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Facile production of a large-area flexible TiO$_2$/carbon nanofiber sheet for water purification†

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Through the precoating of TiO$_2$ on carbon fiber sheet and the subsequent hydrothermal reaction of the coated species with NaOH and tetrabutyl titanate, we successfully demonstrated the engineering growth of TiO$_2$ nanofibers on carbon fiber sheet. The resulting sheet exhibits excellent flexibility and enables robust, large-area (~300 cm$^2$) fabrication, representing a significant advantage over previous brittle, small area nanofibrous macroscopic structures. The adsorption and photodecomposition of Rhodamine B in water showed that the resulting sheet is very convenient for the purification of contaminated water owing to its combined adsorption and cleaning function. This work provides new insight into the construction of a large area, flexible and robust water purification membrane material.

Introduction

Due to the rapid population growth and mounting environmental crisis, water shortage has become one of the top issues and is probably expected to be the most important problem in the future. Therefore, the development of new and multifunctional water purification materials is becoming an important task for the materials community. To meet the demand of practical water purification, the essential features of next generation water purification materials should be high efficiency, high durability, easy recovery, low cost, and environment beneath.

In the past decade, macroscopic structures consisting of nanounits (e.g., nanowires, nanotubes, nanosheets, etc.) have been demonstrated as promising candidates for catalysts, energy-harvesting systems, and energy-consuming post-treatments (organic solvent cleaning, high temperature calcination, etc.) are needed to remove the anhydro contamination from the carbon-based macroscopic structures for the aim of regeneration, which limited their widespread application. Comparing with carbon macroscopic structures, TiO$_2$ macroscopic structures exhibit easy regeneration feature, since TiO$_2$ nanounits can provide photogenerated charges to decompose the pollutants on their surface under the illumination of ultraviolet light. Recent reports have demonstrated the superiorities of TiO$_2$ macroscopic structures for water purification. However, the reported TiO$_2$ macroscopic structures are always brittle and the size is small, which are the main obstacles to their widespread practical applications.

Carbon fiber sheet (CFS) is a kind of robust multipurpose material with high mechanical strength, good temperature and corrosion resistance. Therefore, the growth of TiO$_2$ nanofibers on CFSs may give rise to robust macroscopic nano-architectures, which may serve as a class of recoverable and durable adsorbent and photocatalytic materials as they will greatly facilitate the treatment of wastewater. Traditional powder photocatalysts need to be dispersed into the waste water and therefore it is impractical to use them for river purification since recovery is almost impossible and causes secondary pollution. In comparison, the modified CFSs can be immersed into wastewater and organic pollutants will be captured by the high porous structures formed by the overlapping and interpenetration of the nanofibers. After the irradiation of UV light, the adsorbed organic pollutants could be eliminated. Once the water is cleaned, the CFSs together with TiO$_2$ nanofibers can be easily lifted from the water.

In this work, through the precoating of TiO$_2$ on CFSs and the subsequent hydrothermal reaction of the coated species with NaOH and tetrabutyl titanate (TBT), we achieved a large area,
flexible and robust TiO₂ nanofiber macroscopic structure. The adsorption and photodecomposition of Rhodamine B (RhB) in water demonstrated the great convenience of the products in the purification of contaminated water.

Experimental

Materials and methods

CFSs were commercially available (purchased from Jiaxing Wanwei Textile Co., Ltd.). The other reagents were all purchased from Shanghai Chemical Co. and used as received.

