CdS/Titania-Nanotube Composite Films for Photocatalytic Hydrogen Production

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CdS/Titania-나노튜브 복합 막을 이용한 광촉매적 수소제조

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ABSTRACT

알칼리 수열합성법에 의해 높은 비표면적을 갖는 티타니아 나노튜브(TiNT)를 합성하였다. 가시광용 광촉매로서의 응용성을 조사하기 위해 CdS 나노입자와 조성(r=TiNT/(CdS+TiNT))을 바꿔가며 일련의 무기 복합필름을 제조하였다. 또한 비교를 위해 티타니아 나노튜브 대신 티타니아 나노입자와 CdS로 구성된 복합체를 역시 제조하였다. 합성된 티타니아 나노튜브는 200℃ 이상의 소결온도에서 부분적으로 튜브 구조의 붕괴가 시작되었지만, CdS와의 복합체는 450℃ 까지도 비교적 안정한 구조를 유지하였다. (CdS+TiNT)복합필름은 티타니아 나노입자 복합계와 비교할 때 가시광 흡수 측면에서는 유사한 정도를 나타내었지만, 수소생산 활성과 광전류 발생은 오히려 훨씬 낮은 값을 나타내었다. 결과적으로, 티타니아 나노튜브는 그의 높은 비표면적에도 불구하고 자기들끼리의 응집성이 강하여 CdS와의 전기적 상호작용이 약하며, 특히 얇은 튜브벽 두께(~3nm)와 낮은 결정성에 기인하는 약한 광전류 특성은 이의 광촉매로서의 응용성을 상당히 제한하는 요소로 나타났다.

KEY WORDS : titania nanotube(티타니아 나노튜브), photocatalyst(광촉매), photochemical (광화학적), cadmium sulfide(카드뮴 황화물), hydrogen(수소)

1. Introduction

With the advent of the so-called hydrogen economy, new technologies producing hydrogen from natural resources other than fossil fuels are becoming more important. The photocatalytic or photoelectrochemical method that produces hydrogen from water by using solar energy is one of these. Since Fujishima and Honda demonstrated that water could be effectively split into hydrogen and oxygen on TiO_2 photo-electrode[1], many researchers have attempted to develop more efficient photocatalytic materials. Among these, TiO_2 and CdS are still the most representative

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photocatalytic materials and work under UV light and visible light, respectively. TiO_2 is an exceptional material that has many important applications like white pigment, catalytic support, photocatalyst, and dye sensitized solar cell[2,3]. Recently, titania nanotubes have been prepared via a rather simple hydrothermal processing using NaOH aqueous solution[4,5]. Since this TiO_2 form has larger surface area, it is of particular interest in the aspect of catalytic or photocatalytic application. Meanwhile, CdS has also been widely used for a yellow pigment, CdS/CIS solar cell, and other photoelectronic devices[6]. This is apparently owing to its suitable band gap property (~2.4 eV) for absorption of visible light as a n-type semiconducting material.

Recently, we reported that when both TiO_2 and CdS particles were used together in a nano-composite film form, they showed a synergistic effect in photo-splitting reaction of aqueous H_2S solution[7]. It was also found that close contacts among the particles and uniform distribution of both components are important. This favorable result was attributed to the effective photo-charge separation between the two contacting particles with different band gaps and band positions as shown in the scheme of Fig. 1 Their photocatalytic performance depended on such physical properties of particles as crystallinity, size and morphology.

In the present study, we prepared titania nanotubes(TiNT) following the previous hydrothermal process[4]. Then, these nanotubes were mixed with CdS sol to prepare CdS- TiNT composite films. Their photocatalytic performances
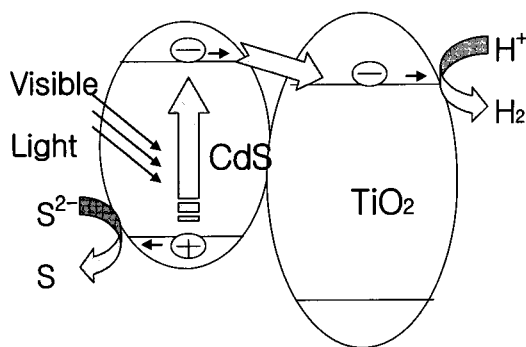

Fig. 1 A schematic drawing of CdS-TiO_2 composite photocatalyst operating under the visible light. The scheme shows an effective photo-charge transfer from CdS to TiO_2, and other details including various chemical reaction steps are omitted for simplification

for hydrogen production were compared with their existing counterparts, i.e., CdS-TiO_2 particulate composite films. The tubular morphology with a larger surface area was of great interest in connection with photocatalytic performance of these composite films.

