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Stabilizing nanostructured lithium insertion materials *via* organic hybridization: A step forward towards high-power batteries



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HIGHLIGHTS

- Structural disordering occurs in anatase TiO₂ nanorods (TiO₂ NRs) upon continuous cycling.
- Lowering the cathodic cut-off potential accelerates the structural disorder in TiO₂ NRs.
- Carbon coating prevents structural disordering upon cycling in TiO₂ nanorods.
- Dopamine is used as anchoring group for the RAFT polymerization derived carbon coating.
- Surface defects of TiO₂ NRs are healed by dopamine.

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ABSTRACT

Herein, we present the electrochemical characterization of carbon-coated TiO₂ nanorods, obtained by carbonizing RAFT (reversible addition fragmentation chain transfer) polymerization derived block copolymers anchored on anatase TiO₂ nanorods. These carbon-coated TiO₂ nanorods show an improved electrochemical performance in terms of first cycle reversibility, specific capacity, cycling stability, and high rate capability. More importantly, however, the structural disordering observed in the uncoated TiO₂ nanorods by means of galvanostatic and potentiodynamic cycling as well as *ex situ* XRD analysis, does not occur for the carbon-coated material. Preventing this structural disordering does not only result in a stabilized cycling performance but, moreover, in substantially enhanced energy storage efficiency (86% vs. only 68% at the 100th cycle) due to the preserved characteristic potential profile of anatase TiO₂.

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1. Introduction

Lithium-ion batteries are currently considered as one of the most promising electrochemical energy storage devices for future large-scale applications, as for instance electric vehicles [1–3]. However, beside improvements related to their energy density, current research activities focus on further advances of the obtainable power of such energy storage devices. In fact, the (dis-)charge capability of graphite, the state-of-the-art anode material is

inherently limited by the release of the Li⁺ solvation shell upon the intercalation of lithium ions through the initially formed solid electrolyte interphase (SEI) [4–6] as well as its very low operational potential and the concomitant safety issue of lithium plating [7,8]. Accordingly, alternative anode materials are investigated offering higher lithium ion (de-)insertion potentials and thus preventing the formation of an SEI layer as well as the risk of metallic lithium deposition at elevated charge/discharge rates. Titanium oxides, as for instance Li₄Ti₅O₁₂ (LTO) or different polymorphs of TiO₂, have gathered a wide interest [9–16] since such materials offer decent specific capacities, due to their higher density with respect to graphite, and lithium (de-)insertion occurs at potentials within the electrochemical stability window of commonly used organic carbonate-based electrolytes. While LTO is already comprised in

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commercial lithium-ion batteries [2], anatase TiO₂ is certainly a very attractive alternative due to its natural abundance, its already available large-scale production, such as pigments for the paint industry and dye-sensitized solar cells [17–19], as well as its theoretically higher specific capacity (335 mAh g⁻¹ vs. 175 mAh g⁻¹ for LTO). However, micro-sized anatase TiO₂ severely suffers of limited specific capacities especially at high rates [20–22]. Nanostructuring of such active material particles showed substantial improvements in terms of achievable specific capacity, due to the increasing capacity contribution resulting from a second phase formation, which occurs only at the particle surface [23–26]. The high rate capability is also improved by an increasing solid solution domain [24–27], a generally reduced lithium ion and electron diffusion and transport pathways and an increased electrode/electrolyte contact area [28,29]. Further improvement was achieved by embedding such nanoparticles in carbonaceous host matrices or applying a carbon coating layer in order to enhance the electronic conductivity of such mostly insulating active material [30]. Wang et al. [31], for instance, investigated self-assembled TiO₂-graphene hybrid nanostructures, showing enhanced rate performance, *i.e.*, more than 100 mAh g⁻¹ at C rates as high as 30C. Fu et al. [32], Das et al. [33], or Cao et al. [34] followed a rather facile approach using sucrose or glucose as carbon precursor, while Thackeray and co-workers [35] reported an *in situ* carbon coating procedure utilizing titanium (IV) oxyacetate as TiO₂ and carbon precursor and a specially designed autogenic reactor. Using the oleic acid capping agent to form a carbonaceous coating layer on TiO₂ nanorods, Bresser et al. [26] obtained an advanced rate performance, particularly when only the charge (delithiation) rate was increased, and high specific capacities of more than 250 mAh g⁻¹, depending on the cathodic cut-off potential. However, it appears noteworthy that this list of anatase TiO₂-carbon heterogeneous secondary structures presents only a brief overview on previously reported work and is certainly not exhaustive. Generally, for active materials storing lithium ions by insertion mechanism, as *inter alia* anatase TiO₂, thus undergoing relatively low volume changes upon reversible lithium uptake, homogenous and rather thin coating layers are preferable. This allows an improved electron transport, while at the same time lithium ion diffusion into the active material particles is not slowed down [36], thus resulting in an improved high rate capability of such electrode materials [37]. Very recently, we reported a new approach for the realization of such a carbon coating based on the carbonization of a block copolymer anchored onto the nanoparticles surface and synthesized by RAFT (reversible addition fragmentation chain transfer) polymerization (Fig. 1), showing an improved cycling stability and reduced capacity fading per cycle relatively to the uncoated TiO₂ nanorods [38].

