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Evolution of nanoscale zero-valent iron (nZVI) in water: Microscopic and spectroscopic evidence on the formation of nano- and micro-structured iron oxides

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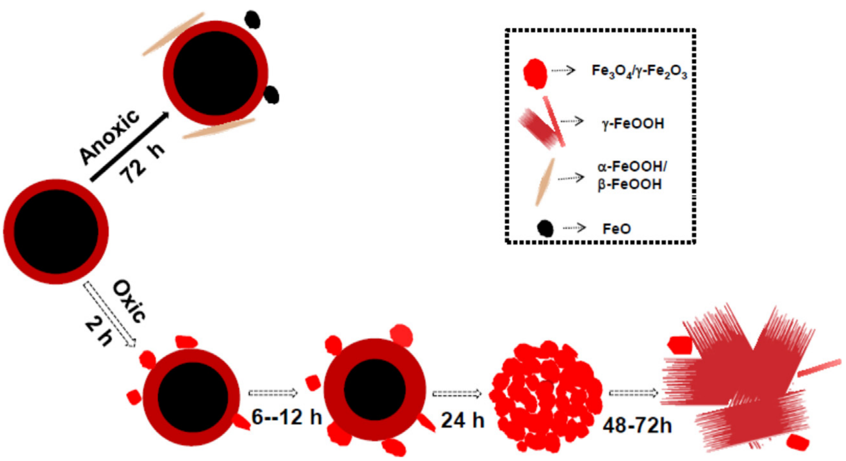
HIGHLIGHTS

- A comprehensive study of corrosion products for nZVI under both oxic and anoxic conditions is performed.
- Under anoxic conditions, the oxidation products contain a mixture of wustite (FeO), goethite (α-FeOOH) and akaganeite (β-FeOOH).
- Under oxic conditions, the final products are mainly crystalline lepidocrocite (γ-FeOOH) with acicular-shaped structures.
- Morphological and structural evolution of nZVI under both oxic and anoxic conditions are substantially different.

GRAPHICAL ABSTRACT



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ABSTRACT

Knowledge on the transformation of nanoscale zero-valent iron (nZVI) in water is essential to predict its surface chemistry including surface charge, colloidal stability and aggregation, reduction and sorption of organic contaminants, heavy metal ions and other pollutants in the environment. In this work, transmission electronic microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy are applied to study the compositional and structural evolution of nZVI under oxic and anoxic conditions. Under anoxic conditions, the core–shell structure of nZVI is well maintained even after 72 h, and the corrosion products usually contain a mixture of wustite (FeO), goethite (α-FeOOH) and akaganeite (β-FeOOH). Under oxic conditions, the core–shell structure quickly collapses to flakes or acicular-shaped structures with crystalline lepidocrocite (γ-FeOOH) as the primary end product. This work provides detailed information and fills an important knowledge gap on the physicochemical characteristics and structural evolution of engineered nanomaterials in the environment.

1. Introduction

Nanoscale zero-valent iron (nZVI) is an engineered nanomaterials widely used in environmental remediation and hazardous waste

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treatment [1–4]. nZVI has a classic core–shell structure, which consists of a metallic iron core encapsulated by a thin iron oxide shell of a few nanometers [5]. This core–shell nanomaterial with two nanoconstituents has multifaceted functions for contaminant separation and transformation. The metallic iron core serves as an electron source and exerts a reducing character, whereas the oxide shell promotes the adsorption of contaminants via electrostatic interactions and surface complexation [6].

In wastewater treatment and groundwater remediation, nZVI can partially or completely transform from metal iron (Fe^0) to nontoxic iron oxide/hydroxides commonly found in sediments and soils, resulting in significant variations in the nanoparticle structure and composition [7–10]. The iron oxidation or corrosion also varies depending on the type of irons, contaminants, solution composition and environmental conditions [11–20]. For example, an nZVI (e.g., RNIP from Toda Kogyo Corp.) produced by the hydrogen reduction of ferric oxides [13], the iron oxide shell generated by the gradual exposure to the atmosphere could inhibit further oxidation of the nZVI particles [14]. The shell-modified RNIP particles formed new iron minerals, goethite, Fe(0) and magnetite when put into water [15]. Research on the chemical transformation of nZVI in groundwater treatment suggested that the differences in groundwater chemistry such as pH, carbonate and phosphate can affect the corrosion products [16–20]. For example, in our previous study, the aging effect of nZVI nanoparticles synthesized by borohydride reduction of $FeCl_3$, was investigated over a period of 90 days in static water [21]. Similarly, nZVI was oxidized primarily to the iron oxide-hydroxide lepidocrocite under flowing aerated water [22]. Results showed that the structure, shape and composition of nZVI changed with time after exposed to water. New applications of nZVI for industrial wastewater treatment provide new challenges on the study of its aging effects [23,24]. In the reactors for industrial water treatment, the nZVI suspension is typically agitated intensely to achieve uniform dispersion in water. The corrosion products under this condition not only affect its removal capacity, but also the final state and fate of iron materials after their emplacement. Until now, comprehensive study of corrosion products for nZVI under oxic and anoxic water is limited, and is clearly needed to enhance our

