A high-tap-density nanosphere-assembled microcluster to simultaneously enable high gravimetric, areal and volumetric capacities: a case study of TiO₂ anode

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Designing nanomaterial-based electrodes has emerged as a promising method to substantially improve the electrochemical performance of lithium-ion batteries (LIBs). However, the practical use of nanotechnology in LIBs generally results in electrode materials with low tap densities, which leads to low areal and volumetric capacities as well as limited areal mass loading. A rational electrode design strategy should compensate for these inherent disadvantages while making full use of the merits of nanomaterials. Herein, taking TiO₂ as an example, we elucidate the construction of an anode that takes into consideration the advantages of both nano- and microarchitectures. The obtained microcluster (0.9 μm in diameter) is a hierarchical ensemble of graphitic carbon-conformal hollow TiO₂ nanospheres (50 nm in diameter) with (001)-rich facets, showing a tap density of 1.7 g cm⁻³ (15 times that of Degussa P25 TiO₂ nanoparticles) and, thus, a large electrode density of 5.4 g cm⁻³. At a current density of 1675 mA g⁻¹, an anode with a mass loading of 15.6 mg cm⁻² not only manifests a stable areal capacity of 3.2 mA h cm⁻² and gravimetric capacity of 160 mA h g⁻¹ over 1000 cycles, but also delivers an exceptional volumetric capacity of 859 mA h cm⁻³, which is 1.6 and 2.5 times those of state-of-the-art graphite and TiO₂ anodes, respectively. Inheriting advantages from both nano- and micro-scale structures is crucial to simultaneously achieve high gravimetric, areal and volumetric capacities. This work addresses typical inherent issues of nanomaterial electrodes, offering an important step forward towards practical applications.

1. Introduction

Recent remarkable advances in nanotechnology have enabled the rational design of lithium-ion battery (LIB) electrodes with fascinating nanoarchitectures and functions, providing a useful method to address intrinsic issues of micro-sized materials, e.g., limited rate response, low capacity, and poor cycling stability. Unfortunately, the integration of nanotechnology into LIB electrodes naturally creates abundant interparticle space, which gives rise to low tap density and, consequently, limited volumetric capacity and thick electrodes with similar mass loadings. Examining studies of LIBs, we observe an interesting phenomenon: most of these studies only focus on gravimetric capacity, while overlooking volumetric and areal capacities. It is particularly important to pursue high-energy batteries for personal devices, where space is usually limited. Furthermore, most reported data involve low mass loading of the active materials. These overly optimistic capacities cannot translate to excellent performance when scaled to practical size. A reimagining of nanoscale engineering of active materials is required to overcome these inevitable barriers.

The rational design of nanostructured electrode materials must compensate for these inherent disadvantages while addressing the challenges of micro-sized materials. Only recently, awareness is increasing of the importance of fabricating hetero-structured materials that inherit advantages from both the nano- and micro-scale; however, progress in this area is still limited. Manipulation of the chemical composition, crystal phase, hierarchy, and morphology of active materials is essential to enhance the properties of batteries. Assembling an electrode that meets these requirements in a limited nano/micro-scale space has yet to be achieved, mainly due to the inadequacy of currently available design strategies and techniques.

TiO₂ is one of the most widely studied semiconductors and has numerous advantageous characteristics, such as...
abundance, nontoxicity, negligible structural variation and safe lithiation potential over graphite.\(^9\) Hence, it shows excellent range in energy-related applications,\(^{10-12}\) especially LIB anodes. Downsizing from the conventional bulk state to nanoscale dimensions is the first step to improve the energy storage capacity of TiO\(_2\). However, this treatment also shares some common challenges faced by other nanomaterials in LIBs.

Here, we revisited TiO\(_2\) anode and attempted to demonstrate the unique contribution of high-tap-density microclusters in improving the electrochemical properties of TiO\(_2\). As illustrated in Scheme 1, the microclusters are densely constructed of graphitic carbon-conformal TiO\(_2\) hollow nanospheres with \{001\}-rich high energy facets. The as-prepared microcluster anode was capable of concurrently executing functions from its crystalline, nanoscale and microscale domains: (i) increasing surface reactivity to Li ions and electronic conductivity by its \{001\} facets and well-designed carbon-conformal configuration; (ii) serving as a reservoir and effectively accommodating strain during Li ion (de)intercalation due to its hollow structure; (iii) providing higher tap density and greater mass loading via close packing of the microclusters. The above three-level functionality synergistically endows our anodes with high gravimetric, areal, and volumetric capacities even at a high mass loading.

2. Experimental section

Chemicals
Titanium(IV) isopropoxide (TIP; 97%), glucose, hexadecylamine (HDA; 90%), Pluronic P123, and potassium chloride (KCl) were purchased from Sigma-Aldrich. Isopropanol, ammonia solution

![Scheme 1](Image_url) Illustration of the synthesis and functions of a high-tap-density microcluster composed of carbon-conformal hollow TiO\(_2\) nanoparticles. The rationale is that the hierarchical micro-/nanostructures are capable of providing synergetic effects between three levels of functionality. First, primary TiO\(_2\) crystals several nanometers in size with \{001\}-rich facets confined by graphitic carbon can greatly improve the kinetics of Li ions and enhance electronic conductivity, hence promoting fast and reversible Li ion storage. Second, the hollow structure provides additional active Li ion storage sites and furthermore accommodates volume variations during the Li (de)insertion processes. Third, dense packing of the microclusters enables high tap density and electrode density.
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(25 wt%), dimethyl sulphoxide (DMSO), and absolute ethanol were obtained from Shanghai Chemical Corp. All chemicals were used as received without further purification.

