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Supplemental document

Facile upscale synthesis of Layered iron oxide Nanosheets and its Application for Phosphate Removal

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S1. Chemical composition analyses of the layered Fe^{III} nanosheets and its precursors

The chemical compositions of the products were analyzed by dissolving proper amounts of the solids in 0.1 M HCl. The Fe^{II} contents within in GR(Cl) and GR(C12) was determined by using a modified phenanthroline method, while the content of total Fe was analyzed by using an Optima 8300 inductive coupled plasma optical emission spectrometer (ICP-OES; PerkinElmer, USA). The contents of chloride and dodecanoate ions within the solid were measured by using a Dionex ICS-2100 ion chromatorgraphy (IC), and an Agilent 6890 series gas chromatograph equipped with a flame-ionization detector (GC-FID, USA), respectively.

Fe^{II} contents of the as-synthesized GR(Cl) and GR(C12) were determined by using a modified phenanthroline method. GR(C12) samples (10 mg) were added to a volumetric flask (50 mL) containing O2-free HCl (2 mL, 0.1 M) in the glovebox. After 30 min the volumetric flask was filled with pure ethanol. Then, mix aliquot of the solution with 1,10-phenanthroliniumchlorid, Nitrilotriacetic acid and Glysine solution. The mixtures were then analysed over a U-2900 UV/vis spectrophotometer (Hitachi, Japan) at a wavelength of 508 nm.

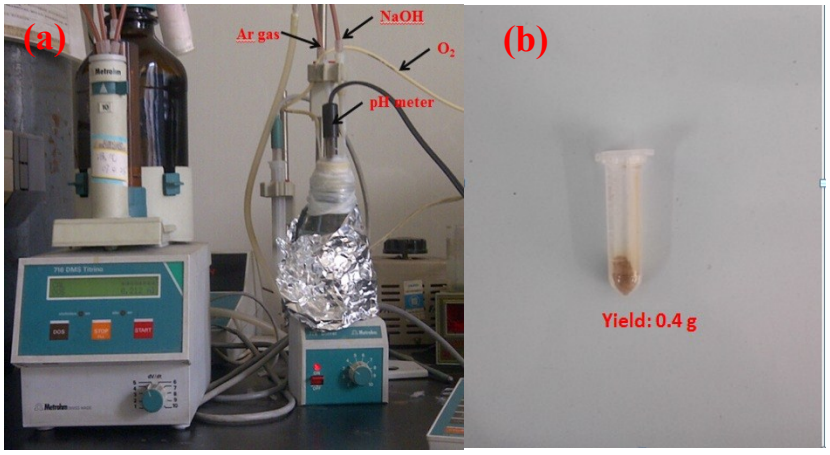
For chloride determination, ten microgram of the sample were dissolved in HCl (0.5 mL, 0.1 M), and then diluted with ethanol to 50 mL. Finally, the solution was determined by an Dionex ICS-2100 ion chromatography. For dodecanoate content analysis, the GRC12 and Fe^{III}/Fe^{III} LDH (C12) samples (10 mg) was dissolved in O_2 free HCl (5 mL, 0.1 M) in a glass vial (50 mL). The precipitated dodecanoic acid was dissolved and extracted with hexane (5 mL) on a shaking table. The dodecanoic acid was derivatized to the fatty acid methyl ester (FAME) by reaction with methanolic NaOH (6 mL, 0.5 m) in the presence of boron trifluoride/methanol complex (10 mL) as catalyst. The FAME was extracted into hexane (5 mL) and measured by using an Agilent 6890 series gas chromatograph equipped with a flame-ionization detector (GC-FID, USA) and a Zebron 7HG-G002-11 capillary column (Phenomenex Inc., USA).

S2. Comparison of one-pot synthesis method and upscale synthesis of and GR(C12) and the layered Fe^{III} nanosheets

The layered Fe^{III} nanosheets were produced via delamination of the solid-state-oxidized GR(C12) to dodecanoate intercalated Fe^{III}/Fe^{III} LDH (Fe^{III}/Fe^{III} LDH(C12)). Hence, the yield of the GR(C12) significantly influences the yield of the layered Fe^{III} nanosheets.