Growth of TiO₂ nanofibers on the CFSs

Before use, CFS was cleaned with 1 M NaOH solution and distilled water and was dried in an oven at 90 ºC. The clean CFS was immersed into 15 vol.% tetrabutyl titanate/hexane solution for 5 mins, and thus the surface of CFS was wetted by tetrabutyl titanate/hexane solution. When CFS was taken out, hexane would volatilize rapidly and only tetrabutyl titanate would be left on the textile. Then, the textile was exposed to water vapor to promote the hydrolysis of tetrabutyl titanate and the generation of TiO₂. This wetting-hydrolysis process was repeated three times in order to increase the loading capacity of TiO₂. After that, the textile coated by TiO₂ was rolled up and placed into an autoclave filled with 10 M NaOH solution and 0.5 ml tetrabutyl titanate. The size of the textile is dependent on the volume of the autoclave. For a 100 mL autoclave, the texture can be several hundreds of square centimeters in size. For a 1 L autoclave, the textile can be several square meters. After heated at 200 ºC for 48 hours, the autoclave was cooled down to room temperature and the textile was taken out, washed alternatively with 0.1 M HAc and distilled water for five times, and calcined at 500 ºC under air atmosphere for 3 hours. It could be seen that the CFS had changed its color from the initial black to white, which suggested the presence of TiO₂.

Characterization

The loading capacity of TiO₂ on the textile was determined by comparison of the initial weight and the final weight of the textile. The morphology observations of the textile and the nanofibers were carried out on a HITACHI S-4800 scanning electron microscope (SEM). X-ray diffraction (XRD) patterns of the textile was recorded on an X’Pert PRO SUPER rA rotation anode X-ray diffractometer with Ni-filtered Cu-Kα radiation (λ = 1.5418 Å). Diffuse reflectance spectra (DRS) and UV-vis absorption spectra were recorded on a Cary 5000 UV-vis-near-infrared spectrophotometer fitted with an integrating sphere. The samples for SEM, XRD, and DRS characterizations were the textile directly. The samples for TEM characterization were prepared as follows: TiO₂ nanofibers were exfoliated from the textile by ultrasound, dispersed in absolute ethanol, and dropped onto a carbon film supported on a copper grid.

Evaluation of photocatalytic activity of modified foam

RhB is a chemically stable and poorly biodegradable dye contaminant in wastewater. Here we use its decomposition as a simulation to demonstrate the great advantages of the modified textile in the purification of the contaminated water. At first, we studied the robustness and reusability of the modified textile by repeated adsorption-lifting-irradiation experiments. A piece of the modified textile (dimensions: 2 cm × 4 cm) was immersed into 100 mL RhB solution (concentration: 9 mg/L) for 10 minutes. The modified textile was lifted from the solution and irradiated by a 10 W UV lamp (wavelength: 254 nm, light intensity: 0.08mW/cm²). During the irradiation, the modified textile was placed 10 cm away from the lamp, and its each side was irradiated 30 minutes. The existence of the RhB molecules on the surface of the modified textile was monitored by measuring the diffuse reflection spectrum. The above adsorption-lifting-irradiation process was repeated ten times. Subsequently, we investigated the photodegradation behavior of RhB under the continuous photocatalysis of the modified textile. During these studies, the modified textile was immersed in the solution all the time. The concentration of the RhB solution was monitored by detecting the absorbance at 550 nm per 20 min.

Results and discussion

Characterization of TiO₂ nanofibers on the CFSs

Scheme 1 describes the process of the engineering growth of TiO₂ nanofibers on the CFSs. Firstly, a piece of CFSs is soaked in TBT/hexane solution for wetting. The sizes of the textile are unrestricted as long as it can be held by the reactor. When the textile is taken out, hexane volatilizes rapidly and only TBT molecules are left on the skeletons of the CFSs. Once the resulting textile was exposed to water vapor, TBT molecules hydrolyze immediately and yield TiO₂ particles on the skeletons of the textile (Figure S1c and S1d, ESI†). The wetting–hydrolysis process is repeated three times to increase the loading capacity of TiO₂ on the textile (Figure S1e and S1f, ESI†), and is essential for the engineering growth of nanofiber on CFS. Secondly, the resulting textile was allowed to react with 10 M NaOH solution and 0.5 ml TBT under hydrothermal condition for the engineering growth of sodium titanate nanofibers on CFSs. When TBT was absent from the hydrothermal reaction, a small amount of nanofibers can be grown on the textile. Sodium titanate nanofibers could be converted into TiO₂ nanofibers through the post-treatment of acid washing and calcination. Consequently, the TiO₂ nanofiber modified CFSs is successfully engineered.

