

## Electronic Supplementary Information (ESI)

### Facile production of a large-area flexible TiO<sub>2</sub>/carbon cloth for dye removal

Le Yang,<sup>a</sup> Zonghan Hong,<sup>a</sup> Jun Wu,<sup>a</sup> and Lian-Wen Zhu<sup>\*,b</sup>

<sup>a</sup> College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China

<sup>b</sup> School of Biology and Chemical Engineering, Jiaxing University, Jiaxing, Zhejiang 314001, People's Republic of China

## Table of Contents

**Figure S1.** (a, b) SEM image of CFSs before the coating of TiO<sub>2</sub>. The surface of the CFSs is clean. (c-f) SEM images of CFSs coated by TiO<sub>2</sub> through the wetting-hydrolysis process. The surfaces of the CFSs are covered by TiO<sub>2</sub> particles. There are a small amount of TiO<sub>2</sub> particles on the surface of the CFSs when the wetting-hydrolysis process is not repeated (c and d). A large amount of TiO<sub>2</sub> particles are seen when the wetting-hydrolysis process is repeated three times (e and f). .....S1

**Figure S2.** Photographs of the TiO<sub>2</sub> nanofiber macroscopic structure obtained in a 100 mL autoclave. (a) The size of the TiO<sub>2</sub> nanofiber macroscopic structure is 300 cm<sup>2</sup>, and it is quite possible to realize larger scale synthesis for industrial production by further enlarging the equipment. (b) The TiO<sub>2</sub> nanofiber macroscopic structure is flexible and easily curled, which is highly desirable for the construction of flexible devices, indicating the designed capillary force directed process is a simple and effective for the construction of a large area, flexible and robust nanofiber macroscopic structures. ....S2

**Figure S3.** Photographs of the cloth obtained from different reaction conditions. (a) 0.1 ml TBT; (b) 0.5 ml TBT. 0.1 mL TBT gave rise to thin nanofiber layers, while 0.5 mL TBT led to the formation of thick layers, indicating the layer thickness can be easily controlled via the amount of the TBT added. ....S3

Fig. S4 Temporal spectral changes of RhB solutions adsorbed by the TiO<sub>2</sub> nanofiber/CFS. Equilibrium was established at 24 h, since no significant change in the absorbance intensity was observed in the following hours. The quantity of the adsorbed RhB was calculated by measuring the concentration of the RhB solution before and after adsorption using the following equation:

$$q_e = \frac{C_0 - C_e}{S}$$

Where  $q_e$  (mg/g) is the amounts of RhB adsorbed per unit weight of the photocatalyst at adsorption equilibrium,  $C_0$  (mg/L) is the initial RhB concentration,  $C_e$  (mg/L) is the RhB

concentration at equilibrium and  $S$  (g/L) is the ratio between the weight of the photocatalyst and the volume of the aqueous solution. The RhB loading is 0.4 mg/g. ....S4

**Figure S5.** UV-vis absorption spectra of the RhB solutions before and after interaction with CFS and TiO<sub>2</sub>/carbon fiber composite, where insets are the optical photographs of the dye solutions. (a): CFS; (b): TiO<sub>2</sub>/carbon fiber composite. The minor changes of the absorbance intensity in Figure S5a proven that CFSs only have a small adsorption of chemical pollutants, which is in good agreement with the fading phenomenon of the dye solutions (the inset in Figure S6a), indicating that CFSs only have a small adsorption of chemical pollutants. Under the same conditions, an equal size of TiO<sub>2</sub>/carbon fiber sheet fade the dye solutions obviously (the inset in Figure S6b), revealing that the strong absorbability of TiO<sub>2</sub>/carbon fiber composite towards the dyes. ....S5

**Figure S6.** (a) Nitrogen adsorption–desorption isotherms of TiO<sub>2</sub> nanofiber/carbon composite at 77 K. (b) BJH pore-size distribution plots determined from the desorption branch. The BET surface area of the TiO<sub>2</sub>/carbon composites is 17.638 m<sup>2</sup>/g and the average pore diameter is 5.9948 nm, which enable their high adsorption capacity for RhB. ....S6

