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# Enhanced lithium ion storage in $TiO_2$ nanoparticles, induced by sulphur and carbon co-doping

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## HIGHLIGHTS

- Anatase nanoparticles are simultaneously doped by sulphur and carbon.
- In SC-$TiO_2$ material carbon exists in elemental and oxide forms.
- Sulphur is integrated in form of sulfate compounds in +6 oxidation state.
- SC-$TiO_2$ shows significant capacity increase and very fast lithiation kinetics.

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## ABSTRACT

Sulphur and carbon codoped anatase nanoparticles are synthesized by one-step approach based on interaction between thiourea and metatitanic acid. Electron microscopy shows micrometer-sized randomly distributed crystal aggregates, consisting of many 25–40 nm $TiO_2$ nanoparticles. The obtained phase composition and chemical states of the elements in the structure are analyzed by means of X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD shows that after doping the tetragonal anatase structure is preserved. Further data assessment by Rietveld refinement allows detection of a slight increase of the *c* lattice parameter and volume related to incorporation of the doping elements. XPS confirms the coexistence of both elemental and oxide carbon forms, which are predominantly located on the $TiO_2$ particle surface. According to XPS analysis sulphur occupies titanium sites and the element is present in $S^{6+}$ sulfate environment. Analysis based on cyclic voltammetry and galvanostatic intermittent titration (GITT) suggests an accelerated $Li^+$ transport in the doped $TiO_2$ structure. The synthesized S and C co-doped anatase has an excellent electrochemical performance in terms of capacity and very fast lithiation kinetics, superior to the non-doped $TiO_2$. The material displays 83% capacity retention for 500 galvanostatic cycles and nearly 100% current efficiency.

## 1. Introduction

Anatase, the most extensively used polymorph modification of $TiO_2$, has been widely researched as an alternative anode material for lithium-ion batteries [1–10]. Due to its excellent electrochemical stability, high operating voltage and low cost $TiO_2$ based anode materials attracted high attention. A considerable number of studies underlined the positive impact of $TiO_2$ for battery safety [5,8,9]. The higher $TiO_2$ lithiation potential reduces the risk of metallic Li dendrites formation and thermal runaway [5,8]. Furthermore, the minimal heat exchange upon charge-discharge [9] and lack of solid-electrolyte interfacial (SEI) layer formation enhance the positive effect of $TiO_2$ for the battery safety and reliability [9]. It is generally accepted that the main weakness of $TiO_2$ concerns its relatively low conductivity and hindered kinetics of Li-ion transport. These drawbacks result in a poor rate capability and a limited capacity of $TiO_2$ based electrodes [10].

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Three basic approaches, including particle size reduction and nanostructuring [11], application of conducting coatings and composites with conducting additives [12], and appropriate doping of the structure [13–30] have been established as the most promising for boosting $TiO_2$ electrochemical performance. Significant improvement of $TiO_2$ functional parameters based on the reduction of Li-ion diffusion length has been achieved by nanostructuring [11]. Further enhancement of Li ion mobility and storage was realized on atomic level by means of integration of carbon [13,14,28], nitrogen [15–17,28], hydrogenation [18] and introducing other elements [19–30].

Sulphur doping during $TiO_2$ chemical synthesis was initially applied to modify the photocatalytic properties of the material [24–26]. The narrowing of the electronic band gap of $TiO_2$ is of great importance for improving the optical and photocatalytic properties of this material in the visible wavelength range [25,26]. It was concluded that the effective doping of $TiO_2$ with non-metal elements like sulphur, creates strongly delocalized impurity states essential for a good mobility of the photogenerated holes and minimization of electron-hole recombination [26]. Furthermore, the doping of $TiO_2$ with additional elements, including sulphur, considerably increases the conductivity of the material, required as well for the improvement of lithiation/delithiation kinetics [27] and for the enhancement of its electrochemical performance in water based media [26]. Along with several nonmetallic dopants (including C, N, F), sulphur doping has resulted in an effective electrochemical storage and improvement of lithiation kinetics [27]. The synthetic approach involves a three step method, comprising nitriding in gaseous $NH_3$ of already synthesized $TiO_2$ nanoparticles, followed by oxidation in air and final S doping in gaseous $H_2S$. Even though a rather complex synthetic procedure has been used, a visible improvement of the capacity and rate capability of the material was achieved [27].

