THE FABRICATION OF Ag NANOPARTICLES LOADED TiO\textsubscript{2} NANOTUBES BY PHOTOREDUCTION METHOD AND THEIR PHOTOCATALYTIC ACTIVITY

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ABSTRACT

In this paper, we survey the effect of the photoreduction (illumination) time and the annealing temperature on the formation of Ag nanoparticles supported on TiO\textsubscript{2} nanotubes (Ag/TNTs). The morphology, crystal structure and compositions were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS), respectively. The results showed that Ag nanoparticles are supported on TNTs and the amount of Ag nanoparticles could be controlled. The morphology of TNTs can be changed by the photoreduction time and the annealing temperature.

Keywords: silver nanoparticles, TiO\textsubscript{2} nanotubes, photoreduction, photocatalyst.

1. INTRODUCTION

TiO\textsubscript{2} is a common material applied in environmental treatment because of its high photocatalytic and chemical stability \cite{1,2}. Due to the fact that TiO\textsubscript{2} has a relatively large band gap (3.2 eV), the photocatalytic reactions of TiO\textsubscript{2} are limited by low absorption capability in the visible light (UV) region and a high recombination rate of photogenerated electron–hole pairs formed in photocatalytic activity. Among TiO\textsubscript{2} materials at nanoscale, TiO\textsubscript{2} nanotubes (TNTs) have the advantages because the proportion reunion of electronic pair - hole is lower than TiO\textsubscript{2} nanoparticles. However, TiO\textsubscript{2} nanotubes (TNTs) are also a large bandgap material (3.85 eV), so its photocatalytic activity only occurs in the UV light \cite{3}. To overcome this limitation, some materials have been doped into TNTs such as metal oxides \cite{4}, nonmetallic as N\textsubscript{2} \cite{5} and particularly the metal nanoparticles \cite{1}.

Among metals, silver (Ag) was used in antibacterial applications, infection control and decontamination in the old times \cite{6,7}. The presence of Ag nanoparticles in Ag/TNTs composite material has significantly improved the photon absorption by the surface plasmon effect and thereby increased the number of pairs of electrons - holes on nanostructured TiO\textsubscript{2} semiconductor
In addition, the Ag nanoparticles which acted as electron trapping centre increased the duration of the particles diffusion and reduced the recombination performance of electrons-holes [9].

In this research, first Ag/TNTs materials were synthesized from TNTs powder and the AgNO$_3$ solution by photoreduction method. Then, the photocatalytic ability of these materials with a methylene blue (MB) dye solution was investigated. This method has many advantages such as: (a) synthesizing directly Ag nanoparticles on TNTs without using organic solvents and the surface protection of Ag nanoparticles; (b) controlling the Ag nanoparticles formed on TNTs surface, and (c) synthesis process is simple, easy, cost–efficient with large-scale application.

2. EXPERIMENTAL

2.1. Chemicals and materials

TNTs powders were successfully synthesized by hydrothermal method. The results had been published in ref.[10]. AgNO$_3$ salt (99.9 %) was purchased from Alpha Chemika, India. De-ionized (DI) water was purchased from Thermo Scientific Equipment and methylene blue (MB) powder (99.9 %) was purchased from Shanghai Chemical, China.

2.2. Preparation of Ag/TNTs

At the beginning, 1.0 gram TNTs powder was added into AgNO$_3$ solution with different concentrations (0.01 M – 0.04 M). The solution was magnetically stirred and put under UVC light at different illumination times (6 hours to 36 hours). The obtained precipitate was filtered and washed with DI water several times and dried at 100$^\circ$C for 2 hours in the air. For the survey of the effect of the annealing temperature, we annealed samples at various temperatures (300, 400 and 500$^\circ$C) in 2 hours.

2.3. Materials characterizations

Crystal structures of TNTs and Ag/TNTs were determined by X-ray diffraction (XRD) using a Bruker D8 – Advance 5005 with Cu Kα radiation ($\lambda = 0.154064$ nm). Morphology of samples were recorded by Transmission Electron Microscopy (TEM) on a JEM 1400 instrument. Chemical compositions of these materials were analyzed by Energy Dispersive X-ray spectroscopy (EDX) data on a Field Emission Scanning Electron Microscopy (FESEM) (JOEL JSM 7401F).

