Development of Ag/TiO_2 Composite electrode for Photoelectrochemical Water Splitting

การพัฒนาอิเล็กโทรดจากวัสดุคอมโพสิตระหว่างไทเทเนียมไดออกไซด์ และอนุภาคนาโนซิลเวอร์ สำหรับการแยกน้ำด้วยไฟฟ้าเคมีทางแสง

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ABSTRACT

The purpose of this work is to investigate photoelectrochemical performance of composite electrode between titanium dioxide (TiO_2) and silver nanoparticles (AgNPs). AgNPs were employed due to a surface plasmon resonance effect that can improve visible light absorption and decrease electron-hole recombination of TiO_2. Preparation of Ag/TiO_2 composite electrode with different amount of AgNPs from 20, 40, 60, 80 and 100 ppm were carried out by ball milling process. After that, characterization by XRD, Raman, UV-Vis, SEM, EDX and FTIR technique were examined. Finally, photoelectrochemical performance were performed using cyclic voltammetry measurement. CV curves showed a current density at 1.23 V (vs. Ag/AgCl) for TiO_2 and Ag/TiO_2 electrode which are 1.15 and 1.83 $\mu A/cm^2$. It can be concluded that an addition of AgNPs resulted in better photocurrent which related to higher photoelectrochemical performance in water splitting for hydrogen production.

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพของเซลล์ไฟฟ้าเคมีทางแสงจากวัสดุคอมโพสิตระหว่างไทเทเนียมไดออกไซด์และอนุภาคนาโนซิลเวอร์ด้วยเทคนิคบอลมิลลิ่ง ในงานนี้ใช้อนุภาคนาโนซิลเวอร์เนื่องจากคุณสมบัติช่วยเพิ่มประสิทธิภาพการดูดกลืนแสงในช่วงวิซิเบิลและลดการรวมตัวกันของคู่อิเล็กตรอนและโฮลของไทเทเนียมไดออกไซด์ โดยในการวิจัยได้เปรียบเทียบปริมาณความเข้มข้นของอนุภาคนาโนซิลเวอร์ที่ใช้คือ 20 40 60 80 และ 100 ppm แล้วนำไปวิเคราะห์องค์ประกอบทางเคมี โครงสร้างผลึก สัณฐานวิทยา และสมบัติทางแสงด้วยเทคนิค XRD, Raman, UV-Vis, SEM, EDX และ FTIR ตามลำดับ จากนั้นทำการวิเคราะห์สมบัติเคมีไฟฟ้าทางแสง จากผลการศึกษาเบื้องต้นพบว่าที่ความต่างศักย์ 1.23 โวลล์ เทียบกับซิลเวอร์/ซิลเวอร์คลอไรด์ ฟิล์มไทเทเนียมไดออกไซด์และฟิล์มคอมโพสิตระหว่างไทเทเนียมไดออกไซด์และอนุภาคนาโนซิลเวอร์ มีค่าความหนาแน่นกระแสเท่ากับ 1.15 และ 1.83 $\mu A/cm^2$ จากผลการทดลองสรุปได้เบื้องต้นว่าอนุภาคนาโนซิลเวอร์ช่วยเพิ่มความหนาแน่นกระแสซึ่งสัมพันธ์กับประสิทธิภาพของเซลล์ไฟฟ้าเคมีทางแสงของการแยกน้ำในการผลิตไฮโดรเจน

Keywords: Photoelectrochemical water splitting, Semiconductor materials, Silver nanoparticles
คำสำคัญ: เซลล์ไฟฟ้าเคมีทางแสง วัสดุสารกึ่งตัวนำ อนุภาคนาโนซิลเวอร์

