Preparation and Characterization of PANI/TiO_2 Nano-composite Fibers

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Keywords: hydro-thermal method, characterization, nano-composite fibers.

Abstract. In this paper, we prepared PANI/TiO2 nano-composite fibers by the combination of Sol-Gel method and electrospinning technique. The results indicated that the PANI/TiO2 nano-composite fibers have uniform size and good configuration. The average diameter of the PANI/TiO2 nano-composite fibers is about 300nm. Byscanning electron microscope(SEM), X ray diffraction analysis(XRD), infrared spectrum analysis(FT-IR), thermogravimetric analysis(TG), respectively, we analyzed and characterized the configuration, structure, crystallization, thermal stability and other properties, furthermore, we identified the optimum condition for PANI/TiO2 nano-composite fibers preparation. The article has laid the material foundation for the in-depth study of properties of PANI/TiO2 nano-composite fibers.

1. Introduction

Polymer / inorganic nano-composites are the hot spots in the research of nano materials science. The conductive polyaniline, representative organic semiconductor materials in the conjugated polymer, has raised wide concern for its various structures, special doping mechanism, good oxidation resistance and heat resistance. Composite material made with TiO_2 nano material and PANI, has different electrical conductivity and optical properties from pure PANI. It can also expand the application especially in photoelectricity such as solar cell and photoelectro-catalysis.

At present there are very few reports on preparing PANI/TiO_2 nano-composite fibers by electrospinning technique. Based on anatase TiO_2 nanofibers, we uses hydro-thermal method to make PANI/TiO_2 nano-composite fibers which have uniform size and good configuration. The average diameter of the PANI/TiO_2 nano-composite fibers is about 300nm. It has also analyzed and characterized the configuration, structure, crystallization, thermal stability and other properties and identified the optimum condition for PANI/TiO_2 nano-composite fibers preparation.

2. Experimentation

Main reagent: polyvinylpyrrolidone (PVP,A.R., Beijing Yili Chemical Co., Ltd.MN=1300000); Tetra-n-butyl titanate(C.P., China Shanghai Chemical Reagent Co., Ltd.); Glacial acetic acid(A.R., Beijing Chemical Factory); Aniline(ANI, A.R., Guangdong Shantou Xilong Chemical Factory); $FeCl_3 \cdot 6H_2O$(A.R., Beijing Chaoyang District Tonghui Chemical Factory);HCL(A.R., Beijing Chemical Factory).

Preparing TiO_2 nano material: Add 5g PVP to the 27ml anhydrous ethanol and stir with magnetic force for 10h to get homogeneous polymer solution; add 4ml tetra-n-butyl titanat solution slowly to a mixture of 7ml absolute ethyl alcohol and 6ml glacial acetic acid when stirring, and stir for 2h to get inorganic solution; at room temperature, add the solution of the inorganic material slowly to the homogeneous polymer solution and get PVP/Ti $(OiPr)_4$ precursor solution. Prepare PVP/Ti $(OiPr)_4$ nano-composite fibers with electrospinning and the spinning device is self-designed. Put the fiber into muffle furnace and get anatase TiO_2 nano-fibers.

Preparing PANI/TiO_2 composite nano-fibers: put about 0.5g PANI/TiO_2 nano-composite fibers into 30ml autoclave for preparation. Add 1.1g $FeCl_3 \cdot 6H_2O$ into deionized water and magnetic stir for 15min until get homogeneous solution. Pipet 0.123ml HCL solution to the $FeCl_3 \cdot 6H_2O$ solution and then 0.38 PANI solution was added to the mixture solution of $FeCl_3 \cdot 6H_2O$ and HCL and stir 5min until a stable solution is stable. At last put it into the autoclave and put the autoclave into electric heating constant temperature air blast drying box at 120℃ for 6h. After it, cool it in water for 5min and then move the reaction product into the beaker. Wash several times with distilled water until the solution is clear. And then take out TiO_2 fibers. Now the fiber is turn from white to dark green. Put it into vacuum drying oven at 60℃ for 6h.

