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ARTICLE

An innovative synthesis of carbon-coated TiO₂ nanoparticles as host for Na⁺ intercalation for sodium-ion batteries

Tanguy Soudant^a, Solenne Fleutot^a, Stéphanie Bruyère^a, Lucie Speyer^a, Sébastien Hupont^a, Mickaël Bolmont^a, Thomas Girardet^a, Loris Raspado^a, Claire Hérold^a, Sébastien Cahen^{a*}Received 00th January 20xx,
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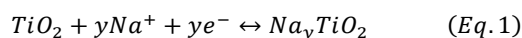
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In this work, an innovative route to synthesize anatase TiO₂@C composite is presented. The synthesis was conducted by a soft chemistry microwave-assisted method using titanium(IV) butoxide as titanium precursor. The residual (un)converted titanium precursor remaining after TiO₂ synthesis was used as carbon precursor and thermally treated under H₂ to obtain nanoparticles of TiO₂@C composite. We showed a superior reversible specific capacity with TiO₂@C (120 mAh.g⁻¹ at C/20 rate, 3rd cycle) than pristine TiO₂ (66.5 mAh.g⁻¹ at C/20 rate, 3rd cycle), in agreement with the importance of carbon coating addition with TiO₂ nanoparticles as negative electrode material for sodium-ion batteries.

Introduction

Currently, considering the environmental crisis, governments want to reduce greenhouse gas emissions. Therefore, electrification of the society is a way to free ourselves from fossil fuel. The corresponding technological changes cause a very important demand in energy storage devices especially for electric vehicles (full electric or hybrid). Indeed, in 2016 battery demand was around 41 to reach 550 GWh per year in 2022¹. Nowadays, Li-ion batteries (LIBs) are widely used in mobile devices especially in electrical vehicles thanks to their high energy density storage. Among elements used for batteries, lithium, cobalt, nickel, copper and even carbon (graphite) will become critical elements in medium term (2025-2035)². Moreover, lithium exploitation is not environmentally friendly, is it so necessary to develop sustainable alternatives for electrochemical storage technologies. Sodium-ion batteries (SIBs) appear as an interesting solution to free ourselves some critical elements cited previously. Unlike LIBs, graphite cannot be used as negative electrode material in SIBs due to poor sodium intercalation with very low theoretic massic capacity of 35 mAh.g⁻¹ for NaC₆₄ (372 mAh.g⁻¹ for LiC₆)³⁻⁵. Consequently, hard carbons remain the most widely studied anode materials because there are very good candidates for sodium ion storage. It presents several advantages regarding the abundance of the carbon element, the low elaboration cost of hard carbons or its expected electrochemical performances (300mAh.g⁻¹ for an energy density of 300 Wh.kg⁻¹ for fully sodiated hard carbons⁶⁻⁸. Elsewhere, transition metal oxides are another possible class of anode materials and are considered for both LIBs and SIBs⁹⁻¹¹. Among them, titanium dioxide (TiO₂) is an attractive

alternative negative electrode material regarding the titanium abundance, its non-toxicity and the cost-effective of the material. Such anode could be envisaged in stationary application where high massic/volumic capacities are not requested. Another interest of titanium dioxide compared with hard carbons is the safety aspect of TiO₂ as anode as its mean nominal voltage is 0.7 versus 0.1-0.05 V (vs. Na⁺/Na)⁸, avoiding Na plating risk¹² with increased cyclability¹³. TiO₂ is a highly studied inorganic material due to its numerous applications in photocatalysis, cosmetic as white pigment, optics, sensors or rechargeable batteries¹⁴. Many polymorphs of TiO₂ exist but the most common phases are rutile (tetragonal, *P4₂/mnm*), brookite (orthorhombic, *Pbca*) and anatase (tetragonal, *I4₁/amd*). The anatase polymorph, thermodynamically stable at low temperature, is the most studied for batteries applications due to its easy synthesis and electrochemical stability¹⁵⁻¹⁸. Especially, anatase polymorph reveals the highest sodium storage^{13,19,20} as described in Eq.1 where γ corresponds to the number of inserted Na⁺:



The nanoscale allows reaching better storage performance than macroscale due to reducing diffusion lengths, large specific surface area and high kinetic properties²¹⁻²³. In the literature, Titanium NanoParticles (TNPs) are mostly synthesized by hydrothermal route^{24,25}. In this work syntheses have been performed by a microwave-assisted procedure due to many advantages such as time gain, reducing power consumption, homogenous heat and smaller size particles obtaining compared to hydrothermal route²⁶. Unfortunately, TNPs are electrochemically instable toward electrolyte due to a huge specific surface area that causes an important irreversible consumption of Na⁺ during the formation of the Solid Electrolyte Interphase (SEI) at the electrode/electrolyte interface^{19,27}. So many works are focused on the improvement

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of the electrochemical stability of TNPs. Indeed, if three-dimensional TiO₂ anatase structure exhibit open galleries favourable for Na⁺ insertion/deinsertion²⁸, it suffers from low conductivity and slow ion diffusion²⁹.

