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Preparation and characterization of silver coated magnetic microspheres prepared by a modified electroless plating process

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ABSTRACT

Silver-coated Fe microspheres were fabricated by the modified electroless plating process without the pretreatment and sensitization steps. Surface modification step with TiO_2 shells provides a continuous and full coverage of Ag shells on Fe microspheres. Ethylene diamine and ammonia were used as a complexing agent to form silver shells during the electroless plating process. Their reflectance was investigated to understand the role of the surface morphology of the silver shells on their optical properties. The growth of the Ag shells at the early stage of the reaction was investigated. Structure and optical properties of the resulting silver-coated Fe microspheres were evaluated based on scanning electron microscopy, silver shell thickness, reflectance and crystal structure analysis. The silver shells prepared with ethylene diamine were more homogenous and compact than those with ammonia.

1. Introduction

Magnetic pigments have been widely used as a machine-readable feature in the field of security [1]. However, dark and black color of the magnetic pigments limits their usage in a wide range of application, in which a bright color is required for the aesthetic design. Therefore, a development of magnetic pigments with a high reflectivity related to a bright color is the most prominent challenge to future advances in the magnetic materials.

In order to obtain the high reflectivity, a shell of metal materials is typically coated on the surface of magnetic pigments. Several methods, including sputter coating, chemical vapour deposition, wet chemical reduction, and electroless plating, have been explored toward the fabrication of metal-coated magnetic particles [2]. Among these methods, electroless plating process is preferred, because it can be applied to coat a metal layer on the components with complex shapes [3]. Further advantages are that electroless plating process does not depend on special instrumentation such as vacuum chambers or ion sources [4]. Electroless plating solutions are in a stable state of a dynamical system other than the state of least energy, thus the silver deposition is limited to the catalytically active surface sites which lower the activation barrier of the reaction [5]. Once a silver deposit has formed, the reaction continuously proceeds due to the autocatalytic action to form a steadily growing polycrystalline film [6]. The conventional way to activate a surface for electroless plating is the two-step process in which the surface is first exposed to a sensitization solution typically $SnCl_2$ and then exposed to an activation solution typically $PdCl_2$ [7–11]. The silver was reduced by Pd and attached on the surface of a sample, and then an agglomerative silver-coating layer was formed on a sample [12–14]. However, these methods have a few drawbacks, such as the hazard of toxic Sn and the high cost of Pd. Electroless silver plating was modified by replacing the pretreatment and activation steps by only using surface hydroxylation with NaOH solution [15]. A new activation method was introduced to form silver nuclei by taking ethylene glycol as a reducing agent [16].

Ammonia is a typical complexing agent for the electroless silver plating. Most researchers used an electroless silver plating solution containing ammonia complexing agents. However, ammonia is not sufficient for practical use because the surface of the silver deposition is not smooth and difficult to handle because of its irritating odor. Although numerous studies have been reported in the fabrication of silver coating using ammonia complexing agents, there are only a few reports related to ethylene diamine complexing agents. Ethylene diamine was used as the complexing agent to suppress silver halide precipitation [4]. Ethylene diamine and ammonia were used as complexing agents for the electroless silver plating solution at the same time [17].

In this work, a silver shell on the surface of Fe microspheres is prepared via a modified electroless plating process. The electroless process

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Table 1
The composition of the electroless silver plating solution.

	Materials	Wt%	Function
Silver salt solution	Silver nitrate	1.35	Silver salt
	Ammonia/ethylene diamine	2.12/1.25	Complexing agents
	Sodium hydroxide	0.25	Velocity regulator
Reductant solution	Glucose	1.27	Reducing agents
	Potassium sodium tartrate	0.09	Additive
	Ethanol	2.01	Additive

is modified by replacing the conventional pretreatment and sensitization steps by only using a TiO_2 coating. Ethylene diamine complexing agent was used for the electroless silver plating solution. Surface morphology of the resulting silver coated Fe microspheres were investigated by scanning electron microscopy (SEM). Relationship between reflectance and silver coating thickness was also studied.

