Research Article

Preparation and Characterization of Nanosized Hematite Colloids Using Green Vitriol as Ferrum Source

Xiao-Quan Chen, Shi-Bin Wu, Ren-Bo Cao, and Jin-Song Tao

State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510641, China

Correspondence should be addressed to Xiao-Quan Chen; tt1nano@126.com

Received 2 March 2014; Revised 23 March 2014; Accepted 23 March 2014; Published 30 April 2014

Academic Editor: Zhenhui Kang

Copyright © 2014 Xiao-Quan Chen et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The paper reports a green synthetic route for nanosized hematite colloids with an excellent monodispersity, using green vitriol and ammonia as raw materials. The reaction conditions of the synthetic route were studied and the as-prepared samples were characterized by XRD, TEM, TG-DTA, DLS, and XPS. The results indicated that the key factors for the monodispersity of the colloidal product were preheating reactants and washing repeatedly the intermediate Fe(OH)$_3$. When the initial pH was set as 4 or 5, the transformation product of Fe(OH)$_3$ was the pure $\alpha$-Fe$_2$O$_3$ with the minim adsorptive sulfate ions. Contrarily, the mixtures of $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH were obtained at the pH 6 or 7, which were related to the mechanism of transformation reaction. In addition, the concentration of Fe(OH)$_3$ should be less than or equal to 0.2 mol/L in order to prepare the qualified nanosized hematite colloids. The researches proved that the excellent monodispersity of the colloidal product resulted from a fine dispersion state of the synthetic system during the whole process and that it was a significant way to obtain the nanosized metallic oxide colloids from the corresponding metal hydroxide due to avoidance of hyperspeed centrifugal separation or dialysis operation.

1. Introduction

The colloidal nanosized $\alpha$-Fe$_2$O$_3$ has wide potential applications such as the environmental remediation [1, 2], medicine [3], photoelectrolysis reactor [4–8], fundamental research of colloidal science [9–13], nanofluid [14], coating, and printing application [15]. Up to now, various physical and chemical processes, such as ball milling [16, 17], coprecipitation [18, 19], sol-gel method [20], micelle template [21], hydrothermal methods [22–32], the solution combustion synthesis technique [33, 34], the forced hydrolysis of Fe(III) solution [35–37], microwave-assisted method [38, 39], and pyrolysis of iron organic complexes [40], have been reported for the preparation of the nanoscaled $\alpha$-Fe$_2$O$_3$ with different forms and morphologies. The colloidal nanosized $\alpha$-Fe$_2$O$_3$ has often been prepared with the hydrolysis of FeCl$_3$ in order to ensure the monodispersivity, which can result from the weaker bridging effect of chloride ions, which are unable to induce the aggregation of the nanosized particles, compared with other anions such as sulfate ions. In addition, the hyperspeed centrifugal separation or dialysis treatment was often used for removing impurity components in colloids, which was feasible in laboratory but not in the commercial process.

In all of the preparation processes for the nanosized $\alpha$-Fe$_2$O$_3$, the iron sources included the ferric chloride (FeCl$_3$), ferric nitrate [Fe(NO$_3$)$_3$], ferric pentacarbonyl [Fe(CO)$_5$], and iron organic compounds. Few of the reports related to the ferrous sulfate (green vitriol, FeSO$_4$$\cdot$7H$_2$O), even if it is very cheaper, because it is the byproducts of the fabricating processes for sulfuric acid (H$_2$SO$_4$) and titanium white (TiO$_2$) and also can be obtained from refining the coarse green vitriol. A ton of H$_2$SO$_4$ and TiO$_2$ product is accompanied by about 0.28 tons of Fe (existing in the cinder) and 1.9 tons of green vitriol, respectively, which can be calculated according to the molecular formula of the raw materials, pyrite and ilmenite (FeS$_2$ and FeTiO$_3$). The amount of byproduct is tremendous and clamps down on the manufacturers with the environmental contamination. The green vitriol, the accompanying product of TiO$_2$ or obtained from the acid leaching the cinder waste, is mainly used for the chemical reagent in the flocculating process of wastewater treatment, which is not sustainable and eco-friendly due to
the secondary solid waste. So the research is also significant to broaden the application channel of the green vitriol.

