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Titanium dioxide (TiO$_2$) is an important material for photovoltaics, photocatalysis, sensors and lithium ion batteries. Various morphologies of TiO$_2$ nanomaterials have been synthesized, including zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires and nanotubes, as well as three-dimensional (3D) nanostructures. However, the successful fabrication of 2D TiO$_2$ nanomaterials, TiO$_2$ nanomaterials with various morphologies have been synthesized, including zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires and nanotubes, as well as three-dimensional (3D) nanostructures. But the two-dimensional (2D) TiO$_2$ nanostructures, which are expected to have more promising properties and applications, are rarely reported. Herein, we report a surfactant-assisted exfoliation method to synthesize TiO$_2$ 2D nanosheets. It has been revealed that tetrabutylammonium hydroxide (hereafter TBAOH) as a surfactant plays a crucial role in retaining the 2D nanosheet structures. Compared with TiO$_2$ nanotubes and anatase TiO$_2$ nanoparticles, the as-prepared TiO$_2$ single layered nanosheets delivered much higher capacities as an anode of the coin-type Li ion cell, with a reversible capacity of 82.2 mAh g$^{-1}$ at the 630th cycle at the current density of 2000 mA/g.

Recently, two-dimensional (2D) nanosheets composed of one- or a few-layers of atoms, such as graphene and transition metal chalcogenides, have gained great attention owing to their large surface areas and related unique properties. The common feature of these 2D nanosheet materials is that their counterpart bulk crystals are layered structures, making it possible to prepare these 2D nanosheets via an exfoliation route. However, it is still a big challenge to synthesize sheet-like structures for those materials with non-layered crystal structures. Titanium dioxide (TiO$_2$) is an important material for photovoltaics, photocatalysis, sensors and lithium ion batteries. TiO$_2$ nanomaterials with various morphologies have been synthesized, including zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanowires and nanotubes, as well as three-dimensional (3D) nanostructures. However, the successful fabrication of 2D TiO$_2$ nanosheets has rarely been reported. Unlike the above mentioned 2D nanomaterials, TiO$_2$ polymorphs, such as anatase, rutile, brookite, are non-layered crystal structures due to the strong ionic interactions between the metal cations and oxygen anions, therefore, it is hard to prepare TiO$_2$ 2D nanosheets via a conventional exfoliation route. Bottom up chemical synthesis strategy was then proposed to obtain 2D TiO$_2$ nanosheets. For instance, in 2008, Stucky group reported the successful synthesis of TiO$_2$ single layer nanosheets through a bottom-up method starting from titanium isopropoxide in a nonaqueous system and with oleylamine as a surfactant. However, it is hard to make the nanosheets in large quantity using such a bottom up synthesis technique. To date, we are still lack of a convenient fabrication method through which TiO$_2$ nanosheets in large quantity can be synthesized.

Here we report a new exfoliation method to fabricate monolayer TiO$_2$ nanosheets. The method is inspired from the synthesis method of TiO$_2$ nanotubes. Scheme 1a illustrated the formation process of TiO$_2$ nanotubes. When TiO$_2$ crystals are treated with NaOH aqueous solution at an elevated temperature, layered titanates are formed and can be further exfoliated into single layer titane nanosheets. The resultant nanosheets are instable in morphology due to the existence of dangling bonds such as negatively charged Ti-O- and positively charged Ti+. The nanosheets tend to be rolled up to form nanotubes, which are more stable. In this well established process, titane nanosheets are actually formed as an intermediate product, which however are hard to be retained due to their instability in morphology. One possible strategy of retaining the titane nanosheets is to reduce the surface energy of the intermediate nanosheets by introducing a proper surfactant. In this work, the surfactant selected is TBAOH, which is a commonly used cation surfactant and has a large molecule size due to its four butyls. The TBA$^+$ could attach to the negatively charged Ti-O- bonds on both sides of the nanosheets and thus reduce their surface energy effectively, making the nanosheets stable in the solution.

On the basis of the above idea, the synthesis of the targeted TiO$_2$ nanosheets was conducted in an alkaline solution using anatase TiO$_2$ nanoparticles (Sigma) as the raw material and TBAOH as the surfactant. The deployed temperature was 130°C and the reaction time was 24 hours. TiO$_2$ nanosheets in large quantity (for example, in grams) can be synthesized using this method. Details of the experiments are provided in Supporting Information. The XRD pattern, SEM and TEM images of the raw material were presented in Table 1.
TiO$_2$ nanoparticles were shown in Figure S1. The XRD pattern revealed that the raw TiO$_2$ nanoparticles were merely anatase with a little rutile (Figure S1a). The particle size of the TiO$_2$ nanoparticles was about 50 to 200 nm with irregular morphologies, as shown in Figure S1b and S1c. The XRD pattern of the as-prepared TiO$_2$ nanosheets was shown in Figure S2. It revealed that the crystallinity of the nanosheets was not good. A hump around 25° was observed, corresponding to (101) peak of anatase.

