Carbon-Infused MoS₂ Supported on TiO₂ Nanosheet Arrays for Intensified Anodes in Lithium Ion Batteries

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Abstract

Graphite anodes in commercialized lithium ion batteries are meeting the bottleneck for future high-performance electronic devices. Strategies has been applied to improve the cycle and rate capacity of the anode active materials. Herein, a two-step hydrothermal approach is presented to synthesize $\text{TiO}_2@\text{MoS}_2/\text{C}$ as enhanced anodic electrode. The $\text{TiO}_2@\text{MoS}_2/\text{C}$ electrode delivers a satisfying cycle performance of 643.4 mAh/g on average at a current of 100 mA/g upon 100 cycles. The comparison study shows that $\text{TiO}_2@\text{MoS}_2/\text{C}$ are superior to its individual part when assembled into batteries. The result also demonstrates that the support from TiO_2 nanosheet arrays is essential to achieve both improved cycle and rate performance. Without TiO_2 scaffold as an intermediate, MoS_2/C is not able to firmly attach to Ti substrate and tends to be exfoliated upon cycling. Besides, the presence of carbon remarkably improves the poor conductivity of TiO_2 and MoS_2 , which is beneficial to elevate rate capacity at high currents.

Keywords: $\text{TiO}_2@\text{MoS}_2/\text{C}$; carbon infused MoS_2 ; TiO_2 nanosheet arrays; intensified anodes

1. Introduction

Lithium ion batteries, witnessing the booming of modern technology, are essential for supporting ubiquitous portable electronic devices nowadays. Nevertheless, with an ever-increasing demand for advanced devices with high energy and power density like hybrid electric vehicles, commercialized lithium ion batteries used these days reluctantly provide satisfactory performance [1]. That is partially because the anode is made up of graphite with theoretical capacity of only 372 mAh/g. In addition, lithium dendrites are likely to form on the surface of the graphite, inducing a safety issue. Thus, extensive study has been devoted to seeking for effective approaches to achieve intensified anodes.

On one hand, transition metal oxides and dichalcogenides are promising candidates because of their high capacity and relatively high working voltage in comparison with the graphite, which to some extent avoids the lithium dendrites formation [2-3]. However, concomitant large volume expansion/contraction upon cycling are inevitable, leading to electrode pulverization and irreversible capacity loss [4]. To solve this problem, two dimensional nanoarchitectures are employed to effectively remedy the electrochemical performance of the transition metal oxides and dichalcogenides [5]. 2D structures like nanosheets, are not only beneficial to provide large exposed reactive surfaces as well as specific facets, but also able to shorten the diffusion pathway because of their thin thickness. More importantly, open space in between nanosheets is conducive to accommodate volume changes, buffering mechanical strain. On the other hand, in particular, TiO_2 nanosheet arrays have been

synthesized to function as stable scaffolds to be loaded with other materials of high capacity to compensate its intrinsic shortcomings [6-8]. It should be noted that utilizing array scaffolds with large exposed surface area can suppress the aggregation of active materials after cycling, ensuring a high capacity retention. In addition, binders and additives are eliminated in the arrays so as to conserve space for more reactive materials. Besides, in virtue of the morphological resemblance with graphene, layered MoS₂ nanosheets are envisaged to achieve better battery performance for its advantages in structural property [9-12]. Therefore, in order to enhance the capacity and simultaneously maintain good stability, the combination of both two dimensional TiO₂ and MoS₂ into a hybrid electrode, in which TiO₂ as a solid foundation firmly support high-capacity MoS₂, may meet the crucial requirement. There are limited few reports regarding the composite TiO₂@MoS₂ electrode exhibiting good cycle performance, indicating the feasibility of combining TiO₂ with MoS₂, but none of which is based on nanosheet array hybrid structure and film electrodes [13-16].

Despite good cycle performance, rate capacity should be taken into account as well because actual situation needs rapid charge/discharge. The oxides or sulfides suffer a severe decay at high rates owing to their intrinsic low electrical conductivity. Thus, it is conventional and effective to combine the prepared electrode with another conductive material to enhance the conductivity. It is generally acknowledged that the incorporation of carbon material is a predominant methodology to achieve improved performance with high efficiency [17-20]. For instances, Liu et al. utilized conformal coating strategy to hydrothermally synthesize mesoporous TiO₂ hollow spheres with

the assistance of glucose. With the presence of graphitic carbon, the result showed extended cycle performance at a high rate of 5 C [21].

