Preparation and Catalytic Property of Au-decorated Titanium Dioxide Dendritic Nanofibers

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Abstract. To remove organic pollutants from industrial wastewater, the Au-decorated titanium dioxide dendritic nanofibers (Au-Ti DNFs) were synthesized through in situ decoration of gold (Au) nanoparticles on the titanium dioxide dendritic nanofibers (Ti DNFs). The electrospun Ti NFs were firstly prepared by sol-gel method combined with electrospinning technology, then in situ converted to Ti DNFs in the NaOH solution via a hydrothermal route, and finally treated in the solution of HAuCl₄ꞏ₄H₂O to produce Au-DTi NFs. SEM and TEM analyses showed that the Au-Ti DNFs had the dendritic and fibrous morphology and consisted of a large number of Au-Ti nanowires. 4-Nitrophenol was used as the model organic material to test the catalytic performance of Au-Ti DNFs. The results showed that Au-Ti DNFs catalytically reduced 4-nitrophenol to 4-aminophenol and their catalytic performance was higher than that of Ti DNFs due to the decoration of Au nanoparticles.

1. Introduction

4-Nitrophenol (4-NP) is one of the representative organic and toxic pollutants in the wastewater [1]. Catalytic reduction of 4-NP to 4-aminophenol (4-AP) has been considered as the model reaction to remove 4-NP from the wastewater. Nobel metal nanoparticles normally possess excellent catalytic capacity and have been extensively utilized for conversion of 4-NP to 4-AP. Gold (Au) nanoparticles as one type of noble metal nanoparticles are easily synthesized via the simple reduction reaction with controllable size and morphology and show excellent catalytic activity [2]. However, the agglomeration of Au nanoparticles highly limits their catalytic applications.

Several types of materials have been employed as substrate for immobilization of Au nanoparticles with enhanced stability. Titanium dioxide (TiO₂) is one of the most famous semiconductor inorganic materials and has been extensively utilized in the industrial and biomedical applications due to their excellent photocatalytic activity and good biocompatibility [3-4]. TiO₂ NFs could be simply fabricated via the electrospun process and have been successfully utilized for immobilization of Au nanoparticles [3]. However, the as-synthesized Au-decorated TiO₂ NFs still showed low catalytic capacity due to the low specific surface area of the electrospun TiO₂ NFs. In our recent study, novel TiO₂ dendritic NFs (Ti DNFs) were successfully synthesized and showed ultrahigh specific surface area [4]. It is highly hypothesized that Ti DNFs would be interesting in the immobilization of Au nanoparticles. Thus, in this study, to confirm this hypothesis, Ti DNFs were employed as substrate for immobilization of Au
nanoparticles to derive Au-decorated Ti DNFs (Au-Ti DNFs). Microstructure and catalytic capacity of the as-synthesized Au-Ti DNFs were investigated.

2. Materials and methods

2.1. Materials
Titanium isopropoxide, acetic acid, polyvinylpyrrolidone, ethanol, sodium hydroxide, gold chloride solution (HAuCl₄·4H₂O), 4-nitrophenol (4-NP), sodium borohydride (NaBH₄) were purchased from Aladdin (Shanghai, China).

2.2. Synthesis of Au-Ti DNFs
Au-Ti DNFs were synthesized through in situ decoration of Au nanoparticles on the Ti DNFs via a hydrothermal method. The synthesis process is shown in Figure 1. Au-Ti DNFs were synthesized according to the method described in the previous study [4]. Briefly, appropriate amount of Ti DNFs were added to the solution of HAuCl₄·4H₂O (1 mmol/L) which was held in a 50 mL-autoclaved device. The mixture was hydrothermally treated at 120°C for 4 h to produce Au-Ti DNFs. The as-synthesized Au-Ti DNFs were filtered from the solution, washed with water and finally freeze-dried at -10°C.

Figure 1. Flow chart for preparation of Au-Ti DNFs.

