



## The photocatalytic Enhancement of TiO<sub>2</sub> Nanotubes by Simultaneously Doping Ag Nanoparticles During Anodization Process: Photocatalytic Degradation of 2,4-Dichlorophenol

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**Abstract :** Ag-Doped TiO<sub>2</sub> nanotubes (TNTs) were fabricated with facile two-step anodization process. In addition, the catalytic activity of Ag-Doped TiO<sub>2</sub> nanotubes was examined in photocatalytic degradation of 2,4-dichlorophenol. Characterizing of Ag-Doped TiO<sub>2</sub> nanotubes were evaluated by FESEM, TEM, XRD, DRS and Spectrophotometry analyses. Results show that doping Ag nanoparticles uniformly distributed over the TNTs without any distraction in a tubular structure. Anatase crystalline phase was obtained by annealing the Ag-Doped TNTs at 550 °C. DRS results showed the addition of Ag nanoparticles had a sufficient effect of band gap which it decreased the band gap from 2.9 to 2.7. Pure TiO<sub>2</sub> nanotubes showed 74% removal of 2,4-dichlorophenol. photocatalytic degradation study indicated that Ag-dopant has an efficient impact on photocatalytic activity of TNTs with Ag-Doped TNTs could degrade 91% of 2,4-dichlorophenol under UV irradiation.

**Keywords :** TiO<sub>2</sub> nanotube, Ag-Doped, Photocatalytic degradation, 2,4-dichlorophenol

### Introduction

Ever since the discovery of the photocatalytic splitting of water on titanium dioxide (TiO<sub>2</sub>) electrodes by Fujishima and Honda in 1972 [1], TiO<sub>2</sub> have attracted much attention for widespread environmental applications due to its non-toxicity, long-term stability, low cost, chemical inertness, easy availability and high photoactivity [2]. However, its practical application was greatly restricted by the following aspects. Firstly, bare TiO<sub>2</sub> can only be excited under ultraviolet (UV) irradiation, which accounts for only 2–4% of the solar spectrum due to its wide band gap of catalyst. 3.2 eV (for anatase) [3]. Secondly, pulverous TiO<sub>2</sub> nanomaterial was difficult to separate from the suspending system, resulting in the thorny issue of reuse of nanocatalyst. Besides, it could also cause the secondary pollution. Thirdly, the high recombination of photogenerated hole and electron (h<sup>+</sup>/e<sup>-</sup>) pairs lowered the photocatalytic efficiency during the photo-decomposition of pollutants. From then on, considerable efforts have been carried out to improve the visible light photocatalytic performance and lifecycle of TiO<sub>2</sub> nanomaterials.

Noble metals, such as gold (Au) and silver (Ag), possess an additional ability to absorb visible light due to the existence of localized surface plasmon resonance (LSPR). Moreover, these metals function as electron donors to promote electron transfer from metal to TiO<sub>2</sub> and act as electron traps in the metal–TiO<sub>2</sub> nanostructures, minimizing the surface charge recombination in TNTs [4]. Among these noble metals,

Ag is the most suitable for incorporating with TiO<sub>2</sub> to improve the photocatalytic activity and open possibility for further applications in the antibacterial field due to its strong antimicrobial effect individually. Kang et al. [5] fabricated Ag/N Co-doped TiO<sub>2</sub> nanotube arrays by photodeposit AgNO<sub>3</sub> on the surface of TNTs. All these doping methods may lead to agglomeration Ag nanoparticles on the surface of TNTs because of its non-uniform dispersion causing less light diffusion into the TNTs and also reducing active site of TiO<sub>2</sub> catalyst. Therefore, in this work, Ag-TiO<sub>2</sub> nanotubes (Ag-TNTs) will be fabricated using two-step electrochemical anodization method. The morphology, chemical composition, and crystalline phase of the Ag-TNTs are investigated using various characterization techniques. In addition, the photocatalytic activity of the Ag-TNTs in comparison with pure TNTs is also evaluated using the degradation of 2,4-dichlorophenol (2,4-DCP) aqueous solution under UV light irradiation. The photocatalyst mechanism is also discussed in detail.