**Figure S7.** (a) Schematic reaction of the photodegradation of the dye; (b) Reaction scheme of the oxidation of the dye. When the TiO<sub>2</sub>/carbon cloth is irradiated with ultraviolet light (254 nm), conduction band electrons (e<sup>-</sup>) and valence band holes (h<sup>+</sup>) are generated on TiO<sub>2</sub> nanofibers. The photogenerated electrons and holes can react with H<sub>2</sub>O and O<sub>2</sub> molecules adsorbed on the surface of TiO<sub>2</sub>, leading to the formation of reactive oxygen species, such as O<sub>2</sub><sup>-</sup> and •OH. The formed reactive species attack on the aromatic chromophore ring, leading to the degradation of the RhB structure and the formation of a number of intermediates without a wavelength shift, mainly aromatic and aliphatic acid. The formation, transformation, and removal/breaking of the chromophore in those intermediates could proceed simultaneously with a fast ring-opening process and a complete mineralization in the presence of TiO<sub>2</sub>. The final products of the RhB photodegradation were CO<sub>2</sub>, H<sub>2</sub>O, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, which are rather safe for the

environment. ....S7

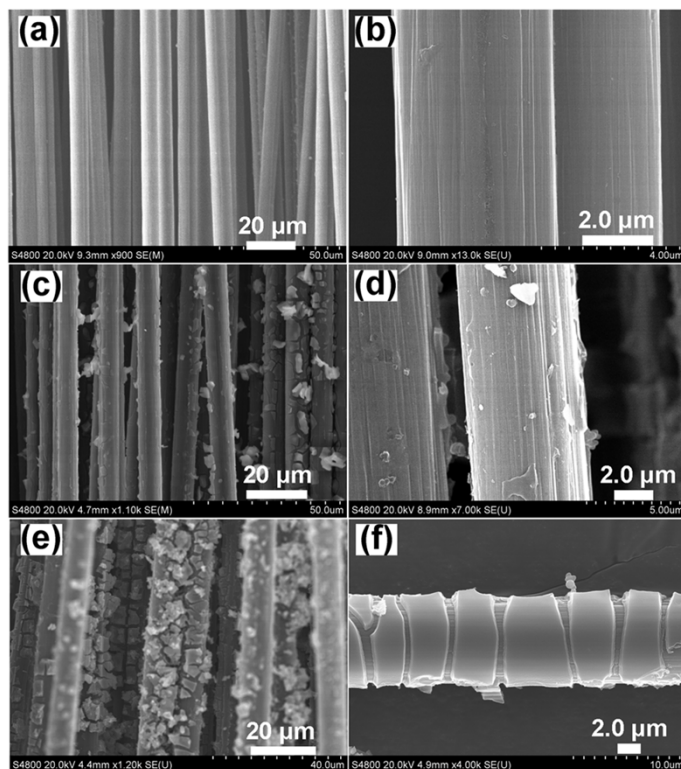
**Figure S8.** Diffuse reflection spectra of modified textile after ten times of adsorption (curve 1) and irradiation (curve 2) with UV light. It can be seen that the modified textile still has a strong adsorbability towards RhB and a high photocatalytic activity. Because the TiO<sub>2</sub> nanofibers were firmly anchored with the CFS and no catalyst loss was observed during the repeated photocatalytic and adsorption test. Therefore, the modified textile is a class of recoverable and durable photocatalytic and adsorption materials, which has great potential in water purification.

.....S8

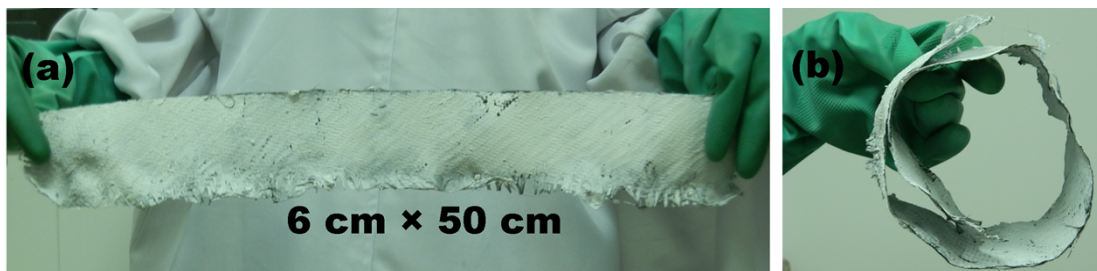
**Figure S9.** (a) Temporal spectral changes of RhB catalyzed by P25/carbon fiber sheets under the illumination of a ultraviolet lamp. (b) Curve of the degradation ratio of RhB versus reuse times of P25/carbon fiber sheets under UV light irradiation for 80 min.