Provoked by the aforesaid study, herein, we propose a structure of $\text{TiO}_2@\text{MoS}_2$ arrays with the presence of carbon through facile synthetic procedures for anodic electrodes in lithium ion batteries. This ternary array configuration has rarely been reported to the best of our knowledge. The prepared $\text{TiO}_2@\text{MoS}_2/\text{C}$ electrode was optimized by varying the amount of loaded MoS_2 . When measured as an electrode in a half cell, it exhibited a high capacity of 457 mAh/g at 100 mA/g even after 100 cycles, 643.4 mAh/g on average. The intensified performance is ascribed to the following aspects. First, TiO_2 sheet array attached to the Ti substrate served as a stable scaffold for supporting MoS_2 during long cycles, and a strong adhesion to the current substrate for avoiding capacity loss from active materials detachment. Second, MoS_2 in the form of tiny-sheet assembly with large surface area and inter space voids facilitated full contact with electrolyte for ensuring efficient and rapid reaction as well as volume expansion induced by electrochemical reactions with Li ions. Third, the presence of carbon greatly improved the poor conductivity of TiO_2 and MoS_2 , beneficial to rate capacity at high currents. Fourth, the hybrid worked synergistically to obtain a superior performance as compared to either individual part, indicating that the combination of these materials could help to compensate with each other and unleash their potential.

2. Experimental

2.1 Synthetic procedures

The synthetic process was divided into two steps as shown in Figure 1. In Step I, TiO₂ nanosheet arrays were formed through a facile hydrothermal method, followed by annealing treatment as our previous reports.⁸ In brief, a pure Ti foil was immersed into 1 M NaOH solution and then sealed in a Teflon-lined stainless steel autoclave subjected to 180 °C for 14 h. The resultant foil was rinsed and then immersed in 1 M diluent hydrochloric acid solution for 30 min to replace Na⁺ with H⁺. After it was annealed at 500 °C for 1 h, TiO₂ nanosheet arrays on Ti substrate were prepared. In step II, MoS₂/C was concurrently loaded onto TiO₂ nanosheet array with one spot. As-prepared TiO₂ nanosheet was put in the autoclave with the solution of 0.15 g sodium molybdate dihydrate, 0.3 g thiourea and 0.2 g glucose dissolved in 40 mL deionized water. The autoclave was heated at 200 °C for 20, 22 and 24 h, which could straightforwardly control the loading amount of MoS₂/C. After that, the resulted sample was thoroughly rinsed with deionized water and ethanol, dried at 70 °C for 24 h and then transferred to a tube furnace for annealing at 600 °C for 2 h under the flowing of H₂/N₂ with a volume ratio of 1:9. Prior to any further measurements, the sample naturally was cooled down to room temperature. For comparison, direct growth of pure MoS₂/C on the Ti substrate was performed as the aforementioned procedure with omission of Step I. As a control, TiO₂@MoS₂ was also synthesized without glucose addition. All reagents were used directly without further purification.

Insert Figure 1.

2.2 Characterization, battery assembly and measurement

The structure and phases of the prepared samples were determined by X-ray diffraction measurement (XRD, X'PertPRO MRD, PANalytical, Netherlands, Cu K α radiation). Raman spectra (LabRAM HR JY-Evolution, excitation wavelength $\lambda=532$ nm) were used to reveal more structural information and verify the existence of carbon. Their morphology was observed by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) as well as high-resolution transmission electron microscopy (HRTEM, Titan G² 60-300 Probe Cs Corrector) equipped with energy dispersive spectroscopy (EDS, EDAX genesis 7000). X-ray photoelectron spectroscopy (XPS) measurement was also conducted on a VG ESCALAB 250 spectrometer (Thermo Electron, UK) with monochromatic Al K α (1486.6 eV) irradiation to analyse binding energy of elements in different status.

