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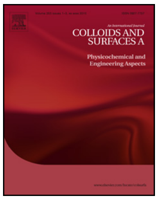

Fabrication of nitrogen-doped titanium oxide/silica core–shell particles and their electrical conductivity

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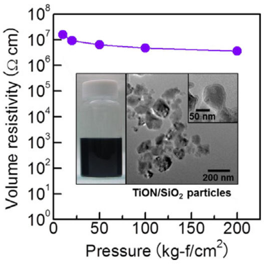
HIGHLIGHTS

- We fabricated partially nitrided titanium oxide (TiON)/SiO_2 core–shell particles.
- The TiON particles were silica-coated by a sol–gel process using silicon alkoxide.
- The silica shell thickness increased with increasing silicon alkoxide concentration.
- The TiON/SiO_2 particles had the volume resistivity larger than 2.8×10^6 Ω cm.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work proposes a method for fabricating partially nitrided titanium oxide (TiON) particles coated with silica shells (TiON/SiO_2) using a sol–gel process and describes their electronic insulation properties. Commercially available TiON particles with an average size of 90.3 ± 29.9 nm were used as the core particles. The silica coating of the TiON particles was performed using a sol–gel method with 15 M tetraethylorthosilicate (TEOS) in H_2O and 1.2×10^{-3} M NaOH in an ethanol solution containing 1.0×10^{-2} M TiON particles at 35 °C. Successful silica coating was confirmed using transmittance electron microscopy, dynamic light scattering, electrophoretic light scattering, X-ray photoelectron spectroscopy and optical spectroscopy. The silica shell thickness increased in the range of 3.6–11.4 nm with increasing TEOS concentrations from 2.0×10^{-3} to 9.0×10^{-3} M. The volume resistivity of a powder of the TiON/SiO_2 particles was larger than 2.8×10^6 Ω cm, even under pressure, i.e., it did not decrease remarkably with an increase in pressure applied to the powder from 10 to 200 kg-f/cm^2. The silica shells were hypothesized to prevent the TiON particles from contacting other TiON particles.

1. Introduction

Black particles are mainly based on materials such as chromium compounds and carbon [1–7]. These black particles have been used as raw materials for optical devices, such as the black matrix of a liquid crystal display [1–3,5]. The particles are desired to be electrically insulating for these applications and to be colloidally stable

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for the fabrication of the black matrix. However, there is room for improvement on properties such as electrical insulation and colloidal stability in the existing raw materials for the black matrix for their practical use.

Titanium oxide (TiO_2) is a ceramic that has excellent photocatalytic properties. Because TiO_2 has a band gap of 3.2 eV (anatase), which is in the ultra-violet region, the energy from the visible wavelengths contained in sunlight is not utilized in photo-catalysis. Nitrogen-doping of TiO_2 is one way to narrow its band gap and has been used by several researchers [8–13]. The color of the nitrogen-doped titanium oxide (TiON) powder varies from white (for TiO_2) to black with an increase in amounts of doped nitrogen. Therefore, TiON may be applicable as not only a photo-catalyst but also as the black particles in a black matrix. Although the TiON is a promising raw material for the black matrix, its electronic applications are limited because of its electrically conductivity and its high density. Mixing TiON with insulating powder is a simple technique that makes it electrically insulating. However, this mixing does not prevent TiON particles with high densities from sedimenting.

Coating the particles with shells of a material that is electrically insulating is a solution for solving the problems related to the electrical conductivity of TiON. Silica is a candidate material for the fabrication of this type of shell because it is electrically insulating. In addition, TiON particles coated with silica shells may be colloidally stable because of the colloidal stability of silica particles in the liquid phase. Various researchers have proposed silica-coating methods [14–23]. Most of these silica-coating methods involve (1) the synthesis of core particles, (2) surface-modification of the core particles to increase the affinity between the core particle surface and the silica shells, and (3) the formation of silica shells using a sol–gel method that involves silicone alkoxides. Our research group has also studied the silica coating of various particles, such as Au, Ag, Co, Cu, AgI, Q-dot, Gd compounds and fluorescence beads, and their properties, such as their optical and magnetic properties and their use in imaging for medical diagnosis [24–37].

In the present work, our proposed silica-coating technique was extended to the fabrication of TiON particles coated with silica shells ($TiON/SiO_2$). Their optical and electrical properties were studied.

