Facile Preparation and Enhanced Catalytic Properties of Self-Assembled Pd Nanoparticle-Loaded Nanocomposite Films Synthesized via the Electrospun Approach

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ABSTRACT: In recent years, people pay more attention to environmental pollution and the treatment of sewage has become the focus of recent research. Palladium nanoparticles have good catalytic properties but are easy to agglomerate. Therefore, we used the electrospinning technology to prepare a uniform composite nanofiber film based on polyacrylic acid (PAA) and polyvinyl alcohol (PVA), which demonstrated that they are good carriers of palladium nanoparticles to make the nanoparticles well dispersed. Furthermore, carbon nanotubes (CNTs) were added to increase the specific surface area of the composite nanofiber film and improve its mechanical properties. The successfully synthesized PAA/PVA/CNT-COOH@palladium nanoparticle (PdNP) composite fiber films were characterized by scanning electron microscopy, transmission electron microscopy, and thermogravimetry analysis. p-Nitrophenol and 2-nitroaniline were utilized as typical pollutants to further evaluate the catalytic performance of PAA/PVA/CNT-COOH@PdNP composite fiber films. The PAA/PVA/CNT-COOH@PdNP composite fiber films exhibited enhanced catalytic performance and could be reused for eight consecutive cycles. This work provided new clues for the preparation and application of composite electrospun film materials.

1. INTRODUCTION

Electrospinning is a special fiber manufacturing process of nanofibers by driving a jet of charged polymer solution out of a needle in an electric field. Under the electric field, the droplets at the needle change from a spherical shape to a conical shape (Taylor cone), and the fiber filaments are extended from the conical tip, by which it is possible to produce polymer filaments of nanometer diameter. Electrospinning technology has shown widespread applications in the manufacture of filter membranes, biomedical, and sensors, because of its low spinning cost, a broadly applicable material system, and easy control of the process. Nanofibers prepared by the electrospinning technology have controllability of fiber diameter, high tensile strength, and large specific surface area.

Industrial wastewater from textiles, paper, and printing contains large amounts of organic pollutants, causing serious damage to water, air, and human health. Therefore, improving the removal rate of organic pollutants in industrial wastewater has become a key issue to be solved. Palladium nanoparticles (PdNPs) play an important role in the field of catalysis and adsorption because of their large specific surface area and high surface activity. It is a common method to immerse electrospun fiber films in a precursor solution and then obtain a precious metal/electrospun fiber composite material by in situ reduction. Han et al. prepared electrospun fibers based on polyvinyl alcohol (PVA) and polyethyleneimine (PEI). The fibers were then immersed in a silver nitrate (AgNO₃) solution for in situ reduction to obtain surface Ag-loaded PVA/PEI electrospun fibers. Xiao et al. used polyacrylic acid (PAA) as a matrix material to obtain PAA/PVA fibers by thermal cross-linking, and the heat-treated electrospun fibers were immersed in AgNO₃ solution, followed by the addition of sodium borohydride to prepare Ag-loaded PAA/PVA electrospun fibers. In addition, carbon nanotube (CNT)-composited materials have attracted great attention because of their excellent properties in many fields such as in catalysis.

In this work, our targeted experiments were designed to load Pd nanoparticles onto the electrospinning film to improve the catalytic properties of the films. The PVA/PAA/CNT-COOH composite fiber films were prepared according to the previous work. The obtained composite fiber films were immersed in a PdCl₂ solution after heat treatment, and the Pd-loaded PVA/PAA/CNT-COOH composite fiber films (PVA/PAA/CNT-
COOH@PdNPs) could be prepared by adding sodium borohydride. 2-Nitroaniline (2-NA) and p-nitrophenol (4-NP) were used to study the catalytic reduction of the composite fiber films. Furthermore, the stability of the composite fiber films was evaluated by cyclic catalysis of 4-NP. This work provides new ideas for the preparation and application of self-assembled materials.32−37

