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PHOTOCATALYTIC HYDROGEN GENERATION FROM WATER BY TiO_2/Co_3O_4 COMPOSITE PHOTOCATALYSIS

(Penjanaan Hidrogen Fotokatalitik dari Molekul Air Mengunakan Komposi Fotomangkin TiO_2/Co_3O_4)

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Abstract

Titanium dioxide (TiO_2) is one of the most studied materials as photocatalyst of water splitting for hydrogen generation. However, TiO_2 has a large band gap of around 3.2 eV, limits its absorption energy to visible light, and the photoexcitation products, such as electron and hole, are recombined rapidly. One method to overcome this problem is by creating a composite heterojunction with other semiconductor materials. In this study, the photocatalytic hydrogen generation of water splitting by TiO_2/Co_3O_4 composite photocatalyst was evaluated. The composite was prepared through hydrothermal synthesis assisted by ball mill crushing, and the powder was annealed at 550 °C. The percentage of Co_3O_4 loading on the TiO_2 varied at 0.5% w/w (TC-05), 1% w/w (TC-1), and 2% w/w (TC-2) to study the suitable amount of Co_3O_4. The surface morphology of the composites was investigated through field emission scanning electron microscopy (FESEM) analyses. Results showed that nanosphere and cubic–shaped morphologies were obtained. For the hydrogen performance analysis, two different conditions of photocatalytic hydrogen generation, which are in pure water and water with addition of 10 vol% of methanol solution as the sacrificial reagent, were measured by using a hydrogen sensor (UNISENSE). TC-1 showed the highest hydrogen production in the pure water, which is 6.75 μmol h^{-1} g^{-1} compared with others. The addition of 10% methanol enhanced the hydrogen production by three times compared with pure water (20.22 μmol h^{-1} g^{-1}. The superior heterojunction of TiO_2 and Co_3O_4 performance can be used in practical applications to enhance the photocatalytic properties of TiO_2.

Keywords: cobalt oxide, hydrogen production, PEC, titanium dioxide

Abstrak

Titanium dioksida (TiO_2) adalah salah satu bahan yang paling banyak dikaji sebagai fotomangkin pembelahan molekul air untuk penjanaan hidrogen. Walau bagaimanapun, TiO_2 mempunyai jurang jalur yang besar sekitar 3.2 eV, yang mengehadkan tenaga

penyerapannya kepada cahaya nampak, dan hasil fotopengujaan, iaitu, elektron dan lubang mengakibatkan bergabung semula dengan cepat. Salah satu cara untuk mengatasi masalah tersebut ialah dengan mencipta gabungan komposit dengan bahan semikonduktor lain. Dalam kajian ini, untuk penjanaan hidrogen bagi pembelahan molekul air fotomangkin gabungan komposit TiO_2/Co_3O_4 telah dinilai. Kaedah sintesis hidroterma dibantu oleh proses penghancuran penggilingan bebola yang digunakan untuk menyediakan komposit berikutan penyepuhlindapan serbuk pada 550 °C. Peratusan pengabungan Co_3O_4 pada TiO_2 telah divariasi pada 0.5% w/w (TC-05), 1% w/w (TC-1), dan 2% w/w (TC-2) untuk mengkaji kadar Co_3O_4 yang sesuai. Morfologi permukaan komposit telah disiasat menggunakan analisis FESEM. Berdasarkan FESEM menunjukkan nanosfera dan berbentuk kubik. Untuk analisis prestasi hidrogen, dua keadaan berbeza penjanaan hidrogen fotokatalitik iaitu dalam air tulen dan air ditambah 10 vol % larutan metanol sebagai reagen, dan telah diukur menggunakan sensor hidrogen (UNISENSE). Hasilnya, TC-1 menunjukkan pengeluaran hidrogen tertinggi dalam air tulen iaitu 6.75 μmol h^{-1} g^{-1} berbanding yang lain. Penambahan 10% metanol meningkatkan pengeluaran hidrogen 3 kali lebih tinggi berbanding dengan air tulen 20.22 μmol h^{-1} g^{-1}. Gabungan komposit TiO_2 dan Co_3O_4 boleh digunakan dalam aplikasi praktikal meningkatkan sifat fotomangkin TiO_2.

