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Interfacial sol–gel processing for preparation of porous titania particles using a piezoelectric inkjet nozzle

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A B S T R A C T

The aim of the present work is to apply the liquid–liquid interfacial crystallization using a piezoelectric inkjet nozzle to the sol–gel processing. The instillation process was compared with the batch process to elucidate the effectiveness of the inkjet technique on the liquid–liquid interfacial sol–gel processing. The effect of frequency and water concentration in titanium tetraisopoxide (TTIP) solution on titania particle properties was investigated for sol–gel processing with a piezoelectric inkjet nozzle. Titania particles produced by each process were calcined at 500 °C. The crystal structure, morphology, pore size distribution and specific surface area of titania particles were evaluated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen physisorption measurement. The photocatalytic activity of titania particles was evaluated by the photodegradation of methylene blue solution under UVC light irradiation.

Monodispersed titania particles could be produced by instillation sol–gel processing of hexane using a piezoelectric inkjet nozzle. Titania particles prepared at 1500 Hz were spherical while titania particles prepared at 1000 Hz and 3000 Hz were non-spherical. The number of particulate fracture increased with water concentration in TTIP solution. The inkjet nozzle-mediated instillation processing was found to be a promising way to create porous titania particles with a high photocatalytic activity.

Keywords: Piezoelectric inkjet nozzle; Sol–gel processing; Titania particles; Liquid–liquid interface; Photocatalytic activity

1. Introduction

The functional materials have been used in wide-ranging industrial fields (Hosokawa et al., 2012). The materials are affected significantly by the physical and chemical properties of particles. The ability to control the particle characteristics is of huge importance (Masuda et al., 2006). Bottom-up process has been used for controlling the physical and chemical properties of particles in manufacturing process (Allan, 2001). There have been some studies on controlling the particle properties in bottom-up process such as the crystallization and sol–gel method (Worlitschek and Mazzotti, 2004; Fuchs et al., 2008; Rahman and Padavettan, 2012). Crystallization is an attractive isolated process for manufacturing because this process combines both particle generation and purification (Kubota and Ohshima, 2001). Crystallization technique is generally achieved by reducing the solubility of products in this solution by cooling, evaporation, anti-solvent addition and

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some combination of these methods (Kim and Ulrich, 2001; Yu et al., 2007; Takiyama et al., 2010). A method for driving crystallization is via a chemical reaction where two or more reactants are mixed to form a solid product insoluble in the reaction mixture such as sol–gel processing. Sol–gel processing also has been widely used because of creating nanostructured materials with controlled porosity and shape (Pierre, 1998). Sol–gel processing presents an important approach to the fabrication of nanostructured materials in form of bulk solids and surface coatings (Brinker and Scherer, 1990). The process is to synthesize particle with various functions at low temperature and simple process. Based on sol–gel chemistry, titania particles can be prepared by the hydrolysis and condensation reactions of appropriate precursors. Some researchers have succeeded in fabricating titania particles as photocatalytic materials (Rivallin et al., 2005; Azouani et al., 2010; Nikaido et al., 2009). Ruzimuradov et al. (2014) have investigated the effect of crystalline phases and the hydrolysis rate on the photocatalytic activity of porous titania. Loryuenyong et al. (2012a) have reported that the enhancement of photocatalytic activity of meso-macroporous titania and titania nanoparticles is associated with the increase in photo-absorption efficiency and efficient diffusion of molecules caused by the increase of surface area. However, it is hard to deal with nano-particles mainly because of tendency to agglomeration as a result of their high surface area (Kear et al., 2001). It is extremely difficult to control the morphology of titania particles because of rapidly hydrolysis rate of titanium alkoxide (Rivallin et al., 2005). It is therefore important to propose a promising fabrication method to control the hydrolysis rate of titanium alkoxide and the morphology of titania particles.

