Surfactant-Free Electrodeposition of Ag Dendrites as Photocatalyst for Methylene Blue Degradation

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Abstract. Ag dendrites have successfully fabricated through square-wave electrodeposition method. The electrochemical properties of Ag dendrites were examined via electrochemical impedance spectroscopy and cyclic voltammetry techniques in a solution containing 0.5 M KCl. It was found that Ag dendrites demonstrated equivalent series and charge transfer resistance of 91.3 Ω and 473.7 Ω, respectively. The highest specific capacitance value of Ag dendrites obtained 0.98 F/g at scan rate 10 mV/s. The recorded photocatalytic activities towards methylene blue (MB) degradation under UV light irradiation showed that photocatalytic performance of Ag dendrites reaches approximately 41.88%.

1. Introduction
The rapid development of the textile industry in recent decades has negative impacts on water quality due to untreated dye wastewater. Approximately 10-15% of dye wastewater discharged to the environment during the dyeing process takes place where the dye contained less than 50% potentially carcinogenic azo group [1]. Azo dye pollutants that released into the environment is continuously able to inhibit sunlight penetration into the water and disrupt the lives of aquatic plants [2]. One of azo dye which generally used as textile dyes and laboratory materials is methylene blue (MB). MB is difficult to degrade and can cause a serious health problem. Therefore some researchers have tried to find a decomposition technique of dyes, such as adsorption [3], biodegradation [4], and photocatalysis [2]. Using appropriate catalyst materials, photocatalysis is simpler and effectively applied to degrade organic pollutants. One of good material used as a photocatalyst is metallic nanoparticles. Among various metal, silver is one of the most potentials as a photocatalyst because silver has the highest visible light absorption [5]. Also, silver has high optical cross-sectional characteristics, showed superior electrocatalytic activity, stable, and has good reproducibility. One way to obtain a high catalytic activity could be done by optimizing the morphology of nanostructures. Dendritic structures can enhance photocatalytic activity due to their unique properties, such as low density, large surface area, and provides more active sites [6]. However, most of previously reported synthetic method of Ag dendrites used environmentally unfriendly organic additive such as surfactants [7] and templates [8]. Those additives not only make the synthetic procedure complicated but also introduce impurities and release toxic chemicals to the environment [9]. Herein, we report a simple approach for controllable synthesis of Ag dendrites by applying square wave electrodeposition. As-made Ag dendrites with well-defined branched morphologies exhibited enhanced catalytic activity, which is promising as photocatalyst for methylene blue degradation.
2. Experimental

2.1. Synthesis
Ag dendrites were prepared by electrodeposition method directly on ITO substrates PET-coated. The chemicals used were AgNO\textsubscript{3} (99.9% Ag, Merck) and HNO\textsubscript{3}. In this work, the substrates were rinsed with ethanol and double distilled water before electrodeposition process.

All electrodeposition processes were performed in a three-electrode cell using a Pt wire as the counter electrode, ITO as the working electrode, and Ag/AgCl as the reference electrode. The upper potential limit, lower potential limit, and pulse duration were 1.75 V (Ag/AgCl), –0.3 V (Ag/AgCl) and 100 ms, respectively. The applied potentials were controlled with an eDAQ potentiostat model EA163 and Ecorder 401. After the electrodeposition, the resultant sample was rinsed using double-distilled water and dried.

2.2. Characterization
The morphology of the Ag dendrites was characterized by FEI Quanta 650 scanning electron microscope operated at 20 kV. To confirm Ag in deposits thus verified by energy dispersive X-ray Oxford Instruments EDX. Electrochemical impedance spectroscopy (EIS) measurement was performed using an electrochemical impedance analyzer (EDAQ; ERZ100) embedded to a potentiostat (EDAQ;163). A Platinum wire was used as the counter electrode, Ag/AgCl was used as a reference electrode and Ag dendrites films were used as the working electrode. All electrodes were soaked in a cell containing an electrolyte solution of 0.5 M potassium chloride (KCl).

2.3. Photocatalytic activity measurement
The photocatalytic activity of Ag dendrites was appraised by the degradation of MB. In this work, Ag dendrites film was prepared in 5 ppm MB solution. Then the solution was irradiated with UV and the absorbance of the solution was measured with GBC Cintra 2020 UV-VIS Spectrophotometer at a wavelength of 664 nm. Every 20-second reaction, approximately 3 mL of the solution measured its absorbance until 30 min irradiation. The same procedure was performed on the 1-9 ppm MB standard solution to obtain the calibration curve. Furthermore, the catalytic activity of MB degradation for ITO substrate was also measured. The results of absorbance measurements were then used in the linear regression equation of the MB solution so that MB concentrations were obtained. Thus, the photodegradation efficiency of MB is calculated as a degradation percentage.

