

Preparation of the mixed oxide photocatalyst and its quantum yield

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Mixed oxide 광촉매의 제조 및 광분해 효율 평가

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요약

광촉매로 널리 알려진 TiO_2 의 광분해 거동의 변화를 관찰하기 위하여 Nb_2O_5 를 첨가하여 sol-gel 방법으로 제조한 후 DCA(dichloroacetic acid)의 광분해 효율을 측정하였다. Sol-gel process 과정에서 첨가된 Nb_2O_5 의 농도 및 열처리 온도에 따라 광분해 효율을 관찰한 결과, Nb_2O_5 를 첨가한 후 $400^\circ C$ 에서 한시간 동안 열처리 한 광촉매의 광분해 효율이 가장 높게 나타났다. 또한 열처리 온도와 무관하게 Nb_2O_5 의 양이 증가할수록 광분해 효율은 감소하는 것으로 관찰되었다. 이는 excess electron의 증가로 환원반응 혹은 recombination rate가 증가하기 때문이라고 사료된다. 분해 대상 물질의 pH가 낮을수록 광분해 효율이 증가하는 것을 알 수 있었다.

Abstract

The photocatalytic activity of TiO_2 was investigated as a function of added amount of Nb_2O_5 , heat treatment temperature and the decomposition rate of 1 mM dichloroacetic acid(DCA). Mixed oxides of TiO_2 and Nb_2O_5 was prepared by the sol-gel process. The addition of Nb_2O_5 into TiO_2 has deleterious effect on the decomposition rate of DCA, which was decreased as the amount of Nb_2O_5 was increased. The excess electrons due to the doping of Nb_2O_5 into TiO_2 can promote the reduction process instead of oxidation or recombination rate with electron holes. The most efficient photocatalyst was the one heat treated at $400^\circ C$ for an hour as far as the heat treatment temperature is concerned. The lower the pH of the solution, the higher the quantum yield.

1. Introduction

The solar detoxification has been discussed as an alternative method to clean up the toxic inorganic compound[1,2]. The semiconducting photocatalysts with an appropriate wavelength of sunlight could obtain complete mineralization of hazardous materials present in water. It has been known that the anatase phase TiO_2 , with the band gap energy of 3.2 eV, has the highest photocatalytic efficiency [3,4]. Thus, light below 400 nm, which is only 5% of the solar energy reaching the surface of the earth, is available to generate electron-hole pair. Unless these electrons and electron holes are involved in the photochemical reactions, they recombine and liberate the heat. Researches have been conducted to modify the photocatalysts to obtain higher photocatalytic efficiency by introducing promoters[5,6,7]. A trial to identify the effect of Nb_2O_5 in TiO_2 has been conducted in the present study by utilizing a sol-gel process.

2. Experimental Procedure

Reagent grade tetra-ethyl-ortho-titanate (TEOT) from Fluka Chem. Co., ethyl alcohol(EtOH), hydrochloric acid, hexylen glycol(HG) and deionized water were utilized for the preparation of sol-gel TiO_2 . Niobium(V) ethoxide from Aldrich Chem. Co. was used for the mixed oxide preparation. The schematic diagram for the sol-gel process is displayed in Fig. 1. The thermal behavior of the sample by using a simultaneous thermal analyser(STA) from Stanton Redcroft Ltd. was shown in Fig. 2.

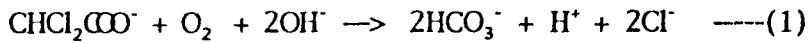
The zero point of charge (zpc) of the sol-gel powder was measured by the Bi-Zeta Plus Instrument of the Brookhaven Instruments Corporation. The pH_{zpc} of 0.2 wt% Nb_2O_5 added TiO_2 , which was heat treated at 400°C for an hour, was identified as around $\text{pH}=4.5$.

Reagent grade dichloroacetic acid(DCA) from Aldrich Chem. Co. was selected as a model compound for the photocatalytic reactions. DCA is a strong organic acid and is dissociated as an anodic form, i.e., $\text{CHCl}_2\text{COO}^-$ in water. It has been reported that the oxidation of one molecule of DCA leads to the formation of one proton [5]. The pH-stat technique for on-line measurements of $[\text{H}^+]$ evolution during the illumination was involved to predict decomposition rate of 1mM DCA at $\text{pH}=3$. The experimental set-up was described in detail in the previous work[6].

