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Comparision of Zn_2TiO_4 and rutile TiO_2 photocatalysts for H_2 production under UV and near-visible light irradiation

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Zn_2TiO_4 a spinel-type structure photocatalyst, was synthesized by a solid-state reaction method, and obtained as a single phase in the temperature range of 900-1200 °C. The average particle size for case of the as-synthesized Zn_2TiO_4 sample, sintered at 1200 °C was found to be 5 μm, whereas it lay in the range of 0.5-2 μm for the case of TiO_2 calcined at 650 °C. The band gap of Zn_2TiO_4 and TiO_2 (rutile) samples determined by UV-Vis diffuse reflectance spectra (DRS) was 3.10 eV (400 nm). The Zn_2TiO_4 sample calcined at 1200 °C exhibited a higher hydrogen production rate than that of rutile TiO_2 from a water-methanol mixture under UV ($\lambda \geq 210$ nm) and near-visible ($\mu \geq 400$ nm) light irradiation. In spite of having the same bandgap energy, the photocatalytic activity of Zn_2TiO_4 was found to be higher than that of rutile TiO_2, manily because of its more negative conduction band edge than rutile TiO_2.

Key words: Zn_2TiO_4, Rutile TiO_2, Photocatalysis, Hydrogen production, Visible light.

Introduction

Photocatalysts convert solar energy into useful chemical energy, such as hydrogen gas [1-3] as an alternative green fuel. Thus production of hydrogen by making use of semiconductor photocatalysts, has recently received much attention [4-7]. In general, to develop a high efficiency photocatalyst for hydrogen production, the semiconductor material should fulfill various requirements, such as (i) a proper band gap position; (ii) bandgap energy; (iii) long-term stability, (iv) good optical property *etc.* According to Matsumoto [8], Zn_2TiO_4 is a fascinating candidate having an ideal bandgap energy (ca. 3.1 eV), as well as the band positions for photo-reduction of water under UV and near-visible light. Interestingly its band gap (ca. 3.1 eV) [9] is the same as rutile TiO_2. In spite of such a similarity, to the best of our knowledge, there is no report on comparison of the photocatalytic activities of the two systems. It can be predicted that the photocatalytic activity of rutile TiO_2 may be lower than the activity of Zn_2TiO_4, as the conduction band edge of rutile TiO_2 is located very near to the reduction potential of hydrogen [8]. In this paper we have carried out a comparative study of photocatalytic properties of Zn_2TiO_4 and rutile TiO_2 systems under UV and near-visible light irradiation.

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Here, we synthesized Zn_2TiO_4 by a solid-state reaction method, and TiO_2 by a sol-gel process. Further structural and optical characterization was carried out with an objective of a photocatalytic application of these systems. A detailed study was carried out to compare the photocatalytic activity of the two materials for hydrogen production from a water-methanol mixture under UV/near-visible light irradiation. In addition, a direct comparison of the computed electronic structures of the two systems is a salient feature of the present work.

Experimental

Zn_2TiO_4 samples were synthesiszed by a conventional solid-state reaction (SSR) method. Stoichiometric amounts of ZnO (99.9%, Aldrich) and TiO_2 (99%, Aldrich) were mixed and ground in methanol. The pelletized powders were calcined at 700-1300 °C for 4 h in a static furnace. On the other hand, for the purpose of comparison, an amorphous TiO_2 precursor (ATP) sample was also prepared by a sol-gel method (SGM) [10]. Thus 10 ml of titanium isoproxide $Ti(OCH(CH_3)_2)_4$ (97.0%, Aldrich) was dissolved in 50 ml of ethyl alcohol and then 3 ml of aqueous ammonium hydroxide solution were added. A homogeneous sol or colloidal solution was obtained after a few hours of vigorous stirring. TiO_2 nanoparticles with anatase and rutile phase structure were formed by heating these ATP samples in air at various temperatures in the range of 300-650 °C for 4 h in an electric furnace.

The Zn_2TiO_4 and TiO_2 samples prepared by the con-

ventional SSR methods were characterized by an X-ray diffractometer (Mac Science Co., M18XHF). X-ray diffraction (XRD) results were compared with the Joint Committee Powder Diffraction Standards (JCPDS) data for phase identification. The band gap energy and optical properties of the as-prepared materials was measured by a UV-visible diffuse reflectance spectrometer (Shimadzu, UV 2401). The morphology was determined by scanning electron microscopy (SEM, Hitachi, S-2460N) and high-resolution transmission electron microscopy (HR-TEM, Philips, CM 200).

