Supporting Information

Formation of Lepidococite (γ-FeOOH) from Oxidation of Nanoscale Zero-Valent Iron (nZVI) in the Oxygenated Water

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Experimental Details

Materials and Chemicals.

All chemicals used in the study, e.g., $FeCl_3{\cdot}6H_2O$ (≥99%), $NaBH_4$ (≥98%), standard γ-FeOOH, are analytical grade, all obtained from Sigma-Aldrich. Chemical stock solutions are prepared using deionized water. Ultrahigh-purity N_2 (≥99.999%) is used to reduce dissolved oxygen in water.

Preparation of nZVI and oxidized nZVI.

Procedures used in the preparation of iron nanoparticles have been published previously. [1, 2] In brief, it entails slowly adding 1:1 volume ratio of 0.25 M sodium borohydride (0.25 M) into 0.045 M ferric chloride solution. The jet-black nanoparticle aggregates are collected by vacuum filtration and refrigerated in a sealed polyethylene container under 95% ethanol until use. The residual water content of the nanoparticles as used typically varies

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between 40 and 50%. Average size of the synthesized nZVI is 60 nm with 80% particles less than 100 nm.

Fully oxidized nZVI was prepared by charging 0.5 g nZVI into 100 mL deionized water in an open container and stirred at 300 rpm for 72 hours at room temperature.

Solid-Phase Characterization of fresh nZVI and oxidized nZVI.

Structural and morphological characterizations were conducted with a Hitachi HD-2700 Cs-STEM, which can simultaneously acquire secondary electron (SE), bright field (BF) and high-angle annular dark-field (HAADF) imaging as well as electron diffraction on a single nZVI particle [3,4,5]. A SE image can offer near three-dimensional characteristics of the nZVI particles while the BF mode allows imaging structures on the basis of phase contrast similar to a conventional transmission electron microscopy. High-angle annular dark-field (HAADF) imaging, which uses high-angle elastic (or phonon) scattering, enables high-spatial-resolution (0.14 nm) imaging. Complimentary examinations were also performed with XRD, XPS and Raman spectroscopy.

Samples for the STEM analysis were prepared by allowing a drop of a dilute ethanol solution of the nanoparticles on a lacey-carbon film supported on a 300-mesh copper STEM grid. More details on the Hitachi HD-2700 STEM can be found elsewhere [5]

XRD analyses were conducted using a D8 Advance X (Bruker) operated at 40 kV and 40 mA with Cu Kα. Continuous scans from 5° to 90° at 2θ were collected with a step size of 0.01° and a count time of 0.2 s per step.

X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Shimadzu Kratos Axis Ultra DLD spectrometer employing a monochromated Al K_α X-ray source (hv = 1486.6 eV), hybrid (magnetic/electrostatic) optics, and a multichannel plate and delay line detector. The binding energies (BEs) over samples were calibrated using the C1s peak at 285.0 eV. The instrument was also calibrated by using Au wire. XPS spectra were recorded at θ= 90° of X-ray source.

Raman spectra were obtained using a LabRam-1B (Jobin Yvon, France) with 632 nm He-Ne laser. Approximately 1 mW of laser irradiation was used to excite the samples. Spectra were collected over the range 4000–100 cm^{-1} and averaged over 10 scans, each with an exposure time of 10 s.

