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Functional Fiber Mats with Tunable Diffuse Reflectance Composed of Electrospun VO_2/PVP Composite Fibers

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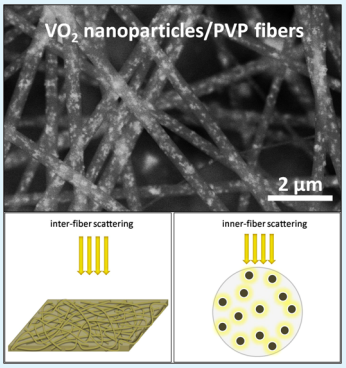
Supporting Information

ABSTRACT: Thermochromic VO_2 nanoparticles have been dispersed into polyvinyl pyrrolidone (PVP) fibers by electrospinning of a VO_2–PVP blend solution. The structure and optical properties of the obtained composite fiber mat were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet–visible (UV–Vis) spectrophotometry, and Fourier transform infrared (FT-IR) spectroscopy. The fiber mat revealed two diffuse reflectance states in infrared spectral region at temperatures under and above the phase transition temperature of VO_2 and its IR reflectance is smaller in high temperature. The difference of diffuse reflectance between the two states (ΔR_{dif}) was obvious to be more than 25% in the wavelengths from 1.5 μm to 6 μm. The diffuse reflectance of the fiber mat could be controlled by adjusting the diameter of the fiber or the content of VO_2 in the fibers and this particular optical property was explained by a multiple scattering-absorbing process.



KEYWORDS: *electrospinning, VO_2/PVP composite fibers, diffuse reflectance*

1. INTRODUCTION

As a remarkably simple and versatile technique, electrospinning has been exploited for nearly one century to process polymers and related materials into 1D structural fibers for a variety of applications.[1−3] During electrospinning, a high voltage is applied to a polymer solution to produce a polymer jet. With the fast evaporation of solvent, the charge density in the polymer jet is increased, resulting in the formation of nanofibers that accumulate to form fiber mats. In the recent years, inorganic/organic composite fibers prepared by electrospinning have been attracting great interests of researchers. The inorganic part in the composites can be ZnO,[4] PbS,[5] CdTe,[6] and Ln^{3+}-doped $NaYF_4$[7] quantum dots for optoelectronic application, or TiO_2 to be used for catalysis,[8] or Ag nanoparticles for antibacterial use.[9] The organic part is determined by the need to use in different kinds of environment[10] and for morphology control.[11,12]

Vanadium dioxide (VO_2) is a typical thermochromic material that undergoes a reversible metal-to-semiconductor phase transition (MST) at about 68 °C (in a bulk crystal).[13] This thermally driven phase transition concurs with a crystallographic transition from a low-temperature monoclinic structure (VO_2(M)) to a high-temperature tetragonal rutile structure (VO_2(R)) and is accompanied by a dramatic change in optical properties in the infrared region from a low-temperature transparent state to a more reflective state at high temperatures.[14,15] As the semiconductor nanoparticles like ZnO and TiO_2 keep their photoluminescence or photocatalysis property in the electrospun fibers, the VO_2/organic composite fiber mats are expected to be functional textiles to reveal variable optical states.

In the present work, the VO_2/PVP composite fiber mats were prepared by electrospinning for the first time and its particular diffuse reflection property was opposite to the conventional films composed of VO_2 nanoparticles.[16] The fiber mat revealed two diffuse reflectance states in infrared wavelengths under and above the phase transition temperature of VO_2 and it reflected less light in high temperature. The difference of diffuse reflectance between the two states (ΔR_{dif}) was obvious to be more than 25% from 1.5 to 6 μm. This drastic variation as well as the transition temperature could be controlled by doping in the VO_2 nanoparticles indicated its potential application in thermal regulation. In addition, the PVP might be replaced by other organic polymers like polyimide (PMMA) or polyacrylonitrile (PAN) to be durable for practical application.

2. EXPERIMENTAL SECTION

In a typical procedure for preparing fibers that were 500 nm in diameter, a certain amount of VO_2 or W-doped VO_2 nanoparticles obtained by the method of literature[17] were well dispersed in 9.4 g alcohol by ultrasonic dispersion, then 0.6 g PVP (M_w = 1 300 000) was added in. After being stirred for 6 h, the solution was loaded in a syringe. The electrospinning process lasted for half an hour under a

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voltage of 12.5 kV. The feeding rate of the suspension in the syringe was controlled as 2.5 mL/h by using a syringe pump and the distance between the tip of the needle and the collector was 15 cm. The electrospun fibers were collected by aluminium foil or glass for characterization.