Synthesis

Glucosamine (GlcN). The amination of glucose was performed based on a previous report.3 Briefly, 0.96 g of glucose, 4.80 g of ammonium carbonate and 15 mL of DMSO were placed in an automated microwave tube (40 °C, 250 psi pressure and 10 watts power for 4.5 h). Then, the reaction mixture was freeze-dried overnight to afford syrup-like GlcN containing very little DMSO residue.

High-tap-density microclusters. The experiment was a slight modification of a previously published method.4 Typically, 2.2 mL of TIP and 0.31 g of GlcN were placed in a vial (50 mL of iso-propanol) capped with a septum (solution A). Then, 0.16 g of HDA and 0.19 g of P123 were both dissolved in 50 mL of iso-propanol, followed by the addition of 0.4 mL of 100 mM KCl (solution B). After 1 h, solutions A and B were mixed with vigorous stirring for 5 s and allowed to age for another 18 h at 25 °C. The formed white precipitate was harvested by centrifugation and then washed repeatedly with ethanol. In order to investigate the role of the organic templates in the above sol–gel reactions, the feed mass ratios of HDA/P123/GlcN were changed in a large range according to the ternary phase diagram (Fig. 2).

To fabricate high-tap-density clusters composed of graphitic carbon-conformal hollow TiO2, 100 mg of the above sample was dispersed in 20 mL of deionized water and 10 mL of ethanol, to which various amounts of ammonia solution (25%) were rapidly added (1, 5, and 10 mL, respectively). The dispersion was transferred to a Teflon-lined autoclave (50 mL) and heated at 160 °C for 8 h. The brown solid was collected by centrifugation, washed with water and ethanol five times, and dried in a vacuum oven at 40 °C. The resulting powder was pyrolyzed by calcination at temperatures from 200 °C to 800 °C at 150 °C intervals for 3 h in flowing Ar.

Characterization

Morphological and structural studies were performed using a JEM-2100F high-resolution transmission electron microscope at an acceleration voltage of 200 kV (HRTEM) and a Hitachi S-4800 field-emission scanning electron microscope (SEM). The phase structures of TiO2 were determined by X-ray diffraction (XRD) recorded on a Bruker D8 advanced diffractometer using Cu Kα radiation. N2 adsorption–desorption isotherms were acquired on a TriStar II 3020 surface area and porosity analyzer at 77 K (Micromeritics, USA). The surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The pore size was calculated by the Barrett–Joyner–Halenda (BJH) method. ESI-Q-TOF-MS was performed using a micrOTOF-Q III (Bruker Daltonics) mass spectrometer. The ESI source was operated at 4.5 kV and 180 °C. Infrared spectra were recorded on a Bruker Vertex 80v FT-IR spectrometer.

Electrochemical measurements

The working anode was composed of high-tap-density microclusters, 5% carbon black, and 5% polyvinylidene difluoride binder. The slurry was coated onto the lithium foil current collector and then dried in a vacuum oven at 80 °C for 12 h to remove solvent before pressing. Afterward, the electrodes were typically punched in disk-like shapes with diameters of 12 mm and weights of about 4 mg; these were vacuum-dried at 80 °C for another 24 h. The cell assembly was operated in a glove box. The electrolyte solution was 1 M LiPF6 and ethylene carbonate/diethyl carbonate/ethyl methyl carbonate (1 : 1 : 1 by volume). The cells were assembled with the as-prepared TiO2, lithium metal and separator made of a Celgard 2300 film. Galvanostatic charge/discharge tests were carried out at 25 °C using an automatic LAND battery testing system (Wuhan, China) at various current rates.

3. Results and discussion

For the preparation of high-tap-density microclusters composed of carbon-conformal hollow TiO2 nanoparticles, two crucial steps should be noted: (1) preparation of solid GlcN-templating Ti species (Fig. 1c and f) as a precursor to generate amorphous TiO2 microspheres; (2) gradual inward crystallization to induce hollow graphitic carbon-conformal TiO2 nanoparticles (Fig. 4). The rationale underlying this synthesis strategy is the separation of the various chemical reactions involved, such as structural evolutions starting from crystal transitions and shape shrinkage to surface granulating and interior hollowing. This greatly hinders detrimental cross-interference during the formation of the TiO2 microclusters.

Synthesis of GlcN-templating Ti5 species

Generally, natural systems take advantage of solid, poorly ordered phases instead of high supersaturation levels of mineral salts to biomimeralize crystalline materials.15 For example, ferrihydrite (Fe(OH)3), a poorly crystalline iron oxide, has been identified as a starting material to obtain stoichiometric and structurally pure Fe2O3 crystal in magnetotactic bacteria and chiton teeth. This solid precursor-based strategy allows life systems to efficiently accumulate large quantities of constituent components at a feasible time and place, which can then be crystallized into biominerals with unprecedented properties. In the present work, we mimicked this solid precursor-based concept using GlcN, a pivotal molecule in the biosynthesis of many minerals, with the aim of constructing high-quality TiO2 materials.