2. Experimental

2.1 Preparation of CdS–TiNT Composite Films

Nano-crystalline CdS sol was prepared by a precipitation reaction of 0.5 M $Cd(NO_3)_2$ and 0.5 M Na_2S aqueous solutions at room temperature and a subsequent hydrothermal treatment at 240℃ for 12 h. Details for preparation and its physical properties are shown in a reference[8]. Titania nanotubes were prepared by the hydrothermal reaction under strongly basic condition, whose procedure was previously reported by Kasuga et al[4]. In this study, a commercial TiO_2 powder, P-25 obtained from the Degussa, was used as a starting material and NaOH as an alkaline source. These

CdS sol and titania nanotubes slurries were mixed together mechanically using ultrasonification with variation of the mole ratio, r =TiNT/(CdS+TiNT). CdS-TiNT composite films were thus prepared by casting the final sol mixed with PEG onto fluorine doped SnO_2 conducting glass(F:SnO_2), and a subsequent heat- treatment at 450℃ for 30 min under air. The film thickness was adjusted to be on the level of ~10 μm. For comparison of photocatalytic performance, CdS-TiO_2 particulate composite films were also prepared similarly following a previous study[7].

The morphology and thickness of the composite films were observed by using SEM(JEOL JSM-6700F). Detailed morphology and crystalline phases of titania nanotubes and CdS particles were identified by using TEM(JEOL JEM 2010) and XRD(CuK α, Rigaku), respectively. UV-NIR fiber optic spectrometer(Ocean Optics, HR 4000) and PL spectrophotometer(Perkin-Elmer lambda 20) were used to obtain optical absorption spectra (DRS mode) and photoluminescence spectra of the composite films, respectively. Specific surface areas of the particles were measured by using the BET method(Micromeritics, ASAP 2400).

2.2. Preparation of Composite Film Electrodes and Photocurrent Measurement

The composite film electrode(working area ~1 cm×1 cm) for measurement of photocurrent was prepared by connecting a copper lead wire and the exposed F:SnO_2 film with silver paste. The photocurrent was measured in a water-jacketed cell of three-electrodes system consisting of the composite film electrode, a saturated calomel electrode(SCE), and Pt gauze as a photo-anode, a reference electrode and a cathode, respectively. The light was illuminated on the photo-anode from a Xe lamp(ILC Technology, U.S.A) with the intensity of 100 mW/cm^2(AM 1.5). The photocurrent to potential(I-V) curve was measured in an aqueous electrolyte solution consisting of 0.1 M Na_2S and 0.02 M Na_2SO_3 solutes at 25℃ using a potentiostat/galvanostat(EG&G Model 273A). Unless otherwise specified, all photocurrent values were compared at 0.0 V vs. SCE, since most of the present composite films indicated stable photocurrent values at this potential[9].

2.3. Preparation of the Photoreactor and Measurement of Photocatalytic Activity for Hydrogen Production

The photocatalytic films for hydrogen production were also prepared by the same procedure as the case of photoelectrodes above, but with larger working areas ~9 cm×9 cm. Then, these films were coated with Pt particles as co-catalyst by plasma sputtering(80 watt, 30 sec., 3×10^{-3} torr of Ar). Finally, a photoreactor was constructed using this glass plate coated with photocatalytic films, a bare glass counter-plate, and a stainless steel frame together, and sealed with silicone rubber gasket. As in the case of photocurrent measurement, the light for production of hydrogen was illuminated from a Xe lamp with the power intensity of 100 mW/cm^2(AM 1.5). Hydrogen production experiments were carried out in a closed circulation system using an aqueous solution of 0.1 M Na_2S and 0.02 M Na_2SO_3 as a

reference feedstock for comparison of water photo-splitting activity of these films[7]. The amount of hydrogen produced with time was calculated quantitatively by the pressure increase of the closed system and confirmed qualitatively by a gas chromatograph(molecular sieve 5A column, HP 5890).

