

EFFECT OF Ag NANOPARTICLE ON THE PHOTOCATALYTIC ACTIVITY OF TiO₂ NANOTUBES

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ABSTRACT

The TiO₂ nanotubes were fabricated by the hydrothermal method. Then, Ag nanoparticles with the varying ratio were attached on the TiO₂ nanotubes by photoreduction. The characteristics of structure, morphology, chemical composition and of TiO₂ nanotubes modified Ag (Ag-TNTs) was investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM), energy dispersive X-ray (EDX) and the absorption spectral of Methylene blue (MB) solution. The results showed that Ag-TNTs have fairly uniform length with Ag particles immobilized on the tube. The photocatalysis TiO₂ nanotubes (TNTs) is higher than Ag-TNTs in UV range and lower than Ag-TNTs in the visible light. And the photocatalytic activity of Ag-TNTs with 5 wt.% Ag is highest in the visible range.

Keywords: TiO₂, Ag, nanotubes, photocatalyst.

1. INTRODUCTION

TiO₂ attracted much attention due to its excellent applications in antibacterial treatment, deodorization and water purification, hydrogen production from water splitting reaction photocatalyst, self-cleaning surface systems, treatment of organic contaminants etc. [1 - 4]. Photocatalytic property of TiO₂ is determined by the ability of recombination electron-hole pairs. However, TiO₂ has a wide bandgap (3.2 eV), thus it only absorbs ultraviolet light (only 5 % of solar radiation reaching the surface of the earth is within the UV range) and electron-hole pairs are easily recombined due to high density of trap states; resulting its photocatalyst low in the visible light and near-infrared regions. The high recombination rate of electron-hole pair limits the application of TiO₂ [5]. Therefore, several studies have attempted to modify the surface of TiO₂ or dope the metals, non-metals [6, 7] and noble metals [8, 9] as to improve its efficiency of photocatalytic activity and the use of solar energy.

Surface modification by noble metals (Ag, Au, Pt) can markedly broaden the absorption region because it can strongly interact with light in visible and infrared region due to surface plasmon resonance (SPR) [10 - 13]. Ag is one of the most promising transition metals for the improvement of photocatalytic activity of TiO₂ because Ag nanoparticles can act as electron trapper to slow the rate of electron-hole pair recombination. Thus, more holes and electrons are available for the photocatalytic reactions [14, 15]. Recently, several studies have observed that the combination Ag-TiO₂ structure showed the good bactericidal effect [16, 17] and expands its operations into the region visible light [18]. However, some studies have observed that a suitable amount of silver will accelerate the process of electron traps, on the contrary, will limit the ability to absorb light, and they act as a junction for the recombination of electron-hole pairs so limit photocatalytic activity [19].

In this study, we report fabrication of TiO₂ nanotubes structure and modification by Ag (Ag-TNTs). TiO₂ nanotubes structure (TNTs) is fabricated by the hydrothermal method with hydrothermal conditions are presented in our previous reports [20, 21], the surface modification process was carried out by photoreduction method with different ratio weight of Ag. The photocatalytic property is estimated by monitoring the changes between the initial MB absorption spectra and the final MB absorption spectra intensity as presented in the work [22].

2. EXPERIMENTAL

TNTs is fabricated from commercial TiO₂ powder by the hydrothermal method in 10M NaOH solvent with hydrothermal conditions are published in our works [20,21]. However, compared to the work [20, 21] we used a solution of HNO₃ instead of HCl to treatment after the hydrothermal process. The obtained TNTs are used as precursors to fabricate Ag-TNTs structure. Ag-TNTs structures were fabricated as follows: initial precursors include TNTs and AgNO₃ powder (Merck, 99 %). The modification surface process is accomplished by the photoreduction method: dissolving AgNO₃ powder with the ratio different weight with TNTs: 2.5 % (Ag-TNTs-1), 5 % (Ag-TNTs- 2) and 10 % (Ag-TNTs-3) in 50 ml DI water by a magnetic stirrer, and then dispersed TNTs in AgNO₃ solution. After 15 minutes stirring, the mixture was put into the UV phototherapy system, continue stirring for two hours with moderate phototherapy. Filter the solid powder by centrifuge, then rinse several times with DI water and dried at 800 °C temperature in an oven in 4 h. The morphology, the crystalline and the chemical components of Ag-TNTs were characterized by transmission electron microscopy (TEM, JEM-1400), X-ray diffraction (XRD, Bruker D8- ADVANCE) and scanning electron microscope (EDX, Horima EMAX7593-H), respectively. Assess and compare photocatalytic ability of materials via the absorption Methylene Blue (MB) solution in different lighting conditions.