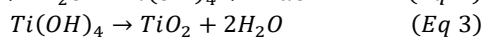
One cost-effective approach used for improving the capacity and rate capability is the formation carbon coating surrounding TNPs. A porous carbon matrix will bring preferential sites for Na⁺ insertion/deinsertion, improve the contact between active material and electrolyte by its penetration through pores and optimize conduction paths for fast electron transport^{30,31}.

It is expected that the carbon will add a synergetic effect, providing a conductive network that will also stabilize the SEI, improving the Initial Coulombic Efficiency together with increased capacity and rate performances. Indeed, it has been demonstrated that carbon coating allows improving the electronic conductivity of TNPs through the formation of a Ti-C bond, contributing to better electrochemical performances^{27,30}. To coat nanoparticles, many routes exist such as sol-gel^{31,32}, hydrothermal^{33,34} or microwave-assisted³⁵ routes. In this work, we employed a one-pot TNPs synthesis followed by direct thermal treatment without adding supplementary reactant. This original approach is assumed to improve the TNPs stability using Ti(OCH₂CH₂CH₂CH₃)₄ (TetraButOxyTitanium TBOT) as both titanium and carbon precursors. To do so, as-prepared TNPs were thermally treated under H₂ flow.

Experimental

Synthesis of TiO₂@C nanoparticles

Usually, TiO₂ nanoparticles (TNPs) are mainly synthesized by hydrothermal route^{24,25}. In this work, all syntheses have been conducted by microwave-assisted which allows energy and time gains compared to hydrothermal route²⁶. To synthesize TNPs, samples are prepared in a glove bag under argon atmosphere to prevent hydrolysis of TBOT. 4 mL of TBOT (Aldrich Chemistry, 97%, CAS: 5593-70-4) and 8 mL of acetic acid (Sigma Aldrich, ≥ 99.8%, CAS: 64-19-7) are introduced into a microwave vial then transferred into a single-mode microwave (Monowave 400 from Anton Paar) for the thermal treatment at a temperature between 180 and 240 °C for 30 minutes and finally cooling at 55 °C. The reaction mechanisms involved can be described by the following reactions³⁶:



The obtained mixture containing TiO₂ nanoparticles is then washed once with absolute ethanol (VWR, 99.95%, CAS: 64-17-5) and twice with ultra-pure water (resistivity: 18.2 MΩ.cm) by centrifugation for 5 minutes for each washing then dried at 80 °C. The TNPs powder with carbon precursor was loaded in a silica boat and thermally treated under H₂ flux (70 mL.min⁻¹) for 4h at 400 °C (5 °C.min⁻¹) in a horizontal furnace.

Characterizations

The TNPs phase was identified by powder X-ray diffraction (pXRD) using a Bruker diffractometer (D8 Advance) with Mo Kα

radiation (0.70926 Å) in transmission mode and Cu Kα radiation (1.54060 Å) in reflexion mode (θ-θ geometry). Thermogravimetric analyses (Setaram - Setsys EV1750) coupled with mass spectroscopy (Pfeiffer Vacuum - Omnistar GSD 301C) were conducted at a heating rate of 5 °C.min⁻¹ from room temperature to 800 °C and a cooling rate of 10 °C.min⁻¹. Carbon in the samples was evidenced by Raman spectroscopy using a Horiba spectrometer (Labram HR800) operating with a 457 nm wavelength. High-resolution transmission electron microscopy (HR-TEM) was performed (JEOL – ARM 200F) to study morphology, size, and crystallinity of particles. Scanning TEM (STEM) mode was used for chemical analysis by Electron Energy Loss Spectroscopy (EELS).

Electrochemical characterization

To perform electrochemical characterizations, a 70/10/20 slurry (70 wt% active material, 10 wt% carboxymethyl cellulose as binder and 20 wt% carbon black as conductive material) was prepared in deionized water and then coated on aluminium foil³⁷. Once slurry has dried, the material was assembled on current collector in coin cell CR2032 or in powder in Swagelok® half-cell versus Na metallic foil vs 1M NaClO₄ in EC-DMC 1:1 in mass. Galvanostatic Cycling with Potential Limitation (GCPL) tests were conducted on Biologic – BCS-810 between 0 and 3 V vs. Na⁺/Na at C/20 rate.

