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Color Evolution and Thermal Behavior of Silica (SiO_2)- and Zircon ($ZrSiO_4$)-coated Nano α-Fe_2O_3 Pigments

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This manuscript reports coloration and thermal behavior of the silica and zircon effect on α-Fe_2O_3 pigment. The prepared three types of pigments were heat-treated at various temperatures (800–1000 °C), and their color evolutions were characterized by colorimeter and UV–visible spectroscopy.

Red color α-Fe_2O_3 has attracted much interest owing to recent demand for nontoxic, Cd-free pigments.[1] In particular, the coloration of nanosized α-Fe_2O_3 is controllable depending on the synthetic conditions.[2–4] In general, ceramic pigments must possess thermal stability at high temperature. However, nanosized red pigment easily undergoes aggregation at high temperature, and its color turns to brown. To obtain a stable and bright color, it is necessary to encapsulate α-Fe_2O_3 in a more stable phase such as silica (SiO_2) or zircon ($ZrSiO_4$). Several groups have studied silica inclusion red pigment in a silica matrix using $FeSO_4 \cdot 7H_2O$ as an iron oxide precursor.[5,6] Recently, well-designed core–shell red pigments were prepared using nanosized α-Fe_2O_3 and silica (SiO_2) from tetraethyl orthosilicate (TEOS) as starting materials.[7] Silica is particularly attractive for use as a coating and various applications due to its high thermal stability and transparency.[8,9] Another promising encapsulator, $ZrSiO_4$, is commonly used in the ceramic industry for glazes due to its high chemical and thermal stability at firing temperature.[10] Zircon ($ZrSiO_4$) was sintered from ZrO_2 and SiO_2 layers which are coated separately in a corresponding solution.[11,12] In this work, we propose two well-designed core–shell nanopigments using silica (SiO_2) and zircon ($ZrSiO_4$) prepared by a hydrolysis method and compare the resulting color evolution to that of α-Fe_2O_3 nanoparticles. Sphere-shaped α-Fe_2O_3 nanoparticles were prepared via a hydrothermal method as described elsewhere.[2,13] Silica-coated α-Fe_2O_3 was synthesized following a modified version of a method from the literature.[7] The α-Fe_2O_3 (40 mg) nanoparticles were dispersed in 100 mL of distilled water by sonication for 5 min followed by the addition of 1 wt % cetyltrimethylammonium bromide (CTAB) (1 mL). Then, 10 mL of (0.02 M) aqueous zirconium sulfate solution was added dropwise to the above solution at room temperature for 2 h. After zirconia (ZrO_2) shell of about 16–25 nm thick, silica layers (SiO_2) were fabricated using the Stöber method in an ethanol–water solution of TEOS. α-Fe_2O_3, α-Fe_2O_3@SiO_2, and α-Fe_2O_3@ZrO_2@SiO_2 were sintered at 800, 900, and 1000 °C for 1 h at a heating rate of $10\,°C\,min^{-1}$. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy dispersion spectroscopy (EDS) equipment. Color measurements were performed by UV–vis spectroscopy, using the CIE Lab method.

A typical TEM image (Figure 1a) shows the sphere-shaped α-Fe_2O_3 particles with an average diameter of 150 nm.

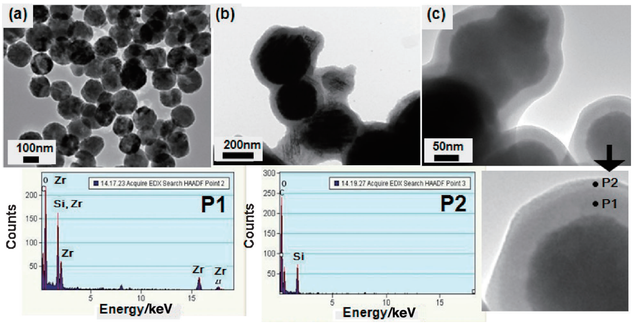
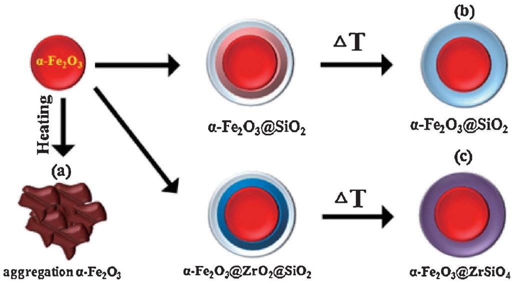


Figure 1. TEM images of (a) α-Fe_2O_3 nanoparticles (bar: 100 nm), (b) α-Fe_2O_3@SiO_2 nanoparticles, (c) α-Fe_2O_3@ZrO_2@SiO_2 nanoparticles and EDS spectra of spots (P1)–(P2), respectively, in insert image.

