Nanocoating Fe_2O_3 powders with a homogeneous ultrathin ZrO_2 shell

Feng ZHAO, Yanfeng GAO,[†] Weidong LI and Hongjie LUO

Research Center for Industrial Ceramics, Shanghai Institute of Ceramics, Chinese Academy of Sciences,
1295 Dingxi, Shanghai 200050, P. R. China

A facile process was introduced to prepare zirconia-coated hematite particles ($\text{Fe}_2\text{O}_3(\text{@})\text{ZrO}_2$) in an aqueous solution. The amorphous ZrO_2 shell was homogeneously deposited on the hematite surface, and the thickness of ZrO_2 precursor shell is about 2–3 nm. The method shows a strategy for surface modification with an ultrathin inorganic layer.

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Key-words : Chemical deposition, Core-shell particle, Hematite, ZrO_2 , Ultrathin film

[Received April 30, 2008; Accepted June 19, 2008]

1. Introduction

In the past decades, nano-coated particles on the scale from nanometer to micrometer have attracted intense research interest because of the variety of potential or practical applications in different fields, such as food, cosmetic, drug, power materials, and so on.^{1)–4)} It is well known that high activity of nanoparticles makes some of them unstable in air or some specific circumstances. Changes such as oxidization, aggregation and/or decomposition usually occur. For satisfying applications, the surface modification of these nanoparticles is required to tailor their surface chemistry, so that they can have requisite properties, such as anticorrosion, antioxidization, antireduction, dispersivity, solubility and colloidal stability. The difficulties related to the following three issues, however, are obvious in developing methods for engineering these surfaces. First, the matrix particles should be monodispersed in the reaction environment. The difficulty is that the nanoparticles have a very high tendency to aggregate, and the tendency may be further strengthened by coating with a shell, so multicore formation within the shell is usually seen. Second, the formation of a coating should be preferably limited on the surface of matrix particles through the heterogeneous nucleation; the homogeneous nucleation to form particles in solution should be suppressed. Third, the control over thickness, morphology and crystalline properties of coatings is of importance to achieve target applications. The thickness, for example, may have crucial effects on the overall physicochemical performance of the original particles.

Meanwhile, great progresses have been made in recent years in the fabrication of core/shell hetero-structured particles with tailored shell thickness, morphology, and surface properties.^{5),6)} Many oxides such as titania, zirconia and silica have been deposited on the surfaces of various particles to form core/shell structures.^{7)–9)} Nevertheless, the thickness for most of shell coatings ranges from above 20 nm to micrometers. In a general process,¹⁰⁾ the shell nanoparticles were nucleated on active radicals of the core surfaces firstly, then as the reaction proceeding, these discrete deposits increased in size and coalesced to form a contin-

uous shell. Thus, the as-obtained particles had a relatively thick shell inevitably even though the shell was homogeneous. However, the control of the shell to have an ultrathin thickness is fundamental to retain the properties of the original matrix particles. An effective way to tailor the thickness and morphology of coatings is linked to aqua chemistry of coating species, their hydrolysis and complexation, and interactions with core particles possessing sensitive surface chemistry.

Therefore, by extending our experience in the preparation of ceramic films on flat substrates in solution,^{11)–13)} we modified the solution conditions and proposed a facile route to synthesize the core/shell particles of $\text{Fe}_2\text{O}_3(\text{@})\text{ZrO}_2$ by ZrOCl_2 hydrolysis.

2. Experimental procedures

For a typical process, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co. Ltd., China) was dissolved in 100 mL of deionized water to make the concentration of Zr^{4+} to be about 5 mM. To this solution an appropriate amount of HCl was added to regulate the pH value of solution to a confined scope. 20 mg of hematite powders (Deqing, China.) was then added and dispersed ultrasonically. The suspension was magnetically stirred in a water bath at 75°C for 6–24 h. Continuous stirring was necessary during the hot-water-treatment to prevent the hematite particles from settlement. After reactions, the powders were washed 3 times with deionized water by centrifuging. The as-obtained powders were dried at 90°C for 24 h in an oven.