Using GlcN as a directing agent, the involved sol–gel reactions were rather complicated, with numerous sequences of molecular intermediates. Understanding structural changes via monitoring their generation and consumption, which were usually exclusive to each reaction stage, was greatly important to explore the reaction mechanism and subsequently optimize the size, morphology, and structural properties of amorphous TiO2. Therefore, we utilized high resolution ESI-MS to explore the molecular intermediates in the early stages of the Ti species. The full-scan mass spectra obtained by directly injecting TIP and GlcN into isopropanol are plotted in Fig. 1a and b, respectively. Obviously, only one dominant signal at m/z...
203.0524 appeared in the TIP spectrum (Fig. 1a), corresponding to a adduct ion of \([\text{TiO(OiPr)}_2 + \text{Na}]^+\). It should be mentioned that the solvent used to dissolve TIP had a profound effect on the intrinsic chemical composition of the Ti source (Fig. S1, ESI†). After considering all the evidence, we selected iso-propanol as the solvent for our synthesis route.

As shown in Fig. 1b, ionization of GlcN mainly produced a distinctly intense signal derived from \([\text{GlcN} + \text{H}]^+\) at \(m/z\) 180.0867 and a less intense ion of \([\text{GlcN} + \text{Na}]^+\) at \(m/z\) 202.1020. Moreover, two additional fragment ions of \(m/z\) 162.0762 and 342.1385 appeared, corresponding to the loss of one \(\text{H}_2\text{O}\) molecule and a hydroxyl group, respectively.

The \([\text{GlcN} + \text{H}]^+\) ion was identified as the most stable intermediate derived from the signal of –NH₂ protonation, which can serve as a characteristic index to confirm whether –NH₂ groups were successfully connected to glucose. The MS spectrum of glucose (Fig. S2, ESI†) differed considerably from the GlcN signals with respect to the species of adduct ions, e.g., the maximum intensity corresponding to the ion of \([\text{M} + \text{Na}]^+\) and its representative peak at \(m/z\) 203.0516.

In addition, the GlcN/TIP molar ratios were varied from 0.1 : 1 to 8 : 1, directly controlled by the Ti precursors. For example, substantial peaks ranging from 600 to 1500 showed that numerous Ti species appeared (Fig. S3, ESI†). Importantly, the purity of the Ti species greatly improved when the GlcN/TIP molar ratios reached 4 and 8 equivalents. The 4 : 1 molar ratio, shown in Fig. 1c, afforded a clean spectrum with a single peak at \(m/z\) 988.9643 that may originate from the Ti₅ complex: \([\text{Ti}_5\text{O}_8(\text{OH})_8(\text{OiPr})(\text{OCH}_2\text{CH}_3)(\text{GlcN})_2 + \text{Na}]^+\). This species showed excellent stability in isopropanol, as evidenced by the negligible substitution side reactions (Fig. 1e) compared to the MS data of TIP in ethanol (inset of Fig. S1, ESI†).

Among GlcN, HDA, and P123, only GlcN can initiate a chemical reaction with the Ti species. To support this viewpoint, the products of HDA and GlcN-induced sol–gel reactions were studied by FTIR spectroscopy, respectively (Fig. 3g, and 3h). The vibration peaks of TiO₂ prepared via HDA, i.e., 2918 and 2848 cm⁻¹ of C–H stretching, 1460 and 719 cm⁻¹ of –CH₂– scissoring and rocking, and 1620 cm⁻¹ of N–H scissoring, were observed without any peak shifts compared to blank HDA. This observation was in total contrast to previous work reporting primary amine-capped silver nanoparticles and quantum dots.¹⁷,¹⁸ We confirmed that for the sol–gel reactions involving alkylamine, physical binding modes rather than chemical
bonds greatly affected the hydrolysis and condensation. When GlcN was employed to prepare TiO$_2$, a new signal arose at 1128 cm$^{-1}$ (Fig. 3h), which is a typical peak attributed to Ti–O–C vibration. This clearly proved the structural information observed by MS (Fig. 1c).

In virtue of the experimental data discussed above, we proposed a possible reaction pathway to form the Ti$_5$ precursors, focusing on the action of chemical bonding reactions between GlcN and the Ti species (Fig. 1f). The binding of the bidentate GlcN ligand with Ti atom is the most probable species acting as a starting condensation monomer. The first route involves the formation of edge-sharing dimers between octahedrons. A series of leaving molecules, such as iPrOH and GlcN, enable the connection of a third/fifth octahedron to the growing Ti network, finally forming the GlcN-directing precursor (Fig. 1c, m/z 988.9643). A crucial feature of bidentate GlcN ligands is that they can alter the availability of octahedral units, e.g., retarding the pathway to condense into Ti species. As illustrated in Fig. 1f, GlcN-directing Ti$_5$ species may expose two electrically neutral –NH$_2$ groups. This solid crystalline phase of the Ti$_5$ precursor is more prone than TIP itself to participate in the subsequent reactions, e.g., inducing an H-bond network between GlcN-free Ti species and HDA/PEO molecules. The condensation processes proceeds until a point is reached where no further consecutive shape transitions occur; ultimately, well-defined microspheres are obtained (Fig. 2f).