X-ray diffraction (XRD) analyses were conducted on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5418 Å). The morphology and microstructure were determined using a scanning electron microscope (SEM; Hitachi, S-4300) and a field-emission scanning electron microscope (FE-SEM; Hitachi, S-4800). The diffuse reflectance (R_{dif}) of the fiber mats in the wavelength range from 350 to 2500 nm and from 2.5 to 12 μm were measured using a UV−vis spectrophotometer (Hitachi, U-3010) and a Fourier transform infrared (FT-IR) spectrometer (Nicolet, Magna 560) with an integrating sphere and a temperature controlling unit.

3. RESULTS AND DISCUSSION

It is well-known that the content of organics in solution determines the viscosity of the spinning solution and thus determines the diameter of the electrospun fibers. VO_2/PVP composite fibers with different diameters were obtained by adjusting the amount of PVP in the spinning solution (when the amount of VO_2 was 0.2 g). SEM images of these samples were shown in Figure 1. When the weight of the solution

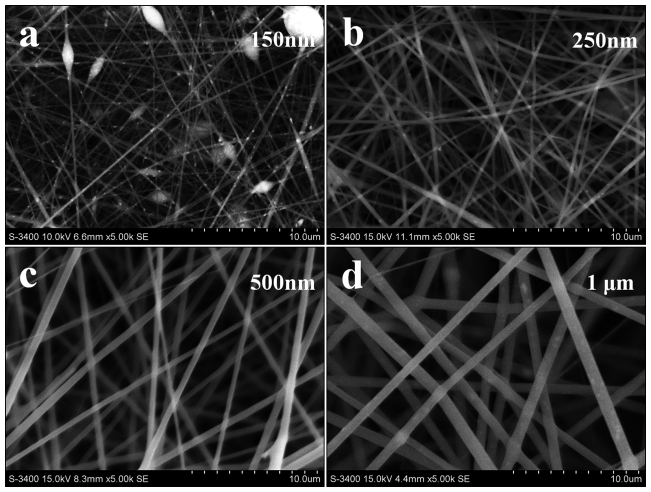

Figure 1. (a−d) SEM images of the electrospun VO_2/PVP composite fibers with different diameters obtained by adjusting the amount of PVP in the spinning solution.

(alcohol and PVP) and PVP were 10 g and 0.4 g (4 wt %), the products were fibers (d = 150 nm) and several spindles. The diameter of the fibers came to be 250 nm when 0.5 g of PVP was added. The spindles were eliminated by increasing the amount of PVP to 0.6 g (d=500 nm), so this condition was adopted for the further research. Nine-tenths of a gram of PVP corresponded to a diameter of 1 μm; however, further increasing the amount of PVP did not make thicker fibers.

The electrospun VO_2/PVP composite fibers with a diameter of 500 nm were chosen to do further research. Figure 2a shows their SEM image under low magnification, which showed the fibers were uniform and longer than 1 cm. It was confirmed that the spindles resulting from the solution's insufficient viscosity were completely eliminated. These fiber mats containing 25 wt % VO_2 or W-doped VO_2 (PVP, 0.6 g; VO_2, 0.2 g) were characterized by XRD and the results were showed in Figure 2b (transmission spectrum and SEM image of the nanoparticle composed films are shown in the Supporting Information,

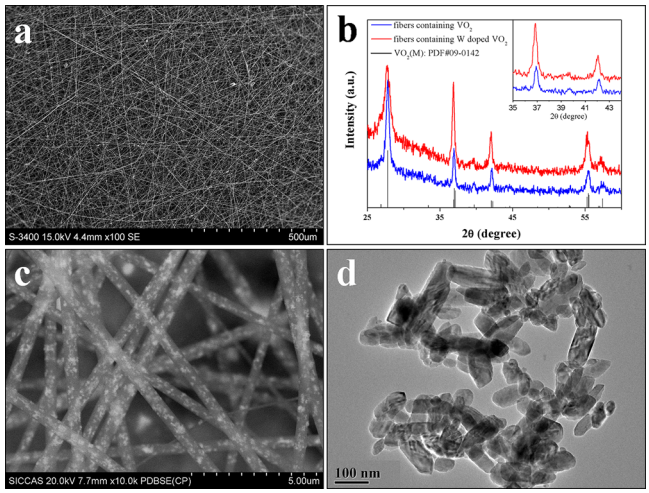

Figure 2. (a) SEM image of the electrospun VO_2/PVP composite fibers (d = 500 nm); (b) XRD patterns of the fiber mats containing 25 wt % VO_2 and W-doped VO_2 (PVP, 0.6 g; VO_2, 0.2 g); (c) SEM image of the VO_2/PVP fibers under backscattered mode. (d = 500 nm; VO_2, 0.2 g); (d) TEM image of VO_2 nanoparticles.