Previously, a facile route has been represented in brief for the preparation of nanosized \( \alpha-\text{Fe}_2\text{O}_3 \) particles with the ferric sulfate \([\text{Fe}_2(\text{SO}_4)_3]\) and ammonia \((\text{NH}_3\cdot\text{H}_2\text{O})\) as raw materials [41]. In this present paper, we will report the detailed researches on the synthetic process of nanosized \( \alpha-\text{Fe}_2\text{O}_3 \) colloids when \( \text{FeSO}_4 \) and \( \text{NH}_3\cdot\text{H}_2\text{O} \) are used, including the pretreatment of reactants and the intermediate, reaction conditions (such as pH and reagent concentration), and synthetic mechanism. During the process, the intermediate was purified and transformed directly into the nanosized particles, avoiding the hyperspeed centrifugal or dialysis operation. Because the byproduct \((\text{NH}_3)_2\text{SO}_4\) is an agricultural fertilizer, and the starting materials are inexpensive, and also the process can be beneficial to the sulfuric acid and titanium white fabricating industry, the process is green, of low cost, and suitable for the commercial fabrication of the nanosized \( \alpha-\text{Fe}_2\text{O}_3 \) colloids.

2. Experimental

2.1. Materials. Ferrous sulfate, ammonia, hydrogen peroxide \((\text{H}_2\text{O}_2)\), ferrous chloride \((\text{FeCl}_2)\), and other all chemicals were of chemical pure grade and were used as received without further purification.

2.2. Preparation of Nanosized \( \alpha-\text{Fe}_2\text{O}_3 \) Colloids. 10 mL of \( \text{H}_2\text{O}_2 \) \((10.6 \text{ mol/L})\) was poured into a 300 mL solution of 0.1 mol/L \( \text{FeSO}_4 \) to obtain solution A, and 5 mL of \( \text{NH}_3\cdot\text{H}_2\text{O} \) \((15.7 \text{ mol/L})\) was diluted to 50 mL with distilled water to obtain solution B. After solution A and solution B were heated to boiling and to 60°C, respectively, they were mixed rapidly and stirred for 10 min at 500 rpm. The reaction mixture was centrifuged to obtain \( \text{Fe(OH)}_3 \) precipitate, which was dispersed with 500 mL of distilled water and centrifuged again; the operation was done repeatedly five times. The washed \( \text{Fe(OH)}_3 \) precipitate was dispersed in distilled water to form a \( \text{Fe(OH)}_3 \) suspension. 0.6 mL solution of 0.1 mol/L \( \text{FeCl}_3 \), which was used as catalyst and could accelerate the transformation of \( \text{Fe(OH)}_3 \) gel [42], was added into the suspension and \( \text{HCl} \) solution \((0.1 \text{ mol/L})\) was used for the adjustment of pH. At last, the suspension was heated to boiling and kept refluxing for 5 hours under 300 rpm to form the colloidal sample, from which the powder sample could be obtained by vacuum drying. The preparation procedure was shown in Figure 1.

2.3. Characterization and Analysis of the Nanosized \( \alpha-\text{Fe}_2\text{O}_3 \) Colloids. The XRD spectrum was determined by X-ray diffractometer (Bruker D8 ADVANCE, Germany) with Cu Kα radiation, scanning from 10° to 70° at 2°/min speed. The dynamic light scattering analysis instrument (Malvern Zetasizer Nano, England) was used for the determinations of the mean size and Zeta potential, for which the concentration of test solution was about 0.5% (W/W%) at the presence of \(10^{-3} \text{ mol/L} \text{ HCl}\). The TEM observation was finished with the JEM-100CXII transmission electron microscope (Japan) on a copper wire film, on which the sample solution was dropped and dried at normal temperature. The TG-DTA analysis was finished at the Q-500 coupled thermal analyzer (USA) with rising rate of temperature \(10^\circ\text{C/min} \) and sweeping rate of \(\text{N}_2 \) \(39 \text{ ml/min}\). The XPS spectra were determined by XPS analytic instrument (Axis Ultra DLD, England) with Al Kα as X-ray radiation source and powder 150 W.

