

The enhancement of photocatalytic activity of porous g-C₃N₄@TiO₂ nanotubes heterostructure

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Abstract. The g-C₃N₄ nanosheets were uniformly grown on TiO₂ nanotubes with porous structure via the improved methods of impregnation calcination and facial vapor deposition. The photocatalytic performance of the g-C₃N₄/TiO₂ nanotubes was evaluated by the degradation of methyl orange solution (MO) and exhibited higher photodegradation rate than the pure g-C₃N₄ or TiO₂ nanotubes under xenon light irradiation, which may be attributed to the increased specific surface area and efficiently separation of photon-generated electrons/holes by the heterostructure. This work provides a simple and efficient scheme of manufacturing porous heterostructure nanotubes for environmental and energy applications.

Keywords: Electrospinning; g-C₃N₄; Nanotubes; Microstructure.

1. Introduction

TiO₂ is regarded as a multifunctional semiconductor metal oxide, which has attracted extensive attention from scientists because of its high oxidizing power, environmental friendliness, non-toxicity and low cost.[1, 2] Recently, the application of TiO₂ photocatalysts has mainly focused on decomposing toxic and hazardous organic pollutants in contaminated air and water, which is of great importance for environmental protection.[3] Although significant progress has been achieved, the high recombination rate of photo-generated electron/hole pairs still hinders the wider industrial application of TiO₂ photocatalysts.[4, 5] Graphitic carbon nitride (g-C₃N₄), with its narrow band gap of 2.8 eV, has been extensively studied as an important metal-free semiconductor.[6] Compared to pure TiO₂ and g-C₃N₄, the g-C₃N₄/TiO₂ heterostructure has demonstrated superior photocatalytic performance, reducing charge carrier recombination and enhancing electron transfer rates.[7] However, the preparation of the g-C₃N₄/TiO₂ heterojunction mainly relies on the calcination of a mixture of nitrogen-rich precursors and TiO₂, which often results in the aggregation of g-C₃N₄ and a decrease in active sites, limiting its industrial application.[8]

The porous structure is beneficial for the photocatalyst, as it increases the specific surface area and efficiently transports guest species to the active sites.[9] In this study, porous g-C₃N₄/TiO₂ nanotubes were prepared using a novel method. The porous structure of the nanotubes was formed during the g-C₃N₄ modification process, resulting in a larger specific surface area. When compared to pure g-C₃N₄ and TiO₂ nanotubes, the porous g-C₃N₄/TiO₂ nanotubes exhibited higher photocatalytic activity for MO degradation. This work may provide a simple and efficient method for manufacturing composite semiconductor photocatalysts.

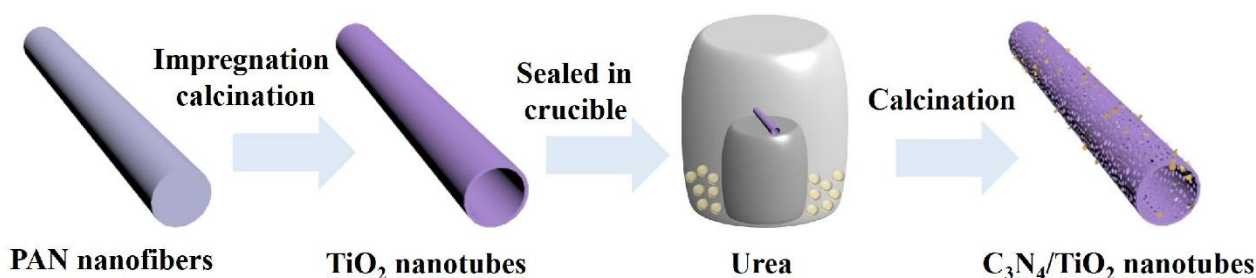


Fig. 1 The schematic illustration of the preparation of g-C₃N₄/TiO₂ nanotubes.

2. Experimental

2.1 Fabrication of g-C₃N₄/TiO₂ nanotubes.

The porous g-C₃N₄/TiO₂ nanotubes were prepared using the improved impregnation calcination and facial vapor deposition method. Firstly, 1.6 g of polyacrylonitrile (PAN) was dissolved in 10.0 mL of N, N-dimethylformamide (DMF) to obtain the electrospinning precursor solution. The solution was then transferred into an injector connected to a 16.0 kV high voltage power supply. The distance between the injector and acceptor was set at 14 cm, and the flow rate of the precursor solution was controlled at 0.5 mL/h. The resulting PAN fiber membrane was soaked in a tetrabutyltitanate ethanol solution (v/v = 1:10) for 5 minutes and dried in an air oven at 200 °C for 2 hours. Afterward, the hollow TiO₂ nanotubes were obtained through calcination. The calcination process involved a heating rate of 2 °C/min up to 550 °C, and the tubes were kept at that temperature for 2 hours.

