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High reflective efficiency and durability of multilayered core-shell composite particles with controlled shell thickness

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ABSTRACT

Multilayered core-shell composite particles with a high reflective efficiency and durability were prepared by a subsequent formation of multilayered shells on silver-coated iron (Fe/Ag) microspheres. The SiO_2 and TiO_2 multilayered shells were formed onto the Fe/Ag microspheres by the sol-gel reaction of tetraethylorthosilicate (TEOS) and titanium *n*-butoxide (TBOT), respectively. The thickness uniformity of SiO_2 and TiO_2 shells was improved by ultrasonication during the sol-gel reaction process. The mechanical durability of the composite particles was also investigated by an ink grinder. The SiO_2 and TiO_2 multilayered shells showed high efficiency for preserving the reflectivity and increasing the durability of the Fe/Ag microspheres.

1. Introduction

Magnetic pigments have been widely used for machine-verification of banknote in the field of security. For example, it is known that most of suspect notes (~90%) are caught when they do not have an authentic signature with a magnetic pattern [1]. However, most of the magnetic particles exhibit a deep gray or dark brown color, which limits their use in applications such as color inks, cosmetic pigments, and anti-fake inks where bright color is required. To overcome these barriers in optical properties, white magnetic particles have been introduced by adopting multilayered core-shell structure [2]. An Ag shell having a uniform thickness at least 50 nm reflects incident light to brighten the color of the substrate [3]. In order to prepare a dense and complete Ag shell by electroless plating, surface activation methods have been used. The best-known method is that the surface is exposed to a sensitization solution typically $SnCl_2$ and then exposed to an activation solution typically $PdCl_2$ [4–6]. Recently, polydopamine has been used to form a dense Ag shell layer on core-shell microspheres [7]. White color magnetic microspheres comprising a Fe/TiO_2/Ag core-shell structure with a continuous, uniform compact silver layer were successfully fabricated by TiO_2-assisted electroless plating in a simple and eco-friendly method [2]. The coating procedure involved a sol-gel reaction for TiO_2 and electroless plating for Ag with ultrasound treatment. The temporal growth of the silver shell at the early stage of the silver growth reaction was investigated to examine how silver islands grow and coalesce [8]. However, in the ink manufacturing process through ink grinder, deformations are generated in the silver shell due to the ductility of silver, resulting in a reduced lightness. A chemical degradation of the silver surface can also lead to decreasing the lightness of the white magnetic particles. Weathering and salt spray test results show that the silver surface changes to Ag_2O, $AgC_2H_3O_2$ and Ag_2CO_3 [9].

A protective silica shell on the surface of the silver layer has been proposed to improve their thermal durability. Thermal durability tests have shown that the silver layer is stable up to 200 °C when a protective shell is employed [10]. However, there arises a problem that the brightness could decrease depending on the refractive index and the thickness of the protective shell. There is a remarkable change in the reflectance when the thickness of the protective shell becomes the order of the wavelengths of visible light. This is due to wave interference in thin films and the difference in the refractive index of the protective shell, the air, and the silver layer. Despite many studies on the fabrication of multilayered films with a controlled thickness, most of the studies were focused on optical properties of thin films obtained by deposition technique [11,12]. A wet chemical route is an efficient method for making multilayer films [13,14]. However, studies on the formation of multi-layered protective shells with controlled thickness have been carried out mainly using deposition technology, so it is necessary to study the formation of multilayer protective shells by the wet chemical method. SiO_2 and TiO_2 have various applications as layers with low-and high-refractive index in optical layer systems, such as

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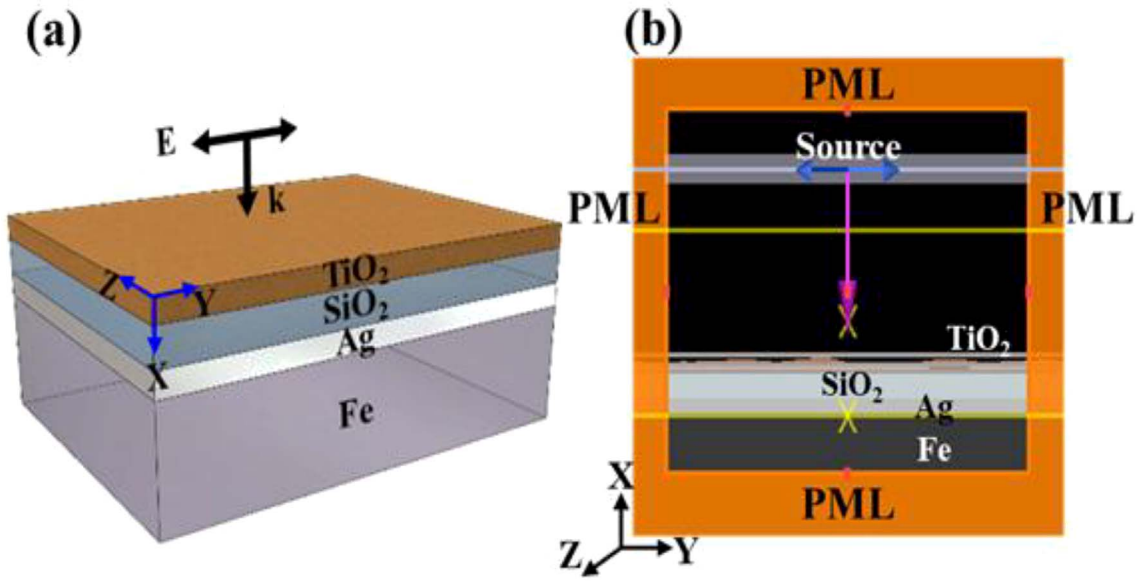

