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Abstract Template-free synthesis of TiO_2 architectures with controlled morphology evolution has been developed through solvothermal reaction in 1,4-dioxane. By simply varying the molar ratio of the concentrated HCl over Titanium isopropoxide (TTIP) from 0 to 5.0, series of morphologies including nanoparticle-built microspheres, nanoparticle-built microspheres decorated with nanorods, nanorod cauliflowers, and nanorod dendrites have been obtained. The influence of several key factors on the morphology control of TiO_2 has been systematically

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investigated. These parameters include the mass (molar) ratio of HCl/TTIP, solvothermal reaction temperature and time, acid species (concentrated nitric acid), and solvent type (tetrahydrofuran and 1,3-dioxane). The mechanism for the formation of the TiO_2 architectures with controlled morphology evolution has been discussed. The application of the TiO_2 architectures as water splitting photocatalyst and lithium–ion battery anode has been demonstrated. And the corresponding structure–property correlation has been discussed.

Introduction

Studies on the synthesis and application of nanostructured TiO₂ has received tremendous attention due to their unique electrochemical properties and promising utilization in photocatalysis, dye-sensitized solar cells, lithium-ion batteries, sensors, and biomedical devices [1-9]. It is well recognized that the morphology and crystallinity of TiO₂ play crucial roles in the performance [10-20]. Recently, hierarchical TiO₂ architectures composed of both primary nanoscale building blocks and secondary micrometer scale aggregates attracted particular attention because they possess the advantages of both nano- and µm-scale structural features [13, 21-24]. Hard/soft templating strategy has been extensively applied to synthesize hierarchical TiO₂ nanostructures [25–30]. With the template synthesis, thermal treatment at high temperature is required to crystallize pristine TiO₂ and remove non-functional templating molecules. However, the templating agent removal is a tedious task because it often induces severe structure collapse at high temperature. This drawback has shed significant doubts on the ultimate applicability of the template



synthesis strategy. As compensation, sophisticated tuning of calcination protocol is mandatory to retain structure integrity after thermal treatment. Therefore, template-free reaction has attracted considerable attention as an alternative route to synthesize bare TiO_2 architectures [31–40]. Nevertheless, the types of the morphologies synthesized by template-free reaction are quite limited so far [23, 32, 33, 36, 41]. What is more important, small molecule surfactants have been often used in the synthesis protocols. Delicate tuning of the experimental parameters is essential to control the morphology of TiO_2 [37, 42]. Thermal removal of small molecules is still required [24, 34, 41, 42]. Finally, with some template-free synthesis recipes, large amounts of corrosive organic acid or ammonium hydroxide are used as solvents, which is environmentally harsh [32, 38, 39, 43].

Here, we report a simple facile way to achieve templatefree synthesis of TiO₂ architectures with controlled series of morphology in a non-corrosive solvent. Compared to the synthetic methods reported before, this strategy developed by us has a few particular advantages. First, the use of surfactants is totally excluded, which facilitates structure retention during high-temperature thermal treatment. Second, no complicated composition system is needed. Instead, only three different chemical species are used in this work. Specifically, 1,4-dioxane is used as common solvent for solvothermal reaction; Titanium tetraisopropoxide (TTIP) is used as precursor and concentrated HCl is applied as catalyst for the sol-gel reaction of TTIP. Third, instead of the morphology control via sophisticated variation of the solution composition, simultaneous control over morphology and crystallinity of the TiO₂ architectures has been realized in this work by simply varying the molar ratio between HCl and TTIP. With this method, series of different morphologies including nanoparticulate microspheres, microspheres decorated with nanorods, nanorod cauliflowers, and nanorod dendrites have been synthesized. Fourth, compared to acetic acid and ammonium hydroxide, 1,4-dioxane is a non-corrosive solvent and it is not environmentally harsh. Fifth, besides the general results on morphology control, the impact of series of different factors under different molar ratios of HCl/TTIP has been systematically investigated in this manuscript, which has rarely been addressed previously. These parameters include solvent type(1,4-dioxane, 1,3-dioxane, and tetrahydrofuran), acid type(concentrated HCl, concentrated HNO₃), solvothermal reaction temperature (110, 140, and 170 °C), and time (from 0.5 to 8 h). Based on the results, the mechanism of the morphology evolution has been proposed. Furthermore, the applications of the hierarchical TiO₂ nanostructures as water splitting photocatalyst and lithium-ion battery anode have been demonstrated.