Figure S1). The XRD patterns indicated that the VO_2 and W doped VO_2 nanoparticles kept their phase unchanged during the electrospinning process. The diffraction peak shift caused by W doping was still obvious despite the nanoparticles being buried in PVP. To confirm the existence of VO_2 in the electrospun fibers, FE-SEM image of the fibers under backscattered mode is shown in Figure 2c, whereas TEM image of VO_2 nanoparticles was shown in Figure 2d for contrast. As expected, the nanoparticles with average size at 80 nm were uniformly distributed in the fibers, which was favorable to reveal their thermochromic property.

Figure 3a was the diffuse reflection spectra in the wavelength range from 350 nm to 2500 nm of VO_2/PVP composite fiber

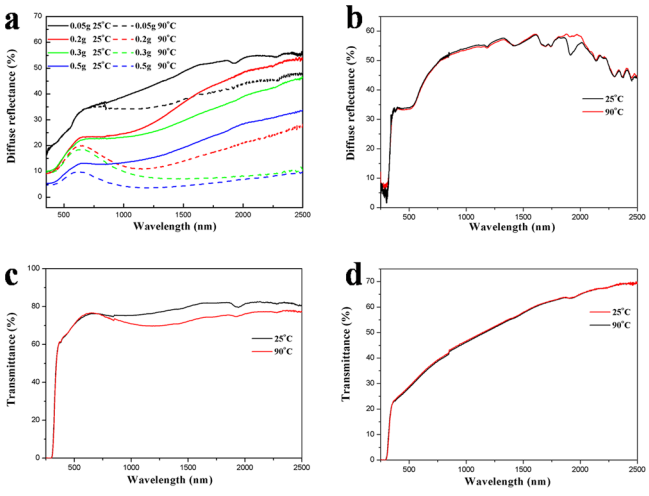

Figure 3. (a) Diffuse reflection spectra of VO_2/PVP composite fiber mats (d = 500 nm) with different VO_2 content. (b) Diffuse reflection spectrum of PVP fiber (d = 500 nm) mat. (c) Transmission spectrum of the thin VO_2/PVP composite fiber mat (d = 500 nm, 0.05 g VO_2). (d) Transmission spectrum of the thin PVP fiber mat (d = 500 nm).

mats (d = 500 nm) with different VO_2 content from 0.05 g to 0.5 g, which were prepared under the typical procedure to electrospin for 30 minutes. The fiber mats revealed different

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diffuse reflection properties under and above 68 °C as it is the phase transition temperature of VO_2 nanoparticles. Their property was different from the VO_2 film which shows a higher reflectance above 68 °C, however exhibiting its opposite. The diffuse reflectance of the fiber mats became lower when they were heated to above the phase transition temperature. Increasing the amount of VO_2 resulted in reduction of the diffuse reflectance under and above 68 °C and raised the difference of diffuse reflectance between the two states within a certain range from 7.7 wt.% (VO_2, 0.05 g) to 33.3 wt.% (VO_2, 0.3 g) at 2500 nm. However, further increasing the amount to 0.5 g lowered the difference, for the diffuse reflectance above 68 °C had been reduced to less than 10%.

The diffuse reflection spectrum of a PVP fiber mat without VO_2 nanoparticles (d = 500 nm) was showed in Figure 3b for contrasting. The diffuse reflectance showed no clear difference under and above 68 °C, which was a little higher than that of the fiber mat containing 0.05 g of VO_2, so the particular diffuse reflection property could be attributed to VO_2 particles rather than PVP. To further understand this property, we measured the transmission spectrum of VO_2/PVP composite fiber mat (d = 500 nm; VO_2, 0.05 g) and the result is shown in Figure 3c, with the spectrum of the PVP fiber mat given in Figure 3d for contrast. For this measurement, the electrospinning time for the samples has been reduced to get semitransparent fiber mat. It was found that the transmission property of the VO_2/PVP composite fiber demonstrated a similar behavior as VO_2 films, becoming less transparent above the phase transition temperature, however, its reflection property was similar as the thick one. That indicated the VO_2 nanoparticles keep its thermochromic property when they buried in the fiber. When the composite fiber mat was at metallic state under high temperature, it transmitted and reflected less light than the semiconductor state, so the remaining light should be absorbed because of the multiple scattering-absorbing process. Two modes of this process may exist and the sketch maps were revealed in Figure 4: inter-fiber scattering and inner-fiber