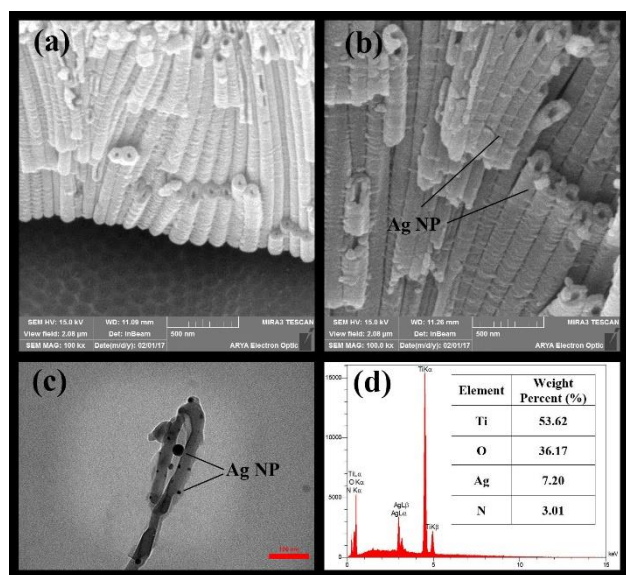
### Materials and method

Commercial titanium foils (with 97% purity, 0.25 mm in thickness) were cut into pieces of 3 by 9 cm. First of all, for degreasing, sheets were immersed in acetone, ethanol and deionized water for about 10 min, respectively. To obtain a completely smooth and sleek surface, chemical polishing in a mixture of HF, HNO<sub>3</sub> and deionized water solution with a volume ratio 1:4:5 was used. For Anodizing, titanium sheets were used for both the anode and the cathode. The first step was

performed in an ethylene glycol-based electrolyte containing 2 vol % deionized water and 0.5 wt% ammonium fluoride at a constant voltage of 40 V at room temperature for 1.5 h. Then, the resulting TNTs from the first step were removed by acid treating process using HF and deionized water solution. To achieve the orderly and aligned Ag-Doped TNTs, the second step of anodizing was done in the same Voltage and electrolyte of first step with adding an appropriate amount of AgNO<sub>3</sub> particles. The anodizing process was continued for 6 h. Furthermore, the pure TNTs were prepared in the same procedure as mention above without adding AgNO<sub>3</sub> particles. Subsequently, to obtain a crystalline structure, the temperature of the samples was raised to 550 °C at a rate of 3.5 °C/min. They were kept at that temperature for 2 h.

## Results and Discussion

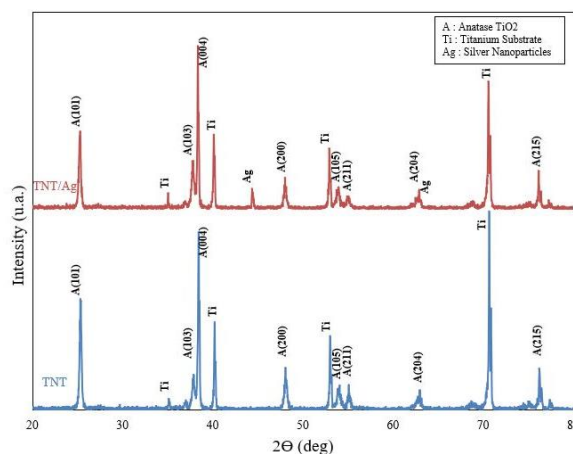
In Fig. 1(a)–(b), the surface and cross section field-emission scanning electron microscopy images (FESEM) of the TNTs and Ag-Doped TNTs are observed. These figures indicate that by removing the nanotubes grown in the first-step anodization, many ordered hexagonal imprint patterns are left on Ti substrates, greatly improving the uniformity and orderliness of the TNTs during the second-step anodization. Ag nanoparticles can be observed in Fig 1(b). the particles are fairly uniformly distributed over the of nanotubes without any destruction in tubular structure. It can be seen that the nanotubes wall thickness increase by doping Ag nanoparticles. This shows the existence of Ag nanoparticles inside TiO<sub>2</sub> structure. Fig. 1(c) shows TEM image of Ag-Doped TNTs sample. Ag nanoparticles were well doped top, inside and between the TNT as indicated by arrows. Fig 1(d) shows the EDX result of Ag-Doped TNTs. The results show that by this process 7.2 % Ag nanoparticles



were doped on TNTs.

Fig.1: FESEM images of anodic a) Pure TNTs and b) Ag-Doped TNTs, c) TEM image and d) EDX results of Ag-Doped TNTs

Fig. 2 represents the XRD patterns of the TNT and Ag-Doped TNT samples. It can be observed that both samples exhibit the diffraction peaks at  $2\theta$  of 25.3°, 37.8°, 38.1°, 48.2°, 53.9°, 55.2°, 62.7° and 75° which are equivalent to the Miller indexes (101), (103), (004), (200), (105), (211), (204) and (215) which indicates that the samples consist only of the anatase form after calcination at the temperature of 550 °C and demonstrates that the Ag doping does not change the phase composition [2]. There are two peaks at 44.24° and 63.8° corresponding to the characteristic of Ag, are observed, which confirms that the existence of Ag in the TNTs. Besides there are four peaks at 35.8°, 40.2°, 53.7° and 70.6° corresponding to the characteristic peaks of Ti substrate [5]. No more phases observed in the XRD



patterns shows high purity of the samples.

