Synthesis of TiO$_2$ Nanotubes Decorated with Ag Nanoparticles (TNTs/AgNPs) For Visible Light Degradation of Methylene Blue

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Abstract. TiO$_2$ nanotubes (TNTs) decorated with Ag nanoparticles (AgNPs) were fabricated first by anodisation of titanium wire to produce the TNTs then by dispersing AgNPs on the TNT arrays. The AgNPs were produced by reduction in *kyllinga brevifolia* extract. The AgNPs have diameter in the range of 10 – 30 nm measured from transmission electron microscope image and average particle size of 22.3 nm. They were dispersed on TNTs by wetness impregnation technique. The morphology of the fabricated TNTs/AgNPs was evaluated by scanning electron microscope (SEM). SEM images of the sample shows highly ordered TNTs with 7.30 ± 0.46 µm long with 74.59 ± 9.22 nm inner diameters and wall thickness 33.51 ± 4.56 nm. After impregnation, the dispersed AgNPs appear to be distributed uniformly across the surface of the TNTs. The TNTs/AgNPs composite were used to remove methylene blue (MB) dye from an artificial wastewater. On TNTs/AgNPs 63% degradation was recorded compares to pure TNTs with only 17% degradation after 1 hr reaction under visible light. The addition of AgNPs has contributed to the activation of the composite under visible light perhaps due to the surface plasmon of the AgNPs as well as electrons transfer process to the conduction band of TiO$_2$.

1. Introduction

TiO$_2$ is the most widely researched photo-catalysts semiconductor because it is highly photoactive, has a strong oxidizing potential, long term photo-stability and is also nontoxicity and economical [1]. However, the application of TiO$_2$ is limited by its high band gap energy (3.0–3.2 eV), it is only able to act as a photo-catalysts under ultraviolet (UV) light, which accounts for about 4-5% of sunlight, greatly limiting its practical applications [2]. From the view point of exploiting the solar light, visible light responsive TiO$_2$ photocatalysts are highly preferred.
One of the possible solutions for improving the photo-catalytic efficiency of TiO$_2$ photocatalysts in the visible region is to shift its optical absorption from the UV region to the visible light region by making a composite of TiO$_2$ with other materials [3]. In order to improve the photo-catalytic efficiency and extending the spectral response of TiO$_2$ to the visible spectrum, decoration of Ag on the surface of TiO$_2$ is employed in this study. The Ag enhances the photo-catalytic activity by reducing the band gap and/or reducing electron-hole recombination [2].

In this context, the TiO$_2$ nanotubes (TNTs) were prepared by anodizing method of titanium wire in mixture of ethylene glycol (EG) / anhydrous NH$_4$F. Throughout the anodisation process, air bubbles were introduced to the electrolyte. As to investigate the effect of alkaline salt, based on carbonate, we added in 0.1 M K$_2$CO$_3$ to the electrolyte half way through the anodisation process. It is acknowledged that alkaline species can increase the pH of electrolyte and may reduce the formation of TNTs as TNTs require acidic environment to induced the chemical etching for growth.

However as shown by Taib et al [4] and Nyein et al [5], the addition of alkaline species did not bring negative consequence to the growth of nanotubes. Alas, the TNTs formed were well crystalline and rather long. It was then concluded, that the growth process is not affected too much by the pH of the electrolyte. Nonetheless, TNTs formed were extremely large with diameter reaching 140 nm. It is believed that the large diameter is perhaps due to the increase in lateral growth of pore occurring at the beginning of the anodic process.

Here, anodic process was done in anhydrous electrolyte for 10 mins with air bubble injected to electrolyte as oxygen provider. After 10 mins, K$_2$CO$_3$ was added to electrolyte. First to investigate if the diameter can be reduced by performing this step and two is to see the effect of the carbonate to the adherence of the nanotubes on Ti. As reported by Bashirom et al [6], the presence of carbonate species can affect the adherence of anodic ZrO$_2$ on Zr.

In this work, *kyllinga brevifolia* silver nanoparticles (AgNPS) were synthesized by reduction of *K. brevifolia* extract. The decoration of AgNPs on surface of TNTs was done using wetness impregnation technique. In addition, catalytic activity of AgNPs decorated on TNTs was investigated and compared by degradation of methylene blue (MB). It was found that the presence of silver significantly improved the photo catalytic performance of samples to degrade MB under visible light.

### 2. Experimental study

TNTs were fabricated by anodizing method. Commercial pure Ti wire (0.50 mm thick, 4 cm length, 99.5%, NILACO, Japan) was used as the anode electrode and platinum as counter electrode in an anodisation bath comprising of fluoride EG electrolyte (97 mL EG with 0.3 wt% anhydrous NH$_4$F). Prior to anodization, Ti wire was degreased by sonicating in acetone and ethanol for 15 mins each then air dried. Anodisation bath was saturated with air, as to provide sufficient oxygen for oxide growth and 3.0 vol% 1.0 M K$_2$CO$_3$ was added at the middle of anodizing experiment. This was to investigate the influence of such salt on the morphology of anodic film as well as on investigating the adherence of the film. The anodization voltage was kept constant at 60 V for 20 mins anodizing time. The anodized Ti wires were then rinsed in deionized water and subsequently annealed at 400 °C in air for 2hrs to induce phase formation.