The hydrothermal reaction was accompanied by a color change from the initial black to white and resulted in the formation of Na₂TiO₃ nanofibers on CFSs, which is further confirmed by X-ray powder diffraction (XRD) test (Fig. 1, curve b). After annealed at 500 ºC for 3h, Na₂TiO₃ was transformed to TiO₂. The XRD patterns of the as-prepared TiO₂ nanofiber modified CFSs are shown in Fig. 1, curve c. All the diffraction peaks can be indexed to TiO₂ (JCPDs file, No 35-0088), indicating the successful growth of TiO₂ nanofibers on the textile. The XRD
The precoated TiO$_2$/CFS composite showed a strong peak centered at 25.5°, demonstrating the good crystalline properties of TiO$_2$ nanofibers. Notably, no typical diffraction peaks of the CFS are observed in the TiO$_2$/CFS sample, which is attributed to the fact that the main peak of anatase TiO$_2$ at 25.5° may be shielded by the main characteristic peak of CFS.

Fig. 1 XRD patterns. (a) Pure CFS; (b) CFS grown by Na$_2$Ti$_2$O$_7$ nanofibers; (c) CFS grown by TiO$_2$ nanofibers.

Fig. 2a and 2b show the digital photographs of CFSs and TiO$_2$ nanofiber modified CFSs. White and uniform layers were formed and firmly attached on both sides of CFSs, indicating the successful growth of TiO$_2$ nanofibers on CFS through the designed approach shown in scheme 1. Furthermore, the size of the final products depends on the volume of the autoclave, since the present method is great versatile in scaling up the synthesis for industrial production by further enlarging the equipment. As far as we know, it is difficult to achieve such large-size TiO$_2$ nanofiber macroscopic structures with traditional methods. In addition, the CFS grown by inflexible TiO$_2$ nanofibers is flexible and easily curled (Figure S2b, ESI†), which is highly desirable for the construction of flexible devices, such as wearable energy harvesting and self-cleaning systems.

A low-magnification SEM image (Fig 2c) reveals that the white layers on both sides of CFS were consisting of long and flexible TiO$_2$ nanofibers and the nanofibers are uniform, long, and ribbon-like and the diameters of the nanofibers are below 200 nm and longitudinal dimensions are several tens to several hundreds of micrometers. Further SEM observations (Fig 2d) indicate that there are two kinds of nanofibers in the TiO$_2$ nanofiber layers. One kind of nanofibers was formed on the surface of carbon fibres (indicated by green cycle in Fig 2d), while another kind was formed between carbon fibres (indicated by red box in Fig 2d). The nanofibers on the surface of the CFS were the hydrothermal reaction products of the added TBT with NaOH, while the nanofibers between carbon fibres were formed from the precoated TiO$_2$ particles and their engineering growth was directed by the capillary forces between carbon fibers.

Both the precoated TiO$_2$ particles and TBT are essential for the engineering growth of nanofibers on CFS. In the hydrothermal treatment process, the absorbed TiO$_2$ particles on the surface of carbon fibers were transformed to long nanofibers and the as-prepared nanofibers were in situ anchored with CFS via the overlapping and interpenetration of the flexible TiO$_2$ nanofibers and carbon fibres. When no TiO$_2$ particles were precoated on CFS, few nanofibers were randomly introduced on the CFS, which can be easily washed off from the CFS because of the weak interaction between TiO$_2$ and carbon fibers. The nanofibers obtained via the hydrothermal reaction of TBT and NaOH further interweaved with the nanofibers grown on CFS, leading to the formation of dense nanofiber layers on CFS. The layer thickness can be easily controlled via the amount of the TBT added. When TBT is absent from the hydrothermal reaction, only a small amount of nanofibers were formed on the CFS. 0.1 mL TBT gave rise to thin nanofiber layers, while 0.5 mL TBT led to the formation of thick layers (Figure S3, ESI†). When more than 0.5 mL TBT was added to the reaction system, large amount of white precipitate was formed at the bottom of the autoclave, indicating the maximum amount of TiO$_2$ nanofibers have been achieved on the CFS. Such a textile with a size of 4 cm$^2$ can support 100 mg of TiO$_2$ nanofibers.

