Preparation of purely inorganic silica doped titania fibers via electrospinning

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The preparation technique to obtain purely inorganic silica doped titania fibers using electrospinning together with sol–gel method was proposed. For the system without silicon doping, fibers were too brittle to form long fiber. And it was clarified that small amount of doped silicon could modify the flexibility of fibers drastically and long fibers with appropriate mechanical property could be obtained. After calcination at 500°C for 2 h anatase phase was appeared and the specific surface area of fibers with composition of [Ti]/[Si] = 6 showed highest value 71.9 m²/g among all the samples tested, which is even higher than typical fine particles. The result of decomposition experiment of Rhodamine B dye solution showed that the silica doped titania fiber has adequate photocatalytic activity to decompose organic matters.

Key-words : Titania, Silica, Photocatalyst, Electrospinning and sol–gel

1. Introduction

The photocatalytic activity of TiO₂ has been the objects of intensive researches from its finding by Honda and Fujishima. From the beginning, waste water treatment has been thought to be one of the most promising applications. It is well-known that activated species from TiO₂ under UV radiation have quite intensive oxidation activity to decompose a variety of organics down to H₂O and CO₂. However, in spite of its potential, waste water treatment process with TiO₂ is still scarcely under practical application due to several reasons. The most severe problem is probably that UV radiation is essential. Against this problem, several innovative works such as nitrogen or sulfur doping to make TiO₂ be responsive to visible light have been achieved. Although there is a pioneer work about the fabrication of titania doped silica fiber using electrospinning together with sol–gel synthesis, titania rich composition has not been reported. This work offers a novel and high throughput process to obtain purely inorganic silica doped titania fiber of high specific surface area.

2. Experimental procedures

All the chemical reagents were analytical grade purchased by Kishida Chemical and used without further purification. Water was used after deionization followed by distillation. A typical sol preparation procedure is as following. 5.21 g of concentrated hydrochloric acid (36 mass %) and 0.39 g of water were dissolved into 5.0 g of ethanol (Solution A). In the mean time, 51.56 g of titanium tetraisopropoxid (TTIP) and 6.25 g of tetraethoxysilan (TEOS) were dissolved into the 5.0 g of ethanol in conical flask (Solution B). Solution A was added dropwise into Solution B with magnetic stirring under the ice bath. It took about 30 min to avoid precipitation during mixing. It has been reported that TTIP in ethanol solution is stable and no segregation occurs with appropriate amount of concentrated hydrochloric acid provably due to the complexation by chloride ion. Then the solution was reacted under gentle mixing with magnetic stirring at ambient temperature introducing humidified...
air of 90% relative humidity, controlled by potassium chloride saturated aqueous solution, at the flow rate of 300 ml/min.13) Although the detailed mechanism is still unclear, the employment of humidified air could drastically decrease the reaction time.12) And it is also notable that the onset amount of water, including originated from concentrated hydrochloric acid, was fixed to be unity based on the atomic ratio to the total amount of alkoxide, both TTIP and TEOS, to obtain spinnable sol. As reaction proceeded, viscosity of the solution increased. Just before the throughout gelation, at typical viscosity ca. 500 mPa·s, sol was spun via electrospinning. The viscosity was measured using oscillation viscometer (CBC, VISCOMATE VM-10A). Experimental setup for electrospinning is shown in Fig. 1. In this study, tip-collector distance was fixed to be 200 mm and applied voltage also fixed to be 20 kV constant using high-voltage power supply (Pulse Electronic Engineering, Model 502). Tip inner diameter is ø1.5 mm and flow rate of sol was not controlled.

Obtained fibers were characterized by powder X-ray diffraction (XRD) (Rigaku, RINT 2000) using Cu-Kα radiation under the scan rate of 2.0 deg./min. Scanning electron microscope (SEM) (Keyence, VE-8800) was used to observe the fiber morphology and fiber thickness. Nitrogen adsorption method (Bell, Belsorp Mimi) was used to measure the specific surface area of fibers. Diffuse reflection spectroscopy (JASCO, V-650) was carried out to measure the band gap energy. And the zeta potential measurement (Malvern, Zetasizer 3000HS) was carried out.

The photocatalytic activity of fibers was verified by the decomposition experiment of Rhodamine B dye as the following procedure. 1.0 g of fiber was immersed in the 100 g of 5 ppm Rhodamine B dye aqueous solution charged in the quartz beaker. Then UV light of 254 nm wave length with the intensity of 614 μW/cm² at 50 mm distance was irradiated from two lamps (AS ONE, SLUV-4). At certain time intervals, 5 ml of solution was taken then the concentration of Rhodamine B dye was measured with UV–vis spectrometer (Hitachi High-Tech, UV-2400PC).

