Silica Effect on Coloration of Hematite Nanoparticles for Red Pigments

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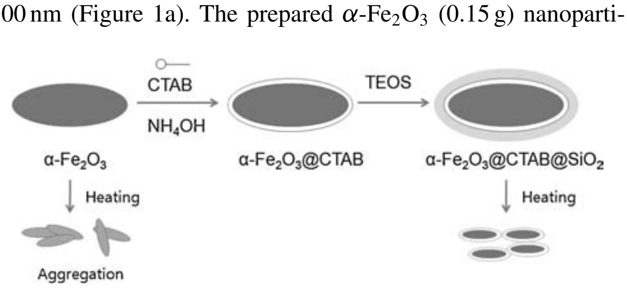
A novel red pigment displaying consistent properties up to a heating temperature of 1000 °C was synthesized, which indicates that the multilayer silica coating actually minimizes the agglomeration of the nanoparticles.

In the ceramic industry, there is a restricted choice for red/yellow colors because Cd-based pigments can affect the environment and human health. Recent investigations reveal that these toxic pigments can be replaced by nontoxic pigments such as $CaTaO_2N$.[1] α-Fe_2O_3 belongs to an important class of inorganic red pigments which are composed of nontoxic and safe elements.[2,3] Ceramic pigments must possess thermal and chemical stability at high temperature.[4] However, it has been shown that the tonality of hematite changes due to agglomeration at high temperature. To minimize agglomeration and oxidation, we proposed a multilayer coating system with silica. The silica-coating approach is particularly attractive because silica surfaces are easy to functionalize and nontoxic.[5–9] In addition, silica has transparency which is applicable to bio and optical application.[10,11] Recently silica and surface-modified hydrophobic nanoparticles are important for dispersion and bio-applications. In contrast, hydrophilic nanoparticles were easily coated with silica using tetraethylorthosilicate (TEOS) in ethanol solution.[12] However, some particles have weakly interaction with silica, which is necessary to modify the surface of nanoparticles.[13,14] In the present study, we chose cetyltrimethylammonium bromide (CTAB) as a surface modifier and successfully synthesized α-Fe_2O_3@CTAB@SiO_2 (Scheme 1).

The starting materials, $FeCl_3 \cdot 6H_2O$ (97%), NaH_2PO_4 (99.999%), tetraethylorthosilicate (TEOS, 99.999%), NH_4OH (28% solution in water, 99.99%), and cetyltrimethylammonium bromide (CTAB, 99%) were purchased from Aldrich. All materials were used as received without further purification. The reddish spindle α-Fe_2O_3 nanoparticles were prepared via a hydrothermal method as described previously.[2,15] The size distribution and shape of the as-prepared nanoparticles are homogeneous. The length of spindle hematite was determined to be around 300 nm (Figure 1a). The prepared α-Fe_2O_3 (0.15 g) nanoparticles were dispersed in a mixture of 9 mL of ethanol and 12 mL of water by sonication for 5 min, followed by the addition of CTAB (15 mg) and NH_4OH (28%, 50 µL). After about 30 min, 30 µL of TEOS was added dropwise to the α-Fe_2O_3 solution at room temperature. After the formation of a thin intermediate layer in basic solution, TEOS was added directly to the solution for further silica growing, without any purification.



Scheme 1. The formation of α-Fe_2O_3@CTAB@SiO_2.

