



# Mo-doped Gray Anatase TiO<sub>2</sub>: Lattice Expansion for Enhanced Sodium Storage



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## ABSTRACT

Gray-colored Mo<sup>6+</sup>-doped anatase TiO<sub>2</sub> is prepared uniformly with particle size of 10–20 nm, and is firstly employed as anode material in sodium-ion batteries (SIBs), presenting excellent electrochemical performances. It delivered reversible specific capacities of 231.8 mAh g<sup>-1</sup> at 0.1 C (33.5 mA g<sup>-1</sup>) after 100 cycles and 108.3 mAh g<sup>-1</sup> at 5 C (1.68 A g<sup>-1</sup>), comparing to 170.5 mAh g<sup>-1</sup> at 0.1 C and only 41.7 mAh g<sup>-1</sup> at 5 C for the bare TiO<sub>2</sub>. The improved electrochemical performances might be beneficial from the doping of Mo<sup>6+</sup>, which can effectively enhance the conductivity of TiO<sub>2</sub> resulting from induced conduction band electrons, interstitial oxygen defects and vacancies. In addition, the doping can also lead to the lattice expansion, which can facilitate the diffusion of Na<sup>+</sup>. In combination with natural abundance and environmental benignity, Mo<sup>6+</sup>-doped TiO<sub>2</sub> can be expected to be utilized as an anode material for enhanced sodium storage.

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## 1. Introduction

Rechargeable batteries, which can function repeatedly through reversible energy storage and release, have been widespread applied to portable electronic devices, electric or hybrid electric vehicles as well as energy storage stations. As a most typical type, lithium ion batteries (LIBs) hold a dominant share in the battery market, since LIBs have high energy densities, long cycle lifespans and rapid charge-discharge rate [1,2]. However, LIBs suffer from the quite limited lithium sources and the increasing costs, which have to be addressed for a predicted booming battery market requirements [3–5], therefore to find possible alternatives is particularly important. Sodium ion batteries (SIBs) are the closest analogue of LIBs, and their comparable electrochemical performances and the nearly inexhaustible sodium resources in the earth's crust and ocean make SIBs a most promising substitute.

Sodium is a larger version of alkali metal than lithium (ionic radius, 1.02 Å versus 0.76 Å) [6], and thus searching an appropriate

anode material for SIBs is challenging and essentially significant for SIBs developments. During the recent decade, great endeavors have been devoted to seek the suitable candidates. Titanium dioxide is regarded as one of the most appealing choices, thanks to its natural abundance, environmental benignity and relatively robust structure during the insertion and extraction process of sodium ion [7–9].

Nevertheless, the inferior electronic conductivity and narrow ionic channels of TiO<sub>2</sub> are not suitable for rapid sodium ion transfer, which extremely hinder the practical application of TiO<sub>2</sub> as anode material in SIBs [10]. In order to enhance its sodium storage properties, substantial efforts have been dedicated to surmount these inherent drawbacks. A typical approach is to modify the morphologies like diminishing the crystallite size or designing novel micro/nanostructure such as nanocubes [11], nanofibers [12], nanotubes [13] and nanorods [14] to shorten the Na<sup>+</sup> diffusion path and support fast Na<sup>+</sup> transport. Another effectual way is to hammer at improving electric conductivity through combining with high conductive materials such as hard carbon [15,16] or doping aliovalent ions with Nb [17], N [18], B [19], and Sn [20].

Apart from doping with Nb, N, B and Sn, it also has been described in previous report that Mo<sup>6+</sup> can increase the electrical

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conductivity of TiO<sub>2</sub> by partially substituting Ti<sup>4+</sup> [21]. An internal Mo<sup>6+</sup>-doped TiO<sub>2</sub> had been obtained through hydrothermal process by Zhang et al. [22] As anode material for LIBs, it delivered a high reversible specific capacity of 408 mA h g<sup>-1</sup> at 60 mA g<sup>-1</sup> after 200 cycles and exhibited excellent rate capacities.

In this work, Mo<sup>6+</sup>-doped TiO<sub>2</sub> was obtained through a sol-gel route and its electrochemical performances were explored in details, showing that Mo<sup>6+</sup>-doped TiO<sub>2</sub> showed higher specific capacities, remarkable cycling performances and relatively excellent rate capacities.

## 2. Experimental section

### 2.1. Preparation of electronic anode materials

Bare and Mo<sup>6+</sup>-doped TiO<sub>2</sub> were prepared through a sol-gel method. Under magnetic stirring, 0.21 g ammonium molybdate were previously dissolved in a mixture solution containing 48.2 ml ethanol, 6 ml deionized water and 0.6 ml nitric acid to form the solution A. Meanwhile, the mixture solution B was made up of 48.2 ml ethanol and 21.3 ml tetrabutyl titanate. Afterwards, the solution A was added dropwise into the solution B to obtain a homogeneous solution. The mixed solution was under constant stirring for 1 h to form a viscous gel and subsequently aged for 24 h at ambient temperature. It was then stored in a vacuum oven at 70 °C over night to get a dry gel. Finally, the dry gel was gently grounded and annealed at 500 °C in air for 6 h to produce Mo<sup>6+</sup>-doped TiO<sub>2</sub>, which was denoted as MTO. For comparison, the bare TiO<sub>2</sub> samples were marked as TO and were produced through a same process without adding ammonium molybdate.

