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DESIGN OF A BI-FUNCTIONAL α -Fe₂O₃/Zn₂SiO₄:Mn²⁺ BY LAYER-BY-LAYER ASSEMBLY METHOD

PROJEKTOWANIE DWUFUNKCYJNYCH PROSZKÓW α -Fe₂O₃/Zn₂SiO₄:Mn²⁺ METODĄ WARSTWA PO WARSTWIE

This work describes the design of bi-functional α -Fe₂O₃/Zn₂SiO₄:Mn²⁺ using a two-step coating process. We propose a combination of pigments (α -Fe₂O₃) and phosphor (Zn₂SiO₄:Mn²⁺) glaze which is assembled using a layer-by-layer method. A silica-coated α -Fe₂O₃ pigment was obtained by a sol-gel method and a Zn²⁺ precursor was then added to the silica-coated α -Fe₂O₃ to create a ZnO layer. Finally, the Zn₂SiO₄:Mn²⁺ layer was prepared with the addition of Mn²⁺ ions to serve as a phosphor precursor in the multi-coated α -Fe₂O₃, followed by annealing at a temperature above 1000°C. Details of the phase structure, color and optical properties of the multi-functional α -Fe₂O₃/Zn₂SiO₄:Mn²⁺ were characterized by transmission electron microscopy and X-ray diffraction analyses.

Keywords: red pigment, α -Fe₂O₃, Zn₂SiO₄:Mn²⁺ 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 fluorescent 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 α -Fe₂O₃ and silica (SiO₂) from tetraethyl orthosilicate (TEOS) as a starting material. The silica-coated α -Fe₂O₃ 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. ZrSiO₄ is commonly used in the ceramics industry for glazes due to its high chemical and thermal

stability at firing temperature. Zircon (ZrSiO₄) was sintered from ZrO₂ and SiO₂ layers which were coated separately in corresponding solutions [9-11]. Another promising encapsulator, Zn₂SiO₄:Mn²⁺, is used in glazes and phosphors due to its strong luminescent properties. In the past, Zn₂SiO₄:Mn²⁺ was prepared by means of a solid-state reaction between ZnO and SiO₂ (ZnO + SiO₂ = Zn₂SiO₄) 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 Zn₂SiO₄:Mn²⁺, which is commonly used in many types of nanoparticles (e.g., phosphors, quantum dots). In this work, we propose well-designed multi-functional α -Fe₂O₃ pigments using a Zn₂SiO₄ 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 α -Fe₂O₃@SiO₂

Spherical α -Fe₂O₃ nanoparticles were prepared via a hydrothermal method. Silica-coated α -Fe₂O₃ was synthesized following a modified version of an earlier published method [13]. The prepared α -Fe₂O₃ particles were coated with silica using a sol-gel method. In a typical procedure, about 40 mg of α -Fe₂O₃ was dispersed in a water and ethanol mixture, after

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which 300 μL of NH_4OH and 150 μL of tetraethyl orthosilicate (TEOS) were added. The samples were characterized by XRD and TEM.

2.2. Synthesis of $\alpha\text{-Fe}_2\text{O}_3@Zn_2\text{SiO}_4:\text{Mn}^{2+}$

To obtain the $Zn_2SiO_4:\text{Mn}^{2+}$ layer, the prepared core-shell structures were annealed at 1000°C with Zn^{2+} and Mn^{2+} ions as a dopant in an ammonia solution. The doping concentration was 2-10 mol%, substituting Mn^{2+} for Zn^{2+} in the $Zn_2SiO_4:\text{Mn}^{2+}$ 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 $\text{Mn}(\text{acac})_2$ and $\text{Zn}(\text{acac})_2$ were dissolved in deionized water with the final concentration of Zn^{2+} and Mn^{2+} at 2-10 mol and 2-10 mol, respectively. In a typical procedure, about 18 mM of $\alpha\text{-Fe}_2\text{O}_3@SiO_2$ was dispersed in 20 mL DI water. Next, 0.1 mL NH_4OH , 3.28 mM of $\text{Zn}(\text{acac})_2$ and 0.036 mM of $\text{Mn}(\text{acac})_2$ were added to the solution. The entire process used to obtain the $\alpha\text{-Fe}_2\text{O}_3@Zn_2SiO_4:\text{Mn}^{2+}$ materials is shown in Fig. 1.