**Synthesis of amorphous microspheres via Ti$_5$ species as a precursor**

In this work, we used the GlcN-templating Ti$_5$ species as a precursor to prepare amorphous TiO$_2$. It was thus of particular importance to evaluate the structural evolution of TiO$_2$ in the presence of different structure-directing agents, such as P123 and n-alkylamines (e.g., HDA). Actually, GlcN was introduced into the reaction systems prior to HDA and P123. In order to acquire visual results, we integrated GlcN with HDA and P123 to compose a ternary phase diagram (Fig. 2). This can be employed to optimize amorphous TiO$_2$ microspheres in terms of particle size, shape and dispersibility.

When pure HDA or P123 reagent (at the right or left vertex, respectively) was used, both TiO$_2$ beads had smooth surfaces (Fig. 2a and b). Notably, the blank P123-templating sol–gel approach indeed generated polydisperse TiO$_2$ spheres. However, the size uniformity was significantly improved by adding HDA to the system, such as a 43.2%/56.8% mass ratio of HDA/P123 (Fig. 2d). Most importantly, as shown in Fig. 2c, subsequently replacing HDA and P123 with GlcN under otherwise identical experimental factors resulted in discrete TiO$_2$...
nanoparticles with ultrafine rough structures. Their diameters significantly decreased to less than 0.1 μm. When the DLS technique was performed on this GlcN-templating TiO2 in water (pH 7.4), a broad size distribution was obtained with a maximum hydrodynamic diameter of 0.4 μm, clearly indicating severe agglomeration of the TiO2 spheres (Fig. S4a, ESI†). In this case, it was necessary to introduce a second amine reagent to prevent aggregation of the primary TiO2 particles. As shown in Fig. 2e, adding an appropriate amount of HDA to GlcN with a mass ratio of 26.7%/73.3% formed slightly polydisperse spheres with sizes ranging from 0.22 to 0.45 μm. The occasional presence of particle fragments remained apparent.

Fig. 2f provides a representative SEM image of the TiO2 microspheres at a HDA/P123/GlcN mass ratio of 24.9%/28.7%/46.4%. These TiO2 microspheres exhibited a well-defined flaky surface. Their corresponding sizes predominantly increased to ca. 1.2 μm. Surprisingly, in contrast with previously reported TiO2 fabrication methods,20 the interior structures of the as-prepared TiO2 microspheres actually consisted of a dense nanoparticulate network (inset of Fig. 2f). The above difference clearly indicates that with the aid of HDA and P123, GlcN can chemically react with Ti species (Fig. 1f) to generate a more robust self-organization of constituent TiO2 nanospheres. In the following sections, the amorphous TiO2 prepared based on the circled domain in Fig. 2 was chosen as the starting platform unless otherwise noted. Outside this domain, however, the comprehensive properties of the amorphous TiO2 microspheres were compromised.

To further understand the roles of different organic templates (HDA, P123, and GlcN, etc.) in the formation of amorphous TiO2 spheres, a control experiment was conducted in the absence of any template additives in an otherwise identical environment (Fig. S5b, ESI†). These amorphous TiO2 beads lost their spherical shapes, and the occasional presence of stacking dimers or trimers became apparent. Based on this convincing evidence, as well as the morphological evolution shown in Fig. 2, it was revealed that the templates used entirely fulfilled their various functions in inducing sol-gel routes. The coupling of HDA with P123 can improve the quality and reproducibility of the product. GlcN, a bidentate ligand, chemically capped the Ti species and played an important role as a structural promter to participate in H-bonding-based assembly processes and to control self-assembly pathways at the molecular level. It became obvious that slow conversion of the precursor (i.e., GlcN-templating Ti5 species) is an efficient regulatory factor in the bottom-up synthesis of TiO2 amorphous microspheres with unprecedented properties, including well-defined size, regular morphology, high packing hierarchy and dispersibility.

Synthesis of pomegranate-like microspheres

Hence, we carried out a series of hydrothermal procedures to treat amorphous TiO2 microspheres prepared with varying mass ratios of structure-templating molecules. For both the GlcN-free microspheres, i.e., 100% of HDA in Fig. 3a and 100% of P123 in Fig. 3b, most of the spherical morphology was destroyed completely, leaving abundant irregular, fluffy and damaged TiO2 aggregates. However, once GlcN was introduced into the reaction recipe, the hydrothermal-treated microspheres

![Fig. 3](image-url)
could inherit representative features from their parent structures (Fig. 3c), such as uniformity and monodispersity. Of particular importance here is that with an appropriate mass ratio of HDA/P123/GlcN (24.9%/28.7%/46.4%), the titania surface was prone to be granular, associated with a clear eroded surface (Fig. 3d). Moreover, numerous interconnected TiO₂ nanoparticles were uniformly distributed throughout the whole microspheres (Fig. 3e). Taking a close look at each TiO₂ nanoparticle, we found that they retained solid structures at the hydrothermal treatment stage (Fig. 3f). In view of the substantial crystal densification, growth, and fusion of TiO₂ during the hydrothermal procedure, it was very surprising to observe a shrinkage of only 8.3% in diameter, compared to 36% for the control TiO₂ microspheres (Fig. S6, ESI†). Even in the presence of 10 mL of ammonia, GlcN made a specific contribution to inhibiting structural shrinkage as phase transition occurred.