AgNPs were prepared by reduction of Ag salts in *K. brevifolia* extract (KBE) as reductant. 5 g of *K. brevifolia* dried powder was soaked in 100 mL deionized water at 70 °C for 1 hr. The extracts were filtered through Whatman No. 1 filter paper. This solution was considered as 100% *K. brevifolia* extract (KBE). 1 mL KBE was added to 9 mL 2 mM silver nitrate solution at room temperature for 90 mins reaction time. Once the reaction was completed, AgNPs were dispersed on TNTs by wet impregnation technique. The as-synthesized TNTs/AgNPs were dried in an oven at 60 ± 3 °C. The morphology of the fabricated TNTs/AgNPs was evaluated by field emission scanning electron microscopy (FESEM, Hitachi S3700N), energy-filtered transmission electron microscopy (EFTEM, PHILIPS CM12) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai™ G2 20 S TWIN) operated at 200 kV with a LaB$_6$ filament hybrid with selected area electron diffraction (SAED). The chemical
composition of the samples has been obtained with energy dispersive X-ray spectroscopy (EDX) using SEM instrument equipped with Bruker Quantax EDX system. The catalytic activity was studied by measuring decolouration of 30 ppm MB in the presence of TNTs/AgNPs and TNTs only. 1 mL 0.1M NaBH\textsubscript{4} was also added to the MB solution as to investigate its influence on the removal efficiency (\%RE) of MB. 4.0 mL capacity quartz tube was used to contain the solution and catalysts and the tube was left in the dark for 60 mins. Then the quartz tube was exposed to visible light and time-dependent absorption data points of the peak at 664 nm were recorded after every 10 mins.

3. Results and discussion

Figures 1(a) and (b) are FESEM images (surface and cross section) of anodised Ti wire in the presence of air bubble and K\textsubscript{2}CO\textsubscript{3}. As can be seen similar to the case of KOH [4] or NaOH [5] addition, the presence of basic salt, K\textsubscript{2}CO\textsubscript{3} did not hinder the formation of TNTs. As reported by Bashirom \textit{et al} [6] the adherence of the anodic film to the underlying substrate was weakened and can peeled off when adding K\textsubscript{2}CO\textsubscript{3} in electrolyte due to evolution of CO\textsubscript{2} gas during anodisation process. But in our case, the TNTs produced have better mechanical stability and were not peeled off from Ti wire. To increase the adherence of TNTs on Ti wire substrate as well as induce the phase formation, the TNTs were annealed at 400 °C in air for 2 hrs. Annealing causes the fluoride rich layer to sublime and makes TNTs attached to the substrate through a newly formed thermal oxide layer in between [7]. TNTs grown in this condition have length of 7.30 ± 0.46 µm, 74.59 ± 9.22 nm inner diameters and wall thickness 33.51 ± 4.56 nm. Table 1 shows the comparison of length and diameter of TNTs using various conditions of anodisation. It can be seen clearly that the length and diameter of TNTs prepared from this experiment shows better length and diameter with shorter anodisation time.

![Figure 1. FESEM images of (a) surface (b) cross section of pristine TNTs](image)

| Electrolyte, voltage, substrate | Time, mins | Length, µm | Inner diameter, nm | Wall thickness, nm | Reference |
|-------------------------------|------------|------------|-------------------|-------------------|-----------|
| Eg/NH\textsubscript{4}F/KOH, 60 V, Ti foil | 30 | 6.1 | 50 | 50 | [4] |
| Eg/NH\textsubscript{4}F/NaOH, 60 V, Ti foil | 60 | 23 | 175 | - | [5] |
| Eg/NH\textsubscript{4}F, 20 V Ti wire | 30 | 0.3 | 60 | - | [8] |
| Eg/NH\textsubscript{4}F/K\textsubscript{2}CO\textsubscript{3}, 60 V, Ti wire | 20 | 7.30 ± 0.46 | 74.59 ± 9.22 | 33.51 ± 4.56 | Present work |

To prepare TNTs/AgNPs, we prepared the AgNPs via salt reduction technique utilising KBE as reductant. TEM image in Figure 2 (a) shows the appearance of the AgNPs produced by KBE. As seen from TEM image, the shape of colloidal AgNPs is quasi-spherical and the particles are highly dispersed. The particle size of AgNPs as obtained from TEM is in the range 10-30 nm with average particles of 22.3 nm as shown in Figure 2 (b). The AgNPs were then dispersed on TNTs by wet impregnation technique. After AgNPs deposition as seen from Figures 3 (a) and (b), the surface morphology and walls
features have not changed but the existence of AgNPs as spherical particles distributed around the walls of the nanotubes is rather obvious.