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Introduction

Nowadays, development of new alternative energy sources becomes critical tissue because fossil fuel including, petroleum, coal and natural gas will be exhausted in the future (IRENA, 2019). Hydrogen is a renewable energy attracted special attention as it is clean, excellent energy carrier and highly efficient compared to other energy resources (Zohuri, 2018). There are several processes for hydrogen production for example, stream reforming, plasma reforming, thermolysis and electrolysis (*Bičáková,* Straka, 2010). These days, solar energy conversion with photocatalytic reaction is promising because it can be applied on water splitting for hydrogen production. Photoelectrochemical (PEC) cell is an electrochemical device that can produces hydrogen from water using sunlight. Electronic transition of semiconductor materials which is used as a photoanode cause a chemical reaction, which split water molecules into H_2 and O_2 (Hidalgo, 2015). For this application, semiconductor materials have been widely studied including, TiO_2, ZnO, CdS and WO_3. Among of these materials, TiO_2 as a photocatalyst that is widely popular because it is non-toxic, low-cost, chemical, and thermal stability and outstanding photocatalytic properties (Eidsvåg et al., 2021). However, the main drawback of the TiO_2 is absorb only UV light region because the large bandgap energy of TiO_2 (3.0, 3.2 and 3.4 eV for rutile, anatase and brookite, respectively) and fast charge recombination of electron-hole pairs, which reduces photocatalytic reaction (Shen et al., 2018). Thus, the increasing of an absorption ability of TiO_2 to visible light region without reducing photocatalytic reaction has been of interest. Many studied shows that TiO_2 can be improve photocatalytic activity by doping with metallic or non-metallic elements such as gold, silver, copper and platinum (Doña-Rodríguez, Pulido Melián, 2021). It has been well known that AgNPs have been extensively studied because is easy to prepare compared to other elements. Additionally, a surface plasmon resonance effect of AgNPs can be improve a photocatalytic reaction of TiO_2 (Tai et al., 2021). Moreover, AgNPs on surface of TiO_2 act as electron acceptor, increasing visible light absorption and decreasing charge recombination. These cause by the fermi level of AgNPs is below the conduction band of TiO_2 (Lidiaine et al., 2015; Zada et al., 2017).

In this work, aims to development of Ag/TiO_2 composite electrode by ball milling which is simple, low energy consumption and a low-cost technique. Moreover, the different amount of AgNPs loading were examined. Characterization by XRD, Raman, UV-Vis, SEM, EDX and FTIR technique were tested to understand structural and chemical composition of the composite. Finally, the photoelectrochemical properties was used to study by CV technique.

Objectives of the study

1. To study effect of Ag/TiO_2 films with different amount of AgNPs by ball milling process
2. To study chemical composition, morphology and photocatalytic activity of Ag/TiO_2 films.

Materials and method

Preparation of Ag/TiO_2 by ball milling process

Silver nanoparticles (AgNPs) from PRIME Nanotechnology and Ethanol (C_2H_5OH, 95%) form RCL Labscan were used as purchased for preparation of TiO_2 and Ag/TiO_2. Firstly, TiO_2 (Degussa P25) 5 g was dispersed into 50 ml of AgNPs solution and gently stirred at 50°C for 30 minutes. Afterwards, Ag/TiO_2 solution was added into 120 ml of bottle wide mount and used ball mill machine to crush and grind the materials into a fine form. After 24 hours, Ag/TiO_2 were filtered and washed with ethanol several times and dried at 100°C for 48 hours. Finally, repeat this process with a different amount of AgNPs (20, 40, 60, 80 and 100 ppm, respectively).

Figure 1 TiO_2 and Ag/TiO_2 samples by ball milling process.

Preparation of Ag/TiO_2 films electrode

Ag/TiO_2 1 g was added into 20 ml of deionized water and gently stirred at 50°C for 1 hour. Before the thin film deposition, the FTO substates were washed with deionized water and ethanol by using an ultrasonic bath. After that, TiO_2 and Ag/TiO_2 films were casted onto FTO substrates by spin coating technique, using a different speed rates of 2000 rpm for 30 second followed by 3000 rpm each for 30 seconds at room temperature. Afterwards, Ag/TiO_2 films were dried at 80°C for 30 minutes to remove organic residues. Finally, electrode preparation of TiO_2 and $AgTiO_2$ films were carried out for photocatalytic activity test by using copper wire, copper tape and kapton tape as shown in Figure 2.