Experimental

All chemicals and materials addressed in this work were used as received without further purification. DMF of analytical grade, concentrated HCl (37 %), concentrated nitric acid (65 %), 1,3-dixoane, and tetrahydrofuran (THF) of analytical grade were received from Sinopharm Group Co., Ltd. Titanium tetraisopropoxide (TTIP, 97 %) was purchased from Alfa Aesar.

Sample preparation was as following. TTIP (0.2, 0.4, 0.8, 1.6, and 3.2 g) and concentrated HCl (0.2, 0.5, 1.0, and 1.6) were added to 10 g 1,4-dioxane. After stirring for around 10 min at room temperature, the solution was transferred to a Teflon-lined stainless steel autoclave and heated at elevated temperatures (110, 140, and 170 °C) for different periods of time (0.5, 1.0, 2.0, 4.0, and 8.0 h), followed by natural cooling to room temperature. The white precipitates obtained were centrifugated, washed, and vacuum dried at 80 °C. Thereafter calcination in air at 500 °C for 3 h was applied with a ramp rate of 5 K/ min, followed by natural cooling to room temperature in furnace. To investigate the role of concentrated HCl, the mass of concentrated HCl was set as 0.2, 0.5, 1.0, and 1.6 g, respectively, while the mass of TTIP was set at 0.8 g. In order to study the impact of TTIP, the mass of TTIP was varied with 0.2, 0.4, 0.8, 1.6, and 3.2 g; while the mass of the concentrated HCl was fixed at 1.0 g. When the solvothermal reaction temperature was adjusted (140, 170 °C), the mass of the concentrated HCl was chosen as 0.2, 0.5, 1.0, and 1.6 g; while the mass of TTIP was 0.8 g. When the impact of the solvothermal reaction time was systematically investigated, the detailed experimental conditions were adjusted as following: temperature: 110 °C, time: 0.5, 1.0, 2.0, 4.0, and 8.0 h, mass of the concentrated HCl: 0.2, 0.5, 1.0, and 1.6 g, mass of TTIP: 0.8 g. Regarding the studies on HNO₃, the sample preparation condition was as following: temperature: 110 °C; mass of HNO₃: 0.2, 0.5, 1.0, and 1.6 g; mass of TTIP: 0.8 g. When 1,3-dioxane or THF was used as solvent instead of 1,4-dioxane, the experimental condition was as following: temperature: 110 °C; mass of the concentrated HCI: 0.2, 0.5, 1.0, and 1.6 g; mass of TTIP: 0.8 g.

Field emission scanning electron microscopy (FESEM) experiment was carried out using Hitachi S4800 scanning electron microscope (Tokyo, Japan) at an accelerating voltage of 4 kV. The sample powder was put on a conductive tape and sputtered with gold before imaging.

Transmission electron microscopy (TEM) experiments were conducted with an FEI Tecnai F20 instrument (TEM, Oregon, USA) or TEM (2100F, JEOL, Japan) with a 200 kV field emission gun.



Fig. 1 Morphology evolution of the hierarchical TiO_2 architectures synthesized with different mass concentrations of concentrated HCl with respect to the total mass of 1, 4-dioxane: 2 wt% (**a**), 5 wt% (**b**), 10 wt% (**c**), and 16 wt% (**d**) at 110 °C, mass ratio of TTIP: 8 wt%

X-ray diffraction experiment was performed to characterize the crystallographic phases of the powders (Bruker AXS D8 Advance, $\lambda = 1.541$ Å, 2.2 kW) with 2 θ starting from 5° to 90°.