2. Experimental

2.1. Materials

Silver nitrate, ethylene diamine, ammonia, ethanol, sodium hydroxide, glucose, potassium sodium tartrate and titanium n-butoxide (TBOT) were all purchased from Aldrich. These chemicals were of analytical reagent grade and used without further purification. The Fe microspheres (Magnetic pigment 025 BASF) were obtained from BASF SE. Deionized (DI) water (18.2 MΩ·cm at room temperature) was used.

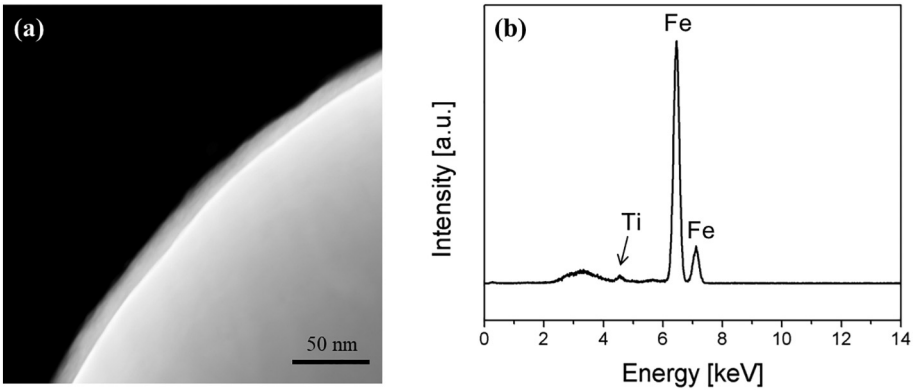

Fig. 1. (a) TEM dark field image and (b) XRF spectra of the TiO_2 coated Fe microspheres.

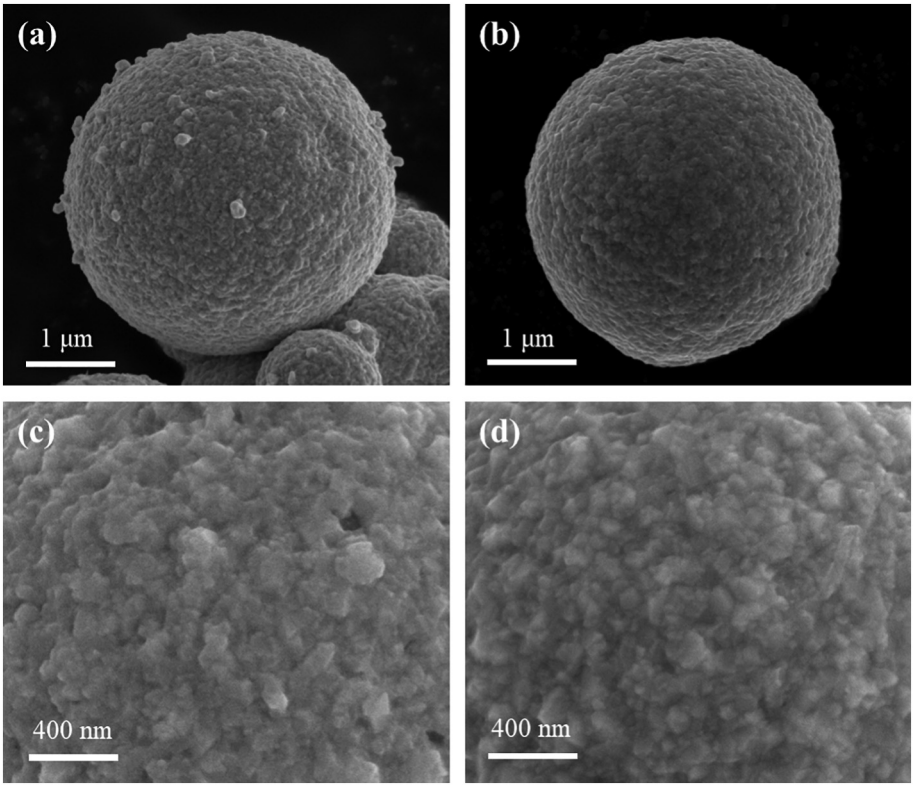

Fig. 2. SEM images of the Ag coated Fe microspheres obtained by electroless plating process (a,c) with ammonia and (b,d) with ethylene diamine (for both cases, Ag weight percentage is 15%).