3. RESULTS AND DISCUSSION

The obtained tube structures at the same fabrication conditions (130 °C, 22 hours) are maintaining the fairly uniform length of several hundred nanometers with a diameter of 11.78 nm (Fig. 1) in comparison to the TNTs structure in [20]. Their crystal structures show the TiO₂ nanotube crystalline in anatase phase at the peaks as $2\theta = 25.08^\circ$, A (101); 37° , A (004); 48.05° , A (200); 57° , A (211) and rutile at $2\theta = 27.47^\circ$, R (110); 35.89° , R (101) and not appearance of impurities such as salts (Na₂Ti₃O₇, H₂Ti₃O₇) (Fig. 4).

The TEM figures of Ag-TNTs with the varying weight ratio of AgNO₃:TiO₂ show that the appearance of Ag nanoparticles did not affect the morphology of TNTs (Fig. 2). The length and the

diameter of TNTs are about $150 \div 200$ nm and $8 \div 12$ nm with Ag attached up the wall of TNTs. The average diameter of Ag-TNTs with Ag 2.5 wt.%, 5 wt.% and 10 wt.% is 2.31, 2.31 and 5.11 nm respectively. However, at the lowest concentration, there are only a few Ag nanoparticles on the surface of TNTs, when the concentration increased (5 wt.% and 10 wt.%) the density of Ag nanoparticles on TNTs is dense, nearly covering the TNTs.

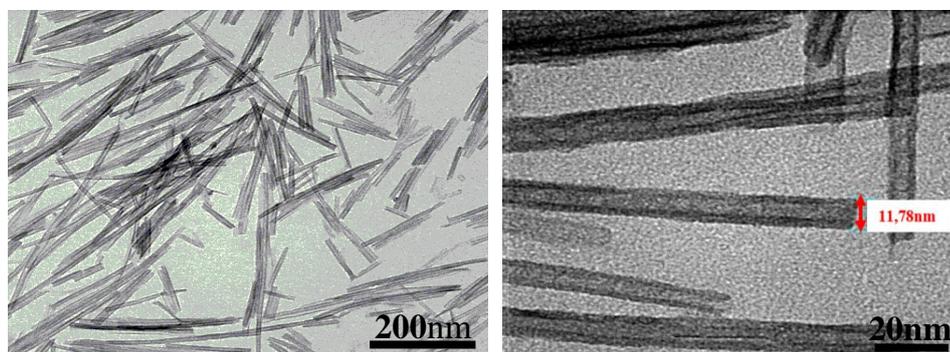


Figure 1. TEM images of TNTs fabricated by the hydrothermal method at 130 °C for 22 h.

The EDX spectra of Ag-TNTs-2.5 wt.% shows the Ag elements at the peaks as 2.65 keV and 3.00 keV beside the Ti, O, Na elements of TNTs. And the obtained result shows Ag element accounting for about 0.8 % by atoms or about 3.12 % by weight. This one proved the presence of Ag particles in Ag-TNTs samples. In XRD patterns of TNTs and Ag-TNTs samples indicated that two diffraction peaks appear at 38° and 44° angle, corresponding to Ag (111), Ag (200) beside the characteristic peaks of TiO₂ at 25.28°, 48.05° and 27.47° with (101), (200) anatase and (110) rutile, respectively (Fig. 4). However, the crystallization of the Ag crystal in XRD is very poor though high amount of Ag in TNTs. This can be explained that the Ag atoms attached from AgNO₃ solution are in an amorphous structure because they are fabricated at the room temperature and they were only high crystalline when annealed at high temperatures [23]. The phase transformation between rutile and Na₂Ti₂O₅ of TiO₂ has not been also observing, this confirms that the Ag particles are only attached on the surface of TNTs, and not incorporated into the lattice of TNTs. This result is matching with results of the TEM images (Fig. 2) and the authors [24], whereas the Ag particles deposited only on the surface of the TNTs and did not appear in the structure of TNTs. So, Ag particles have been successfully attached to TNTs by using the photoreduction method with a stirring and irradiation under UV light in 2 hours.

