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Full Length Article

Developing thermally resistant polydopamine@nano turbostratic BN@CeO_2 double core-shell ultraviolet absorber with low light-catalysis activity and its grafted high performance aramid fibers

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ABSTRACT

Constructing novel surface structure to overcome two bottlenecks (low surface activity and poor resistance to UV) of aramid fiber (KF) is a meaningful topic. Herein, a new hybridized UV absorber (PDA@tBN@CeO_2) with strong UV absorption, low catalytic activity and high heat resistance was synthesized by forming nano turbostratic boron nitride (tBN) and polydopamine (PDA) shells on CeO_2 core, successively. The double shell-core structure not only significantly reduces the photocatalytic activity of CeO_2, but also obviously improves the UV-blocking effect of CeO_2 and provides active groups for chemical grafting with KF. On this basis, three modified KFs (T-KF1, T-KF2, T-KF3) were fabricated by constructing unique surface structure with different loading of PDA@tBN@CeO_2 through chemical bonds, guaranteeing the good interface between KF and PDA@tBN@CeO_2. The effects of PDA@tBN@CeO_2 concentration on structure and overall performances (surface activity, UV resistance, thermal and mechanical properties) of T-KF fibers were investigated. All T-KFs have greatly improved surface activity and UV-resistance, the improvement degree is dependent on the loading of PDA@tBN@CeO_2. For T-KF2 with 1 wt% of PDA@tBN@CeO_2, its initial decomposition temperature and the value after 168 h-UV irradiation are 49 °C and 90 °C higher than those of original KF, respectively; moreover, tensile strength and energy to break of T-KF2 are severally 1.14 and 1.21 times of those of original KF, the simultaneously improved degrees are the best values among modified KFs reported so far. In addition, T-KFs show outstanding retentions of tensile performances after 168 h UV irradiation, especially, the retention of energy to break of T-KF2 is 1.62 times of that of KF. The excellent integrated performances of T-KF are proved to be attributed to the unique structure of PDA@tBN@CeO_2 as well as the interaction between PDA@tBN@CeO_2 and KF.

1. Introduction

Aramid fiber (KF) is a typical representative of high performance organic fibers. Its excellent merits such as light weight, ultrahigh strength, high modulus and heat resistance [1] make it suitable for applications in many fields including aerospace [2], safety protection [3,4], electronic information [5], goods [6], tire skeleton [7], *etc.* However, its low surface activity and poor UV resistance [8–11] originated from its special chemical structure [12] lead to poor manufacturability and low reliability of service [13].

For a long time, many works were carried out to improve surface activity of KFs [14–19]; in recent years, researchers began to improve UV resistance of KFs. Typically, Mao's group [20] introduced octahedral ammonium chloride-caged sesquisiloxane onto the surface of KF, and found that UV resistance was improved, but meanwhile, the tensile strength degraded and the crystallinity of KF decreased by 14.5%. Our group has made lots of efforts to improve the UV resistance of KF, specifically, coating KF with dopamine-graphene oxide (PDA-GO) [21], hyperbranched polysiloxane (HPSi) [22] or $Ce_{0.8}Ca_{0.2}O_{1.8}$ [23] with chemical route, or constructing MgAlFe/double hydroxide (LDH) coating on the surfaces of KFs with a technique of self-assembly layer-by-layer (LBL) [24]. All these surface modified KFs have improved surface activity and UV resistance, however PDA-GO hybrid or HPSi modified KFs also exhibit decreased heat and oxidation resistance, while the photocatalytic activity of $Ce_{0.8}Ca_{0.2}O_{1.8}$ is too high to maintain the good stability of performance of KFs, and the adhesion between KF and the MgAlFe/LDH coating constructed with LBL is limited. Therefore, it is still a challenge to develop new high performance KF with both surface activity and UV resistance

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through constructing new surface with low photocatalytic activity and good adhesion.

Herein, a new organic-inorganic hybridized UV absorber (PDA@tBN@CeO_2) was first synthesized, which has a double core-shell structure, in which CeO_2 is the core, tBN is the first shell, and polydopamine (PDA) is the second-layer shell. On this basis, a series of modified fibers (T-KFs) were prepared by grafting of PDA@tBN@CeO_2 onto the surfaces of KFs, the effects and mechanism of PDA@tBN@CeO_2 content on the structure and integrated properties of KFs (surface activity, UV resistance, mechanical and thermodynamic properties) were intensively discussed.

2. Experimental

2.1. Materials

KFs used herein were Kevlar-49 fibers (Dupont company, USA). γ-Glycidoxypropyl trimethoxysilane (GPTMS) of analytical grade was purchased from Beno Biotechnology Co. Ltd, Suzhou (China). Urea of analytical grade was obtained from Shanghai Titan Polytron Technologies Inc. (China). Cerium chloride (99%) was bought from Sinopharm Chemical Reagent Co. Ltd. (China). Acetone, petroleum ether, sodium hydroxide, boric acid and H_2O_2 with mass fraction of 30% were all analytical grades and purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd, China.

2.2. Synthesis of PDA@tBN@CeO_2

18.6 g cerium chloride was dissolved in deionized water, into which 6 g sodium hydroxide was introduced to form greyish white precipitate. The mixture was stirred at 40 °C for 20 min, into which 5.1 mL H_2O_2 solution was added while the pH value of the mixture was adjusted to 12 by NaOH solution. After that the mixture was stayed at 40 °C for 12 h, followed by filtration, washing with deionized water and freeze-dried, successively. The dried particles were calcined for 2 h in a muffle furnace at 700 °C to obtain nano-CeO_2.