Previously, coating of TiO$_2$ onto polymers, cotton textiles and foams have been achieved by the method of impregnation or plasma sputtering, where TiO$_2$ is composed of irregular nanoparticles. Comparing with nanoparticles, nanofibers permit easy electron transport in one dimension, which is favorable towards improving the photocatalytic performance. In addition, TiO$_2$ nanoparticles supported by polymers or cotton textiles are not suitable for durable photocatalytic materials because the polymers and textiles may also be decomposed by TiO$_2$. Furthermore, because of the weak interactions between TiO$_2$ and substrate, the TiO$_2$ may fall off the support during the photocatalytic process. In our case, TiO$_2$ nanofibers were firmly anchored with the CFS via the overlapping and interpenetration, so the as-prepared textile can serve as a class of recoverable and...
durable photocatalytic materials without catalyst loss.

**Optical properties**

Fig. 3b shows the surface diffuse reflection spectra of the pure textile and the CFSs grown by the TiO$_2$ nanofibers. Pure textile does not have characteristic absorption bands. But the modified textile exhibits an intense absorption towards light below 400 nm. Consequently, the modified textile can utilize light efficiently and provide photogenerated charges for photocatalytic reactions.

**Photocatalytic performance**

As a chemically stable and poorly biodegradable dye, RhB is a main contaminant in wastewater. In this work, we use the photodegradation of RhB as a model reaction to evaluate the great advantages of the textile modified by TiO$_2$ nanowires in the purification of polluted water. Firstly, we investigated the robustness and reusability of the prepared textile by repeated adsorption–lifting–irradiation experiments. As shown in Fig. 3a, the modified textile was immersed into the wastewater to capture RhB. Then the CFSs together with the TiO$_2$ nanofibers and RhB was lifted from the water. Finally the textile was irradiated to remove RhB. Fig. 3c shows the diffuse reflection spectra of the modified textile at the three stages. Initially, only a sharp band around 400 nm was found, which is attributed to the TiO$_2$ nanofibers on the textile. At the second stage, an additional band around 550 nm appeared, which is due to the chromophores in the RhB molecules. These results revealed that the RhB in the solution was captured by the modified textile. The quantity of the adsorbed RhB was calculated by measuring the concentration of the RhB solution before and after adsorption and the RhB adsorption capacity of the modified textile is 0.4 mg/g (Figure S5, ESI†). It is noted that the pure CFSs only causes a slight fading of the RhB solution (Figure S6, ESI†). The high adsorption capacity of the TiO$_2$ nanofiber/carbon fiber sheet benefited from its large BET surface area (17.638 m$^2$/g) and pore structure (Figure S7, ESI†). When the TiO$_2$/carbon fiber sheet is irradiated with ultraviolet light (254 nm), conduction band electrons (e$^-$) and valence band holes (h$^+$) are generated on TiO$_2$ nanofibers. The photogenerated electrons and holes can react with H$_2$O and O$_2$ molecules, leading to the formation of reactive oxygen species, such as O$_2^-$ and •OH. The resulting reactive oxygen species can oxidize RhB to CO$_2$, H$_2$O and mineral end-products. After irradiation under UV light for 60 mins, the diffuse reflection spectrum of the modified textile changed back to the original form (blue line), indicating that the adsorbed RhB molecules were removed. The adsorption–lifting–irradiation process can be repeated many times while retaining the photocatalytic activity of the modified textile (Figure S4, ESI†), confirming that the modified textile is a reusable and durable photocatalytic material.

