Viser Technology Pte. Ltd.
Research and Application of Materials Science
DOI: 10.33142/rams.v3i1.4496

Research Article Open Access

A Novel Preparation Method of Organic-inorganic Aramid Nanofibers (ANFs) Hybrid Membrane Using Ethanol as Proton Donor

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Abstract:
In the work, the surface of the titanium dioxide (TiO_2) nano particles were modified with 3-Aminopropyltriethoxysilane (KH550) first. And the ANFs were loaded with the different nano TiO_2 assisted via the ultrasonic process. Then the organic and inorganic hybrid membrane were fabrication by vacuum assisted flocculation (VAF). Ethanol as a proton donor can realize the flocculation of ANFs. The results of the nanocomposites were characterized by Transmission electron microscope (TEM), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The SEM results indicated that the agglomeration of nanoparticles on ANF were reduced obviously, Through the preparation of aramid nanofiber membrane with the proton donor of ethanol, it is observed that the interlaced network structures of the membrane surface were constructed. The result of the UV data is that the addition of nano-titanium dioxide improves the UV absorption capacity of the fiber membrane.
Keywords: *Aramid nanofiber; Nano-TiO_2; Hybridization; Functional; Nanocomposites*

1 Introduction

So far, the preparation of organic-inorganic hybrid composite membranes has been applied to various potential applications [1-5]. The successful combination of ANFs with gold nanoparticles [6], carbon nanotubes [7], graphene and silver nanowires provide new methods for organic-inorganic hybridization of ANFs. Due to the high specific surface area of nanoparticles, agglomeration is a serious problem which make nanoparticles poorly dispersed in the organic matrix. Surface modification of nanoparticles is usually needed to achieve uniform dispersion of nanoparticles. It has been reported that transparent magnetic composite membrane are successfully prepared by combining inorganic magnetic nanoparticles with nano fibrillated cellulose matrix to form a three-dimensional network structure [8]. There are many active functional groups on the surface of ANFs, which have good adhesion with other nanomaterials. However, the aramid fiber has weak UV resistance, and the composite film prepared by ANFs has poor anti UV resistance. At the same time, Nano-TiO_2 has good UV absorption performance and good binding sites on the surface of ANFs. Combining the two can improve the anti UV performance of the composite film. Inspired by the combination of nano fibrillated cellulose and nano particles, it becomes feasible to combine ANFs with functionalized inorganic nanoparticles to obtain hybrid films with anti UV resistance.

In this work, Nano-TiO_2 and ANFs are proposed to be combined to prepare TiO_2/ANFs. Then the TiO_2/ANFs hybrid films are fabricated by vacuum flocculation with ethanol as proton donor. After surface modification of Nano-TiO_2 by KH550, inorganic nanoparticles are able to disperse in ethanol uniformly. In addition, uniformly distributed nano-sized TiO_2 particles also endow the nano-sized TiO_2/ANFs with good anti-ultraviolet properties.

2 Experimental section

2.1 Materials

Aramid fiber (Kevlar-29): Model 956, specification 1500D, linear density 1670 dtex, was purchased from Dupont Company, USA. Potassium hydroxide (KOH), and Dimethyl sulfoxide (DMSO, 99.7%) were purchased from Aladdin co., Ltd, Shanghai, China. Ethanol(density (20 ℃) is 0.789～0.791 g/ml, grade is analytical grade

Received on March 12, 2021; Accepted on April 21, 2021

(AR), content ≥ 99.7%) were supplied by Fuyu Chemical, Tianjin, China. Nano Titanium dioxide (TiO_2, content 99.8%, particle size of 25 nm) were purchased from Macklin co., Ltd, Shanghai, China.

2.2 Sample preparation

2.2.1 Preparation of ANFs/DMSO suspension

1.5g KOH was dissolved in the DMSO, and 1.5g clean aramid fiber was added in the DMSO solution. Then the dark red ANFs solution was formed by continuous stirring at 25 ℃ for one week.