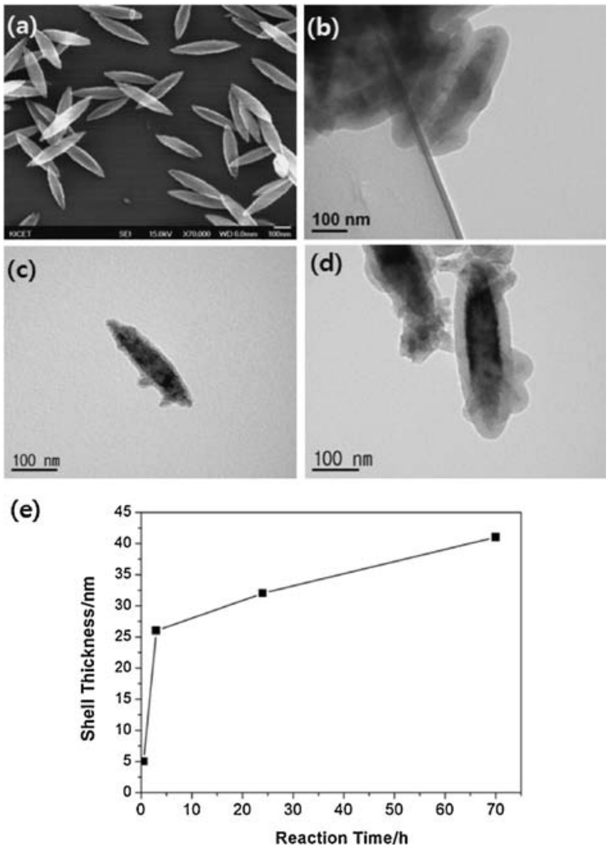


Figure 1. SEM image of (a) spindle α-Fe_2O_3 particles (bar = 100 nm) and TEM image of (b) silica-coated Fe_2O_3. (c) TEM images of α-Fe_2O_3@SiO_2 with a SiO_2 shell thickness of 5 nm, (d) 20 nm, (e) effect of reaction time on the SiO_2 shell thickness of silica-coated iron oxide.

Silica thickness can be controlled through the various synthetic conditions.[16] We were able to reliably control thickness by changing reaction time. Figures 1b–1d show the TEM images taken at various stages of the coating process with different reaction times. The thickness of the silica coating increased with time, as long as there was sufficient TEOS in the ammonia solution. Thickness of the silica layer was 5, 26, 32, and 41 nm at 0.5,

Table 1. The CIE Lab values of three different samples as a function of calcination

Sample[a]	CIE Lab value[b]					
	L^*	L'^*	a^*	a'^*	b^*	b'^*
1	55.3	53.0	9.5	6.2	5.5	1.2
2	56.6	56.2	14.6	8.0	10.0	4.5
3	55.9	55.1	16.9	15.3	10.3	9.2

[a] **1**: commercial α-Fe_2O_3, **2**: 300-nm nanosized α-Fe_2O_3, and **3**: silica-coated 300-nm nanosized α-Fe_2O_3. [b] L^*, a^*, and b^*: values before heating at 1000 °C. L'^*, a'^*, and b'^*: values after heating at 1000 °C.

3, 24, and 70 h, respectively (Figures 1b–1e). For this study, 24-h reaction time samples were chosen and characterized.

Core–shell type hematite nanoparticles contain surfactants CTAB which were assigned by IR and TGA. The thermal behavior of the α-Fe_2O_3 and silica-coated α-Fe_2O_3 samples were studied by thermogravimetric analysis in oxygen/nitrogen atmosphere at a heating rate of $5\,^\circ C\,min^{-1}$.

In the case of silica-coated α-Fe_2O_3, the first step was visible between 350–400 °C, which might be derived from the thermal decomposition of CTAB molecules that were used prior to the silica coating on α-Fe_2O_3 (Figure S1).[17] The infrared spectrum of silica-coated nanoparticles exhibits several bands from 2920 to 2950 cm^{-1} and from 1480 to 1490 cm^{-1}, characteristic regions for $\nu_{as}(\text{–}CH_3)$ and $\nu_{as}(\text{–}CH_2\text{–})$ bands from CTAB molecules, respectively. For silica-coated nanoparticles, a band is observed around 1200 cm^{-1} (Figure S2).[17] The XRD patterns show that silica-coated α-Fe_2O_3 nanoparticles have diffraction peaks similar to that of the parent α-Fe_2O_3 nanoparticles. There is a small peak around $2\theta = 22^\circ$ corresponding to the amorphous SiO_2 (Figure S3)[17] which means the iron oxide particles were well retained in the silica matrix.

There are several methods for color measurement, but in ceramic practices the CIE Lab method is usually accepted to specify the color of a product. Three parameters, L^*, a^*, and b^*, measure brightness, red/green and yellow/blue color intensities, respectively. Table 1 shows the value of the CIE Lab measurements of three different samples. The commercial α-Fe_2O_3 powder that is used as a red pigment for Japanese porcelain enamel was used as a reference. The L^*, a^*, and b^* CIE Lab values of α-Fe_2O_3 nanoparticles by Katsuki were published.[2] The L^*, a^*, and b^* CIE Lab value of spindle α-Fe_2O_3 are higher than those of commercial α-Fe_2O_3. Silica-coated hematite has a similar value to that of α-Fe_2O_3 which means silica does not affect red color tonality. In the case of commercial and spindle nanoparticles, especially samples which were heat treated at 1000 °C, a'^* and b'^* factors evidently decreased (Figures 2a and 2b, Table 1). However, in the case of silica-coated hematite, there is not a big difference observed after heating at 1000 °C (Figure 2c, Table 1).