To modify the g-C₃N₄ and form porous structures on the TiO₂ nanotubes, the improved vapor deposition method was utilized. 20 mg of TiO₂ nanotubes were transferred into a crucible (30 mL), which was placed inside a sealed crucible (100 mL) containing 7 g of urea. This setup was then calcined at a heating rate of 2 °C/min up to 550 °C, and kept at that temperature for 30 minutes. The resulting samples were named porous g-C₃N₄/TiO₂ nanotubes. (preparation process is as shown in Fig. 1).

2.2 Evaluation of photocatalytic activity.

The photocatalytic performance of the samples was evaluated by measuring the degradation of MO. Initially, 40 mg of the samples were mixed with 40 mL of MO solution (10 mg/L) and stirred in the dark for 2 hours to reach the adsorption/desorption equilibrium. Subsequently, the mixture was exposed to simulated solar light (xenon lamp, 120 W, at a distance of 10 cm). The concentration of MO in the solution was measured by UV-vis spectroscopy after collecting a 3 mL sample at regular time intervals and centrifuging it.

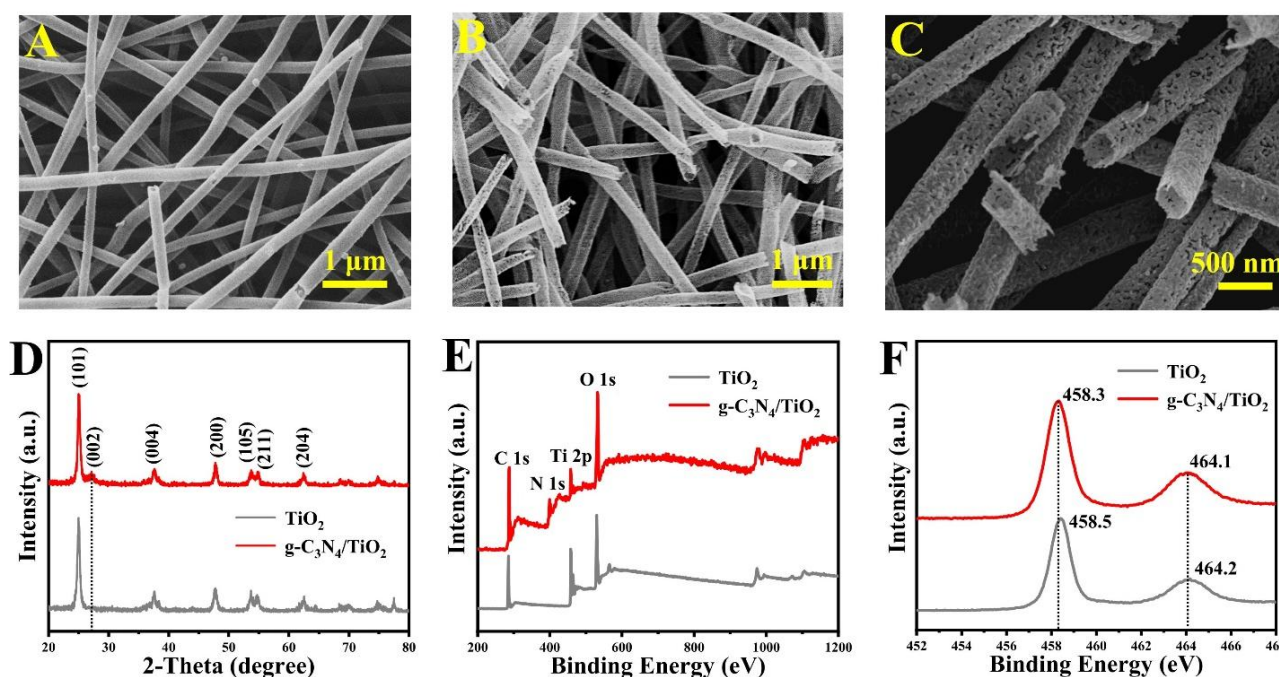


Fig. 2 The SEM images of TiO₂ nanotubes (A) and porous g-C₃N₄/TiO₂ nanotubes (B and C). XRD patterns of the TiO₂ and g-C₃N₄/TiO₂ (D). XPS spectra of samples (E) and the HRXPS of Ti 2p (F).