2.3. Characterizations
A field emission scanning electron microscopy (FE-SEM, JEOL, Japan) was applied for observation of morphology and size of the samples. A high resolution transmission electron microscopy (HRTEM, EM-1200EX, Japan) was utilized for observation of the detailed structures of the resultant samples. An ultraviolet-visible spectrophotometer (UV-8000S, Shanghai Metash, China) was used to obtain the UV–vis absorption spectra.

2.4. Catalytic capacity
The mixed aqueous system of 4-NP and NaBH₄ were used for evaluation of catalytic of the resultant samples. Ultraviolet-visible light spectrum analyzer (UV-Vis) was used to monitor the photocatalytic performance of both Ti DNFs and Au-Ti DNFs. Both types of samples were suspended in water by sonication to obtain a sample suspension with a concentration of 1 mg/mL. NaBH₄ solution with a concentration of 0.1 mol/L and a 4-NP solution with 0.25 mmol/L were prepared. In the catalysis experiment, 0.4 mL of NaBH₄ solution, 0.4mL of 4-NP solution, 0.6 mL of water and 15 μL of the sample suspension were together added to the 4 mL-cuvette, and absorption curves were measured by UV-Vis at pre-determined intervals.
3. Results and discussion
Figure 2 shows the SEM images of (a) Ti DNFs and (b) Au-Ti DNFs. Ti DNFs had the dendritic and fibrous morphology and constructed by a large number of ultrafine nanowires (Figure 2a), as reported in the previous study [4]. After hydrothermal reaction with HAuCl₄·4H₂O, the as-synthesized Au-Ti DNFs (Figure 2b) also showed the dendritic and fibrous morphology and consisted of lots of ultrafine nanowires. The hydrothermal treatment in the solution of HAuCl₄·4H₂O has no dramatic effect on both size and morphology between Ti DNFs and Au-Ti DNFs.

![Figure 2. SEM images of (a) Ti DNFs and (b) Au-Ti DNFs.](image)

To confirm the formation of Au-Ti DNFs, the elements in Au-Ti DNFs were further analyzed. As shown in Figure 3, the as-synthesized Au-Ti DNFs (Figure 3a) consisted of Ti (Figure 3b), O (Figure 3c), and Au (Figure 3d) elements. Moreover, Au element (Figure 3d) was well distributed on the Au-Ti DNFs.

![Figure 3. Element mapping images of Au-Ti DNFs.](image)

Figure 4 shows TEM images of Au-Ti DNFs. Au-Ti DNFs displayed the dendritic and fibrous morphology with the diameter of several micrometers and constructed by a large number of nanowires with the diameter of around 7 nm (Figure 4a). A high magnification image showed that the ultrafine Au nanoparticles with the diameter of 5-10 nm (Figure 4b) were well decorated on the surface of the nanowires.

![Figure 4. TEM images of Au-Ti DNFs.](image)
Catalytic activity of Ti DNFs and Au-Ti DNFs was evaluated using 4-NP as model chemical. The catalytic reaction was monitored with a UV-vis machine. As shown in Figure 5, with increasing the reaction time, the intensity of the adsorption band at 400 nm assigned to 4-nitrophylate ions was significantly different between Ti DNFs and Au-Ti DNFs. For Ti DNFs, no dramatic change in intensity of peak at 400 nm was found [5]. For Au-Ti DNFs, the intensity of peak at 400 nm was gradually decreased and a new peak at 290 nm assigned to 4-AP was gradually increased, indicating that the conversion of 4-NP to 4-AP occurred. Namely, Au-Ti DNFs showed the catalytic capacity for reduction of 4-NP due to the presence of Au nanoparticles.

4. Conclusions
Au-Ti DNFs were successfully synthesized through in situ decoration of Au nanoparticles on Ti DNFs and showed the hierarchical and fibrous morphology. When reacted with 4-NP/NaBH₄ solution, they presented the enhanced catalytic capacity for reduction of 4-NP to 4-AP.

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