3. Results and Discussion

The intensity of the Xe light involved in this experiment was found $1.5\mu\text{E}/\text{sec}$ from the actinometry measurement[6], where E stands for Einstein. The decomposition rate of DCA divided by the light intensity provides the quantum yield of the photocatalyst under the given experimental conditions. If other possibilities

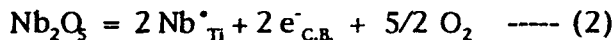
are ignored, $[H^+]$ evolution indicates the degradation of DCA, since one molecule of DCA produces one proton by the following equation (1).



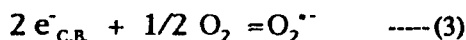
As shown in Fig.3, the concentration of $[H^+]$ in the solution increases as the illumination time increases. It is also noted that the amount of Nb_2O_5 added in TiO_2 as photocatalyst increased, the decomposition rate of DCA decreased as compared to that of pure sol-gel TiO_2 .

The photocatalytic activity of the Nb_2O_5 added TiO_2 was investigated as a function of heat treatment temperatures and is depicted in Fig. 4. As the heat treatment temperature increases, the quantum yield decreases. This can be explained by the thermal behavior of the sample as shown in Fig. 2. Nb_2O_5 added TiO_2 powder experiences phase transformation at the starting temperature of $480^\circ C$ from anatase to rutile. Thus, Nb_2O_5 added TiO_2 powder, heat treated lower than the phase transformation temperature, is remained as anatase phase, which is known to have a higher photocatalytic activity[3,4]. However, a sample that heat treated at $450^\circ C$ for an hour may has a mixture of anatase and rutile phases as can be seen in our preliminary work [4]. The changes in surface areas can be one of the reasons why the quantum yield is decreased as the amount of Nb_2O_5 in TiO_2 is increased. BET surface areas are not revealed in this study, however, Fig. 5 describes SEM pictures of pure sol-gel TiO_2 powder and 0.2wt% Nb_2O_5 added in TiO_2 by sol-gel process. It indicates the particle shape and size are not significantly different from each other.

With the defect structure theory, Ti(IV) can be substituted by doped Nb(V) to produce excess electron as expressed in equation (2)



Where Nb_{Ti}^+ indicates effective positive charge and $e_{c.B.}^-$ is the electron in the conduction band. The excess electrons could be either reacted with O_2 which is absorbed on the surface of TiO_2 as in the equation (3) or recombined with holes as in the equation (4).



The excess electrons retard the photocatalytic reaction in both cases, since it may be consumed in reduction reaction or recombination with holes. Thus, less possibilities to promote oxidation of DCA can be anticipated as the amount of Nb_2O_5

increases. The EPR study of Nb doped TiO_2 implied Nb substitutes Ti^{4+} sites in the form of Nb^{4+} [7]. However, such sites act as donor impurities and they are ready to form electron in the conduction band as indicated in equation (2).

The pH effect of the solution on the quantum yield was investigated and the result of 0.2wt% Nb_2O_5 added in TiO_2 powder by sol-gel process is shown in Fig. 6. As the pH of the solution increases, the quantum yield decreases drastically and levels off in the neutral and basic regions. This indicates the surface condition of a mixed oxide plays an important role in photocatalytic activities. The pH of zero point of charge of 0.2wt% Nb_2O_5 added in TiO_2 powders by sol-gel process was about 4.5. The surface of the above catalyst predominantly positively charged below $\text{pH}=4.5$, thus, a high degradation rate of the anionic DCA can be expected in acidic regions.

4. Summary

The photocatalytic activity of Nb_2O_5 added TiO_2 powders by sol-gel process was lower than that of pure sol-gel TiO_2 powders for 1mM DCA as a target material at fixed pH of 3. The addition of Nb_2O_5 retards the decomposition rate of DCA because of the formation of excess electrons in the conduction band. Thus, this photocatalyst could be useful for the reduction process. The defect structure model was utilized to explain the reason. The energy shift of the conduction band is reasonable theoretically []. However, the exact role of the excess electrons was not clear at the moment.

