

Novel optical properties of amorphous ferric hydroxide in near infrared region

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ABSTRACT: New spectroscopic characteristics of amorphous ferric hydroxide ($\text{Fe}(\text{OH})_3$), interestingly in the near infrared (NIR) region, are presented in this study. The absorption spectrum of ferric hydroxide covers wide spectral regions from ultraviolet to NIR (200 ~ 900 nm). Unique emission bands were newly observed in the NIR regions (800 ~ 1400 nm). Several bands of this NIR emission are quiet well overlapped with the combinational vibrational absorption bands of water. From photothermal conversion study, very interestingly, temperature of aqueous mixture solution including the amorphous ferric hydroxide was significantly increased from ambient temperature to 38 °C for 30 minutes under irradiation of a standard helium lamp.

Thermal therapy is one of the popular therapeutic approaches to treat various medical conditions, such as desensitizing neuralgia,¹⁻³ obstructive tonsillar hypertrophy,⁴ and killing malignant tumor.⁵⁻⁹ Recently, photothermal therapy techniques have been combined with near infrared (NIR) irradiation and its thermal coupling agents have been widely investigated for the anti-cancer treatment application, such as the hyperthermia therapy.¹⁰⁻¹² Especially, NIR light from 650 nm up to 900 nm, called the “tissue optical window”,^{13,14} is recently utilized because it can penetrate relatively deep into skin, tissue and hemoglobin, resulting in providing site-specific heating and/or treatment of diseased regions without undesired side effects to normal organs and tissues.¹⁵ As a result, NIR absorbing and emitting agents have been emerged as one of the most attractive segments in the anti-cancer treatment. The commonly used NIR absorbing agents are shape-controlled gold nanoparticles¹⁶⁻¹⁹ and various functionalized carbon nanotube complex.²⁰⁻²² Dyes, quantum dot and rare earth metal reagents have also been mainly used as NIR luminescent materials.²³⁻²⁹

Here we introduce the new and easily obtainable NIR photo-absorbing and emitting agent. Amorphous ferric hydroxide ($\text{Fe}(\text{OH})_3$) has been ordinarily used as an adsorbent in contaminated water, in pigments, and in pharmaceutical preparations.³⁰ Furthermore, ferric hydroxide is just frequently used as a facile precursor to synthesis various iron oxides/oxyhydroxides utilizing in many environmental and biological applications.³¹⁻³⁶ In particular, to the best of our knowledge, the spectroscopic properties of amorphous ferric hydroxide at NIR regions have not been reported yet. In this study, we report on absorption, emission, and the photothermal effects of ferric hydroxide.

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In this study, amorphous ferric hydroxide was synthesized by treatment of an aqueous solution of 0.05M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with 1N NaOH following a previous literature.³⁷ The resulting product was repetitively washed with deionized water, and then dried at 100 °C for 24 h in oven.

The shape, size, and elemental composition of the as-made ferric hydroxide was analyzed using field emission scanning electron

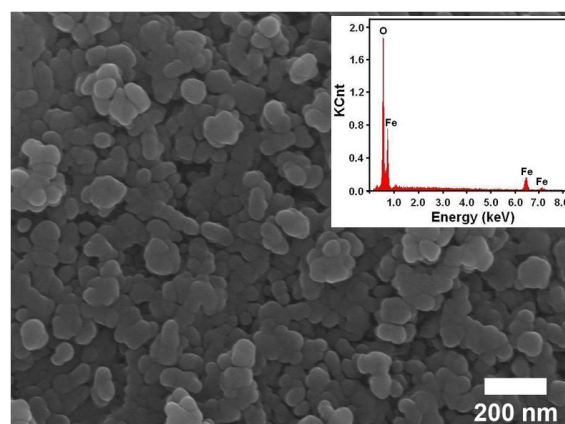


Figure 1. SEM image of ferric hydroxide and corresponding EDS spectrum (inset).

