**Functional Carbon Nanofibers with Semi-Embedded Titanium Oxide Particles via Electrospinning**

*Guoqing Chang, Wajid Ullah, Yunfeng Hu, Liwei Lin, Xu Wang, and Chang-Zhi Li*

The formulation of optoelectronic components into 1D nanostructures allows the promotion of new materials with multifunctionalities. In this work, it is demonstrated that new synthesis of photocatalytic carbon nanofiber decorated with semi-embedded titanium oxide (TiO$_2$), namely, TiO$_2$@carbon fiber, is conveniently accessed through the electrospinning of polyacrylonitrile polymer and TiO$_2$ particle comixture, and then followed by photon-activated self-erosion to expose the embedded TiO$_2$ and carbonization. The hybrid nanofibers are characterized by field emission scanning electron microscopy, transmission electron microscopy, and X-ray diffraction analysis. Furthermore, the photocatalytic activities of the resultant fibers are tested with photodegradation of Rhodamine B in aqueous solution, which reveals that the carbon nanofiber with semi-embedded TiO$_2$ drastically improved catalytic efficiency and recyclability, comparing to those fibers without or with embedded TiO$_2$.

1. Introduction

Electrospinning has attracted attention of researchers since it offers unique capabilities for accessing continuous fibers from polymer solutions (or melts) with diameters ranging from micrometers down to a few nanometers.\(^\text{[1–4]}\) Especially, It has been revealed that carbon nanofibers (with diameter below 1000 nm) from electrospinning are proven materials with high thermal stability, large surface area, and good chemical resistance.\(^\text{[3–7]}\) On the other hand, to develop efficient methodologies and materials for tackling environmental pollution in water remains as one of the most critical challenges for sustainability of society. Among them, the utilization of polymer fibers or carbon hybrid materials turns out to be attractive for the adsorption and removal of organic dyes in aqueous solution.\(^\text{[8–10]}\) However, the recovery and disposal of adsorbed dyes as well as the absorbents remains as problematic. Consequently, the in situ photocatalytic degradation of organic pollutants exhibits advantages to potentially purify wastewater discharged from industry and households.

TiO$_2$ particles show strong photooxidation capability for organic compounds, which, however, easily aggregate in aqueous solution due to their high specific surface area.\(^\text{[11–18]}\) Meanwhile, the suspended particles in water are also difficult to be recollected and recycled.\(^\text{[19–25]}\) In this regards, composites and hybrid materials have been proposed and developed to address this challenge, including the incorporation of metal oxide with fibers.\(^\text{[20–33]}\) In particular, the hybrid TiO$_2$-fiber frameworks are intriguing family of photocatalysts, in which photocatalytic nanoparticles are combined with recyclable fiber mats.\(^\text{[22–27]}\) However, some deficiencies for these hybrids are that the detachment of loosely coated particles could decrease photocatalytic activities during recycling. In addition, the particles fully embedded into fibers could also lower the catalytic efficiency,\(^\text{[28]}\) due to the encapsulation of catalyst from reaction with organic pollutants. It recently revealed that metal oxide filled in hollow fiber can enhance the recyclability of the catalyst, in which photocatalysts are encapsulated at the inner of composites, while allowing dyes diffusing into.\(^\text{[34,35]}\) Therefore, the photocatalytic metal oxide nanoparticles and carbon fibers can be a desirable combination in the formulation of recyclable photocatalyst for the in situ photocatalytic degradation of organic pollutants in water, whereas the remaining challenge is the request of proper design of functional fiber nanostructure, which not only immobilize photocatalytic nanoparticles onto fibers, but also remain large surface of catalyst to participate in the redox reaction with pollutants. Herein, we demonstrate new synthesis of photocatalytic carbon nanofibers decorated with semi-embedded titanium oxide nanoparticles, namely, TiO$_2$@carbon fiber, is conveniently obtained through the first electrospinning of polyacrylonitrile (PAN) polymer and TiO$_2$ particle comixture in dimethylformamide (DMF), and then followed by photon-activated self-erosion to exposure embedded TiO$_2$ and carbonization to form chemically robust...
TiO$_2$@carbon fibers. This process has the advantage of ease of scale-up for potentially low-cost mass production. Furthermore, those TiO$_2$@carbon fibers with semi-embedded TiO$_2$ nanoparticles exhibit the improved photocatalytic efficiency and recyclability upon photodegradation tests of Rhodamine B (Rh B) in aqueous solution.

