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Original Research Paper

Influence of alkoxide structures on formation of TiO_2/WO_3 heterojunctions for photocatalytic decomposition of organic compounds

Taeseok Choi [a], Jung-Sik Kim [b], Jung Hyeun Kim [a,*]

[a] Department of Chemical Engineering, University of Seoul, 163 Siripdaero, Dongdaemun-gu, Seoul 130-743, South Korea
[b] Department of Materials Science and Engineering, University of Seoul, 163 Siripdaero, Dongdaemun-gu, Seoul 130-743, South Korea

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Reducing recombination and lowering band gap can be achieved with heterostructured photocatalysts, and the TiO_2 photocatalyst film coupled with WO_3 component maintains its advantageous characteristics. In order to investigate the effect of molecular structures on heterojunction formation, the three types of TiO_2 precursors were used to make TiO_2/WO_3 heterojunction. The TiO_2/WO_3 composite films with high transmittance were successfully fabricated by the sol–gel spin coating method. Formation of Ti–O–W linkage was preferable from the precursor with small steric hindrance, and it was confirmed with the well scattered WO_3 components in TiO_2 crystal matrix and also with reduced TiO_2 crystal size. High portion of Ti–O–W bond resulted in the most effective photocatalytic activity. Therefore, it is important to use a proper precursor to improve photodecomposition efficiency in manufacturing the heterostructured photocatalysts.

1. Introduction

Since Goodeve et al. suggested photosensitized catalyst reaction in 1938 [1], lots of research were reported such as water splitting to hydrogen production [2], removing pollutants in aqueous solution [3], and air purifying system [4]. Especially, photocatalyst coated glass with high transmittance has attracted great attentions because of its self-cleaning characteristics [5,6], super hydrophilicity [7], and long term stability [8]. In addition, photocatalytic glasses has been developed to apply not only for self-cleaning of outdoor environments such as skyscrapers and dome stadiums but also for air-purifications of indoor environment like hospital.

Many attempts have been devoted to develop high-performance photocatalysts on glass substrates by impurity doping on base material [9], phase mixing [10], and heterojunction synthesis [11–14]. Among these methods, the heterojunction is the most attractive method for improving the efficiency of semiconductor photocatalyst by simple combinations of multiple components. Combined heterojunctions from different semiconductors with suitable valence band (VB) and conduction band (CB) not only inhibit the recombination of electron-hole pairs but also modify the band gap structure of semiconductors [15]. The selection of proper components for heterojunction formation is very important because the improper band arrangement has negative effect on electron-hole separation. In heterojunction systems, it is impossible to separate electron-hole pairs if the CB and VB of minor component are located between those of the major component [16]. For example, the VB of WO_3 is located at more positive side than that of TiO_2, and thus the holes in the WO_3 VB can be transferred to that of TiO_2. Therefore, TiO_2/WO_3 heterojunction photocatalysts can effectively initiate various oxidation reactions for photodecomposition of contaminant molecules. In addition, heterostructured TiO_2 photocatalyst maintains its advantageous characteristics such as outstanding oxidizing power, nontoxicity, and chemical stability [5,17] without fast recombination of photo excited electron-hole pairs [11,13].

Many researchers tried to find optimum composition of heterostructured materials [13,18,19], but there are few studies for investigating the effect of molecular structure on heterojunction formation. In this study, we selected three types of TiO_2 precursors (titanium n-propoxide, titanium n-butoxide, and titanium isopropoxide) to examine the effect of molecular arrangement during hydrolysis–condensation reaction. Under the same use of WO_3 precursor (tungsten hexaisopropoxide), Ti–O–W heterojunctions were investigated to see the steric hindrance effect for the three precursors. The heterostructured crystalline phase of TiO_2 was investigated with X-ray diffraction. X-ray photoelectron spectroscopy and high resolution transmission electron microscope were also used to examine the heterojunction systems. The film

* Corresponding author. Fax: +82 2 6490 2364.
E-mail address: jhkimad@uos.ac.kr (J.H. Kim).

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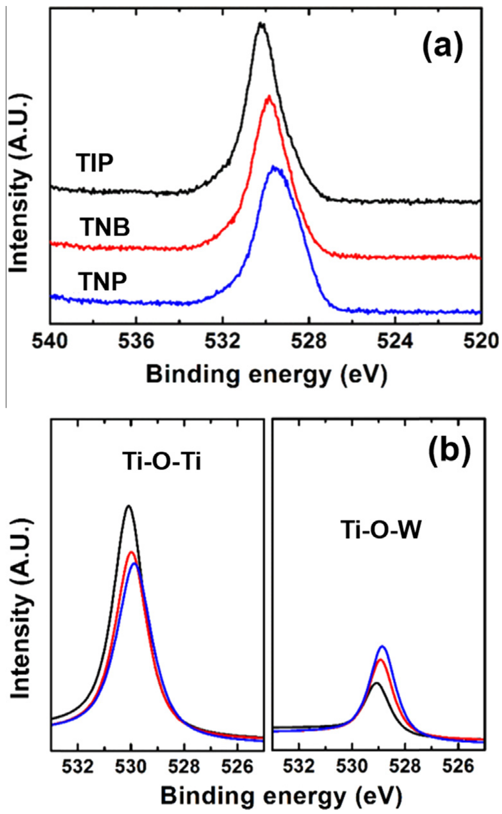