The absorption spectra of decoloration of MB aqueous solution tested UV light irradiation for 45 min are shown in Figure 5. The absorption spectra for Ag-TNTs-2, Ag-TNTs-3 shows the small changes compared to Ag-TNTs-1. However Ag-TNTs-1's absorption spectral change is smaller than those of TNTs. This illustrated that the photocatalytic performance of Ag-TNTs are lower than TNTs and of all Ag-TNTs are not much different under UV light (Fig. 5). This can be explained that in UV light, only TiO₂ reacts in the photocatalysis process and Ag does not contribute to increase the speed of photocatalyst. Moreover, they can coat TNTs leading to decrease effective area of TNTs and the photocatalyst ability. In other words, the higher Ag concentration is the slower photocatalytic activity. So, the Ag-TNTs-1 with the concentration of 2.5% Ag is photocatalytic reactions slightly better than Ag-TNTs-2 and Ag-TNTs-3.

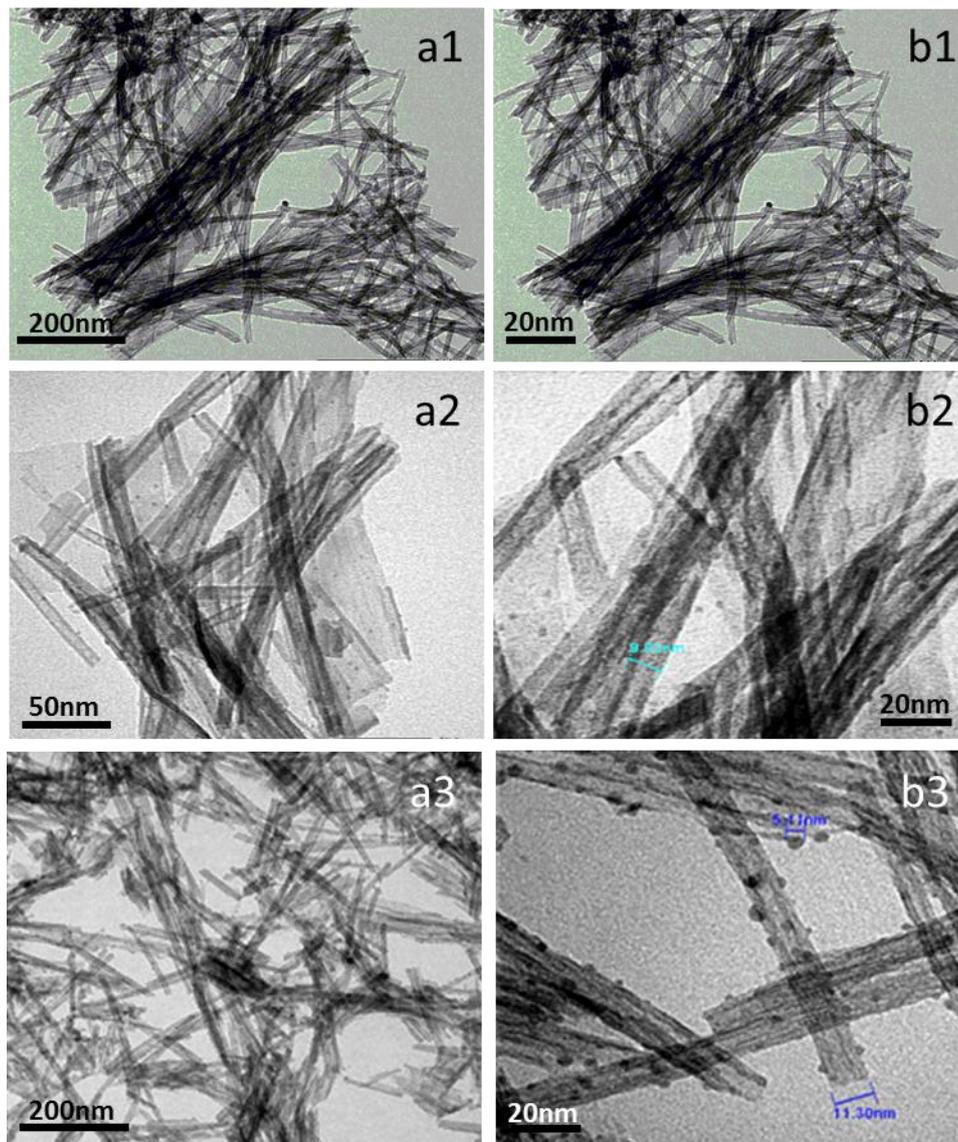


Figure 2. TEM images of Ag-TNTs with different weight ratio (%) of AgNO₃: TiO₂ Ag-TNTs-1(a1,b1); Ag-TNTs-2 (a2,b2) and Ag-TNTs-3 (a3,b3).

On the contrary, the photocatalytic activity of Ag-TNTs is better than TNTs under sunlight condition (Fig. 6). Within 20 min, all Ag-TNTs's absorption spectral change is larger than TNTs, whereby TNTs shows the smallest changes and Ag-TNTs-2 shows the biggest change under sunlight. It is found that the 5wt.