2. Experimental Section

PAN fibers containing TiO$_2$ particles, TiO$_2$@PAN fibers, were produced via the electrospinning of TiO$_2$-PAN comixture. Typically, a suspension of Degussa P25 TiO$_2$ powder (0.05 g) in DMF (4.5 g) was first treated with ultrasonic homogenizer, and then stirred for 1 h. Then, PAN (0.5 g) was added to the suspension, with additional constant stirring (4 h). The obtained suspension was kept for 6 h for stabilization. As shown in Scheme 1, the electrospinning setup consists of a high voltage power supply, a syringe, a syringe pump, and a rotating roller with aluminum foil as a collector. A voltage of +15 kV was applied to the needle tip of the syringe, resulting in fibrous materials deposited on the target aluminum foil roller. The photoactivated self-erosion of TiO$_2$@PAN nanofiber to expose the embedded TiO$_2$ is achieved via the following process: The as-prepared fiber mat was cut into small pieces (1 cm $\times$ 1 cm) after drying at room temperature and put into a 100 mL beaker filled with distilled water. The beaker was put 10 cm in front of a UV light source (60 W, wavelength of 365 nm) for 48 h to erode PAN fiber surface with the photoredox TiO$_2$, and yield fibers with partially embedded TiO$_2$ particles, namely, semi-embedded TiO$_2$@PAN fibers. Afterward, the fiber mats were collected and heated at 100 °C for 2 h in vacuum oven. Furthermore, carbonization of TiO$_2$@PAN fibers was processed in a tube furnace at temperature of 300 °C in air for 30 min and then 1200 °C under nitrogen streaming to produce semi-embedded TiO$_2$@carbon fibers (from semi-embedded TiO$_2$@PAN fibers) and embedded TiO$_2$@carbon fibers (from the uneroded and embedded TiO$_2$@PAN fibers).

3. Structural Characterization

These fiber samples were characterized using field emission scanning electron microscopy (FESEM) (Hitachi S-4700) that operated at 10 kV. The samples were prepared on glass slides sputtered by gold for 1 min. The structural and the elemental distribution of the composite fibers were resolved using a high-resolution transmission electron microscope (TEM, JEOL, JEM-2100F) system to determine distribution and presence of TiO$_2$ particles in fibers. To investigate crystal structure of TiO$_2$-containing fibers, X-ray diffraction (XRD) apparatus [D/MAX-2200 Ultima/PC, Rigaku, Japan] was used to obtain X-ray diffraction patterns. UV–vis spectrophotometer (UV-2550, Shimadzu) was also used for the measurement of dye degradation intensity.

4. Photocatalytic Activity Measurements

For the photocatalytic dye degradation experiments, the as-synthesized carbon fibers with TiO$_2$ nanoparticles were utilized using Rh B in aqueous solution. Four different tests were conducted with 20 mg of testing materials dispersed in a reactor with solution of 25 mL of Rh B (4 mg L$^{-1}$) at room temperature: (1) semi-embedded TiO$_2$@carbon fiber mats, (2) embedded TiO$_2$@carbon fiber mats, (3) carbon fibers only, and (4) without any carbon fiber or TiO$_2$. The solutions were magnetically stirred in the dark for 30 min until an adsorption/desorption equilibrium was reached and a 365 nm UV lamp was
utilized as the light source to illuminate the solution continuously afterward. In this process, 2 mL of the reaction solution was taken for every 30 min, filtered, and measured under UV–vis spectrophotometer (UV-2550, Shimadzu). The dye degradation ratio was calculated as $C/C_0$ where $C_0$ is the initial Rh B concentration, and $C$ is the Rh B concentration after the photocatalytic reaction.

