SUMMARY OF Ph.D. DISSERTATION

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Title

Optimization and Functionallization of Nanofibrous Mats/Membranes Prepared by Electrospinning

Abstract

In this study, the optimization and functionallization of nanofibrous mats/membranes prepared by electrospinning were discussed to obtain the uniform properties of nanofibrous nonwoven mats, sensing nanofibrous membranes, functional films coated nanofibrous mats, and polyoxometalate nanotubes.

Firstly, a novel multi-jet electrospinning fashion was built up to fabricate the nanofibrous nonwoven mats with uniform properties. Blend biodegradable nanofibrous nonwoven mats with different weight ratio of poly(vinyl alcohol) (PVA)/cellulose acetate (CA) were fabricated via multi-jet electrospinning. A relative high voltage (20 kV) was used to supply the power for multi-jet electrospinning. The weight ratio of PVA/CA in blend nanofibrous mats can be controlled by changing the number ratio of jets of PVA/CA. Moreover, the real composition of PVA and CA in blend nanofibrous mats was determined by immersing the blend nanofibrous mats into water to remove the PVA component. Morphology, dispersibility, and mechanical properties of blend nanofibrous mats were examined by FE-SEM, FT-IR, WAXD, and tensile test. The results showed the blend nanofibrous mats have good dispersibility because the blend nanofibrous mats have uniform properties for each sample and regular transforms with changing the number ratio of jets of PVA/CA. As a result, the PVA and CA nanofibers were homogenously dispersed into each other. FT-IR results demonstrated that there was no chemical reaction between PVA and CA nanofibers, just physical blending. Additionally, the mechanical properties of CA nanofibrous mats were improved by increasing the content of PVA nanofibers. Furthermore, the multi-component blend nanofibrous mats also can be obtained by increasing the electrospinning jets in this multi-jet electrospinning fashion. Potential applications of the blend nanofibrous mats include filters and biomedical materials.

Secondly, the nanofibrous membranes were studied as high efficient gas sensing materials. A novel gas sensor composed of electrospun nanofibrous membranes and quartz crystal microbalance (QCM) was fabricated. The electrospun nanofibers with diameter of 100-400 nm can be deposited on the surface of QCM by electrospinning the homogenous blend solutions of cross-linkable poly(acrylic acid) (PAA) and PVA. A series of nanofibrous membranes with various weight percentage of PAA to PVA were fabricated and characterized regarding their morphology and sensitivity to NH_3. Sensing experiments were examined by measuring the resonance frequency shifts of QCM which due to the additional mass loading. The results showed that the sensing properties were mainly affected by the content of PAA component in nanofibrous membranes, concentration of NH_3, and relative humidity. Additionally, the sensitivity of nanofibrous membranes was much higher than that of continuous layer-by-layer (LBL) films.

In order to increase the sensitivity of sensing fibrous membranes, electrospun fibrous PAA membranes

were studied as sensing material coated on QCM for ammonia detection at ppb level. The fibrous membranes with different morphology can be deposited on the electrode of QCM by electrospinning the PAA solutions with various solvent composition of H_2O and ethanol. The results of sensing experiments indicated that the sensitivity of the fibrous membranes coated QCM (FM-QCM) sensors was 4 times higher than that of the casting films coated QCM (CF-QCM) sensors. Meanwhile, the FM-QCM sensors exhibited high sensitivity towards low concentration of ammonia, as low as 130 ppb at the relative humidity of 40 %. The pre-sorbed water in fibrous membranes was proved to be the key factor to affect the sensitivity of FM-QCM sensors for ammonia. The sensor performance has been found to depend on the morphology of the fibrous membranes, concentration of ammonia, coating load of the fibrous membranes on QCM, and relative humidity. Preliminary study of the stability investigation was also presented.

Finally, the functional films coated nanofibrous mats were fabricated by a combination of electrospinning and electrostatic LBL self-assembly techniques for the first time. Oppositely charged anatase TiO_2 nanoparticles and PAA were alternately deposited on the surface of negatively charged CA nanofibers using the electrostatic LBL self-assembly technique to form a LBL structured ultrathin hybrid films on electrospun nanofibers. The fibrous mats were characterized by XRD, FT-IR, FE-SEM, TEM and BET surface area. The crystalline phase of anatase TiO_2 remained unchanged in the resultant TiO_2/PAA films coated on CA fibrous mats. Moreover, the TiO_2/PAA films coated fibers showed rough surface with grains due to the deposition of aggregated TiO_2 particles. The average diameter of fibers increased from 344 to 584 nm and the BET surface area of fibrous mats increased from 2.5 to 6.0 m^2/g after being coated with 5 bilayers of TiO_2/PAA films. And such LBL films coated fibrous mats would show great potential to be used as catalysts, filters and sensors. Furthermore, the LBL structured tubes might be made by thermal degradation or solvent extraction of the template nanofibers.

Additionally, the self-assembled polyelectrolyte multilayered (PEM) films were fabricated on electrospun CA nanofibers via the electrostatic LBL adsorption of oppositely charged poly(allylamine hydrochloride) (PAH) and PAA. The growth of PEM films on CA nanofibers was studied by regulating the pH value of polyelectrolyte solutions and the number of PAH/PAA bilayers. The composition and morphology of PEM films coated fibrous mats were examined by FTIR, FE-SEM, and AFM. The results indicated that the growth of PEM films fabricated at a PAH pH of 7.5 and a PAA pH of 3.5 (PAH7.5/PAA3.5) was much quicker than that of films of PAH and PAA adsorbed at pH 5 (PAH5/PAA5). The CA nanofibers were embedded in the thick PAH7.5/PAA3.5 films. The average diameter of PAH5/PAA5 films coated fibers and average PAH5/PAA5 film thickness gradually increased with increasing the number of PEM bilayers. Moreover, the surface roughness of fibers was increased after deposition of PAH/PAA films.

Furthermore, we have recently fabricated the Keggin-type polyoxometalate ($H_4SiW_{12}O_{40}$) nanotubes by calcining the LBL structured ultrathin hybrid films coated electrospun fibrous mats. The hybrid films coated electrospun fibrous mats were obtained from the alternate deposition of positively charged PAH and negatively charged $H_4SiW_{12}O_{40}$ on the surface of negatively charged CA nanofibers using the electrostatic LBL self-assembly technique. The fibrous mats were characterized by SEM, TEM, FT-IR, and WAXD. It was found that the morphology of hybrid PAH/$H_4SiW_{12}O_{40}$ films coated fibrous mats was strongly influenced by the number of deposition bilayers and the pH of dipping solutions. The fibrous mats were contracted and the $H_4SiW_{12}O_{40}$ nanotubes with a wall thickness about 50 nm can be fabricated after calcination at high temperature. Additionally, the FT-IR and WAXD results indicated that the pure $H_4SiW_{12}O_{40}$ nanotubes were gotten with a Keggin structure.