Results and discussions

Effect of the synthesis temperature

To study the temperature influence on the TNPs crystallinity, four different synthesis temperatures were tested. On the XRD patterns shown in Fig. 1, the diffraction peaks can all be indexed with anatase TiO₂ only (COD n° 96-900-8216). FWHM of the peaks decreases from 0.3149 to 0.2558 for 101 reflection and from 0.6298 to 0.3149 for the 200 reflection when the temperature increases, which characterizes a higher crystallite size (from 16 nm for 180 °C to 27 nm for 240 °C, calculated by Scherrer equation from 101 peak). Moreover, a low angle background signal is detected due to the presence of residual

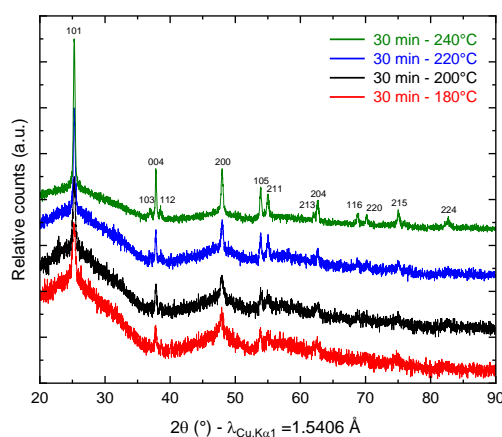


Fig. 1. pXRD patterns of anatase TiO₂ after synthesis at 180 (red), 200 (black), 220 (blue) and 240 °C (green).



amorphous material. This background decreases progressively by increasing the temperature in agreement with the sharpening of the Bragg peaks accordingly to a higher crystallinity. Fig. 2 presents ThermoGravimetric Analyses (TGA) for the sample synthesized at 180 °C. This thermogram is considered as representative of all samples of the study (data retrieved from other ones are summarized in Table 1). Such an analysis allows quantifying the residual quantity of titanium precursor after synthesis. Two mass losses signals are present: the first one is attributed to H₂O outgassing at 45 °C and the second one to the combustion of residual TBOT at 318 °C. Whatever the temperature synthesis considered, the TBOT mass loss does not change, in agreement with a reaction yield close to 70 %.

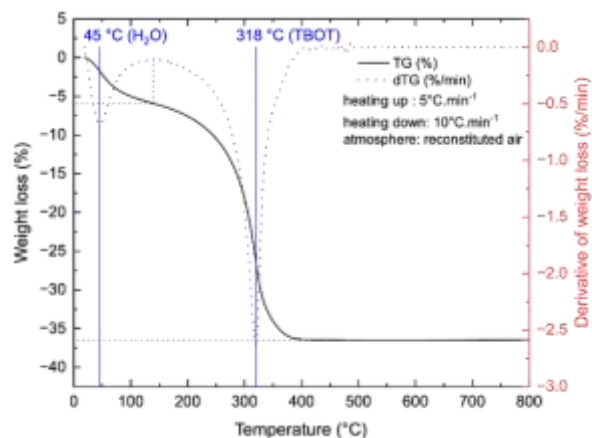


Fig. 2 TGA of TNPs after synthesis (180 °C – 30 min).

Thermal treatment

After synthesis, thermal treatment of TNPs under H₂-flux at 400 °C was carried out to remove TBOT residues and integrate TiO₂ into carbon. Indeed, residual TBOT present at around 30 %_{wt} is assumed to be usable as a carbon precursor to form the carbon coating. pXRD patterns (Fig. 3) are recorded before and after thermal treatment under H₂ using a diffractometer with Mo K_{α1} radiation in order to probe the sample in transmission mode. pXRD patterns show no-TiO₂ reduction into Ti, as thermodynamically expected up to 500 °C. It should be noted that TiO₂ polymorph is preserved, and the crystalline phase ratio is improved after thermal treatment. The SiO₂ reflection peak at 9.78 °(2θ) is attributed to the silica boat used

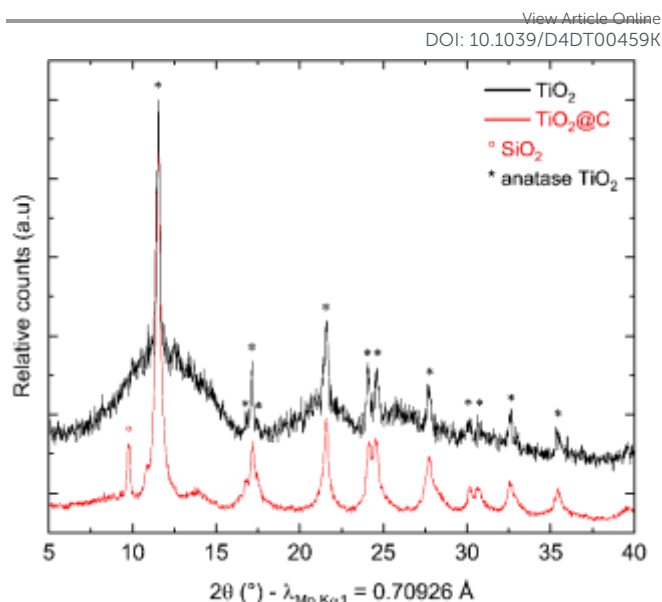


Fig. 3 pXRD patterns before (black) and after (red) heat treatment under H₂

for the thermal treatment. Finally, the splitting of the peak around 11 °(2θ) could be due to the 002 reflection of a poorly crystallized carbon. To confirm the presence of carbon after this step, TG-MS analysis was performed, and the results are presented in Fig. 4.