![Figure 2](image)

**Figure 2.** (a) EFTEM image of AgNPs (b) Histogram for particle size distribution of AgNPs

In Figure 4, the morphology and crystallinity of TNTs/AgNPs were explored using HRTEM and SAED. Figure 4 (a) displays the HRTEM image of TNTs/AgNPs showing (101) lattice fringe of anatase TNTs (d = 0.35 nm) and AgNPs (d = 0.24 nm). The darker image on TNTs is AgNPs dispersed on the surface of TNTs. SAED pattern as shown in Figure 4 (b) further confirms this observation.

![Figure 4](image)

**Figure 4.** (a) HRTEM images of TNTs/AgNPs and (b) SAED

Figure 5 shows the EDX spectrum for TNTs/AgNPs sample. The peak at 0.277 eV is related to carbon species, whereas the peak at 0.525 eV and 0.677 eV are related to oxygen and fluorine species respectively. The common peak around 0.452 eV belongs to titanium species and peak at 2.984 eV is assigned to silver atom decoration on TNTs. The wt% each element is 2.49%, 39.72%, 21.71%, 1.62% and 34.47% for carbon, titanium, oxygen, fluorine and silver respectively as summarize in insect table in Figure 5.
For catalytic study, the MB degradation measured by %RE in aqueous solution with NaBH₄ was carried out in the presence of TNTs/AgNPs and TNTs (control) under visible light. MB has a main maximum peak at 664 nm due to the azo bond of the dye. As seen from Figure 6, for both samples, the %RE increased very slowly in dark. Thus, no obvious degradation of dye can be observed indicating extremely poor degradation of dye under dark despite the presence of catalysts. When the solution was placed under visible light for another 80 mins, degradation was seen to be much enhanced for the solution with TNTs/AgNPs. The maximum %RE for TNTs/AgNPs is 63% compared to pristine TNTs only around 17%. This indicates the success in forming visible light activated catalysts for dye degradation. The effect of NaBH₄ to degradation of MB is as sacrificial reagent (hole scavenger). The positive holes at valence band ($h^+_{VB}$) of TNTs will consumed through the oxidation reaction with NaBH₄ as electron donor irreversibly. The remaining photo-generated electrons will then reduce MB to less harmful substances.

**Figure 5.** EDX spectrum and data for TNTs/AgNPs sample

**Figure 6.** %RE of MB dye by TNTs/AgNPs and TNTs (control) under visible light.

Figure 7 shows the pseudo-first order and pseudo-second order kinetics study of TNTs/AgNPs and TNTs for degradation of MB respectively. The results imply that the photo-degradation of MB obeys the pseudo-first order kinetics. The corresponding linear relationships of ln ($C_t$/C₀) versus reaction time are shown in Figure 7 and the rate constant, $k$, is calculated from the slopes of the fitted straight lines. The rate constant obtained are $7.5 \times 10^{-3}$ and $6.0 \times 10^{-5}$ cm$^{-1}$ for TNTs/AgNPs and TNTs (control) respectively. The improvement progress for TNTs/AgNPs compared to bare TNTs was attributed to the localized surface plasmon resonance (SPR) that enables AgNPs to absorb light in the visible region [9]. Similar findings were reported by Nyein et al [5] whereby deposited AgNPs were found to enhance photochemical properties of their nanotubes in visible region of sunlight. According to them, the influence of AgNPs on TNTs are to extend the absorption of light of TNTs in the visible region and help in reducing recombination of photo-generated charge carriers due to effect of SPR produced by
oscillation of surface electrons. Table 2 shows the reaction rate constant (k), \( R^2 \) value and removal efficiency (%RE) for pseudo-first order and pseudo-second order kinetics of TNTs/AgNPs and pristine TNTs.

### Table 2: Pseudo-first, pseudo-second order kinetics and %RE for TNTs

| Sample          | Pseudo-first order | Pseudo-second order | % RE |
|-----------------|--------------------|---------------------|------|
|                 | \( k \)           | \( R^2 \)           | \( k \) | \( R^2 \) |       |
| TNTs/AgNPs      | 7.5 x 10^{-3}     | 0.9807              | 5.0 x 10^{-4} | 0.9754 | 62.97 |
| TNTs            | 6.0 x 10^{-5}     | 0.4002              | 3.0 x 10^{-6} | 0.4000 | 17.77 |

4. Conclusion

TNTs/AgNPs have been successfully fabricated firstly by anodisation in anhydrous fluorinated/ethylene glycol/carbonated electrolyte and then dispersing AgNPs on the TNT arrays by wetness impregnation technique. The morphology of TNTs/AgNPs shows the TNTs produced highly ordered 7.30 ± 0.46 µm long with 74.59 ± 9.22 nm inner diameters and wall thickness 33.51 ± 4.56 nm. Photocatalytic study shows that TNTs/AgNPs are able to reduce MB with around 63% compared to bare TNTs (control) only 17% under visible light illumination. The reaction rate values for the degradation MB are 7.5 x 10^{-3} ind 6.0 x 10^{-5} min^{-1} for TNTs/AgNPs and TNTs respectively. AgNPs has contributed to the activation of the composite under visible light perhaps due to the SPR of the AgNPs as well as electrons transfer process to the conduction band of TiO₂.

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