Kata kunci: kobalt oksida, pengeluaran hidrogen, PEC, titanium dioksida

Introduction

The growth in global population and quality of life has caused a remarkably increase in energy consumption, where fossil-based fuels are the primary energy contributors to date. Given the nonrenewable nature of fossil fuels, they will be depleted if humans do not undertake steps to safeguard these resources. Alternative fuels are necessary to fulfil future energy demands if fossil fuels are no longer available, particularly for the transportation sector, which consumes around 60% of global energy [1, 2]. Hydrogen was identified four decades ago as a fundamental element of a feasible future energy framework for giving safe, savvy, and ecologically harmless energy. The Energy Policy Act of 1992 classifies hydrogen as an alternative fuel. The ability to power fuel cells in zero-emission cars and the fuel cell's rapid filling time and high efficiency have sparked interest in hydrogen as an alternative transportation fuel. A fuel cell with an electric motor is two to three times more efficient than a gasoline-powered internal combustion engine. Internal combustion engines may use hydrogen as a fuel [3, 4].

The availability of H_2 has become a new barrier because it is not naturally accessible on earth. Hydrogen may be found in a variety of forms, including hydrocarbons, water molecules, and acid and base molecules. Thus, H_2 must be eliminated from all of the abovementioned sources [5]. Coal gasification, steam reforming of natural gas, cryogenic distillation, and water splitting are the methods used for producing commercial hydrogen [6]. Coal gasification and steam reforming of natural gas processes can produce significant quantities of hydrogen. However, these approaches need a strong and safe system due to the tremendous energy consumption (temperatures > 1000 °C) necessary to perform reactions [7]. Electricity generated from renewable energy sources, such as hydropower, wind power, and solar power, might be used to electrolyze water molecules. However, these procedures are inefficient and costly [8]. Photocatalytic water splitting technologies have gained considerable interest for producing green and sustainable hydrogen energy from water. The intrinsic features and architectures of semiconductor-based photocatalysts and photoelectrodes have a large influence on the efficiency of solar-to-hydrogen conversion in photocatalytic and/or PEC catalysis [9].

Titanium dioxide (TiO_2) became the most widely used photocatalyst in the 1970s when water splitting drew the attention of researchers. This condition is due to the low cost, chemical stability, Earth abundance, and nontoxicity of TiO_2. Unfortunately, the potential of TiO_2 is limited because of its high band gap width, poor conductivity, and problematic excited dissociation and electron transport. Thus, many studies have focused on improving the TiO_2's photocatalytic efficacy by changing its surface and microstructure, adding cocatalysts, and creating heterojunctions with metals or other semiconductors [10]. Engineered heterojunctions in photocatalysts were revealed to be a viable approach for increasing catalyst activity by allowing

photogenerated electron–hole pairs to be separated spatially. Co_3O_4 is a good choice for fabricating TiO_2-based hybrids for water splitting because Co_3O_4 is one of the most well-known p-type semiconductors, with incredible substance dependability, low solvency, and solid electrical, attractive, and reactant attributes. The cost-effectiveness and availability of Co-based chemicals may simplify large-scale applications [11-13]. Compared with the typical hydrogen electrode, Co_3O_4 has conduction band (CB) and valence band (VB) areas of 0.97 and 1.23 eV, respectively, thereby resulting in a p–n heterointersection with TiO_2. The performance of a combination of varying weight percent of TiO_2/Co_3O_4 thin films in PEC and photocatalytic water splitting was investigated in this work. TiO_2 P25 was used to make a heterojunction with Co_3O_4 by using a hydrothermal technique.

Materials and Methods

Materials

Cobalt nitrate hexahydrate Co $(NO_3)_2.6H_2O$ and TiO_2 P25 were obtained from Sigma-Aldrich. Urea (analytical grade), polyethylene glycol, and ethanol were purchased from Chem-Supply. All chemicals were used without further purification.

Preparation of TiO_2

Ethanol (1 mL) was mixed with 0.2 g of TiO_2 P25 and 0.05 g of polyethylene glycol, and the mixture was crushed. Blade coating was used to coat the slurry on the fluorine-doped tin oxide (FTO) surface at 0.5 mm thickness, which was then annealed at 500 °C for 2 h.

Synthesis of cobalt oxide

In accordance with prior research, cobalt oxide was produced by using a hydrothermal technique [11]. Cobalt nitrate hexahydrate (1.74 g) and urea (0.72 g) were dissolved in 50 mL deionized water. A stainless-steel autoclave was used to transfer the homogenous solution. The autoclave was placed in a furnace for 6 h at 100 °C. The autoclave was turned off and allowed to cool to ambient temperature. The sample was washed with deionized water before being dried in an oven. Cobalt oxide produced by hydrothermal technique was ball milled for 2 h before being mixed with TiO_2.