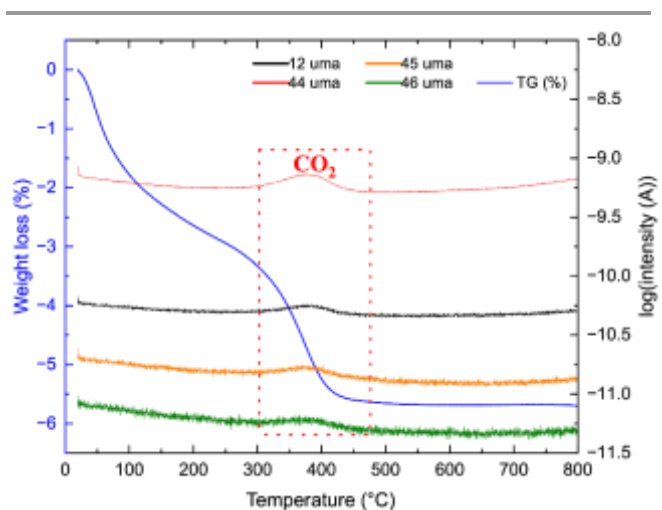


Fig. 4 TG-MS analysis under air of TNPs after thermal treatment.

The weight loss can be decomposed in two phenomena as previously observed. The first one at around 45 °C is still

Table 1 Quantitative data of TG analysis for the different synthesis temperatures.

Synthesis temperature (°C)	H ₂ O weight loss (%)	Weight loss temperature (°C)	TBOT weight loss (%)	Decomposition temperature (°C)
180	6	45	31	318
200	7	43	30	317
220	6	42	30	318
240	4	54	27	314



attributed to H₂O outgassing, and the second one at around 370 °C (higher than for pristine TiO₂ nanoparticles) is correlated with CO₂ detected by mass spectroscopy. This second weight loss can be assigned to the combustion of around 3 wt% of carbon. This carbon amount is in accordance with Devina *et al.* who obtained 0.2-4.1 wt% carbon depending on the carbon impregnation method³⁸. The weak combustion temperature is probably due to the amorphous nature of the carbon material formed on the surface of the particles³⁹. Complementary to mass spectroscopy, Raman spectroscopy is performed to evidence the obtaining of carbon. Indeed, it consists in a powerful tool to characterize carbon materials. Six active Raman vibration modes due to the D_{2d} local symmetry of anatase TiO₂ are observed on the spectrum (Fig. 5): 1A_g + 2B_{1g} + 3E_g^{40,41} at range 100-750 cm⁻¹ identified by purple zone.

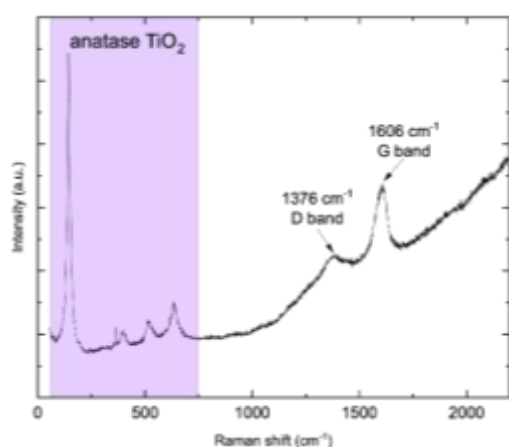


Fig. 5 Raman spectrum of TiO₂@C (457 nm wavelength).

D and G bands respectively present at 1376 and 1606 cm⁻¹ corroborate the presence of carbon material as revealed after TGA analysis. D band (disordered sp² carbon) is expected around 1350 cm⁻¹^{31,42-45} but a shift is observed due to the excitation wavelength used⁴⁶. Here I_D/I_G ratio is 0.22 but due to its parabolic evolution, it is not possible to conclude about carbon crystallinity. Indeed, as described by Merlen *et al.*, D band intensity increases with disorder, reaches a maximum and then, decreases when carbon being close to amorphous⁴⁷. High-Resolution Transmission Electronic Microscopy (HR-TEM) was used to study carbon morphology. Selected Area Electron Diffraction (SAED) reveals diffraction plans of anatase TiO₂ (Table 2) in accordance with XRD measurement, and the good crystallinity of the particles. First TEM micrograph (Fig. 6 (a)) exhibits aggregated particles into an amorphous matrix. HR-TEM micrograph (Fig. 6 (b)) evidences atomic planes of the particles demonstrating titanium dioxide's crystallinity and allows to determine the size of the crystals, which is 8.5 ± 1.4 nm in accordance with XRD calculation. STEM-EDX elementary mapping images highlight the presence of carbon (Fig. 7). Thus, TG-MS, Raman spectroscopy and HR-TEM confirm the presence of carbon in samples thermally treated under H₂ using TBOT as a carbon precursor.

