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Silica-coating of nitrogen-doped titanium oxide particles and their electrical conductivity

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ABSTRACT

The present work investigates effects of concentrations of raw chemicals in a sol–gel process on morphology of partially nitrided titanium oxide (TiON) particles coated with silica shells (TiON/SiO_2) and describes their electronic insulation properties. Commercially available TiON particles with an average size of 90.3 ± 29.9 nm, of which the volume resistivity was 6.27×10^{-2} Ω m under pressure applied to their powder of 200 kg-f/cm^2, were used as the core particles. The silica-coating of the TiON particles was performed using a sol–gel method using tetraethylorthosilicate (TEOS) at 1.2×10^{-3}–12.0×10^{-3} M NaOH and 9–21 M H_2O in an ethanol solution containing 1.0×10^{-1} M TiON particles at 35 °C. Optimum concentrations of NaOH and H_2O for successful silica-coating were 15 and 9.0×10^{-3} M, respectively. The silica shell thickness increased in the range of 105 ± 37–114 ± 40 nm with increasing TEOS concentrations from 1.0×10^{-2} to 9.0×10^{-2} M TEOS. The volume resistivity of a powder of the TiON/SiO_2 particles with a silica shell thickness of 4.9 nm was as high as 2.17×10^3 Ω m at the applied pressure of 200 kg-f/cm^2; the silica shells were considered to prevent the TiON particles from contacting other TiON particles.

1. Introduction

Black pigments have been used for producing black matrix of a liquid crystal display [1]. The black pigments, among which colloid solutions of black particles representative, are required to be electrically insulating and colloidally stable for the production of the black matrix. Materials such as chromium compounds and carbon are representative as the black pigments [2–5]. Properties such as electrical insulation and colloidal stability in the existing black pigments are desired to be improved for their practical use.

Powder of titania particles with no doping has a color of white. The color of white becomes black with nitrogen-doping, because the nitrogen-doping narrows their band gap [6–8]. The nitrogen-doped titanium oxide (TiON) particles with black color tone may be an alternative candidate as the black pigments in a black matrix. They are electrically conductive, and are apt to sediment due to their high density, which limit their electronic applications. Their electrical conductivity can be controlled simply by mixing TiON with insulating powder. However, this mixing does not prevent TiON particles from sedimenting.

Coating the particles with shells of a material provides a physical barrier between each particle. If a material that is electrically insulating is used as the shells, electrical conductivity of the particles is reduced. Accordingly, coating the particles with shells of an electrically insulating material is a solution for solving the problem related to the electrical conductivity of TiON. To solve the problem on the colloidal stability, the coating must stabilize the particles colloidally. The material of shells, of which particles are colloidally stable, may be suitable for the improvement of colloidal stability of the core particles. From these viewpoints, silica is a candidate material for the fabrication of this type of shell, because of its electrically insulating property and the colloidal stability of silica particles in various liquid phases.

Various researchers have employed on silica-coating of particles [9–17]. In most of their silica-coating methods, firstly core particles are synthesized by reactions such as metal salt–base reaction, precipitation reaction between metal salt solutions, reduction of metal ion and polymerization of organic monomer. Secondly, the core particles are surface-modified for increasing the affinity between the core particle surface and the silica shells. Finally, the formation of silica shells is performed by a sol–gel method using silicone alkoxides. Our research group has also studied the silica-coating of various particles such as Au, Ag, Co, RuPt and cadmium

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chalcogenide quantum dot, and their properties such as their optical, magnetic, catalytic and medical imaging properties [18–22]. According to the researches on developments of silica-coating, morphology of silica-coated particles was strongly dependent on raw chemicals such as catalyst, H_2O and silicon alkoxide.

The present work develops a method for fabricating TiON particles coated with silica shells (TiON/SiO_2) by extending our proposed silica-coating technique. Effects of concentrations of various raw chemicals on morphology of TiON/SiO_2 particles were investigated precisely for optimization of fabrication conditions. Their electrical properties were also studied.