As-prepared samples were cut into circles and assembled into a CR2016 half coin cell system. The sample was directly employed as working electrode with metallic Ti substrate as a current collector, while a slice of lithium foil was utilized as counter and reference electrodes. The electrolyte consisted of LiPF₆ (1 M) dissolved in a mixture of ethylene carbonate (EC), ethylmethyl carbonate (EMC) and dimethyl carbonate (DMC) with a volume ratio of 1: 1: 1. The separator was a polypropylene film (Celgard2000). Battery assembly was conducted in a glove box (Mbraun, Germany) filled with inert argon. The assembled batteries were kept still for 12 h before any measurement. The galvanostatic charge/discharge measurement at different currents was performed on a BTS-55 Neware battery testing system (Shenzhen, China) at room temperature. Cyclic

voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were investigated with an electrochemical working station (CHI660E) within the range of 0.05 to 3.0 V and 10 mHz to 100 kHz, respectively. Note that each voltage mentioned in this paper was versus Li/Li⁺. Calculation details regarding the mass loading of active materials were included in Supplementary Information.

3. Results and discussion

The XRD patterns are displayed in Figure 2a. The samples prepared with different reaction durations in Step II shared similar XRD pattern. All peaks from the three samples were indexed to anatase TiO₂ (JCPDS No. 73-1764) and MoS₂ (JCPDS No. 6-97) in addition to metallic Ti substrate (JCPDS No. 1-1198). The peak positioned at 25.3°, 48.1° and 63.0° was assigned to plane (101) (200) and (204) of anatase TiO₂, respectively [22]. Sharp peak shape indicated good crystallinity of the prepared samples. Besides, the diffraction peaks located at 28.7°, 32.3° and 57.5° resulted from plane (004) (100) and (110) of semi-conductive 2H-MoS₂, respectively, which was in accordance with reported results [23]. The results above explicitly showed that TiO₂@MoS₂ composites were successfully fabricated. However, due to the low crystallinity of carbon, the XRD data were unable to show the trace of carbon.

Insert Figure 2.

Therefore, Raman spectrum was introduced to make up the deficiency. Owing to

the intensive similarity of the structure and components for the three samples, for simplicity, only the spectrum of the sample with reaction time of 22 h in Step II was shown as proof of concept in Figure 2b. There were two peaks at 1349 cm^{-1} and 1590 cm^{-1} , well recognized as characteristic D band and G band of carbon material respectively [24]. These two peaks demonstrated the existence of carbon, which was introduced by pyrolysis of glucose followed by an annealing treatment. Furthermore, D band was associated with the disordered state of carbon while G band corresponded to the graphitic carbon in an ordered state [25]. The ratio of their intensity $I_G:I_D$ implies the graphitization of the carbon. The $I_G:I_D$ of the sample was calculated to be 1.10, indicative of decent graphitization. In addition, the Raman shifts of 380 cm^{-1} and 405 cm^{-1} corresponded to E_{2g}^1 and A_{1g} modes of MoS_2 , which were first order Raman vibrational modes within the S-Mo-S layers [26-27]. Schematic illustration of the modes was inserted in Figure 2b. The rest of the peaks all belonged to diverse vibrational modes of anatase TiO_2 .

X-ray photoelectron spectroscopy (XPS) was employed to investigate the composition and chemical state of the elements. As high-resolution XPS spectra to Mo of $\text{TiO}_2@\text{MoS}_2/\text{C}$ displayed in Figure 2c, the binding energy of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ was 229.4 eV and 232.5 eV respectively, indicating the tetravalent Mo in the crystal. The peak of S $2s$ at 225.5 eV was also observed. In Figure 2d, the binding energy of 161.2 eV was ascribed to S $2p_{3/2}$, in association with sulfur species in MoS_2 . The values above were in conformity with the previous report [28]. More importantly, in comparison with the XPS spectrum of $\text{TiO}_2@\text{MoS}_2$ without carbon (Figure S1), the Mo

binding energy in $\text{TiO}_2@\text{MoS}_2/\text{C}$ shifted towards lower energy ($\Delta E \approx 0.2$ eV), which was reportedly attributed to the electron transfer process that might occur between MoS_2 and carbon materials, favorable for facilitating the electronic conductivity of the electrode [29]. Furthermore, C $1s$ XPS spectrum (Figure 2e) was further deconvoluted into three carbon species centered at 284.8, 286.3 and 288.4 eV [30]. The main peak at 284.8 eV was assigned to graphitic C-C bonds, while the rests were for alcohols -C-OH and aldehydes -C=O groups, indicating the residues from insufficient reduction of glucose [31].