The Nitrogen adsorption–desorption isotherm was measured on ASAP 2020 M apparatus at 77.3 K. Around 200 mg of the dry sample was firstly loaded into the glass analysis tube, which was then fixed to the degas port. The temperature was firstly increased to 90 °C with a ramp rate of 10 K/min, followed by holding for 30 min. Thereafter, the temperature was increased to 200 °C and held for 8 h until the outgas rate was less than 5 μ m Hg. The sample was backfilled with N₂ before transferred to the analysis port. N₂ adsorption–desorption isotherm was measured with the relative pressure range set between 0 and 1.0. The BET surface area was calculated over the range of relative pressures between 0.05 and 0.20.

Photo catalytic activity measurement was carried out according to the following procedure. 50 mg of TiO_2 powders were dispersed into 120 ml aqueous methanol solution with the volume concentration of 25 vol% in a closed gas circulation system (Perfect Light Company Labsolar-III (AG)). The UV–Visible light irradiations were received from a 300 W Xe lamp (Perfect Light Company Solaredge 700) without and with a UVCUT-420 nm filter (CE Aulight. Inc). The evolved gases were detected in situ by using an online gas chromatograph (GC-2014C,

Shimadzu) equipped with a thermal conductivity detector (TCD).

2032 type lithium-ion battery coin cell device using lithium foil as counter electrode was fabricated to evaluate the electrochemical performance of the TiO₂ architectures. The slurry mixture was prepared by mixing active material, Super P and poly(vinylidene fluoride) (PVDF) (mass ratio: 8:1:1) together in N-methyl Pyrrolidone (NMP). Thereafter, the slurry mixture was spread on a piece of copper foil, followed by drying at 80 °C overnight. After drying, the copper foil was pressed, cut into appropriate dimension, and dried in oven at 80 °C further for 4 h. Then the device was fabricated in glove box using the electrolyte from Shanshan Tech Co., Ltd, where 1.0 M LiPF₆ was dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DMC) (1:2 v/v). The rate performance was measured at the current density sequence of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 0.1 C in the voltage range between 3.0 and 0.005 V (vs. Li/Li⁺) (five cycles each current density, 1 C = 335 mAh/g). The cyclic measurement was carried out at a current density of 0.2 C in the voltage range of 3.0-0.005 V (vs. Li/Li⁺) for 50 rounds. The specific capacity was calculated on the basis of only the active material. The discharge process was referred to the lithiation process and correspondingly the charge process was defined as the delithiation process.

Results and discussion

Figure 1 shows the impact of concentrated HCl on the morphology change of the TiO_2 architectures. It is found that with 2 wt% of concentrated HCl over the total mass of



Fig. 2 XRD patterns of the hierarchical TiO_2 architectures with different morphologies: nanoparticle-built microspheres (*black*), microspheres decorated with nanorods (*red*), nanorod cauliflowers, and nanorod dendrites (*blue*) (Color figure online)

Fig. 3 TEM images of the hierarchical TiO₂ architectures synthesized with different mass of concentrations of concentrated HCl with respect to the total mass of 1, 4-dioxane: 2 wt% (a), 5 wt% (b), 10 wt% (c), and 16 wt% (d), mass ratio of TTIP: 8 wt%

1,4-dioxane, TiO₂ microspheres are formed with the average size of ca. 1.4 µm (Fig. 1a and Figure S1a). A closer look at the TiO₂ microspheres reveals that they are built by the close pack of TiO₂ nanoparticles with a small size of around 22 nm. Furthermore, TiO₂ microspheres with similar morphologies are still observed without concentrated HCl (Figure S2). It suggests that with small amount of concentrated HCl, TiO₂ nanoparticles are formed in solution, which are further assembled into microspheres in close-pack style. With the mass concentration of concentrated HCl further increased to 5 wt%, the nanoparticle-built microspheres are still present. However, the surface of the microspheres are decorated with TiO₂ nanorods (Fig. 1b), which are bundled together to form cauliflower-like architectures. When the mass concentration of the concentrated HCl is further lifted to 10 wt%, the nanoparticle-built microspheres disappear totally and only nanorod-built microspheres with the average size of 4.0 µm are observed (Fig. 1c and Figure S1c). The microspheres are composed of vertically aligned TiO₂ nanorods with the diameter of 38 nm as shown by the highmagnification SEM image (inset of Fig. 1c). When the mass concentration of the concentrated HCl is increased to 16 wt%, the morphology of the nanorod-built microspheres