P25/carbon fiber sheets were prepared as follows: A piece of clean carbon fiber sheet (dimensions: 2 cm × 4 cm) was immersed in 50 mL alcohol containing 0.5g P25 powder. After alcohol volatilized, P25 were left on the surface of carbon fiber sheet. Consequently, P25/carbon fiber sheets were successfully prepared. Then, P25/carbon fiber sheets were applied for the photodegradation of RhB. Only 40% of RhB molecular were photodegraded by P25/carbon fiber sheets within 80 min (Figure S7a), which is much lower than TiO<sub>2</sub> nanofiber/CFSs because of lower loading capacity of P25 on carbon fiber sheets (25 mg TiO<sub>2</sub> nanofibers VS 5 mg P25). Furthermore, repeated photocatalytic tests reveal that TiO<sub>2</sub> nanofibers/CFSs possess better catalytic durability than P25/carbon fiber sheets. After five times reuse, the degradation ratio of RhB by TiO<sub>2</sub> nanofibers/CFSs is still as high as ca. 97%; while only 20% by P25/carbon fiber sheets (Figure S7b). For TiO<sub>2</sub> nanofibers/CFSs, TiO<sub>2</sub> nanofibers were firmly anchored with the CFS and no catalyst loss was observed during the repeated photocatalytic test (Fig. 4d). In contrast, P25 easily get away the carbon nanofiber sheet during the catalytic process because of weak interaction between P25 and carbon fiber sheet, leading to the decline of the catalytic durability. Therefore, the TiO<sub>2</sub> nanofibers/CFS is a class of recoverable and durable photocatalytic materials, which has great potential in water purification. ....S9

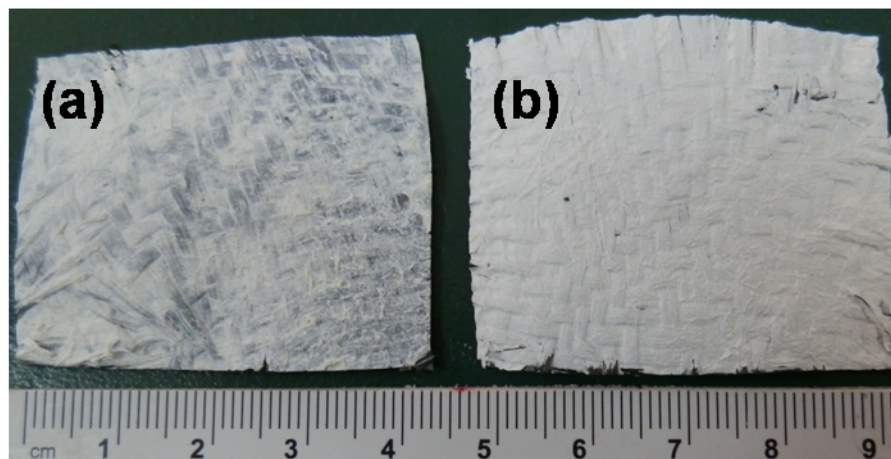
**Figure S10.** Temporal spectral changes of dye solutions catalyzed by the TiO<sub>2</sub> nanofiber/CFSs. (a) Methylene blue, (b) Methyl orange, (c) Fluorescein. ....S10



**Figure S1.** (a, b) SEM image of CFs before the coating of TiO<sub>2</sub>. The surface of the CFs is clean. (c-f) SEM images of CFs coated by TiO<sub>2</sub> through the wetting-hydrolysis process. The surfaces of the CFs are covered by TiO<sub>2</sub> particles. There are a small amount of TiO<sub>2</sub> particles on the surface of the CFs when the wetting-hydrolysis process is not repeated (c and d). A large amount of TiO<sub>2</sub> particles are seen when the wetting-hydrolysis process is repeated three times (e and f).