Figure 1. (a) and (b) Low and high magnification SEM images of as-synthesized TiO$_2$ nanosheets respectively, (c-d) Distinct TEM image of the product, (e) HRTEM of selected by the white frame in (d), (f) the corresponding SAED of the nanosheets in figure (c).

Figure 1 showed distinct SEM and TEM images of the as-synthesized TiO$_2$ nanosheets. From Figure 1a and 1b, it could be seen that the product was the aggregates of nanosheets. To get clear TEM image, the product was dispersed in water with ultrasonic treatment. The TEM image in Figure 1c showed very thin nanosheets with about 200 nm in length and 20 to 50 nm in width. A higher magnification TEM image in Figure 1d revealed that the nanosheets had turn-up edge. The high resolution TEM image of the marked area (white frame) in Figure 1d was shown in Figure 1e. Lattice fringes with a spacing of 0.35 nm, corresponding to the $d_{(101)}$ of the anatase phase, were clearly observed from the turn-up edge of the nanosheets, which indicated that the nanosheets grew along [101] direction. The sample was further characterized using SAED and Raman. Figure 1f was an electron diffraction pattern obtained by focusing the electron beam on the sample of Figure 1c. The pattern was composed of imperfect rings with discrete points, which could be indexed as anatase (200) and (211) planes, respectively. Raman spectrum of the as-prepared nanosheets was shown in Figure S3. The main peaks, 200 cm$^{-1}$, 394 cm$^{-1}$, 515 cm$^{-1}$, 637 cm$^{-1}$ were the typical Raman bands of anatase, confirming the formation of anatase. The thickness of the obtained TiO$_2$ nanosheets was further characterized using TEM. As shown in the Inset in Figure 2a, the thickness of TiO$_2$ nanosheet was about 0.40 nm, which was very close to the height of one layer of [TiO$_6$] octahedron (0.38 nm, Figure 2b). This result suggested that the obtained TiO$_2$ nanosheets were single layered. AFM was also used to characterize the thickness of TiO$_2$ nanosheet. However, the as-obtained TiO$_2$ nanosheets were hard to be fully dispersed during the AFM testing. As shown in Figure S4, a thickness of 0.952 nm was obtained. Such value is larger than the theoretical thickness of a two-layer TiO$_2$ nanosheet, indicating the loose restacking of two individual TiO$_2$ nanosheets.

In order to understand the formation process and mechanism of TiO$_2$ nanosheets, the effects of the experiment parameters on the formation of TiO$_2$ nanosheets were further investigated. It was no doubt that TBAOH played a key role in the synthesis of the TiO$_2$ nanosheets. As can be seen from Figure S5, the resulting products showed a strong dependence on the amount of TBAOH at 130 °C. When there was no TBAOH, the products were the mixture of nanotubes and unreacted nanoparticles (Figure S5a). When 4 g of TBAOH was added, there were nanosheets formed in the product, as well as nanotubes and unreacted nanoparticles (Figure S5b). Further increasing the amount of TBAOH to 8 g, as shown in Figure S5c, nanotubes were nearly disappeared and only nanosheets and unreacted nanoparticles existed in the product. According to the formation mechanism of TiO$_2$ nanotubes reported by the previous papers, the single layer nanosheet will roll up to nanotube if there was no TBAOH. Obviously, TBAOH, as a surfactant, effectively prevent the formation of nanotubes and thus promote the formation of nanosheets.

Samples synthesized at different durations and temperatures...
were collected when the amount of TBAOH was fixed at 8 g. For the sample treated at 130 °C for 4 h (Figure 3b), layered structures were formed on the surfaces of nanoparticles, as compared to the smooth surface of the raw nanoparticles (Figure 3a). This indicated that layered titanates were formed upon the reaction between NaOH and TiO$_2$. Some single-layer nanosheets were even observed surrounding the nanoparticles, suggesting that the formed layered titanates tended to be delaminated from the mother particles. As the reaction time was prolonged to 12 h, more nanosheets were formed, which were closely bound up with the TiO$_2$ nanoparticles (Figure 3c). With increasing the reaction time to 24 h, most of the TiO$_2$ nanoparticles disappeared and TiO$_2$ nanosheets were formed almost completely (as shown in Figure 1). Temperature dependent experiments were carried out by varying the reaction temperature from 80 °C, 130 °C to 180 °C. The reaction time was fixed at 24 hours and the amount of surfactant is 8 g. When the reaction was carried out at 80 °C, a few nanosheets were formed, as shown in Figure S6a. However, if the reaction temperature was too high, such as 180 °C, the product only consisted of nanobelts instead of nanosheets (Figure S6b). At such a high temperature, single layer nanosheets tend to be stacked together to become more stable even in the presence of surfactant. From these studies, it was concluded that the moderate temperature (130 °C) was critical to synthesize the single-layer nanosheets.