In summary, we have reported the successful synthesis of uniform silica-coated α-Fe_2O_3 nanoparticles using a CTAB which could be helpful to grow TEOS over CTAB-modified particle surfaces. The thickness of the silica layer was reproducibly controlled using reaction time as the main parameter. Nanosized silica-coated α-Fe_2O_3 showed higher tonalities of reddish-to-yellow than those of commercial powders. In addition, after calcinations at 1000 °C, the tonality of silica-coated red pigment was not changed.

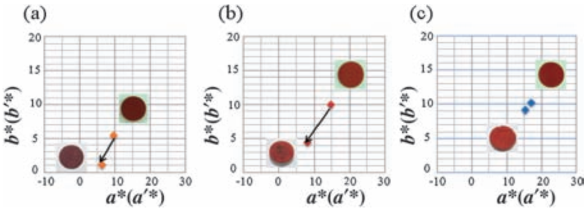


Figure 2. Color of red pigments prepared from three different samples at room temperature and 1000 °C. CIE Lab values before and after heating at 1000 °C results of (a) commercial α-Fe_2O_3, (b) 300-nm nanosized α-Fe_2O_3, and (c) silica-coated 300-nm nanosized α-Fe_2O_3.

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References and Notes

1 M. Jansen, H. P. Letschert, *Nature* **2000**, *404*, 980.
2 H. Katsuki, S. Komarneni, *J. Am. Ceram. Soc.* **2003**, *86*, 183.
3 J. Wang, W. B. White, J. H. Adair, *J. Am. Ceram. Soc.* **2005**, *88*, 3449.
4 F. Bondioli, T. Manfredini, C. Siligardi, A. M. Ferrari, *J. Am. Ceram. Soc.* **2005**, *88*, 1070.
5 W. Wu, Q. He, C. Jiang, *Nanoscale Res. Lett.* **2008**, *3*, 397.
6 K. Kang, J. Choi, J. H. Nam, S. C. Lee, K. J. Kim, S.-W. Lee, J. H. Chang, *J. Phys. Chem. B* **2009**, *113*, 536.
7 S. L. Westcott, S. J. Oldenburg, T. R. Lee, N. J. Halas, *Langmuir* **2003**, *19*, 6693.
8 D. Gerion, F. Pinaud, S. C. Williams, W. J. Parak, D. Zanchet, S. Weiss, A. P. Alivisatos, *J. Phys. Chem.* **2001**, *105*, 8861.
9 A. Palani, J.-S. Lee, J. Huh, M. Kim, Y.-J. Lee, J. H. Chang, K. Lee, S.-W. Lee, *J. Proteome Res.* **2008**, *7*, 3591.
10 Y. Yang, M. Gao, *Adv. Mater.* **2005**, *17*, 2354.
11 W. J. Parak, D. Gerion, D. Zanchet, A. S. Woerz, T. Pellegrino, C. Micheel, S. C. Williams, M. Seitz, R. E. Bruehl, Z. Bryant, C. Bustamante, C. R. Bertozzi, A. P. Alivisatos, *Chem. Mater.* **2002**, *14*, 2113.
12 Y. Lu, Y. Yin, B. T. Mayers, Y. Xia, *Nano Lett.* **2002**, *2*, 183.
13 Y. Deng, D. Qi, C. Deng, X. Zhang, D. Zhao, *J. Am. Chem. Soc.* **2008**, *130*, 28.
14 M. Iijima, Y. Yonemochi, M. Kimata, M. Hasegawa, M. Tsukada, H. Kamiya, *J. Colloid Interface Sci.* **2005**, *287*, 526.
15 T. Sugimoto, A. Muramatsu, K. Sakata, D. Shindo, *J. Colloid Interface Sci.* **1993**, *158*, 420.
16 D. K. Yi, S. S. Lee, G. C. Papaefthymiou, J. Y. Ying, *Chem. Mater.* **2006**, *18*, 614.
17 Supporting Information is available electronical on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.