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Preparation of PVA/ $H_3PW_{12}O_{40}$ Fiber Mats

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Abstract: Poly(vinyl alcohol) (PVA) fiber mats containing 20 and 80 wt% $H_3PW_{12}O_{40}$ were prepared by using electrospinning technique. The fiber mats were characterized by IR, XRD spectra and scanning electron microscope (SEM). The diameter of the fiber mats is *ca*. 400 nm.

Keywords: Fiber mats, heteropolyacid, electrospinning, PVA, SEM.

The preparation of inorganic-organic hybrid materials based on heteropolyacid has been received considerable attention in recent years[1]. Heteropolyacid, as catalyst, is especially important in industrial application[2]. However, a main disadvantage is its very low surface area[3]. To date, there is not any report on heteropolyacid-based fiber mats. Obviously, the synthesis of heteropolyacid-based inorganic-organic hybrid ultra fine fiber mats is significant in increasing surface area of catalyst.

10 g (11.0 mL) of the 10 % PVA solution was added to 0.25 g and 4.00 g of $H_3PW_{12}O_{40}$, respectively. The solutions were stirred vigorously for 24 h at room temperature. The viscous solutions of 20 and 80 wt% $H_3PW_{12}O_{40}$ were obtained, respectively. The $H_3PW_{12}O_{40}$/PVA solution was contained in a plastic capillary tube. A copper pin was connected to a high-voltage generator, which was placed in the solution. The distance from tip to collector is 7 cm. A voltage of 18 kV was applied to the solution and dense web of fibers was collected on the aluminum foil. 20 and 80 wt% $H_3PW_{12}O_{40}$ fibers were dried under vacuum for 24 h at 40 ^oC.

Figure 1 gives the SEM photographs of the fiber mats. The result of diameter distributions indicated that the diameter of the fibers increases with increasing $H_3PW_{12}O_{40}$ content, *i.e*. higher the $H_3PW_{12}O_{40}$ content is, thicker the diameter of the fibers is. The average diameter of the fibers changes from *ca*. 380 to 510 nm with increasing $H_3PW_{12}O_{40}$ content from 20 to 80 wt%.

The IR spectrum of the $H_3PW_{12}O_{40}$/PVA fiber mats showed four characteristic bands of $H_3PW_{12}O_{40}$, *i.e.* ν_{as}(W-O_d): 983 cm^{-1}, ν_{as}(W-O_b-W): 897 cm^{-1}, ν_{as}(P-O_a): 1078 cm^{-1}, and ν_{as}(W-O_c-W): 832 cm^{-1}. The appearance of the characteristic peaks of heteropoly acid indicates the existence of $H_3PW_{12}O_{40}$ in PVA matrix[4]. Compared with the intensity of characteristic band of PVA, the intensity of the four characteristic bands of heteropolyacid increases with increasing $H_3PW_{12}O_{40}$ content.

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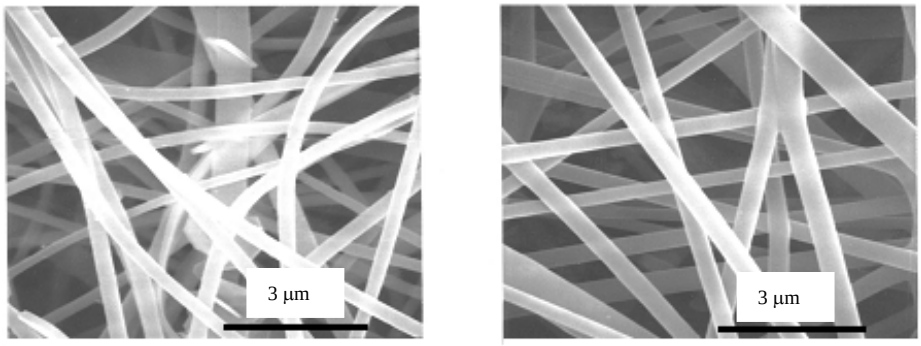
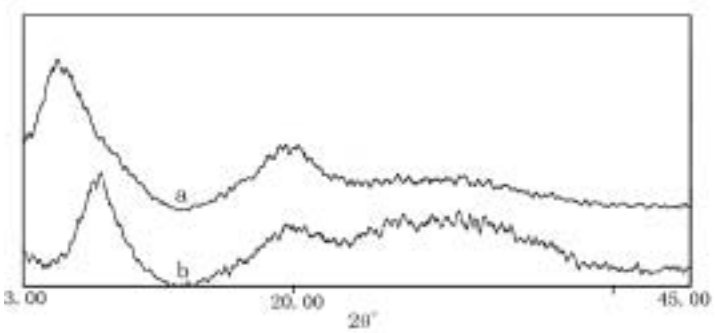
Figure 1 Scanning electron microscopy of the fiber mats with different $H_3PW_{12}O_{40}$ content. a, 20 wt%; b, 80 wt%.



a b

For pure PVA, there is a peak in its X-ray diffraction around $2\theta=20^o$, which corresponds to the (101) plane of PVA semi-crystalline[5]. As seen in **Figure 2**, PVA fiber mats become an amorphous state because of increasing $H_3PW_{12}O_{40}$ content. This indicates that $H_3PW_{12}O_{40}$ can inhibit the crystal growth of PVA. At the same time, a special peak at $2\theta<10^o$ appears. The 2θ shifted with increasing $H_3PW_{12}O_{40}$ content. For 80 wt% $H_3PW_{12}O_{40}$/PVA fiber mats, the peak appeared at about 7.7^o that is close to the characteristic peak of heteropoly acid[6]. The appearance of the peak at $2\theta<10^o$ showed the existence of the Keggin anions in PVA matrix, and also indicated that the molecules of the fiber mats are in order with short interlayer distance[7].

Figure 2 XRD diffraction of the fiber mats with different $H_3PW_{12}O_{40}$ content. a, 20 Wt%; b, 80 wt%.



BET results: Pure, 20 and 80 wt% $H_3PW_{12}O_{40}$ fiber mats are dried in vacuum for 24 h at 40 °C, respectively. The BET surface area is 0.52, 3.61 and 2.76 m^2/g, respectively. *i.e.* thicker the diameter of the fiber is, less the BET surface area of the fiber mats is. However, the BET surface area of the fiber mats is higher than that of pure $H_3PW_{12}O_{40}$ powder. This shows that the fiber mats, as a candidate of the catalyst, can be applied in future catalytic reaction.

References

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