Fig. 4 HRTEM images of the hierarchical TiO_2 architectures synthesized with different mass of concentrations of concentrated HCl with respect to the total mass of 1, 4-dioxane: 2 wt%

(a nanoparticle-built microspheres), 5 wt% (b and c microspheres decorated with nanorods), 10 wt% (d nanorod cauliflowers), and 16 wt% (e nanorod dendrites), mass ratio of TTIP: 8 wt%



Fig. 5 Morphology evolution of the hierarchical TiO₂ architectures synthesized with different mass concentrations of TTIP with respect to the total mass of 1, 4-dioxane: 2 wt% (a), 8 wt% (b), 16 wt% (c), and 32 wt% (d), mass ratio of concentrated HCl: 10 wt%

is changed to dendrite-like nanorod aggregates (Fig. 1d). The high-magnification SEM image shows that the shape of the individual nanorod is changed (inset of Fig. 1d). With 10 wt% of concentrated HCl, the shape of the nanorod is of square prism feature. However, with 16 wt% of concentrated HCl, the shape of the TiO₂ nanorod is changed to nanoribbon-like structure. Due to the morphology change of the individual TiO₂ nanorod, the corresponding assembly pattern of the nanorods are modified. Regarding the square-prism-like nanrods, it is easy to close pack. As a result, isotropic assembly domiantes and cauliflower-like nanorod-built microspheres are formed. However, with the nanoribbon-like structure, it is relatively difficult form close pack. Therefore, the nanorods are assembled in a scattered style, leading to the formation of nanorod dendrites.

The crystallographic phase of the TiO_2 architectures is investigated by XRD as shown in Fig. 2. The results show that the nanoaparticle-built microspheres are of pure anatase phase, while the XRD pattern of the microsphere decorated with nanorod indicates the coexistence of both anatase and rutile phases. Because the nanoparticle-built microsphere is of anatase, it is reasonable to ascribe the rutile phase to the nanorods. The anatase phase disappears in the XRD pattern of the nanorod-built cauliflower microspheres and nanorod dendrites, where only the rutile phase is exhibited. This result further confirms the assumption that the rutile phase within the sample of microsphere decorated with nanorod comes from the nanorod.

The detailed morphologies of the TiO₂ architectures are further investigated by transmission electron microscopy (TEM). Figure 3a clearly shows the structure of the nanoparticle-built microspheres, which is consistent with the SEM image in Fig. 1a. Figure 3b confirms that nanorods are decorating the nanoparticulate microspheres. Figure 3c shows spherical structure feature, where nanorod-like structures are only slightly observed. The nearly perfect spherical shape of the nanorod-built microspheres hides structure details under TEM. Regarding the TiO₂ nanorod dendritic structure, spheres are also observed. Furthermore, nanoribbon-like structure is visible by TEM. The different structure features observed by TEM between Fig. 3c, d are due to the different assembly pattern of the TiO₂ nanorods. The high-resolution transmission electron microscopy (HRTEM) images prove that the nanoparticle-built microspheres are of anatase phase (Fig. 4a), while both anatase and rutile phases are observed in the microspheres decorated with nanorods (Fig. 4b, c). Only rutile phase is observed in the cauliflower-like nanorod microspheres (Fig. 4d) and nanorod dendrites (Fig. 4e).

