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DESIGN OF A BI-FUNCTIONAL $\alpha$-Fe$_2$O$_3$/Zn$_2$SiO$_4$:Mn$^{2+}$ BY LAYER-BY-LAYER ASSEMBLY METHOD

This work describes the design of bi-functional $\alpha$-Fe$_2$O$_3$/Zn$_2$SiO$_4$:Mn$^{2+}$ using a two-step coating process. We propose a combination of pigments ($\alpha$-Fe$_2$O$_3$) and phosphor (Zn$_2$SiO$_4$:Mn$^{2+}$) glaze which is assembled using a layer-by-layer method. A silica-coated $\alpha$-Fe$_2$O$_3$ pigment was obtained by a sol-gel method and a Zn$^{2+}$ precursor was then added to the silica-coated $\alpha$-Fe$_2$O$_3$ to create a ZnO layer. Finally, the Zn$_2$SiO$_4$:Mn$^{2+}$ layer was prepared with the addition of Mn$^{2+}$ ions to serve as a phosphor precursor in the multi-coated $\alpha$-Fe$_2$O$_3$, followed by annealing at a temperature above 1000°C. Details of the phase structure, color and optical properties of the multi-functional $\alpha$-Fe$_2$O$_3$/Zn$_2$SiO$_4$:Mn$^{2+}$ were characterized by transmission electron microscopy and X-ray diffraction analyses.

Keywords: red pigment, $\alpha$-Fe$_2$O$_3$, Zn$_2$SiO$_4$:Mn$^{2+}$ layer, phosphor, bi-functional

1. Introduction

The encapsulation technique is regarded as of very important given its association with interesting actual and potential applications in different fields, such as optics, catalysis, microelectronics, coatings, cosmetics, inks, drug-release systems and diagnoses [1]. Specifically, multi-functional inorganic particles with ceramic oxide are desirable in many applications in order to improve the stability of the encapsulated product [1-3]. Recently, we reported a core-shell structure with a non-toxic bi-functional magnetic ceramic phosphor which under silica coating and surface modification steps [4]. ZnO is an environmentally friendly ceramic phosphor that has been extensively studied as a fluoroscent material for use in compound semiconductors due to its low price and non-toxicity [5]. Bi-functional materials can be designed with ferrite nanoparticles, which can be controlled with an external magnetic field that can be immobilized close to the target. There have been several studies on improvements of the properties of core nanoparticles by encapsulation within a silica shell [6-7]. To minimize agglomeration and oxidation of the core materials, a silica coating can be applied. Recently, well-designed core-shell red pigments were prepared using nano-sized $\alpha$-Fe$_2$O$_3$ and silica (SiO$_2$) from tetraethyl orthosilicate (TEOS) as a starting material. The silica-coated $\alpha$-Fe$_2$O$_3$ pigment retained its red coloration after being heated to 1000°C [8]. Silica is particularly attractive for use as a coating material in various applications due to its high thermal stability and transparency. ZrSiO$_4$ is commonly used in the ceramics industry for glazes due to its high chemical and thermal stability at firing temperature. Zircon (ZrSiO$_4$) was sintered from ZrO$_2$ and SiO$_2$ layers which were coated separately in corresponding solutions [9-11]. Another promising encapsulator, Zn$_2$SiO$_4$:Mn$^{2+}$, is used in glazes and phosphors due to its strong luminescent properties. In the past, Zn$_2$SiO$_4$:Mn$^{2+}$ was prepared by means of a solid-state reaction between ZnO and SiO$_2$ (ZnO + SiO$_2$ = Zn$_2$SiO$_4$) at temperatures exceeding 1000°C [11]. However, the use of the solid-state method makes it difficult to control the physical properties of products due to limitations in the synthesis conditions, such as a high annealing temperature [12]. Therefore, we suggest the use of a core-shell structure to form Zn$_2$SiO$_4$:Mn$^{2+}$, which is commonly used in many types of nanoparticles (e.g., phosphors, quantum dots). In this work, we propose well-designed multi-functional $\alpha$-Fe$_2$O$_3$ pigments using a Zn$_2$SiO$_4$ glaze prepared by a sol-gel method. The samples were characterized by TEM (transmission electron microscopy) and XRD (X-ray diffraction) analyses.

2. Experimental procedure

2.1. Synthesis of $\alpha$-Fe$_2$O$_3$@SiO$_2$

Spherical $\alpha$-Fe$_2$O$_3$ nanoparticles were prepared via a hydrothermal method. Silica-coated $\alpha$-Fe$_2$O$_3$ was synthesized following a modified version of an earlier published method [13]. The prepared $\alpha$-Fe$_2$O$_3$ particles were coated with silica using a sol-gel method. In a typical procedure, about 40 mg of $\alpha$-Fe$_2$O$_3$ was dispersed in a water and ethanol mixture, after
which 300 μL of NH₄OH and 150 μL of tetraethyl orthosilicate (TEOS) were added. The samples were characterized by XRD and TEM.