In the above hydrothermal experiments, understanding what happens to the GlcN and Ti species, placing special focus on the phase transition from amorphous to anatase, has been proven to be an important determinant to synthesize pomegranate-like TiO₂ materials. With respect to two previously published results, hydrothermally initiated carbonization derived from glucose⁵ and the capability of an amorphous constituent component to prevent collapse of the anatase framework,⁶ structural information for the TiO₂ samples before and after hydrothermal treatment was obtained by FTIR and XRD, respectively. Analysis of the TiO₂ phase transformation was performed through monitoring the shi

ting of the transmittance peaks of the amorphous phase at 612 cm⁻¹ and of the crystalline phase at 705 cm⁻¹.²³,²⁴ For the sample prepared via using pure HDA (Fig. 3g), adding 5 mL of ammonia during the hydrothermal processes resulted in products that mainly consisted of amorphous phase or demonstrated poor crystallinity, as indicated by the appearance of a blurry shoulder at 702 cm⁻¹. In fact, the corresponding XRD pattern (shown in Fig. 3i, black curve) exhibited a featureless amorphous background as the prevalent phase. However, this finding did not apply to the hydrothermally treated amorphous TiO₂ including GlcN additive (Fig. 3h). The stretching vibration of Ti–O–Ti underwent a distinct high-frequency shift from 612 to 705 cm⁻¹, clearly revealing the occurrence of phase crystallization transitions from amorphous to crystalline.²⁵ XRD measurement corroborated this well-resolved crystallinity (Fig. 3i, red one). The diffraction peaks belonging to the {101} and {200} planes of anatase can be distinctly observed. In addition, the fading of the band at 1128 cm⁻¹ (Ti–O–C stretching) in Fig. 3h, associated with the appearance of signals at 1633 and 1418 cm⁻¹ (vibrations of C==C and –COOH from the carbon framework), were regarded as direct evidence of the immature carbonization of glucose, e.g., dehydration and polymerization between hydroxyl groups, as well as partial aromatization.²⁶ The formation of Ti–O–C bonds can greatly inhibit the mobility range of Ti atoms in inorganic frameworks, which is required to preserve intact crystal structures during phase transitions. In accordance with these results and analysis, we demonstrated that carbonization of GlcN indeed directed the formation of TiO₂ crystalline arrays.

The representative isotherms of hydrothermally treated TiO₂ measured by N² adsorption–desorption are shown in Table 1. Amorphous TiO₂ spheres were also characterized for comparison. The specific surface area of the hydrothermally treated TiO₂ was very small, less than 2 m² g⁻¹ (see Table 1), suggesting a dense non-porous structure that was amorphous according to the XRD pattern. When the ammonia was increased to 1 mL, a type II isotherm was observed, which demonstrates the nonporous character of the tightly packed interior structures.²⁷ For the sample treated with 2 mL of ammonia, the diffraction pattern became slightly sharper, e.g., three weak, broad peaks appeared at 2θ = 27.5, 48.1, and 62.5°. Upon increasing the ammonia to 5 mL, the treated sample possessed a typical IV isotherm with a featured H1 hysteresis loop (Fig. S7a, ESI†), manifesting a well-developed mesoporous structure.²⁷ The increased surface area and pore volume were calculated to be ca. 109.4 m² g⁻¹ and 0.38 cm³ g⁻¹, respectively. The superior mesoporosity was principally derived from the phase transformation from amorphous to anatase, which could be monitored by the appearance of several diffraction peaks at 25.4, 37.9, 48.1, and 62.7° (Fig. S7b, ESI†). Interestingly, doubling the ammonia amount to 10 mL could break the structural stability of the TiO₂ crystal, resulting in resolution attenuation of the diffraction patterns (Fig. S7b, ESI†). As explicitly summarized in Table 1, growth-constrained phase transition, i.e., TiO₂ crystallization confined within the carbon

Table 1 Physical properties of the hydrothermally treated microspheres with a mass ratio of HDA/P123/GlcN at 24.9%/28.7%/46.4%

<table>
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<tr>
<th>Sample</th>
<th>Ammonia content (mL)</th>
<th>SEM (μm)</th>
<th>DLS (μm)/PDI</th>
<th>Crystal phase</th>
<th>Porosity properties</th>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>Surface area² (m² g⁻¹)</td>
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<td>1.5/0.08</td>
<td>Amorphous</td>
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<td>1.9</td>
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<td>1.3/0.05</td>
<td>Amorphous</td>
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<tr>
<td></td>
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<td>1.3/0.08</td>
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<td>5</td>
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<td>1.5/0.09</td>
<td>Anatase and amorphous</td>
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<tr>
<td></td>
<td>10</td>
<td>1.04, 0.52</td>
<td>1.7/0.21</td>
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</table>

² Microsphere diameter refers to the average diameter obtained by manually measuring over 100 particles observed in the SEM image. ³ BET specific surface area. ⁴ Pore diameter was calculated with the BJH method from the desorption branch. ⁵ n.a.” indicates not applicable. ⁶ “—” indicates that the pore diameter could not be determined from the BET data.
framework, yields the greatest benefit of enlarged mesopore sizes along with increasing specific surface area.