2. RESULTS AND DISCUSSION

2.1. Characterization of PVA/PAA/CNT-COOH@PdNP Composite Films. Figure 1 shows the synthesis process of PAA/PVA/CNT-COOH@PdNP composite spinning fiber films. First, PAA/PVA/CNT-COOH composite fiber films were prepared by electrospinning and heat treatment. The obtained PVA/PAA/CNT-COOH spinning fiber film was immersed in PdCl₂ solution, and through the condensation reaction between hydroxyl and carboxyl groups, Pd nanoparticles were slowly loaded onto the spinning fiber films. It is worth noting that the PAA/PVA/CNT-COOH composite fiber film was used as a carrier for PdNPs, which effectively avoids a large amount of aggregation of PdNPs and exhibited good catalytic performance and stability. Finally, the prepared PAA/PVA/CNT-COOH@PdNP composite fiber films were used to characterize the catalytic properties and stability of 4-NP and 2-NA.

Figure 2 shows the morphological characteristics of PAA/PVA, PAA/PVA/CNT-COOH, and PAA/PVA/CNT-COOH@PdNP composite fiber films. It could be clearly observed from Figure 2a,b that PAA/PVA electrospinning fibers were long and straight, which showed the fiber structure with the main diameter range of 400−500 nm. Figure 2c,d shows that a large number of spindle-like structures occurred, which indicated that CNT-COOH could not disperse well in the spinning solution. In addition, CNT-COOH could combine with some hydroxyl groups in the PVA molecule, which was a thermal cross-linking reaction.38 CNT-COOH would not fall off the spinning fiber films and played a supporting role, which made the spinning fiber film structure more stable. Moreover, the addition of CNT-COOH could improve the mechanical properties of the composite fiber films.39,40 The morphologies and the element distribution of PAA/PVA/CNT-COOH@PdNP nanocomposite fiber films are shown in Figures 2e,f and 3, respectively. From Figure 2e,f, it could be clearly seen that Pd nanoparticles were loaded on the surface of the fiber. The same result could be obtained from Figure 3, which confirmed the existence of a large number of Pd nanoparticles.

TEM measurements were performed to further investigate the morphological characteristics of the composite fiber films. From Figure 4a,b, it could be clearly seen that the PAA/PVA spinning fiber films were long and straight, which was consistent with the scanning electron microscopy (SEM) results. Figure 4c,d shows that CNT-COOH embedded in the spinning fibers caused spindle-like structures on PAA/PVA/CNT-COOH fiber films. In addition, after the PAA/PVA/CNT-COOH spinning fiber film was immersed in PdCl₂
solutions, PdNPs were observed from Figure 4e,f. Therefore, it could be concluded that PdNPs were successfully loaded on the surface of PAA/PVA/CNT-COOH composite films, which made the composite fiber films exhibit good catalytic activity and stability.

The thermal stability of the samples were analyzed by thermogravimetry (TG) as shown in Figure 5. The TG curves of PAA/PVA, PAA/PVA/CNT-COOH, and PAA/PVA/CNT-COOH@PdNP composite fiber films were measured in argon atmosphere. The mass loss below 150 °C could be considered as evaporation of moisture in the sample. From 280 to 480 °C, it showed that the mass of the spinning fiber samples was drastically reduced, which could be attributed to the thermal decomposition of the carbon skeleton in PVA and PAA molecules. The mass of the spinning fiber films reached a stable state above 480 °C. Furthermore, the mass loss of PVA/PAA fiber films was about 77.9%, whereas those of PAA/PVA/CNT-COOH and PAA/PVA/CNT-COOH@PdNP fiber films were 82.5 and 83.4%, respectively. The results demonstrated that the addition of CNT-COOH and PdNPs affected the thermal stability of composite fiber films.