It was further observed that the distribution of dopant elements in the $TiO_2$ lattice changes the electronic structure and therefore gives an impact to the electron and ion transport in the solid state. The homogeneous distribution of dopants in the entire $TiO_2$ particle is essential for attaining a good conductivity and improved rate performance of the material. Considering the occupation site of the doping element in the $TiO_2$ structure, it is very important that nonmetallic dopants to be substitutional for a lattice atom instead to have an interstitial position in $TiO_2$. The dopants, located in the interstitial spaces between $TiO_6$ octahedra, can block the intercalation of lithium ions and hence inhibit the electrochemical kinetics of lithium exchange [27].

Using first principles calculations, structural, electronic and optical properties of S-doped anatase are studied [31]. Different states of sulphur (anionic and cationic) are considered depending on their position in $TiO_2$ lattice: in interstitial site and in substitution for either oxygen or titanium atoms. It was experimentally observed that among the explored structures, two anionic and one cationic configurations induce an improved light absorption in the visible region. It was found that the cationic sulphur configurations $S^{4+}$ and $S^{6+}$ are strongly stabilized in a wide range of oxygen chemical potential, while anionic species exist only at very low chemical potential values. Systems involving sulphur on Ti position, incorporated in the form of $SO_2$ units are expected to be thermodynamically more stable and with improved optical properties. Considering possible synergetic effect caused by a second doping element, DFT analysis revealed a positive influence of the carbon doping on the electronic and photocatalytic properties of $TiO_2$. The observed carbon effect is attributed to the inhibition of impurity states localized in the middle of the band gap by the single sulphur doping [32].

Taking into consideration the complex structural aspects of the sulphur $TiO_2$ doping, their impact on the lithiation mechanism and kinetics of the structure remains still controversial.

Current work concentrates on sulphur and carbon co-doped $TiO_2$ nanoparticles (SC-$TiO_2$), obtained by a direct procedure based on interaction between thiourea and metatitanic acid. The synthesis method is an example of a simple and effective one-step strategy for boosting the capacity and cycling rate performance of anatase electrodes. The study aims at revealing the structural characteristics of the doping induced lithium ion storage in anatase.

## 2. Experimental

### 2.1. Chemicals and materials

Ethylene carbonate (EC), dimethyl carbonate (DMC), $LiPF_6$ and Li metal foil were supplied by Alfa Aesar. Thiourea was provided by Wako Pure Chemical Industry. The solvents and electrolytes necessary for electrochemical experiments were dried until a value of 15 ppm $H_2O$ was reached. The moisture in the electrolytes was controlled by Karl – Fischer titration (831 KF Coulometer from Metrohm). A Cu foil as a current collector was supplied by Li Tec. Other chemicals were obtained from commercial sources and were used without further purification.

### 2.2. Synthesis of $TiO_2$–SC nanoparticles

A mixture of 10.4 g metatitanic acid and 3.6 g thiourea was triturated in an agate mortar to obtain a homogeneous mass, which was heated up at 500 °C for 1 h. Thus, a yellow powder was synthesized using a solid phase method.

### 2.3. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)

A high-resolution scanning electron microscope Hitachi S-4800 II was used for the surface morphology characterisation. JEOL-JEM-1011 TEM microscope, operated at an accelerating voltage of 80 kV with a resolution of 0.2 nm, was used to obtain images of individual nanoparticles. The powder samples were prepared by air-drying a drop of a sonicated suspension onto copper grids.

The phase identification of sulphur doped $TiO_2$ structure was carried out by powder X-ray, using a Siemens D5000 diffractometer in reflection mode with Cu K$\alpha$ radiation. XRD patterns were recorded in the 2Θ range of [15; 100°] with a step size of 0.02° and a stay time of 1s/step.

XPS measurements were carried out in normal emission using monochromatic AlK$\alpha$ ($h\nu = 1486.7$ eV) radiation. More details about the experimental setup can be found in Ref. [33]. Core level spectra were recorded at constant pass energy with a total energy resolution of 0.6 eV and at absence of charge neutralization and further binding energy (BE) correction. All core level spectra were analyzed by subtracting a linear background and peak positions. The areas were obtained by a least-squares fitting of model curves (70% Gaussian, 30% Lorentzian) to the experimental data. The data were fitted using CasaXPS (Version 23.16 Dev52, Casa Software Ltd., www.casaxps.com). For calculation of the atomic concentration a homogeneous distribution of the elements within the XPS detected volume was assumed. The data for photoemission cross sections and asymmetry factors were obtained from the work of Yeh and Lindau [34]. The error in the quantitative analysis is estimated in the range of ±10%, while the accuracy for BE assignment is ±0.2 eV.