Synthesis of the composite heterojunction of TiO_2 and Co_3O_4 as a sample

TiO_2, Co_3O_4, polyethylene glycol, and ethanol were ball milled for 20 min, coated over the FTO surface, and annealed for 2 h at 550 °C. TC-05 (0.5% $Co_3O_4.TiO_2$), TC-1 (1% $Co_3O_4.TiO_2$), and TC-2 (2% $Co_3O_4.TiO_2$) were the three weight variants of TiO_2:Co_3O_4. The sample was characterized and used as a working electrode.

Characterization

A field emission scanning electron microscopy (FESEM) model of ZEISS MERLIN was used to examine the surface morphology with 10k magnification and signal A intense duo.

Electrochemical study

In a three-electrode setup with 0.5 M Na_2SO_4 electrolyte solution, linear sweep voltammetry (LSV) analysis was performed by using an Ametek Versastat 4 under a 100 mW/cm^2 xenon light. The working electrodes were TiO_2/Co_3O_4 thin films, the counter electrodes were platinum wires, and the reference electrodes were Ag/AgCl electrodes.

Photocatalytic H_2 generation measurements

The sample (100 mg) was weighed and placed in a reactor to conduct the photocatalytic H_2 generation measurements. The sample was added with 100 mL of sodium sulfate and placed under solar AM 1.3 illumination (100 mW cm^{-2}) using 75 W Xenon light at 500 nm bandwidth for 2 h, and hydrogen readings were taken every 20 min. The steps were repeated by adding methanol as scavenger, and the readings were taken. In this study, a hydrogen sensor was used to measure the hydrogen produced through a photochemical process.

Figure 1. Photoreactor set up for the photocatalytic H_2 generation measurements

Results and Discussion

Characterizations of catalysts

Figure 2 displays the FESEM images of the as-prepared (a) TiO_2 (b) TC-05, (c) TC-1, and (d) TC-2 samples. From Figure 2a, the TiO_2 shows well-defined nanocubic morphology, with the width of 1.011 µm. Figures 2b–c shows that the loaded Co_3O_4 is finely dispersed on the TiO_2 surface with a diameter of approximately 7.14 nm. Figure 2d shows that an obvious agglomeration occurs during the introduction of Co_3O_4 species. The result is mostly similar to a previous study [12]. However, the different weight percentages of composite heterojunction show different sizes of loaded Co_3O_4 [12].

LSV analysis was used to study the potential of the photocatalyst, and the overpotentials of TC-05, TC-1, and TC-2 were calculated. Figure 3a shows the photocurrent responses of (a) TiO_2, (b) TC-05, (c) TC-1, and (d) TC-2 samples. TC-1 had the highest photocurrent density (70 µA cm^{-2}) among the composites, implying that coating TiO_2 with Co_3O_4 nanoparticles (NPs) improved the photogeneration performance. However, the photocurrent decreased when the Co_3O_4 composites increased to 2 wt.%. This condition occurred because of the agglomeration of the photocatalyst, as shown in the FESEM image (Figure 2d). The agglomeration of the photocatalyst decreased the active site and surface area. EIS analysis was used to test the charge carrier transport capabilities of the composites (Figure 3b), The Nyquist plot of TC-1 was less than that of TC-05 and TC-2. This finding revealed that the TC-1 sample had the lowest electron migration resistance among the samples, indicating that it had a high photocatalytic hydrogen evolution reaction (HER) performance. These findings suggested that the TC-1 sample had the best charge detachment behavior of photogenerated carriers among the photocatalyst samples. The amount of active free radicals available for photocatalytic H_2 creation will rise if charge carrier separation was effective [14].