### 2.2. Materials characterization

X-ray diffractometer (XRD, Rigaku D/max 2550 VB<sup>+</sup> 18 KW) with monochromatic Cu K $\alpha$  radiation ( $\lambda=1.542$  Å) was measured to check the phase of the powdered samples. XRD patterns were obtained in the 2  $\theta$  range of 20°–80° with a scan rate of 2° per minute. X-ray photoelectron spectroscopy (XPS) experiments were carried out on an X-ray photoelectron spectrometer (K-Alpha 1063). The crystalline structure and composition of the as-obtained samples were characterized by using elemental mapping (EM, Quanta 200 field-emission SEM system) and transmission electron microscopy (TEM, JEM-2100F).

### 2.3. Electrochemical measurements

Electrochemical tests were carried out by CR2016-type coin cells, which were made up of a sodium metal cathode, the working anode, separated by a polypropylene film (Celgard 2500) and assembled in an Ar-filled MBraun glovebox. The working electrode contained 70 wt% active materials (MTOs and TOs), 15 wt% carboxymethyl cellulose (CMC) as binder and 15 wt% super P as conductive additive. The homogenous slurry was coated uniformly on copper foil and dried at 80 °C for 12 h in a vacuum oven, successively, punched into wafers and the average mass loading of the active material was 0.8 mg cm<sup>-2</sup>. The electrolyte solution was consisted of 0.97968 g NaClO<sub>4</sub>, 8 ml propylene carbonate (PC) and 400  $\mu$ l fluoroethylene carbonate (FEC). Galvanostatic charge-discharge cycling, rate performance and cyclic voltammetry tests of the cells were performed in a voltage range between 0.01 and 3.0 V (vs. Na<sup>+</sup>/Na) by using Arbin battery cyler (BT 2000) and Solartron Analytical. Electrochemical impedance spectroscopy (EIS) studies were conducted on a Solartron Analytical in a frequency range from 0.01 Hz to 100 kHz.

## 3. Results and discussion

### 3.1. Crystalline structure and compositions of MTO

X-ray diffraction (XRD) patterns of MTOs and TOs were presented in Fig. 1a. All the peaks were fitted well with the standard XRD peaks of anatase phase TiO<sub>2</sub> (PDF #21–1272) and no additional peaks were observed, indicating that it is effective to produce highly pure TiO<sub>2</sub> phase by the sol-gel method. Five peaks of the two samples could be seen in Raman images (Fig. 1b), which could be assigned to the typical Raman characteristics of anatase TiO<sub>2</sub>. In addition, no shift near 140 cm<sup>-1</sup> was observed before and after doping, denoting that the doping of Mo<sup>6+</sup> did not change the crystallite structure of TiO<sub>2</sub>, consisting well with the XRD results. Moreover, note that all of the typical XRD diffraction peak became broader in the case of MTOs, implying that MTOs had smaller crystallite size about 121 Å comparing to that of TOs (about 162 Å) according to the Scherrer formula ( $D = K\lambda/\beta\cos\theta$ ), demonstrating that the doped Mo<sup>6+</sup> could restrain the growth of crystallite size of TiO<sub>2</sub> [23]. Rietveld refinement of the XRD data revealed a lesser increase in the cell volume (shown in the Table. 1), meaning that the Mo<sup>6+</sup> doping had expanded the unit cell, thus, incorporating Mo<sup>6+</sup> into the TiO<sub>2</sub> framework could trigger the lattice expansion of the TiO<sub>2</sub>.

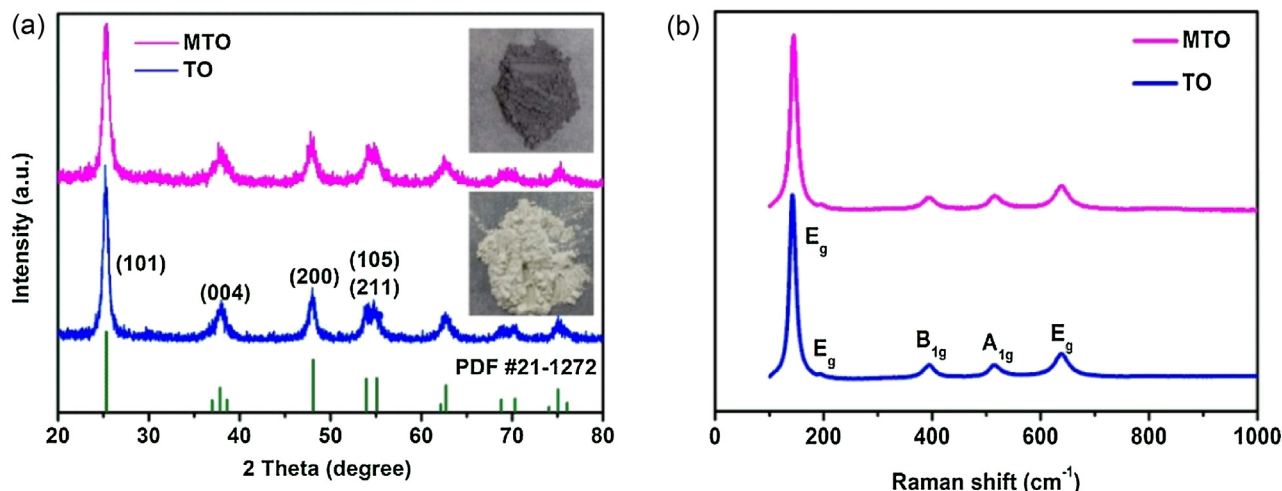


Fig. 1. (a) XRD patterns of MTO and TO, (b) Raman shifts of MTO and TO.

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