microscopy (FESEM, Hitachi, SU-70, 15 kV accelerating voltage) attached with an energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) patterns of the samples were obtained using an X-ray diffractometer (PANalytical, X'Pert Pro MPD) with a $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation source. UV-Vis absorption spectra of ferric hydroxide, which was dispersed in ethylene glycol, were recorded using an S-3100 UV-Vis spectrophotometer (Scinco, Korea) at room temperature. A conventional quartz cuvette of 1 cm optical path was used. NIR photoluminescence spectra were measured on a Horiba iHR-320 spectrometer (Jobin Yvon Horiba) equipped with a liquid nitrogen cooled InGaAs photo detector in the wavelength range of 800 ~ 1500 nm with a monochromatic light of 580 nm (Xe-lamp) as an excitation source. To heat up by photothermal process of samples, halogen illuminator (FHL-101, 100 W, Asahi-Spectra, Japan) was used as a NIR and visible light source. The illuminating light from FHL-101 is delivered to the surface of sample by the fiber optic ring light guide (MRG53-1000S, Moritex, Japan). The distance between the sample surface and the fiber optic ring was about 8 cm. The illumination power was 200 mW/cm^2 at the sample surface. Infrared camera (SC7600, FLIR Systems, Croissy-Beaubourg, France) was used for all temperature measurements.

Figure 1 shows a SEM image and an EDS spectrum of the as-made ferric hydroxide particles. The shape of the particles is spherical and its average diameter is about 100 nm. The particles tend to aggregate each other. The EDS spectrum reveals that the particles are composed of iron (Fe) and oxygen (O).

The crystal structure of iron oxide/hydroxide powders as well as the as-made ferric hydroxide was investigated by XRD analysis. Figure 2 shows the XRD profiles of the as-made ferric hydroxide, α -Fe₂O₃, and β -FeOOH, respectively. Compared to the crystalline characteristics of the α -Fe₂O₃ and β -FeOOH, the increased background and broadened diffraction peak, as shown in the Figure 2a, is due to amorphous characteristic of the as-made ferric hydroxide. According to a previous report,³⁸ ferric hydroxide is known to be converted to β -FeOOH and α -Fe₂O₃ phases by aging under a proper condition. In this study, however, the observed XRD profiles indicate that the ferric hydroxide synthesized through the solution process does not contain any by-products of iron oxides/hydroxides.

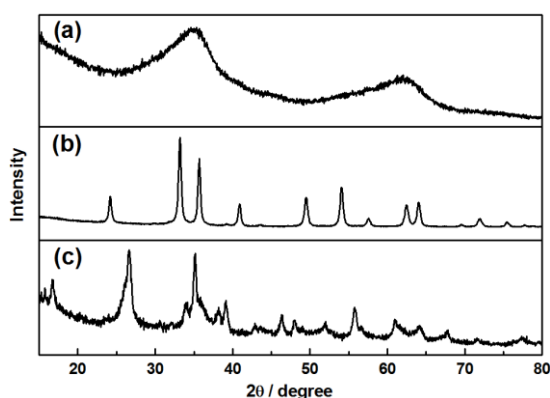


Figure 2. XRD patterns of (a) as-made ferric hydroxide, (b) α -Fe₂O₃ and (c) β -FeOOH powders.

UV-Vis absorption and photoluminescence spectra of the amorphous ferric hydroxide are shown in Figure 3. The absorption spectrum shows broad absorption feature in over the visible and up to NIR range, with a maximum absorption peak at 590 nm. Under 580 nm excitation, at ambient temperature, the photoluminescence spectrum of the amorphous ferric hydroxide shows broad emissions in the NIR region (800 ~ 1400 nm) with intense luminescence peak at around 1000 nm. By now, to the best of our knowledge, similar intense luminescence spectrum in the NIR region has not been reported from iron oxide relevant materials. From repetitive measurements, we consider that these broad and intense emissions are plausibly responsible for the optical transitions between the partly filled *d*-shells (*d-d* transitions) of iron (Fe).³⁹

The specific absorption in the visible region and unique NIR emission characteristics of the amorphous ferric hydroxide can be applicable to heat up a system by photothermal conversion process. In principle, such the NIR emission well overlap with the combinational vibration modes of water molecule, as indicated by shade regions in Figure 3,⁴⁰ hence, it is generally expected that NIR emission can be consumed to excite vibrational modes of neighbor water molecules. Therefore, in this mixture aqueous solution, it does not surprise observing the temperature elevation under light irradiation. In order to measure temperature change, halogen

illuminator was irradiated to the ferric hydroxide powder (10 mg) and ferric hydroxide/water mixture (1 mg/ml), respectively. The overall power of the light source was approximated at 200 mW/cm².

