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Preparation and Photocatalytic Activity of $[PW_{12}O_{40}]^{3-}$-Grafted Anatase Powder from Selective Leaching of $BaTiO_3$

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Abstract

Titanium oxide (anatase) particles were prepared using selective Ba leaching from $BaTiO_3$. The anatase powder was flaky. Its photocatalytic activity for the decomposition of gaseous 2-propanol (IPA) was improved by grafting tungsten-based Keggin-type heteropolyacids (PW_{12}: ($[PW_{12}O_{40}]^{3-}$). PW_{12}-grafted anatase powder immobilized onto Pyrex glass plates with amorphous TiO_2 exhibited better retention of the UV induced hydrophilicity than the pure anatase. Results suggest that the electron scavenger property of PW_{12} plays an important role in the overall photocatalytic performance of the material.

Key-words: *$BaTiO_3$, Anatase, Photocatalyst, Hydrophilic*

1. Introduction

Titanium oxide (TiO_2) is a well-known semiconductor photocatalyst[1,2]. Electron and hole pairs are generated when TiO_2 is illuminated by UV. The electron and hole pairs respectively reduce and oxidize adsorbates on the surface, thereby producing radical species such as OH radicals and H_2O_2, which can decompose most organic compounds. Various studies have examined the application of TiO_2 for water and air purification[3-8]. Together with the photocatalytic decomposition activity, a highly hydrophilic state is obtainable on a TiO_2 surface under UV illumination. This phenomenon is designated as *photoinduced hydrophilicity*[9-11].

In electronic devices such as multilayered ceramic condensers, $BaTiO_3$ is widely used as a Pb-free ferroelectric material[12]. Because of its toxicity, Ba concentrations in water and soil are carefully monitored and restricted. Usually, $BaTiO_3$ waste is solidified for disposal by mixture with concrete or glass. As a candidate of the recycle process for $BaTiO_3$, Kikuta *et al.*[13] reported the processing of TiO_2 powder by acid leaching of $BaTiO_3$ in 2006. Subsequently, we prepared rod-like rutile[14,15] and flake-like anatase[15] from the same $BaTiO_3$ by varying the processing conditions.

Very recently, Pruethiarenun *et al.* hybridized tungsten-based Keggin-type heteropolyacid (PW_{12}: $[PW_{12}O_{40}]^{3-}$) with brookite-type TiO_2. Their results revealed that the material exhibited higher photocatalytic decomposition activity and that it had higher photoinduced hydrophilicization rates than pure brookite under UV illumination[16,17]. These results were inferred to have derived from electron scavenging of PW_{12} and the resultant Z-scheme photocatalytic systems in the material[18,19]. However, their material provided better retention of hydrophilicity in the dark than pure brookite did. They attributed this property to the slow reoxidation efficiency of PW_{12}^{-} [17]. Although the improvement of photocatalytic decomposition activity of TiO_2 by PW_{12} grafting was confirmed also in the PW_{12}/anatase system[20-22], the wettability conversion behavior has not been confirmed on the system. Based on this background, we prepared single-phase flaky anatase from acid treatment of $BaTiO_3$ powder. Then photocatalytic decomposition activity under UV illumination and the wettability conversion before and after UV illumination were evaluated for the sample with and without PW_{12} grafting.

2. Experimental

2.1 Sample preparation

A commercial $BaTiO_3$ powder (details of characteristics were presented in a previous report[14], 2.0 g, BT-01; Sakai Chemical Industry Co. Ltd., Japan) was mixed with a 5M HNO_3 solution (100 mL) by stirring at room temperature. Then the suspension was heated to 72˚C. The temperature was maintained for 4 min. The suspension was filtrated and cooled to about 50˚C; its pH value was adjusted to 3 using a 25 mass % NH_4OH solution. The obtained suspension was heated to 90˚C again and aged at that temperature for 1 hr. Subsequently, the suspension was centrifuged and sedimentation was washed in distilled water by sonication for 5 min. This washing procedure was repeated twice. Then the powder was dried using a freeze-dryer (DC400; Yamato Scientific Co. Ltd., Japan). Anatase powder was obtained when the dried powder was