2.2.2 Surface modification treatment of Nano-TiO_2

The ethanol absolute, deionized water and KH550 were mixed with a fixed ratio (90:10:1 ml) and place in the flask. The mixture was disposed by ultrasonic for 10 minutes. The pH was adjusted at 4 by adding adequate hydrochloric acid and sodium hydroxide [9]. Subsequently, A certain amount of well dispersed KH550 was added into the mixture dispersed Nano-TiO_2, stirring for one hour in the oil bath at the temperature of 60 ℃. Then the excess KH550 was removed by deionized water and ethanol washing for several times. At last the treated TiO_2 nanoparticles were dried in the vacuum oven at 100 ℃ for 6 h. In short, the original sample was named as U-TiO_2 and the KH550-modified Nano-TiO_2 was named as T-TiO_2.

2.2.3 Fabrication TiO_2/ANFs nanocomposites

20 ml of ANFs/DMSO solution were added into 100 ml of ethanol solution and an ultrasonic treatment of 2 hours were proceed to obtain uniform suspensions. Then ANFs membrane were fabricated by vacuum assisted flocculation method. In the process of suction filtration, washing with ethanol were used to remove DMSO solution, and the vacuum suction filtration for 6～8 h was also applied to obtain uniform and transparent ANF membrane. The same method was also used to prepare Nanocomposites with different mass fractions of nano TiO_2 particles. Then ANFs/DMSO and TiO_2 were dispersed and ultrasonic processed in the ethanol together with different weight ratio. Finally, the films were dried in a vacuum oven at 60 ℃ for 8 hours.

2.3 Characterization

A scanning electron microscope (SU8010 and JEOL JSM-7500F) was used to observe the surface morphology of TiO_2 and TiO_2/ANFs. The TEM (FEI Tecnai G2 F20) was applied to observe the morphology of ANFs. An UV-vis spectrophotometer (PE Lambda 950) was used to evaluate the absorption properties of the nano paper in the wavelength range of 200～800 nm.

3 Results and discussion

3.1 Morphologies of TiO_2 and ANF

According to the SEM results in Figure 1(a) (b), it is observed that the agglomeration of nanoparticles has been significantly reduced after the treatment of silane coupling agent. Via grafting silane coupling agent on the surface, the nano particles are well dispersed, providing a good precondition for the preparation of uniform and dense nano composite membrane. In Figure 1(c) (d), it can be concluded from the TEM results that ANFs with the size of nanometer have been successfully prepared. After mixing the modified nano particles with ANFs, it is observed that nano particles are uniformly attached on the surface of the nanofibers, conforming to our assumptive scheme of organic and inorganic nano paper in Figure 2. In Figure 2, There is a hydrogen bond between the carbonyl group on the fiber surface and the amino group between the nanoparticles. So that the nanoparticles can be stably dispersed in the suspension of ANFs [8].

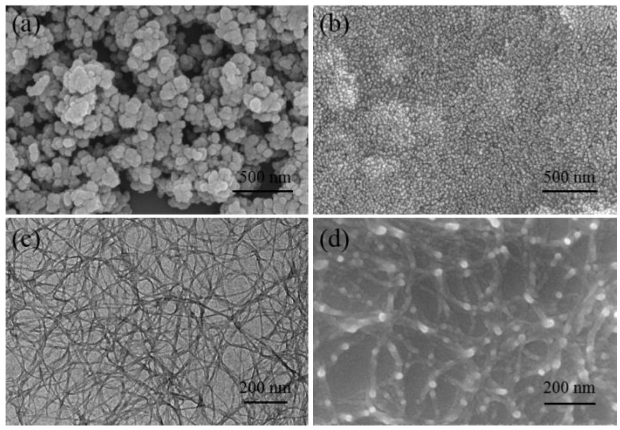


Figure 1 SEM images of the TiO_2 (a) U-TiO_2, (b) T-TiO_2, (c) TEM photographs of the ANFs, (d) Combination of ANFs and nanoparticles

