

LOADING EFFECT OF Ag NANOPARTICLES ON PHOTOCATALYTIC ACTIVITY OF TiO₂ NANOROD ARRAYS PREPARED BY HYDROTHERMAL METHOD

Rutile-TiO₂ nanorod thin films were formed on Ti disks via alkali treatment in NaOH solutions followed by heat treatment at 700°C. Ag nanoparticles were loaded on nanorods using a photo-reduction method to improve the photocatalytic properties of the prepared specimen. The surface characterization and the photo-electrochemical properties of the Ag-loaded TiO₂ nanorods were investigated using a field-emission scanning electron microscope (FE-SEM), X-ray photoelectron spectroscopy (XPS), UV-Vis spectroscopy and electrochemical impedance spectroscopy (EIS). The TiO₂ nanorods obtained after the heat treatment were 80 to 180 nm thick and 1 μm long. The thickness of the nanorods increased with the NaOH concentration. The UV-Vis spectra exhibit a shift in the absorption edge of the Ag-loaded TiO₂ to the visible light range and further narrowing of the bandgap. The decrease in the size of the capacitive loops in the EIS spectra showed that the Ag loading effectively improved the photocatalytic activity of the TiO₂ nanorods.

Keywords: TiO₂ nanorods, Ag nanoparticles, Hydrothermal, Electrochemical impedance spectroscopy, UV-Vis spectroscopy

1. Introduction

TiO₂-based nanostructures have been extensively studied owing to their promising physical and chemical properties, such as a high specific surface area, low cost of synthesis, high photo-activity, and environmental stability [1,2]. One-dimensional TiO₂ nanostructures such as nanorods [3-5] have also been extensively investigated because of their superior electrochemical properties that are attributed to their dimensional anisotropy. Nanorods have a highly porous surface and smoother orientation [6] than other TiO₂ nanostructures, resulting in a larger surface area without an increase in the dimensions. Increases in the photo-activity of TiO₂-based nanostructures within the visible range of solar radiation and the efficiency of TiO₂ as a photocatalyst were achieved by doping or decorating noble-metal elements on TiO₂-based nanostructures [7,8]. Noble-metal nanoparticles, such as Ag nanoparticles, act as an active component of a plasmonic photocatalyst because of surface plasmon resonance [7,9].

The hydrothermal technique is a well-known method for fabricating TiO₂ nanorods on thin films [10,11]. Unfortunately, the applications of TiO₂ nanorods are limited, and no report has demonstrated the fabrication of TiO₂ nanorods on bulk Ti. In this

study, sodium titanate and rutile-TiO₂ nanorod thin films were formed on Ti disks via alkali treatment in NaOH solutions and subsequent heat treatment. Then, Ag nanoparticles were loaded onto the obtained nanorods using a photo-reduction method to improve their photocatalytic properties.

2. Experimental

Commercially pure Ti disks (grade 2, purity > 99.9 wt%, Kobe Steel Co., Japan) with a diameter of 15 mm and thickness of 3 mm were used as starting materials. The Ti disks were immersed in 10 mL of different NaOH solutions at 60°C in an oven (vacuum drying oven, Jisico, Korea) for 24 h to enable the formation of sodium titanate layers on the surfaces of the specimens. The alkali-treated samples were annealed at 700°C for 2 h in a muffle box furnace at a heating rate of 5°C min⁻¹. The specimens were immersed in a 0.1 M AgNO₃ (Duksan, Korea) solution for 30 min and exposed to UV light (VL-4.LC, Vilber Lourmat, France) for 30 min. The microstructure was observed using FE-SEM (S-4700, Hitachi, Japan). The analysis was performed using XPS (VG Multilab 2000, Thermo VG Scientific), where the