3. Results and Discussion

3.1. Preheating of Reactants and Repeated Washing of Intermediate \( \text{Fe(OH)}_3 \). \( \text{FeSO}_4 \) and \( \text{NH}_3\cdot\text{H}_2\text{O} \) solutions were preheated and mixed rapidly so as to form grainy \( \text{Fe(OH)}_3 \) with the inferior crystal cell structures, which was beneficial to the monodispersity of the product nanosized \( \alpha-\text{Fe}_2\text{O}_3 \). Our experimental results proved that the intermediate \( \text{Fe(OH)}_3 \) obtained from the unpreheated reactants could not be transformed into the stable colloidal nanosized \( \alpha-\text{Fe}_2\text{O}_3 \) no matter what the reaction temperature and initial pH were. In fact, while the preheated reactants were mixed, the palingenetic \( \text{Fe(OH)}_3 \) had already initiated the transformation reaction at its forming moment. Figure 2 is the XRD spectra of the \( \text{Fe(OH)}_3 \) prepared with preheated and unpreheated reactants, respectively, which display the weak adsorption peaks at (110) and (300) crystal faces in the spectrum of the as-prepared sample from the preheated reactants, confirming the inferior crystal cell structures that hold certain crystal properties, such as the distinct particle borders, instead of the massive gel entirely that is unfavorable to the dispersity of the nanosized particle product in the liquid phase.

The reaction product of \( \text{FeSO}_4 \), \( \text{H}_2\text{O}_2 \), and \( \text{NH}_3\cdot\text{H}_2\text{O} \), \( \text{Fe(OH)}_3 \) precipitate, was washed repeatedly in order to remove the sulfate ions, which could form the bridging bidentate structure \((\text{FeSO}_4\cdot\text{OFe})\) on \( \alpha-\text{Fe}_2\text{O}_3 \) particle surfaces to result in aggregation [43]. Whether or not heating the reactants could also affect the washing efficiency of the intermediate \( \text{Fe(OH)}_3 \), the sulfate ions adsorbing on the granules could be easily removed at heating condition. Reversely, it was very difficult to remove the ions because
they are embedded in the massive gel. Therefore, it was necessary that the reactants were preheated to boiling and the Fe(OH)$_3$ precipitate was washed repeatedly to fabricate the nanosized α-Fe$_2$O$_3$ particles with excellent monodispersity, when FeSO$_4$ was used as Fe source.

3.2. Effect of pH on the Component of Transformation Product of Fe(OH)$_3$. In this work, the effect of pH value on the component of transformation products of Fe(OH)$_3$ was investigated with XRD and TG-DTA. When pH value was set as 4 and 5, the XRD spectra of the products displayed the pure α-Fe$_2$O$_3$ crystalline (Figure 3, JCPDS, File number 89-0597). When pH value was 6 and 7, the characteristic peaks of α-FeOOH (JCPDS, File number 29-713) in the XRD appeared and indicated that the partial Fe(OH)$_3$ has transformed into α-FeOOH crystalline.