The electronic band-structure calculation of Zn_2TiO_4 was performed using the WIEN 97 package based on the full potential linearized augmented plane wave method [11]. This method uses the generalized gradient approximation, an improvement to the local spin-density approximation within density functional theory that is known to be an efficient and accurate scheme for solving the many-electron problem of a crystal. The crystallographic parameters for the calculation including lattice parameters and atomic positions were adopted from the literature [12].

The photo-reduction reactions of water were carried out at room temperature in an upper-irradiation type Pyrex reaction vessel hooked up into a closed gas circulation system. Photocatalytic reduction was carried out by irradiating suspended powders using a Hg-arc lamp (500W) equipped with a UV-visible light irradiation. The H_2 evolution was examined in an aqueous methanol solution (distilled water 80 ml and CH_3OH 20 ml) by stirring 0.3 g of the catalyst loaded with 0.2 wt% Pt. Before photocatalytic reactions, all the catalysts were loaded with 0.2 wt% Pt a using conventional impregnation method using aqueous $PtCl_2$. The concentration of the reaction product (H_2) was determined by a gas chromatograph equipped with a thermal conductivity detector (a molecular sieve 5-Å column and Ar carrier).

Results and Discussion

Structural characterization of Zn_2TiO_4 and TiO_2 samples were carried out to compare the crystallization behaviors of the samples prepared at various calcination temperatures. Fig. 1 shows the XRD patterns of Zn_2TiO_4 samples prepared by sintering the mixed precursor (ZnO and TiO_2) at various temperatures. The samples formed above 800 °C exhibited an inverse spinel Zn_2TiO_4 structure with a lattice constant of 8.48 Å, and space group Fd3m [13]. The sample calcined at low temperatures (700 °C) showed some unknown impurity phases. The formation of Zn_2TiO_4 was observed in the samples calcined between 800 and 1300 °C. The study clearly reveals the temperature-depdendent crystallization behavior of Zn_2TiO_4

Further, the structural characterization of TiO_2 was studied in detail as seen in Fig. 2. Here, the X-ray patterns show the crystallization behavior of TiO_2 as a function of the calcination temperature for the amorphous TiO_2 precursor (ATP) sample. The TiO_2 precursor sample did not show

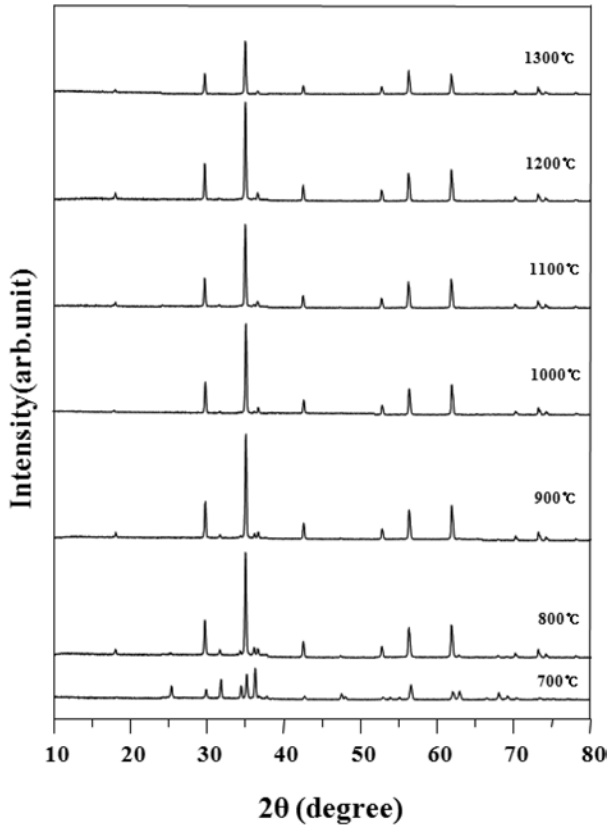

Fig. 1. XRD patterns of Zn_2TiO_4 samples sintered at various temperatures for 4 h; (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C , (e) 1100 °C , (f) 1200 °C , (g) 1300 °C.