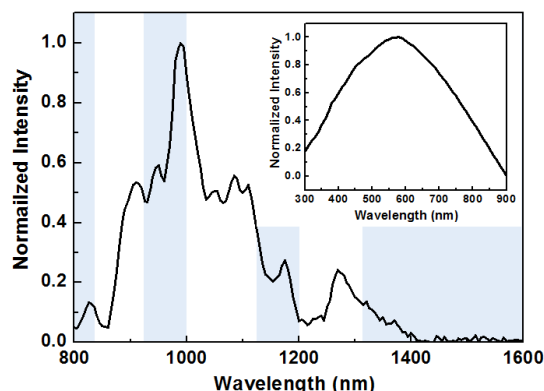


Figure 3. Photoluminescence spectrum of the amorphous ferric hydroxide dispersed in ethylene glycol. Excitation wavelength is 580 nm. Inset is UV-Vis absorption spectrum of the ferric hydroxide.

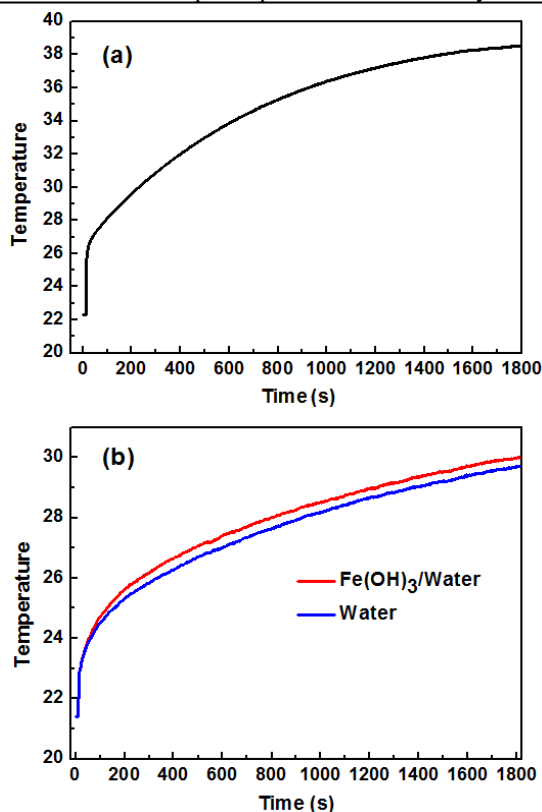


Figure 4. Temperature change of (a) ferric hydroxide powder and (b) ferric hydroxide/water mixture as well as pure water.

Figure 4a shows the temperature changes of ferric hydroxide powder itself under visible and NIR irradiation for 30 minutes. The temperature of the ferric hydroxide is significantly increased from 22 °C to approximately 38 °C. This indicates that the absorbed optical energy is sufficiently transferred into molecular vibration modes, eventually generating thermal energy.⁴¹ Figure 4b shows the temperature elevation of ferric hydroxide/water mixture as well as pure water with irradiation of visible and NIR. The temperatures of the ferric hydroxide/water mixture (500 μ l) and the pure water (500

μl) were increased to 30 °C and 29.5 °C, respectively. The visible and NIR light energy can be converted to thermal energy because water has a large number of vibration absorption bands in this region, which are mostly composed of overtone and combination bands.⁴⁰ As a result, the temperature of pure water also increased gradually. Under the same conditions, the temperature of the ferric hydroxide/water mixture was more enhanced than that of pure water. This is because the optical energy absorbed by ferric hydroxide is converted to heat through intra-band nonradiative relaxation processes and/or energy transfer to bound (or adjacent) water molecules, which can further enhance temperature of surrounding water. Although, the temperature of the ferric hydroxide/water mixture is about 0.5 °C higher than that of pure water, which is due to the fact that small amounts of ferric hydroxide in mixture (0.1 w/v%) are used. Therefore, further study is underway to investigate the effect not only of compositions of ferric hydroxide/water mixture, but also of visible and/or NIR monochromatic radiation.

In summary, we have analyzed the spectroscopic characteristics of the amorphous ferric hydroxide. The ferric hydroxide exhibited wide absorption from UV to NIR region (200 ~ 900 nm). Moreover, the notable emissions were newly observed in the NIR region (800 ~ 1400 nm). With the specific spectroscopic properties of the intense NIR emissions, we could detect extra temperature elevation as a result of photothermal conversion processes. These results suggest that the ferric hydroxide material can be effectively utilized as a photothermal agent in the visible and NIR regions. Hopefully, the interesting characteristics of the ferric hydroxide material would be widely applicable in photothermal therapeutic and biomedical fields.

KEYWORDS: Ferric hydroxide, Photothermal conversion, Near infrared, Photoluminescence

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