3. Results and Discussion

The morphology of the samples was characterized by scanning electron microscopy (SEM). As shown in Fig.2A, the TiO₂ nanotubes with diameter of about 400 nm are uniform and smooth. The g-C₃N₄/TiO₂ (Fig. 2B and 2C) shown a uniform porous nanotube structure, which may be caused by the gas pressure generated from the urea sublimation during the heating process. Fig. 2D shows the X-ray diffraction (XRD) pattern of TiO₂ and g-C₃N₄/TiO₂ nanotubes. The sharp and strong diffraction peaks located at 25.34°, 37.83°, 48.13°, 55.13° and 62.67° could be attributed to the (101), (004), (200), (211) and (204) lattice planes of the anatase TiO₂ (JCPDS 21-1272). For g-C₃N₄/TiO₂ nanotubes, except for the characteristic peak of anatase TiO₂, a new peak at 27.39° could be appeared, which corresponding to the (002) lattice planes of g-C₃N₄. [9] The surface elemental and chemical states were studied by X-ray photoelectron spectroscopy (XPS) spectra (Fig. 2E). Compared with pure TiO₂, the peak of N was obviously in g-C₃N₄/TiO₂. The Ti 2p peaks (Fig. 2F) of g-C₃N₄/TiO₂ shown slight shift, which may be caused by the electron transfer from g-C₃N₄ to TiO₂.

Fig. 3A shows UV-vis diffuse reflectance spectroscopy (DRS) analysis. For pure TiO₂ nanotubes, the adsorption wavelength was under 390 nm, implying that the TiO₂ nanotubes only have a response to UV light. After g-C₃N₄ was coupled with TiO₂ nanotubes, the adsorption intensity extended to the visible light region, which means a wider photo absorption from ultraviolet to visible light was realized. Meanwhile, the homologous band gap energy (E_g) of the as-prepared photocatalysts were calculated by the formula $E_g = 1240/\lambda_g$, the pure TiO₂ and g-C₃N₄/TiO₂ have the E_g value of 2.97 eV and 2.83 eV, which could be attributed to the photosensitive effect between g-C₃N₄ and TiO₂ heterostructure and the special optical ability of porous nanotubes structure. [8]

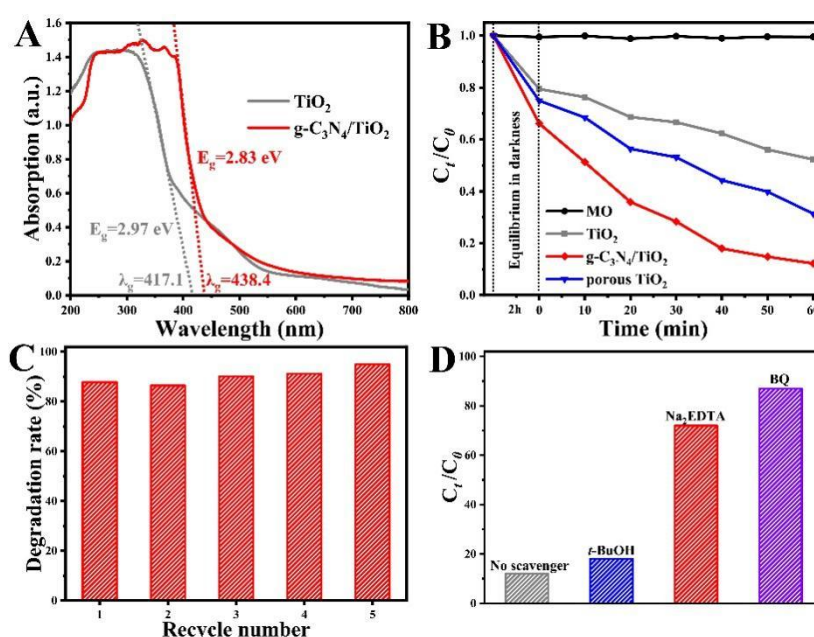


Fig. 3 UV-vis DRS (A) and band gap of the as-prepared samples. Degradation test of the photocatalysts under simulated solar light (B). Recycling tests (C) and active species trapping experiments (D) of the g-C₃N₄/TiO₂ nanotubes under simulated solar light.