2.2 g boric acid and 4.2 g urea were added into a solution consisting of 240 mL ethanol and 120 mL water, then 6 g nano-CeO_2 was introduced to above solution to form a suspension, which was stirred for 1 h under ultrasound, followed by evaporation with a rotary evaporator and drying under vacuum at 80 °C for 48 h, successively. The resultant product was calcined in a nitrogen stream at 900 °C for 5 h, and then washed with ethanol and deionized water to obtain crude product, which was at last dried in vacuum to generate tBN coated CeO_2, coded as tBN@CeO_2.

Tris(trimethyl methyl amine hydrochloride)-Buffer solution (10 mM, pH = 8.5) was prepared by adding NaOH solution into 10 mM Tris-HCl solution until the pH value reached 8.5. 0.8 g dopamine hydrochloride was dispersed in a mixed solution consisting of 300 mL Tris-buffer (10 mM, pH = 8.5), 100 mL ethanol and 2 g tBN@CeO_2 with stirring at 25 °C for 6 h. After that, the mixture was filtered and washed with deionized water, followed by drying in vacuum to obtain CeO_2 with double shells, named as PDA@tBN@CeO_2.

2.3. Preparation of modified fibers

Kevlar-49 fibers were sequentially immersed in acetone, petroleum ether and deionized water, successively, followed by heating and refluxing for 3 h to remove impurities on the surface of the fibers, and dried in vacuum to obtain clean fibers.

Above clean fibers were immersed in ethanol solution containing 10 wt% sodium hydroxide, and oscillated for 5 h under 65 °C, then the fibers were washed by deionized water, followed by drying in vacuum under 80 °C, successively, to get fibers with amino and carboxyl groups, coded as mKF.

mKFs were dunked in a solution consisting of 30 mL GPTMS and 70 mL ethanol, and then reacted at 70 °C for 12 h under the protection of nitrogen atmosphere. After that, fibers were directly dipped into deionized water suspension containing PDA@tBN@CeO_2 and maintained at 60 °C for 5 h. The resultant fibers were washed with ethanol and dried in vacuum to obtain target fibers. When the content of PDA@tBN@CeO_2 was 0.5 wt%, 1 wt% and 1.5 wt%, the resultant fiber was denoted as T-KF1, T-KF2 and T-KF3, of which the grafting rates were 3.7%, 4.3% and 5.2%, respectively.

2.4. UV radiation of fibers

Fibers were fixed on an aluminum plate and placed in an ultraviolet aging test box (QUV/spray, Q-Lab, USA). According to Standard ISO 4892 (Part3), fibers were severally radiated for 24 h, 72 h, 120 h and 168 h, and the radiated fibers were named UV-KF, UV-mKF, UV-T-KF1, UV-T-KF2 and UV-T-KF3, respectively.

2.5. Characterizations

Fibers were chopped and fully grinded with potassium bromide powders, and their FTIR spectra were recorded on a Nicolet 5700 Fi-ATR Spectrometer (USA), the optical resolution was 4 cm^{-1}.

Surface morphologies and elemental compositions of fibers were obtained using a scanning electron microscope (SEM Hitachi s-4700, Japan) equipped with an Energy Disperse Spectroscopy (EDS) detector.

X-ray diffraction (XRD) (Rigaku Co. Ltd, Tokyo, Japan) with Cu Ka (λ = 1.54 Å) as the source of emission was used to detect structures of fibers.

UV-vis spectra from 200 to 800 nm were recorded using a Ruili 1100 UV spectrometer (Cary 50, USA).

Thermogravimetric analyses (TGA) were performed on a TA instrument (Discovery TGA, USA). The system was operated under a nitrogen atmosphere with a heating rate of 10 °C/min. The initial degradation temperature (T_{di}) is the temperature at which the weight loss of the sample reaches 5 wt%.

Tensile strengths of single-fiber at room temperature were measured on a universal test single fiber machine (CMT-4101SUSTCN) according to Chinese Standard GB/T14337-2008. The tensile rate was 10 mm/min, and the original gauge length was 20 mm. About 25–50 samples were tested for each fiber, and the average value of these tests was regarded as the datum of each fiber. The diameter of each fiber was measured with scanning electron microscope (SEM).

The photocatalytic activity was characterized through the catalytic oxidation of methyl orange (MO) under 1000 W high-pressure mercury lamp irradiation. Specifically, 50 mg sample was dispersed in 1 L MO solution (50 mg/L), then the suspension was ultrasonic dispersion for 10 min followed by vigorous stirring in the darkroom for 30 min to achieve adsorption-desorption equilibrium. The suspension was irradiated under a mercury lamp, and then 5 mL of suspension was collected at every 5 min interval and filtered to the quartz dish by polytetrafluoroethylene filter. After that the concentration of dye was analyzed using the ultraviolet visible spectrophotometer (YU-1900, Persee, China) at the absorption peak of MO absorption.

Specific surface area was measured by nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method and measurements were conducted on a BELsorp-max, MicrotracBEL Corp. (Japan). Pretreatment conditions were that the heating rate was 5 °C/min and degassed at 195 °C for 2 h.

The particle sizes of nanoparticles were observed using a transmission electron microscopy (TEM, TecnaiG220, FEI Company, USA). Nanoparticles were dispersed in ethanol under ultrasound for 25 min. Then, the suspension was dropped on the copper wire.