The influence of TTIP on the morphology change of the TiO_2 architectures has been investigated as shown in Fig. 5 and Figure S3. With 2 wt% of TTIP, TiO_2 dendrites are obtained which are built by the nanoribbon-like TiO_2 structures (Fig. 5a). With 8 wt% of TTIP, nanorod-built cauliflower microspheres are formed. The microspheres are built by the close pack of the square-prism-like TiO_2 nanorods (Fig. 5b). When the mass concentration of TTIP

Scheme 1 Morphology evolution of the TiO₂ architectures along with increasing mass (molar) ratio of HCI/TTIP through solvothermal reaction in 1,4-dioxane, a nanoparticle-built microsphere, b nanorod cauliflower, c nanorod dendrite





Fig. 6 Morphology evolution of the hierarchical TiO_2 architectures synthesized with solvothermal reaction at 140 °C with different mass concentrations of concentrated HCl with respect to the total mass of 1,

4-dioxane: 2 wt% (a), 5 wt% (b), 10 wt% (c), and 16 wt% (d). *Inset* high-magnification SEM image of each sample, mass ratio of TTIP: 8 wt%



Fig. 7 Morphology evolution of the hierarchical TiO_2 architectures synthesized with solvothermal reaction at 170 °C with different mass concentrations of concentrated HCl with respect to the total mass of 1,

4-dioxane: 2 wt% (a), 5 wt% (b), 10 wt% (c), and 16 wt% (d). *Inset* high-magnification SEM image of each sample, mass ratio of TTIP: 8 wt%

is further increased to 16 wt%, microspheres composed of TiO_2 nanoparticles are observed by SEM (Fig. 5c), which are decorated by TiO_2 nanorods. Finally, with 32 wt% of

TTIP, nanoparticle-built TiO_2 microspheres are again formed (Fig. 5d). In general, it can be seen the trend of the morphology change with increasing amount of TTIP is reversed compared to the morphology evolution trend with increasing amount of concentrated HCl. However, when the mass ratio of HCl/TTIP is considered, the observed morphology trends against increasing amount of HCl and TTIP are consistent. With the HCl/TTIP mass ratio of 5/16 or 1/4 (even 0/1), 5/8, 5/4, and 2/1, the morphology of the hierarchical architectures evolves with the sequence of nanoparticle-built microspheres, microspheres decorated with nanorods, nanorod-built cauliflower, and nanorod dendrites (Scheme 1). It is reported that the sol-gel reaction kinetics of TTIP can be modified by varying the amount of concentrated HCl [42]. With little amount of HCl, the edge-sharing linkage of the TiO₆ octahedra is favored due to excessive amount of OH group in solution. As a result, the formation of anatase phase dominates [41]. However, with increasing amount of HCl, the linkage of the TiO₆ octahedra is changed and the formation of rutile phase is overwhelming compared to the anatase phase. Furthermore, the chloride ions in solution tend to be selectively adsorbed onto the (110) plane of the rutile TiO₂ nucleus [41]. It guides an anisotropic one-dimensional growth along the (001) orientation to form nanorods [41]. However, from our results, it can be rationalized that it is the relative mass (molar) ratio of HCl/TTIP which governs the crystallinity and morphology control of TiO₂. This is to say, the control over crystallinity and morphology of the TiO₂ architectures can also be achieved by adjusting the amount of TTIP in solution. It seems that with the HCl/ TTIP molar ratio below 1.0, formation of nanoparticle-built microspheres of anatase are favored. With the molar ratio of HCl/TTIP increased to around 1.78, both nanoparticlebuilt microspheres of anatase phase and nanorods of rutile phase coexist. When the molar ratio of HCl/TTIP is increased to above 3.0, nanorod cauliflowers built by close



Fig. 8 Morphology of the hierarchical TiO_2 architectures synthesized with solvothermal reaction at 110 °C with 2 wt% of concentrated HCl with respect to the total mass of 1, 4-dioxane for different reaction

time: 0.5 h (a), 1 h (b), 2 h (c), 4 h (d), and 8 h (e). *Inset* high-magnification SEM image of each sample, mass ratio of TTIP: 8 wt%



Fig. 9 Morphology of the hierarchical TiO_2 architectures synthesized with solvothermal reaction at 110 °C with 5 wt% of concentrated HCl with respect to the total mass of 1, 4-dioxane for different reaction

time: 0.5 h (a), 1 h (b), 2 h (c), 4 h (d), and 8 h (e). *Inset* high-magnification SEM image of each sample, mass ratio of TTIP: 8 wt%

packing of square-prism-like nanorods are formed. And when the molar ratio of HCl/TTIP is increased to a high level of more than 5.0, dendrites formed by radially packed nanoribbons are observed.