The quantum yield changes as a function of pH of the solution was explained via surface condition of oxides involved in the reaction. The electrostatic property of a particle surface could cause the specific adsorption of anionic species to the surface from the water phase and provide more reaction sites.

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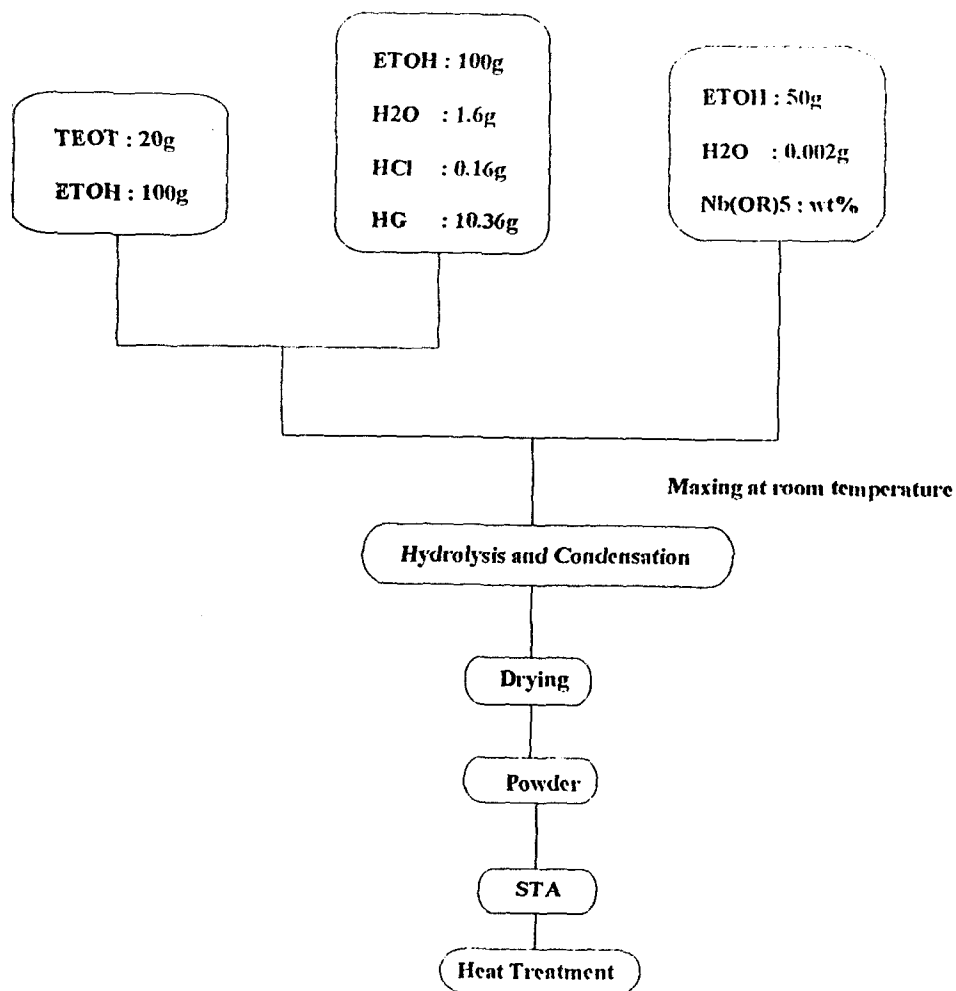


