Chinese Journal of Catalysis 38 (2017) 73–82

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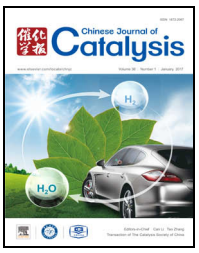

Article

Fabrication and catalytic behavior of hierarchically-structured nylon 6 nanofiber membrane decorated with silver nanoparticles

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ARTICLE INFO

Article history:
Received 5 August 2016
Accepted 29 August 2016
Published 5 January 2017

Keywords:
Electrospinning
Hierarchical structure
Ag nanoparticle
PA6 nanofiber membrane
Catalysis

ABSTRACT

A hierarchically-structured nylon 6 (PA6) nanofiber membrane decorated with silver nanoparticles (Ag NPs) was fabricated by electrospinning and impregnation methods. The as-fabricated hierarchically-structured Ag/PA6 nanofiber membrane (HS-Ag/PA6 NM) exhibits a morphology in which Ag NPs are deposited on the surfaces of both thick fibers and thin fibers. The content and size of the Ag NPs can be controlled by varying the concentration of the silver colloid solution. Compared with the non-hierarchically-structured Ag/PA6 nanofiber membrane, HS-Ag/PA6 NM has a higher specific surface area and exhibits a higher degradation rate for methylene blue of 81.8%–98.1% within 2 h. HS-Ag/PA6 NM can be easily recycled and exhibits good reusability. It retains a degradation rate for methylene blue of 83.5% after five consecutive cycles. The hierarchically-structured nanofiber membrane is therefore a potential nanocatalyst.

1. Introduction

The rapid development of economies and technology has led to increased attention to wastewater treatment, especially to effluent containing dyes and their decomposition products produced in the textiles industry [1]. Silver is a group IB transition metal with a valence shell electronic structure of $4d^{10}5s^{1}$. Silver-based materials are widely applied in catalysis because of their specific physical and chemical structures [2].

Silver nanoparticles (Ag NPs) are often loaded on a support material such as microspheres [3], beads [4], films [5], and fibers [6], which limits their agglomeration and improves their catalytic activity. In situ reduction [7] and post-processing [8] are two common methods for loading Ag NPs onto supports. In situ reduction is simple and convenient, but most Ag NPs are distributed within the support, with only a few exposed on the surface, which is therefore an inefficient use of Ag NPs. In contrast, decorating Ag NPs on the surface of fiber supports through post-processing can yield silver-based materials with high catalytic activities [9].

Nanofibers are fibers with diameters of less than 100 nm. The nanometer scale of the nanofibers makes them an efficient catalytic support [10]. Electrospinning is a versatile, effective, and widespread method for manufacturing long continuous nanofibers [11]. There are many reports of electrospun nanofiber membranes being used as catalytic supports for Ag NPs. Jang et al. [12] fabricated cellulose-based nanofibers by electrospinning and subsequent ultraviolet irradiation. The result-

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This work was supported by the National Natural Science Foundation of China (51673148), National Basic Research Program of China (2014CB660813), National Key Technology Support Program (2015BAE01B03), Innovation Fund for Technology of China (14C26211200298), and Innovation Fund for Technology of Tianjin (14TXGCCX00014,14ZXCXGX00776).
DOI: 10.1016/S1872-2067(16)62545-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 1, January 2017

ing cellulose nanofiber matrices were loaded with Ag^+ or Ag NPs, and demonstrated potential as catalytic membranes for the sensing of specific chemicals. Liu et al. [13] fabricated Ag/PS nanofibers by a combination of electrospinning and in situ reduction. The resulting membranes exhibited excellent catalytic activity for the degradation of dye pollutants. Gao et al. [14] fabricated Ag/PAN fiber networks, which exhibited activity for the degradation of 4-NP under general conditions.

Recent advances in electrospinning technology have allowed the fabrication of specifically-structured nanofiber membranes, such as core-shell structures [15], hollow structures [16], porous structures [17], and web-like structures [18,19]. Hierarchically-structured nanofibers with multiscale organizations have been inspired by the hierarchical structures of trees consisting of many trunks and branches. Such nanofibers have exhibited high levels of functionality and performance. This has been because of the high surface area provided by their thin fibers, and excellent mechanical properties provided by their thick fibers [20–22]. Specifically-structured nanofiber membranes have been applied in filters [23], sensors [24], and catalysts [25]. Bai et al. [26] fabricated tree-like hierarchically-structured TiO_2 nanofiber (NF)/ZnO nanorod (NR) materials by the electrospinning of TiO_2 NFs and hydrothermal growth of ZnO NRs. The resulting structures yielded high photocatalytic activity because of their high specific surface area, high rate of mass transfer, and thus readily accessible reaction sites. Shi et al. [25] fabricated branch-like carboxylated multiwalled carbon nanotube/chitosan nanofibrous membranes by simultaneous electrospinning and spraying. The resulting membranes exhibited improved rejection of 161%–166% and 80%–90% toward methylene blue (MB) and methyl orange, respectively. We recently fabricated hierarchically-structured nanofiber membranes by adding tetrabutylammonium chloride (TBAC) into PVDF/dimethyl formamide/acetone solution, via one-step electrospinning. The resulting tree-like PVDF nanofiber membranes exhibited high mechanical strength and high specific surface areas [27].