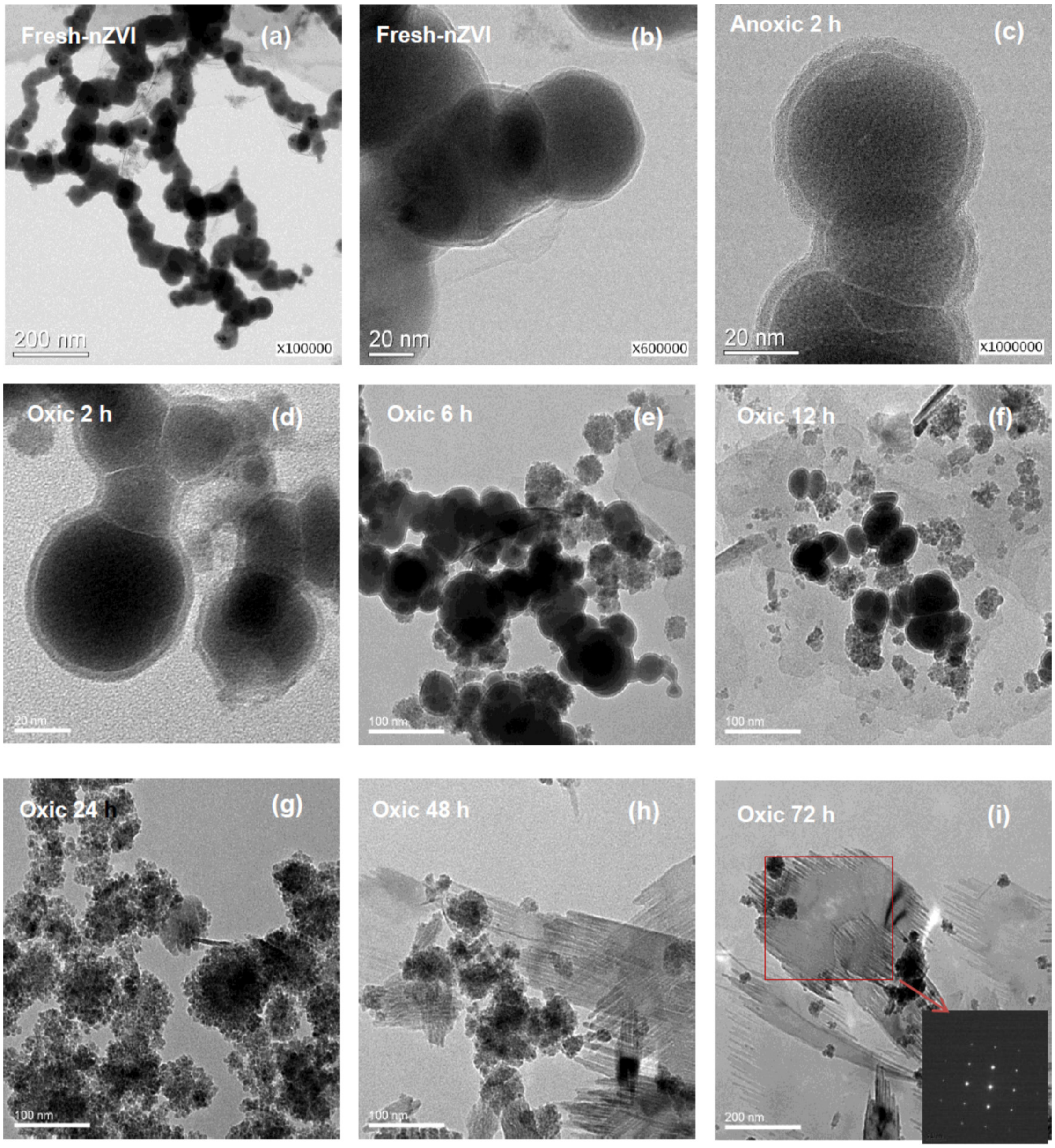

Fig. 1. TEM images of (a, b) fresh- nZVI, (c) nZVI eroded in anoxic water for 72 h, and (d–i) nZVI oxidized in oxic water over different time periods.

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