Digest Journal of Nanomaterials and Biostructures Vol. 16, No. 3, July - September 2021, p. 989 - 994

A composite of graphene-beaded porous carbon-nanofibers and TiO_2 nanoparticles as an efficient visible-light photocatalyst

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Novel composites of graphene-beaded porous carbon nanofibers decorated with TiO_2 (G/PCF/TiO_2) were synthesized using an electrospinning method and their photocatalytic performance was demonstrated based on the degradation of methylene blue (MB) under visible light irradiation. The enhanced photocatalytic properties of G/PCF/TiO_2 can be ascribed to the synergistic effect of graphene-beaded porous carbon nanofibers, which facilitates charge transfer, increases the light absorption in the visible range, as well as favors the adsorption of dye. The present strategy provides an effective strategy for the preparation of carbon-based composite and its application for high-performance photocatalysts.

(Received April 22, 2021; Accepted August 17, 2021)

Keywords: Carbon materials, Nanocomposites

1. Introduction

As one of the most promising photocatalysts, titanium dioxide (TiO_2) is non-toxic, chemically and thermally stable, and known to be photoactive[1]. On the other hand, low quantum efficiencies and limited visible light absorption have restricted its utilization to date[2]. One approach researchers have taken is to anchor TiO_2 to conductive carbon materials[3]. Porous carbon fibers decorated with nanosized TiO_2, such as the ones presented[4], here are expected to simultaneously provide excellent dye adsorption as well as drive efficient separation of photogenerated electron-hole pairs. Moreover, highly conductive graphene can be covalently connected with porous carbon fibers, forming carbonaceous nanostructures of graphene-beaded porous carbon nanofibers[5]. Embedding nanosized TiO_2 in this graphene-beaded porous carbon nanofibers matrix provides synergistic effects and boost their photocatalytic activities.

2. Experimental details

Fig. 1 showed the fabrication of the G/PCF/TiO_2 composites schematically. 2 g of polyacrylonitrile (PAN, >99% purity, Aladdin) and 0.3 g Polymethyl methacrylate (PMMA, MW~35000, Aladdin) were dissolved in 12 mL N,N-dimethylformamide (DMF, >99.8% purity, Macklin) to form the solution A1. 2 g polyvinylpyrrolidone (PVP, MW~40000, Aladdin), 0.5 g titanium dioxide (TiO_2, >99% purity, Aladdin) and 0.1 g graphene oxide were uniformly dispersed in 18 mL DMF to obtain the solution A2. Co-axial electrospinning was employed to deposit the photocatalysts, with 30 kV applied across a distance (needle tip to collector) of 30 cm. The inner (A1) and outer solutions (A2) were simultaneously fed through the nozzles with the rate of 0.01 $mm \cdot s^{-1}$. The collected nanofibers were stabilized in an air environment at 200 °C for 2 h, and carbonized at 600 °C in N_2 atmosphere for 2 h, the as-products were labeled as G/PCF/TiO_2. For

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comparison, G/PCF was prepared by the same method, but without adding TiO_2. PCF/TiO_2 was also prepared by the same method, but without adding GO.

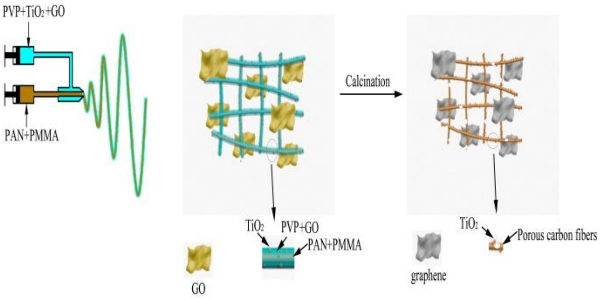

Fig. 1. Schematic illustration of the co-axial electrospinning and carbonization processes.

The samples were characterized by Scanning Electron Microscopy (SEM, Hitachi S4800), Transmission Electron Microscopy (TEM, JEM-2100F), X-Ray Diffractometry (XRD, D5000), UV-vis diffuse spectroscopy (UV-2550, Shimadzu), photoluminescence spectroscopy (Hitachi, F-7000).