Fig. 1. XPS spectra of O1s peaks from TIP, TNB, and TNP precursors and binding energy peaks for Ti–O–Ti and Ti–O–W linkages from deconvolution of O1s peaks (b).

thickness and optical properties were measured by field emission scanning electron microscope and UV–vis spectroscopy. The photodecomposition of methylene blue (MB) was performed under 150 W Xe lamp, and the extent of decomposition was measured every 15 min.

2. Experimental

2.1. Solution preparation via sol-gel synthesis

The coating solutions for TiO_2/WO_3 heterojunction films were prepared with ethanol (anhydrous, 99.5%, Sigma–Aldrich®), n-butanol (anhydrous, 99.8%, Sigma–Aldrich®), deionized water, precursors of TiO_2, nitric acid (HNO_3, 70%, Sigma Aldrich®), and tungsten hexaisopropoxide (5% w/v in isopropanol, Alfa Aesar) in the molar ratio of 19:1:0.5:1:0.1:0.025 [5]. Titanium precursors were titanium isopropoxide (TIP, 97%, Sigma–Aldrich®), titanium n-butoxide (TNB, 97%, Sigma–Aldrich®), and titanium n-propoxide (TNP, 98%, Sigma–Aldrich®). Prepared TNP and TIP solutions were transparent, but the TNB solution was slightly yellowish transparent. The SiO_2 solution was also prepared by mixing ethanol, deionized water, tetraethyl orthosilicate (TEOS, 99%, Sigma–Aldrich®), and HCl in the molar ratio of 10:4:1:0.03 for introducing SiO_2 barrier layers onto soda-lime glass substrates. All solutions were stirred and aged for 24 h for solution stability. The as-prepared TiO_2/WO_3 and SiO_2 solutions were stable and transparent for two weeks without precipitation at room temperature.

2.2. Film fabrication

Heterostructured films were manufactured with spin coating and sintering processes as reported previously [5]. The glass

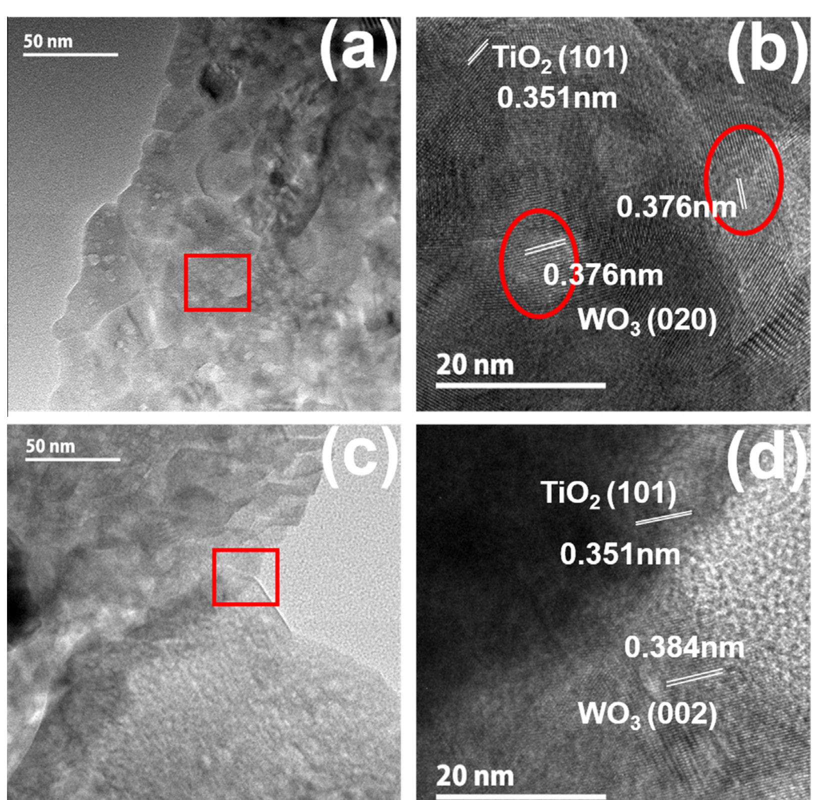

Fig. 2. HR-TEM images of TiO_2/WO_3 heterojunctions produced from TNP (a) and TIP (c) precursors. Images (b) and (d) are magnified from the red square regions in (a) and (c) images. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)