2.2. Catalytic Performances of PAA/PVA/CNT-COOH@PdNP Composite Films. In recent years, self-assembled materials have been used in many fields, such as biology,41 photoelectrochemistry,42−46 chemical modification,47−49 and catalysis.22 2-NA and 4-NP were chosen as typical models to explore the catalytic performances of PAA/PVA/CNT-COOH@PdNP composite fiber films. First, we studied the catalytic experiment of 2-NA and the product after being reduced was o-phenylenediamine (OPD).50 A full-wavelength scan of 2-NA (0.005 mol/L) by a UV−vis spectrophotometer revealed that the maximum absorption peak was at 415 nm as shown in Figure 6a. After adding the NaBH4 solution, the maximum absorption peak position had not changed and the color of the solution became yellow-green. Furthermore, the absorbance of 2-NA and excessive NaBH4 was almost

Figure 3. (a) Representative SEM image and (b−f) elemental mapping images of the prepared PAA/PVA/CNT-COOH@PdNP composite fiber film.

Figure 4. TEM images of the prepared (a,b) PAA/PVA, (c,d) PAA/PVA/CNT-COOH, (e,f) PAA/PVA/CNT-COOH@PdNP composite fiber films.

Figure 5. TG curves of the prepared PAA/PVA, PAA/PVA/CNT-COOH and PAA/PVA/CNT-COOH@PdNP composite fiber films.
unchanged within 48 h. We also measured the specific process of catalytic reaction after adding PAA/PVA/CNT-COOH@PdNP composite fiber films. A full-wavelength scan was performed every 5 min after adding PAA/PVA/CNT-COOH@PdNPs into a 2-NA and NaBH₄ mixture solution with the obtained results exhibited in Figure 6b. From Figure 6b, it could be seen that the characteristic absorption peak at 415 nm gradually decreased, the absorbance hardly changed after 30 min, and the color changed from bright yellow to colorless. The results indicated that 2-NA was completely catalyzed to OPD in the presence of PAA/PVA/CNT-COOH@PdNPs.

The catalytic performance of the compositing spinning fiber films was also evaluated by 4-NP (Figure 6c). The maximum absorption wavelength of 4-NP (0.005 mol/L) was monitored at 317 nm by a UV–vis spectrophotometer. When the NaBH₄ solution was added into the 4-NP solution, the NaBH₄ molecule provided a negative hydrogen ion to attack the 4-NP molecule and then formed a sodium 4-NP molecule. Compared with the 4-NP solution, the characteristic absorption peak of 4-NP and the NaBH₄ mixture solution showed a red shift to 401 nm. At the same time, the color of the mixture solution changed from yellow to yellow-green. In addition, the absorption peak at 401 nm was almost unchanged after 48 hours, indicating that the 4-NP did not react with NaBH₄. The full-wavelength scan was performed every 5 min after adding PAA/PVA/CNT-COOH@PdNP composite fiber films. Figure 6d shows that the absorbance value of the mixture solution gradually decreased at 401 nm and the absorbance no longer changed after 25 min, indicating that the reaction had reached equilibrium in the presence of PAA/PVA/CNT-COOH@PdNP composite fiber films. The same conclusion could be obtained from the color of the mixture solution before and after the reaction. It could be explained that as the catalytic reaction proceeds, the nitro group in the sodium 4-NP molecule was reduced to the amino group by PdNPs, and the final product was 4-aminophenol (4-AP). 4-NP was a toxic and strong stimulating pesticide intermediate; however, it could be

Figure 6. UV–vis spectrum of (a) 2-NA, 2-NA, and NaBH₄; (b) catalytic reduction of 2-NA by PAA/PVA/CNT-COOH@PdNPs; (c) 4-NP, 4-NP, and NaBH₄; (d) catalytic reduction of 4-NP by PAA/PVA/CNT-COOH@PdNPs.

Figure 7. PVA/PAA/CNT-COOH@PdNP composite fiber films catalyze 4-NP; (a) relationship between ln(Ct/C₀) and time t; (b) catalytic stability for different continuous cycles.
reduced to the less toxic 4-AP with the PAA/PVA/CNT-COOH@PdNP composite fiber films as catalyst.\textsuperscript{31–33} In conclusion, the good catalytic performances of PAA/PVA/CNT-COOH@PdNP composite fiber films could be confirmed by catalytic degradation of 2-NA and 4-NP.