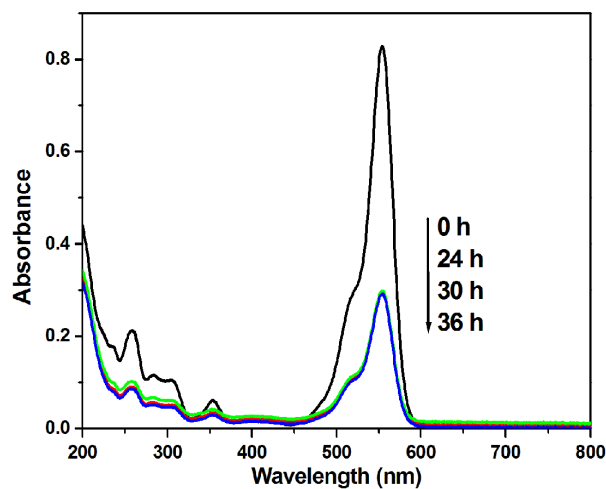


**Figure S2.** Photographs of the TiO<sub>2</sub> nanofiber macroscopic structure obtained in a 100 mL autoclave. (a) The size of the TiO<sub>2</sub> nanofiber macroscopic structure is 300 cm<sup>2</sup>, and it is quite possible to realize larger scale synthesis for industrial production by further enlarging the equipment. (b) The TiO<sub>2</sub> nanofiber macroscopic structure is flexible and easily curled, which is highly desirable for the construction of flexible devices, indicating the designed capillary force directed process is a simple and effective for the construction of a large area, flexible and robust nanofiber macroscopic structures.



**Figure S3.** Photographs of the cloth obtained from different reaction conditions. (a) 0.1 ml TBT; (b) 0.5 ml TBT. 0.1 mL TBT gave rise to thin nanofiber layers, while 0.5 mL TBT led to the formation of thick layers, indicating the layer thickness can be easily controlled via the amount of the TBT added.