According to the discussion above, our idea of synthesizing TiO$_2$ nanosheets by introducing a surfactant to retain the intermediate titanate nanosheets was proved to be feasible. The more detailed formation mechanism was illustrated in Scheme 2. The crystalline structure (anatase) of TiO$_2$ is on the basis of TiO$_6$ octahedra, which share vertices and edges to build up the three-dimensional framework. During the alkali-hydrothermal process, the Ti–O–Ti bonds were broken and the intermediate titanate layered structures with positively charged Ti– dangling bonds and negatively charged Ti–O– dangling bonds were formed. The XRD pattern in Figure S2 verified the formation of titanate. Upon the addition of TBAOH surfactant, TBA$^+$ ions, together with OH$^-$ and Na$^+$ ions, bond with these dangling bonds to neutralize the charge. Therefore, the surface energy of the intermediate titanate nanosheets was reduced and thus the rolling up process was stopped. With the reaction proceeded, more and more Ti–O–Ti bonds were broken and the resulting nanosheets started to peel off from the nanoparticles. Upon washing with acids such as HCl or HNO$_3$, the cations on the nanosheets were removed, and thus the titanate nanosheets were changed into TiO$_2$ nanosheets. To demonstrate the promising properties of 2D TiO$_2$ nanosheets, the as-obtained TiO$_2$ nanosheets were fused as the anode material and assembled into a CR2106 coin-type cell for electrochemical tests. The charge/discharge profiles of TiO$_2$ nanosheets under the current density of 100 mA g$^{-1}$ at the first three cycles were shown in Figure 4a. The first discharge and charge capacities were 197.6 and 151.6 mAh g$^{-1}$, respectively, demonstrating an initial coulombic efficiency of 79.3%. Such value is comparable to those reported efficiencies in literature for TiO$_2$ in anode applications. In the subsequent two cycles, the coulombic efficiency of TiO$_2$ nanosheets quickly rose to above 90%, with stable reversible capacities of 150.8 and 149.1 mAh g$^{-1}$, respectively. No evident potential plateau was observed in these charge/discharge profiles, which has also been demonstrated in the electrochemical studies of other two-dimensional materials, such as graphene and MoS$_2$. The TiO$_2$ nanosheets anode was further tested with increasing current densities up to 10000 mA g$^{-1}$. The corresponding charge/discharge profiles were shown in Figure 4b. As comparison, anodes fabricated from TiO$_2$ nanotubes and anatase nanoparticles (raw material) were also tested under the same condition. Despite the fact that TiO$_2$ nanotubes demonstrated a slightly higher first cycle capacity of 183.5 mAh g$^{-1}$, TiO$_2$ nanosheets showed much superior electrochemical performances at high current densities. For instance, as shown in Figure 4c, the reversible capacity of TiO$_2$ nanotubes was quickly faded to 80.4 mAh g$^{-1}$ at the current density of 1000 mA g$^{-1}$. In contrast, TiO$_2$ nanosheets delivered a reversible capacity of 111.7 mAh g$^{-1}$ at the same current density. The reversible capacities of TiO$_2$ nanosheets were 127.2, 114.4, 103.3, 85.8, 77.7, 69.8, and 60.4 mAh g$^{-1}$ at the current densities of 500, 1000, 2000, 4000, 6000, 8000, and 10000 mA g$^{-1}$, respectively, showing minor drops in capacities as current density increased. The TiO$_2$ particles showed much inferior electrochemical performances at high current densities. For instance, as shown in Figure 4c, the reversible capacity of TiO$_2$ nanotubes was quickly faded to 80.4 mAh g$^{-1}$ at the current density of 1000 mA g$^{-1}$. In contrast, TiO$_2$ nanosheets delivered a reversible capacity of 111.7 mAh g$^{-1}$ at the same current density. 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... electrochemical performances as compared to the nanotubes and nanosheets, delivering only 6.9 mAh g\textsuperscript{-1} at the current density of 10000 mAh g\textsuperscript{-1}. The cells were subjected to further cycling test at a current density of 2000 mA g\textsuperscript{-1} for 630 cycles. As shown in Figure 4d, stable reversible capacities were achieved by all three materials. Among them, TiO\textsubscript{2} nanosheets delivered much higher capacities than the other two, with a reversible capacity of 82.2 mAh g\textsuperscript{-1} at the 630th cycle.

In conclusion, a new exfoliation method for producing single layer TiO\textsubscript{2} nanosheets was reported, which was developed from a well established TiO\textsubscript{2} nanotube synthesis process. By adding a surfactant TBAOH, the intermediate titanate nanosheets were retained and thus the formation of TiO\textsubscript{2} nanosheets was promoted. The obtained TiO\textsubscript{2} nanosheets showed promising applications as Li ion battery anode, demonstrating better electrochemical performance than TiO\textsubscript{2} nanotubes and anatase nanoparticles. TiO\textsubscript{2} nanosheets in large quantity can be fabricated through this exfoliation method.

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Notes and references

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