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Electrochemical synthesis of Fe_xNi_{1-x} nanostructures for environmental remediation

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ABSTRACT

Fe_xNi_{1-x} nanostructures with different compositions ($0 < x < 1.0$) were electrodeposited from simple aqueous electrolytes with different ferric ion and nickel ion ratios. Composition, morphology, crystal structure, magnetic properties and electronegativity of the synthesized Fe_xNi_{1-x} nanostructures were systematically investigated. As the composition of Fe (x) in Fe_xNi_{1-x} nanostructures decreased from 1.0 to 0, the morphology changed from dendritic to nanoparticles and thin plates. The X-ray diffraction (XRD) patterns revealed that the dominant crystal structures shifted from metallic body centered cubic (bcc) for iron-rich Fe_xNi_{1-x} to mixed bcc and faced center cubic (fcc) for near equiatomic FeNi to rhombohedral/hexagonal for nickel-rich FeNi. The magnetic saturation and isoelectric point were also strongly dependent on nanostructure composition. Specifically, the magnetic saturation decreased and the isoelectric point increased with decreasing Fe content. When Fe content in Fe_xNi_{1-x} nanostructures was greater than 0.5 ($x > 0.5$), Fe_xNi_{1-x} nanostructures showed mainly metallic (zero-valent) Fe present as determined by XRD and selected area electron diffraction (SAED) patterns. Accordingly, $Fe_{1.0}$, $Fe_{0.71}Ni_{0.29}$ and $Fe_{0.55}Ni_{0.45}$ exhibited reactivity toward 1,1,1,2-tetrachloroethane, with $Fe_{1.0}$ yielding the greatest rate of reductive dechlorination.

1. Introduction and background

Nanostructured materials having a large surface-to-volume ratio possess very different properties from their bulk counterparts and are of great interest due to their many potential applications [1–4]. Magnetic nanostructures such as iron oxide nanoparticles (i.e., magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3)) are widely used in ferrofluids for audio speakers [5], magnetic resonance imaging [6,7], magnetic storage media [8], and site-specific gene and drug delivery [9,10]. Fe_xNi_{1-x} alloys with different compositions have been also used in many industrial fields due to their diversity in magnetic properties. Permalloy (20% iron, 80% nickel), for example, has been used in magnetic recording heads [11,12] and invar (64% iron, 36% nickel) has applications in precision instruments such as shadow masks for color televisions [13]. Nickel hydroxide, on the other hand, is the main active material for cathodes in alkaline rechargeable batteries [14–16].

Extensive efforts to synthesize iron oxide and Fe_xNi_{1-x} nanostructures have been devoted not only to the above applications, but also to the development of materials for environmental remediation [2,17–23]. Nanoscale iron oxides such as magnetite and maghemite have been used as adsorbents to remove arsenic from water [2,17]. Nanoscale zero-valent Fe, Pd/Fe, and Ni/Fe particles have also been studied and synthesized for environmental remediation of toxic compounds including chlorinated compounds, organic dyes, and heavy metals [18–23]. The bimetallic nanoparticles, such as Pd/Fe and Ni/Fe particles, have been observed to have around 1–3 orders of magnitude higher rate of chlorinated hydrocarbon degradation relative to microscale commercial Fe particles, due to their higher surface area-to-volume ratio and the catalytic nature of the metal additives to Fe [19,21].

Various wet chemical methods have been employed to synthesize nanoscale iron oxides, nickel oxides, metallic Fe, metallic Ni, and bimetallic Ni/Fe particles [24]. For the synthesis of nanoscale iron oxides, chemical precipitation [25,26], hydrothermal [27], thermolysis [28,29], and electrodeposition [2,30] were successfully used. However, nanoscale metallic Fe (zero-valent iron) previously used for environmental remediation have mostly been synthesized by the chemical reduction method from ferric or ferrous solutions in the presence of sodium borohydride with subsequent galvanic displacement of less noble metallic iron nanoparticles with more noble metals (e.g., Ni, Pd) to generate bimetallic nanoparticles (e.g., Ni/Fe and Pd/Fe) [18–23].