SEM images are shown in Figure 3 to display morphological information of the samples. The TiO_2 nanosheet arrays were homogeneously distributed on the Ti substrate without pack agglomeration (Figure 3a). The thickness of individual sheet was measured to be 10 ~ 25 nm, and such thin thickness could reduce diffusion length for lithium ion immigration. The morphologies of $\text{TiO}_2@\text{MoS}_2/\text{C}$ of different reaction time are displayed in Figures 3b~3d. As shown in Figure 3b, enormous MoS_2 thin sheets were assembled to form spheres with approximate diameters of 1 μm . With the reaction extending to 22 h (Figure 3c), MoS_2 spheres seemed to integrate into strips with similar width. Although the MoS_2 spheres were integrated into together, individual MoS_2 sheet still stayed divergent in different directions for ensuring open space in proximity, thus beneficial to efficient utilization of active materials and their full contact with electrolyte. However, when the reaction time prolonged to 24 h (Figure 3d), high-density MoS_2 hunks were formed, which greatly reduced the interstitial space between MoS_2 blocks. Note that the thickness of one single MoS_2 sheet was several nanometers,

which was also in favor of the reduction of lithium ion diffusion pathway within the electrode [32]. Moreover, there was no additional particle formed outside the structure. Thus, it was speculated that carbon existed conformally within MoS₂ sheets as a whole instead of surface coating. Additionally, low-resolution SEM images were provided to observe the connection area between TiO₂ and MoS₂/C (Figure S2). From the uncovered area by MoS₂/C, it can be found that TiO₂ sheet arrays were beneath those MoS₂ spheres, indicating that the MoS₂/C formed another layer on the top of TiO₂ nanosheet arrays. As a consequence, TiO₂ nanosheet arrays functioned as a stable scaffold to sustain the upper MoS₂/C.

Insert Figure 3.

High resolution transmission electron microscopy (HRTEM) was employed to gain insight to the structure. In Figure 4a, the image showed that numerous MoS₂ sheets assembled to form a sphere-like structure. Wherein, it also presented its ultrathin nature with a transparent appearance. There was no additional carbon layer coating on the surface of MoS₂ sheets (Inset in Figure 4a). The well-defined layer structure of MoS₂ sheets was clearly observed (Figure 4b) and the overall thickness was measured to be 3.90 or 4.87 nm at different locations, consistent with the SEM results. The distinctive layer structure implied an approximate interlayer distance of 0.67 nm, in accordance with current reports [33]. The enlarged interlayer spacing can be beneficial for Li⁺ ingress and supportive for rate performance [34]. In addition, such thin structure yet

enabled convenient lithium transport pathways and fast solid diffusion upon cycling. EDS element mapping was conducted to visually display the distribution of different elements. As shown in Figure 4c, Mo, S and C were uniformly distributed throughout the structure with the exactly same contour, suggesting that carbon was uniformly present within MoS₂ sheets in coordination with the synthetic procedure and TEM images.

Insert Figure 4.

In order to investigate their electrochemical performance as anodes, half cells were assembled and charged/discharged at a constant current of 100 mA/g, which was frequently applied in this system. The comparison of the three electrodes is intuitively shown in Figure 5. During the first ten cycles, there was no much difference amongst them and they delivered a capacity of over 700 mAh/g. But after that, the capacity of the sample prepared with 20 h reaction time began to decline and later the sample with 24 h faded as well. On the contrary, the sample with 22 h maintained a high capacity of more than 650 mAh/g after 50 cycles, superior to the other two electrodes. The reason why the electrodes differed from each other might be their morphological difference and unequal loading amount of MoS₂/C. The loading amount of active material can play an important role in the battery performance as previously reported [35]. It is necessary to control reaction condition to achieve a balance between stability and capacity, in order to optimize the electrochemical performance. Herein, the sample

prepared with 22 h was regarded as the optimal electrode considering the comparison of all three electrodes. The following electrochemical measurements were all based on this sample to further understand its advantage.

Insert Figure 5.