The activities of the composite towards the photodegradation of MB were conducted, with, 100 mg of the composite dispersed in 300 mL of a MB solution (10 mg/L). After stirring in the dark for 30 min, to attain an adsorption-desorption equilibrium, the system was irradiated by a 500 W Xe lamp equipped with a 420 nm cut-off filter. At various time points during the irradiation process, a 5 mL of the suspension was extracted and centrifuged, with the supernatant examined by UV-vis spectrophotometry to determine the residual concentration.

3. Results and discussion

The morphology of G/PCF/TiO_2 was examined by SEM, as presented in Fig. 2a and b, revealing a fibrous structure with fibrils about 100 nm in diameter. It was noted that sheet-like structures bridged these nanofibers. Furthermore nanoparticles decorated both the surfaces of the fibers and the sheets. TEM of these structures was presented in Fig. 2c-d. Fig. 2c illustrated the connection between the nanosheets and fibers. Higher resolution TEM in Fig. 2d revealed the porous nature of these fibers possessed and it was ascribed to templating effects from the PMMA, which was removed in the process of carbonization. In Fig. 2e nanoparticles, with an average particle diameter of about 20 nm, could be seen to be uniformly distributed on the surfaces of both the sheets and fibers. A high-resolution TEM image of these nanoparticles, in Fig. 2f, showed a lattice structure with d spacing of 0.35 nm, close to Chen[6] had previously been reported for the (101) plane spacings of anatase.

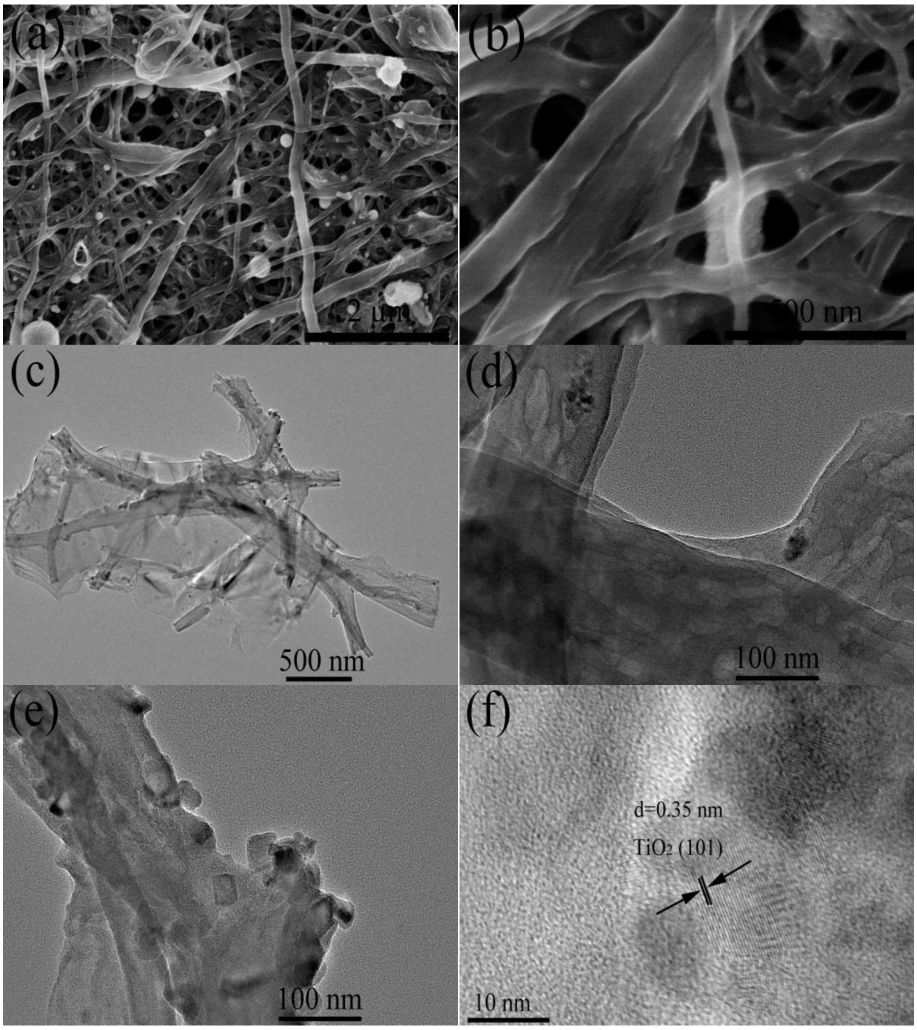

Fig. 2. (a)(b)SEM, (c)(d)(e) TEM, (f)HRTEM of G/PCF/TiO_2.