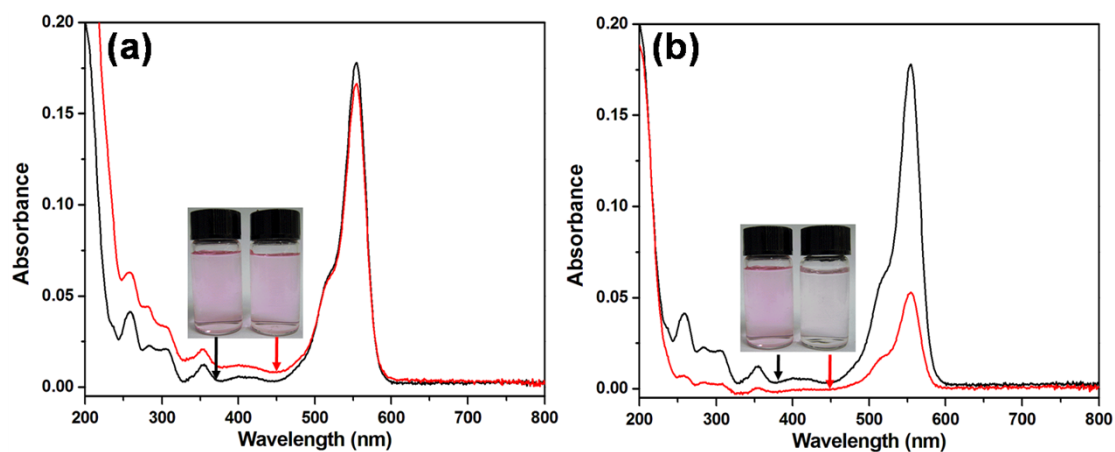




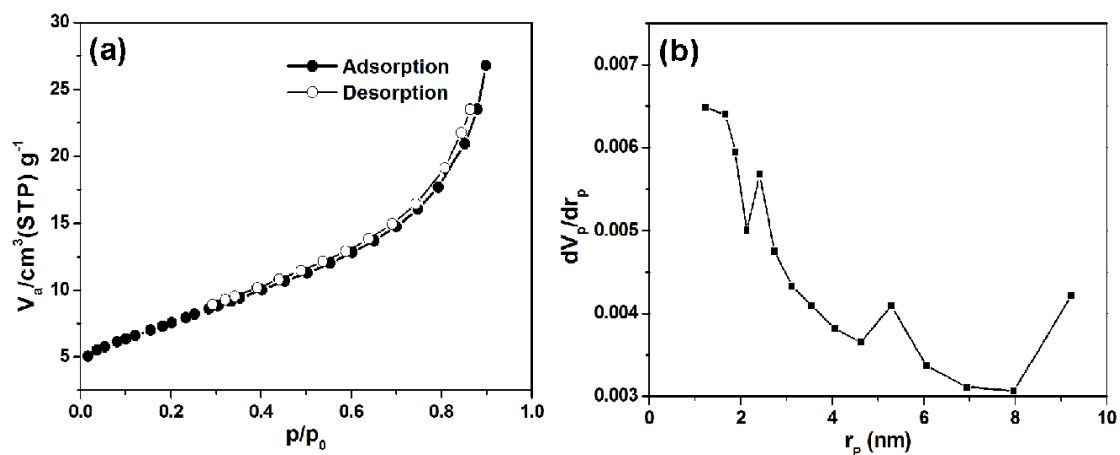
**Figure S4.** Temporal spectral changes of RhB solutions absorbed by the TiO<sub>2</sub> nanofiber/CFS. Equilibrium was established at 24 h, since no significant change in the absorbance intensity was observed in the following hours. The quantity of the adsorbed RhB was calculated by measuring the concentration of the RhB solution before and after adsorption using the following equation:

$$q_e = \frac{C_0 - C_e}{S}$$

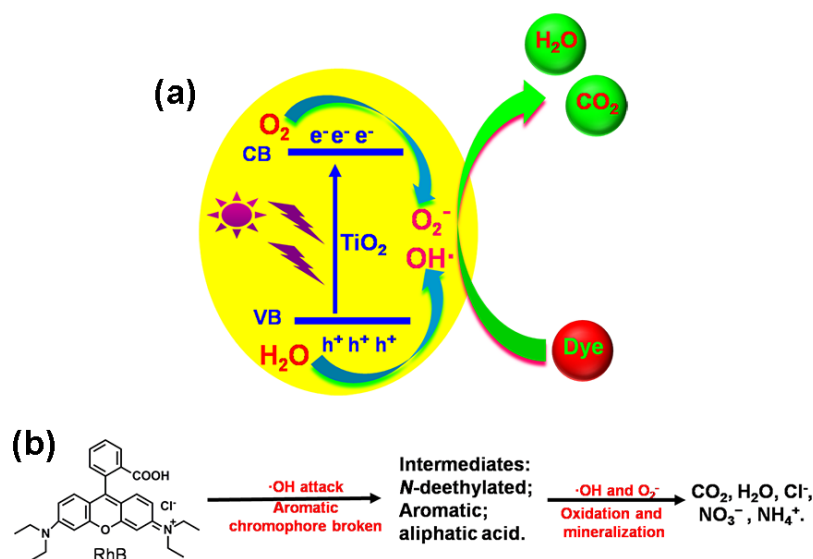
Where  $q_e$  (mg/g) is the amounts of RhB adsorbed per unit weight of the photocatalyst at adsorption equilibrium,  $C_0$  (mg/L) is the initial RhB concentration,  $C_e$  (mg/L) is the RhB concentration at equilibrium and  $S$  (g/L) is the ratio between the weight of the photocatalyst and the volume of the aqueous solution. The RhB loading is 0.4 mg/g.