% Ag (Ag-TNTs-2) achieve the highest efficiency of the MB photodegradation under the sunlight. So, the photocatalysis TiO₂ is good in UV environment that only 5 % in the solar spectrum and photocatalysis Ag-TNTs are good in the visible-light region in which Ag-TNTs-2 is highest. This can be explained by the Fermi level of the Ag nanoparticles is lower than the bottom of the conduction band of TiO₂ so electrons will transfer to the conduction band of the TiO₂ nanoparticles go to Ag, become free electrons and

simultaneously accumulation in this position to form a Schottky barrier between TiO₂ and Ag [25]. The free electrons and holes appear in the valence band of the TiO₂ will diffuse to the surface and react with O₂ and H₂O on the surface of Ag and forming hydroxyl radical O₂⁻ and superoxide *OH capable of oxidation reducing organic matter. This process significantly reduces the possibility of recombination electron-hole pairs, resulting in efficient separation and photocatalytic property will be improved [26]. Besides the presence of Ag nanoparticles on the surface of TNTs, Ag-TNTs help extend the absorption wavelength to a visible-light region, enhanced photocatalytic features through surface plasmon resonance [27]. This result also shows that effective absorption depends on the content of silver, if the amount is lower than 5 % Ag (Ag-TNTs-1 form), the Ag will act as recombination centers electron-hole pairs; whereas if the amount exceeds 5 % Ag (Ag-TNTs-3 form), the apperance of Ag molecules on the surface of the TNTs will constitute barriers limit the light absorption efficiency of TNTs reduces splitting electron-hole pairs. Both conditions cause reduced efficiency absorbance dye molecule or reducing the photocatalytic features [28, 29].

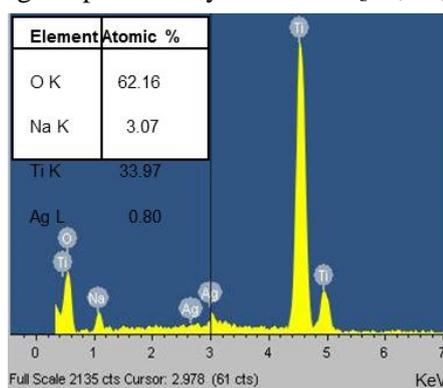


Figure 3. EDX spectra of Ag-TNTs-1.