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sample surface was excited with X-ray radiation from a monochromatic Al source. The energy resolution was 0.6 eV, measured for the Ag 3d5/2 core-level spectrum. UV-Vis absorption spectra were measured to study the optical response of the Ag-loaded nanorods using UV-VIS-NIR spectrometer (U-3501, Hitachi, Japan). EIS was employed to evaluate the properties of the various photocatalysts under AC polarization. EIS experiments were performed using a PARSTAT 2273 (Princeton Applied Research) power supply in a 0.1 M sodium sulfate (Na_2SO_4 , Duksan, Korea) solution over a frequency range of 100 kHz to 100 mHz with an amplitude of 10 mV and a DC potential of +0.2 V_{sce} (one V_{sce} is the potential of a standard calomel reference electrode). These studies were conducted in the dark and under UV illumination (8 W UV lamp, $\lambda = 365$ nm). In the electrochemical cell, a platinum electrode was used as the counter electrode and an Ag/AgCl/KCl (sat'd) electrode was used as the reference electrode. Nyquist plots were extracted from these experiments, and the data were evaluated and fitted to the suggested equivalent circuit using the ZSimpWin program (EChem Software).

3. Results and discussion

Fig. 1 shows FE-SEM images, XPS survey and Ag-3d spectra of specimens treated with various NaOH concentrations followed by heat treatment at 700°C. The shape and size of the

specimens following the deposition of Ag nanoparticles on the nanorods suggest that the deposition process did not alter the nanorod structure. The size of the Ag nanoparticles firmly attached to the nanorods was approximately 30 to 40 nm, and they were uniformly distributed along the surface of the nanorods. According to the XPS analysis in Fig. 1(d) and 1(e), the atomic percent values of Ag on samples treated with 3, 5, and 7 M NaOH were 11.46, 6.95, and 5.61, respectively. The Ag spectra comprise two peaks, including Ag 3d5 and Ag 3d3, separated by 5.8 eV. The first peak of Ag 3d5 at 367.15 eV is related to the metallic Ag atoms in the Ag clusters. The second peak of Ag 3d3 at 373 eV is related to Ag oxide or other bonds from the Ag surface atoms [12]. The concentration of the NaOH solution before loading played an important role in the attachment of the Ag nanoparticles to the nanorods. As shown in the graph, the intensities of the Ag peaks gradually decrease as the NaOH solution concentration increases.

Fig. 2 shows the XRD patterns of the Ag-loaded nanorod specimens treated with 3, 5, and 7 M NaOH. The Ti peaks from the substrate are mainly present owing to the low thickness and density of the nanorod layer. As expected, the fraction of the sodium titanate phase increased with the NaOH concentration used for the alkali treatment. The specimens appeared to exhibit narrower peaks following the loading of Ag nanoparticles. Furthermore, loading the Ag nanoparticles tended to stabilize the TiO₂-rutile and sodium titanate phases by modifying their lattice parameters.