2.4 Photocatalytic measurement procedure

Firstly, the initial absorption of 10 ppm MB solution was measured at 664 nm wavelength. After that, 0.03 g catalyst was added into 30 mL MB solution and stirred evenly in dark for 60 minutes to balance the absorption and desorption. Then, the solution was extracted in a cuvet to measure the absorption after every UV illumination time (UVA lamp, $\lambda = 350$ nm, 7 W). The distance from a light source to the surface of the solution is 15 cm. The absorption spectra of all samples were determined by U2910 spectrometer (HITACHI, Japan).
3. RESULTS AND DISCUSSION

3.1 The effect of photoreduction time on the formation of Ag/TNTs

According to our previous research [10], the crystal structure of TNTs was not different from that of commercial TiO$_2$. The diffractive peaks of samples at $2\theta = 25.30^\circ$ and $48.03^\circ$ are featured for the (101) and (200) lattice planes of anatase phase and the peak at $2\theta = 27.43^\circ$ defines the (110) plane of rutile phase. The intensity of all these peaks is lower than that of commercial TiO$_2$. Besides, the morphology of TNTs is uniformed tubes. The average diameter of TNTs is about 10 nm and its length is several hundred nanometers.

We prepared Ag/TNTs samples from 0.04 M AgNO$_3$ solution and change the UV illumination time (6, 24, 36 hours). The color of products changes from white (Fig. 1a, 1b) into gray-brown color (Fig. 1c) after photoreduction process under the above condition. This color characterization of the sample indicates the appearance of Ag particles on the surface of TiO$_2$ (Fig. 1) [6, 7, 11].

![Figure 1. Images of commercial TiO$_2$ (a), TNTs (b), Ag/TNTs (c).](image)

Morphologies of the product were indicated on TEM images as Fig. 2a and Fig. 2b. They shows that Ag particles are supported on the TNTs surface, the distribution of the particle size is non-uniformed distribution and their average diameter is about 5 nm. With the samples photoreduced for 24 hours (Fig. 2c, d) have appearance of Ag nanoparticles appear average size about 5 - 10 nm and they distribute uniformly on the surface of TNTs. These results show the similarity with some recent study results, which fabricated Ag/TNTs combination materials by different methods in ref. [2, 9, 12]. The stability of this morphology also exists after 36-hour photoreduction (Fig. 2e, f). Besides, the amount of Ag nanoparticles in 36-hour illumination sample is greater than the 24-hour sample. Moreover, the diameter of 36-hour illumination sample is smaller (about ~ 5 nm) than the 24-hour illumination sample.

To confirm the influence of illumination time on the formation of Ag nanoparticles on TNTs, we analyzed the X-ray energy dispersive (EDX) of these samples. Table 1 presents the atom ratio Ti/Ag falls down when the photoreduction time is increased from 6 hours to 36 hours. It shows that the longer the illumination time is, the more Ag nanoparticles are increased. These results demonstrate a good agreement with the results of TEM images (Fig. 2).
Table 1. The percentage of atoms in the samples.

<table>
<thead>
<tr>
<th></th>
<th>6h (% atom)</th>
<th>24h (% atom)</th>
<th>36h (% atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>53.17</td>
<td>56.36</td>
<td>48.10</td>
</tr>
<tr>
<td>Ti K</td>
<td>15.38</td>
<td>17.13</td>
<td>14.10</td>
</tr>
<tr>
<td>Ag L</td>
<td>2.57</td>
<td>2.98</td>
<td>2.97</td>
</tr>
<tr>
<td>Impurities of measurement devices</td>
<td>28.8</td>
<td>23.53</td>
<td>34.83</td>
</tr>
<tr>
<td>Atom ratio of Ti/Ag</td>
<td>5.98</td>
<td>5.74</td>
<td>4.74</td>
</tr>
</tbody>
</table>

Figure 2. TEM images of Ag/TNTs with various illumination time: (a,b) 6 hours; (c,d) 24 hours; and (e,f) 36 hours.

XRD patterns (Fig. 3) shows that the intensity of (101) and (200) peaks of the anatase phase and (110) of the rutile phase of samples decreases compared to initial TNTs. Besides, there is not any change of the positions of specific peaks. This presents that Ag nanoparticles have a good distribution on the TNTs surface [13] and Ag nanoparticles don’t replace Ti atoms position in the crystal structure of TNTs [2].
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3.2. The effect of the annealing temperature on the morphology and structure of Ag/TNTs

We annealed the Ag/TNTs samples at 300 °C, 400 °C and 500 °C for 2 hours in the air and analyzed XRD patterns and TEM images of these samples.