S2.1 One-pot synthesis of GR(C12)

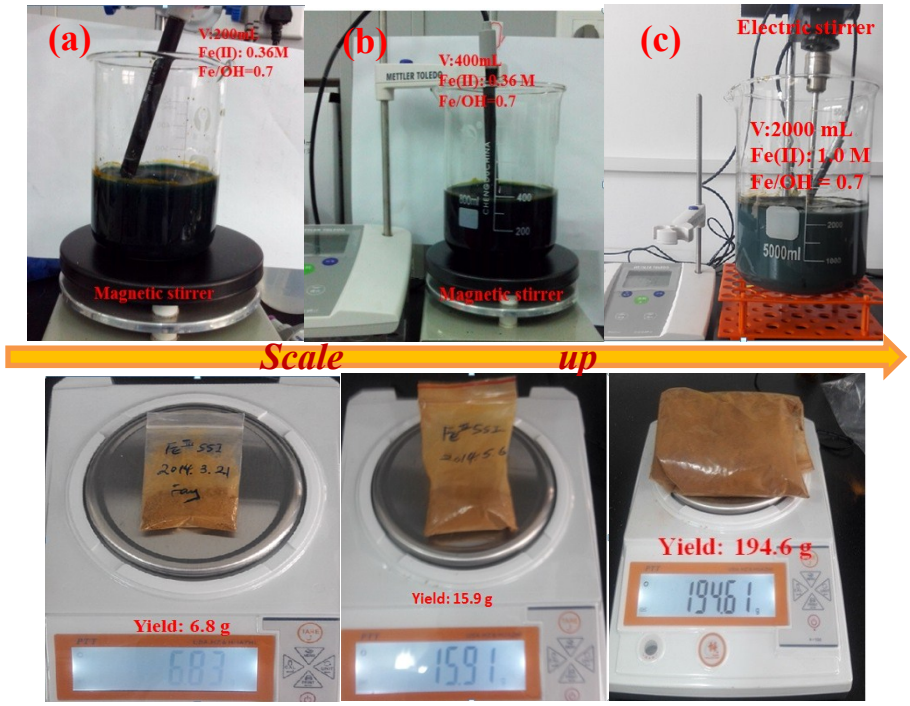
The synthesis of GR(C12) comprises the controlled partial aerial oxidation of a solution containing both aqueous Fe(II) ions and the interlayer dodecanoate ions, at constant pH of 8 and at room temperature (Scheme S1). An aliquot of 190 mL of the sodium dodecanoate solution was transferred into a 300 mL glass-infusion flask (6 cm inner diameter) fitted with a rubber septum and bubbled with Ar gas (50 ml/min) during 3 h to remove traces of oxygen. After this period the septum of the reaction flask was replaced with a rubber septum fitted with a Metrohm (Herisau, Switzerland) pH-stat system comprising an end-point titrator (716 DMS-Titrino), and a base inlet and gas in- and outlets. Around 12–15 mL of 0.5 M $FeSO_4$ stock solution were slowly transferred to the reaction flask ($[Fe^{II}]$=30 mM) and at the same time the solution was titrated with 1 M Ar-bubbled NaOH solution maintaining the pH of the solution at 8±0.1. When the pH was stable, CO2-free air was pumped into the solution using a peristaltic pump at a rate resulting in a constant rate of base consumption of around 0.04 mL/min. The reaction was stopped once when Fe^{II}/Fe^{III} reached a ratio of 2.



Scheme S1. (a) Setup of the one-pot synthesis method for GR(C12); (b) the yield of the layered Fe^{III} nanosheets.

S2.2 Upscale synthesis of GR(C12)

The detailed procedure of the upscale synthesis of GR(C12) has been clearly described in the text (section of 2.2).



Scheme S2. Demonstration of upscale synthesis of the layered Fe^{III} nanosheets by varying the initial concentration of Fe^{II} ions and the volume of the reactor.

Table S1. Comparison of one-pot and upscale syntheses of the layered Fe^{III} nanosheets

Synthesis Method	Comparison
One-pot synthesis	• Low yield: 0.4 g; • Limitation of scaling up (maximum volume 190 mL; Fe(II)=30 mM); • Containing high amounts of SO_4^{2-} within GR(C12) leading to impurity after oxidation; • $FeSO_4$ is the only choice of iron source to successfully product GR(C12).
Upscale synthesis	• High yield up to 195 g in our trials. • The synthesis can be scaled up to large reaction volume, and high initial Fe(II) ; • Starting Fe(II) salt is $FeCl_2$ which can be easily exchanged by C12 anions; • Neglect amount of impurity after oxidation.