Fig. 1 Preparation for Nb_2O_5 added TiO_2 powders by sol-gel process

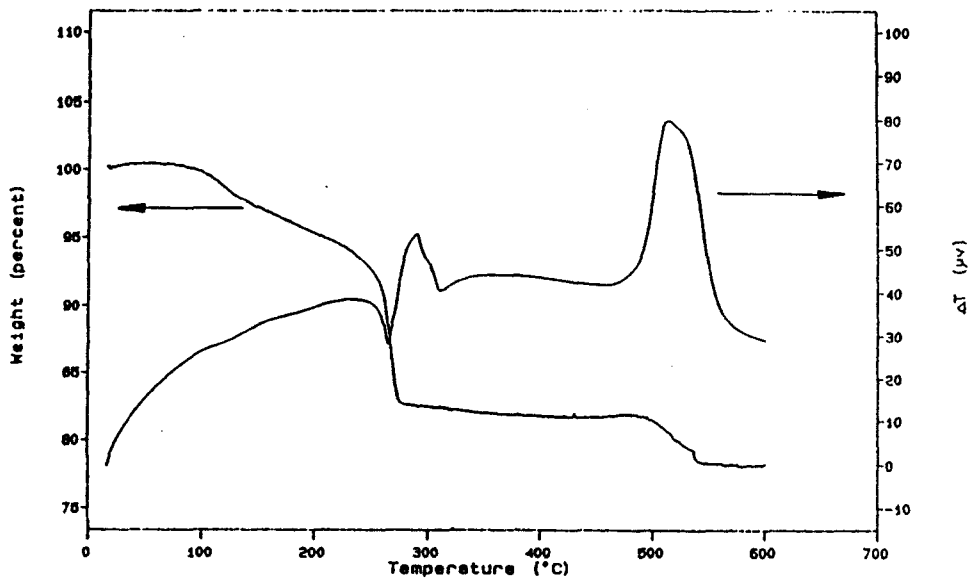


Fig. 2 Thermal behavior of 0.2 wt% Nb_2O_5 added TiO_2 powders

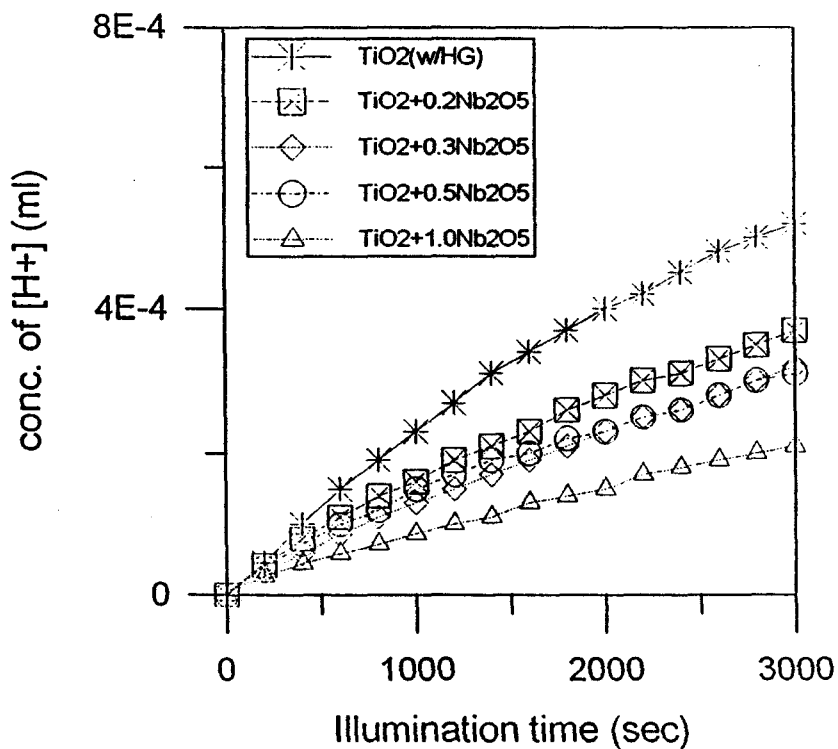


Fig. 3 Concentration of $[\text{H}^+]$ as a function of the illumination time for Nb_2O_5 added TiO_2 powders