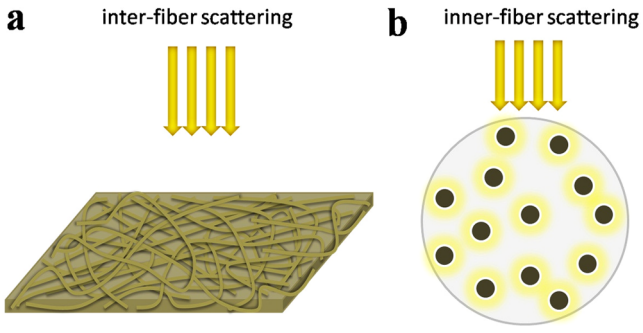

Figure 4. Two modes of the multiple scattering-absorbing process when light is absorbing by the fiber mat: (a) the inter-fiber scattering; (b) the inner-fiber scattering.

scattering. The inner-fiber scattering (Figure 4b) occurred among the VO_2 nanoparticles in each single fiber. By this mode the fibers were endowed with thermochromic property thus the inter-fiber scattering (Figure 4a) meant light was multiply scattered by the VO_2/PVP composite fibers. The incident light underwent these scatterings over and over again unless it was reflected back and every scattering was accompanied by absorption. Thus the absorption accumulated to be obvious although the absorption coefficient of VO_2 nanoparticles at metallic state is slightly larger than the semiconductor state in this wavelength region. Increasing the content of VO_2 in the fibers within a certain range enhanced the inner-fiber scattering as well as the inter-fiber scattering, so the diffuse reflectance under and above 68 °C reduced and the difference of diffuse reflectance between the two states increased.

The phase transition temperature of VO_2 can be tuned by doping, and the transition temperature of this optical functional fiber mat could also be altered. Practically, the diffuse reflection spectrum of fiber mats containing W-doped VO_2 nanoparticles whose phase transition temperature was tuned to be 40 °C were measured, as the result was shown in Figure 5. The

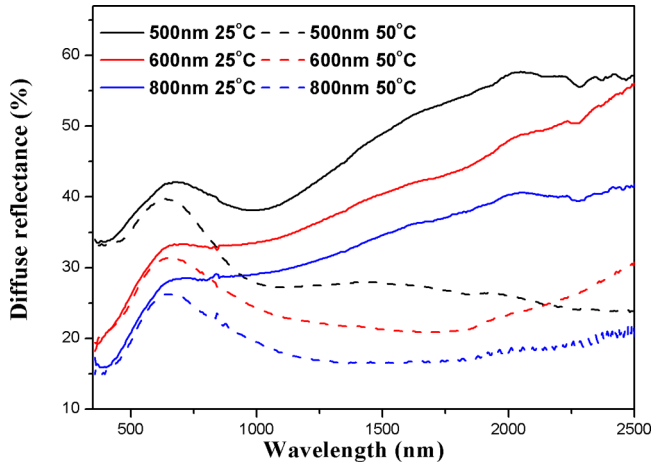

Figure 5. Diffuse reflection spectra of W-doped VO_2/PVP composite fiber mats with different fiber diameters.

diameter of these fibers was changed to investigate how it affected the optical property at the same time. For this measurement, the diameter of the fibers was controlled by altering the content of PVP in the electrospun solution as mentioned before while the content of W-doped VO_2 nanoparticles in the fibers was fixed to be 14.3 wt % (for example: 0.1 g of VO_2 and 0.6 g of PVP). The diffuse reflection property of fiber mats containing W-doped VO_2 nanoparticles was similar to the fiber mats containing undoped ones that they reflected less light after heating above the transition temperature. However, the diameter did affect the reflection property that when it increased, the diffuse reflectance of the fiber mats both under and above the transition temperature decreased. This phenomenon could be explained by the inner-fiber scattering that the thick fibers contained more VO_2 nanoparticles so enhanced the multiple scattering-absorbing process. Now two methods have been discovered to alter the diffuse reflectance of the fiber mat: controlling the content of VO_2 in the fiber mats or adjusting the diameter of the fiber. In addition, it was noteworthy that only two reflection state existed in our experiment when the fiber mats were uniformly heated. The diffuse reflection spectra of fiber mat containing W-doped VO_2 nanoparticles at metallic state remained the same when it were measured at 43, 47, 55, and 65 °C.

