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A Facile Method for Synthesizing TiO₂ Sea-Urchin-Like Structures and Their Applications in Solar Energy Harvesting *

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We present a new method to prepare TiO₂ sea-urchin-like structures, which involves the initial formation of tubular nanostructures and subsequent self-assembly of the nanotubes into micrometer-scale sea-urchin-like structures. We also investigate the important role of alkali aqueous conditions in the preparation of TiO₂ sea-urchin-like structures. This facile and cost-effective approach provides a new route for the preparation of self-assembled TiO₂ structures. In addition, the performance of the as-synthesized TiO₂ sea-urchin-like structures as the active layer of an efficient solar energy harvester is also studied and discussed.

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Ever since the structure of carbon nanotubes was elucidated by Iijima in 1991,^[1] a great deal of attention has been paid to the synthesis and characterization of one-dimensional (1D) nanomaterials due to their unique shape-dependent properties.^[2–5] Recent studies have shown that various 1D nanomaterials can be synthesized readily.^[6–8] Among these nanomaterials, TiO₂ nanotubes are of particular interest due to their wide bandgaps with desirable band-edge positions and biocompatibility, which enable their application in photocatalysis,^[8] solar energy harvesting,^[9] photoelectrolysis, etc.^[10] Synthesis of TiO₂ nanostructures can be achieved by various routes, including the template-assisted method,^[11] anodic oxidation approaches^[12] and the wet chemical method.^[13] A simple hydrothermal method for producing large amounts of TiO₂ nanotubes was first proposed by Kasuga *et al.*^[13] in 1998, followed by an investigation of the mechanism of TiO₂ nanotube formation in alkali solution to establish the crystal structure of the nanotubes.^[14] However, cost-effective large-scale synthesis methods with a rational control in the size, morphology and particularly the assembly of TiO₂ nanostructures have yet to be developed. Mao *et al.*^[15] reported the three-dimensional (3D) assembly of TiO₂ 1D nanostructures using a modified H₂O₂-assisting hydrothermal method. In this Letter, we report a simple and facile method to synthesize TiO₂ sea-urchin-like nanostructures, which is based on the hydrothermal method reported by Kasuga *et al.* Since the hydrothermal method is widely used in preparing TiO₂

nanomaterials, the approach we present here should be very helpful for the preparation of self-assembled TiO₂ nanostructures. Applications of these TiO₂ sea-urchin-like structures as active layers of dye-sensitized solar cells have also been investigated.

The synthesis and self-assembly of nanotubes into micrometer-scale sea-urchin-like structures was performed through a modified hydrothermal approach, including the initial transformation from TiO₂ nanoparticles to tubular nanostructures and the subsequent self-assembly of the nanotubes into sea-urchin-like structures in alkali aqueous solutions. The typical synthetic process is shown in Fig. 1. All reagents were analytical grade and used as received without further purification. There was 1 g TiO₂ nanoparticle powder (Aldrich, purity $\geq 99.9\%$, average size of about 100 nm) added into 80 mL 10 M NaOH aqueous solution (Beijing Chemical Reagents Company, purity $\geq 96.0\%$) and the mixture was stirred for 30 min at room temperature. The obtained suspension was then transferred into a 100 mL Teflon-lined stainless autoclave and heated up to 160° for 30 hours. When this hydrothermal treatment was completed, the Teflon-lined stainless autoclave was cooled down to room temperature naturally. The as-synthesized products were then divided into two groups, denoted as samples A and B, respectively. Sample A was kept in the Teflon-lined stainless autoclave for a week under room temperature. Then the white precipitates were subsequently purified by centrifugation and washed using 0.1 M HCl aqueous solution for three times and

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later with de-ionized water until the pH value of the supernatant was close to 7. The obtained precipitates were then annealed at 300° in air before further characterization. While sample B was purified with centrifugation immediately after the hydrothermal treatment. The centrifugation and annealing process were performed under the same conditions as for sample A.

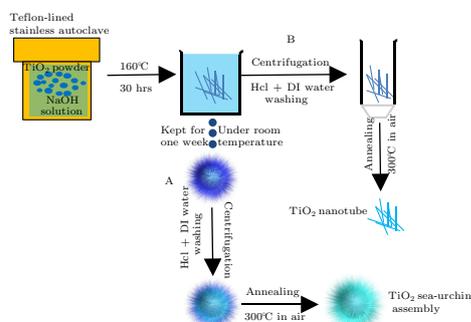


Fig. 1. The synthesis sequence of sea-urchin-like TiO_2 nanostructures.