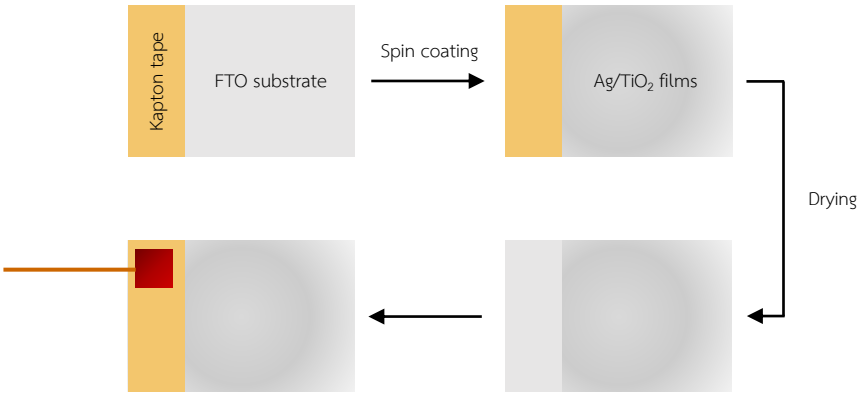

Figure 2 Electrode preparation of Ag/TiO_2 films

Characterization of Ag/TiO_2 films

Crystallinity and phase purity of TiO_2 and Ag/TiO_2 were characterized by x-ray diffractometer (PANalytical, EMPYREAN) with Cu-Kα radiation (λ =1.5406 A°). X-ray diffraction (XRD) patterns were recorded in the angular range (2θ) = 20 to 80°. The chemical structure was examined by Raman spectroscopy (HORIBA, XploRa plus) with an incident laser wavelength of 532 nm. The distribution and morphology of TiO_2 and Ag/TiO_2 were evaluated by using scanning electron microscope (LEO, 1450VP) after coating with gold. The UV-Vis absorption spectra of AgNPs were characterized using a UV-Vis spectrophotometer (Shimazu, UV-1800) in the range of 200 to 800 nm. Fourier transform infrared spectroscopy measurements were carried out using (Bruker, TENSOR27) in the range 400 to 4000 cm^{-1} at a resolution 0.5 cm^{-1}. The Cyclic voltammetry (CV) and Linear sweep voltammetry (LSV) curves were evaluated by using potentiostat and galvanostat.

Result and discussion

Crystallinity and phase purity of Ag/TiO_2

The XRD patterns of bare TiO_2 and Ag/TiO_2 as shown in Figure 3. The diffraction peaks of anatase phase located at 25.65°, 48.04° and 54.40° correspond to [101], [200] and [105] planes (Guillaume et al., 2018). The main diffraction peak of rutile phase was observed at 28.11 correspond to [110] plane because the high calcination temperature of TiO_2. Moreover, The Ag diffraction peaks are not clear due to at 38.06°, 48.21° and 63.15° were overlapped to diffraction peaks of TiO_2, which correspond to [111], [200] and [220] planes, respectively (Roy et al., 2014).

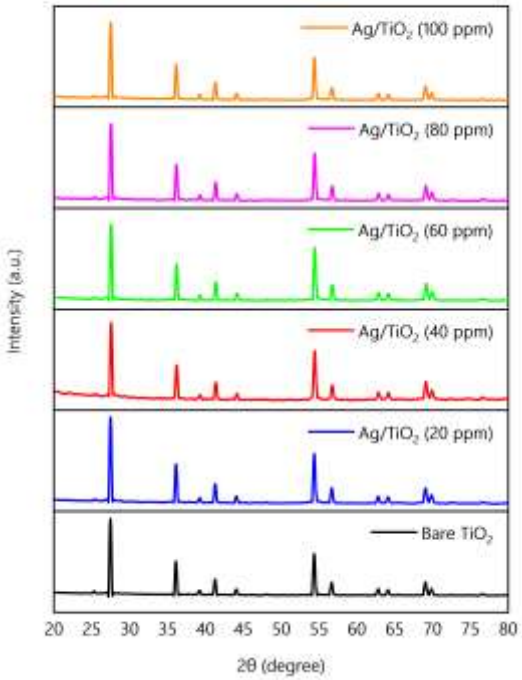

Figure 3 XRD patterns of TiO_2 and Ag/TiO_2 nanoparticles.