5. Results and Discussion

The resulting electrospun fiber morphologies are shown in Figure 1. In Figure 1a, the TiO$_2$@PAN fibers with smooth morphology and diameters in sub-micrometer scale confirm the success of the electrospinning process. Figure 1b shows a magnification image of Figure 1a, which clearly shows that the fibers treated before UV radiations were generally smooth. In Figure 1c,d, the SEM images show the surfaces of these composite fibers have been corroded to expose TiO$_2$ nanoparticles while the fibers structure remained continuous after the UV irradiation. The UV photon generated electron and hole in TiO$_2$ nanoparticles take part in redox reactions at the contacted PAN polymers with the assistance of water molecule, which made unique porous structure on the PAN fibers to expose the embedded TiO$_2$ particles (Figure S1, Supporting Information). Briefly, the excited TiO$_2$ allows donating electron from CB band to the nearby O$_2$, resulting in the generation of reactive O$_2$ radical to react with organics. Meanwhile, depending on the nearby chemical environment, that is, basic aqueous solution, one hole extraction to the TiO$_2$ VB band can promote the generation of reactive -OH radical from OH$^-$ anion, which tend to destroy cyano group and/or carbon–hydrogen (or carbon) bond of PAN, eventually erode fiber around TiO$_2$. The presence of elements of Ti, O, and C can be identified in the energy-dispersive X-ray (EDX) spectrum of the TiO$_2$@PAN nanofibers after UV illumination for 48 h in Figure S2 (Supporting Information). Figure 1e,f shows the enlarged view SEM image of semi-embedded TiO$_2$ particles in the carbon fibers.

High-resolution TEM images for TiO$_2$@PAN and TiO$_2$@carbon nanofibers were used to study the hybrid fibers with semi-embedded and embedded TiO$_2$ particles. As shown in Figure 2, the presence of TiO$_2$ particles within TiO$_2$@PAN and TiO$_2$@carbon fibers can be confirmed from the TEM images. Figure 2a shows TiO$_2$ particles have been embedded by PAN fiber before the photon-activated self-erosion, where TiO$_2$ particles were identified as the dark areas and PAN fiber with light contrast. In Figure 2b, the magnified TEM images show that semi-embedded TiO$_2$ nanoparticles with sizes of $\approx 20$ nm are dispersed in PAN fibers (shown by black arrow). In Figure 2c, the TEM image shows semi-embedded TiO$_2$ in carbon nanofiber (hollow structure on fibers with bright area shown by black arrow). The structures of the semi-embedded TiO$_2$@carbon fibers were studied by XRD in Figure 2d with peaks at 25.3° and 48° which correspond to anatase phase of TiO$_2$ while the peak at 16° is the characteristic of carbon fiber. The commercial TiO$_2$ nanoparticles used in this work are composed of the anatase phase as observed. No characteristic peaks other than TiO$_2$ and carbon were observed in the XRD pattern, referring the high purity of TiO$_2$@carbon fibers (Figure S3, Supporting Information).

The semi-embedded TiO$_2$@carbon fibers were compared with other samples, including embedded TiO$_2$@carbon fibers, carbon fibers, and blank Rh B solution for photocatalytic tests as shown in Figure 3. After illumination with UV light for 180 min, Rh B solution with semi-embedded TiO$_2$@carbon networks exhibited the best dye degradation efficiency, with the average of three times more efficiency over other samples. Clearly, the semi-embedded TiO$_2$@carbon
Hybrid fibers are in favor of dye degradation. It is because those semi-embedded TiO2@carbon fibers have more accessibility of catalyst to participate in the redox reaction with organic dyes, due to not only the larger contact surface between TiO2 with dyes, but also the longer migration distance of photoinduced electron and hole in conductive carbon fibers. Images of Rh B at different time periods with semi-embedded carbon fibers are also shown in Figure S4 (Supporting Information). The photocatalytic degradation curve of Rh B by pristine P25 is shown in Figure S5 (Supporting Information), indicating similar level of photocatalytic activity toward organic dyes, but the recyclability of P25 particles is expected to be poorer than those of TiO2@fiber.