The crystalline phases of powders were determined by X-ray diffractometry (XRD, Model D/Max 2550V, Rigaku, Japan). The morphology and elements analysis of the coated powders was characterized by transmission electron microscopy (TEM) and energy dispersive spectrometer (EDS, JEM-2010F, JEOL, Japan).

3. Results and discussion

Figures 1(a–c) show TEM images of hematite powders coated with a zirconia precursor obtained by treating for 6, 12 and 24 h, respectively. The images show the original commercial hematite particles are about 100 nm in size and irregular in shape. A thin layer was clearly observed to be formed around the particle. These layers were in an amorphous state from the

[†] Corresponding author: Y. Gao; E-mail: yfgao@mail.sic.ac.cn

Fig. 1. TEM images of zirconia-precursor-coated hematite particles at pH = 0.4 after soaking for 6 h (a), 12 h (b), 24 h (c) respectively, and (d) HRTEM image of the same sample as (a).

results of both X-ray and electron diffraction. The shell thickness, about 2–3 nm, seems to be independent upon the soaking time at the given concentration of ZrOCl_2 solution. The above information was also confirmed by a high resolution TEM (HRTEM) image which is shown in Fig. 1(d). The HRTEM displays that an amorphous layer covered a well-crystallized hematite matrix.

The hydrolysis of ZrOCl_2 aqueous solution has been reported by many researchers,^{[14], [15]} and the method adopt is complicated and it takes a long time to form primary zirconia particles. In our process, the initial pH value of solution was about 0.4, and the temperature was 75°C. Under these conditions, no precipitates were observed to be formed in the ZrOCl_2 blank solution even the reaction time was above 24 h. This result indicated that homogeneous nucleation was suppressed under the given conditions. Meanwhile, the severe acidic circumstance made the corrosion of hematite particles possible. The hot acid solution activated the hematite particle surface, consequently inducing the nucleation of zirconia precursors. Because the surface activation process proceeded homogeneously around the particle surfaces, the nucleation of the zirconia precursor would take place equally around the particle surfaces. Compared with the blank sample, a heterogeneous nucleation mechanism seems to work in the presence of Fe_2O_3 powders. If the time for deposition was more than 24 h, the dissolved Fe^{3+} ions colored the solution to be bright yellow. The competitive reactions between the zirconia deposition and matrix dissolution may be partially responsible for the unobvious changes in the shell thickness with soaking time increasing.

As the amorphous zirconia precursor was instable in an acid circumstance, a heat-treat process to crystallize was conducted by calcining the particles at 500°C for 3 h. However, no diffraction peaks for zirconia were observed in XRD patterns. After calcination, a corrosion experiment by dispersion the coated particles in a hydrochloric acid (2 M) at 75°C for 2 h was executed to test the anticorrosion effect. The result shows that although the dissolution of hematite matrix is restrained by coating with zirconia, especially in the starting period of treatment, the ultrathin zirconia layer cannot withstand a long-term

Fig. 2. (a) TEM image of zirconia coated hematite powders calcined at 500°C for 3 h and (b) an EDS spectrum of spot A pointed in the image.

acidic treatment. Further structural analysis was carried out by TEM observation. **Figure 2(a)** shows a TEM image of zirconia coated sample after calcining at 500°C for 3 h. Discontinuous spots of the shell film on the particles were observed unfortunately, suggesting the occurrence of shell cracking and shrinking during calcining. An EDS spectrum confirmed the discreteness of zirconia layer after calcination which was shown in Fig. 2(b).

4. Conclusion

In this study, amorphous zirconia precursor-coated hematite powder with the shell thickness of 2–3 nm was prepared by the thermal hydrolysis of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in an aqueous solution. Prolonging the deposition time did not increase the coating thickness, probably because competitive reactions between the zirconia deposition and matrix dissolution. Although cracking and shrinking of the ultrathin zirconia shell occurred during calcining at 500°C in air, the powders still showed anticorrosion effect in a strong acidic solution. The introduced process experimentally confirms the possibility to form an ultrathin shell through a solution route.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (No.50772129) and the Century Program (One-Hundred-Talent Program) of the Chinese Academy of Sciences.

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