The impact of solvothermal reaction temperature on the morphology of the TiO₂ architectures has been studied. Besides 110 °C, solvothermal reaction at 140 °C (Fig. 6) and 170 °C (Fig. 7) are performed accompanied with systematic variation of the mass concentration of the conexperiments reveal HCl. Both centrated similar morphology change with respect to increasing mass concentration of the concentrated HCl. The specific morphology details do not change significantly between 140 and 170 °C. The results imply that increasing the solvothermal reaction temperature does not modify the fundamental solgel reaction process of TTIP and further assembly behavior of the TiO₂ nanoaparticles and nanorods.

From Figs. 8, 9, 10, and 11 the impact of solvothermal reaction time on the morphology of the TiO₂ architectures with different mass concentrations of the concentrated HCl is displayed. As shown by Fig. 8, when the mass concentration of the concentrated HCl is fixed at 2 wt%, nanoparticle-built microspheres are formed with the solvothermal reaction extended from 0.5 to 8 h. The microspheres synthesized with different reaction times show almost identical morphology. It indicates that the nanoparticle-built microspheres are formed upon solvothermal reaction and the structure is quite stable along with further solvothermal reaction. When the mass concentration of the concentrated HCl is set at 5 wt%, microspheres decorated with nanorods are already formed with the reaction time of 0.5 h (Fig. 9). With further extension of reaction time to 8 h, the microspheres decorated with nanorods continue to exist and the structures do



Fig. 10 Morphology of the hierarchical TiO_2 architectures synthesized with solvothermal reaction at 110 °C with 10 wt% of concentrated HCl with respect to the total mass of 1, 4-dioxane for different

not change significantly. With 10 wt% of concentrated HCl, nanorod-built cauliflower microspheres are formed with the reaction time of 0.5 h. With further extended reaction time, the morphology of the cauliflower microspheres are still observed and does not exhibit significant change. With 16 wt% of the concentrated HCl, TiO₂ dendrites built by nanoribbons are formed with the solvothemral reaction time from 0.5 to 8 h. The results further show that the assembled TiO₂ nanrod architectures are also formed in the early stage of the solvothermal reaction time.

To elucidate the role of HCl on the morphology of the TiO_2 architectures, concentrated nitric acid is used to replace HCl as a catalyst for the sol–gel reaction of TTIP. Unlike HCl, only nanoparticle-built microspheres are formed with different mass concentrations of the

reaction time: 0.5 h (a), 1 h (b), 2 h (c), 4 h (d), and 8 h (e). Inset high-magnification SEM image of each sample, mass ratio of TTIP: 8 wt%

concentrated HNO₃ (Fig. 12). It indicates that isotropic growth of the TiO₂ nanocrystals is retained with increasing amount of concentrated HNO₃. It is reported that chloride ions can modify the crystalline plane growth behavior of nanosized TiO₂ via coordination bonds, leading to the anisotropic growth of TiO₂ nanostructures [41]. However, from the results it seems that they do not interfere the nanocrystal growth process of TiO₂. As a result, no nanorods are observed and only TiO₂ nanoparticles are formed. The results emphasize the effect of HCl on the morphology control of the TiO₂ architectures.

The influence of solvent on the morphology control of the TiO_2 architectures is evaluated. As shown in Fig. 13, with 2 wt% of concentrated HCl in THF, nanoparticle-built microspheres are observed. However, with further increasing amount of concentrated HCl, the morphology transition from nanoparticle to nanorod is not observed.



