



Research paper

Different coating on electrospun nanofiber via layer-by-layer self-assembly for their photocatalytic activities



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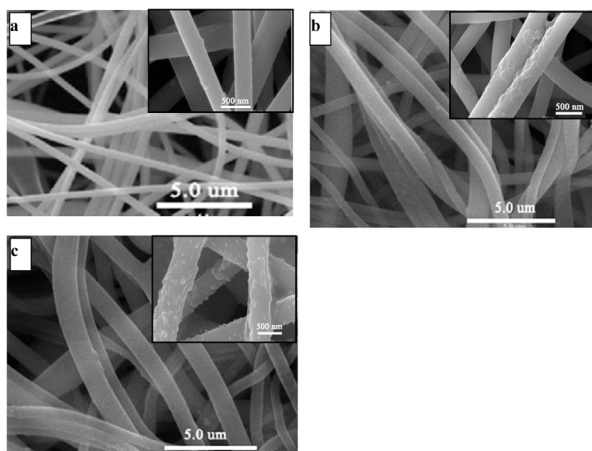
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GRAPHICAL ABSTRACT

The silver nanoparticle were deposited onto the fibrous PAA/PVA/PW₁₂ precursor by layer-by-layer (LBL) self-assembly technique, as SEM image depicted as Ag-(PEI)₂(PW₁₂)₂, (b) Ag-(PEI)₄(PW₁₂)₄ and (c) Ag-(PEI)₆(PW₁₂)₆ film. An interesting phenomena was indicated that the less the number was, the higher photocatalytic activity would be. This Ag-(PEI)₂(PW₁₂)₂ photocatalyst was highly efficient and relatively stable, for example in the degradation of methylene blue under visible light.



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ABSTRACT

The water-stable PAA/PVA/PW₁₂ nanofiber was firstly prepared by electrospinning and thermal treatments. The negatively charged phosphotungstic acid (PW₁₂), positively charged polyethylenimine (PEI) and silver nanoparticle (Ag NPs) were alternatively deposited onto the fibrous substrate by layer-by-layer (LBL) self-assembly technique. The photocatalytic activity of different coated LBL film was observed under visible light irradiation. The results indicated that the conversion rate of methylene blue (MB) was gradually decreased with increasing the number of bilayers pairs. The behavior might ascribe to the more polycation electrolyte PEI that prevented from permeating for the MB molecule. On the other hand, in terms of the effects of surface charges on the photocatalytic activity, negatively charged surface (PEI)_n(PW₁₂)_n indicated higher photocatalytic activity than that of positively charged surface (PEI)_n(PW₁₂)_{n-1}. For the Ag NPs deposited on the LBL film, Ag-(PEI)_n(PW₁₂)_n

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film were found to be a better photocatalytic activity than other multilayer films, specially, Ag-(PEI)₂(PW₁₂)₂ exhibited the most excellent activity due to the influence of the synergy in the hybrid materials.

1. Introduction

In recent years, considerable interest has been paid attention to nanosized semiconductor particles, which are displayed for energy and environmental applications because of the higher surface area and efficient charge separation [1]. For the sake of low cost, nontoxicity and easier handling, it is more appropriate to immobilize semiconductor material on a certain film. Decher Hong and co-workers introduced a structure-controlled, simple and low-cost technique to fabricate ultrathin film by the alternate adsorption e.g. positively and negatively charged species from solutions. It was known as the layer-by-layer (LBL) self-assembly [2–4]. The LBL self-assembly technique provided a unique possibility that the thickness of a single layer could be accurate to the nanometer scale, additionally, the multilayer films had the ability to carry an excess of charge that was localized at upper polymer/electrolyte interface, and was compensated by mobile ions in the solution [5]. Based on the LBL technique, the various components, such as polyelectrolyte systems, as well as almost any type of charged species, such as organic dye, dendrimers, biological macromolecules and inorganic materials, are applicable for constructing a functional multilayer film. When the hybrid film were made up of polyelectrolytes and charged inorganic components [6], the substrates would be more willing to adsorb preferably polyelectrolytes than to adsorb the inorganic components [7,8]. Its aim is to decrease the interruption from the substance and to cause a uniformly charged surface of LBL film [9,10]. Thus, the inorganic components could be more available to deposit on the precursor film.