Compared to other wet chemical methods, electrodeposition is simple, fast, inexpensive, and manufacturable and can be an

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excellent alternative method of synthesizing nanoscale materials, such as nanowires [31–33], nanotubes [34], and nanoparticles [2,30]. In our prior work, it was demonstrated that the particle size, shape, and production rate of crystalline maghemite (γ-Fe_2O_3) nanoparticles were effectively controlled by adjusting the electrodeposition conditions [2]. Additionally, monodisperse crystalline zero-valent iron, FeNi, and FePd nanowires could be synthesized using template-directed electrodeposition method [33].

In this work, Fe_xNi_{1-x} nanostructures were electrodeposited as a function of Fe^{3+} and Ni^{2+} concentration in solution to investigate the capacity of this method to generate reactive Fe_xNi_{1-x} alloy nanostructures with controlled composition. Hence, the composition, morphology, crystal structure, magnetic properties, and electronegativity of electrochemically synthesized Fe_xNi_{1-x} nanostructures were measured, and the potential of these Fe_xNi_{1-x} nanostructures for environmental remediation of a model chlorinated hydrocarbon was examined.

2. Materials and methods

2.1. Chemicals

Chemicals used in this study were $FeCl_3$ (Fisher, ACS reagent grade), $NiCl_2{\cdot}6H_2O$ (Fisher, ACS reagent grade), 1,1,1,2-Tetrachloroethane (1,1,1,2-TeCA, 99%, Aldrich), and hexane (99%, Aldrich). The buffer solution of 25 mM Tris (tris(hydroxymethyl)-aminomethane, 99%, Sigma) in 0.1 M NaCl (99%, Sigma–Aldrich) used for reactivity studies was prepared using deionized water (Milli-Q Plus UV, Millipore) and was deoxygenated by purging with high purity N_2 gas (99.99%) for more than one and half hours.

2.2. Electrochemical synthesis and characterization

Fe_xNi_{1-x} nanostructures were electrochemically synthesized from six different electrolytes by varying the iron/nickel ion ratios in solution which is at a fixed total metal ions concentration of 0.01 M. The solution chemistry was varied according to $[Fe^{3+}]/([Fe^{3+}]+[Ni^{2+}])$ ratios: 0, 0.1, 0.25, 0.5, 0.75, and 1.0, which is shown in Table 1. The pH of the solution was adjusted to 2.0 with HCl or NaOH. A 100 mL glass jar with water jacket at 20 °C was used with a working volume of 50 mL. Steel (Kocour, Chicago, IL) and platinum-coated titanium (Technic Inc., Anaheim, CA) sheets were used as cathode and anode, respectively. The surface area of both electrodes was fixed at 4 cm^2. Electrodeposition of Fe_xNi_{1-x} nanostructures was conducted in galvanostatic mode with a fixed current density of 1 A/cm^2 using a power supply (Hewlett-Packard, 6655A, Houston, TX). The deposition time was fixed at 2 min. As the deposition was initiated, the potential began from approximately 80 V and gradually decreased to 50 V. The resulting nanostructures were washed three times with ultrapure water by centrifugation at 10,000 × g for 10 min and then vacuum-dried at 60 °C overnight. Dried samples were immediately used for the characterization. For reactivity test, dried samples were stored in an anaerobic chamber until used.

The composition of nanostructures was determined using an atomic absorption spectrometer (AAnalyst 800, PerkinElmer, Waltham, MA). The morphology of Fe_xNi_{1-x} was characterized by transmission electron microscopy (TEM) in a FEI-PHILIPS CM300 electron microscope (Hillsboro, OR) operated at 200 kV. The samples were prepared by placing a drop of a diluted suspension of each sample in ultrapure water onto a carbon coated copper grid and allowing water to evaporate at room temperature.