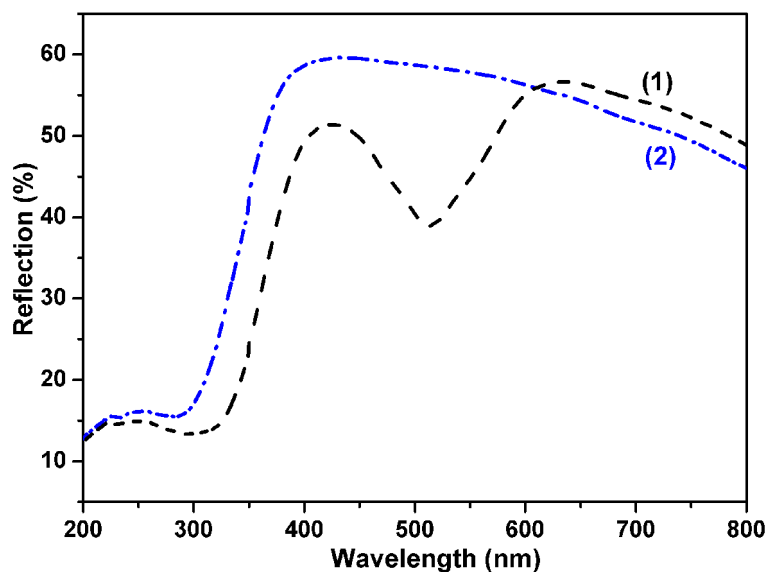
**Figure S5.** UV-vis absorption spectra of the RhB solutions before and after interaction with CFS and TiO<sub>2</sub>/carbon fiber composite, where insets are the optical photographs of the dye solutions. (a): CFS; (b): TiO<sub>2</sub>/carbon fiber composite. The minor changes of the absorbance intensity in Figure S5a proven that CFSs only have a small adsorption of chemical pollutants, which is in good agreement with the fading phenomenon of the dye solutions (the inset in Figure S6a), indicating that CFSs only have a small adsorption of chemical pollutants. Under the same conditions, an equal size of TiO<sub>2</sub>/carbon fiber sheet fade the dye solutions obviously (the inset in Figure S6b), revealing that the strong absorbability of TiO<sub>2</sub>/carbon fiber composite towards the dyes.



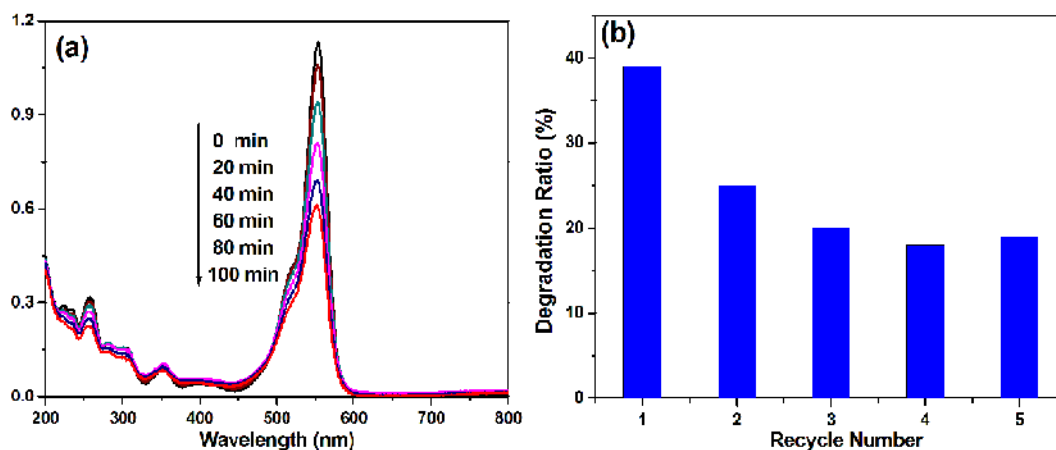
**Figure S6.** (a) Nitrogen adsorption–desorption isotherms of  $\text{TiO}_2$  nanofiber/carbon composite at 77 K. (b) BJH pore-size distribution plots determined from the desorption branch. The BET surface area of the  $\text{TiO}_2$ /carbon composites is  $17.638\text{ m}^2/\text{g}$  and the average pore diameter is  $5.9948\text{ nm}$ , which enable their high adsorption capacity for RhB.



**Figure S7.** (a) Schematic reaction of the photodegradation of the dye; (b) Reaction scheme of the oxidation of the dye. When the TiO<sub>2</sub>/carbon cloth is irradiated with ultraviolet light (254 nm), conduction band electrons (e<sup>-</sup>) and valence band holes (h<sup>+</sup>) are generated on TiO<sub>2</sub> nanofibers. The photogenerated electrons and holes can react with H<sub>2</sub>O and O<sub>2</sub> molecules adsorbed on the surface of TiO<sub>2</sub>, leading to the formation of reactive oxygen species, such as O<sub>2</sub><sup>-</sup> and •OH. The formed reactive species attack on the aromatic chromophore ring, leading to the degradation of the RhB structure and the formation of a number of intermediates without a wavelength shift, mainly aromatic and aliphatic acid. The formation, transformation, and removal/breaking of the chromophore in those intermediates could proceed simultaneously with a fast ring-opening process and a complete mineralization in the presence of TiO<sub>2</sub>. The final products of the RhB photodegradation were CO<sub>2</sub>, H<sub>2</sub>O, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, which are rather safe for the environment.