Subsequently, we investigated the photodegradation behaviors of RhB under continuous photocatalysis of the modified textile. During the studies, the modified textile is immersed in the solution all the time. RhB was completely photodegraded by the modified textile within 80 min (Fig. 4a), demonstrating the high photocatalytic efficiency of the modified textile. RhB was degraded fast initially, but the degradation rate become slow after 40 min as the concentration of RhB decreased. The average degradation rate $k$ is 0.6 mg/h ($k = m/t$, where $m$ and $t$ indicate the weight of the degraded pollutant and the irradiation time, respectively), which is similar with the reported TiO$_2$ nanofiber framework. It is noted that the pure CFSs has no photocatalytic activity and it only causes a slight fading of the RhB solution due to the adsorption of a small amount of RhB by the textile (Figure S6, ESI†).

Owing to the existence of carbon fibers, the as-prepared TiO$_2$ nanofiber/carbon fiber sheets exhibited lower photocatalytic activity than the reported TiO$_2$ nanofiber membranes. For TiO$_2$ nanofiber/carbon fiber sheets, only the TiO$_2$ nanofibers can utilize ultraviolet light for photodegradation of RhB, because carbon fibers do not have photocatalytic activity. For TiO$_2$ nanofiber membranes, all the building blocks of the membrane can serve as active sites to eliminate RhB. Furthermore, the TiO$_2$ nanofibers/CFSs exhibited much higher photocatalytic activity than the reported TiO$_2$ nanotubes/CFSs and P25/CFSs (Figure S8a, ESI†). Comparing with TiO$_2$ nanotubes and P25, TiO$_2$ nanofibers possess ultralong 1D structure, which is benefiting for the overlapping and interweave with carbon fibers, so the TiO$_2$
nanofibers were not only grown between the carbon fibers, but also formed on the surface of the carbon fibers, leading to higher loading capacity of TiO$_2$ nanofibers on carbon fiber sheets (one square centimeter of CFS can support 25 mg nanofibers VS 5 mg nanotubes or P25). In other word, more active sites were formed on TiO$_2$ nanofibers/CFSs than TiO$_2$ nanotubes/CFSs and P25/CFSs with same size. Consequently, The TiO$_2$ nanofibers/CFSs exhibited much higher photocatalytic activity than the reported TiO$_2$/CFSs composite. In addition, the modified textile had good reuse capacity; even after five times reuse, the degradation ratio of RhB is still as high as ca. 97% (Fig. 4c), while only 20% for P25/CFSs (Figure S8b, ESI†). No catalyst loss was observed during the repeated photocatalytic test (Fig. 4d), indicating the TiO$_2$ nanofibers were firmly anchored with the CFS. The TiO$_2$ nanofiber/CFSs were also capable of photodecomposing many organic pollutes, including Methylene blue, Methyl orange, and Fluorescein (Figure S9, ES†). Therefore, the modified textile is a class of recoverable and durable photocatalytic materials, which has great potential in water purification.

**Conclusions**

In the work reported here, we have demonstrated a facile strategy for the engineering growth of TiO$_2$ nanofibers on CFS. The resulting large size nanofiber macroscopic structure is a durable photocatalytic material since it can be easily recovered and the robustness of the modified textile allows it to be reused. The as-prepared TiO$_2$ nanofiber modified CFS possesses both adsorption functionality and cleaning functionality and should have potential for advanced water purification. In addition, the obtained nanofiber macroscopic structure is a kind of versatile scaffold for the construction of macroscopic multifunctional materials, which might also be of interest in solar cell, catalysis, and separation technology.

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**References**

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We successfully produced a large area, flexible and robust TiO$_2$ nanofiber/carbon fiber sheet with great convenience for water purification.

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