In-situ deposition of hematite (α-Fe₂O₃) microcubes on cotton cellulose via hydrothermal method

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Abstract. Hematite microcubes with truncated edges have been successfully deposited on cotton cellulose via one-step hydrothermal process using anhydrous FeCl₃ and glycine as Fe(III) precursor and chelating agent, respectively. The amount of glycine significantly affects the morphology and yield of hematite. The addition of 0.495 g of glycine to 50 ml of 0.1 M FeCl₃ solution with 0.400 g of cotton resulted to hematite-deposited cellulose having ~15% hematite content. The reduction of glycine to 0.247 g increased the amount of hematite on the surface of the cotton cellulose to ~20% by weight. However, the hematite microcubes have a wide size distribution, with particle size in the range of 0.684 µm to 1.520 µm. Without glycine, hematite cannot be formed in the solution.

1. Introduction
Hematite (α-Fe₂O₃) is the most stable oxide of iron under ambient conditions [1]. It has acquired considerable attention due to its wide range of applications being a cheap, n-type semiconductor with high corrosion resistance, high stability, substantial absorption of visible light, low bandgap of 2.1 eV, and low toxicity [2]. Numerous studies have shown its potential, such as in photocatalysis [3], gas sensing applications [4], lithium batteries [5 - 6], and water treatment [7 - 8].

The size and shape of the synthesized hematite nanoparticles play important role in the properties and performance of the material [1]. Extensive studies regarding hematite synthesis have produced different morphologies ranging from microflowers [8], nanocubes [9], nanotubes [10] and nanospheres [6] among others. Numerous techniques have been developed to produce these structures and achieved the desired properties [1]. Some of these methods are direct thermal decomposition [11], electrochemical synthesis [10], sonochemical synthesis [12] and chemical co-precipitation [13]. However, most of these methods require multiple steps, massive amount of energy and expensive chemicals while others are environmentally unsafe. Moreover, wide size distribution of particles is obtained for some processes, which is why hydrothermal method is preferred. In hydrothermal synthesis, glycine is commonly used as chelating agent in preparing hematite [1, 14]. However, there are only few comprehensive studies on its role in the formation of hematite.

Deposition of hematite on cellulosic scaffolds has been performed to cater specific applications ranging from drug delivery [15] to pigment science [16]. It is because the use of cellulose as a substrate can promote nucleation and growth of the metallic oxide in aqueous medium [16]. Hematite
with microcube morphology has been known to create an impact in drug delivery, wherein the \( \alpha-Fe_2O_3 \) microcubes are embedded in drug fillers commonly made of cellulosic materials [15, 17]. The deposition of hematite micro and nanoparticles in various substrates makes product recovery easier due to the apparent bigger structure.

In this study, a simple, cheap and environment friendly way to synthesize and deposit \( \alpha-Fe_2O_3 \) microparticles in cotton cellulose is presented. A single-step hydrothermal method has been performed with the use of anhydrous FeCl\(_3\) as precursor and glycine as chelating agent. The effects of varying the amount of glycine in the formation of hematite have been investigated. The crystal structure and morphology of the products were analyzed and the amount of deposited hematite on the cellulose fibers was determined from the thermogram of each sample.

2. Methodology

In a typical preparation, 0.811 g of anhydrous ferric chloride (FeCl\(_3\), HIMEDIA) was dissolved in 50 ml deionized water to produce 0.1 M FeCl\(_3\) yellow-brown transparent solution. Then 0.495 g of glycine (NH\(_2\)CH\(_2\)COOH, UNIVAR, Ajax Finechem) was added slowly upon continuous stirring, producing a black solution. It was mixed thoroughly for 30 min using a magnetic stirrer at 500 rpm. Then 0.400 g of commercial cotton (Cleene, Selair Manufacturing Corp.) was added and the mixture was heated in a hot plate. It was allowed to boil for 15 min where it turned brown-orange. The solution was transferred to a 100 ml Teflon-lined stainless steel autoclave and heated to 160 °C in oven (Yamato, ADP 210C) for 5 h. After the hydrothermal process, the cotton fibers fragmented into small pieces fine enough for the final product to be a suspension. The solid products were collected via decantation and washed with DI water, shaken vigorously to remove loose hematite. After three times of washing, the solid products were collected and dried in oven at 85 °C for 4 h. To determine the effect of glycine, the amount was reduced in other experiments. Another experiment was also carried out without the cotton to determine its effect in the morphology of the hematite.

The structure and crystallinity of the formed hematite was analyzed using XRD (SHIMADZU, XRD-7000 Maxima). The morphology was observed using FESEM (JSM-7800fPrime Japan) and the thermal behavior and stability of the samples were investigated via TG-DTA (SHIMADZU TA-60WS) run at 10 °C/min ramp rate from room temperature to 1000 °C in static air.