To identify the photocatalytic performance, the TiO₂ nanotubes, porous g-C₃N₄/TiO₂ nanotubes, and porous TiO₂ nanotubes (obtained by calcination of g-C₃N₄/TiO₂) were tested for MO degradation under xenon light irradiation. As shown in Fig.3B, after the adsorption/equilibrium in dark, the degradation efficiencies of the porous g-C₃N₄/TiO₂ nanotubes could reach to 87.9%, higher than the pure TiO₂ tubes (47.8%) and the porous TiO₂ nanotubes (68.7%) under simulated solar light for 60 min. The improvement of porous g-C₃N₄/TiO₂ nanotubes photocatalytic performance could be attributed to the synergy of porous structure on the surface and the

heterostructure of g-C₃N₄/TiO₂, which increase the active site and promotes the photogenerated electron-hole separation and transportation. Meanwhile, the g-C₃N₄/TiO₂ nanotubes presented good stability after being reused for five times (Fig. 3C).

Furthermore, the active species trapping experiments (Fig. 3D) was detected to identify which reactive species play the major role in the photocatalytic degradation process. MO include 1 mM of 1,4-benzoquinone (BQ), tert-butyl alcohol (t-BuOH), or disodium ethylenediaminetetraacetate (Na₂EDTA), were introduced into the photocatalytic degradation system as scavengers of superoxide radical ($\bullet\text{O}_2^-$), hydroxyl radical ($\bullet\text{OH}$) and hole (h^+), respectively. The results indicate that the degradation rate significantly decreased when BQ and Na₂EDTA were introduced, which means the $\bullet\text{O}_2^-$ and h^+ were the main active species in the photodegradation process of g-C₃N₄/TiO₂. [1]

4. Conclusion

The porous g-C₃N₄/TiO₂ nanotubes were synthesized by the improved methods of impregnation calcination and facial vapor deposition for the first time. Compared with pure TiO₂ nanotubes, the porous g-C₃N₄/TiO₂ nanotubes showed better photocatalytic activity. The formation mechanism of porous g-C₃N₄/TiO₂ nanotubes and the reason for heterostructures enhanced photocatalytic performance were also conjectured. Moreover, this research provides a new method for the preparation of porous heterostructure nanotubes.

References

- [1] Cheng Z, Zhao S, Han L. A novel preparation method for ZnO/gamma-Al₂O₃ nanofibers with enhanced absorbability and improved photocatalytic water-treatment performance by Ag nanoparticles. *Nanoscale*. 2018;10:6892-9.
- [2] Hu L, Yan J, Wang C, Chai B, Li J. Direct electrospinning method for the construction of Z-scheme TiO₂/g-C₃N₄/RGO ternary heterojunction photocatalysts with remarkably ameliorated photocatalytic performance. *Chinese Journal of Catalysis*. 2019;40:458-69.
- [3] Dai Z, Zhen Y, Sun Y, Li L, Ding D. ZnFe₂O₄/g-C₃N₄ S-scheme photocatalyst with enhanced adsorption and photocatalytic activity for uranium(VI) removal. *Chemical Engineering Journal*. 2021;415:129002.
- [4] Zhao S, Cheng Z, Kang L, Zhang Y, Zhao X. A novel preparation of porous spong-shaped Ag/ZnO heterostructures and their potent photocatalytic degradation efficiency. *Materials Letters*. 2016;182:305-8.
- [5] Cheng J, Hu Z, Li Q, Li X, Fang S, Wu X, et al. Fabrication of high photoreactive carbon nitride nanosheets by polymerization of amidinourea for hydrogen production. *Applied Catalysis B: Environmental*. 2019;245:197-206.
- [6] Wang C, Hu L, Chai B, Yan J, Li J. Enhanced photocatalytic activity of electrospun nanofibrous TiO₂/g-C₃N₄ heterojunction photocatalyst under simulated solar light. *Applied Surface Science*. 2018;430:243-52.
- [7] Zhou X, Shao C, Li X, Wang X, Guo X, Liu Y. Three dimensional hierarchical heterostructures of g-C₃N₄ nanosheets/TiO₂ nanofibers: Controllable growth via gas-solid reaction and enhanced photocatalytic activity under visible light. *J Hazard Mater*. 2018;344:113-22.
- [8] Cheng Z, Zhao S, Han Z, Zhang Y, Zhao X, Kang L. A novel preparation of Ag@TiO₂ tubes and their potent photocatalytic degradation efficiency. *CrystEngComm*. 2016;18:8756-61.
- [9] Zhao S, Cheng Z, Kang L, Li M, Gao Z. The facile preparation of Ag decorated TiO₂/ZnO nanotubes and their potent photocatalytic degradation efficiency. *RSC Adv*. 2017;7:50064-71.