2.3. Kinetic Evaluation and Cyclic Stability of PAA/PVA/CNT-COOH@PdNP Composite Fiber Films. As an excess of NaBH\textsubscript{4} solution ($C_{\text{NaBH}_4}/C_{4\text{NP}} = 400$) was added during the catalysis, the reaction of NaBH\textsubscript{4} and 4-NP was considered as pseudo-first-order kinetics related to the 4-NP concentration.\textsuperscript{54,55} Figure 7a shows the kinetic fitting data of catalytic 4-NP. According to the Lambert–Beer law $A = K b c$, the value of $C_4/C_0$ was proportional to $A/A_0$\textsuperscript{56} where $A$ is the absorbance, $K$ is the molar absorption coefficient, $c$ is the concentration of the light-absorbing substance, and $b$ is the thickness of the absorbing layer. $C_t$ and $C_0$ are the concentrations at time $t$ and initial, respectively, $A_t$ and $A_0$ are the absorbance of the initial solution and at time $t$ at 401 nm, respectively. The obtained data were calculated and a linear fitting curve of reaction time $t$ and $\ln(C_t/C_0)$ obtained as shown in Figure 7a. The kinetic constant was 0.43 min$^{-1}$ according to the linear fitting principle, which was closely correlated to the catalytic performance. Stability and recyclability are important metrics for evaluating the efficiency of catalysts. In this work, the prepared PAA/PVA/CNT-COOH@PdNP composite fiber films were used to continuously catalyze the fresh 4-NP and NaBH\textsubscript{4} mixture solutions. After eight cycles of catalysis, Figure 7b shows that the catalytic efficiency of PAA/PVA/CNT-COOH@PdNP composite fiber films for the NaBH\textsubscript{4} and 4-NP mixture solution could still reach 95%. With the number of cycles increased, the conversion rate of 4-NP decreased slightly, which might be due to multiple washing of the PAA/PVA/CNT-COOH@PdNP composite fiber films. However, the stability of composite fiber films was still good. The results of catalytic experiments demonstrated that PAA/PVA/CNT-COOH@PdNP composite fiber films had excellent catalytic performance and high stability, and the prepared composite fiber films exhibited broad application prospects in the field of catalysts.

3. CONCLUSIONS

In summary, new PAA/PVA/CNT-COOH@PdNP composite fiber films were successfully prepared by electrospinning technology and in situ reduction. The obtained PAA/PVA/CNT-COOH@PdNP composite fiber film was used for catalytic reduction of 4-NP and 2-NA to evaluate the catalytic performance. The experiment results showed that 4-NP and 2-NA could be reduced by PAA/PVA/CNT-COOH@PdNP composite fiber films in a short time. In addition, the prepared PAA/PVA/CNT-COOH@PdNP composite fiber films were used in the cyclic catalytic test to further evaluate the stability. After eight cycles, the catalytic efficiencies of 4-NP and 2-NA were maintained at 95 and 92%, demonstrating enhanced catalytic performance and stability of the present self-assembled composite electrospun films.

4. EXPERIMENTAL SECTION

4.1. Materials. PVA ($M_w = 87\,000–98\,000$, 98–99% hydrolysis) was purchased from Aladdin Company. PAA ($M_w = 2000$), 4-NP, 2-NA, palladium chloride (PdCl\textsubscript{2})}}, carboxylated CNTs (CNT-COOH), and NaBH\textsubscript{4} were purchased from Alfa Aesar Company. Ultrapure water was prepared by Millipore’s ultra-microporous filtration system. The ultrapure water used in the experiments was obtained by a Milli-Q water purification system.