Cyclic voltammetry was performed to investigate the electrochemical reaction process during the cycling. The scanning was at a rate of 0.5 mV/s ranging from 0.05 to 3.0 V. The first three cycles is presented in Figure 6a. In the first cycle, a reduction peak was located at 0.9 V corresponding to initial Li^+ intercalation into MoS_2 lattice, which led to the phase transition from semi-conductive 2H- MoS_2 to metallic phase 1T- LiMoS_2 abiding by a shear mechanism [36]. With the intercalation continuance, another reduction peak at 0.44 V showed up for a conversion reaction, i.e., $1\text{T-LiMoS}_2 + x\text{Li}^+ \rightarrow \text{Li}_2\text{S} + \text{Mo}$. The whole process could be described as $\text{MoS}_2 + 4\text{Li} = \text{Mo} + 2\text{Li}_2\text{S}$ [37-39]. In the subsequent cycles, there were two new reduction peaks at 1.49 and 1.90 V, in association with the irreversible phase transition of MoS_2 and the intercalation into TiO_2 . The oxidation peaks of 1.71 and 2.23 V were attributed to Li^+ extraction from TiO_2 as well as oxidation of metallic Mo to MoS_2 [13] [40]. Besides, it was reported that a small amount of sulfur originated from the dissociation of Li_2S at 2.23 V might react with Li^+ to form Li_2S according to a Li-S system mechanism during the anodic process [41]. The formation of sulfur would contribute additional capacity to the overall cycle performance to some extent due to its high theoretical capacity. Furthermore, XPS

spectra of Mo and S (Figure S3) after cycling showed broader peaks and could be deconvoluted into several components as compared to the pristine samples, suggesting the presence of different valences and chemical states, which corroborated multiple and complicated processes in the electrochemical reaction [42]. Last but not least, there was no redox peak for carbon in CV profile, which implied that carbon contributed little to the capacity in the electrochemical reaction.

Insert Figure 6.

Galvanostatic cycle performance is shown in Figure 6b. At a constant current density of 100 mA/g, the initial discharge capacity of $\text{TiO}_2@\text{MoS}_2/\text{C}$ was 1083.9 mAh/g with a low Coulombic efficiency of 78% on account of the formation of SEI film irreversibly consuming Li resources in addition to active material exfoliation caused by volume expansion upon lithium intercalation [43]. Moreover, the exfoliation exposed more fresh surface area to the electrolyte, leading to subsequent formation of SEI films. It further worsened the situation. Nevertheless, the electrode soon recovered its stability in subsequent cycles with a reasonable fading. The electrode still delivered a high capacity of 457 mAh/g after 100 cycles. In contrast, although the individual MoS_2/C electrode exhibited a higher capacity at the beginning, it severely declined to less than 300 mAh/g over 30 cycles and finally delivered a low capacity of only 148 mAh/g at the 100th cycle, even lower than that of TiO_2 nanosheet arrays. The reason behind this was the massive volume change upon lithiation, which was commonly

present in metal oxides or sulfides cases [44]. As a control, $\text{TiO}_2@ \text{MoS}_2$ without carbon was cycled under the same condition, exhibiting 18% lower capacity than that of $\text{TiO}_2@ \text{MoS}_2/\text{C}$ (Figure S4). The large volume expansion and contraction triggered the detachment of active materials from the current substrate, leading to a fatal capacity loss. Besides, the capacity of TiO_2 arrays steadily remained at 180 mAh/g, reflecting its unique stability. In comparison with the other two electrodes, the composite $\text{TiO}_2@ \text{MoS}_2/\text{C}$ outdid both TiO_2 and MoS_2/C . The TiO_2 nanosheet arrays delivered a relatively low capacity. The capacity of the sample would decay rapidly without the TiO_2 as a stable scaffold like pure MoS_2/C , alluding to the fact that the scaffold of TiO_2 was important and essential to achieve a satisfactory performance. Furthermore, their synergistic effect enhanced the cycle performance through taking advantage of their merits. The carbon infused in the MoS_2 not only intensified the conductivity to accelerate the ions/electrons transport but also buffered the volume expansion upon cycling. Additionally, the MoS_2 was responsible for the majority of capacity while TiO_2 functioned as a scaffold to support and immobilize the MoS_2 on its top in case that the MoS_2 lost electrical contact. Charge/discharge curves at a constant current are provided in Figure 6c. In the initial discharge process, there was a long slope voltage platform around 0.48 V corresponding to the transition of 2H- MoS_2 to 1T- MoS_2 , accompanied by its decomposition to Mo and Li_2S [45-46]. During the charge process, an arising platform around 2.25 V was present due to Li^+ extraction from TiO_2 and oxidation of Mo as well as formation of Li_2S [47]. The result coincided with the CV profile above. It is worth noting that MoS_2 transformed from semi-conductive to metallic phase, which

was conducive to conductivity enhancement. The 40th cycle was different from the initial cycle and there was a shift toward lower capacity, indicative of irreversible capacity loss.

