Cos as Co-Catalyst for Enhancing the TiO₂ Photoelectrochemical Water Splitting

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Abstract. Titanium dioxide is a semiconductor that widely applied because it is environmentally friendly and has good catalytic activity. However, the wide band gap of TiO₂ limits its application in photocatalytic activities. Cobalt sulfide (CoS) is extensively used as a photocatode in photoelectrochemistry because it has good electrochemical activity, low cost and non-toxic. The formation of p-n junction between TiO₂ and CoS can reduce the band gap of the former, and the load transfer of photoelectrochemical activity can be increased. TiO₂/CoS is a promising photocatalyst in enhancing photoelectrochemical performance. In this work, a TiO₂/CoS thin film was synthesized through hydrothermal method to study the effect of CoS on TiO₂ and improve the photoelectrochemical performance. Characterization were performed using X-ray diffraction, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy and UV reflectance. Results showed that as-synthesized TiO₂/CoS was a mixed phase of TiO₂ (anatase, rutile) and CoS with agglomerate-shaped small particles. The band gap of TiO₂ was reduced after CoS was loaded at 2.75 eV. The density of as-synthesized sample was 1.2572 mA at 1 V compared with Ag/AgCl under light irradiation.

1. Introduction

Hydrogen is an alternative energy that is used as fuel in fuel cell technology to produce electricity with a by-product in the form of water vapor. This technology is very environmentally friendly and can reduce the effects of greenhouse gases. Hydrogen is the most abundant element in the universe, but hydrogen is not found naturally as hydrogen gas on earth. Instead, this element can be extracted from various sources, especially from water [1]. The problem is that hydrogen production via water requires a huge amount of energy, and one of the most promising ways is to utilise solar energy. Photoelectrochemical (PEC) is among the several methods used for producing hydrogen with solar energy.

PEC water splitting, which represent another promising means for producing hydrogen, can be directly converted from solar energy to hydrogen [2]. This method was first performed by Fujishima and Honda in 1972 [3]. PEC water splitting require semiconductor materials as photoelectrodes, specifically n- and p-type semiconductors as photoanodes and photocatodes, respectively. The photoelectrode facilitates the
flow of electrons that are generated by light-induced chemical reactions. The band gap of photoelectrode semiconductors are higher that the redox potential of water (1.23 – 1.4 eV) [4]. PEC use various semiconductor metal oxides, but the most commonly used is TiO₂ due to its high catalytic and oxidative activities, abundance, low cost and non-toxicity [1]. However, TiO₂ semiconductors are only excited by ultraviolet light because they have a band gap of 3.2 eV and 3.0 eV for anatase and rutile, respectively [5]. To enhance the PEC performance, the structure of the material was set in nanosize to improve surface effectiveness and allow absorption in visible areas. Moreover, ion doping [6] and co-catalyst loaded [7] can be used to enhance the PEC performance.

Cobalt sulfide (CoS) is p-type semiconductor compound that exhibits good performance and non-toxic electrochemical activity with relatively low cost [8]. CoS-modified TiO₂ has also been studied to improve photocatalytic performance. The combination of the p-type semiconductors from CoS and the n-type from TiO₂ forms the p-n junction that can increase load transfer and electron-hole separation [9]. This study investigated the synthesis of p–n junction thin films between TiO₂ and CoS using hydrothermal method assisted by ball milling and measure the photoelectrochemical activity in hydrogen production.

2. Experimental

2.1. Preparation of CoS powder
Firstly, 1.46 g of cobalt nitrate hexahydrate (R&M Chemicals) and 0.38 g of thiourea (Merck) were dissolved in a solution of 20 mL ethanol and 5 mL distilled water. The solution was sonicated for 30 min and then moved into an autoclave and heated at 180 ºC for 24 h. The resulting sample were filtered and washed with distilled water and ethanol. Finally, the washed samples were heated in an oven at 60 ºC for 12 h and then calcined for 4 h at 400 ºC.

2.2 Preparation of TiO₂/CoS powder
TiO₂/CoS powder was prepared using 1.6 g of TiO₂ (Sigma Aldrich) and 0.4 g of CoS powder. The TiO₂ powder was dissolved in 70 mL of acetone then stirred for 30 min. Then, the CoS powder was added to the solution. The solution was stirred and heated at 40 ºC until all the solvent evaporated.

2.3 Synthesis of TiO₂/CoS thin film
Firstly, 1 g of TiO₂/CoS powder were mixed with 0.25 g of polyethylene glycol (PEG, Sigma Aldrich) and 8 mL of ethanol. The mixture was transferred into a zirconium oxide container and the ball milling process is carried out at 3000 rpm for 2 h. The slurry formed were coated on fluorine.

2.4 Characterization
The morphologies of TiO₂/CoS thin film were characterized using a field emission scanning electron microscope (FESEM) (ZEISS SUPRA 55VP), whereas the percentage of crystallinity were measured through X-Ray Diffraction (XRD) (Bruker D8 Advance). The XRD data were obtained using Cu Kα radiation (λ=1.5406 Å) at scan rate of 0.040°/s from 2θ 2º to 60º. The UV Reflectance data which were used to measure band gap of the samples, were recorded using a Perkin Elmer Lambda 950 spectrophotometer (λ=300-800 nm).

2.5 Photoelectrochemical measurement
Firstly, the PEC measurements were obtained using 3 electrodes; the silver chloride electrode (Ag/AgCl), platinum wire and TiO₂/CoS thin film were used as the reference electrode, counter, and working electrodes, respectively. The data were recorded using Ametek Versastat 4 under xenon light. Then, 0.5 M
of sodium sulfate (Na₂SO₄) was utilised as the electrolyte solution. Finally, the linear sweep voltammetry (LSV) data at a scan rate of 0.01 V/s were recorded.