Figure 4 shows the Raman spectra of bare TiO_2 and Ag/TiO_2 samples. The peaks at 135, 445 and 610 cm^{-1} that correspond to the symmetries of B_{1g}, E_g and A_{1g}, respectively which is rutile phase of TiO_2 (Challagulla et al., 2017). In the case of Ag/TiO_2, the peaks at 237 cm^{-1} assigned to the stretching vibrations of Ag-N and Ag-O bonds. Moreover, the peaks at 1328 and 1587 cm^{-1} correspond to -COO stretching and C=O stretching vibration of carboxylate group. These peaks are well pronounced with increasing amount of AgNPs that confirm the presence of AgNPs on surface of TiO_2.

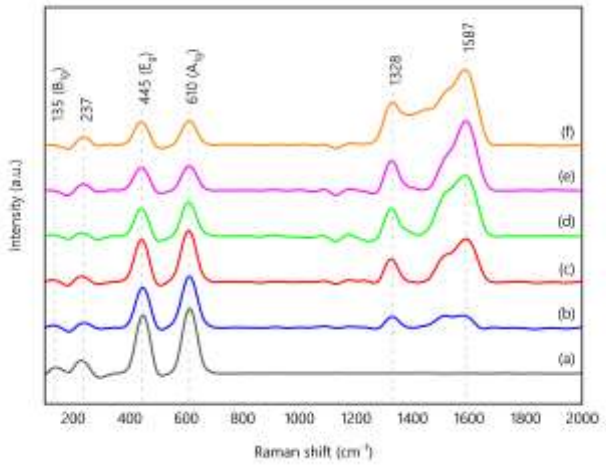

Figure 4 Raman spectra of (a) bare TiO_2 and (b-f) Ag/TiO_2 nanoparticles

Optical properties of AgNPs

The UV-Vis absorption spectra of all samples are shown in Figure 5. The absorption peak observed at ~400 nm in the visible range that correspond to the plasmonic absorption of AgNPs. The energy band gap was calculated using Tauc plot equation (Ahmed et al., 2021).

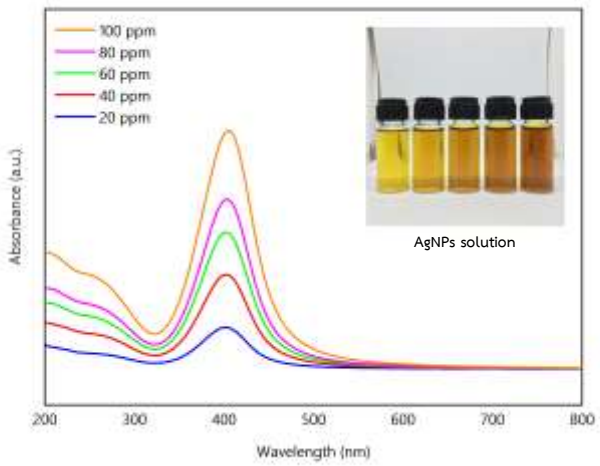

Figure 5 UV-Vis absorption spectra of AgNPs.

Morphology of TiO_2 and Ag/TiO_2

Figure 6a shows SEM image of bare TiO_2 where the particles are well distributed and spherical shape. The spherical shape particles have uniform size in the range of ~20-30 nm. The morphology of Ag/TiO_2 as shown in Figure 6b-f it was observed that the distributed of TiO_2 decreased with the increasing amount of AgNPs. In addition, the particle sizes of Ag/TiO_2 were decreased to ~15-20 nm because the crushing and grinding with ball milling process. The elemental composition of Ag/TiO_2 was detected by EDX analysis, which confirms the presence of oxygen (O), silver (Ag) and titanium (Ti), respectively as shown in Figure 6g.