### 2.2. Synthesis of α-Fe₂O₃@Zn₂SiO₄:Mn²⁺

To obtain the Zn₂SiO₄:Mn²⁺ layer, the prepared core-shell structures were annealed at 1000°C with Zn²⁺ and Mn²⁺ ions as a dopant in an ammonia solution. The doping concentration was 2-10 mol%, substituting Mn²⁺ for Zn²⁺ in the Zn₂SiO₄:Mn²⁺ in a previously optimized process [15]. The synthesis scheme is shown in Fig. 1. According to the compositions in the above formula, stoichiometric amounts of Mn(acac)₂ and Zn(acac)₂ were dissolved in deionized water with the final concentration of Zn²⁺ and Mn²⁺ at 2-10 mol and 2-10 mol, respectively. In a typical procedure, about 18 mM of α-Fe₂O₃@SiO₂ was dispersed in 20 mL DI water. Next, 0.1 mL NH₄OH, 3.28 mM of Zn(acac)₂ and 0.036 mM of Mn(acac)₂ were added to the solution. The entire process used to obtain the α-Fe₂O₃@Zn₂SiO₄:Mn²⁺ materials is shown in Fig. 1.

![Fig. 1. Schematic diagram is synthetic α-Fe₂O₃@Zn₂SiO₄:Mn²⁺](image)

3. Results and discussion

Fig. 2 shows SEM and TEM images of the α-Fe₂O₃ particles and the silica-coated α-Fe₂O₃ particles. The spherical α-Fe₂O₃ particles were about 200 nm in size with a relatively narrow size distribution. The α-Fe₂O₃ particles were coated with silica via a sol-gel coating process in a basic aqueous condition. Fig. 2a shows TEM images of silica-coated α-Fe₂O₃ nanoparticles that have a silica layer with a thickness of around 5 nm.

![Fig. 2. TEM images of (a) α-Fe₂O₃ and (b) α-Fe₂O₃@SiO₂](image)

Synthesis of the Zn₂SiO₄-coated α-Fe₂O₃ was done by the sintering of SiO₂ and ZnO-coated hematite. The silica shell was prepared by the hydrolysis of TEOS in an ethanol-water solution for 4 h, and the ZnO shell was prepared by the hydrolysis of zinc acetate in an aqueous solution for 2 h. The SiO₂ and ZnO layers were coated separately in corresponding solutions. During the Zn₂SiO₄ formation process with the heat treatment of SiO₂ and ZnO, silica was reacted with ZnO, leading to the formation of Zn₂SiO₄. Fig. 3 shows TEM images of Zn₂SiO₄:Mn²⁺-coated α-Fe₂O₃ prepared at 1000°C using a two-step coating process. Fig. 3a and 3b show TEM images of the core-shell structure of the Zn₂SiO₄:Mn²⁺ α-Fe₂O₃ particles with a Zn₂SiO₄:Mn²⁺ shell thickness of about 3 nm.

![Fig. 3. TEM images of α-Fe₂O₃@Zn₂SiO₄:Mn²⁺](image)

![Fig. 4. XRD patterns of Zn₂SiO₄-coated α-Fe₂O₃ were calcined at 1000°C](image)

To form the Zn₂SiO₄:Mn²⁺ layer, the prepared core-shell structures were annealed at 1000°C with Mn²⁺ ions as a dopant. Fig. 4 shows the XRD pattern of α-Fe₂O₃@Zn₂SiO₄:Mn²⁺ after it was heated at 1000°C. At room temperature, all of the diffraction peaks can be indexed to the α-Fe₂O₃ phase (data not shown). When samples were treated at 1000°C, the formation of Zn₂SiO₄ phases was observed. Driven by the heat treatment, the ZnO layer diffuses into the SiO₂ matrix to form the Zn₄SiO₄ shell although some residual ZnO in the crystal phase still appears. Both of the diffraction peaks belong to crystalline willemite.
[α-Zn2SiO4 JCPDS card No. 37-1485]. Most likely, the thin SiO2-coated α-Fe2O3 and second ZnO shell were only partially converted to zinc silicate, with some remaining, as a relatively small amount of silica could lead to the creation of all of the zinc silicate needed. The phase and physical properties of the Zn2SiO4:Mn2+ phosphor were controlled using SiO2-coated α-Fe2O3 of different shell thickness after calcinations at 1000°C [15].

Fig. 5 shows photograph of the Zn2SiO4:Mn2+-coated α-Fe2O3 solution upon exposure to UV light and photoluminescence spectra of Zn2SiO4:Mn2+ phosphor. The Zn2SiO4:Mn2+-coated α-Fe2O3 solution is shown before exposure to UV light (left) and after exposure to UV light, excited at 255 nm (right). The α-Fe2O3 solution shows no changes in terms of its color or emission. (Fig. 5a) On the other hand, emission of the Zn2SiO4:Mn2+-coated α-Fe2O3 solution was noted at 255 nm. (Fig. 5a) We confirmed the fluorescent properties of bi-functional materials using emission spectra. The PL emission peak wavelengths of Zn2SiO4:Mn2+ phosphors were around 521 nm when excited by UV light at 254 nm in Fig. 5b.

4. Conclusions

We report the well-designed synthesis of core-shell structures of α-Fe2O3, α-Fe2O3@SiO2 and α-Fe2O3@Zn2SiO4:Mn2+. Specifically, zinc silicate-coated α-Fe2O3 particles were coated with a double shell of silica (SiO2) and zinc oxide (ZnO) precursors by the hydrolysis of TEOS and zinc acetate, respectively. The silica and zinc oxide shells reacted to produce zinc silicate after a heat treatment at 1000°C with Mn(acac)2 as a dopant. We expect that this multi-core-shell process can be used to create pigments and phosphors of various types to produce many useful functional-structured materials.

Acknowledgements

This work was supported by a grant from “the Fundamental R&D Program for Core Technology of Materials” funded by the Ministry of Knowledge Economy, Korea and by the “Sanhak Joint R&D program” funded by the Small and Medium Business Administration, Korea.

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Received: 20 November 2014.