3. Results and discussion

When 0.495 g of glycine was added, the as-prepared powder has a deep red color. The red color indicates the presence of hematite particles as commonly reported [7]. In the absence of glycine, black solid products was produced which suggest nonexistence of hematite.

Figure 1 shows the corresponding XRD patterns of the final products with 0.495 g glycine and without the added glycine. In figure 1a, sharp peaks attributed to hematite are indexed. Some notable peaks are at \( 2\theta = 24.12^\circ, 33.3^\circ, 35.74^\circ, 40.94^\circ, 49.54^\circ \) and \( 54.14^\circ \) which correspond to planes \((0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4)\) and \((1 1 6)\) [18]. This confirms the formation of hematite as indicated by the reddish appearance of the powder. Other peaks at \( 2\theta = 15.0^\circ, 16.5^\circ, 22.86^\circ \) and \( 34.5^\circ \) belong to cellulose I of the cotton due to planes \((1 0 1), (0 0 2)\) respectively [19].

No peaks corresponding to hematite are observed in the XRD pattern of the sample without glycine as seen in figure 1b. Only broad peaks corresponding to cellulose I are clearly present. Notice that there is a significant increase in the intensity of planes \((1 0 1)\) and \((1 0 \bar{1})\).

Figure 2a shows the SEM micrographs of the products formed upon addition of 0.495 g of glycine without the cotton substrate. The particles have cubic shape with truncated edges. Additionally, the cubic hematite particles have sponge-like structures. The size of the particles ranges from 0.851 \( \mu \text{m} \) to 1.269 \( \mu \text{m} \). Agglomeration of these particles have been observed which resulted to bulk structures that reaches several micrometers in diameter.
Figure 1. X-ray diffraction pattern of the samples with a) 0.495 g glycine and b) without glycine.

Figure 2. Low and high resolution SEM images of the sample (a) without cotton containing 0.495 g glycine and of the samples with 0.400 g cotton containing (b) 0.495 g, (c) 0.247 g, and (d) 0 g glycine.
With the addition of cotton, the cubic hematite particles with an average size of 0.712 µm adhered on the surface of the fibers as shown in figure 2b. The cotton fibers have diameters and lengths of about 20 µm and 200 µm respectively. However, the cotton fibers are not uniformly covered with hematite.

For the sample prepared with 0.247 g glycine, the cotton fibers are also covered with hematite particles. Based on the SEM images (see figure 2c), more hematite particles are deposited on the surface at lower glycine concentration. The size of these particles ranges from 0.684 µm to 1.520 µm with an average size of 1.032 µm. It is larger compared to the average size of the previous sample, which is only 0.712 µm. But these particles are still much bigger compared to the average particle size of 80 - 90 nm that was reported using same synthesis method [5]. With over 100 particles measured, the standard deviation is about 14.77% of the average diameter indicating wide size distribution. Without addition of glycine, only cotton fibers are observed as seen in figure 2d. This agrees with the XRD pattern in figure 1b, which only show peaks due to cellulose I of the cotton.

The addition of glycine is crucial in preparing hematite particles. The mixing of FeCl₃ and glycine in deionized water may result to dissolution and hydrolysis forming iron cations and glycine in acidic (Gly⁺: H₃NCH₂-COOH) and zwitterionic (Gly±: H₃N-CH₂-COO⁻) forms [14, 20]. Glycine acts as a strong chelating agent which may form stable complexes with the iron cations. These complexes become unstable at higher temperature, releasing the iron cations in the aqueous solution followed by nucleation and crystal growth upon hydrothermal process [5]. It has been reported that positively charged protonated glycine interacts with Fe(OH)_3, which is a product of FeCl₃ hydrolysis, via electrostatic and hydrogen bond [21]. Hematite particles are then formed by a two-phase transformation upon hydrothermal treatment [21], Fe(OH)_3 → FeOOH → α-Fe₂O₃.

Glycine delays the growth of crystals due to the formation of the said complexes [5]. Low concentration of glycine would result to inefficient control of the particle size. Nuclei formed at early stages tend to outgrow each other since there is lesser glycine that delays growth, as suggested by the presence of larger hematite particles of the sample with lower glycine content (figure 2c). The nuclei formed at the later stages will no longer grow since the precursor is already depleted resulting to a wide size distribution. But without glycine, hematite cannot be formed. Perhaps, Fe(OH)_3 get strongly bonded to the cotton cellulose and is not able to release even at elevated temperature, hindering the formation of α-Fe₂O₃.