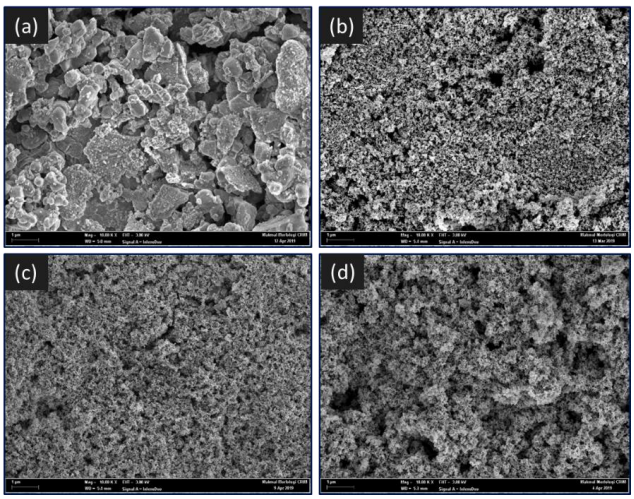

Figure 2. FESEM image of (a) TiO_2 (b) TC-05, (c) TC-1, and (d) TC-2

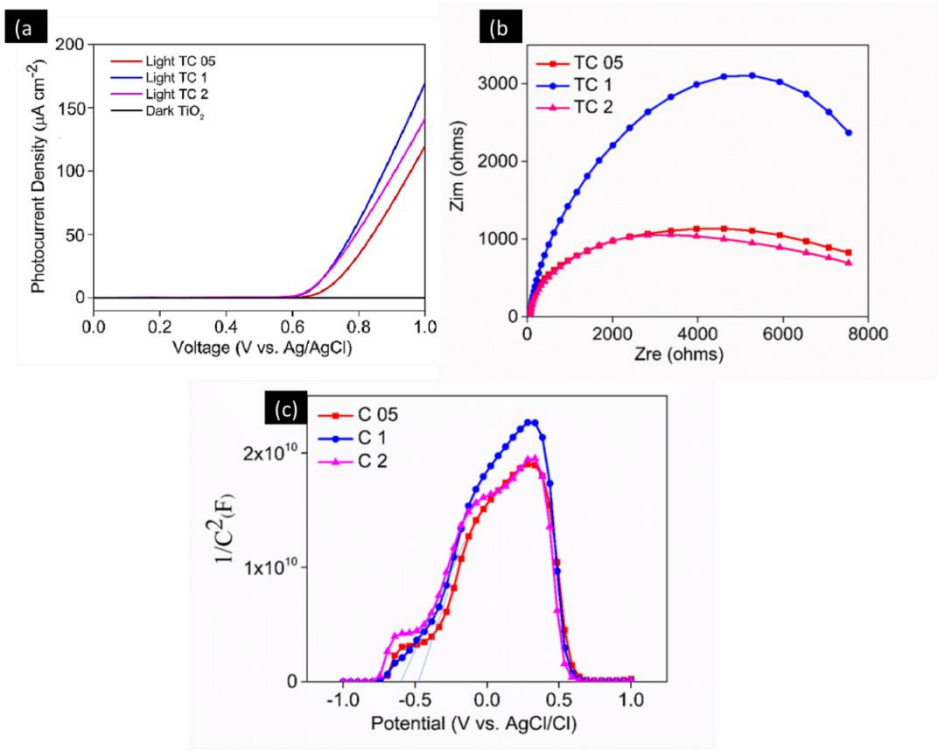

Figure 3. (a) Photocurrent density (b) Electrochemical impedance spectroscopy (EIS), and (c) Mott–Schottky plot of TC-05, TC-1 and TC-2

Photocatalytic hydrogen generation

The photocatalytic hydrogen evolution of the prepared samples was evaluated under artificial sunlight irradiation by using a hydrogen sensor. The photocatalytic hydrogen evolution was tested in two different solutions, and the results were compared. The first analysis (Figure 3a) was tested by using only pure water, and the second analysis (Figure 4b) was tested by using pure water with the addition of 10 vol% of methanol solution as the sacrificial reagent. The comparison of Figures 4a and b showed that the sample with methanol exhibited three times excellent photocatalytic hydrogen evolution as compared without methanol. As shown in Figures 4a and b, the TC-1 sample exhibited the highest H_2 advancement rate (6.75 μmol $g^{-1}h^{-1}$) in pure water and (20.22 μmol $g^{-1}h^{-1}$) in methanol among all the prearranged Co_3O_4/TiO_2 tests. The H_2 production in methanol is higher compared with pure water because methanol effectively separates the hole charges, and the hole–electron pair recombination is reduced [15]. The H_2 advancement rate of TC-2 diminished to 5.70 μmol $g^{-1}h^{-1}$ in pure water and 16.71 μmol $g^{-1}h^{-1}$ in methanol.

The photocatalytic HER of the proposed TiO_2/Co_3O_4 heterojunctions is shown in Figure 5 to analyze the composite heterojunction of TiO_2/Co_3O_4. A previous study [11] provided the specifics of the Co_3O_4 band structure. TiO_2 has a higher Fermi level than Co_3O_4 before they come into contact in the heterojunction. Negative charges migrated from TiO_2 to Co_3O_4 after the heterojunction because p-type Co_3O_4 NPs developed on the surface of n-type TiO_2. This condition caused the Fermi level alignment between TiO_2 and Co_3O_4, resulting in a *p–n* Co_3O_4/TiO_2 junction. According to Wang et al. (2022), a space charge region with a strong built-in electric field in the TiO_2 to Co_3O_4 direction occurs at the TiO_2/Co_3O_4 interface when the energy bands of TiO_2 and Co_3O_4 are bent up and down, resulting in a drift of the