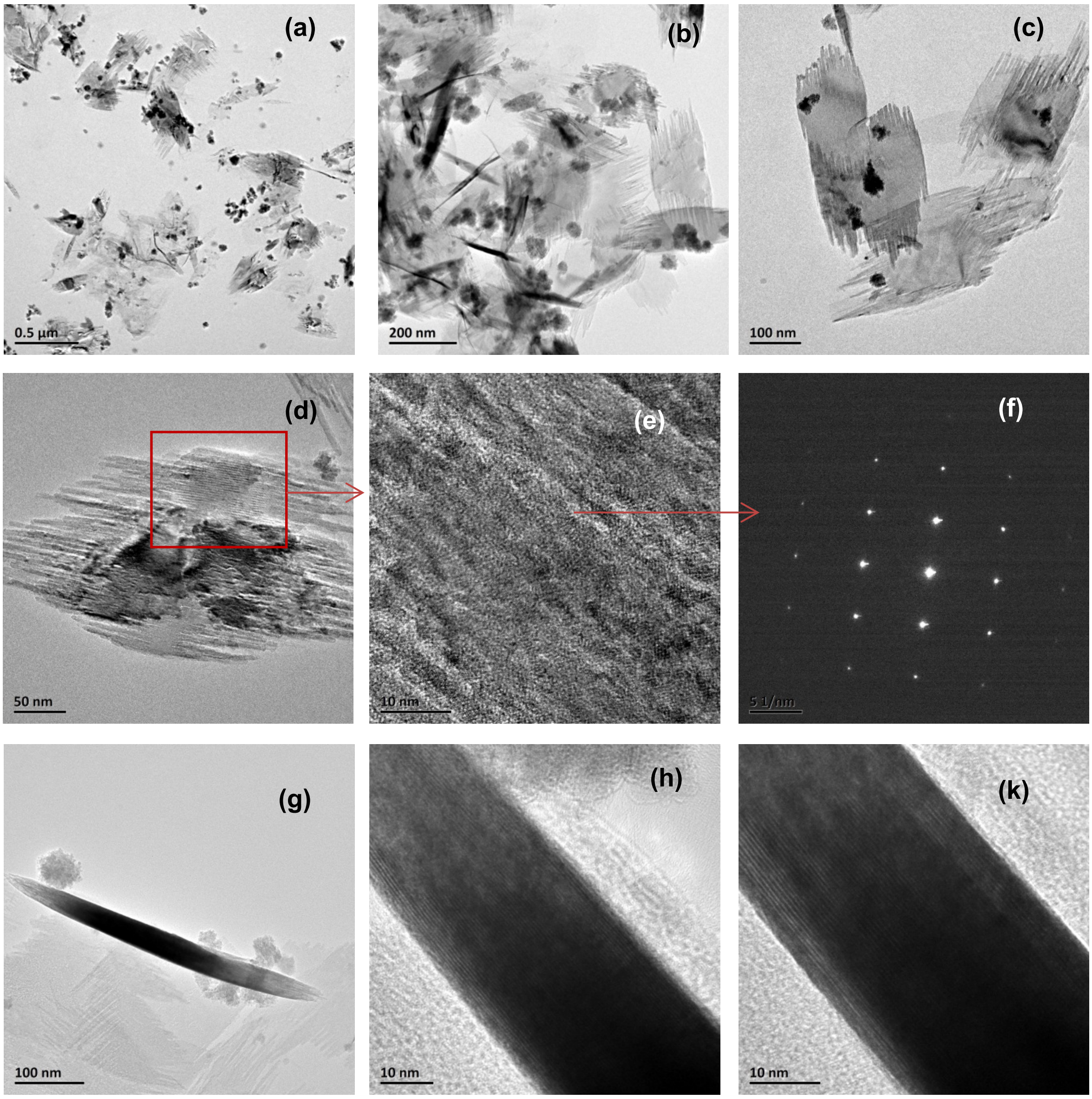

Fig. S1.BF-STEM images of 72-h-oxidized nZVI (a, b, c, d, e, g, h, k) and SAED (f) from (e) .

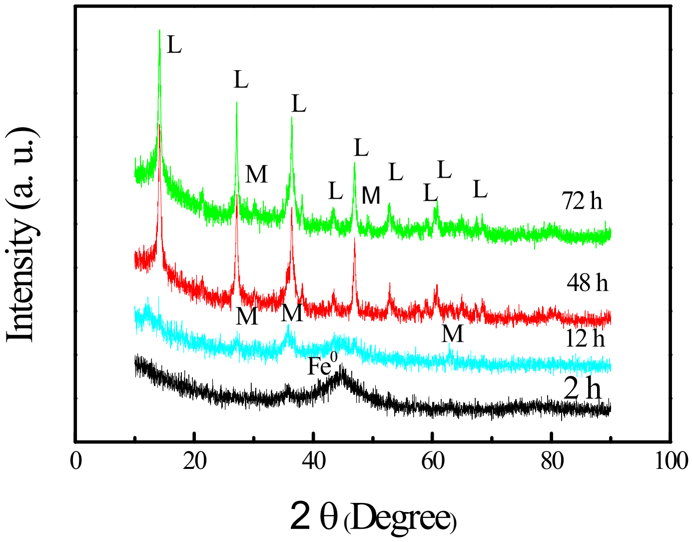

Fig. S2 XRD analysis of nZVI oxidized in oxygenated water for 2 h, 12 h, 48 h and 72 h. Peaks are referred to magnetite/maghemite (Fe_3O_4/γ-Fe_2O_3) (M), lepidocrocite (γ-FeOOH) (L), and nZVI (Fe^0).

Reference

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