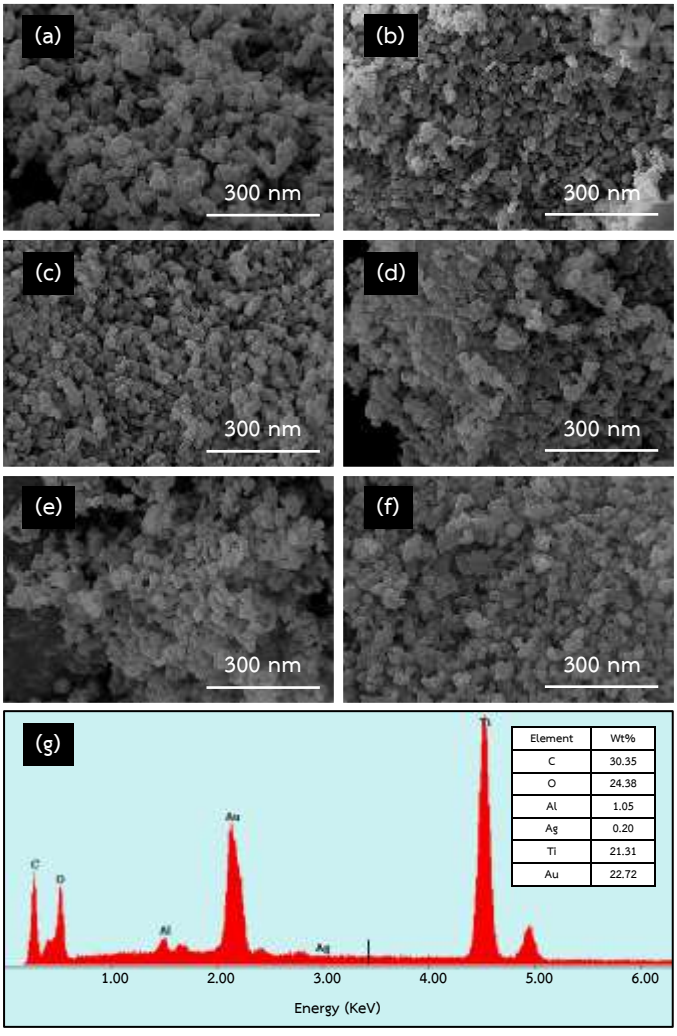

Figure 6 SEM images of (a) TiO_2, (b-f) Ag/TiO_2 at different concentration and (g) EDX spectra of Ag/TiO_2.

Chemical composition of Ag/TiO_2

Figure 7 shows the FTIR spectra recorded for TiO_2 and Ag/TiO_2. The position of the major peaks near 500 to 800 cm^{-1} correspond to the Ti-O-Ti stretching vibration of TiO_2. The peak at 442 cm^{-1} and 1635 cm^{-1} confirms the Ag-O bending vibration and O-H bending vibration of AgNPs, respectively. The peaks at 3310 cm^{-1} occurs form O-H stretching vibrations of TiO_2 due to absorption of water molecules from the moisture. The peaks near 775, 1160 and 1646 cm^{-1} are assigned as an interaction between AgNPs and TiO_2, which the intensity of this peak increased with increasing amount of AgNPs in composite samples (Sarteep et al., 2016).

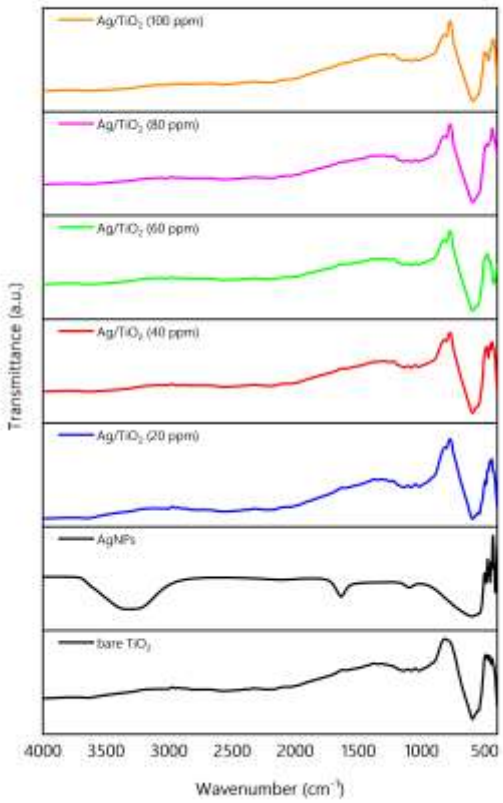

Figure 7 FTIR spectra of TiO_2 and Ag/TiO_2 nanoparticles.

Photocatalytic activity of Ag/TiO_2 films

The photocatalytic activity was carried out in three electrodes configuration using the TiO_2 and Ag/TiO_2 films as the working electrodes, a platinum wire as the counter electrode and an Ag/AgCl as the reference electrode. These electrodes were immersed in 0.5 M H_2SO_4 aqueous electrolyte. The current density was recorded by cyclic voltammetry at a scan rate of 50 mVs^{-1}, when a constant open circuit voltage was achieved, varying the potential from 0-2 V (vs. Ag/AgCl) under illumination condition.