Fig. 11 Morphology of the hierarchical TiO_2 architectures synthesized with solvothermal reaction at 110 °C with 16 wt% of concentrated HCl with respect to the total mass of 1, 4-dioxane for different

reaction time: 0.5 h (a), 1 h (b), 2 h (c), 4 h (d), and 8 h (e). *Inset* high-magnification SEM image of each sample, mass ratio of TTIP: 8 wt%

Similar experiment is conducted in 1,3-dioxane, where different behavior is observed (Fig. 14). With the mass concentration of the concentrated HCl below 10 wt%, nanoparticle-built microspheres are formed. While with 16 wt% of concentrated HCl, TiO₂ nanorods are observed. But the morphology control in 1,3-dioxane is not good as the reaction performed in 1,4-dixoane under the specific experimental condition explored in this manuscript. It seems that the nature of solvent plays an important role on the formation of the hierarchical TiO₂ architectures.

Finally, the application of the TiO_2 architectures as water splitting photocatalyst and lithium–ion battery anode has been be demonstrated. The samples were synthesized with the concentrated HCl mass ratio of 2, 5, 10, and 16 wt%, respectively, at 110 °C together with the mass ratio of TTIP of 8 wt%. According to Fig. 15, compared to the blank control sample, all of the nanostructured TiO₂ microspheres show obvious photocatalytic performance for water splitting. Nevertheless, the nanoparticle-built microspheres decorated with nanorods exhibit the best photocatalytic performance among the four different morphologies. While the nanoparticle-built microspheres show the worst performance. The best performance of the microspheres decorated with nanorods originates from the heterojunction between anatase and rutile and relative high specific surface area $(15.0 \text{ m}^2/\text{g})$ [44]. While the worst performance of the nanoparticle-built microspheres is ascribed to the low specific surface area compared to other samples $(1.5 \text{ m}^2/\text{g})$. The nanorod-built microspheres and nanorod cauliflowers exhibit medium photocatalytic performance. Compared to the sample of the microspheres decorated with nanorods, the nanorod-built cauliflowers and nanorod dendrites are of pure rutile phase. The absence of heterojunction leads to inferior photocatalytic



Fig. 12 Morphology of the TiO_2 architectures synthesized with solvothermal reaction at 110 °C with different mass concentrations of concentrated HNO₃ with respect to the total mass of 1, 4-dioxane:

2 wt% (a), 5 wt% (b), 10 wt% (c), and 16 wt% (d). *Inset* high-magnification SEM image of each sample, mass ratio of TTIP: 8 wt%



Fig. 13 Morphology of the TiO_2 architectures synthesized with solvothermal reaction at 110 °C with different mass concentrations of concentrated HCl with respect to the total mass of tetrahydrofuran

performance. Compared to the nanoparticle-built microspheres of anatase phase, the rutile phase of the nanorods brings less performance [17]. However, the relatively (THF): 2 wt% (a), 5 wt% (b), 10 wt% (c), and 16 wt% (d), mass ratio of TTIP: 8 wt%

higher specific surface area of the nanorods makes compensation to the photo catalytic performance (8.9 m²/g for nanorod cauliflower and 7.6 m²/g for nanorod dendrites).



Fig. 14 Morphology of the hierarchical TiO₂ architectures synthesized with solvothermal reaction at 110 °C with different mass concentrations of concentrated HCl with respect to the total mass of 1,3-dioxane: 2 wt% (**a**), 5 wt% (**b**), 10 wt% (**c**), and 16 wt% (**d**), mass ratio of TTIP: 8 wt%



Fig. 15 Photocatalytic hydrogen conversion performance of the hierarchical TiO_2 architectures under full spectrum light: nanoparticle-built microspheres (*purple*), microspheres decorated with nanorods (*green*), nanorod cauliflowers (red), and nanorod dendrites (*black*), commercial P25 TiO_2 (*dark cyan*), and blank control sample (*blue*) (Color figure online)

As a result, the performance of the nanrod-built cauliflowers and nanorod dendrites are slightly better than that of the nanoaprticle-built microspheres. Compared to the commercial P25 TiO₂, the nanostructured TiO₂ microspheres exhibit inferior photocatalytic performance. It is supposed to be due to relative low specific surface area (around 50 m²/g for P25) and lack of sufficient antase–rutile heterojunction within the microspheres as within the P25 TiO₂ [44].