On the other hand, the TG-DTA curves were also used for revealing the species in the transformation product, colloidal crystalline particles, which was more accurate than XRD spectra. Figure 4 has shown four sets of the TG-DTA curves of the products at different pH values. The TG curves could be divided into two temperature ranges, 100–200°C and 200–600°C. The adsorption water was lost in the lower temperature range. The lost weight rates of the samples were 6.90%, 5.92%, 5.17%, and 3.84%, respectively, when the initial pH value of the transformation reaction corresponded to 4, 5, 6, and 7. At the higher temperature, from 200°C to 600°C, the lost weight should be attributed mainly to the dehydration of hydroxyl groups, which were 3.97%, 3.67%, 4.22%, and 3.95%, respectively. The hydroxyl groups on the face of the α-Fe$_2$O$_3$ crystalline were lost gradually in the whole of the temperature range, but the loss of hydroxyl groups in the α-FeOOH crystalline molecular occurred rapidly at 270°C, which was confirmed by the sharp peaks in the DTA curves of the samples with pH 6 and 7, especially with pH 7. It was attributed to the decomposition of α-FeOOH, which agreed with the literature that reported the weight loss step of α-FeOOH in the temperature range 250–330°C [44].

The TG-DTA researches proved that when pH was set as 4 or 5, the pure α-Fe$_2$O$_3$ could be obtained; in contrast, when pH was 6 or 7, the as-prepared samples contained a certain amount of α-FeOOH. The conclusions from the TG-DTA results of the samples were in agreement with the ones from the XRD spectrum in Figure 3. Although there were few researches about hydrolysis of Fe$^{3+}$ in the presence of SO$_4^{2-}$, many literatures reported that the effect of NO$_3^-$, Cl$^-$, and organic molecules on the product components of Fe$^{3+}$ forced hydrolysis. Among them, there was a similar report with the aging of the precipitation of FeCl$_3$ at pH 6 to 6.5; the mixture of α-FeOOH and α-Fe$_2$O$_3$ could be obtained [45].

In summary, the experimental results demonstrated that the Fe(OH)$_3$ from FeSO$_4$, NH$_3$·H$_2$O, and H$_2$O$_2$ could transform into a single phase of nanosized α-Fe$_2$O$_3$ at pH 4 or 5 and the α-FeOOH crystal phase could be observed at pH 6 or 7.

3.3. Effect of pH Values on the Monodispersity. The TEM photographs of the as-prepared samples with different initial pH values were displayed in Figure 5, which revealed that the nanosized α-Fe$_2$O$_3$ particles obtained at pH 4 or 5 had an excellent monodispersity and the mixtures of nanosized α-Fe$_2$O$_3$ and α-FeOOH at pH 6 or 7 were in the flocculating state. This could be ascribed from two aspects. Firstly, at the start of the transformation reaction, the Fe(OH)$_3$ grain itself at pH 4 or 5 had a better monodispersity than the one at pH 6 or 7 due to the higher Zeta potentials (the former two were 43.6 mV and 36.2 mV; the latter two were 25.2 mV and 11.1 mV). The higher the Zeta potential was, the better the monodispersity was, which could be deduced from DLVO theory.

In the other way, at pH 4 and 5, the transformation reaction of Fe(OH)$_3$ followed mostly the dissolution reprecipitation mechanism during the initial stage; corresponding to
pH 6 or 7 the direct bulk-phase transformation mechanism was followed, which could be judged from the pH falls of the reaction system. The feature of the dissolution reprecipitation mechanism was just the pH fall in the reaction system [46]. It was determined that the falling values of pH in an hour range at the initial pH 4 and 5 were 0.7 and 1.3, while at pH 6 and 7 the falling values were 0.3 and 0.2. The dissolution reprecipitation mechanism was beneficial to the monodispersity of the formed nanosized α-Fe₂O₃; conversely, the bulk-phase transformation mechanism could not release the aggregate in the reaction system.

From the above results, we could deduce that it was essential for the preparation of the colloids with excellent monodispersity to keep the synthetic system a fine dispersion state during the whole process.