The structure, morphology and chemical compositions of the as-prepared samples were characterized using scanning electron microscopy (LV-SEM, JSM-5900LV), transmission electron microscopy (JEOL TEM 3010) and energy dispersive x-ray spectroscopy (EDX). The results are shown in Fig. 2. Figure 2(a)(1) and Figure 2(b)(1) are the SEM images of samples A and B, respectively. Sea-urchin-like structures with diameters around $2\ \mu\text{m}$ can be observed from sample A as shown in Fig. 2(a)(1), for which the precipitates of the hydrothermal treatment were kept with further processing in the Teflon-lined stainless autoclave for an additional week. However, if the products of hydrothermal treatment were processed immediately with diluted HCl aqueous solution and de-ionized water, only random tubular structures were observed, as shown in Fig. 2(b)(1). From the EDX results, both samples A and B can be determined as TiO_2 materials. To further investigate the structures of the samples, TEM analyses were carried out. It can be clearly seen that the sea-urchin-like structures (sample A) are the ordered assembly of tubular materials under the alkali condition at room temperature. It should be noted that these 3D sea-urchin-like structures can preserve their morphology even after sonication. From the comparison of these images, it can be seen that the as-synthesized products were sea-urchin-like structures when kept in the alkali aqueous solutions for a week (sample A). If the white precipitates were washed immediately after the hydrothermal treatment, the resulting products were tubular structures. This indicates that the alkali condition is essential for the assembly of nanotubes into sea-urchin-like structures. This conclusion can also be supported by the fact that only tubular nanostructures were observed when sample B (washed immediately after hy-

drothermal treatment) was kept in neutral solution for one week. Therefore, sea-urchin-like structures cannot be formed without the alkali treatment. It has been reported that NaOH aqueous solutions play an important role in the formation of TiO_2 nanotubes.^[14] The alkali conditions used in our experiment may have similar effects for the transformation from tubular nanostructures to sea-urchin-like structures at room temperature.

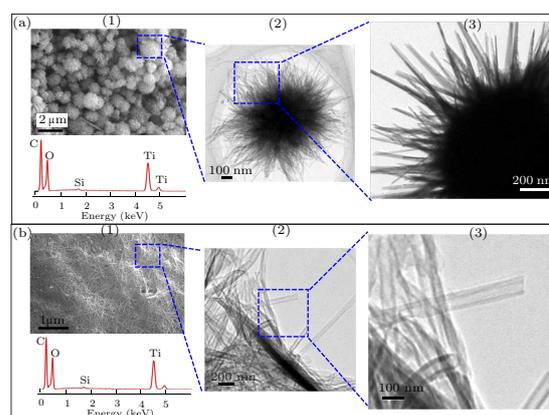


Fig. 2. The characterization of structural morphology and chemical compositions for the as-prepared samples.

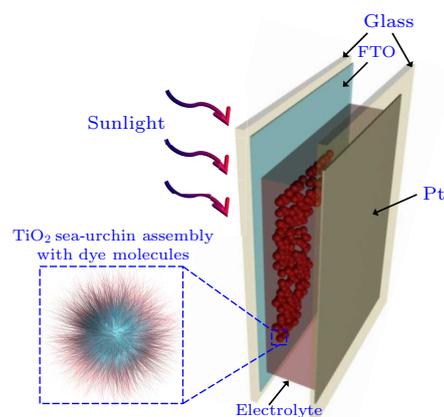


Fig. 3. The structure of TiO_2 sea-urchin-like structure based DSSCs.

From the above results and discussions, the following formation mechanism of sea-urchin-like structures is proposed. At an early stage, the layer-like flake structures were formed and started to roll up into nanotubes in the NaOH solutions at very high temperature. The size and shape of the nanotubes were controlled by reaction conditions such as temperature and reaction time. At the second stage, the as-prepared TiO_2 nanotubes were self-assembled into sea-urchin-like structures under alkali aqueous conditions. The function of NaOH solution is to make the nanotubes aggregate and form sea-urchin-like structures as the final products. The reaction in this stage was carried out at room temperature. Therefore, the sea-urchin-

like structures are the aggregation of TiO_2 nanotubes under alkali aqueous conditions. This method is different from previous reports on the synthesization of TiO_2 sea-urchin-like structures,^[15,17] which involved H_2O_2 for an enhanced oxidation process in the presence of NaOH solution. The approach demonstrated here provides a facile template-free cost-effective way to synthesize a 3D assembly of TiO_2 sea-urchin-like structures with high repeatability and a new route for the self-assembly of nanotubes/nanowires into microstructures.