The three samples with the added cotton were subjected to thermal analysis. The TG and DTA thermograms for the sample with 0.495 g glycine are presented in figure 3a. There are three significant stages of mass reduction at temperature ranges of 25 - 260.9 °C, 260.9 - 351.6 °C and 351.6 - 542.8 °C. The first stage has two distinct levels. Firstly, a small decrease is observed until 74.73 °C that reduce the mass to 94.86%. This corresponds to the dehydration of cellulose. Secondly, a gradual mass loss occurs until 260.9 °C, effectively decreasing the mass to 88.91%. This is probably due to the elimination of physically or chemically adsorbed water. In the second stage, an abrupt decline in the mass to about 27.68% is determined at 351.6 °C. This is attributed to the oxidative decomposition of cotton which involves formation of combustible gases of carbonyl and carboxyl groups (e.g. aldehydes, ketones, ethers, etc.), evolution of gases (e.g. CO and CO₂) and formation of carbonaceous residue or char [22]. In the final stage, the mass continues to decrease until it attains a stable mass of 15.2% around 542.8 °C. This is due to the decomposition of the previously formed residue [23].

A decreasing DTA curve indicates lowering of the sample’s temperature with respect to the reference. Conversely, an increasing DTA curve means a rising relative temperature. The endotherms at 52.35 °C and 324.9 °C are brought by the absorbance of heat due to the evaporation of water and carbonization of cotton respectively. The peak at 351.6 °C signifies an increased temperature due to the burning of char.
Figure 3. Thermal behavior of the samples with 0.400 g cotton and (a) 0.495 g, (b) 0.247 g, and (c) 0 g glycine.

On the other hand, from the thermogram of the sample prepared with 0.247 g of glycine (see figure 3b), a sudden drop occurs reducing the mass to 50.48% at the end of 315.7 °C. Then a multi-step reduction in mass occurs until it achieves a constant mass of 19.85% at about 451 °C. Its DTA curve shows an endotherm at 56.43 °C, which is due to the dehydration of cotton. An exothermic peak centered at 315.7 °C is observed and attributed to the oxidation of cotton. It is followed by two other peaks at 338.8 °C and 378.8 °C, which are basically the burning of the residue.

For the sample without glycine (see figure 3c), there is an immediate loss in mass eliminating 9.06% at the end of 100 °C. The mass is approximately stable until 217.15 °C, where it starts undergoing sharp decrease. Only 41.87% of the mass is left around 318.9 °C. From there, a multi-stage reduction in mass occurs where it ends with a stable mass of 7.77% around 460 °C. From the DTA thermogram, the endotherm brought by the removal of adsorbed water is broader and is shifted to a higher temperature of 76.9 °C. The shifting of the first endothermic peak and its broadening, as the amount of glycine is reduced, suggest that more water is adsorbed by the cellulose. On the other hand, the exothermic peak, which is associated with the burning of cotton, remains almost constant at 317.5 °C. The appearance of four additional peaks implies that unreacted precursor derivatives adsorbed by the cotton (i.e. Fe(OH)$_3$) underwent successive transformations beyond 315 °C.

Hematite is known for its stability even at very high temperatures [2, 5]. By assuming that cotton was completely removed by the burning, we suggest that the weight percentage of the hematite would be approximately 15% because the sample with 0.495 g glycine is found to be mainly composed of cellulose and hematite. The sample with 0.247 g glycine would have higher hematite content of around 20%. The results from the TG curves agree with the observations from the SEM showing more hematite particles deposited in the sample with lower amount of glycine. Finally, the sample
containing no glycine generated 7.77% of stable mass. It is relatively higher than the residue when pure cotton is burnt, which is less than 2% as reported [22]. This implies that cellulose fibers might have absorbed significant amount of iron precursors, which eventually undergo transformations and remains as residual ash.

4. Conclusions
Successful deposition of hematite microcubes on cellulose was carried out via one-step hydrothermal process using anhydrous FeCl$_3$ as Fe(III) precursor and glycine as chelating agent respectively. The effect of varying amount of glycine was investigated. The addition of 0.495 g of glycine to 50 ml of 0.1 M FeCl$_3$ solution with 0.400 g of cotton resulted to hematite-deposited cellulose having ~15% hematite content. The deposited hematite particles have an average size of 0.712 µm, with cubic structure having truncated edges and sponge-like surface morphology. The reduction of glycine to 0.247 g improved the amount of hematite to ~20% by weight, covering more surfaces of the cotton fibers with hematite particles. However, the particles have wide size distribution due to the reduced formation of complexes that controls crystal growth. Without glycine, no hematite was formed. It was also observed that cotton fibers absorbed significant amount of amorphous materials, probably iron precursors that were not able to transform to hematite after the hydrothermal treatment.

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