In Fig. 3a porous fiber structures can again be seen. This region was mapped using EDS to assess the dispersion of elements C, Ti and O (Fig. 3b-d respectively). Carbon was accordant with the fiber structures, while Ti and O were distributed widely across the G/PCF structure, in line with the proposed G/PCF/TiO_2 composites structure.

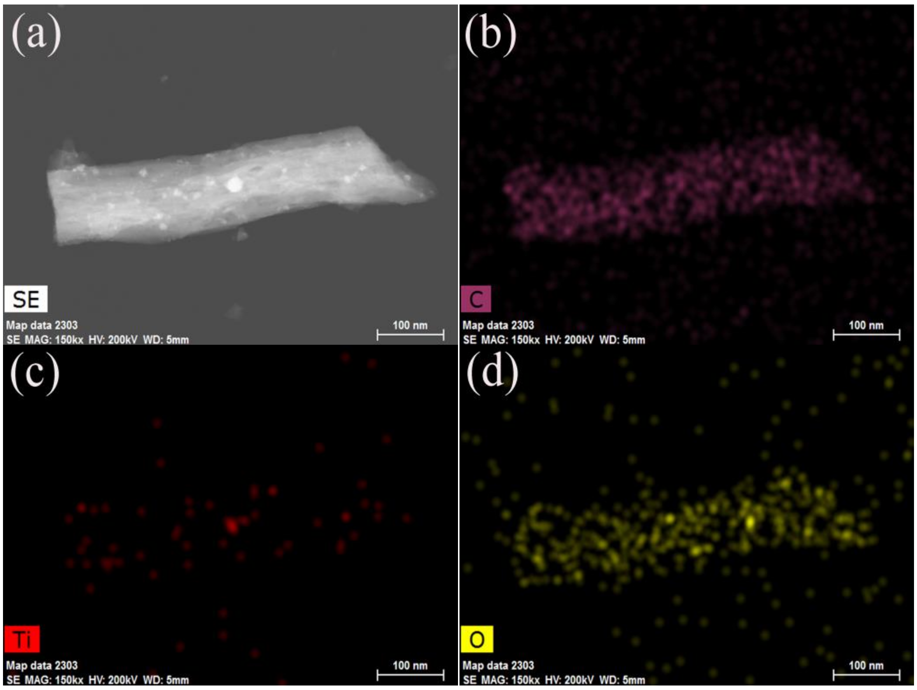

Fig. 3 (a) TEM of EDS mapping of selected area, (b) element C mapping, (c) element Ti mapping, (d) element O mapping of G/PCF/TiO_2

The phase structure and crystallinity of the G/PCF/TiO_2 were characterized by XRD, as shown in Fig. 4a. All the observe diffraction peaks indexed to anatase TiO_2 (JCPDS: 27-1271)[7]. (002) Peaks for graphene or carbon fibers coincided with the (101) peak of TiO_2, making it difficult to reliably distinguish[8].

Fig. 4b showed PL-emission spectra for G/PCF/TiO_2 as well as TiO_2 and PCF/TiO_2 at an excitation wavelength of 345 nm. The PL-intensity decreased as the following order: TiO_2, PCF/TiO_2, and G/PCF/TiO_2, which may be evidence of improved charge separation in the G/PCF/TiO_2 structure, owing to the intimate interaction between TiO_2 and G/PCF[9-10].

The nitrogen adsorption/desorption isotherms were studied (Fig. 4c) and the Brunauer-Emmett-Teller specific surface area was determined to be 60.5 m^2/g. The pore size distribution profiles (inset of Fig. 2c) centered around 3-10 nm, indicating the formation of mesoporosity in the G/PCF/TiO_2.