2. Materials and methods

2.1. Materials

Core particles used in the silica-coating were TiON particles with under the trade name Titanium Black that were supplied 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. Fig. 1(a) shows an X-ray diffractometry (XRD) pattern of the TION particles, of which powder was obtained by drying the sediment left at the bottom of centrifuge tube after centrifugation and removal of the supernatant *via* decantation in air at room temperature. Several peaks detected at 37.1, 43.1, 62.4, 74.8 and 78.9 degrees were attributed to the (111), (200), (220), (311) and (222) planes of cubic TiN according to the standard data (ICSD: 01-087-063). Except for the TIN peaks, a peak assigned to the (101) plane of tetragonal TiO_2 (anatase) according to the standard data (ICSD: 00-001-056) was faintly detected at 24.6 degree. This XRD measurement indicated that the TiO_2 was doped with nitrogen to produce a mixture of anatase TiO_2 and TiN. According to our previous work [23], the particles were angular in shape, had an average size of 90.3 ± 29.9 nm (transmission electron microscopy (TEM) particle size), had the largest distribution of 38.2 nm (dynamic light scattering (DLS) particle size), and had an isoelectric point (IEP) of 4.3. 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.

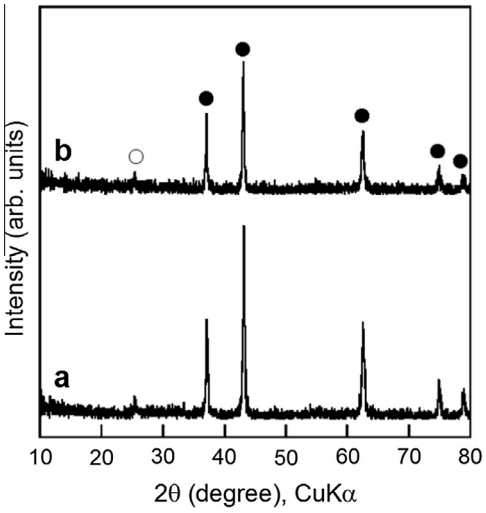

Fig. 1. XRD patterns of (a) the TiON particles and (b) the TiON/SiO_2 particles produced at a NaOH concentration of 6.0×10^{-3} M. The concentrations of H_2O and TEOS were 15 and 3.0×10^{-3} M, respectively. ●: cubic TiN, ○: tetragonal TiO_2 (anatase).

2.2. Methods

2.2.1. Preparation

A colloid solution of the TiON/SiO_2 particles was prepared by a sol–gel method, as follows. The aqueous dispersion of TiON particles and TEOS were added to an H_2O/ethanol solution (TiON/SiO_2). Finally, the aqueous NaOH was added to the TiON/TEOS/H_2O/ethanol solution to initialize a sol–gel reaction of TEOS. 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^{-1}, 1.2×10^{-3}–12.0×10^{-3}, 9–12 and 1.0×10^{-2}–9.0×10^{-2} M, respectively, which provided an initial Ti concentration of 6.9 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.

2.2.2. Characterization

The particles were characterized using XRD, TEM, DLS, electrophoretic light scattering (ELS), and X-ray photoelectron spectroscopy (XPS). The XRD measurement was carried out with a Rigaku Ultima IV X-ray diffractometer operating at 40 kV and 30 mA with Cu Kα radiation. 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 Malvern Zetasizer Nano ZS90 instrument (Malvern, Worcestershire, UK). An aqueous HCl or NaOH solution was added to the sample to alter the pH for the ELS measurements. The surface composition of particles was studied using the XPS, which was performed 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. To clean the surface of the nanoparticles, pre-etching was performed for a few seconds prior to the main measurements, in which the sample was regarded as the particles with the etching time of 1.

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 at 200 kg-f/cm^2 using a Mitsubishi Chemical Analytech MCP-T610 resistivity meter.

3. Results and discussion

3.1. Effect of NaOH concentration

Fig. 2 shows TEM images of the TiON/SiO_2 particles fabricated at various NaOH concentrations. In all the NaOH concentrations examined, the TiON particles were coated with silica shell, though

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