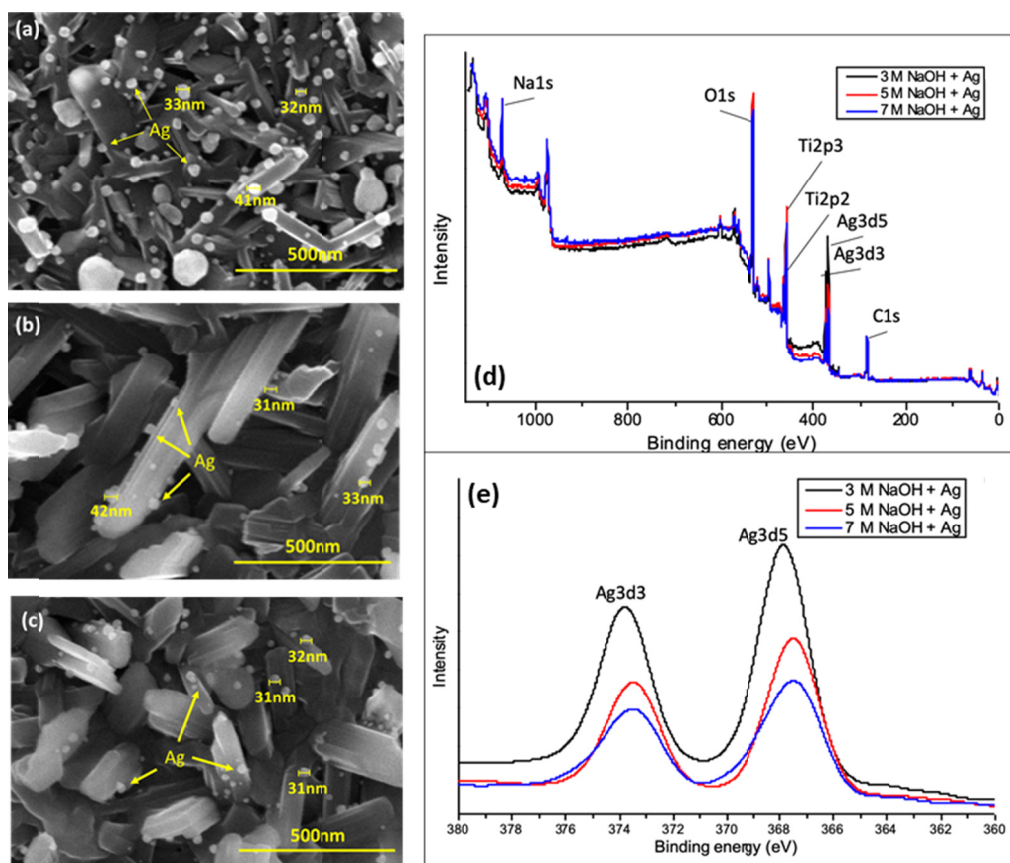


Fig. 1. FE-SEM images of specimens treated with various NaOH concentrations followed by heat treatment at 700°C and loading with Ag nanoparticles; (a) 3 M, (b) 5 M, and (c) 7 M and XPS spectra of alkali-treated specimens followed by Ag nanoparticle loading; (d) survey and (e) Ag 3d spectra

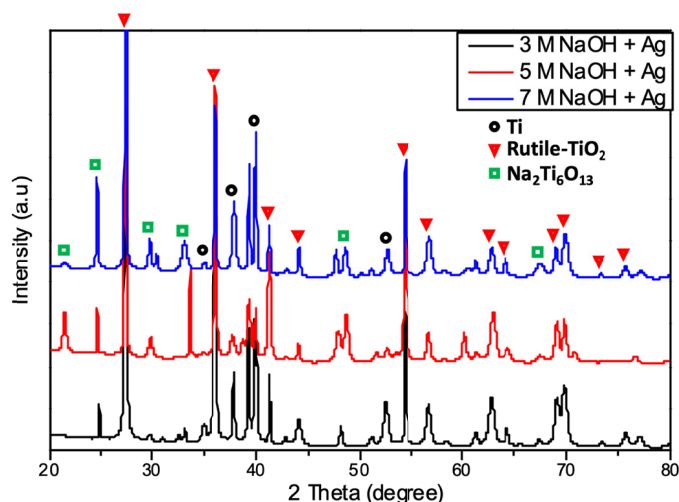


Fig. 2. X-ray diffraction patterns of specimens treated with various NaOH concentrations followed by heat treatment at 700°C and loading with Ag nanoparticles

Fig. 3 shows UV-Vis absorption spectra of specimens treated with 3, 5, and 7 M NaOH followed by heat treatment at 700°C and Ag nanoparticle loading. Compared to the undoped sample, the Ag-loaded specimens demonstrate a noticeable shift in the absorption edge toward the visible light region. Loading Ag nanoparticles on the nanorods significantly improved the visible light (400 to 700 nm) absorbance capability of the samples. The absorption edge and bandgap of the studied samples are summarized in Table 1. Rutile-TiO₂ had a narrower bandgap of 3.056 eV compared to that of typical anatase-TiO₂, which has a bandgap of 3.22 eV, according to Chen et. al. [13]. The specimen subjected to alkali treatment in 5 M NaOH before Ag loading exhibited a significantly higher absorption of visible light compared to the other samples. However, the sample subjected to alkali treatment in 7 M NaOH presented the narrowest bandgap. This behavior suggests that loading Ag nanoparticles onto the TiO₂ nanorods