Figure 1b shows TEM image of silica-coated α-Fe_2O_3 nanoparticles that have a silica layer with a thickness of around 45 nm. CTAB was chosen as a surface modifier, and α-Fe_2O_3@CTAB@SiO_2 was successfully prepared. Synthesis of $ZrSiO_4$-coated α-Fe_2O_3 is done through sintering from ZrO_2 and SiO_2-coated α-Fe_2O_3.[11,12] The ZrO_2 layer and SiO_2 layer are obtained separately in corresponding solution by hydrolysis. A TEM photograph (Figure 1c) of the as-prepared particles clearly indicates that the α-Fe_2O_3 particles were coated with double shells. The ZrO_2 and SiO_2 shells were about 25 and 9 nm in thickness, respectively. The EDS results in P1 and P2 confirm the formation of ZrO_2 and SiO_2 layers, as indicated by the TEM photograph in Figure 1c.

When the α-Fe_2O_3 nanoparticles were heated to 1000 °C, the result was extensive agglomeration of the nanoparticles to form microsized units (Figures 2a and 2d-I). At the same time, silica-coated α-Fe_2O_3 nanoparticles retained their shapes after being heated to 1000 °C, as illustrated in Figure 2b. Figure 2d shows the XRD pattern of α-Fe_2O_3, α-Fe_2O_3@SiO_2, and α-Fe_2O_3@$ZrSiO_4$ after being heated at 900 °C. Unfortunately, α-Fe_2O_3@ZrO_2@SiO_2 core–shell structure was not found in the XRD pattern at 1000 °C, due to aggregation and melting in the glassy matrix after heating (Figure 2c). In case of α-Fe_2O_3@SiO_2 at 900–1000 °C, amorphous SiO_2 was crystallized which was indexed and comparable with room temperature data (Figure 2d-II).[7] When samples were treated at 900 °C, the formation of $ZrSiO_4$ phase was observed in Figure 2d-III. LiF easily reacts with SiO_2 to from SiF_4 during heat treatments which can induce $ZrSiO_4$ formation at low temperature (<850 °C).[10,14]

The color of the α-Fe_2O_3 and core–shell structure was assessed on the grounds of L^*, a^*, and b^* parameters, calculated from the diffuse reflectance spectra. In this method the parameter L^* represents the brightness of the sample; a



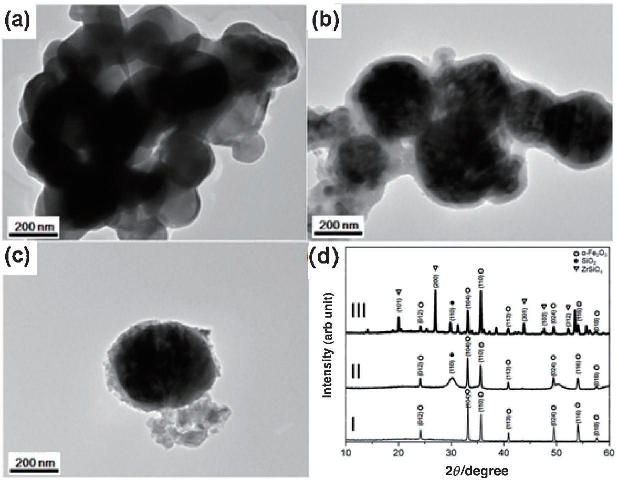


Figure 2. TEM images of after heating at 1000 °C (a) α-Fe$_2$O$_3$ nanoparticles, (b) α-Fe$_2$O$_3$@SiO$_2$ nanoparticles, (c) α-Fe$_2$O$_3$@ZrO$_2$@SiO$_2$ nanoparticles, and (d) XRD data of three samples at 900 °C (I: α-Fe$_2$O$_3$, II: α-Fe$_2$O$_3$@SiO$_2$, III: α-Fe$_2$O$_3$@ZrO$_2$@SiO$_2$).