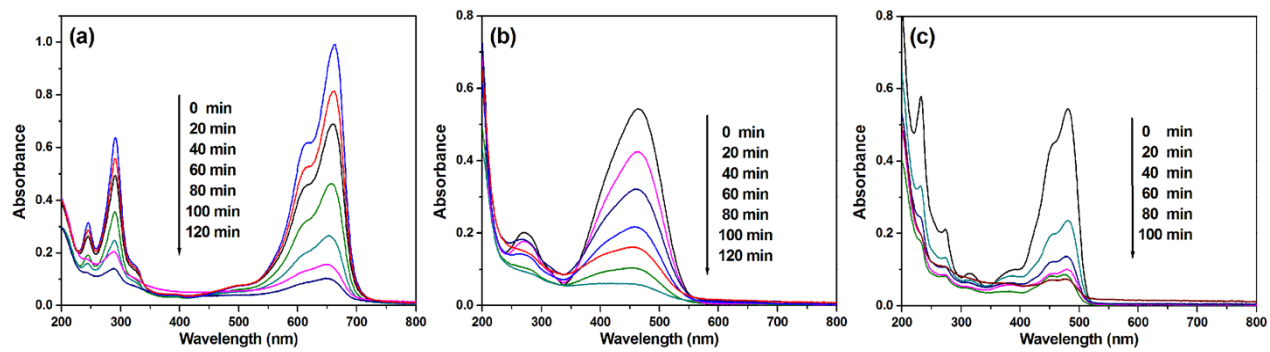


**Figure S8.** Diffuse reflection spectra of modified textile after ten times of adsorption (curve 1) and irradiation (curve 2) with UV light. It can be seen that the modified textile still has a strong adsorbability towards RhB and a high photocatalytic activity. Because the TiO<sub>2</sub> nanofibers were firmly anchored with the CFS and no catalyst loss was observed during the repeated photocatalytic and adsorption test. Therefore, the modified textile is a class of recoverable and durable photocatalytic and adsorption materials, which has great potential in water purification.



**Figure S9.** (a) Temporal spectral changes of RhB catalyzed by P25/carbon fiber sheets under the illumination of a ultraviolet lamp. (b) Curve of the degradation ratio of RhB versus reuse times of P25/carbon fiber sheets under UV light irradiation for 80 min.

P25/carbon fiber sheets were prepared as follows: A piece of clean carbon fiber sheet (dimensions: 2 cm × 4 cm) was immersed in 50 mL alcohol containing 0.5g P25 powder. After alcohol volatilized, P25 were left on the surface of carbon fiber sheet. Consequently, P25/carbon fiber sheets were successfully prepared. Then, P25/carbon fiber sheets were applied for the photodegradation of RhB. Only 40% of RhB molecular were photodegraded by P25/carbon fiber sheets within 80 min (Figure S7a), which is much lower than TiO<sub>2</sub> nanofiber/CFSS because of lower loading capacity of P25 on carbon fiber sheets (25 mg TiO<sub>2</sub> nanofibers VS 5 mg P25). Furthermore, repeated photocatalytic tests reveal that TiO<sub>2</sub> nanofibers/CFSS possess better catalytic durability than P25/carbon fiber sheets. After five times reuse, the degradation ratio of RhB by TiO<sub>2</sub> nanofibers/CFSS is still as high as ca. 97%; while only 20% by P25/carbon fiber sheets (Figure S7b). For TiO<sub>2</sub> nanofibers/CFSS, TiO<sub>2</sub> nanofibers were firmly anchored with the CFS and no catalyst loss was observed during the repeated photocatalytic test (Fig. 4d). In contrast, P25 easily get away the carbon nanofiber sheet during the catalytic process because of weak interaction between P25 and carbon fiber sheet, leading to the decline of the catalytic durability. Therefore, the TiO<sub>2</sub> nanofibers/CFS is a class of recoverable and durable photocatalytic materials, which has great potential in water purification.



**Figure S10.** Temporal spectral changes of dye solutions catalyzed by the TiO<sub>2</sub> nanofiber/CFSs. (a)

Methylene blue, (b) Methyl orange, (c) Fluorescein.