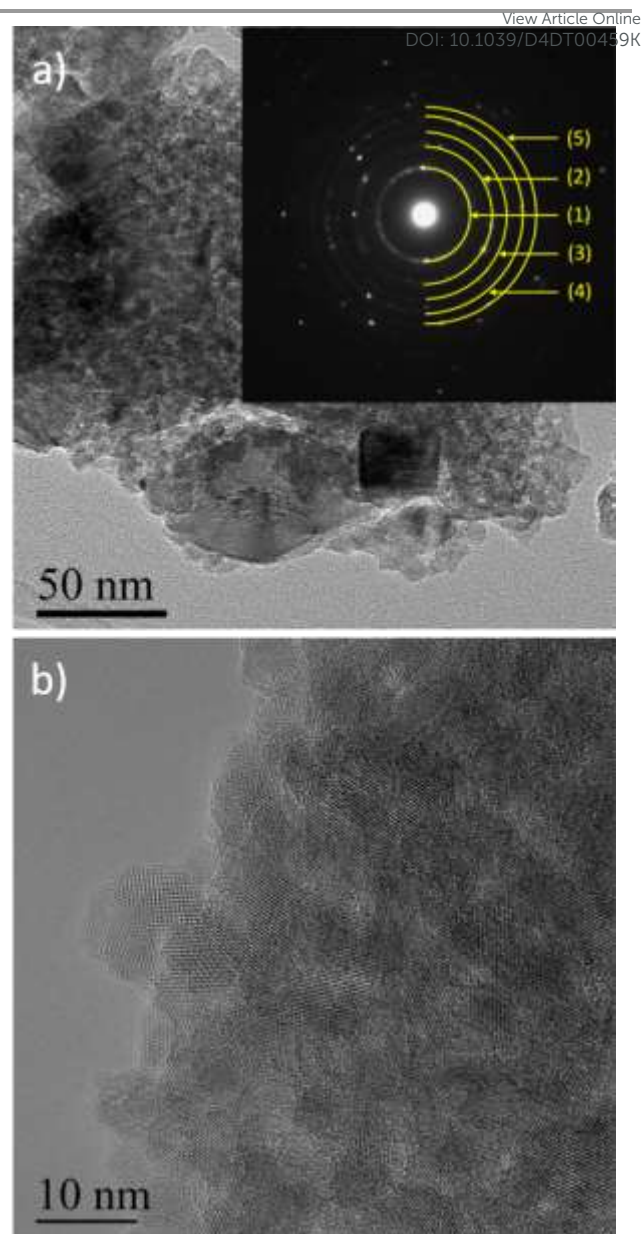


Fig. 6 BF-TEM with SAED a) and HR-TEM of TiO₂@C b).

Table 2 indexation from SAED.

Yellow half-circle (#)	d-spacing (nm)	(hkl)
(1)	0.3524	(101)
(2)	0.2394	(004)
(3)	0.1908	(200)
(4)	0.1711	(105)
(5)	0.1499	(213)



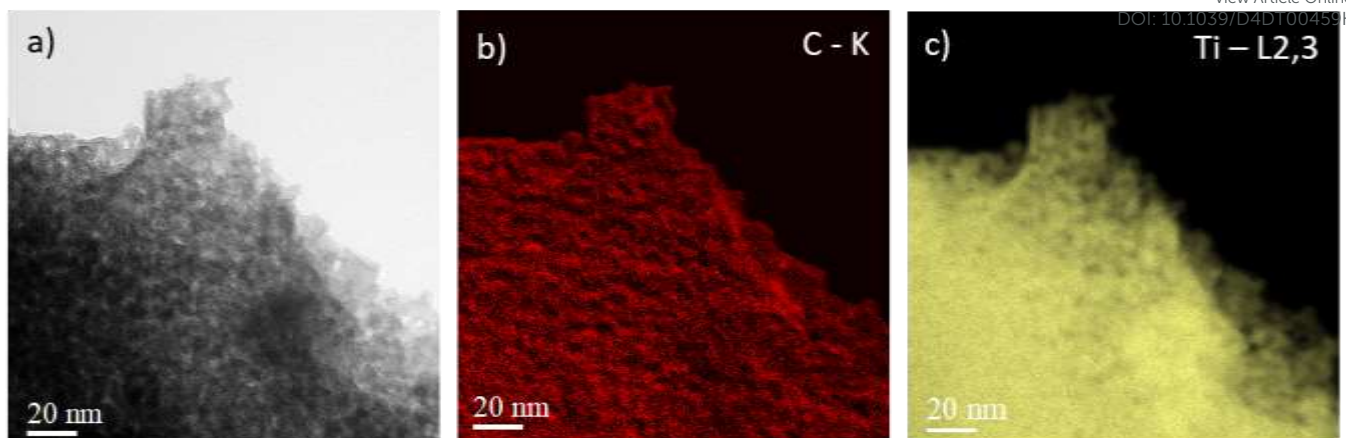


Fig. 7 BF-TEM a) and TEM elemental mapping images of carbon b) and titanium c) for $\text{TiO}_2@\text{C}$.