3. Result and Discussion

The XRD patterns of all samples are depicted in figure 1. The diffraction peaks in figure 1(c) occurred at 25.28° for d₁₀₁ (anatase), 27.44° for d₁₁₀ (rutile), 36.17° for d₁₀₀ (rutile), 37.82° for d₀₀₄ (anatase), 38.60° for d₁₁₂ (anatase), 41.34° for d₁₁₁ (rutile), 48.08° for d₂₀₀ (anatase), 53.93° for d₁₀₅ (anatase) and 55.12° for d₂₁₁ (anatase). These results reveal that the TiO₂ powder is a mix of anatase and rutile. The strong peak at 25.28° indicate that anatase as dominant phase. Figure 1(d) shows diffraction peaks of TiO₂/CoS thin film. Compared with the peaks of pure TiO₂, the diffraction peaks of CoS-loaded TiO₂ exhibit more noise. Moreover, new peaks were detected on the images. The peaks at 30.50°, 34.53°, 46.91° and 54.32° are respectively assigned to the diffractions of the (100), (002), (102) and (110) planes of CoS. The percent crystallinity of the TiO₂ powder is 69.8% with 30.2% amorphous, whereas the % crystallinity of TiO₂/CoS is 61.8% with 38.2 % amorphous. According to Zhou et al. [10] these findings imply that the dopants have introduced some distortions in the structure. The decrease in crystallinity and increase in amorphous content signifies that the CoS was effectively loaded into TiO₂. The presence of CoS on TiO₂ is further verified by the FESEM results in figure 2.

![XRD pattern](image)

**Figure 1.** XRD pattern of (a) TiO₂ anatase (JCPDS No. 21-1272), (b) TiO₂ rutile (JCPDS No. 21-1276), (c) TiO₂ powder and (d) TiO₂/CoS thin film.

Figure 2 reveals the morphologies of TiO₂/CoS using the FESEM results. The as-prepared TiO₂/CoS appeared as an agglomerate of small particles. To confirm the amount of titanium (Ti), oxygen (O), cobalt and sulfur (S) in the thin films, the composition of the TiO₂/CoS is further analysed through energy-dispersive X-ray spectroscopy (EDX). On the one hand, the results of the EDX reveals the formation of titanium oxide caused by the presence of strong Ti and O peaks. The film contains 55.3% Ti and 37.8% O. On the other hand, the presence of Co and S peaks indicated the formation of CoS, which further verifies the effective loading of the compound into TiO₂ to form the TiO₂/CoS photocatalyst that can transfer photogenerated charges.
Figure 2. FESEM images of TiO$_2$/CoS.

Figure 3. Band gap energy of TiO$_2$ and TiO$_2$/CoS photocatalyst.

The optical properties of pure TiO$_2$ and TiO$_2$/CoS were obtained through the UV reflectance. TiO$_2$ is a semiconductor compound that has a band gap of 3.2 and 3.0 eV for anatase and rutile, respectively [5], whereas the observed direct band gap of CoS thin film was approximately 1.13 eV [11]. Figure 3 illustrates that the band gap of pure TiO$_2$ is roughly 3.4 eV. The differences in the lattice structures of
anatase and rutile TiO$_2$ cause varying densities and electronic band structures, leading to distinct band gap [12]. However, the band-gap energy of TiO$_2$ changed from 3.31 to 2.75 eV when CoS was added. CoS can promote visible light absorption that can reduce band-gap energy. In addition, CoS-loaded TiO$_2$ can shift the absorption band gap edge to decrease the recombination of photo-generated electron-hole and enhanced activity in visible light and increase the photoactivity of TiO$_2$.

![Figure 4. Current density of TiO$_2$ and TiO$_2$/CoS](image)

The photoelectrochemical performance of TiO$_2$/CoS was assessed using LSV at a scan rate 0.01 V s$^{-1}$ in 0.5 M of Na$_2$SO$_4$. Figure 4 shows that the current density of the TiO$_2$/CoS was higher than that of pure TiO$_2$. Moreover, TiO$_2$/CoS exhibited current values of 1.1235 (dark) and 1.2572 (light) mA at 1.0 V compared with Ag/AgCl. However, the TiO$_2$ achieved current values of 0.0018 and 0.0082 mA at 1.0 V under dark and light irradiation, respectively. The ability of CoS-loaded TiO$_2$ to separate photo-generated electron-hole is more effective than that of pure TiO$_2$.

4. Conclusion
In this study, the TiO$_2$/CoS thin film was synthesised through hydrothermal method. FESEM images show that the photocatalyst appeared as an agglomerate of small particles. The phases of TiO$_2$ (anatase and rutile) and CoS were identified and confirmed using XRD patterns and EDX, respectively. The EDX results confirmed the formation of TiO$_2$ due to the presence of strong Ti and O peaks as well as that of CoS due to the presence of Co and S peaks. The observed band gap of TiO$_2$/CoS was roughly 2.75 eV. Compared with Ag/AgCl, the photoelectrochemical performance of TiO$_2$/CoS enabled a cell voltage of 1 V to achieve a current of 1.2572 mA in 0.5 M Na$_2$SO$_4$. 


Acknowledgement
This work supported by The Ministry of Education, Malaysia, supported this work through the
FRGS/1/2015/SG01/UKM/03/1 Research grant and Universiti Kebangsaan Malaysia under Research
University Grant GUP-2016-085.

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