Polyoxometalates (POMs) are inorganic metal-oxygen (M-O) poly-anionic clusters, the redox and chemical properties of which can be modified by substituting one or some elements, however, the structural integrity keeps unchanged [11]. Therefore, POMs display wide applications in different fields such as materials science, medicine, electrochemistry and catalysis etc [12–14]. Particularly, in order to improve the optical and electronic property of POMs, many researchers built up the multilayer film with POMs by LBL technique. Liu et al. first studied the preparation and electrochemical property of a negatively Pr (SiMo₇W₄)₂-containing multilayer film in LBL assembly using a quaternized poly (4-vinylpyridine complexed with [Os(bpy)₂Cl]²⁺ counter-cations [15]. Wang et al. fabricated the ultrathin films using positively charged poly(allylamine hydrochloride), and two lanthanide polyoxometalates, K₁₇[Eu(P₂W₁₇O₆₁)₂] and K₁₃[Eu(SiW₁₁O₃₉)₂] as the anions, specifically, the photoluminescent properties of these films were discussed [16]. Gao et al. prepared different types of polyoxometalates, such as K₄[α-SiW₁₂O₄₀], K₁₂V₁₈O₄₂ and Na₉EuW₁₀O₃₆, which were assembled into the shell of microcapsules by LBL assembly. The microcapsules with POMs exhibited a photoluminescent property [17]. Gao et al. selected [γ-GeW₁₀O₃₆]⁸⁻ and [β₂-GeW₁₁O₃₉]⁸⁻ as anion and electrostatically reacted with cationic thionine dye, respectively. The sunlight photocatalytic property of the films for the degradation of the aqueous dyes was observed [18].

The application of electrospinning technique has been rapidly increasing in the past years since it can consistently generate fibers from 50 to 500 nm in diameters, depending on the polymer solution and melts [19]. The obtained nano- or micro-structure materials include polymers, composites and ceramics, and exhibit amazing properties because of very large surface area to volume ratio and high porosity [20]. By choosing appropriate materials, the electrospun fiber is able to alternatively adsorb charged components to build ultrathin coatings. Consequently, the electrospun fiber is made as an ideal substrate which could significantly increase in the number of reactive sites compared

with flat substrates, and result in improvement in practical applications.

The evidence to date indicates there are a few reports of depositing POMs onto electrospun fibers. Gong et al. modified the ITO electrode by self-assembling multilayer film of polyoxometalate on poly (vinyl alcohol) nanofibers and discussed its electrocatalytic and photochromic behavior [21,22]. Ding et al. reported that the concentration of POMs, the number of coating bilayers, and the ionic strength of PEI solutions had a significant effect on the growth and the high porous of LBL films on electrospun nanofibers [23]. However, a relationship between the photocatalyst and the surface charge, the number and components of LBL film has not been established. Based on these, in this work, polyelectrolyte cation polyethylenimine (PEI), polyanion phosphotungstic acid (PW₁₂) or zerovalent silver nanoparticles (Ag NPs) were selected as the uppermost layer of LBL films, respectively. The influences on the corresponding photocatalytic activity were investigated. The negatively charged surface (PEI)_n(PW₁₂)_n indicated more significant property than positively charged surface (PEI)_n(PW₁₂)_{n-1}. Moreover, the more the number of layer was, the less photocatalytic activity was. When Ag NPs were reduced on the LBL film, Ag-(PEI)₂(PW₁₂)₂ shown more excellent activity than other multilayer films.

2. Experiment

2.1. Materials

Poly(vinyl alcohol) (PVA, M_w 80,000 g/mol), Poly acrylic acid (PAA, M_w 450,000 g/mol) and Polyethylenimine (PEI, M_w 10,000 g/mol) were purchased from Aladdin Chemical Co. Phosphotungstic acid (PW₁₂), silver nitrate (AgNO₃), methylene blue (MB), sodium borohydride (NaBH₄) were gotten from Shenyang Chemical Co. These compounds were analytical reagent and pure water was used in all experiments.

2.2. Preparation of water-stable PAA/PVA/PW₁₂ nanofibers

Aqueous PVA solution (ca. 10% w/v) was gotten by dissolving PVA powder in distilled water and heated at 90 °C with the help of stirring. PAA solution (ca. 8% w/v) was prepared by dissolving PAA powder in distilled water at room temperature for 4 h. The PVA and PAA aqueous solutions were blended to obtain a mass ratio of 1:1. 8 g PW₁₂ was slowly added into 20 g mixture polymer solution with stirring, and then the solution was aged for 12 h at ambient temperature.

In the electrospun process, the blended PAA/PVA/PW₁₂ solution was loaded into a plastic syringe that was above a grounded tubular collector. The positive electrode of a high-voltage generator was placed in the solution. The performed voltage (15 kV), feeding rate (0.4 ml/h) and distance (13 cm) were applied from the syringe tip to the collector, respectively. The detailed electrospun setup can be found in elsewhere [19]. The ultrafine PAA/PVA/PW₁₂ fibers were whipped continuously by the electrostatic repulsion until a nanofibrous mat was achieved on aluminum foil. The as-electrospun PAA/PVA/PW₁₂ mats were dried at 140 °C for 1 h under a vacuum oven to obtain the water-insoluble fiber.

2.3. Assembly of PEI, PW₁₂ or Ag NPs onto electrospun nanofibers

The undermentioned solutions were used to prepare multilayer films: aqueous PEI solution (5 mg/ml), silver nitrate solution (0.1 mol/L), sodium borohydride solution (0.2 mol/L), and aqueous PW₁₂ solution (1 × 10⁻² mol/L). The hybrid LBL film was performed by alternately adsorbing polycation electrolyte PEI and anion PW₁₂ onto the

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