3. Results and discussion

3.1 Scanning electron microscope(SEM)

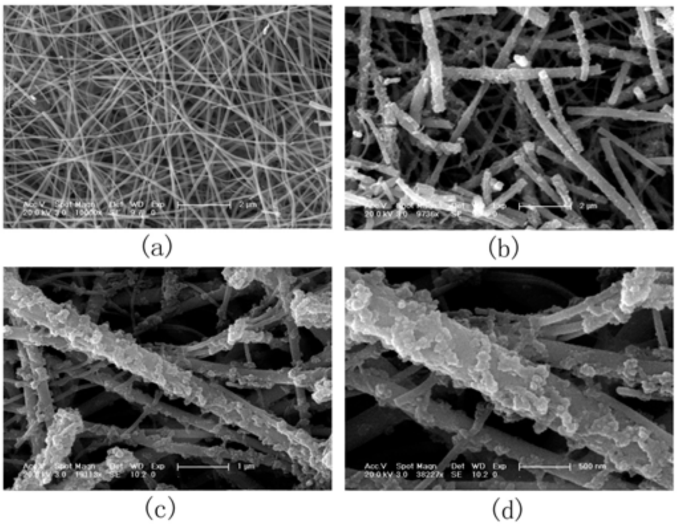

Fig.1 SEM images of PANI/TiO2 composite nanofibers

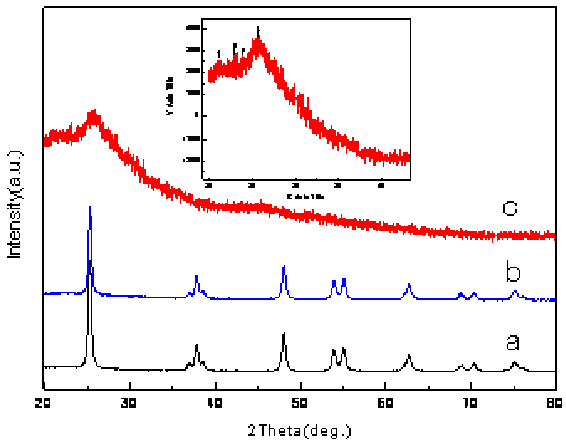

Fig.2 XRD spectrum of TiO2 (a), PANI/TiO2 composite nanofibers(b), PANI(c)

It can be seen in fig.1 (a) that the fiber surface is smooth and the diameter distribution is uniform which is about 150nm. Fig.1 (b), (c) and (d) are all SEM images of PANI/TiO_2 in different magnification. From (b) we see that the fiber diameter grows to about 300nm after the completion of TiO_2 reacting in PANI hydrothermal system. We believe that the surface of the TiO_2 nano fiber is coated with a layer of PANI. Zoom (b) and we can see PANI particles are also grown on the surface of the layered structure (as shown in figure C and figure d) and the distribution is uniform. According to the SEM analysis, the hydrothermal reaction caused the fracture in TiO_2 nano fiber. In conclusion, the PANI/TiO_2 composite nanofibers are shell structure. The average diameter is around 300nm. The form is good and the reunion phenomenon is not obvious.

3.2 X ray diffraction analysis(XRD)

Fig.2 is the XRD spectrum of TiO_2 (a), PANI/TiO_2 composite nanofibers (b), PANI (c). From it we can see that where 2θ is 25.27 degrees, 37.82 degrees, 47.93 degrees, 54.04 degrees, 55.01

degrees, 62.66 degrees, 68.72 degrees, 70.29 degree there are relatively strong diffraction peak. Compared with JCPDS standard, it's proved that TiO2 is anatase structure. Spectrum (b) is PANI/TiO_2 composite nanofibers. We didn't see obvious diffraction peak in it. It can be explained that when an aniline unit is in polymerization centered with TiO_2 nano-fibers, the chain growth and crystallization of PANI are hindered by TiO_2 fibers and crystallinity decreases or even disappears, expressed as the disappearing of two broad diffraction peaks- 21.24°and 25.89°[1,2]. Fig c is the XRD spectrum of pure PANI, from which we can see four obvious diffraction peaks in $2\theta=20\sim30°$which are respectively 21.24°,22.94°,24.05°,25.89°. It means that PANI is partially crystalline [3].But the diffraction peaks are weak and have high density, which means the crystallinity is relatively low. It's similar to the study of MacDiarmid et.al [4]. By comparing (c) and (d), we can know that the interaction between PANI and TiO_2 nano-fibers basically has no influence on TiO_2 fibers. The diffraction peaks of PANI/TiO_2 composite are consistent with pure TiO_2, which means the crystallinity of PANI is relatively low.