Rate performance was examined at diverse current densities as presented in Figure 6d. The $\text{TiO}_2@\text{MoS}_2/\text{C}$ electrode delivered the capacity of 1046.1, 743.6, 367.7, 260.2 and 161.7 mAh/g at the current density of 100, 200, 400, 800 and 1200 mA/g, respectively. The capacity tended to reduce as the current density increased. This tendency was ascribed to the inherent poor conductivity of metal oxides and sulfides. Whereas, $\text{TiO}_2@\text{MoS}_2/\text{C}$ performed better than both of the controls because of synergistic effect and their constructive combination. The carbon induced by pyrolysis of glucose to some extent improved the conductivity and fostered charge transfer. With the absence of TiO_2 arrays, the MoS_2 electrode decayed more drastically than $\text{TiO}_2@\text{MoS}_2/\text{C}$ although it had already been incorporated with carbon, which substantiated that TiO_2 played a crucial role in not only cycle performance but also rate capacity. From this point of view, the improvement stemming from the support of the scaffold was remarkable. When the current density fell back to 100 mA/g, the capacity of $\text{TiO}_2@\text{MoS}_2/\text{C}$ rose up to 437.3 mAh/g, restoring about 41.8% of the original capacity. The great capacity loss was attributed to the irreversible structural damage at high rates but it still recovered partially and behaved better than TiO_2 and MoS_2/C .

Insert Figure 7.

Electrochemical impedance spectroscopy (EIS) was carried out to elucidate the advantages of the prepared electrodes. Nyquist plots at early stage shown in Figure 7 were similar in shape, which consisted of a depressed semicircle from high to medium frequency and an inclined line at low frequency region. The diameter of the semicircle was associated with the charge transfer resistance when lithium ions diffused into the electrode through the electrode/electrolyte interface [48]. $\text{TiO}_2@\text{MoS}_2/\text{C}$ possessed the smallest diameter of 205.1Ω as compared to 294.5 and 332.3Ω for TiO_2 and MoS_2/C respectively, indicative of faster kinetics process. The decreased resistance was ascribed to positive influence by combining TiO_2 scaffold with MoS_2 . On one hand, the nanoarray structure provided large and open surface area for lithium ion swift insertion and extraction. On the other hand, the thin nature of numerous MoS_2 sheets might be conducive to reduce activation energy for lithium ion ingress and abridge the diffusion pathway, which was linked to the thickness [48-49]. Hence, the improved kinetics would be beneficial to the electrochemical performance. To further investigate the differences after cycling, EIS measurement on the electrodes at late stage was conducted (inset in Figure 7). Compared with the early stage, the diameters of the three electrodes increased after 100 cycles, indicative of elevation of the charge transfer resistance, which was probably due to the volume variation upon cycling as well as pulverization of the active materials resulting in new SEI formation [50-51]. More importantly, R_{ct} for the TiO_2 electrode increased slightly suggesting its excellent stability as a good scaffold. It in turn accounted for the smallest R_{ct} of $\text{TiO}_2@\text{MoS}_2/\text{C}$ among three electrodes despite cycling for many times. It was also worthy of

mentioning that at both early and late stages, $\text{TiO}_2@\text{MoS}_2/\text{C}$ still possessed the smallest R_Ω , which was associated with electrolyte resistance and electrical contact resistance, and reflected by the intercept on the horizontal axis [52]. Besides, an equivalent circuit is provided as Figure S5 in Supplementary Information.

It worths highlighting that TiO_2 serving as a stable scaffold established a solid foundation for subsequent MoS_2/C loading and satisfying performance. As illustrated in Figure 8, TiO_2 rooted robustly on the Ti substrate because TiO_2 nanoarrays were formed via direct reaction between metallic titanium and sodium hydroxide, which led to stronger adhesion to Ti substrate than MoS_2 to Ti. Moreover, TiO_2 nanoarrays firmly grasped the MoS_2/C on the top for ensuring good electrical contact and mechanical stability [53]. In contrast, on account of the lattice mismatch, pure MoS_2/C loosely attached to the Ti substrate after hydrothermal synthesis and detached from the substrate upon cycling due to volume expansion/contraction. That was the reason why $\text{TiO}_2@\text{MoS}_2/\text{C}$ performed much better than MoS_2/C . Active materials peeled off led to its disconnection from the current collector, consequently resulting in fatal capacity loss. To verify that, batteries after cycle measurement were disassembled to observe the difference. The electrodes were taken out of cells and rinsed with deionized water. As shown in Figure S6, the surface of $\text{TiO}_2@\text{MoS}_2/\text{C}$ was dark, which revealed good integrity and presence of many active materials, while MoS_2/C was basically washed away to expose the Ti substrate, which intuitively reflected the flaccid attachment between MoS_2 and the Ti substrate. The result was in good agreement with our aforementioned prediction.