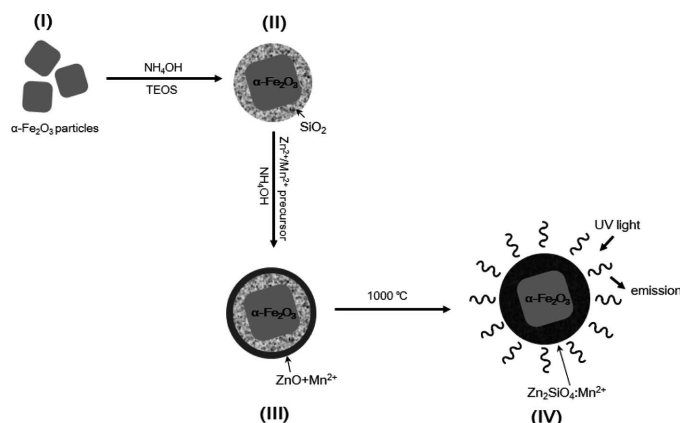


Fig. 1. Schematic diagram is synthetic $\alpha\text{-Fe}_2\text{O}_3@Zn_2SiO_4:\text{Mn}^{2+}$

3. Results and discussion

Fig. 2. shows SEM and TEM images of the $\alpha\text{-Fe}_2\text{O}_3$ particles and the silica-coated $\alpha\text{-Fe}_2\text{O}_3$ particles. The spherical $\alpha\text{-Fe}_2\text{O}_3$ particles were about 200 nm in size with a relatively narrow size distribution. The $\alpha\text{-Fe}_2\text{O}_3$ particles were coated with silica via a sol-gel coating process in a basic aqueous condition. Fig. 2a shows TEM images of silica-coated $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles that have a silica layer with a thickness of around 5 nm.

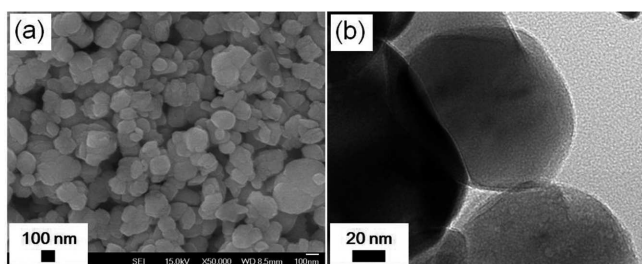


Fig. 2. TEM images of (a) $\alpha\text{-Fe}_2\text{O}_3$ and (b) $\alpha\text{-Fe}_2\text{O}_3@SiO_2$

Synthesis of the Zn_2SiO_4 -coated $\alpha\text{-Fe}_2\text{O}_3$ was done by the sintering of SiO_2 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 SiO_2 and ZnO layers were coated separately in corresponding solutions. During the Zn_2SiO_4 formation process with the heat treatment of SiO_2 and ZnO , silica was reacted with ZnO , leading to the formation of Zn_2SiO_4 . Fig. 3 shows TEM images of $Zn_2SiO_4:\text{Mn}^{2+}$ -coated $\alpha\text{-Fe}_2\text{O}_3$ prepared at 1000°C using a two-step coating process. Fig. 3a and 3b show TEM images of the core-shell structure of the $Zn_2SiO_4:\text{Mn}^{2+}$ coated $\alpha\text{-Fe}_2\text{O}_3$ particles with a $Zn_2SiO_4:\text{Mn}^{2+}$ shell thickness of about 3 nm.