![XRD patterns of Ag/TNTs samples with various annealed temperature](image)

**Figure 4.** XRD patterns of Ag/TNTs samples with various annealed temperature.

XRD patterns (Fig. 4) present that the intensity of (200) peak of the anatase phase decreases when being annealed at 300 °C. Besides, the intensity of (110) peak of the rutile phase is higher than that of the samples annealed at 500 °C. The intensity of (110) rutile peak is maximum at 500 °C.

The result of TEM images (Fig. 5) shows that the morphology and the size of Ag/TNTs are stable when they are annealed at 400 °C. The tube morphology of TNTs is broken and they start
to change into another morphology when they are annealed at 500 °C. However, Ag nanoparticles still maintain their average size of 2~15 nm.

![TEM images of Ag/TNTs samples with various annealed temperature: (a,b) 400 °C; (c,d) 500 °C.](image)

**Figure 5.** TEM images of Ag/TNTs samples with various annealed temperature: (a,b) 400 °C; (c,d) 500 °C.

### 3.3. The photocatalytic activity of Ag/TNTs

The photocatalytic ability of Ag/TNTs compared to TNTs and commercial TiO$_2$ is shown in Fig. 6. The results demonstrate that, the sample photoreduced for 24 hours that degrades MB is greater than the other samples (Fig. 6). Ag nanoparticles loaded TNTs significantly improve the photocatalytic ability of TNTs. This result explains that the electric field is formed on the surface of nanoparticles with plasmon frequency due to light irradiation. This effect makes the electrons transit between the conduction and valence bands. Then, these electrons will interact with absorbed oxygen to create -O$_2$. These -O$_2$ make an oxidation creation with MB solution [11, 12, 14].

![Photocatalytic activity comparison](image)

**Figure 6.** Compare the photocatalytic ability of Ag/TNTs, commercial TiO$_2$ and TNTs.
The influence of annealing temperature on the photocatalytic ability of Ag/TNTs is presented on Fig. 7. An annealed Ag/TNTs sample at 500 °C is the worst MB degradation. Whereas, the annealed Ag/TNTs at 400 °C is the best degradation. These results explained that the annealed sample at 500 °C breaks the TNTs structure and clusters leading to the increase of particle size and the strong decrease of the absorption.

![Graph showing photocatalytic ability of Ag/TNTs with various annealed temperatures.](image)

**Figure 7.** The photocatalytic ability of Ag/TNTs with various annealed temperature.

### 4. CONCLUSIONS

Ag/TNTs samples have been successfully synthesized by photoreduction method. The morphology and structure of Ag /TNTs materials can be controlled by changing the illumination time and annealing temperatures. Ag nanoparticles were loaded on TNTs with an average diameter from 5 nm to 10 nm and uniformly distributed on the TNTs surface. Besides, the more illumination time was, the larger number of Ag nanoparticles formed and loaded on TNTs surface. The sample annealed at 400 °C for 2 hours has stability in the morphology and size of Ag nanoparticles clinging on TNTs surface. The morphological structure of TNTs into Ag/TNTs sample was broken and changed to other shapes when they were calcinated to 500 °C. The photocatalytic characteristics showed that photocatalytic ability of Ag /TNTs would be greater than commercial TiO₂ and TNTs.

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### REFERENCES


TÓM TÁT

CHẾ TẠO CÁC HẠT NANO Ag TRÊN ỐNG NANO TiO$_2$ BẰNG PHƯƠNG PHÁP KHỬ QUANG HỌC VÀ HOẠT TÍNH QUANG XÚC TÁC CỦA CHÚNG

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Trong bài báo này chúng tôi khảo sát ảnh hưởng của thời gian chiếu đen (thời gian khử), nhiệt độ nung lên sự hình thành của vật liệu tổ hợp nano Ag/ống nano TiO$_2$ (viết tắt là Ag/TNTs) được tổng hợp bằng phương pháp khử quang học. Đồng thời khảo sát khả năng quang xúc tác của chúng với dung dịch Methylen Blue. Hình thái học, cấu trúc tĩnh thể của vật liệu tổ hợp Ag/TNTs được khảo sát bằng ảnh TEM, gián độ nhiễu xạ tia X và phổ tán sắc năng lượng tia X. Kết quả cho thấy có sự hình thành các hạt nano Ag bám lên TNTs, đồng thời có thể điều khiển được số lượng các hạt nano Ag cũng như hình thái học của TNTs bằng việc thay đổi thời gian khử và nhiệt độ nung.

Từ khóa: hạt nano Ag, ống nano TiO$_2$, khử quang học, quang xúc tác.