium resources. In recent years, several studies have indicated that sodium-ion batteries may even have comparable energy and power density to lithium-ion batteries when suitable cathode and anode materials are used.[1,2] However, the radius of Na^+ (1.02 Å) is obviously larger than that of Li^+ (0.76 Å), which complicates the development of applicable anode materials for sodium-ion energy-storage systems.[3–5] Anode materials, an important part of SIBs, have achieved significant progress in the past few years; however, applicable host materials for SIBs are still limited.[6–9] To date, various anode materials, including hard carbon,[10,11] metal alloys (Sb[12,13] and Sn[14,15]), conversion materials[16–18] and titanium-based insertion-type materials,[19–21] have been explored for SIBs. Titanium dioxide (TiO_2) has attracted widespread interest as the SIB anode because of its low cost, nontoxicity, stable structure and reasonable operation voltage (≈0.7 V *vs.* Na), avoiding dangerous Na plating.[19,20,22] TiO_2 has also wide applications in photocatalysis,[23,24] perovskite solar cells[25] and SERS sensing.[26]

Several stable or metastable phases of TiO_2, commonly including rutile TiO_2, anatase TiO_2 and bronze TiO_2 (TiO_2(B)), have been reported. All TiO_2 polymorphs consist of TiO_6 octahedra attached with corners or edges. Their insertion process is based on the Ti^{4+}/Ti^{3+} redox pair that usually occurs at a moderate potential, usually at 0.6–0.9 V *vs.* Na/Na^+ depending on the polymorph.[27,28] Especially, TiO_2(B), a metastable phase of TiO_2, has an array of open tunnels along the [010] direction; this means that theoretically, it can accommodate Na^+ ions more easily and allow faster Na-ion transport than the other TiO_2 polymorphs.[29,30] This structural characteristic also induces more open voids than the cases of anatase and rutile phases, and thus, TiO_2(B) is a suitable anode material for metal-ion insertion;[27] however, owing to the inefficient ion conductivity and poor electronic property, the sodium storage performance

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