**Synthesis of a high-tap-density microcluster**

A gram-scale quantity of black product was synthesized through direct calcination at 650 °C for 3 h in an Ar flowing tube furnace (Fig. 4a). The shapes and structures of the as-obtained TiO₂ materials were analyzed by electron microscopy measurements. From the panoramic SEM image, these TiO₂ materials present a granular morphology with a diameter of about 0.9 μm (Fig. 4b). The high-magnification SEM image shows that each microsized TiO₂ was hierarchically packed with TiO₂ nanoparticles with diameters of about 50 nm (Fig. 4c). The TEM image in Fig. 4d displays a multistacked edge region of TiO₂ beads which consists of nanoparticles with diameters of 40 to 60 nm, in good agreement with the SEM data. Importantly, the high-resolution TEM images (Fig. 4e and f) show the evident hollow structure of these constituent nanoparticles. The shell thickness was estimated to be 8 nm. Most of the shell was continuous, and some isolated shells intercalated into adjacent parts, leading to interconnected hollow dimers and trimers.

The chemical compositions of the TiO₂ materials were recorded by EDX analysis. Stronger C signals were observed, as well as stoichiometric Ti : O atomic ratios (Fig. 4g); this provides proof that the organic agents used, especially GlcN, were converted into carbon components. In virtue of the hollow and mesoporous structures, the microclusters possessed a type IV isotherm with a surface area of 85 m² g⁻¹ and a pore volume of 0.29 cm³ g⁻¹. A visible ink-bottle-type hysteresis loop appeared in the isotherm (Fig. 4h), originating from a large hollow cavity capped by narrow windows, including mesoporous channels distributed through the shell layer. This also demonstrates that the obtained sample was capable of retaining its structural integrity even when calcined at 800 °C.

To obtain insight into the underlying mechanism of the structural and crystallographic evolutions during the phase transition, the sample was studied as a function of calcination temperature from 200 °C to 800 °C using XRD and TEM. For the sample calcined at 200 °C (Fig. 4i), the broadening diffraction curve roughly matched that of anatase crystal (JCPDS 21-1272). Upon increasing the calcination temperature to 350 °C, the (200) diffraction line intensified significantly while the (101) line weakened to some extent. When we sintered the TiO₂...
samples from 500 °C to 800 °C, a similar tendency of weakening/strengthening intensity of the peak lines in the low/high diffraction region was observed. For example, with a calcination temperature of 650 °C, the (200) diffraction line became sharper and stronger, accompanied by the appearance of a discernible peak at 24.4° belonging to graphitic carbon.29

Additionally, the (101) diffraction signal significantly decreased. Notably, particular attention should be paid to the diffraction width at 37.5° indexed to anatase (004) because dominance of the {001} plane contributes to broadening of the (004) diffraction line.30–33 Considering the relative peak width and intensity (Fig. 4i), with increasing calcination temperature, the unambiguous broadening of the (004) diffraction peak indicates the presence of smaller TiO2 nanocrystallites along the [001] direction that constitute the hollow TiO2 shell. Through careful comparison, a slight shift of the (101) line to a lower degree with increasing calcination temperature from 200 °C to 500 °C was detected (2θ = 0.8°). The variations in the directions and intensity of the (004) and (200) diffraction peaks, together with the downshift and absence of the (101) peak, provide a consistent picture of the anisotropy and crystallographic orientation of the anatase grains, demonstrating the decreased crystal size along the [001] direction and the extended crystalline region along the [100]/[010] axis.34,35 The anatase grains followed an oriented growth strategy with respect to the surface of the hollow TiO2 nanoparticles, which were strongly textured and predominantly exposed the {001} facets. However, it was difficult to calculate the precise value of the exposed fraction of {001} facets because its Bragg diffraction peak was not well-defined due to the interference of carbon species.

Upon closer examination of the TEM images (Fig. 4j) of the constituent TiO2 nanoparticles, we observed an interesting structural evolution. The size of the core decreased continuously in response to increasing calcination temperature, giving rise to core/shell (200 °C), core/void/shell (350 °C, 500 °C), and entirely hollow structures (650 °C, 800 °C). We exploited microarea analysis at the core and shell locations to obtain structural information. Typically, the sample calcined at 200 °C was amorphous at both its core and shell, which is in good agreement with the XRD results. As the heating continued to 650 °C, the whole TiO2 nanoparticle became highly crystalline and the core totally disappeared, leading to a hollow structure.

Actually, the final TiO2 structure was highly dependent on the preparation conditions, and good care must be taken to obtain hollow cavities. The use of GlcN-assisting Ti clusters as a precursor played a vital role in cavity formation. The synthesis recipe without GlcN generated solid TiO2 microspheres after hydrothermal and calcination reactions (designated as M–TiO2, Fig. S8, ESI†). In virtue of the above observation, we postulated that: (1) the formation of hollow TiO2 is related to the gradual inward crystallization process (Scheme 1, Fig. 4j). The amorphous or less crystalline core was gradually consumed, finally resulting in hollow TiO2 nanoparticles;24 (2) the primary TiO2 crystallites on the surface served as seeds to initiate the carbon-conformal coating, which can support and stabilize the hollow walls of TiO2 in situ, thus effectively preventing the shell from collapsing.