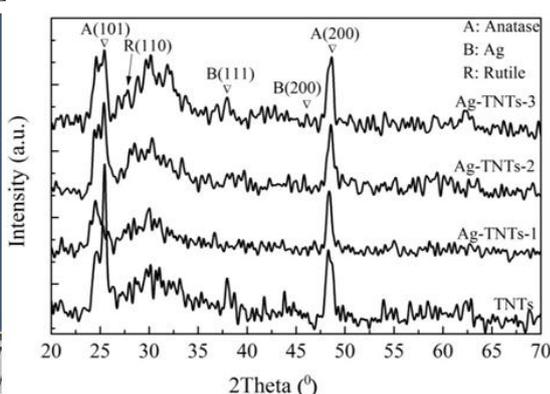


Figure 4. XRD pattern of TNTs, Ag-TNT-1, Ag-TNTs-2 and Ag-TNTs-3.

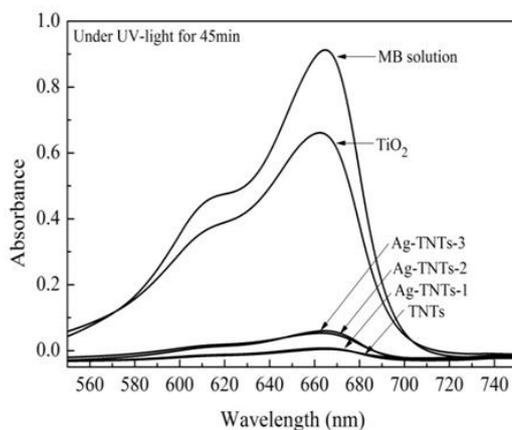


Figure 5. Absorption spectra of MB solution in the presence of different catalysts after being kept under UV-light for 45 min.

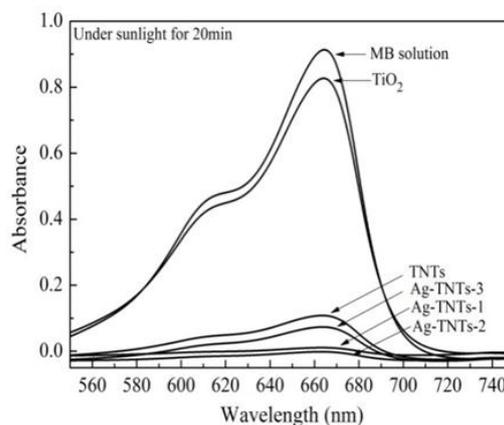


Figure 6. Absorption spectra of MB solution in the presence of different catalysts after being kept under sunlight for 30 min.

4. CONCLUSIONS

TNTs and Ag-TNTs structures are successfully fabricated by the hydrothermal method and photoreduction. The TNTs obtained structures are fairly uniform with $150 \div 200$ nm in length, $9 \div 11$ nm in diameter and Ag nanoparticles attach evenly over the tube. The photocatalyst activity of Ag-TNTs is lower than TNTs under UV light but higher in the visible-light. The highest photocatalytic activity of Ag-TNTs with 5 % Ag in the visible light is going to promise applications of environmental treatment and antibacterial under sunlight.

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TÓM TẮT

ẢNH HƯỞNG CỦA HẠT NANO Ag LÊN TÍNH NĂNG QUANG XÚC TÁC CỦA ỐNG NANO TiO₂

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Hạt nano Ag với các tỉ trọng khác nhau đã được đính thành công trên bề mặt các ống nano TiO₂ bằng phương pháp quang khử. Đặc điểm hình dạng cấu trúc, thành phần hóa học và tính năng quang xúc tác được đánh giá bằng các phương pháp tương ứng là kính hiển vi điện tử truyền qua (TEM), nhiễu xạ tia X (XRD), phổ tán sắc năng lượng tia X (EDX) và phổ hấp thụ của dung dịch Methylene blue (MB). Kết quả nhận được cho thấy ống nano TiO₂ có độ dài khá đồng đều với các hạt nano Ag bám trên ống. Tính chất quang xúc tác của ống nano TiO₂ cao hơn so với cấu trúc Ag-TNTs trong vùng UV và thấp hơn cấu trúc Ag-TNTs trong vùng ánh sáng khả kiến. Hoạt động quang xúc tác của cấu trúc Ag-TNTs ứng với 5 wt.% Ag cho hiệu suất cao nhất trong vùng ánh sáng khả kiến.

Từ khóa: TiO₂, Ag, ống nano, quang xúc tác.