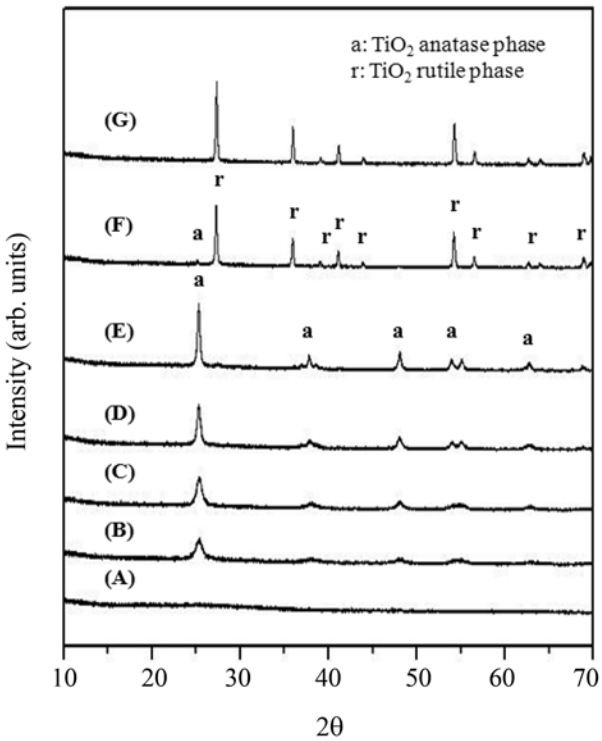

Fig. 2. XRD patterns of TiO_2 samples calcined at various temperatures for 4 h; (A) 300 °C, (B) 350 °C, (C) 400 °C, (D) 450 °C , (E) 500 °C , (F) 550 °C , (G) 650 °C .

(Fig. 2(A)) any XRD peaks indicating that it was amorphous solid. Crystalline TiO_2 grew with an increase in the calcination temperature. The crystallization behavior of TiO_2 in the ATP sample was very similar to our previous report [10] and showed a well-crystallized anatase phase at 500 °C. But at higher temperatures (≥ 550 °C) it turned to the thermodynamically more stable rutile phase.

Fig. 3 shows scanning electron microscopy (SEM) images of TiO_2 and Zn_2TiO_4 samples. The TiO_2 sample displayed the existence of more or less spherical particles with a size range of 0.5-2 μm. In contrast, the Zn_2TiO_4 sample displayed a well-crystallized morphology with the grain size lying in the 5-10 μm size range. Such larger particles are expected due to the high temperature-induced particle growth in this metal oxide.

Fig. 4 shows UV-vis diffuse reflectance spectra of Zn_2TiO_4 samples sintered at different temperatures (1100, 1200, 1300 °C) and for a TiO_2 (rutile) sample. Fig. 4 clearly indicates a similarity in the absorption edge of these systems.

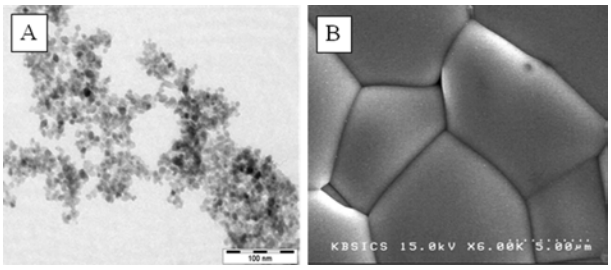

Fig. 3. SEM images of (A) TiO_2 calcined at 650 °C for 4 h; and (B) Zn_2TiO_4 sample calcined at 1200 °C for 4 h.

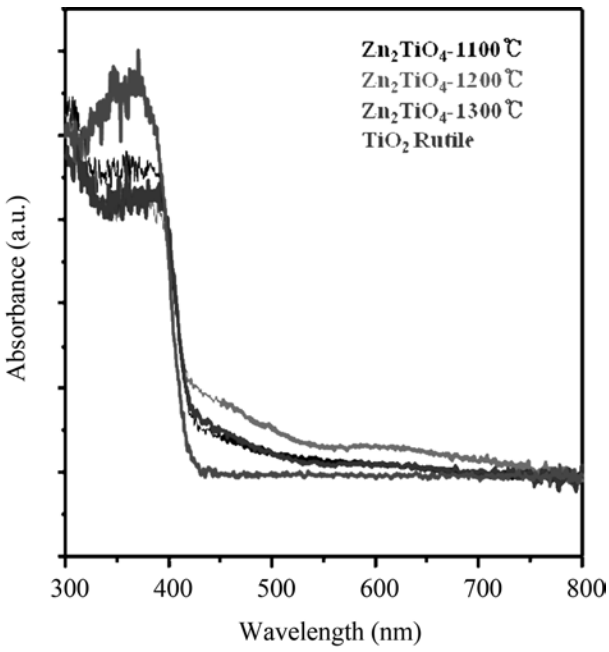

Fig. 4. UV-Vis diffuse reflectance spectra of various samples of (a) Zn_2TiO_4-1100 °C, (b) Zn_2TiO_4-1200 °C, (c) Zn_2TiO_4-1300 °C and (d) TiO_2-650 °C indicating the similarity in the band gap of these systems.