positive a^* value represents red, a negative value shows green. It is said that red pigments show a high red color tone with increasing a^*. Silica did not affect red color tonality due to its high transparency. As temperature increases, the a^* and b^* factors of α-Fe$_2$O$_3$ evidently decreased due to the aggregation and morphological change of nanosized α-Fe$_2$O$_3$ (Figure 3a). At 1000 °C, a^* and b^* values of α-Fe$_2$O$_3$@ZrO$_2$@SiO$_2$ decreased to near 0 and turned to brownish gray because lithium iron silicate was melted in the glassy matrix (Figure 3c). On the other hand, the constant a^* and b^* values in the α-Fe$_2$O$_3$@SiO$_2$ samples indicate that the level of red pigments was relatively stable. The a^* value of α-Fe$_2$O$_3$@SiO$_2$ was about 18, which is comparable to the value found in a spindle-type core structure (Figure 3b).[7]

The color of the prepared powders was characterized by reflectance spectra in the wavelength range from 350 to 800 nm by UV–vis spectroscopy (Figure S1[16]). Figure S1[16] presents the reflectance curves of α-Fe$_2$O$_3$, α-Fe$_2$O$_3$@SiO$_2$, and α-Fe$_2$O$_3$@ZrO$_2$@SiO$_2$, respectively. The reflectance value is strongly influenced by the mean diameter.[15] Silica-coated α-Fe$_2$O$_3$ shows higher reflectance in a longer wavelength region (700–800 nm) than the others pigments do. After heat treatment at 900 °C, reflectance of the silica-coated α-Fe$_2$O$_3$ had increased due to high scattering of silica surface which is related to the increased L^* values in the CIE Lab at 900 °C (Figure 3b).

In summary, we report the well-designed synthesis of core–shell structure; α-Fe$_2$O$_3$, α-Fe$_2$O$_3$@SiO$_2$, and α-Fe$_2$O$_3$@ZrO$_2$@SiO$_2$ have been achieved by development of the hydrolysis method. Especially, zircon-coated α-Fe$_2$O$_3$ particles were coated with a double shell of zirconia and silica. At high temperature, α-Fe$_2$O$_3$ and zircon-coated α-Fe$_2$O$_3$ particles show large coloration change due to morphological change of nanosized α-Fe$_2$O$_3$ and melting in the glassy matrix. Silica-coated α-Fe$_2$O$_3$ is highly stable optical properties at 1000 °C.

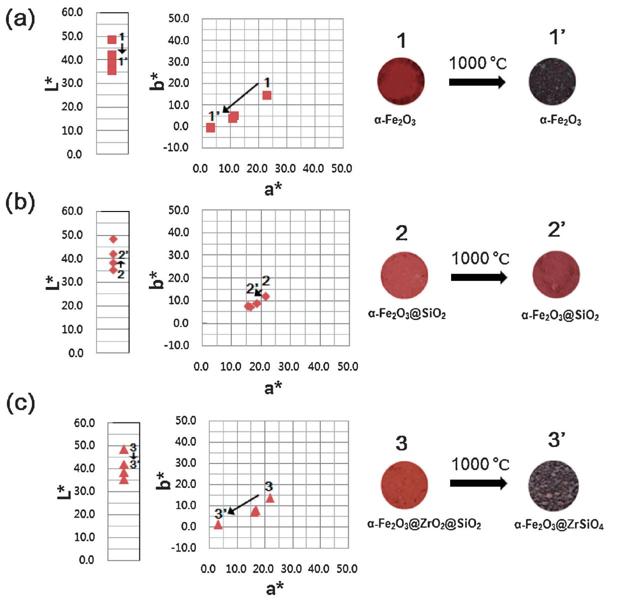


Figure 3. The CIE L^*, a^*, and b^* values of the pigments in comparison with the values of (a) α-Fe$_2$O$_3$, (b) α-Fe$_2$O$_3$@SiO$_2$, and (c) α-Fe$_2$O$_3$@ZrSiO$_4$ at various temperatures at RT, 800, 900, and 1000 °C. Color evolution data (RT, 1000 °C) were showed (Data at 800 and 900 °C are not indexed for clarity).

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