The same samples as the photocatalytic test were also applied to evaluate the electrochemical performance as lithium-ion battery anode. The discharge/charge curves are exhibited in Fig. 16. As shown in Fig. 16a, the initial discharge capacity of the nanoparticle-built microspheres is around 120 mAhg⁻¹; while the initial charge capacity is ca. 50 mAhg⁻¹(current density: 0.2 C, 1 $C = 335 \text{ mAg}^{-1}$). After cycling at 0.2 C for 50 rounds, the discharge/charge capacity is around 56 mAhg⁻¹. Concerning the nanoparticle-built microsphere decorated with nanorods, the initial discharge capacity is increased to 208 mAhg⁻¹. While the initial charge capacity is 105 mAhg⁻¹. After 50 cycles at 0.2 C, the discharge/charge capacities are still around 85 mAhg^{-1} . For the nanorod cauliflowers and nanorod dendrites, the initial discharge capacities are in the range of between 140 and 180 mAhg⁻¹. And the initial charge capacities are around 60 mAhg⁻¹. After 50 cycles at 0.2 C, the discharge/charge capacities are in the range of between 45 and 60 mAhg $^{-1}$. The cyclic and rate performance of TiO_2 are shown in Fig. 17. It is clear that the microspheres decorated with nanorods possess superior performance compared to the other three samples (Fig. 17a). Furthermore, the rate performance of the TiO₂ microspheres decorated with nanorods also show the best performance among the four samples under different current densities (Fig. 17b). In general, it can be seen that the nanoparticlebuilt microspheres decorated with nanorods exhibit the best cyclic and rate performance among the four different



Fig. 16 Charge/discharge curves of the hierarchical TiO_2 architectures as lithium-ion battery anode: nanoparticle-built microspheres (**a**), microspheres decorated with nanorods (**b**), nanorod cauliflowers (**c**), and nanorod dendrites (**d**)



architectures. The best performance is supposed to be due to the existence of anatase phase and relatively high specific surface area [10, 11, 14, 45]. It is reported that the anatase phase exhibits better electrochemical performance as lithium–ion battery anode than the rutile phase [10, 11]. As a result, the nanorod cauliflowers and nanorod dendrites may intrinsically exhibit inferior performance than the architectures based on the nanoparticle-built microspheres. However, the pure nanoparticle-built microsphere possesses very small specific surface area, which dramatically limits its performance. Therefore, as a balance between crystallographic phase and specific surface area, the nanoparticle-built microspheres of anatase decorated with rutile nanorods show the best performance because they have a reasonable specific surface area among the four types of architectures.

Conclusions

In conclusion, a template-free synthesis of TiO_2 architectures has been developed through solvothermal reaction in 1,4-dioxane. By simply varying the molar ratio of concentrated HCl over Titanium isopropoxide from 0 to 5.0, series of structures including nanoparticle-built microspheres, nanoparticle-built microspheres decorated with nanorods, nanorod cauliflowers, and nanorods are achieved. It has been found that the nanoparticle-built microspheres are of anatase phase and the nanorods are of rutile phase. The impact of key factors on the morphology evolution of the TiO₂ architectures has been systematically investigated. It has been found that the solvothermal reaction with the temperature above 110 °C did not change the morphology the TiO₂ architectures significantly. With solvothermal reaction for 0.5 h, all of the architectures with different morphologies have been formed, which are stable enough after further reaction for 8 h. The replacement of concentrated HCl with concentrated nitric acid only generates nanoparticle-built microspheres. This result indicates that chloride ions play crucial roles in the formation of TiO₂ nanorods. Solvothermal reaction in THF and 1,3-dioxane does not exhibit morphology control as good as in 1,4dioxane. The application of the TiO₂ architectures as water splitting photocatalyst and lithium-ion battery anode has been demonstrated. It is discovered that the nanoparticlebuilt microspheres of anatase decorated with rutile nanorods possess the best photo catalytic performance due to the existence of heterojunction and relative high specific surface area among the four types of architectures. Furthermore, the nanoparticle-built microspheres decorated with nanorods also exhibit the best electrochemical performance as lithium-ion battery anode due to the existence of more electrochemical active anatase phase and relatively high specific surface area among all structures.

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Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

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