Electrochemical characterization

Pristine TiO_2

Galvanostatic curves of pristine TNPs (*i.e.* without carbon), are presented Fig. 8. On the first discharge (sodiation) curve, three slopes can be noted ; the first one between 2 and 1.2 V vs. Na^+/Na , the second one between 1.2 and 0,25 V vs. Na^+/Na and the last one until 0 V vs. Na^+/Na . Wu *et al.* has described that the first one at high potential is related to a pseudo-capacitive

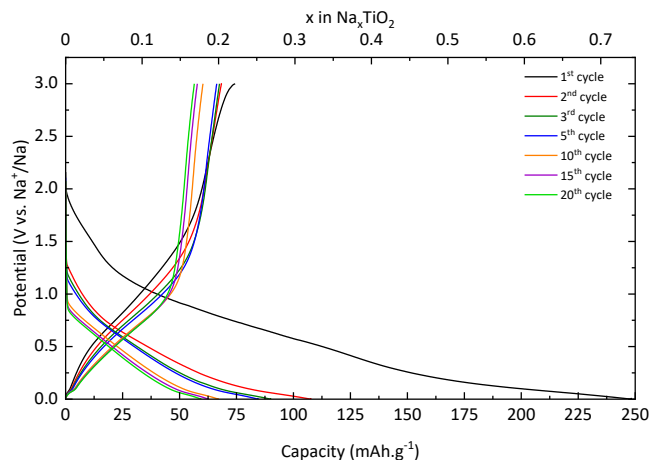
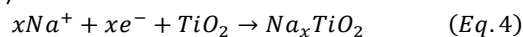


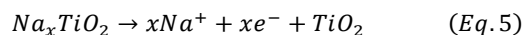
Fig. 8 charge/discharge curves of pristine TiO_2 at C/20 rate.

process where no structural changes are observed¹³. Then, Na^+ insertion occurs with a structural transition and finally a disproportionation reaction with intermediate phase formation. The next cycles curves adopt a S-shape behaviour due to poor low crystallinity. First discharge curve indicates an intercalation of 0.75 Na^+ and a deintercalation of only 0.25 Na^+ into TiO_2 that corresponds to an irreversible capacity of 175 mAh.g^{-1} and a reversible capacity of 75 mAh.g^{-1} . A fraction of Na^+ ions is continuously consumed to form the SEI, as shown by curves shift to lower capacity values, especially after the first cycle. At the 20th cycle, 0.18 Na^+ can be intercalated and 0.17

Na^+ are deintercalated. These results demonstrate the electrochemical instability of TiO_2 nanoparticles towards electrolyte (Fig. 8). The evolution of the capacity versus the number of cycles shows that the first irreversible capacity is significant, and the capacity continuously decreases (Fig. 9). At the first cycle, the coulombic efficiency reaches 30 % due to SEI formation and reaches 95 % at 20th cycle that is an acceptable value for this kind of material and corresponds to results mentioned by Ge *et al.*²⁷. Specific capacity goes down to 60 mAh.g^{-1} at the 20th cycle, below the values mentioned in the literature^{11,13,19,27,37}. The 30 % TBOT residues after the synthesis as electronic insulator can explain this result. Incremental dQ/dE versus E curves presented Fig. 10 allow determining the sodiation reaction potentials. In reduction path, the two peaks at 0.04 and 0.75 V vs. Na^+/Na corresponds to the sodiation reaction (Eq.4):



Desodiation reaction takes place at the same potential as sodiation reaction *i.e.* 0.75 V vs Na^+/Na (Eq.5):



In addition, the peaks at 0.04 V vs. Na^+/Na in reduction and 0.08 V vs. Na^+/Na are also attributed to electrolyte decomposition according to Wu *et al.*¹³. Finally, the signal between 1.3 and 0.9 V vs Na^+/Na that shifts to lower and lower potential values, is due to SEI formation, that corroborates results previously mentioned and demonstrates the electrochemical instability of TNPs toward electrolyte.