The diffuse reflection spectrum of the fiber mat containing W-doped VO_2 nanoparticles in mid-infrared and far-infrared region from 2.5 μm to 12 μm was shown in Figure 6. The diameter of the sample was 800 nm whose diffuse reflection spectrum in near infrared region was shown by the blue line in Figure 5. The fiber mat maintained its reflection property in

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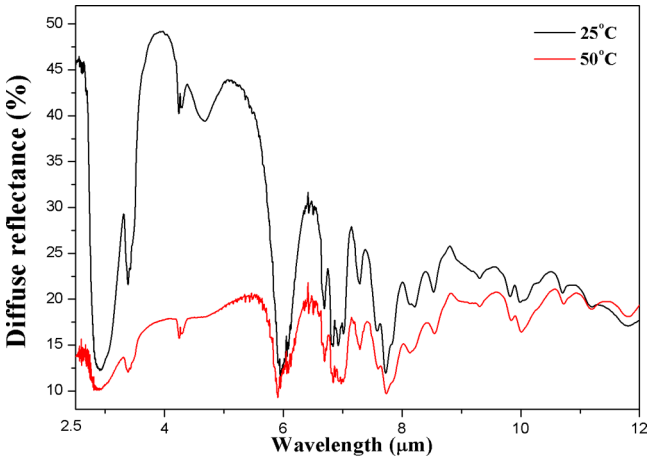

Figure 6. Diffuse reflection spectrum of the PVP fiber mat containing W-doped VO_2 nanoparticles in mid-infrared and far infrared region from 2.5 to 12 μm.

mid-infrared and far-infrared region to reflect less light when heated above the transition temperature. The difference of the diffuse reflectance under and above the transition temperature was still large in the mid-infrared from 3 to 6 μm, which reduced in the far-infrared region.

In this work, we took PVP as an example to demonstrate a functional textile. However, the VO_2/PVP composite fiber mat was water-soluble and its mechanical intensity was relatively low, so not suitable for practical application. So the VO_2/PMMA and VO_2/PAN composite fibers were electorspun to compose durable fiber mats, as the diffuse reflection spectra of them (d = 500 nm; VO_2, 7.7 wt %) from 350 nm to 12 μm are shown in Figure 7. They showed similar variable optical

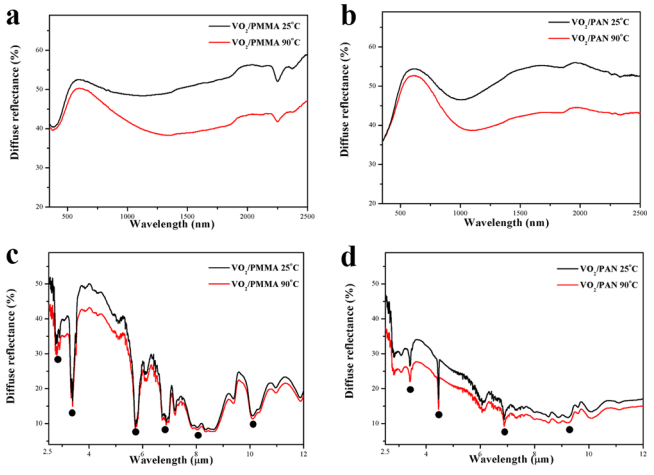

Figure 7. (a, b) Diffuse reflection spectra of VO_2/PMMA and VO_2/PAN composite fiber mats from 350 nm to 2500 nm. (c, d) Diffuse reflection spectra of VO_2/PMMA and VO_2/PAN composite fiber mats in mid-infrared and far infrared region from 2.5 to 12 μm.

properties under and above 68 °C, as expected. However, the diffuse reflection spectra could be different in the mid-infrared and far-infrared region by using different organics for electrospinning. The characteristic absorption peaks of PMMA and PAN were labeled by dots in panels c and d in Figure 7. The photos of the VO_2/PVP and VO_2/PAN composite fiber mats were shown in Figure S2 in the Supporting Information. These attempts indicate the functional thermochromic textile containing VO_2 nanoparticles is well-prepared for practical use.

4. CONCLUSION

In summary, we prepared VO_2/PVP composite fiber mats by electrospinning with particular optical property. The fiber mat revealed two diffuse reflectance states in infrared wavelengths under and above the phase transition temperature of the VO_2 nanoparticles. However, its IR reflectance performance was different with pure VO_2 nanoparticles that reflect less light in high temperature, which was explained by a multiple scattering-absorbing process. Diffuse reflectance of the fiber mat could be controlled by adjusting the diameter of the fiber or the content of VO_2 and the transition temperature could be controlled by doping in the VO_2 nanoparticles. In addition, the PVP might be replaced by other organics like PMMA or PAN for electrospinning to be durable for practical application.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Transmission spectrum of the films composed of VO_2 nanoparticles that were used for electrospinning. The photos of VO_2/PVP and VO_2/PAN composite fiber mats. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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