Insert Figure 8.

In summary, the enhanced cycle and rate performance could be attributed to the following aspects. Firstly, zero-strain TiO_2 nanosheet arrays served as a stable scaffold to ensure good electrical contact and buffer large volume variation (side view in Figure S7). Secondly, carbon introduced by pyrolysis of glucose infiltrated into the structure of thin MoS_2 sheets, effectively improving the electronic conductivity [54]. Thirdly, well-dispersed $\text{TiO}_2@ \text{MoS}_2/\text{C}$ nanoarrays were composed of numerous tiny sheets of thin thickness. Such unique structure could provide more active sites for electrochemical reaction and large surface area without geometrical barrier for full contact with electrolyte, speeding up the lithium insertion. Fourth, the $\text{TiO}_2@ \text{MoS}_2/\text{C}$ were free of fluorine-based binders i.e. PVDF so as to save more space for active materials in limited battery volume, increasing the overall output capacity [55]. All the above synergistically contributed to the decent battery performance achieved. Our design was based on array structure, and therefore it was difficult to compare its performance with that for similar materials in the literatures available since they focused on powder material. In this case, $\text{TiO}_2@ \text{MoS}_2/\text{C}$ nanoarray structure on Ti substrate was fabricated instead of bare powders for the first time.

4. Conclusions

This paper has specifically demonstrated the synthesis of $\text{TiO}_2@ \text{MoS}_2/\text{C}$

nanoarrays on Ti substrate through a two-step hydrothermal method followed by annealing treatment, which was successfully employed as intensified anodic electrodes for lithium ion battery. The composites delivered a high capacity of 457 mAh/g after 100 cycles at a constant current of 100 mA/g, 643.4 mAh/g on average. The rate performance was also elevated when compared to individual TiO₂ and MoS₂/C. TiO₂ nanosheet scaffold was supportive yet crucial to the enhanced performance. Well-constructed arrays of two dimensional sheets were a useful manner to enhance performance. Besides, the reasonable utilization of carbon was favorable for the improvement as well. In general, this work presents a facile routine for achieving outstanding electrodes and shows metal oxides/sulfides as underlying successors of commercialized anodes.

Acknowledgements

This work was financially supported by National Science Foundation of China (Nos. 21377044 and 21573085) and the Key Project of Natural Science Foundation of Hubei Province (No. 2015CFA037).

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Figure captions

Figure 1 Schematic illustration for the synthetic process of $\text{TiO}_2@\text{MoS}_2/\text{C}$.

Figure 2 (a) XRD patterns for the samples prepared under different reaction conditions, (b) Raman spectrum for the sample with 22 h hydrothermal treatment in Step II and its high-resolution XPS spectra for (c) Mo, (d) S and (e) C element.

Figure 3 SEM images for (a) pristine TiO_2 nanosheet arrays and $\text{TiO}_2@\text{MoS}_2/\text{C}$ with the reaction duration of (b) 20, (c) 22 and (d) 24 h in Step II.

Figure 4 TEM images for (a) MoS_2/C (22 h reaction duration) and closer observation at the edge within the inset as well as (b) its corresponding HRTEM image, and (c) EDS mapping for different elements.

Figure 5 Comparative capacity of three electrodes cycled at a constant current of 100 mA/g.

Figure 6 (a) CV profile for the first three cycles of the $\text{TiO}_2@\text{MoS}_2/\text{C}$ electrode, (b) galvanostatic cycle performance of three electrodes, (c) charge/discharge curves for the $\text{TiO}_2@\text{MoS}_2/\text{C}$ electrode and (d) rate performance of three electrodes at different current densities.

Figure 7 Nyquist plots of three electrodes ranging from 10 mHz to 100 kHz at early and (inset) late stage which refers to the 3rd and 80th cycle, respectively.

Figure 8 Schematic illustration for superiority of the structure and flaccid attachment between MoS_2 and the Ti substrate.

Li et al., Figure 1

Li et al., Figure 2

Li et al., Figure 3

Li et al., Figure 4

Li et al., Figure 5

Li et al., Figure 6

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Graphical Abstract