The recyclability of photocatalytic materials plays a crucial role for practical application. We investigated the recycle performances of semi-exposed TiO2@carbon fibers with each cycle of 180 min. After each cycle, the fiber networks were easily recovered by filtration. Figure 4 shows the performance of semi-embedded TiO2@carbon fiber networks during seven cycles. The tests show good reproducibility of fibers and degradation efficiency even became slightly higher after several cycles, which may partially be due to the better dispersal of fiber networks in solution that leads to the improved dye absorption and degradation.

6. Conclusions

In summary, the successful fabrication of continuous photocatalytic carbon nanofibers with semi-embedded titanium oxide nanoparticles, namely, TiO2@carbon fibers, is demonstrated, through the first electrospinning of PAN polymer and TiO2 particle comixture, and then followed by photon-activated self-erosion and carbonization processes. Those semi-embedded TiO2@carbon fibers are in favor of dye degradation. It is because those semi-embedded TiO2@carbon fibers have more accessibility of catalyst to participate in the redox reaction with organic dyes, due to not only the larger contact surface between TiO2 with dyes, but also the longer migration distance of photoinduced electron and hole in conductive carbon fibers. Images of Rh B at different time periods with semi-embedded carbon fibers are also shown in Figure S4 (Supporting Information). The photocatalytic degradation curve of Rh B by pristine P25 is shown in Figure S5 (Supporting Information), indicating similar level of photocatalytic activity toward organic dyes, but the recyclability of P25 particles is expected to be poorer than those of TiO2@fiber.

The recyclability of photocatalytic materials plays a crucial role for practical application. We investigated the recycle performances of semi-exposed TiO2@carbon fibers with each cycle of 180 min. After each cycle, the fiber networks were easily recovered by filtration. Figure 4 shows the performance of semi-embedded TiO2@carbon fiber networks during seven cycles. The tests show good reproducibility of fibers and degradation efficiency even became slightly higher after several cycles, which may partially be due to the better dispersal of fiber networks in solution that leads to the improved dye absorption and degradation.

6. Conclusions

In summary, the successful fabrication of continuous photocatalytic carbon nanofibers with semi-embedded titanium oxide nanoparticles, namely, TiO2@carbon fibers, is demonstrated, through the first electrospinning of PAN polymer and TiO2 particle comixture, and then followed by photon-activated self-erosion and carbonization processes. Those semi-embedded TiO2@carbon fibers are in favor of dye degradation. It is because those semi-embedded TiO2@carbon fibers have more accessibility of catalyst to participate in the redox reaction with organic dyes, due to not only the larger contact surface between TiO2 with dyes, but also the longer migration distance of photoinduced electron and hole in conductive carbon fibers. Images of Rh B at different time periods with semi-embedded carbon fibers are also shown in Figure S4 (Supporting Information). The photocatalytic degradation curve of Rh B by pristine P25 is shown in Figure S5 (Supporting Information), indicating similar level of photocatalytic activity toward organic dyes, but the recyclability of P25 particles is expected to be poorer than those of TiO2@fiber.

The recyclability of photocatalytic materials plays a crucial role for practical application. We investigated the recycle performances of semi-exposed TiO2@carbon fibers with each cycle of 180 min. After each cycle, the fiber networks were easily recovered by filtration. Figure 4 shows the performance of semi-embedded TiO2@carbon fiber networks during seven cycles. The tests show good reproducibility of fibers and degradation efficiency even became slightly higher after several cycles, which may partially be due to the better dispersal of fiber networks in solution that leads to the improved dye absorption and degradation.
nanofibers showed promising photocatalytic activities and recyclability upon photodegradation tests of Rhodamine B in aqueous solution. This process has the advantage of ease of scale-up for low-cost mass production. Our work would provide one good example for the nanostructure design of photocatalytic nanofiber as recyclable photocatalyst for the in situ degradation of organic pollutants in water.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
G.C. and W.U. contributed equally to this work. This work was funded by National Natural Science Foundation of China (Nos. 21674093 and 21722404), International Science and Technology Cooperation Program of China (ISTCP) (Grant No. 2016YFE0102900), Zhejiang and 21722404), International Science and Technology Cooperation by National Natural Science Foundation of China (Nos. 21674093.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
carbon, electrospinning, nanofibers, photocatalysts, TiO₂

Received: February 2, 2018
Revised: April 16, 2018
Published online: May 22, 2018