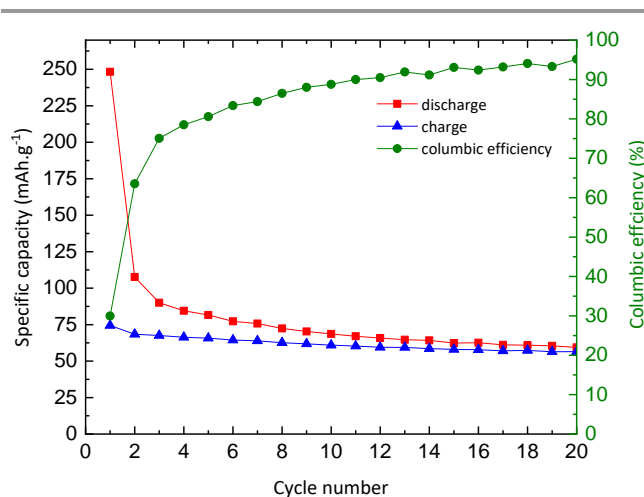


Fig. 9 evolution of charge (blue), discharge (red) capacities, and columbic efficiency (green) as function of the number of cycles.

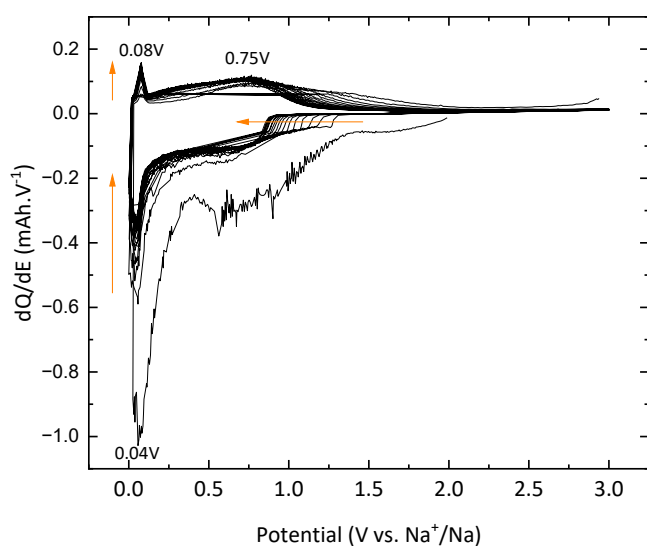


Fig. 10 dQ/dE curves of pristine TiO₂.

TiO₂@C

TNPs with carbon (TiO₂@C) were prepared as described in experimental section. As for pristine TiO₂, galvanostatic measurements were used to characterize electrochemical properties of TNPs@C. On Fig. 11, the first discharge curve reveals a capacity of 220 mA.h.g⁻¹ that corresponds to 0.65 intercalated Na⁺, with a very long plateau at low potential and during the first charge, 0.33 Na⁺ are deintercalated. At the 3rd cycle, the capacity reaches 115 mA.h.g⁻¹, twice that of pristine TiO₂. Then, the capacity at the 20th cycle reaches 76 mA.h.g⁻¹ (retention capacity of 67%), which is much higher than pristine TiO₂. Different values are summarized in Table 3. SEI formation seems to be reduced, demonstrating the stabilization of TNPs embedded in carbon compared to pristine TiO₂. Indeed, the initial coulombic efficiency at 1st cycle is 51% versus 30% for pristine TiO₂. Therefore, the carbon contribution to the stabilization and the improvement in electrochemical performances is significant.

The dQ/dE curve presented in Fig. 12 shows that sodium deinsertion (Eq. 4) takes place at a higher potential i.e. 0.9 V vs. Na⁺/Na than pristine TiO₂ and the insertion mechanism (Eq. 5) occurs at 0.6 V vs. Na⁺/Na which corresponds to the one mentioned by Ge *et al.*²⁷. Moreover, electrolyte decomposition and sodium redox reactions still happen at low potential.

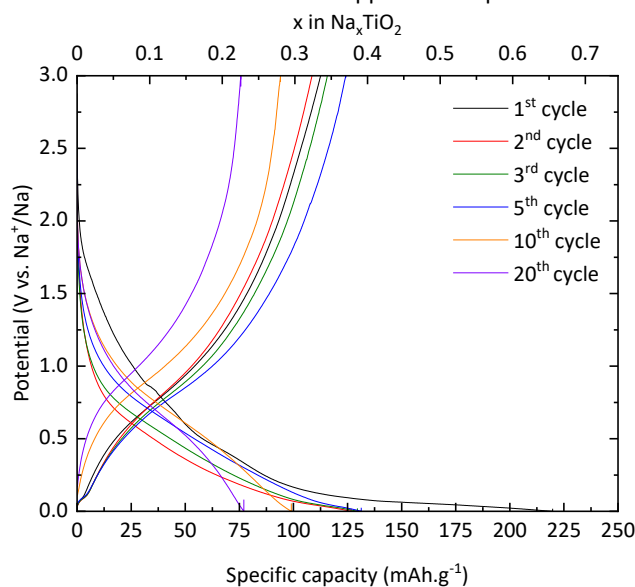


Fig. 11 charge/discharge curves of TiO₂@C.