From these spectra, we estimated the band gap energy of these materials. TiO_2 (rutile) showed a sharp edge at 400 nm, while Zn_2TiO_4 showed two absorption edges; the main edge at 400 nm and a shoulder around 400-500 nm. Thus, it can be concluded that both Zn_2TiO_4 and TiO_2 display a similar band gap of ~3.10 eV, This is also shown in Table 1.

Fig. 5 shows the total density of states (DOS) for Zn_2TiO_4 and rutile TiO_2, where the top of the valence band was set to 0 eV. The muffin-tin radii for Zn, Ti, and O were chosen to be 2.2, 2.0, and 1.8, respectively, in this calculation. The convergence parameter of *RK*max was set to 8.0. The calculation was iterated with a charge convergence criteria of 0.0001. The atomic coordinates for the WIEN97 calculation were adopted from the literature [14]. Similarly, the DOS was calculated for rutile TiO_2. Fig. 5 give a direct qualitative comparison of the DOS of these systems. Specifically DOS of Zn_2TiO_4 implies

Table 1. Photocatalytic H_2 production from methanol-water solution over 0.2 wt% Pt/$ZnTiO_4$ and 0.2 wt% Pt/TiO_2 samples

Catalyst	Bandgap Energy Eg (eV)	H_2 evolution (mmol/gcat·h)	
		UV light irradiation (λ ≥ 10 nm)	Visible light irradiation (λ ≥ 400 nm)
0.2 wt% Pt/Zn_2TiO_4 (1200 °C)	3.10	140	46
0.2 wt% Pt/TiO_2 (650 °C)	3.10	11	2

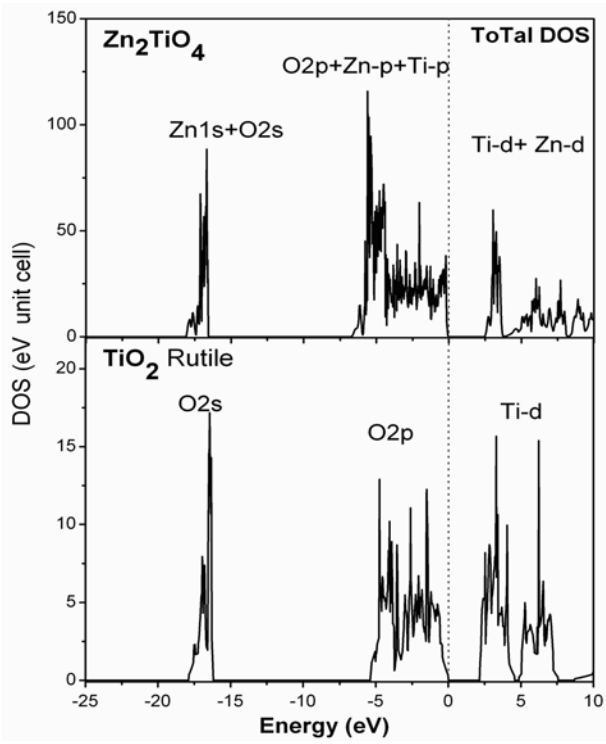

Fig. 5. Theoretically calculated total density of states (DOS) for Zn_2TiO_4 and rutile TiO_2. The top of the valence band was set to 0 eV.

that the valence band is a mixture of the O 2p, Zn 2p and Ti 2p orbitals. The conduction band is comprised of the Zn 3d orbital. It is clear that titania also exhibits a similar DOS, except for the fact that there is no effect of the Zn-states in the conduction band. Effectively, the Zn states affect the conduction band edge position of Zn_2TiO_4 making it a better photocatalyst. From the above study, it can be understood that both oxide systems show very similar optical properties.