TiO_2 sea-urchin-like structures possess advantages such as larger surface areas and an ordered electron conduction network compared with structures in random arrangement and are crucial for applications such as active photocatalysis for the splitting of water/degradation of pollutant^[8] and solar energy harvesting.^[9,17] In the following, the application of TiO_2 sea-urchin-like structures for DSSC will be discussed. The structure of a TiO_2 sea-urchin-like structure based DSSC is shown schematically in Fig. 3. The TiO_2 sea-urchin-like structures were deposited onto the FTO-coated glass substrate from ethanol solution. After evaporation of the ethanol solvent, the TiO_2 sea-urchin-like structures were sensitized in a 0.5 mM N719 dye solution^[16] in ethanol for two hours. A Pt layer evaporated on a precleaned glass substrate served as the counter electrode and was placed in parallel with the FTO glass substrate. The internal space of the device was subsequently filled with a liquid electrolyte (0.5 M LiI, 50 mM I_2 , 0.5 M 4-tertbutylpyridine in 3-methoxypropionitrile) by the capillary effect.^[16] The entire cell was then fully packaged and covered for DSSC performance measurement. The same fabrication process was applied to a TiO_2 nanotube-based DSSC.

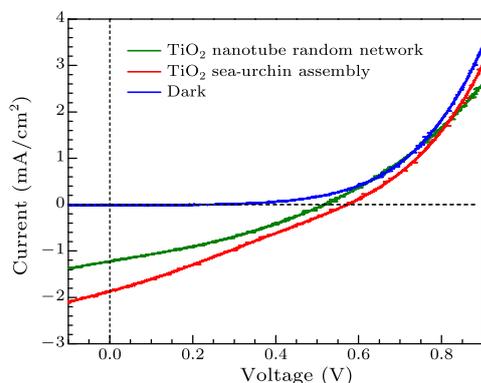


Fig. 4. J - V curves of the sea-urchin-like structures and nanotube-based DSSCs under one full-sun illumination.

The DSSCs were irradiated using a solar simulator (Newport, 300 W Model 91160) with an AM 1.5 spectrum distribution to simulate full-sun intensity ($100 \text{ mW} \cdot \text{cm}^{-2}$). The plots of current density versus

voltage (J - V) were recorded for both TiO_2 sea-urchin-like structures and nanotube-based DSSCs to evaluate their performance. In our experiments, most of the sea-urchin-like structure based DSSCs showed higher efficiency than that of the nanotube-based DSSCs. A typical comparison in performance of TiO_2 nanotubes and sea-urchin-like structure based DSSCs is shown in Fig. 4. It can be seen that the open circuit voltages V_{oc} and short-circuit current densities J_{sc} for both configurations of DSSCs can be obtained as about 0.57 V, 2.1 mA/cm^2 for sea-urchin-like structure based DSSCs and about 0.51 V, 1.4 mA/cm^2 for nanotube-based DSSCs. The fill factors FF are determined as 0.36 and 0.38 for sea-urchin-like structures and nanotube-based DSSCs, respectively. The energy conversion efficiencies are hence calculated as about 0.43% and 0.27% for the sea-urchin-like structures and nanotube-based DSSCs, respectively. An enhanced solar energy harvesting efficiency with an enhancement factor of 1.6 was achieved by replacing the random nanotube network with an ordered assembly of nanotubes in sea-urchin-like structures, with all other conditions remaining the same. This can be understood by the fact that the TiO_2 sea-urchin-like structures are more ordered compared with the TiO_2 nanotubes with random orientations (Fig. 2), which can increase the diffusion length and hence the lifetime of photon-induced electrons, and reduce the probability of parasitic conducting paths, which are detrimental for efficient carrier collection. For a random network of TiO_2 nanotubes, the electrons generated by incident photons move in a random-walk manner, resulting in a decreased output current. In addition, the dye molecules are more easily absorbed into the TiO_2 sea-urchin-like structures when the constituent TiO_2 nanotubes are radially aligned, while the TiO_2 nanotubes in the random network are lying flat in the 2D plane, which significantly reduces the area for absorption of light-harvesting dye molecules. It can be observed clearly from Fig. 2 that there are more spaces in sea-urchin-like structures as compared with nanotubes. These TiO_2 sea-urchin-like structures are also beneficial for increasing the effective amount of TiO_2 nanotubes that can be illuminated by sunlight, which also means that a larger number of dye molecules absorbed on the TiO_2 nanotubes will interact with the illuminating sun light and generate an enhanced output power.

In conclusion, we have presented a facile, cost-effective, simple and template-free method for the self-assembly of TiO_2 sea-urchin-like structures and proposed a probable formation mechanism. This typical synthesis process involves the initial formation of tubular nanostructures and the subsequent self-assembly of nanotubes into micrometer-scale sea-

urchin-like structures under alkali aqueous conditions. Alkali aqueous solutions play an important role in the formation of TiO₂ sea-urchin-like structures. The application of as-synthesized TiO₂ sea-urchins-like structures in DSSCs has also been investigated and we have shown an improved efficiency compared with DSSCs based on random TiO₂ nanotubes, demonstrating promising potential in applications such as high-efficiency solar energy harvesting, photocatalysis and opto-electronics devices.

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