3. Results and Discussion

Fig. 2 shows typical TEM images of titania nanotubes prepared in this study. The as-prepared nanotubes(Fig. 2a & b) revealed 150~300 nm in length, 3~5 nm in inner diameter, and 10~15 nm in outer diameter, and consisted of 3~5 layers of walls(~3 nm of thickness), whose dimension was roughly consistent with those of previous studies[4,5]. These nanotubes partially collapsed into shorter nanotubes or particles upon thermal annealing above 200℃(Fig. 2c & d) and their specific surface areas decreased in proportion to the degree of collapse. The surface area of the nanotubes dried at 60℃ reduced to approximately 30% of the initial area after calcination at 450℃ (376 → 134 m^2/g).

Fig. 3a~d show the crystalline phases of the samples of Fig. 2a~d, respectively, whose crystallinities were rather poor except for the sample of Fig. 2d that was annealed at 450℃. It is known that a well developed crystallinity of photocatalyst is very important for an effective charge transfer within crystallites and thus for a better photocatalytic activity[8].

The sample of Fig. 3d indicated a typical anatase phase of TiO$_2$ crystallites and the average
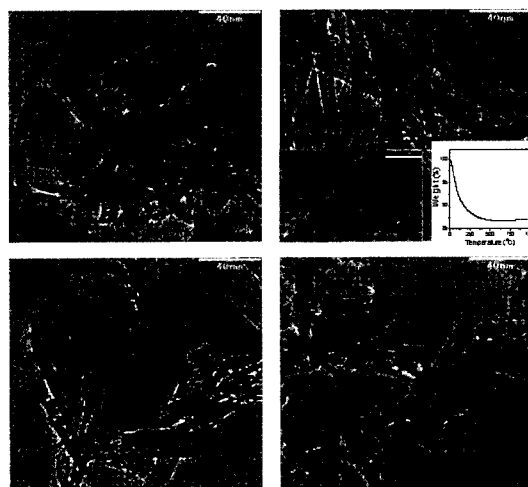

Fig. 2 TEM images of titania nanotubes prepared by the hydrothermal treatment(HT) in NaOH aqueous solution. The samples were annealed in air for 0.5 h at different temperatures: (a) 60℃(befor HCl), (b) 60℃(after HCl), (c) 200℃, & (d) 450℃. After HT, the sample (a) was washed only with water, while (b), (c) & (d) were 0.1M HCl-treated and then washed again with water. The insets of (b) represent the HRTEM image of a nanotube(bar: 10 nm) (left), and TGA(thermogravimetric analysis) data(right)

primary particle size of this sample estimated from the X-ray line broadening analysis[9] was about 18 nm. The XRD patterns of Fig. 3a~c were
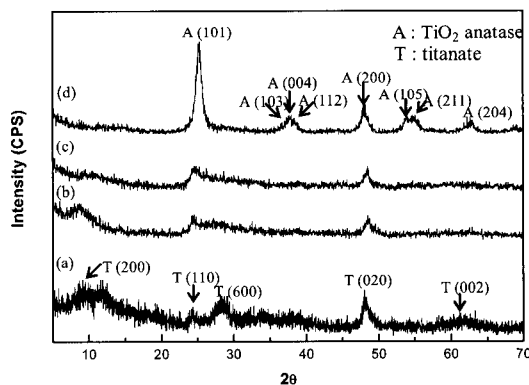

Fig. 3 XRD spectra of the respective samples of Fig. 1 The crystalline planes seen on the sample (a) were quoted from ref. [10] and those of the sample (d) were assigned in consistent with a typical anatase phase of TiO$_2$

apparently differentiated from that of Fig. 3d, and especially the pattern of Fig. 3a was distinguished by the peak at a lower angle, $2\Theta=9.6°$. Furthermore, two nanotube samples of Fig. 2a & 2b also represented different patterns from each other. In fact, the sample of Fig. 3a was found to contain about 15 atomic % of Na(based on EDX analysis) and thought to be a mixture of sodium titanate and titania. In a previous study[10], a similar crystalline pattern to the Fig. 3a was found and they assigned the pattern to such a titanate as $Na_2Ti_2O_4(OH)_2$. The sodium component was not found in a typical nanotube sample, Fig. 3b, and diverse crystalline phases like $H_2Ti_2O_4(OH)_2$[11], $H_2Ti_3O_7$[12], and TiO_2 anatase[13] were suggested for them by earlier studies. Based on the results of Fig. 2 & Fig. 3 and the TGA study shown in the inset of Fig. 2d, whose weight decreased consistently till the temperature reached ~400℃, this well- developed nanotube form is thought to have a titanate phase with some structural water. They collapse into shorter titania nantubes or particles with a gradual removal of structural water upon thermal annealing. Meanwhile, the vacuum dried CdS sample indicated a well-developed hexagonal crystallinity[8].