We have developed a liquid–liquid interfacial crystallization to precipitate solute particles on a liquid–liquid interface which is partially miscible. (Kadota et al., 2007a, 2007b) Interdiffusion between aqueous solutions and organic solvents occurs near the liquid–liquid interface according to the mutual solubility curve (Kitayama et al., 2009). We could successfully produce the glycine porous particles or organic/inorganic composite particles using this liquid–liquid interfacial crystallization (Tanaka et al., 2011; Kadota et al., 2013). The piezo inkjet technique is also significantly effective by applying the crystallization because the morphology control of particles could be expected by creating uniform spherical droplet (Wijshoff, 2010). Piezoelectric inkjet technique has recently been drawing attention as a particle production method in manufacturing processes (Böhmer et al., 2010; Chen and Trout, 2010). Advantages of piezoelectric inkjet techniques are to control various size droplets without thermal energy. Bohmer et al. produced polymer particle using inkjet techniques. Kitsomboonloha et al. (2008) produced metal particles using inkjet techniques. Both groups could succeed in controlling the particle size distribution using inkjet nozzle. In our previous paper, the inkjet technique was applied to liquid–liquid interfacial crystallization (Tamura et al., 2014). The liquid–liquid interfacial crystallization by instillation using the inkjet technique succeeded in controlling the morphology of amino acid particles. Their results give us some expectation that this liquid–liquid interfacial process using inkjet nozzle might be effective for sol–gel process since the reaction fields are limited into uniform spherical interface. Nano-particles are subject to agglomeration and exhibit handling difficult behavior although titania nano-particles could be obtained due to rapidly hydrolysis rate of titanium alkoxide as described above. Fabrication of titania particles, which is comparatively easy to handle, is meaningful in chemical industries.

In the present work, we have applied the liquid–liquid interfacial process by instillation using a piezoelectric inkjet nozzle to the sol–gel processing. The instillation process was compared with the batch process to elucidate the effectiveness of interfacial sol–gel process using a piezoelectric inkjet nozzle. The effect of frequency and water concentration on morphology of titania particles was investigated in the instillation process using a piezoelectric inkjet nozzle. The formation mechanism of porous titania particles was discussed from relationship between droplet size and particle size. The characteristics of titania particles produced by interfacial sol–gel processing using a piezoelectric inkjet nozzle were evaluated. The photocatalytic activity of titania particles was evaluated by photodegradation under ultraviolet light.

2. Experimental

2.1. Materials

Titanium tetraisopoxide (TTIP) (95%), hexane (97%), ethanol (99.5%), acetonitrile (99.5%) hydrochloric acid (HCl) were purchased from Nacalai tesque (Japan). All reagents were used without purification. Both hexane and ethanol were sufficiently dehydrated by the molecular sieve. All solutions were filtered by the membrane filter with 0.1 μm pore before sol–gel process.

2.2. Preparation of titania particles

Titania particles were fabricated via a chemical reaction in the confined space formed on liquid–liquid interface. Titania is one of the most popular and promising materials as a photocatalyst because it is stable in various solvents under photoradiation (Arunmetha et al., 2013). Furthermore, it has a potential ability to induce various types of redox reactions (Ohtani et al., 1997). Titanium tetraisopropoxide (TTIP) was selected as a starting precursor for sol–gel process. The volume of 6 mL of TTIP was dissolved in 60 mL of hexane or ethanol. The liquid–liquid interface between water and hexane was formed but the interface between water and ethanol was not formed because ethanol was miscible in water. TTIP solution was sufficiently dissolved in organic solvents of hexane and ethanol by agitating for 10 min. The concentration of water was adjusted by adding acetonitrile which is miscible in water but creates liquid–liquid interface with hexane. The pH of aqueous solutions was adjusted to 3.0 by adding HCl. Water droplets had been discharged into the TTIP solution from a piezoelectric inkjet nozzle for 1 h. The suspension was filtered by membrane filter with 0.1 μm pore size and the titania particles were dried in a desiccator with blue silica for 24 h. In order to investigate the effect of a process, titania particles were prepared by the batch process without a inkjet nozzle under the same operating condition. The water concentration and frequency of piezoelectric inkjet nozzle might affect the characteristics of titania particles. The water concentration was 10, 20, 50 and 80 vol%. The frequency was 1000, 1500 and 3000 Hz to determine the optimum frequency. The samples were then calcined at 500 °C.

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