3.3 Infrared spectrum analysis(FT-IR)

Fig.3 is the IR spectrum of TiO_2 (a), PANI/TiO_2 nano-composite fibers (b), and pure PANI(c). In 675 and 458 cm-1 there are characteristic vibration peak belonging to anatase TiO_2. Curve (b) is the FT-IR curve of ANI/TiO_2 composite nano materials. Comparing it with (a), there are some new peaks. They can be attributed to main characteristic absorption peaks of PANI compared with absorption peak of pure PANI in (c). It also means PAIN successfully covered the surface of TiO_2 fibers, which is consistent with electron microscope result. However, after adding TiO_2 nanofibers, some of the peaks of polyaniline deviated because the introduction of inorganic materials changed the electronic cloud density of the polymer chain. Because of TiO_2 nanofibers, polyaniline unit is first adsorbed on its surface. Then add the initiator and the polymerization reaction will be carried out on the surface of TiO_2 fiber. This makes the molecular chain of PANI attached to the surface of the TiO_2 fiber and the growth of its molecular chain is also limited to the periphery of the fiber. This action not only inhibits the movement of molecular chains, but also limits the vibration of PANI molecules decreasing the electron cloud density of C-N, C=C and C=N in the molecular chain. Meanwhile, the force between the atoms is reduced, the vibration is weakened and move to the low frequency. It means the TiO_2 nanofibers interact with polyaniline and TiO_2 nanofibers have strong interaction with polyaniline polymer [5, 6, 7]. Titanium is a transition metal. Tetravalent titanium can form a coordination compound with PANI N atom making TiO_2 getting into PAIN molecular chain with positive charge. In peak related with quinone structure, the C=N and C=C become weaker due to it.

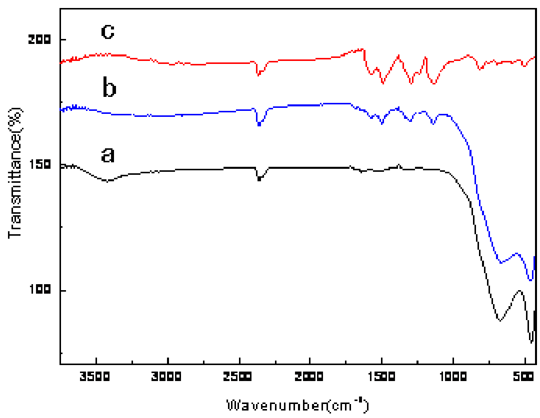

Fig.3 infrared spectrum of TiO2 (a), PANI/TiO2 composite nanofibers(b), and pure PANI(c).

3.4 Thermogravimetric analysis (TG)

Analyze the thermogravimetric of TiO_2 nanofibers and PANI/TiO_2 composite nanofibers with STA 449C Netzsch type thermal analyzer produced by German Netzsch Company. The heating rate is 10℃ /min, the atmosphere is air.

Fig.4 is the thermogravimetric curve of PANI/TiO_2 composite nanofibers. It can be seen from the diagram that the weight loss of TiO_2 nano fibers was below 420℃. It's mainly the process of adsorbed water ethanol desorption and decomposition of part of the surface hydroxyl. By heating it to

200℃, we find it has a weight loss of 2.5% because of water desorption; between 200~500℃, the weight loss is about 5% because of decomposition of PANI molecular framework. Because of the interaction between PANI and TiO_2 in the composite material, the force in the molecular chain of PANI decreases, which reduces the thermal decomposition temperature. Besides, the curve after 500℃ is flat and it means PANI completely decomposes.

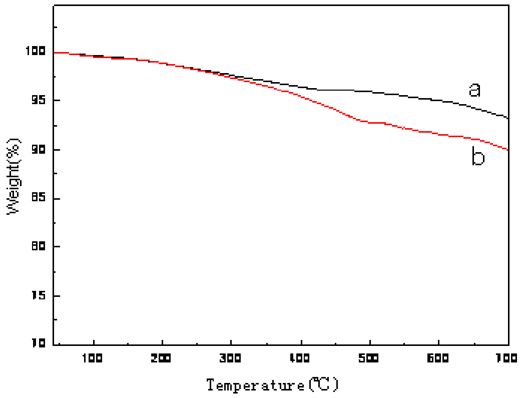

Fig.4 thermogravimetric curve of PANI/TiO2 composite nanofibers

4. Conclusion

In this article, we prepared PANI/TiO_2 nano-composite fibers successfully through electrospinning technique and hydrothermal method. It also confirmed the optimum condition to prepare PANI/TiO_2 composite nanofibers. Through SEM, we can find a layer of organic polyaniline covers the surface of TiO_2 nano fibers and PANI particles are also grown on the surface of the layered structure. In addition, with SEM, XRD, FT-IR, TG and other methods, we have analyzed and characterized the configuration, structure, crystallization, thermal stability and other properties and identified the optimum condition for PANI/TiO_2 composite nanofibers. The fibers have uniform size and good configuration. The average diameter of the PANI/TiO_2 composite nanofibers is about 300nm. The phenomenon of agglomeration is not obvious. There is interaction between molecules in PANI/ TiO_2 composite nanofibers but almost have no influence on TiO_2 fibers. Composite material is not a simple two- phase system. The above work has laid a foundation for the further study of the properties of PANI/ TiO_2 composite nanofibers.

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