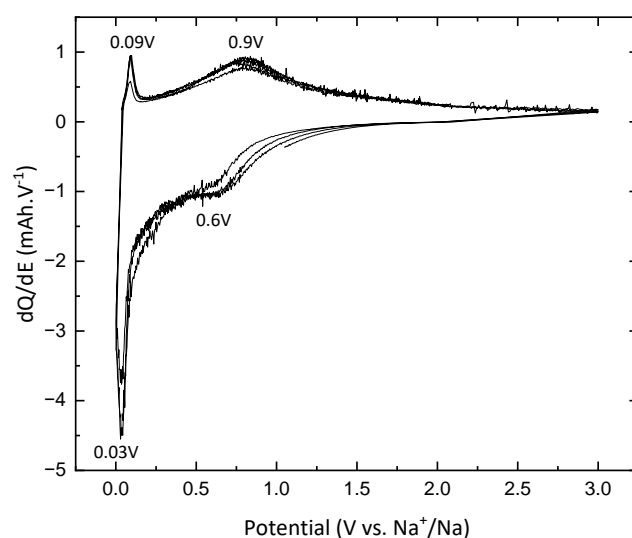


Fig. 12 dQ/dE curves of TiO@C.

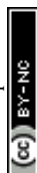


Table 3 Summary of characteristic values.

Pristine TiO ₂			
	Q discharge (mAh/g) - x _{Na}	Q charge (mAh/g) - x _{Na}	Efficiency (%)
Cycle 1	248.3 – 0.74	74.1 – 0.22	30
Cycle 3	90 – 0.27	67.5 – 0.20	75
Cycle 5	81.6 – 0.24	65.8 – 0.20	80.6
Cycle 10	68.6 – 0.20	60.9 – 0.18	88.8
Cycle 20	59.3 – 0.18	56.5 – 0.17	95.2
TiO ₂ @C			
	Q discharge (mAh/g) - x _{Na}	Q charge (mAh/g) - x _{Na}	Efficiency (%)
Cycle 1	219.8 – 0.65	112.6 – 0.34	51.2
Cycle 3	129.5 – 0.39	115.7 – 0.34	89.3
Cycle 5	131.3 – 0.39	124.2 – 0.37	94.6
Cycle 10	128.7 – 0.38	128.2 – 0.38	99.6
Cycle 20	77.1 – 0.23	75.7 – 0.22	98.2

Conclusions

Titanium dioxide nanoparticles were successfully obtained by microwave assisted method. TBOT residues were used as carbon precursor to prepare embedded carbon TNPs. TNPs@C exhibits electrochemical stabilization by improving efficiency during first cycle that corresponds to a decrease in the SEI formation. By carbon addition, capacity reached 115 mAh.g⁻¹ at the 3rd cycle against 67 mAh.g⁻¹ for pristine TNPs. Electrochemical performances of TiO₂@C presented in this work are still lower than those mentioned in other studies^{11,31,48}. If our results are promising, with an ICE of only 51% and a capacity retention of 67%, the materials need further optimization (size and shape of TiO₂ nanoparticles; anchorage, thickness and porosity of the carbon matrix) before widespread commercialisation. The goal of this work is not the full optimization of the electrochemical performances and cycle life of TiO₂ as an anode for sodium-ion batteries, but mainly to bring a proof-of-concept for the innovative and simple synthesis of TiO₂@C intercalation material. Here, this work presents an original way for synthesizing TiO₂ nanoparticles by fast microwave assisted route. Moreover, it constitutes an advanced demonstration on the possibility to use one precursor as both Ti and C precursor. Nevertheless, an optimization of the TiO₂@C material can be considered on several points: control of the residual amorphous material after the microwave assisted step, morphology and crystallinity of TiO₂ anatase, carbon matrix optimization...

Moreover, the electrochemical stabilization of TiO₂ nanoparticles toward electrolyte thanks to carbon addition was proofed.

Author Contributions

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Tanguy Soudant: Formal Analysis, Investigation, Writing Original

Draft, Writing - Review & Editing, Visualization.

Solenne Fleutot: Conceptualization, Methodology, Validation, Investigation, Review & Editing, Visualization, Supervision

Stephanie Bruyère: Formal Analysis, Review & Editing

Lucie Speyer: Formal Analysis, Review & Editing

Mickaël Bolmont: Methodology, Review & Editing,

Thomas Girardet: Methodology, Review & Editing

Loris Raspado: Methodology, Review & Editing

Claire Hérold: Conceptualization, Writing - Review & Editing, Visualization

Sébastien Cahen: Conceptualization, Methodology, Validation,

Formal Analysis, Resources, Writing - Review & Editing,

Visualization, Funding acquisition, Supervision, Project administration

Conflicts of interest

There are no conflicts to declare.

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