Fig.2 : XRD pattern of Pure TNTs and Ag-Doped TNTs

Fig.3 demonstrates the pure TNT and Ag/TNT samples diffuse reflectance spectra over the 250–600 nm wavelength range. There is a broad intense absorption around 400 nm in the DR spectrum of pure TiO<sub>2</sub>. In the DR spectra of Ag/TNT sample, we can observe the absorption shoulder peak in the range between 360 and 500 nm. These absorption shoulders result from the post-broadening SPR peak. In the visible region, the presence of localized surface plasmon resonance (LSPR) would enable the Ag doped TNTs to show broad and strong absorption [6]. We also calculated the band gap energy from the DR spectra according to Eq. (1) [2] for the synthesized samples.

$$[F(R)hv]^{0.5} = A(hv - E_g) \quad (1)$$

Where A is a constant, F(R) is the function of Kubelka–Munk, and  $E_g$  is the band gap. The Ag/TNTs sample band gap decreased slightly compared with Pure TNTs. It can be clearly seen that Ag NPs loaded on the

TiO<sub>2</sub> surface affect the TiO<sub>2</sub> optical properties significantly. Evidently, the photoresponse of the Ag/TNTs is greatly shifted into the visible light ranges because of the SPR properties of metallic silver NPs, leading to a band gap narrowing (2.7 eV) compared with that of pure TNTs (2.9 eV).

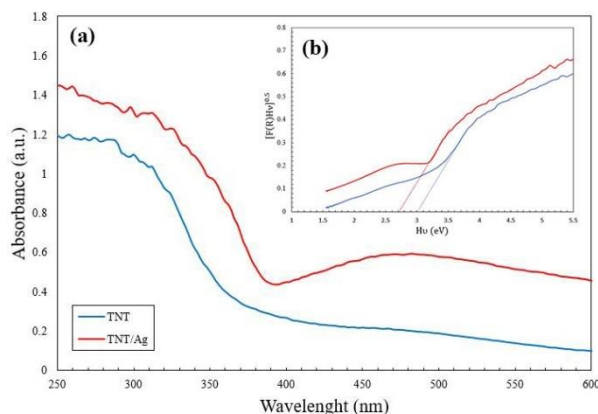
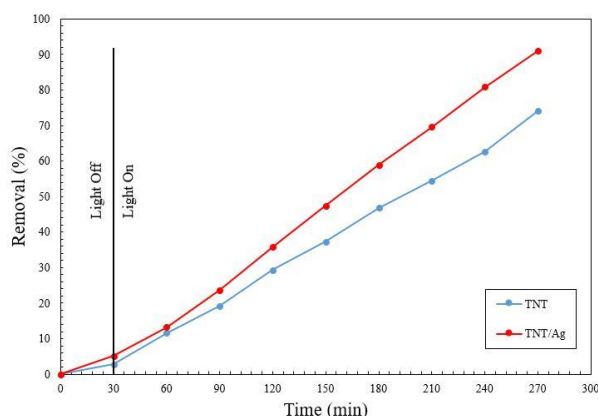


Fig.3 : (a) DRS and (b) Kubelka–Munk plots for the band gap energy calculation of TNT and Ag-Doped TNTs

Fig. 4 shows the photocatalytic removal of 2,4-DCP by fabricated nanotubes versus irradiation time Under 240 min UV irradiation which is calculated using Eq. (2) [2]:

$$X_{2,4-DCP} = \frac{C_0 - C}{C} \times 100 \quad (2)$$

where  $X_{2,4-DCP}$  is the percentage of the degradation of 2,4-DCP,  $C$  is the concentration of 2,4-DCP and  $C_0$  is the initial concentration of 2,4-DCP (40ppm). It can also be observed that little absorption is done in the 30 minutes before the start of the UV radiation (zero time). Thus, it can be concluded that the Ag-Doped TNTs, in addition to creating unstable hydroxyl radicals and superoxide ions in water for the degradation of 2,4-DCP, can also degrade 2,4-DCP by absorbing it on their surface after irradiation by their photon activated surface. It can be seen that doping TNTs with Ag nanoparticles increases photocatalytic degradation percentage of 2,4-DCP significantly from 74% in pure TNT to 91% in 240 min.



This is due to the decrease in the band gap.

Fig.4 : Photocatalytic degradation of 2,4-DCP by the synthesized samples.

## Conclusion

TiO<sub>2</sub> nanotubes were fabricated by two-step anodization process. In order to increase photocatalytic performance of TNTs, Ag nanoparticles were added to second step anodization electrolyte. FESEM images shows that Ag nanoparticles are fairly uniformly distributed over the surface of nanotubes. It can be observed from TEM image of Ag-Doped TNT that Ag nanoparticles were well doped top, inside and between the TNTs. EDX results show that by this process 7.2 % Ag nanoparticles were doped on TNTs. Anatase crystalline phase was obtained by annealing the pure and Ag-Doped TiO<sub>2</sub> nanotubes at 550 °C. It can be indicated from DRS analysis that TiO<sub>2</sub> band gap decreases from 2.9 to 2.7 by doping Ag nanoparticles. photocatalytic degradation of 2,4-dichlorophenol results show that Ag-Doped TNTs have 17% more efficiency than pure TNTs in removing 2,4-DCP pollutant.

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