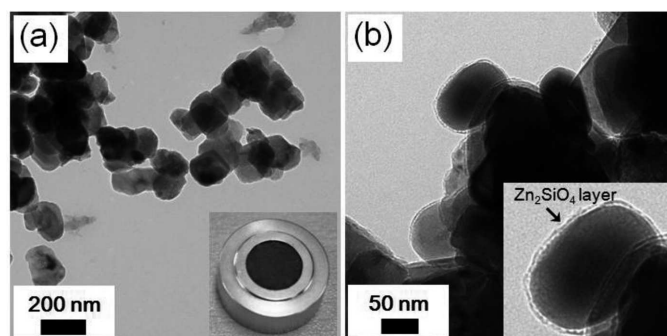


Fig. 3. TEM images of $\alpha\text{-Fe}_2\text{O}_3@Zn_2SiO_4:\text{Mn}^{2+}$ (a) low magnification (insert image; photograph of zinc silicate-coated $\alpha\text{-Fe}_2\text{O}_3$ powder) (b) high magnification (insert image; The zinc silicate layer confirmed by expanded TEM image)

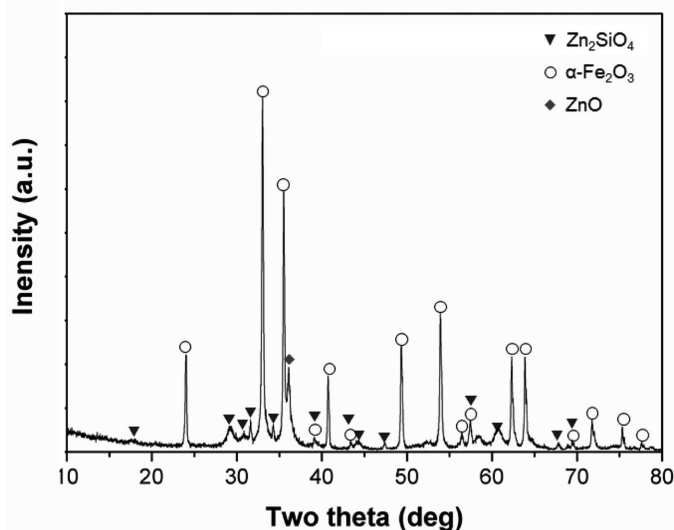


Fig. 4. XRD patterns of Zn_2SiO_4 -coated $\alpha\text{-Fe}_2\text{O}_3$ were calcined at 1000°C

To form the $Zn_2SiO_4:\text{Mn}^{2+}$ layer, the prepared core-shell structures were annealed at 1000°C with Mn^{2+} ions as a dopant. Fig. 4 shows the XRD pattern of $\alpha\text{-Fe}_2\text{O}_3@Zn_2SiO_4:\text{Mn}^{2+}$ after it was heated at 1000°C . At room temperature, all of the diffraction peaks can be indexed to the $\alpha\text{-Fe}_2\text{O}_3$ phase (data not shown). When samples were treated at 1000°C , the formation of Zn_2SiO_4 phases was observed. Driven by the heat treatment, the ZnO layer diffuses into the SiO_2 matrix to form the Zn_2SiO_4 shell although some residual ZnO in the crystal phase still appears. Both of the diffraction peaks belong to crystalline willemitte

[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.

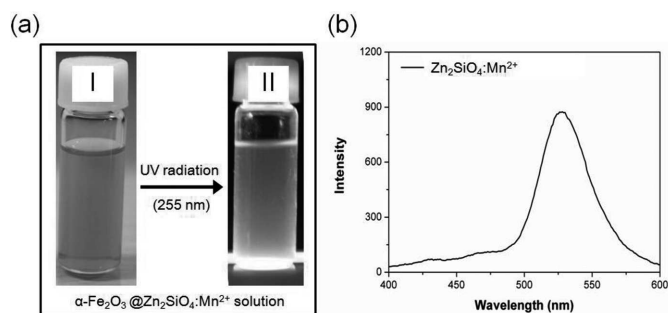


Fig. 5. (a) Photograph of solution of α -Fe₂O₃@Zn₂SiO₄:Mn²⁺ in ethanol (insert; (I) no excitation, (II) excited by UV light at 255 nm). (b) Photoluminescence spectra of Zn₂SiO₄:Mn²⁺ phosphor

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.

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