Among the as-synthesized samples, we investigated the photocatalytic hydrogen production from a methanol-water solution using Zn_2TiO_4 and rutile TiO_2 samples under UV ($\lambda \geq 210$) and visible ($\lambda \geq 400$ nm) light irradiation. Table 1 shows the results of the H_2 evolution as well as the respective band gaps of the samples calculated from the respective spectra. Two samples showed photocatalytic activity for hydrogen production from a methanol-water solution under UV light irradiation ($\lambda \geq 210$). The Zn_2TiO_4 photocatalyst showed a higher photocatalytic activity than that of rutile TiO_2 under both UV and visible light irradiation. The Zn_2TiO_4 photocatalyst showed a H_2 production as high as 46 mmol/gcat·h under visible light irradiation ($\lambda \geq 400$ nm). But, the rutile TiO_2 photocatalyst showed a trace amount of H_2 production.

The photocatalytic quantum yield (QY) of any photocatalyst is an important parameter to understand and compare its efficacy. It can be calculated using the following equation [15, 16]:

$$QY = H_2 \text{ evolution rate}/14.757 \times [(I_1 - I_3)-(I_1 - I_2)] \times A_1/A_2 \times 100 \quad (1)$$

where I_1 is the blank light intensity, I_2 is the scattered light intensity, I_3 is the photocatalyst light intensity, A_1 is the lighted area of the photo reactor, A_2 is the area of the sensor face, and 14.757 is the mole number of photons with $\lambda \geq 400$ nm emitted from the lamp for 1 h. The results of the photocatalytic QY calculation in Table 1, indicate that Zn_2TiO_4 system shows 23 times more QY than rutile TiO_2 system. This is an important observation of the present investigation.

Fig. 6 shows the bandgap positions of Zn_2TiO_4 and rutile TiO_2 photocatalysts reported by Matsumoto [8] and its mechanism for photocatalytic hydrogen production from a methanol-water solution. Although the two samples have the same bandgap energy, the conduction band of Zn_2TiO_4 is located at a more negative position than that of rutile TiO_2 as shown in Fig. 6(A). That is, in the case of Pt/Zn_2TiO_4, an electron excited to the conduction band has a reduction potential more suited to reduce an H^+ ion, and a hole in the valence band also has a lower oxidation potential for CH_3OH degradation to CO_2. The figure clearly demonstrates this fact for Zn_2TiO_4 an further compares it with the case of rutile TiO_2 [17]. Therefore, Zn_2TiO_4 is a potential photocatalyst for photocatalytic reactions which require a higher reduction potential as well as a lower oxidation potential.

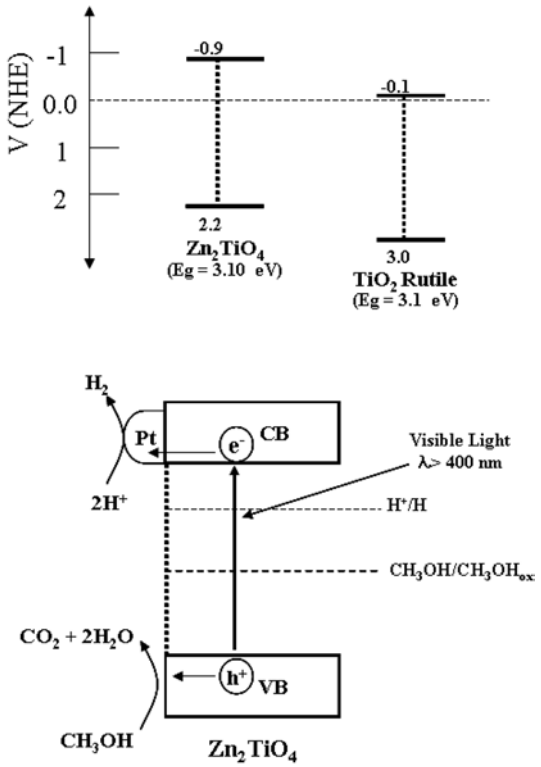

Fig. 6. A. The bandgap positions of Zn_2TiO_4 and rutile TiO_2 photocatalysts. B. The mechanism for photocatalytic hydrogen production from a methanol-water solution.

Conclusions

Spinel-type zinc ferrite material, Zn_2TiO_4 was successfully synthesized by a solid state reaction method and studied together with rutile TiO_2 made by a sol-gel synthesis. In spite of having the same bandgap energy, the photocatalytic activity for hydrogen production under UV and near-visible light over Zn_2TiO_4 was found to be higher than that of rutile TiO_2. Comparatively a more negative conduction edge position of Zn_2TiO_4 than rutile TiO_2 is mainly responsible for this better behavior of the Zn-containing system. Thus, Zn_2TiO_4 can be considered as a better candidate for photocatalytic reactions which require a higher reduction potential as well as a lower oxidation potential viz. for photocatalytic hydrogen production.

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