photogenerated charge carrier for heat transfer until a balance thermal equilibrium is reached [16]. The charge transfer mechanism is shown in Figure 5. Under solar AM 1.3 illumination, photogenerated electrons migrated from TiO_2 and Co_3O_4 VBs to the corresponding CBs. The photogenerated electrons were guided from the p-type Co_3O_4 CB to the n-type TiO_2 CB by the induced built-in electric field, resulting in the spatial detachment of photogenerated electron–hole sets. Similarly, Co_3O_4 NPs filled in as a cocatalyst in this *p–n* Co_3O_4/TiO_2 intersection, assisting in expanding the charge partition. Therefore, more photogenerated electrons might focus on TiO_2, which can then be used in the water reduction cycle to produce H_2.

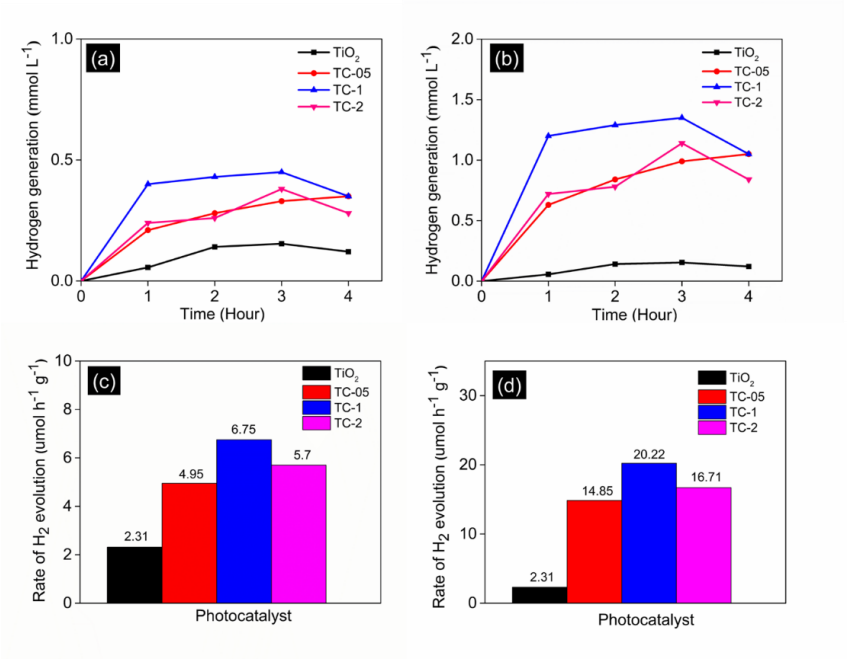

Figure 4. Photocatalytic hydrogen evolution of sample with (a) pure water (b) pure water and methanol, and hydrogen evolution rate of sample with (c) pure water and (d) pure water and methanol.

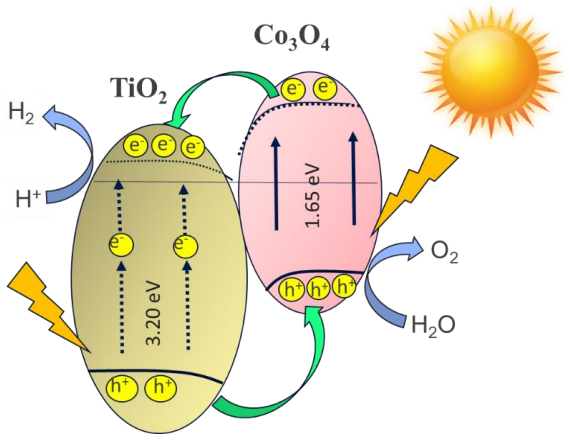

Figure 5. Schematic of the photocatalytic HER mechanism and photogenerated electron–hole separation route of Co_3O_4/TiO_2 *p–n* junction.

Conclusion

In this study, hydrothermal synthesis was used to efficiently construct a Co_3O_4/TiO_2 *p–n* heterojunction. With a photocatalytic H_2 development pace of 20.22 mol $g^{-1}h^{-1}$, the enhanced Co_3O_4/TiO_2 heterojunction had the best photocatalytic H_2 advancement rate. This study used the catalytic effect of Co_3O_4 to distinguish photogenerated electron–hole pairs. A unique Co_3O_4/TiO_2 contact interface and a *p–n* heterojunction was utilized for fast charge carrier transport pathways to enhance the photocatalytic performance. This study may help in the future development and production of *p–n* heterojunction photocatalyst with high visible light-driven energy conversion efficiency.

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