4.2. Preparation of PAA/PVA/CNT-COOH Composite Fiber Films. PVA (0.5 g) was dissolved in ultrapure water with magnetic stirring for 10 h at 90 °C, and 10 wt % solution was prepared. PAA (0.6 g) was dissolved in ultrapure water and stirred for 1 h at room temperature to prepare 30 wt % aqueous solution. Then, the obtained PAA and PVA aqueous solutions were mixed at a mass ratio of 5:2 (PAA/PVA). CNT-COOH was added into the mixture solution to make the concentration of CNT-COOH 1 mg/mL. Stirring at room temperature until the mixture solution was uniform, electrospinning was carried out. The homogeneous PAA/PVA/CNT-COOH mixture solution was slowly poured into a 10 mL syringe, the air bubbles drained, the voltage set to 20 kV, the step pump speed was 0.5 mL/h, and the spinning needle was 15 cm away from aluminum foil. The prepared spinning fibers were vacuum-dried at 25 °C for 24 h, and then the temperature was raised to 120 °C and dried for 3 h to obtain PAA/PVA/CNT-COOH composite fiber films.

4.3. Preparation of PAA/PVA/CNT-COOH@PdNP Composite Fiber Films. PdCl\textsubscript{2} powder was dissolved in ultrapure water to form a 300 μM PdCl\textsubscript{2} solution, and then 0.01 M NaBH\textsubscript{4} solution was added into 10 mL of PdCl\textsubscript{2} solution with high-speed stirring. The obtained solution was brown-yellow, which indicated that Pd\textsuperscript{2+} ions had in situ formed palladium nanoparticles (PdNPs). The prepared PdNPs solution was washed three times with ultrapure water under centrifuge (8000 rpm) to remove excess NaBH\textsubscript{4}. Then, the PAA/PVA/CNT-COOH composite fiber film was immersed in the PdCl\textsubscript{2} solution for 2 h, and the PAA/PVA/CNT-COOH@PdNP composite fiber film could be prepared. The composite spinning film would be washed with ultrapure water several times and then dried at room temperature for later experiments.

4.4. Evaluation of Catalytic Reduction Performance. Catalytic properties of PAA/PVA/CNT-COOH@PdNP composite fibers were characterized by reduction and degradation of 2-NA and 4-NP. Freshly prepared NaBH\textsubscript{4} solution (20 mL) was added as a reducing agent to 10 mL of 2-NA and 4-NP (0.005 M), respectively, and then PAA/PVA/CNT-COOH@PdNP composite fiber spun films were added to obtain a mixture solution. The absorbance of the mixture solution was measured every 5 min by an ultraviolet–visible (UV–vis) spectrophotometer. Two solutions changed from yellow to colorless, indicating the finish of reaction. In addition, the catalytic stability of the PAA/PVA/CNT-COOH@PdNP composite fiber films was also studied. The PAA/PVA/CNT-COOH@PdNP composite fiber films were reused to catalyze the 4-NP solution. Eight cycles of catalytic measurement of PAA/PVA/CNT-COOH@PdNP composite fibers were performed and the absorbance values within the same reaction time were measured, which could be further calculated to obtain the conversion of 4-NP.

4.5. Characterization. In order to observe the morphology of the composite fiber films, we used an S-4800II scanning electron microscope by adjusting the accelerated voltage to 5–15 kV. A Hitachi HT7700 transmission electron microscope was used to analyze the morphology and elements of the fiber film. The thermal stability of the samples was tested by a DTG-60 TG analyzer in argon atmosphere and the heating rate was 10 °C/min. The data of catalytic performance and stability of
the PAA/PVA/CNT-COOH@PdNP composite fiber film were characterized by a UV2550 spectrophotometer.

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We greatly appreciate the financial support of the National Natural Science Foundation of China (no. 21872119), Support Program for the Top Young Talents of Hebei Province, China Postdoctoral Science Foundation (no. 2015MS80214), and Research Program of the College Science & Technology of Hebei Province (no. ZD2018091).

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