Two high-resolution TEM images of the calcined microspheres at 650 °C, shown in Fig. 4j, reveal that the shell layer of the hollow nanosphere comprised well-defined TiO2 crystallites with grain sizes ranging from 5 to 10 nm which were conformally coated by ultrathin graphitic carbon layers (2 to 3 graphene layers, as denoted with red dotted lines). A lattice fringe with 0.47 nm spacing, corresponding to the [002] plane of anatase phase, was evidently visible. It adopted an inclined orientation to the lattice fringe with a spacing of about 0.35 nm, indexed to the [101] plane, with an interfacial angle of 68.3°. In accordance with most previously reported literature studies,15 this interfacial angle is very similar to the theoretical angle between the [101] and {001} planes. The crystallographic information illustrated here indicates that the top and bottom surfaces of the nano-scaled TiO2 crystallites exposed with truncation are bound by the {001} facets.26 In addition to serving as a carbon source, the dominant role of GlcN is to direct crystal growth.27 Because of its hydroxyl groups, GlcN will adsorb on the {001} surface to retard TiO2 growth along the [101] direction, hence maximizing the exposure of {001} facets. From the above observations and analysis, we can confirm that high-tap-density TiO2 microclusters with {001}-rich facets were successfully prepared under high-temperature calcination in Ar atmosphere.

**Electrochemical characterization**

The lithium storage properties of the as-prepared microclusters as anode materials were studied by galvanostatic charge/discharge measurements. Fig. 5a shows representative charge/discharge voltage profiles of a TiO2-based lithium cell within a cutoff voltage window of 1 to 3 V. Two dominant voltage plateaus can be clearly identified at 1.75 V and 1.9 V in the discharge and charge processes, ascribed to lithium-insertion/extraction between the Li-poor phase (tetragonal anatase) and Li-rich phase (e.g., Li0.5TiO2).36 The first discharge capacity was 365 mA h g−1 and the subsequent charge capacity was 260 mA h g−1. Hence, the irreversible capacity loss was 29% in the first cycle, mainly ascribed to interfacial side reactions between the microclusters and electrolyte. The microcluster anode could retain higher discharge and charge capacities of 250 and 241 mA h g−1 in the second cycle and displayed excellent capacity retention thereafter. The interior cavities of the constituent TiO2 nanoparticles can function as an effective buffer space to alleviate volume variations while retaining the structural integrity of the anode. The SEM and AFM images shown in Fig. 5g and h directly corroborate this deduction.39 The surface roughness of the anode films and the morphologies of the microclusters remained almost unchanged even at 5C after 1000 cycles. This is a striking feature to address challenges associated with aggregation of electrode materials, which is another obstacle to the practical use of TiO2.

The demonstrated close packing nanostructure provides an opportunity to improve the coulombic efficiency of electrodes in Li-ion batteries. Detailed values of the charge/discharge capacity and coulombic efficiency of the microcluster anodes at a current rate of 1C are plotted in Fig. 5b. The capacity decayed from 251 to 197 mA h g−1 in 10 cycles and remained...
rather stable thereafter. The coulombic efficiency approached 99% after 20 cycles. As a control, the long-term electrochemical performance of an M–TiO₂ anode was also evaluated (Fig. 5e) because it has similar features to those of the microclusters without carbon coatings or hollow cavities (Fig. S8, ESI†). The charge capacity of the M–TiO₂ anode was only 74 mA h g⁻¹ at 1C in the first cycle and faded quickly from the tenth cycle, with a significant fluctuation of the coulombic efficiency. We attribute the low specific capacities of M–TiO₂ to the following reasons. Solid battery materials have been demonstrated to have numerous structural limitations (e.g., increasing Li⁺ diffusion distance and large volume changes during Li⁺ intercalation) for advanced LIB technology.¹¹ Also, the absence of the electrochemically active carbon coating gives rise to poor battery results due to the intrinsically limited electronic conductivity of TiO₂ materials. Finally, after 1000 cycles at 5C (335 mA g⁻¹ at 1C), the capacity was less than 30 mA h g⁻¹. Furthermore, when evaluated at a high rate of 10C, about 97% of the coulombic efficiency of the microcluster anode was maintained over 1000 cycles, while the control M–TiO₂ anodes generated a rapid decrease in 5 cycles and showed coulombic efficiencies of <30% over 200 cycles. These results convincingly demonstrate the superior lithium storage performance of the microcluster anode in terms of long cycle life.

To explore their rate capabilities, the high-tap-density microcluster anode and M–TiO₂ control anode were discharged and charged at a series of rates (Fig. 5c and f). It was apparent that the M–TiO₂ anode has poor cyclic capacity retention, with capacities of 162, 133, 95, 74, 39 and 26 mA h g⁻¹ at rates of 0.1, 0.2, 0.5, 1, 2.5 and 5C, respectively. In contrast, the anode fabricated with the high-quality microclusters was capable of delivering respective gravimetric capacities of 260, 238, 220, 199, 178, and 160 mA h g⁻¹. Of particular importance here is that after a high cycle rate, the gravimetric capacity of 256 mA h g⁻¹ can be recovered to the initial value when the current rate is decreased back to 0.1C.