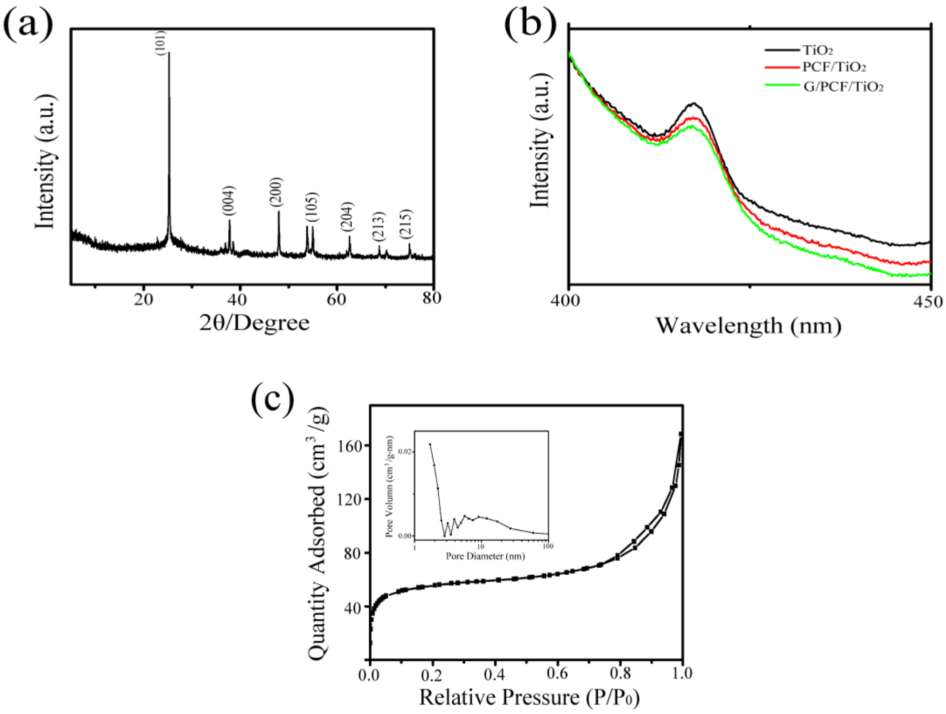

Fig. 4. (a) XRD, (b) photoluminescence spectra, (c) nitrogen adsorption/desorption isotherms and pore size distribution of the samples.

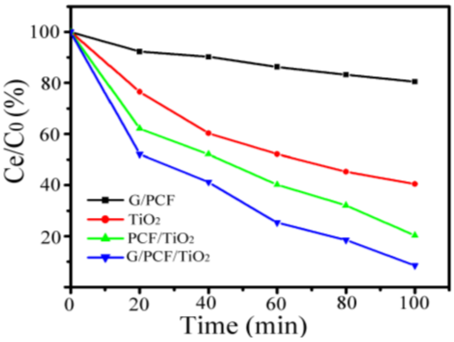

Fig. 5. Photocatalytic degradation efficiency of MB with different catalysts under visible light.

The photodegradation of MB in the presence of either G/PCF/TiO_2, PCF/TiO_2, TiO_2 and G/PCF alone was investigated to evaluate the photocatalytic performance and was shown in Fig. 5. G/PCF/TiO_2 showed much higher photocatalytic activities than those of G/PCF, TiO_2 and PCF/TiO_2. The photocatalytic activity followed the order G/PCF/TiO_2> PCF/TiO_2> TiO_2> G/PCF. It was supposed that the porous carbon fibers, combined with graphene, provided a conductive substrate favoring charge separation and had the effective visible light response[11]. Furthermore, the porous structure could favor the adsorption of MB molecules close to the active species[12].

4. Conclusions

A novel photocatalyst, G/PCF/TiO_2 composite was fabricated using an electrospinning method, with the prepared G/PCF/TiO_2 composites displaying excellent photocatalytic activity. The enhanced photocatalytic performance, compared to TiO_2 alone, can be attributed to the following: (1) the conductive graphene-beaded carbon-fiber substrate suppresses recombination of photoexcited charges in TiO_2 by way of charge transfer; (2) modification of TiO_2 by G/PCF helps improving its visible light response.; (3) the porous carbon structure has the high adsorptive capacity affording a high local concentration of dye molecules near to the catalyst, which is favorable for the catalytic reaction. This study provides a versatile route for the fabricating the novel photocatalysts with efficient visible-light-driven photocatalytic performance.

Acknowledgments

This work was supported by the Natural Science Foundation of China(NSFC, No. 51802096), Science and Technology Bureau projects of Changde ([2019]21), Hunan Provincial Specialty Disciplines of Higher Education Institutions (XJT[2018]469), Innovative Research Team in Higher Educational Instituions of Hunan Province XJT[2019]379).

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