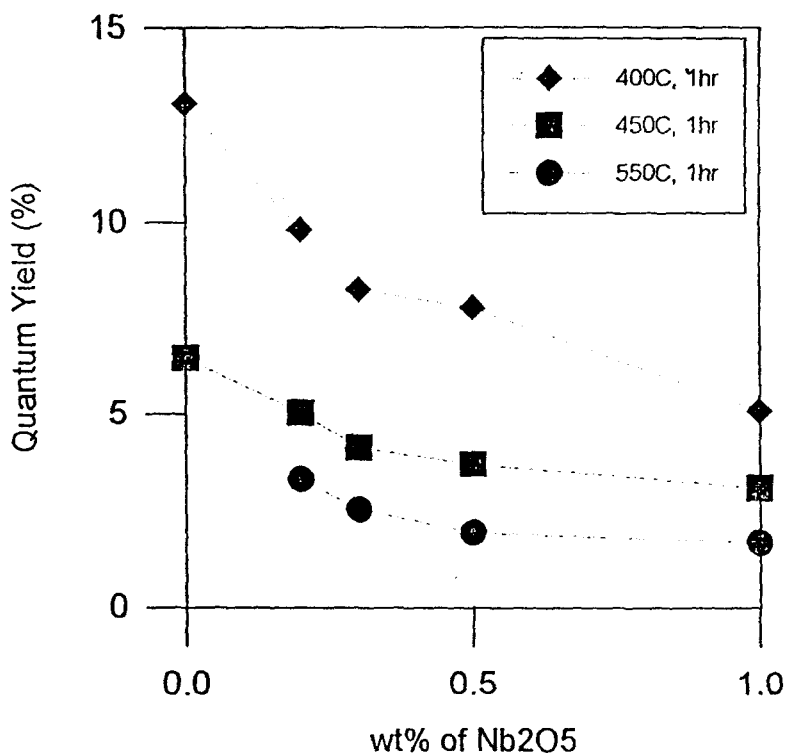


Fig. 4 The changes in quantum yields as a function of the amount of Nb₂O₅ added TiO₂ powders and heat treatment temperature

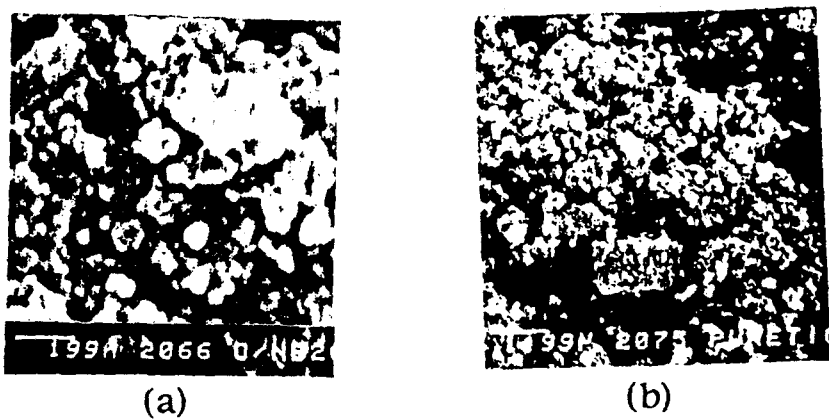


Fig. 5 SEM photographs of (a) pure sol-gel TiO₂ powders and (b) 0.2 wt% Nb₂O₅ added TiO₂ powders

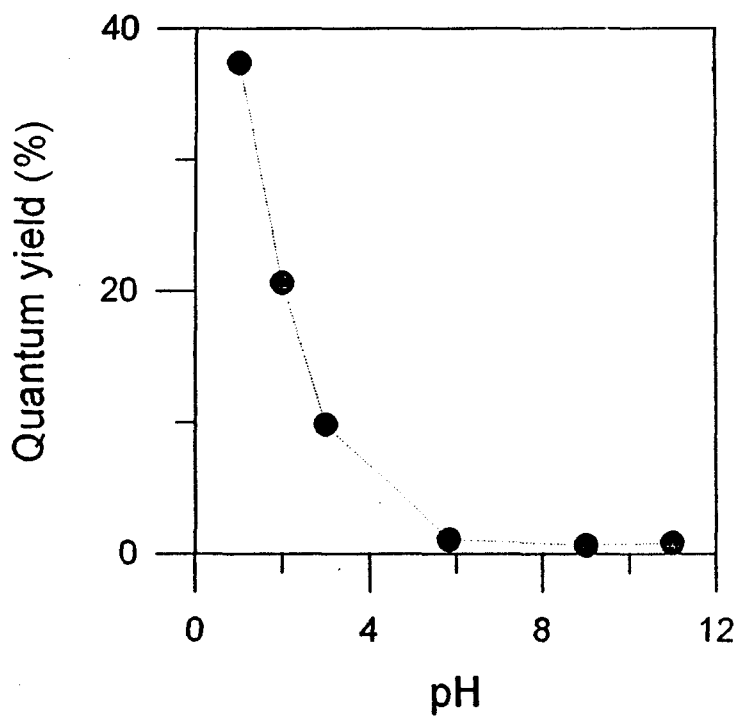


Fig. 6 The effect of pH on the quantum yield