Fig. 1. (a) Schematic illustration of FDTD simulation setup for the Fe/Ag/SiO_2/TiO_2 thin film system in analogy to the core-shell composite microspheres. (b) Real simulation environment with the appropriate boundary conditions.

optical filters and antireflective coatings [15]. TiO_2 is one of the most extensively studied materials in photocatalyst and optical fields due to its chemical stability, low cost, high refractive index, and active reactivity [16]. SiO_2 is usually chosen as the dielectric shell to protect the metal nanostructures from corrosion owing to its non-toxicity and facile fabrication via the Sto¨ber method [17–19].

In this study, multilayered shells with uniform thickness were coated onto the silver-coated iron (Fe/Ag) microspheres to enhance high reflective efficiency and durability of core-shell composite particles. SiO_2 and TiO_2 shells were formed using a sol-gel reaction on the silver-coated iron (Fe/Ag) microspheres. The thickness and state of SiO_2 and TiO_2 shells were observed by the influence of ultrasonication. The surface states of the white magnetic particles shell and the white magnetic particles having the protective shell formed thereon were observed before and after the dispersion step.

2. Experimental sections

2.1. Simulation

Fig. 1 depicts a schematic representation, and real environment of finite difference time domain (FDTD) simulation setup of the corresponding thin film system in analogy to the Fe/Ag/SiO_2/TiO_2 microspheres. The simulated film area is 2 × 2 μm^2 and the thicknesses of Ag, SiO_2, and TiO_2 are 50 nm, 90 nm, and 55 nm, respectively. This FDTD solves Maxwell's electromagnetic wave equations in which the broadband P-polarized plane wave source of wavelengths 400–700 nm is used. The plane of the electric field is oscillating along Y-axis, is irradiating the structure along the X-axis from the top. The top layer (i.e. TiO_2) is assumed to be rough to simulate the roughness of core-shell composite particles, which suffers from specular reflection. The perfectly matched layer (PML) boundary conditions (BCs) have used in all directions. The optical constants that used for the Fe [20], Ag [21], and TiO_2 [22] are taken from the references, whereas the SiO_2 is considered as a constant value of index 1.45.

2.2. Sol-gel reaction of SiO_2 on the silver coated Fe microspheres

In Fig. 2, we demonstrate the fabrication procedures for the Fe/Ag/SiO_2/TiO_2 core-shell composite microspheres. The silver-coated Fe (Fe/Ag) microspheres have been used in previous studies [2]. A silver coating was prepared on the Fe microspheres (Magnetic pigment 025 BASF, Fe 99.5%, sphere shape, D_{50} 3.8–5.3 μm) using an electroless plating process in which silver nitrate was reduced by glucose, as shown in Fig. 2. The SiO_2 shell was directly coated on the Fe/Ag microspheres via hydrolysis and condensation of tetraethylorthosilicate (TEOS, Aldrich). 3.3 wt % of the Fe/Ag microspheres, 0.8 wt % of ammonium hydroxide (NH_4OH, Aldrich) and 0.8 wt % of deionized (DI) water (18.2 MΩ cm, Millipore) were added to 360 ml of ethanol (Aldrich). The 1.1 wt % of TEOS was dissolved in 10 ml of ethanol and then this solution was gradually added to the mixture of particles, ethanol, and DI water. The solution was kept for the next 2 h while stirring. The reaction was fulfilled with and without sonication (Sonics, Vibra cell, 750 W). The SiO_2 coated Fe/Ag (Fe/Ag/SiO_2) microspheres were recovered from the solution by magnetic separation and washed with ethanol. The wet sample was then dried in an oven at 60 °C for 4 h.

2.3. Sol-gel reaction of TiO_2 on the Fe/Ag/SiO_2 microspheres

The TiO_2 shell was directly coated on the Fe/Ag/SiO_2 microspheres via hydrolysis and condensation of titanium *n*-butoxide (TBOT, Aldrich). 3.3 wt % of the Fe/Ag/SiO_2 microspheres and 6.6 wt % of DI water were added to 360 ml of ethanol. The 10.5 wt % of TBOT was added to the mixture of particles, ethanol, and DI water. The temperature of the solution was raised to 85 °C in 10 min and refluxed for 20 min. The reaction was fulfilled with and without sonication. The TiO_2 coated Fe/Ag/SiO_2 (Fe/Ag/SiO_2/TiO_2) microspheres were recovered from the solution by magnetic separation and washed with ethanol. The wet sample was then dried in an oven at 60 °C for 4 h.

2.4. Durability test

The physical durability of the Fe/Ag microspheres and the Fe/Ag/SiO_2/TiO_2 microspheres was investigated by an ink grinder (Buhler Ltd. SDY 300). The 10 wt % of calcium carbonates (Takehara, SL700) and 200 g of alkyd resin (Lawter, Setalin V407E) were added to an ink grinder and dispersed for 5 min. The 10 wt % of magnetic particles was added and the mixture was further dispersed for 5 min. The magnetic particles were separated by a magnet and washed with ethanol. The wet samples were dried at 60 °C for 4 h.