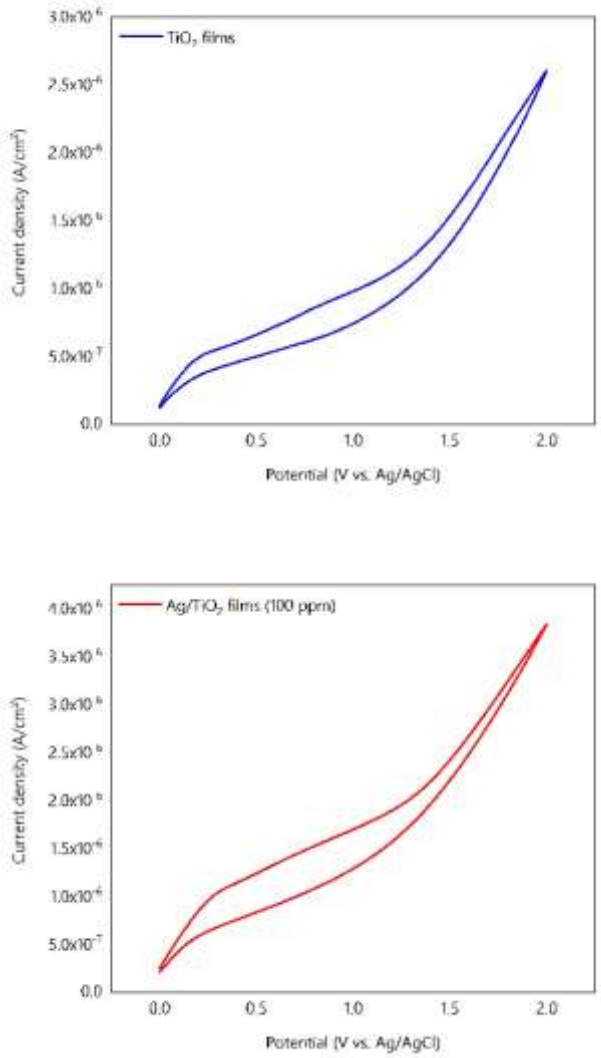

Figure 8 CV curves of the samples: (a) TiO_2 films and (b) Ag/TiO_2 films.

Form CV curves shown in Figure 8, a current density was measured for TiO_2 and Ag/TiO_2 films. A current density at potential 1.23 V (vs. Ag/AgCl) of TiO_2 and Ag/TiO_2 films were 1.15 $\mu A/cm^2$ and 1.83 $\mu A/cm^2$ under illumination condition, which continue to rise until reaching at maximum potential 2 V (vs. Ag/AgCl) corresponding to 2.60 and 3.86 $\mu A/cm^2$. It can be noticed that an addition of AgNPs resulted in better photocurrent which related to higher photoelectrochemical performance.

Conclusion

In this study, Ag/TiO_2 composite electrode containing different amount of AgNPs was preparation by ball milling process. The crystallinity and phase purity of bare TiO_2 and Ag/TiO_2 were characterized by XRD and Raman analyses, which confirm the rutile phase and presence of AgNPs on surface of TiO_2, respectively. FTIR spectra result confirmed the presence functional group and interaction of AgNPs on surface of TiO_2. SEM images show that the distributed and particles size of bare TiO_2 and Ag/TiO_2 nanoparticles in the range of 20-30 nm. The elemental composition of Ag/TiO_2 was detected by EDX analysis that confirms the presence of oxygen, silver and titanium, respectively. The UV-Vis absorption spectra of AgNPs shows an absorption peak at 400 nm. In addition, the preliminary result of photocatalytic activity was evaluated by potentiostat and galvanostat, which Ag/TiO_2 films showed an increase of current density at 1.23 V (vs. Ag/AgCl), under illumination condition compared to TiO_2 films. It can be concluded that a combination with the surface plasmon resonance of AgNPs and TiO_2 are effective way to improve the photocatalytic activity for water splitting reaction.

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