3.4. Effect of the Concentration of Fe(OH)₃ on the Particle Size of Nanosized α-Fe₂O₃. The mean sizes of the nanosized α-Fe₂O₃ particles obtained from different concentrations of Fe(OH)₃ were listed in Table 1, which proved that the particle size increased with the raise of the concentration, and when the concentration was 0.3 mol/L, the mean size was already above 100 nm and the volume fraction of the particles greater than 100 nm reaches up 54.2%. The reasons may be that the reactant with the higher concentration enhanced the merge of crystal nucleus and agglomeration of particles. Therefore, the Fe(OH)₃ concentration should be less than or equal to 0.2 mol/L in order to fabricate the qualified nanosized α-Fe₂O₃ colloidal products.

Table 1: Mean sizes of the nanosized α-Fe₂O₃ particles obtained from different Fe(OH)₃ concentrations.

<table>
<thead>
<tr>
<th>Number</th>
<th>C_(Fe(OH)_3) (mol/L)</th>
<th>Mean size (nm)</th>
<th>P_v (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>51</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>63</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>82</td>
<td>10.2</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>117</td>
<td>54.2</td>
</tr>
</tbody>
</table>

* Volume fraction of the particles greater than 100 nm.
Figure 5: The TEM photographs of the as-prepared samples at different pH values, which displayed the effect of pH values on the monodispersity of as-prepared samples. When the transformation reaction pH was set as 4 or 5, the products nanosized colloidal $\alpha$-Fe$_2$O$_3$ had excellent monodispersity, but, with pH = 6 or 7, the flocs were observed.

3.5. XPS Analysis of the As-Prepared Nanosized $\alpha$-Fe$_2$O$_3$ Sample. The species and contents of the surface elements of the as-prepared nanosized $\alpha$-Fe$_2$O$_3$ particle (Sample I in Table 1) have been determined by XPS analysis (Figure 6). The results demonstrated that the surface of the nanosized $\alpha$-Fe$_2$O$_3$ particle contained Fe, O, C, and S elements and the corresponding contents were separately 72.85%, 19.22%, 7.52%, and 0.41%, in which the microcontent S came from the remains of SO$_4^{2-}$ and the peak of element C was attributed to the C pollutant in the XPS analytic system.

Figure 7 displayed the XPS spectra of Fe 2p and O 1s of the nanosized $\alpha$-Fe$_2$O$_3$, which associated with the prepared methods and were different from the bulk $\alpha$-Fe$_2$O$_3$ [47]. In Figure 7(a), 723.9 eV and 710.0 eV were the binding energies of Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$, respectively, and 715.7 eV was the satellite peak. In Figure 7(b), the binding energy 529.9 eV was assigned to surface oxygen with lower electron density, described as surface oxygen species O$^-$, and higher than one of the lattice O$^{2-}$, 528.1 eV [47]. The amount of surface oxygen species O$^-$ was related to the catalytic activity.

4. Conclusions
The research demonstrates that the nanosized $\alpha$-Fe$_2$O$_3$ colloids with the excellent monodispersity can be prepared with FeSO$_4$ and NH$_3$·H$_2$O as the raw materials. The preheated reactants form the intermediate Fe(OH)$_3$ containing the Fe$_2$O$_3$ crystal structures, which is in favor of washing up sulfate ions; otherwise, the sulfate ions would be embedded in the gel and could not be removed with repeated washing. In order to hold the high Zeta potential and fine dispersion state of reaction system, the transformation pH of the intermediate
should be adjusted to 4 or 5, at which the initial reaction stage follows the dissolution reprecipitation mechanism. The research proves that the excellent monodispersity of the colloidal product results from keeping the synthetic system in the fine dispersion state during the whole process and it is a significant way to obtain the nanosized metallic oxide colloids from the corresponding metal hydroxide due to avoiding of hyperspeed centrifugal or dialysis operations. The reported process is green, of low cost, and feasible for the commercial fabrication of nanosized \( \alpha\)-Fe\(_2\)O\(_3\) colloids due to the facile operation, inexpensive raw materials, and usable byproduct.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This study was financially supported by the Grand Science and Technology Special Plan Projects of Guangdong Province of China (no. 2008A090300016).

References