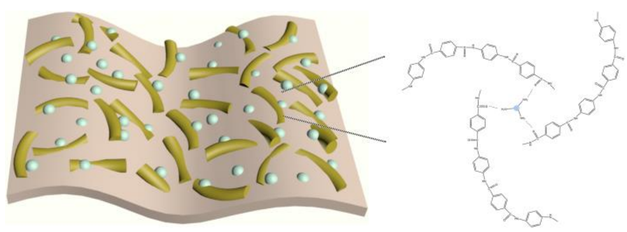
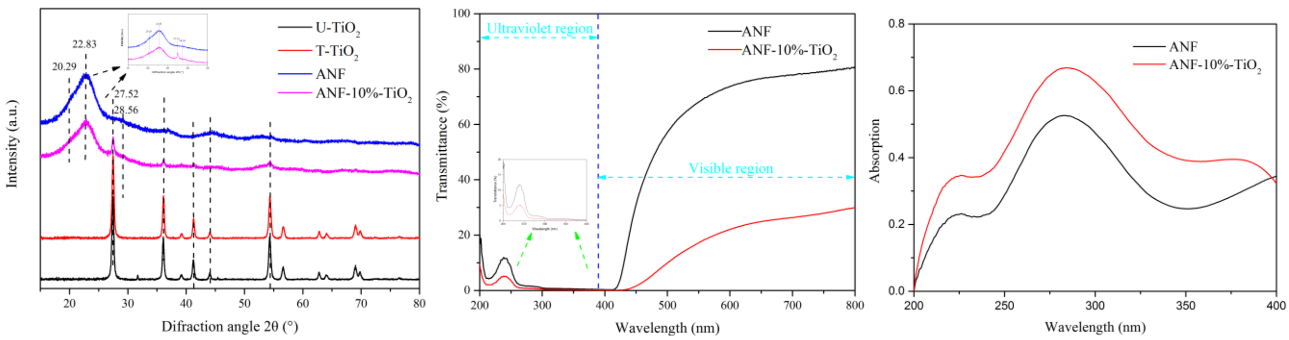


Figure 2 Schematic diagram of organic inorganic nanocomposite paper

3.2 XRD patterns and UV absorption properties of nano hybrid films

Due to the entanglement network of aramid fibers constructed by the strong hydrogen bond among molecules, the size of ANFs is far smaller than the wavelength of visible light, leading a good transparency of the ANFs membrane. From the XRD results of ANF and hybrid films in Figure 3(a), it can be seen that the ANFs film keeps the crystal surface and crystallinity of the traditional aramid fiber. Specifically, ANFs membrane maintains the peak of macro fiber at about 20~30°, which corresponds to the (110), (200), and (004) lattice planes of Kevlar fibers. The nanoparticles are uniformly distributed on nanofibers through chemical bonding and electrostatic adsorption. In Figure 3(b), the pure ANFs film has a transmittance of over 80% of the visible light, showing a high transparency. It is attributed to the smaller size than the visible light wavelength of the ANFs. When inorganic nanoparticles are attached to the hybrid membrane, the network structure is formed between the nanofibers and the nanoparticles, and the fibers and the nanoparticles are more closely combined, so the transparency decreased significantly.



(a) (b) (c)

Figure 3 (a) XRD patterns of nanoparticles and nanocomposite films, (b) Transmission of pure ANFs and hybrid membranes, (c) Absorption spectra of pure ANFs membrane and hybrid membrane

As shown in Figure 3c, the hybrid film with 10% nano particles has a higher absorption intensity in the range of 200～400 nm than the pure ANF film, showing a better UV absorption capacity, which is attributed to the nano TiO_2 as the oxide semiconductor. Nano TiO_2 can absorb ultraviolet light to produce electron/hole pairs, TiO_2 absorbs ultraviolet energy and its electrons are excited from the valence band to the conduction band. The formation of conduction band may be involved in the recombination process or the redox reaction on the surface of TiO_2. The UV energy consumption by TiO_2 can protect the material from UV [10-13]. The optical band gap of Nano-TiO_2 is 385 nm (3.2eV), and below 350 nm it has a strong absorption intensity. The improvement of UV absorption capacity will make the fiber membrane have a better application in the field of UV resistance.

4 Conclusions

In a word, the modified nanoparticles are fixed in the network of ANFs to prepare organic-inorganic hybrid films. The transparency of hybrid membrane depends on the amounts of nano particles attached. Therefore, in the process of preparing composite membranes, it can effectively promote the close bonding of inorganic nanoparticles and ANFs, and prepare uniform and compact composite membranes. The obtained hybrid film has certain transparency, and the pure aramid nanofilm has a transmittance of 80 % in the visible light range. This kind of organic-inorganic hybrid membrane with certain UV absorption effect can be obtained through relatively simple processing and preparation process. This novel method can be an inspiration to the application of organic-inorganic hybrid functionalized composites.

Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements: This work was supported by the Guizhou Province "100-level" Innovative Talents Project, Qianke Union platform talent (NO. [2016] 5653).

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