Herein, we will present a detailed and extended electrochemical characterization of these carbon-coated anatase TiO₂ nanorods,

showing their advanced high rate capability, specific capacity, cycling stability, and first cycle reversibility relatively to the uncoated TiO₂ nanorods. Even more remarkably, however, it will be shown that the application of such a carbon coating suppresses a continuously progressing structural disorder observed in uncoated anatase nanorods by means of galvanostatic and potentiodynamic cycling as well as *ex situ* XRD analysis of cycled electrodes. This structural disordering does not only result in inferior capacity retention but moreover in a substantially reduced energy storage efficiency caused by continuous shortening of the characteristic potential plateau upon lithium (de-)insertion, which is – to the best of our knowledge – herein investigated and discussed for the first time.

2. Experimental section

2.1. Synthesis of carbon-coated and uncoated anatase TiO₂ nanorods

The synthesis of carbon-coated and uncoated anatase TiO₂ nanorods was very recently described in detail by Oschmann et al. [38]. In brief, oleic acid (OLEA, Acros Organics)/oleylamine (OAM, Acros Organics) – capped anatase TiO₂ nanorods were synthesized according to a solvothermal method recently reported by Dinh et al. [39], using titanium butoxide (Acros Organics) as precursor and water vapor as hydrolysis agent. OLEA and OAM were subsequently replaced by tetrafluoroborate (BF₄⁻), using nitrosonium tetrafluoroborate (NOBF₄, Sigma–Aldrich) in dichloromethane solution, according to a ligand-exchange reaction reported by Dong et al. [40]. For the preparation of reference electrodes based on uncoated TiO₂ nanorods, BF₄⁻ was removed by means of centrifugation and dialysis in methanol. For the preparation of carbon-coated TiO₂ nanorods, the BF₄⁻-capped nanorods were dispersed in *N,N*-dimethylformamide (DMF) and mixed with the RAFT (reversible addition fragmentation chain transfer) polymerization-derived block copolymer poly(acrylonitrile-*b*-dopamine acrylamide) (P(AN-*b*-DAAM)), comprising polyacrylonitrile (PAN) as carbon precursor and dopamine as anchor block. The polymer to TiO₂ ratio was 1:4. Subsequently, the block copolymer-functionalized TiO₂ nanorods were purified *via* centrifugation and dried under vacuum. For the carbonization of the block copolymer, the functionalized nanorods were thermally treated under argon (for 240 min at 300 °C & for 90 min at 700 °C; heating rate: 5 °C min⁻¹).

2.2. Morphological and structural characterization

The structure of uncoated and carbon-coated anatase TiO₂ nanorods was investigated by means of X-ray diffraction (XRD) analysis using a Siemens D5000 (Cu-K α radiation, $\lambda = 0.154$ nm). Raman spectroscopy was performed by means of a Horiba Jobin Y

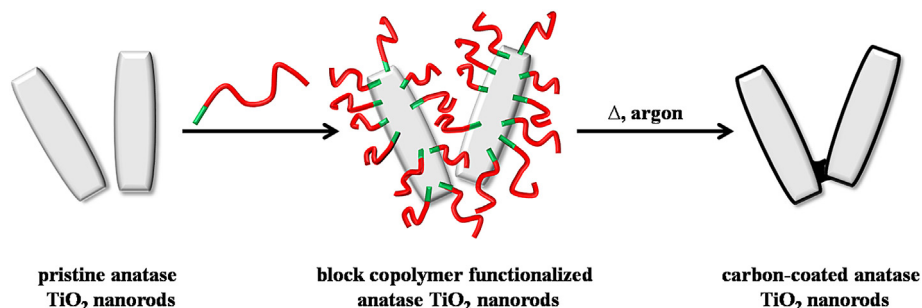


Fig. 1. Schematic illustration of the carbon coating approach: as-synthesized TiO₂ nanorods (left) are functionalized by grafting a block copolymer (center), which is subsequently carbonized by a thermal treatment at 300 °C for 4 h and at 700 °C for 1.5 h under argon, resulting in a thin and homogenous carbon coating (right).

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