Nylon 6 (PA6) is a widely used polymer, which is low cost, exhibits strong chemical and thermal stability, and is hydrophilic [28,29]. The molecular chains of PA6 can coordinate with Ag, making PA6 a potential Ag NP support [30–32]. In the current study, a hierarchically-structured Ag/PA6 nanofiber membrane (HS-Ag/PA6 NM) was fabricated by adding TBAC into PA6/HCOOH solution, via one-step electrospinning and silver colloid solution impregnation methods. The resulting HS-Ag/PA6 NM exhibits excellent catalytic activity in the reduction of MB. This enhanced catalytic performance results from the high specific surface area of HS-Ag/PA6 NM. Because the membrane is easily recovered and reused, it has potential practical use in catalysis.

2. Experimental

2.1. Materials

Nylon 6 granules (PA6, M_w = 16000) were purchased from Ube Industries Ltd. PVP was purchased from Jiaozuo Meida Fine Chemical Co., Ltd. Formic acid (HCOOH) and silver nitrate ($AgNO_3$) were purchased from Tianjin Yingda Rare Chemical Reagents Factory. TBAC was purchased from Tianjin Guangfu Chemical Reagent Co. $NaBH_4$ and NaOH were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co. MB and acid magenta were purchased from Tianjin Tensing Fine Chemical Research Develop Center. All reagents except PA6 and PVP were of analytical grade, and were used without further purification. Deionized water was used through all experiments.

2.2. Preparation of nanofiber membranes

PA6/TBAC solution was prepared by mixing 14 wt.% PA6 and 4 wt.% TBAC with HCOOH and stirring for 10–12 h to form a stable and homogeneous solution. For comparison, a solution without TBAC was also prepared. These solutions were used to prepare nanofiber membranes by electrospinning with an applied voltage of 45 kV, distance from collector to syringe tip of 15 cm, and injection rate of 0.1 mL/h. The inner diameter of the syringe was 0.45 mm. The temperature was kept at 25±2 °C, and the relative humidity was (35±2)%. The nanofiber membranes were collected on surface of a grounded aluminum foil. The membranes were then washed with distilled water, dried at 60 °C, and cut into 2 cm × 2 cm pieces for further use. Membranes fabricated with and without the addition of TBAC were denoted HS-PA6 NM and PA6 NM, respectively.

2.3. Preparation of Ag-decorated PA6 nanofiber membranes

PVP (0.0844 g) was added to 60 mL of deionized water and stirred for 20 min. $NaBH_4$ solution (0.008 mol/L, 40 mL) and 10 mL of $AgNO_3$ solution (0.006 mol/L) were prepared under dark conditions. The PVP and $NaBH_4$ solutions were then mixed thoroughly, and the $AgNO_3$ solution was then added slowly, yielding a silver colloid solution named solution A. Similar solutions were prepared with concentrations of 0.012 mol/L $AgNO_3$/0.016 mol/L $NaBH_4$, and 0.03 mol/L $AgNO_3$/0.04 mol/L $NaBH_4$, and were named solution B and solution C, respectively. Ag/PA6 NM and HS-Ag/PA6 NM were fabricated by the impregnation method, and 0.1 g of nanofiber membranes were immersed in 30 mL of silver colloid solution for 5 h in the dark. The membranes were then washed with deionized water for three times, and dried at 60 °C . PA6 NM immersed in solutions A, B, and C were named samples 1, 2, and 3, respectively. HS-PA6 NM immersed in solutions A, B, and C were named samples 4, 5, and 6, respectively. The fabrication of HS-Ag/PA6 NM is shown schematically in Fig. 1.

2.4. Characterization

The morphologies of the electrospun membranes were observed using field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan). Energy dispersive X-ray spectroscopy (EDS) observations were also carried out using the FE-SEM instrument. The size, shape, and deposition of the Ag NPs on the fiber surface were investigated using transmis-