Fig. 4 shows SEM photographs of various CdS-TiNT composite films prepared with the final heat-treatment at 450℃. The pure CdS film(r=0) indicated a porous morphology consisting of large and irregular CdS particles, while the pure TiNT film(r=1) showed a rather dense shape consisting of agglomerated nanotubes which were aligned randomly. Although the nanotubes in the powder form easily collapsed into particles upon annealing
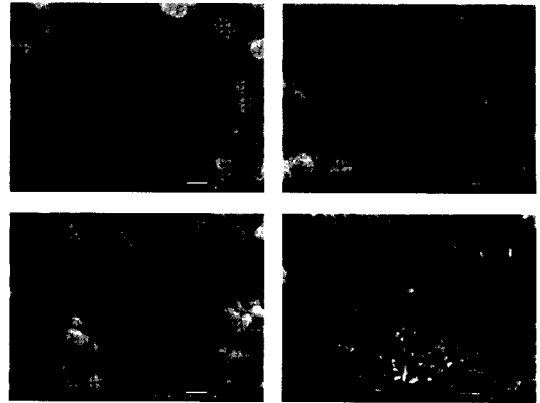

Fig. 4 SEM photographs of composite films with variation of the mole ratio, r=TiNT/(CdS+TiNT): 0 (a), 0.2 (b), 0.4 (c), & 1 (d)

at 450℃(Fig. 2d), the nanotubes in the film form kept their tubular shape despite the heat treatment, probably as a result of aligning on the substrate with the aid of a binder material(PEG) or buffing by CdS particles. Apparently, the nanotubes of CdS-TiNT composites revealed better thermal stability than in their single state. As shown in Fig. 4b & 4c, the CdS-TiNT composite films indicated a mixed state of both components with some agglomeration among nanotubes.

Fig. 5 represents optical absorption spectra (diffuse reflectance mode) for CdS-TiNT composite films. The sample with pure CdS(Fig. 5a, r=0) showed a typical absorption spectrum with the main absorption edge at about 530 nm due to CdS bulk crystalline phase and a long tail due to many defect states. Meanwhile, the sample with pure nanotubes (Fig. 5e, r=1) has a typical absorption edge at about 385 nm, which is nearly consistent with the absorption edge of TiO_2 anatase phase with the band gap energy of 3.2 eV. In the cases of the composite films with r=0.2~ 0.8, visible light absorption above ~400 nm
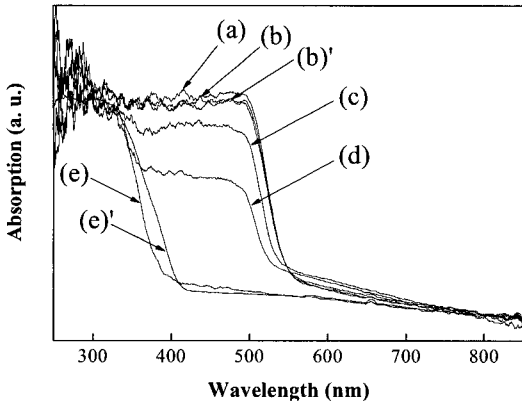
Fig. 5 Optical absorption spectra for the CdS-TiNT composite films with variation of the mole ratio(r): r=0 (a), 0.2 (b), 0.6 (c), 0.8 (d), 1 (e). For comparison, the spectrum (b)' is for r=0.2 of CdS-TiO₂ particulate series and (e)' for P-25(Degussa)
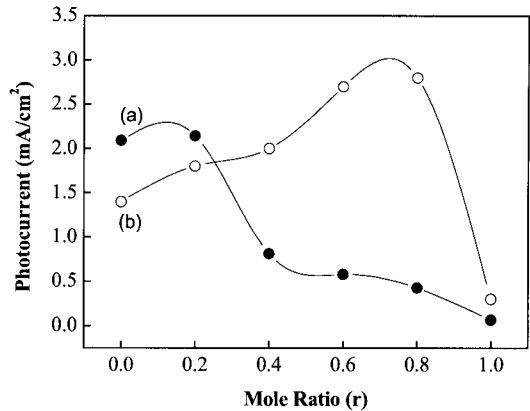