3. Results and discussion

To begin with, the characteristic of purely titania system without TEOS addition is briefly summarized. For the purely titania system, as the reaction proceeded sol became spinnable typically after 4 h. Digital image of obtained fiber is shown in Fig. 2(a) and SEM image is shown in Fig. 2(b) respectively, and it is clearly seen that the fiber is short and has dust-like aspects. This can be attributed to the brittleness of gel which differs vastly from the silica fiber with cotton or wool-like tactile as found in our previous work.13) In order to give fibers flexibility modifying tactile, silicon was employed into the system. Figure 3 shows the viscosities of solution as a function of reaction time for three different compositions. It can clearly be seen that as the introduced amount of silicon increases the reaction time to obtain spinnable sol becomes long, which is due to the relatively low reactivity of TEOS with respect to TTIP. For all the compositions sol could be spun at about the viscosity of 500 mPa·s. The digital images of obtained fibers shown in Fig. 4(a) are clear evidences of drastic improvement in the flexibilities. This is also can be confirmed by the SEM images shown in Fig. 4(b) where neither tail end nor cross section of fibers can be observed. For all the compositions average thickness of fibers was about 5 μm and little difference was observed in tactile among different compositions.

As spun fibers had amorphous structure for all the compositions and thus samples were calcined at 500°C for 2 h in air. It is notable that fibers still maintained cotton-like overview and enough mechanical property to manipulate with tweezers, although the calcination caused the depression of flexibility more or less. XRD patterns for three different compositions after calcination are shown in Fig. 5. In case of silicon rich
Fig. 2. Digital image (a) and SEM image (b) of fibers for purely titania system.

Fig. 3. Viscosity of sols as a function of reaction time for three different compositions. (●) [Ti]/[Si] = 1/3, (■) [Ti]/[Si] = 3 and (♦) [Ti]/[Si] = 6.

Fig. 4. Digital images (a) and SEM images (b) of fibers for three different compositions.
As for silicon rich system, the specific surface area was reduced from 0.11 to 0.02 cm³/g. The specific surface area of a fiber competitive to particulate form requiring centrifugal separation. This clearly shows that proposed process can provide photocatalyst in unique form and with excellent operability.

4. Conclusion

Purely inorganic silica doped titania fibers were successfully prepared via novel technique using electrospinning together with sol-gel method. The following conclusions were derived.

1) For the system without silicon doping, fibers were too brittle to form long fiber and non-woven mat. However the small amount of silicon doping could modify the flexibility of fibers drastically and long fibers with appropriate mechanical property were obtained.

2) Although as spun fiber had amorphous structure, after calcination at 500°C for 2h anatase phase was formed. The specific surface area of fibers with composition of [Ti]/[Si] = 6 showed highest value 71.9 m²/g among all the samples tested, which is even higher than typical fine particles.

3) The result of decomposition experiment of Rhodamine B dye solution confirmed that the silica doped titania fibers decompose organic matters.

Table 1. Specific surface area of fibers after calcination for three different compositions

<table>
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<tr>
<th>[Ti]/[Si]</th>
<th>Specific surface area (m²/g)</th>
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<tbody>
<tr>
<td>1/3</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>43.1</td>
</tr>
<tr>
<td>6</td>
<td>71.9</td>
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composition [Ti]/[Si] = 1/3, crystal structure remained to be amorphous. For other two titanium rich compositions, anatase phase could be observed and peak positions were in relatively good agreement with diffraction data JCPDS PDF#21-1272. And it was also confirmed that the crystallinity was higher in the case of [Ti]/[Si] = 6 where less amount of silicon was doped. The specific surface areas of samples are tabulated in Table 1. As for silicon rich system, the specific surface area was too small to measure using the nitrogen adsorption method, and it was clarified that less amount of silicon doping could provide higher specific surface area. This tendency may be due to the closure of pore originated from silica during calcination process up to 500°C. It will be supported by the fact that the total pore volume was reduced from 0.11 to 0.02 cm³/g during calcination in [Ti]/[Si] = 3 system. The mean pore size after calcination for both systems was about 3.2 nm in diameter. It is notable that 71.9 m²/g for the sample of [Ti]/[Si] = 6 is even higher than typical non-porous titania Evonik P25 whose specific surface area is 40–50 m²/g.

Hereafter the sample of [Ti]/[Si] = 6 with highest crystallinity and specific surface area was used to demonstrate the photocatalytic activity. It was confirmed prior to the decomposition experiment that Rhodamine B dye is not decomposed only by UV radiation without photocatalyst and that adsorption is not prominent under dark condition. Figure 6 shows the decomposition yield as the function of UV radiation time. The decomposition yield was calculated using working curve established beforehand. It was clarified that Rhodamine B dye was completely decomposed after 25 h. By contrast, using Evonik P25 catalyst, the same amount of dye was decomposed within 5 h. The apparent performance decrement in spite of higher specific surface area may be attributed to the narrowing of band gap energy and the change in the zeta-potential. The band gap energy of synthesized fiber was 2.77 eV and that of Evonik P25 was 3.2 eV respectively. This perhaps causes the shortening of lifetime of active species. And it is well known that titania has positive surface charge in neutral solution, however the zeta potential of pulverized fiber was —13.0 mV. And this shall change the affinity of Rhodamine B to the surface. At this stage, it is not clear which factor is dominant and further detailed investigation is required. Nevertheless it should be stated again that photocatalytic fibers could be easily and completely removed from the solution simply with tweezers and this makes the photocatalytic fiber competitive to particulate form requiring centrifugal separation. This clearly shows that proposed process can provide photocatalyst in unique form and with excellent operability.

References