The crystalline structure of Fe_xNi_{1-x} was determined by X-ray diffraction using a D8 Advanced diffractometer (Bruker, Madison, WI) with Cu Kα radiation (λ = 0.154 nm). The surface area was measured by Brunauer–Emmett–Teller (BET) N_2 method (ASAP 2010, Micromeritics, Norcross, GA). Electrophoretic mobility was measured using a ZetaPALS (Brookhaven Instruments Corporation, Holtsville, NY) to get the isoeletric point (IEP), which was conducted at ionic strength of 1 mM KCl (Fisher, ACS reagent grade) from approximately pH 4 to 12. The magnetic properties, such as magnetic saturation (M_S) and coercivity (H_C), were measured using a vibrating sample magnetometer (VSM, ADE Tech, Model 1660, Westwood, MA) at room temperature with applied magnetic field up to ±10 kOe.

Table 1
Solution chemistry used for electrodeposition.

$[Fe^{3+}]/[Fe^{3+}]+[Ni^{2+}]$	Fe^{3+}, M	Ni^{2+}, M
1.0	0.01	0
0.75	0.75	0.25
0.5	0.5	0.5
0.25	0.25	0.75
0.1	0.1	0.9
0	0	0.01

2.3. Reactivity experiments

Reactivity experiments were conducted with three types of the Fe_xNi_{1-x} nanostructures to explore their capacity to reduce a model chlorinated solvent. All reactivity tests were carried out in vials (20 mL, nominal volume) that were free of headspace and sealed with Teflon-faced butyl rubber septa (Wheaton, Millville, NJ). Within an anaerobic chamber, synthesized Fe_xNi_{1-x} nanostructures were weighed into vials that were then filled with deoxygenated buffer solution. Each vial contained 0.1 M NaCl/25 mM Tris buffer (pH 7.0) and a Fe_xNi_{1-x} nanostructure loading of 1.0 g/L. After assembly, vials were removed from the anaerobic chamber and reactivity experiments were conducted immediately. To initiate the reaction, 36 μL of a solution of 55.56 mM 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA) in methanol was added to the sealed vial via a 100 μL syringe, resulting in a final concentration of 100 μM (16.8 mg/L). Control vials free of any Fe_xNi_{1-x} nanostructures were also conducted, and used to determine the initial concentration of 1,1,1,2-TeCA in the experimental reactors. The vials were mixed on a rotary shaker (Cole-Parmer, Model 7637-01) at 45 rpm at room temperature.

At each sampling time, 200 μL was removed from the reactor by simultaneously adding an equivalent volume of deoxygenated buffer so as to prevent the development of headspace over time. Aqueous samples were extracted using 2 mL of hexane, followed by subsequent dilutions in hexane. Diluted extracts were analyzed via a 7890A Gas Chromatograph (Agilent Tech., Santo Clara, CA) with electron capture detection (ECD) and a RTX-1 column (30 m × 0.32 mm i.d. × 5 μm film thickness, Restek, Bellefonte, PA). Standards for these analyses were prepared in hexane and were analyzed in an identical manner to the experimental samples.

3. Results and discussion

3.1. Electrochemical synthesis and characterization

As electrodeposition was initiated, gas evolution occurred at both electrodes and powdered black deposits were formed on the cathode. After a reaction time of 2 min, solution pH remained nearly constant at pH 2.0 ± 0.1. Hydrogen gas bubbled up at the steel cathode, while oxygen gas was produced at the platinum coated titanium anode, resulting in constant solution pH during the electrodeposition. The dependence of resulting deposited Fe content on the ratios of $[Fe^{3+}]$ to $([Fe^{3+}]+[Ni^{2+}])$ in electrolytes is presented in Fig. 1. Since the atomic absorption spectrometer can not detect oxygen (O) and hydrogen (H) content in Fe_xNi_{1-x}, the Fe content at