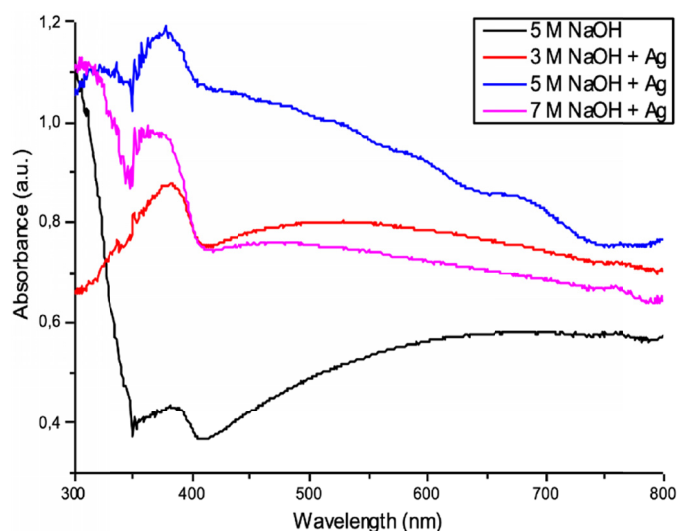


Fig. 3. UV-Vis absorption spectra of specimens treated with 3, 5, and 7 M NaOH at 60°C followed by heat treatment at 700°C and Ag nanoparticle loading

effectively shifted the absorption edge of the TiO₂ specimens toward the visible light range and narrowed the bandgap.

TABLE 1

UV-Vis parameters of specimens treated with 3, 5, and 7 M NaOH at 60°C followed by heat treatment at 700°C and Ag nanoparticle loading

Specimen	Edge absorption wavelength (nm)	Bandgap (eV)
5 M NaOH	405.6	3.056
3 M NaOH + Ag	411	3.016
5 M NaOH + Ag	407.9	3.039
7 M NaOH + Ag	415	2.987

Fig. 4 shows Nyquist plots, Bode plots, and equivalent circuit fitted for alkali-treated specimens heat-treated at 700°C followed by Ag nanoparticle loading in a dark environment and UV light irradiation. In both situations, the impedance spectra show two well-defined capacitive loops in the low- and high-frequency regions, suggesting the involvement of two-time constants. The high-frequency region represents the nanorod layer resistance, which can be attributed to the charge transfer reaction in the electric double layer. The low-frequency capacitive loop is related to the relaxation of mass transport in the solid phase. As shown in Fig. 4(a) and 4(b), the transition from the first to the second capacitive loop occurs at a frequency lower than 21 Hz. The increased concentration of the NaOH solution narrows the capacitive loops in both the high- and low-frequency regions of the specimens. The largest semicircle radius in both the dark and UV-irradiated environments was from the sample subjected to alkali treatment in 3 M NaOH, signifying the slowest charge-transfer in the electrode. The semicircle radius decreased as the concentration of NaOH increased, which suggests an increased charge-transfer rate in the electrode. The ratio of the nanorod size to the size of the Ag nanoparticles attached to the nanorods was also related to the charge transfer rate of the samples. The smallest nanorod size and the highest concentration of Ag nanoparticles attached to the surface of the nanorods resulted in the largest capacitive loop and the lowest charge transfer rate. Based on the Bode plot in Fig. 4(c), the overall impedance decreased in the following order: 3 M > 5 M > 7 M. Furthermore, it was significantly lower after the specimens were exposed to the UV environment. Intermittent changes in the total impedance values suggest the interaction of the solution with two kinds of layers on the surface of the Ti substrate. The first layer was composed of porous nanorod structures and had direct contact with the environment and the second layer. The second layer, which was mainly formed of dense TiO₂, acted as a barrier partially connected to the environment and the porous nanorod layer. The presence of these two layers significantly influenced the photocatalytic behavior of the specimens. The EIS spectrum data were fitted to an equivalent circuit model, as shown in Fig. 4(d). In the equivalent circuit, R_s, R_p, and R_{ct} represent electrolyte resistance, polarization resistance, and charge-transfer resistance between the nanorods and the substrate.