Fig. 6 Photocurrents of CdS-TiNT (a) and CdS-TiO₂ particulate (b) composite films with variation of the mole ratio(r). For the details of (b), refer to ref. 7)

decreased in proportion to the decrease of CdS content but still indicated a considerable amount of absorption even at r=0.8. The light absorption by these samples was comparable to those of corresponding counterparts i.e., CdS-TiO₂ particulate series(refer to Fig. 5b). The difference in titania morphology of composite films showed no significant difference in absorbing the visible light.

The photocurrents were measured electrochemically at a reference experimental condition. With increase of TiNT content, the photocurrent slightly increased at r=0.2 and then decreased monotonically, and finally reached a minimum value at r=1, i.e., pure TiNT film probably as a result of reduced visible-light harvesting due to decreasing CdS content. They showed no significant synergistic effect with formation of the CdS-TiNT composites, which was contrary to the previous results representing a maximum photocurrent at r=0.8(Fig. 5b) and some

kind of favorable interaction being between both components of CdS-TiO₂ particulate films[7]. It was thus thought that the photo-electrons excited from the valence band of CdS particles might not so effectively transfer to the conduction band of TiNT as to prevent those electrons from recombining readily in this series of CdS-TiNT composite films[14]. This nearly monotonic decrease of photocurrents with r was an unexpected result when considering the larger surface area of TiNTs compared to round TiO₂ particles, which was at first anticipated to facilitate the contact with CdS particles. Apparently, in spite of such small sizes of several nanometers in diameter, the nanotube morphology of TiO₂ was less effective in interaction with CdS particles compared to the round shape.

Finally, to investigate the performance of these composite films as photocatalyst, hydrogen production rates were measured in a continuous flow reactor. Fig. 7 shows the amount of hydrogen produced with time from CdS-TiNT composite
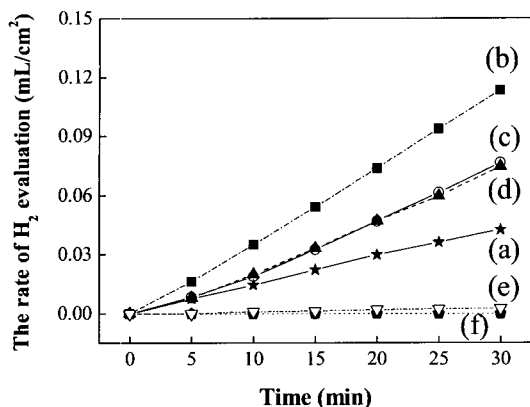
Fig. 7 The amount of hydrogen produced from CdS-TiNT composite films: r=0 (a), 0.2 (b), 0.4 (c), 0.6 (d), 0.8 (e), 1(f)

films. Compared to the results of the CdS-TiO$_2$ particulate series[7], the highest rate, 0.23 cc/cm^2·hr was obtained at r=0.2 and the photocatalytic activities were generally not so good. However, the present photo-activity data indicates that some degree of synergistic effect exists also between CdS particles and TiNTs, although the effect was not so apparent in the photocurrent generation(Fig. 6) which requires even the flow and collection of charge carriers in addition to the charge separation.

4. Summary

Titania nanotube(TiNT) and CdS sol were synthesized by hydrothermal reaction under strongly basic condition and by precipitation reaction of Cd(NO$_3$)$_2$ and Na$_2$S aqueous solutions, respectively. After preparing a series of CdS-TiNT composite films on F:SnO$_2$ conducting glass with variation of the mole ratio (r) of TiNT/(CdS+ TiNT), their visible light absorption, photocatalytic activities for hydrogen production, and the photocurrent generation were examined. In general,

this CdS-TiNT series showed lower photocatalytic activities and photocurrent generation under Xe light irradiation compared to their counterparts, i.e., CdS-TiO$_2$ particulate series. It appeared that TiNTs are not so effective photocatalyic material in spite of their larger specific surface areas compared to TiO$_2$ nanoparticles, because they indicate a poor crystallinity and less intimate interaction or contact with CdS particles owing to the tubular morphology and an easy agglomeration among themselves.

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