It should be noted that many previous publications only provide specific capacities normalized by the mass of the active materials, which does not precisely reflect the properties of packed cells.⁴⁰ Li anodes with large areal capacities are needed for commercial applications. As shown in Fig. 6, we therefore tested anodes with different mass loadings of microclusters. The mass loading of 45 mg cm⁻² showed unstable cycling (Fig. S9a, ESI†). It has been reported by Cui et al.⁴⁰ that achieving stable cycling for a high loading cell requires excellent structural stability of the anode materials. In this regard, we ascribed the fluctuation of areal capacity to changes in the particle morphology that caused electrode-level cracking (Fig. S9b, ESI†). Interestingly, at a relatively low mass loading of

![Fig. 5](https://example.com/fig5.png)

Charge/discharge profiles of (a) microclusters and (d) M–TiO₂ anode at a current rate of 0.1C. Long-term performance and coulombic efficiency of (b) microclusters and (e) M–TiO₂ anode at 1C. The rate properties of (c) microclusters and (f) M–TiO₂ anode at various current rates. Panoramic SEM image, enlarged SEM image (left corner) and AFM image (right corner) of a microcluster anode (g) before and (h) after 1000 cycles at 5C (335 mA g⁻¹ at 1C). The small nanoparticles in the panoramic SEM images are carbon black.
23.7 mg cm$^{-2}$, an areal capacity of 4.9 mA h cm$^{-2}$ was obtained at 5C after 1000 cycles (Fig. 6a). This is 1.4 times the capacity of a commercial Li-ion battery. At a mass loading of 15.6 mg cm$^{-2}$, the microcluster electrode was still capable of delivering volumetric capacities of 1019, 956, 931, 900, 885, and 856 mA h cm$^{-3}$ at rates of 0.1, 0.2, 0.5, 1, 2.5, and 5C, respectively (Fig. 6b). More importantly, the volumetric capacity at a high mass loading (786 mA h cm$^{-3}$, 23.7 mg cm$^{-2}$) was only slightly smaller than that at a low mass loading (954 mA h cm$^{-3}$, 8.2 mg cm$^{-2}$), as shown in Fig. 6c. This verified that almost all the microclusters are active in a thick electrode.

Furthermore, we compared our microcluster electrodes with other recently reported titanium-based materials (including Li$_4$Ti$_5$O$_{12}$ and various TiO$_2$ polymorphs, morphologies and structures). It should be mentioned that a higher mass loading negatively influenced the capacities normalized to the total electrode mass. In this work, the mass loading was 23.7 mg cm$^{-2}$, exceeding that of typical TiO$_2$ electrode systems. However, the gravimetric capacities of our microcluster electrode outperformed those of most other materials (Fig. 6d and Table S1, ESI†), especially at high rates. More importantly, the microclusters exhibited the highest areal and volumetric capacities among TiO$_2$ anodes for LIBs (Fig. 6e and f, Tables S2 and S3, ESI†). For example, at a current density of 670 mA g$^{-1}$, the volumetric capacity of our microclusters was 2.2 times higher than the value for a previously published SiO$_2$/TiO$_2$ composite film.

To the best of our knowledge, simultaneously achieving superior areal, gravimetric, and volumetric capacities has not yet been reported for TiO$_2$ battery applications.

In virtue of all the structural and crystallographic information discussed above, the outstanding electrochemical performance of the as-prepared microclusters acting as anode materials in Li-ion batteries can be understood from the following viewpoints. The rationale is that the hierarchical micro-/nano-structures can provide synergistic effects of transport rate, tap density, surface area, mechanical integrity, etc. First, several nanometers of primary TiO$_2$ crystal confined by graphitic carbon layers can greatly shorten the diffusion length of Li$^+$ ions, hence promoting fast and reversible Li-ion storage. Second, the hollow structure provides additional active Li$^+$ storage sites and also accommodates volume changes during lithium (de)insertion. Third, the pomegranate-like microclusters 0.9 mm in diameter are hierarchical ensembles of carbon-conformal TiO$_2$ nanospheres 50 nm in diameter, giving rise to space-efficient packing for high energy density. Fourth, the {001}-rich facets are advantageous to the fast and efficient kinetics associated with Li$^+$ intercalation and deintercalation with a lower energy barrier. This enabled improvement of the reversibility and rate capability at high current rates. These unique electrochemical functionalities synergistically combined to afford advanced lithium-storage performance.

4. Conclusions

We developed a synthesis protocol via GlcN-assisted Ti clusters as a starting Ti precursor to construct microclusters composed of graphitic carbon-conformal hollow TiO$_2$ nanospheres with {001}-rich facets. These microcluster electrodes with small amounts of carbon conductor additive showed a very high electrode density of 5.4 g cm$^{-3}$. Inheriting the three-level advantages of crystalline phase, nanoscale and microscale, the microcluster anode with a TiO$_2$ mass loading of 15.6 mg cm$^{-2}$ at 5C not only exhibited a stable areal capacity of 3.2 mA h cm$^{-2}$ after 1000 cycles, but also delivered a high volumetric capacity.
of 859 mA h cm\(^{-2}\) (about 1.6 and 2.5 times those of state-of-the-art graphite and TiO\(_2\) anodes, respectively). Moreover, the cycling remained stable even when the areal capacity was increased to 4.9 mA h cm\(^{-2}\) (1.4 times that of the level of commercial LIBs) via increasing the TiO\(_2\) mass loading to 23.7 mg cm\(^{-2}\). The present work offers an effective approach to simultaneously achieve high gravimetric, areal and volumetric capacities, with great potential for practical LIB applications.

**Conflicts of interest**

There are no conflicts to declare.

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