3. Results and Discussion

3.1. Morphological analysis
In this work, Ag was synthesized by the electrodeposition method with 600 s deposition time. Figure 1a shows SEM images of Ag dendrites with the magnification of 10,000-fold magnification. Ag dendrites were formed showing the main trunk with secondary branches. The morphology of the crystal strongly depended on the distance of the formation conditions and thermodynamic equilibrium. According to the literature, dendrites are generally formed under non-equilibrium growth conditions [10]. The whole growth processes occur in a non-equilibrium state, as the fast nucleation and growth contribute to the formation of complicated structures. In this study, we used a lower negative potential compared than the standard reduction potential of Ag, which resulted in a non-equilibrium condition. Figure 1b shows EDX spectra of Ag dendrites with 600 s deposition time. From the spectra, it is indicated that Ag was presented in the deposit, while other elements come from the substrates.
3.2 Electrochemical Properties

To understand the electrochemical properties of Ag dendrites on the ITO substrate, electrochemical impedance spectroscopy (EIS) was applied to investigate the electrical conductivity and ion transfer of the cells. Impedance testing is performed using EIS on the test cells in the frequency range between 1 Hz to 10 kHz in 0.5 M KCl solution as an electrolyte.

Figure 2. Nyquist plots of Ag dendrites at 600 s deposition time.

Figure 2 shows the Nyquist plot between real impedance and imaginary impedance in Ag dendrites of 600 s deposition time. The intercept value from the plot on the axis at high frequencies shows the equivalent series resistance (R_s) value, which includes inherent resistance to the material, electrolyte resistance, and contact resistance on the interface between electrodes and electrolytes [11]. The charge-transfer resistance R_{ct} or Faraday resistance is correlated with the intercalation and deintercalation of ions. The charge transfer resistance (R_{ct}), which results from the diffusion of electrons, can be calculated from the diameter of the semicircle in the high-frequency range. The result shows that R_s and R_{ct} value of Ag dendrites at 600 s deposition times were 91.3 Ω and 473.7 Ω. These results indicate good conductivity due to low internal electrode resistance.
Figure 3. Specific capacitances of Ag dendrites at five scan rates.

The measurement of cyclic voltammetry of Ag dendrites was carried out at five different scan rates and each sample was measured 10 test cycles in the voltage range -0.9 V to -0.2 V. The calculated specific capacitances are plotted in Figure 3. Figure 3 displays a decreasing trend of specific capacitance value with the raise of scan rate. Slow scanning rate allows the electrolyte to penetrate the material pores more thoroughly and enlarge the contact with the electrode surface then producing a greater capacitance value [12]. Whereas at higher scanning speeds, positive ions in the electrolyte can only approach the outer surface of the electrode resulting in a smaller capacitance value [13].

3.3. Photocatalytic activity
The degradation of Methylene Blue (MB) was chosen to evaluate the photocatalytic performance of the as-prepared nanostructures. Methylene blue has a maximum absorption peak at 664 nm. Figure 4 reveals the absorption spectra of the MB solution under UV light until 30 minutes irradiation with Ag dendrites as photocatalyst. It can be seen that the value of intensity is decreases due to chromophore degradation. When illuminated by light, the electrons in the photocatalyst material will be activated to move from the valence band to the conduction band. Thus, it causes holes (positive charges) in the valence band, which then reacts with H₂O to form hydroxyl radicals which have strong oxidation so that it will degrade organic compounds. The electrons in the conduction band (negative charge) also reduce organic compounds [14].

Figure 4. Absorbance spectrum of MB degradation under UV irradiation.

Figure 5 displays the degradation percentage for Ag dendrites 600 s deposition time was 41.88% after 30 minutes of UV irradiation. As a reference, the photocatalytic activity with only ITO is slightly
degraded. There are two ways can be tried to enhance the photocatalytic efficiency of the as-prepared materials. First, the decrease in the recombination of the photo-generated electrons and holes allows them to take part in the photocatalytic reaction. Second, optimizing the morphology and structure of the products can get more reactive species. In our experiments, an enhanced photocatalytic activity could be attributed to dendritic morphology. This structure could provide more active site to adsorb reactive species and allow effective transport for the reactant molecules to get to the active sites due to reduced diffusion path of ions. From figure 5, it can be seen that Ag dendrites have good photocatalytic performance because of wider branch, lower charge transfer resistance, and higher specific capacitance value. Hence, it is clearly understood that dendrites morphology on silver has enhanced its photocatalytic activity.

![Figure 5. Photocatalytic degradation of MB under UV irradiation.](image)

4. Conclusion
In this work, a novel Ag dendrites on ITO substrates has been achieved through square-wave electrodeposition method without any surfactant used. Such dendritic structures with broad branch give effective degradation of organic dye molecules. The as-prepared substrates show that Ag dendrites a good candidate for photocatalysis application towards methylene blue degradation with the degradation percentage of 41.88 % in just 30 minutes of UV irradiation.

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