S2. Chemical composition

Table S2. Chemical composition of GR(Cl), GR(C12), Fe^{III}/Fe^{III}(C12) and Fe^{III} nanosheets samples in this study

Sample	Fe^{II}(wt.%)	Fe^{III}(wt.%)	Fe^{II}/Fe^{III}	Dodecanoate (wt.%)	Cl(wt.%)	OH/O
GR(Cl)	39.2 ± 1.5	12.2 ± 1.3	3.2	0	8.7 ± 0.9	39.7 ± 1.4
GR(C12)	28.4 ± 0.6	8.8 ± 0.7	3.2	34.6 ± 1.1	0.1 ± 0.01	28.7 ± 0.8
Fe^{III}/Fe^{III}(C12)	0	37.2 ± 1.8	0	34.2 ± 2.4	0.1 ± 0.01	28.7 ± 2.5
Fe^{III} nanosheets	0	63.4 ± 2.5	0	<LOD	<LOD	36.6 ± 2.5

S3. **Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) measurements**

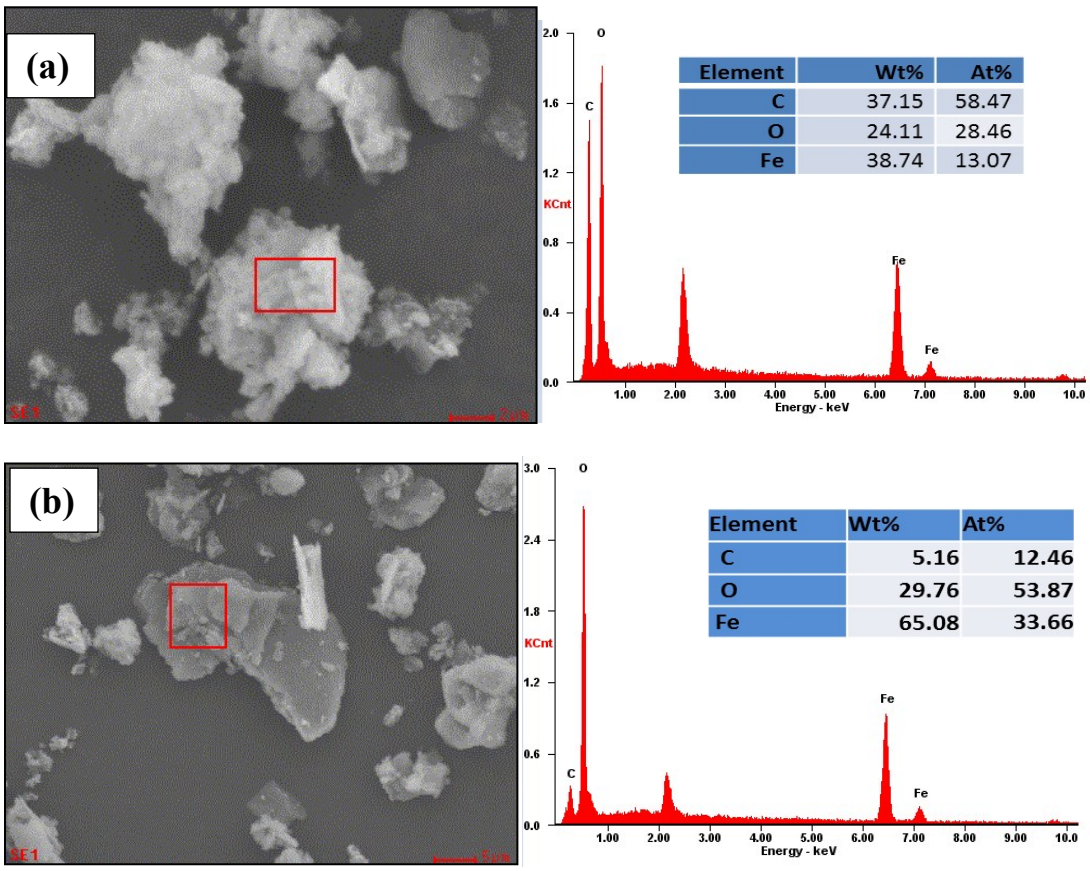


Fig. S1. SEM/EDS analyses of (a) Fe^{III}/Fe^{III} LDH (C12), (b) the layered Fe^{III} nanosheets.