2. Materials and methods

2.1. Materials

TiON particles are commercially available under the trade name Titanium Black from Mitsubishi Materials Electronic Chemicals Co., Ltd. The TiON was composed of 60 wt% TiN and 40 wt% TiO_2 and was obtained as an aqueous dispersion of TiON particles with a content of 10 wt% TiON (Ti concentration: 1.61 mol-Ti/L, TiON concentration: 111 mg-TiON/mL) from the company, as shown in Fig. 1(a). For the silica coating, tetraethylorthosilicate (TEOS) (Kanto Chemical, 95%), aqueous NaOH (Kanto Chemical, 1 M), and ethanol (Kanto Chemical, 99.5%) were used as the silica source, the catalyst for the sol–gel reaction of TEOS and the solvent, respectively. All chemicals were used as received. Water was ion exchanged and distilled using a Yamato WG-250 prior to use in all experiments.

2.2. Methods

2.2.1. Preparation

The TiON particles were silica coated using a sol–gel method, as follows. The TiON dispersion, TEOS and aqueous NaOH were added to an H_2O/ethanol solution ($TiON/SiO_2$). The reaction temperature and time were 35 °C and 24 h, respectively. The initial concentrations of Ti, NaOH, H_2O and TEOS in the reactant solution were adjusted to 1.0×10^{-2}, 1.2×10^{-3}, 15 and 1.0×10^{-3}–9.0×10^{-3} M, respectively, in which the initial Ti concentration corresponded to 0.69 mg-TiON/mL. The as-prepared $TiON/SiO_2$ particles were washed using repeated process consisting of centrifugation (15,000 rev/min, 30 min), the removal of the supernatant via decantation, the addition of water and shaking on a vortex mixer, which resulted in replacement of the solvent with water. This procedure was repeated three times. To obtain a powder of the $TiON/SiO_2$ particles, the residue left at the bottom of centrifuge tube after the removal of the supernatant via decantation was dried in air at room temperature.

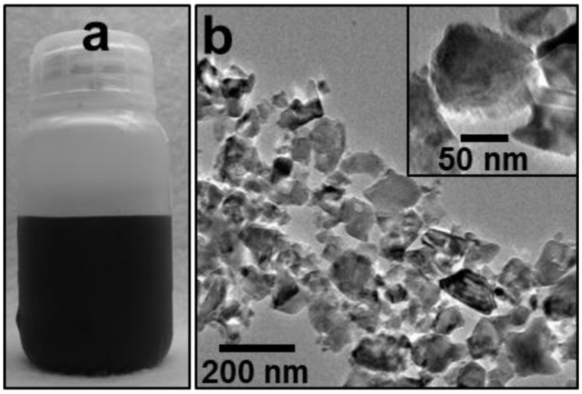

Fig. 1. Photograph of the TiON particle colloid solution (a), and TEM image of the TiON particles in the colloid solution (b).

2.2.2. Characterization

The particles were characterized using transmittance electron microscopy (TEM), dynamic light scattering (DLS), electrophoretic light scattering (ELS), X-ray photoelectron spectroscopy (XPS) and optical spectroscopy. The TEM was performed using a JEOL JEM-2000FX II (Akishima, Tokyo, Japan) microscope operating at 200 kV. The TEM samples were prepared by dropping and evaporating the particle suspensions onto a colloid-coated copper grid. Dozens of particle diameters were measured to determine the volume-averaged particle size. The distribution of the particle sizes and the ζ-potentials of the particles were measured using DLS and ELS, respectively, to obtain information about the state of the particles. Both DLS and ELS were performed using a Brookhaven Zeta-Plus instrument (Holtsville, New York, USA). An aqueous HCl or NaOH solution was added to the sample to alter the pH for the ELS measurements. The study of the surface composition of particles was performed using XPS measurements. The XPS samples were powders that were obtained by drying the particles at room temperature in vacuo after the final removal of the supernatant during the washing process. The XPS spectra were obtained using a JEOL JPS-9010 equipped with a monochromatic Mg Kα radiation source (200 W, 10 kV, 1253.6 eV). To study the composition below the surface, the particles were etched using 500 kV Ar^+ sputtering for 1 min. The transmittances of the colloidal particle solutions from the ultra-violet to the near-infrared were measured using a Shimadzu UV-3101PC (Kyoto, Japan) spectrophotometer.

The volume resistivities of the particle powders were measured using a 4-pin probe to determine the electrical insulation of the particles. The measurements were performed while applying pressure to the powder sample in the range of 0–200 kg-f/cm^2 using a Mitsubishi Chemical Analytech MCP-T610 resistivity meter.