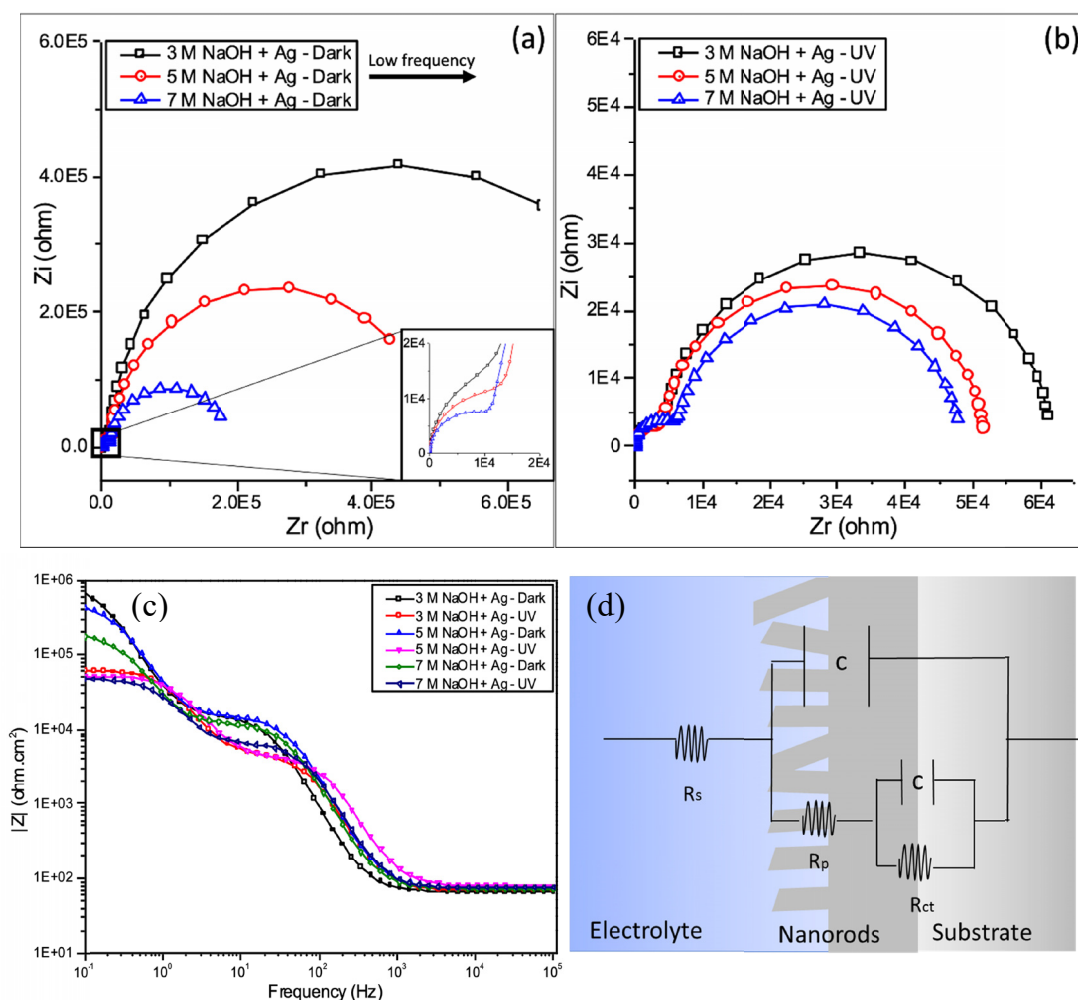


Fig. 4. Nyquist plots of alkali-treated specimens heat-treated at 700°C followed by Ag nanoparticle loading measured in (a) a dark environment, (b) under UV light irradiation, (c) Bode plots of $|Z|$ vs. frequency of alkali-treated specimens, and (d) equivalent circuit fitted for alkali-treated specimens

4. Conclusions

The Ag nanoparticles loaded on the surface of the nanorods showed a uniform distribution. The UV-Vis spectra demonstrate that Ag loading on the nanorod structures substantially improved the visible light absorbance of the nanorods. This improvement was the result of shifting the absorption edge of the TiO_2 to the visible light range and narrowing the bandgap. The electrochemical behaviors of the specimens showed considerable changes in the charge transfer rate after Ag nanoparticle loading. The decrease in the size of the capacitive loops in the EIS spectra showed that the Ag loading effectively improved the photocatalytic activity of the nanorods.

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