Electrochemically fabricated zero-valent iron, iron-nickel, and iron-palladium nanowires for environmental remediation applications

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Abstract Monodisperse crystalline zero-valent iron, iron-nickel, iron-palladium nanowires were synthesised using template-directed electrodeposition methods. Prior to nanowire fabrication, alumina nanotemplates with controlled pore structure (e.g. pore diameter and porosity) were fabricated by anodising high purity aluminium foil in sulphuric acid. After fabrication of alumina nanotemplates, iron, iron-nickel and iron-palladium nanowires were electrodeposited within the pore structure. The dimensions of nanowires including diameter and length were precisely controlled by pore diameter of anodised alumina and deposition rate and time. The composition, crystal structure and orientation were controlled by adjusting electrodeposition parameters including applied current density and solution compositions.

Keywords Alumina nanotemplate; electrodeposition; iron-nickel alloy; iron-palladium; nanowires; zero-valent iron

Introduction

Nanostructures represent a new generation of environmental remediation technologies that could provide a novel and cost-effective solution to some of the most challenging environmental remediation problems (Zhang, 2003; Obare and Meyer, 2004). They offer several advantages over bulk materials. For example, the higher surface-area-to-volume ratio can lead to enhanced reactivity with environmental contaminants that degrade through an adsorption mechanism. The electrical and optoelectrical properties (e.g. bandgap) of semiconducting nanostructures can be tuned by controlling the dimensions of nanostructures (e.g. diameter and length), which is important for photocatalytically environmental remediation. In addition, the surface of nanostructures can be readily modified toward specific environmental remediation application.

Zero-valent iron nanoparticles are very effective for the transformation and detoxification of a wide variety of contaminants, such as arsenic (Kanel et al., 2005), hexavalent chromium (Ponder et al., 2000), chlorinated organic solvents (Schrick et al., 2004) and nitroaromatic compounds (NACS) (Choe et al., 2001).

A common method for synthesis of iron nanoparticles is by reduction of aqueous ferric solutions by reducing agents such as sodium borohydride or sodium hypophosphite (Obare and Meyer, 2004). This approach is a high yield method to synthesise iron nanoparticles; however, the monodispersity is poor. In addition, purity of iron nanoparticles can be poor because of boron, oxide and hydroxide incorporated during synthesis which can lead to amorphous iron nanoparticles with decreased reactivity. Amorphous iron nanoparticles (diameter of approximately 10 nm) were fabricated by sonicate iron pentacarbonyl under argon environment (Suslick et al., 1991; Kataby et al., 1998). Chemical vapour deposition (CVD) has also been employed to synthesise iron nanoparticles (Zaera, 1989).
Electrodeposition is an alternative method of fabricating nanoengineered materials. Comparable to chemical reduction, sonochemistry and CVD, electrodeposition is a cost-effective and manufacturable fabrication technique with the ability to “tailor” composition and properties of materials.

In this paper, we demonstrated the electrodeposition of high purity crystalline zero-valent iron nanowires where the dimensions of iron nanowires were precisely controlled by pore size of alumina nanotemplate and applied current density and time. In addition, we developed new plating solutions to electrodeposit FeNi and FePd nanowires. FeNi and FePd nanowires were fabricated because recent studies show that palladium and nickel can further enhance the speed and efficiency of remediation (Muftikian et al., 1995; Schrick et al., 2002). The crystal structure and orientation were controlled by adjusting electrodeposition parameters including applied current density and solution compositions.

**Fabrication of alumina nanotemplate**

Alumina nanotemplate is a key material for fabrication of nanostructures, because it can provide large-area, nanometre-sized pore structures with high aspect ratios in a cost-effective and reliable manner. Alumina templates were fabricated by anodising high purity aluminium (99.99%) in acidic media such as phosphoric, oxalic and sulphuric acid (Diggle et al., 1969; O’Sullivan and Wood, 1970; Brace, 2000). Under proper experimental conditions, the nanoporous structure of anodised alumina resembles a highly ordered honeycomb pattern of closely packed hexagonal nanosize cells with an individual pore located in the centre of each cell. A significant advantage of porous anodic alumina templates is their tailorable dimensions (Diggle et al., 1969; O’Sullivan and Wood, 1970; Brace, 2000).

Based on our previous work (Myung et al., 2004), alumina nanotemplates were synthesised from high purity aluminum foil (alloy # 1047) anodised in sulphuric acid. Two different concentrations of sulphuric acid (i.e. 1.8 and 3.25 M) were selected as electrolytes to produce small pore structures of 20 and 30 nm pore diameters, respectively. Pore diameter is a function of applied voltage; therefore, prior to anodisation, the relationship between applied current density and voltage was examined (Figure 1).

In the aluminium anodising process, the voltage initially increased rapidly as the applied current density increased, but became saturated at higher current densities. Current density was more sensitive to voltage changes at higher current density; therefore a galvanostatic...
condition (i.e. constant current mode) was selected as the more stable anodisation process. The measured voltage at the same current density was decreased when the concentration of sulphuric acid was increased. The difference in voltage due to different acid concentrations could be related to the ion concentration in the electrolyte which directly affects polarisation resistance and electrolyte resistance. Anodisation was performed at a current density of 100 mA/cm² and constant temperature of 20°C by using a recirculating water chiller. After anodisation at 1.8 M sulphuric acid for 45 min, the resulting thickness of anodised alumina was measured to be approximately 40 micron. In order to fabricate free-standing alumina nanotemplates, the remaining aluminium was removed with 0.1 M CuCl₂ + 20 V% HCl etching solution, and finally, a pore-widening process was performed to remove the alumina barrier layer at the bottom face of the template with 0.3 M H₃PO₄ solution for 30 min. Figure 2 shows SEM images of an alumina template after the pore-widening procedure where the final pore size was approximately 30 nm with a porosity of 15%. As shown in Figure 2(B), pores were vertically straight and parallel to each other.

**Electrodeposition of zero-valent iron and iron-nickel thin films and nanowires**

Iron and iron-nickel by electrodeposition have been extensively researched with various kinds of electrolytes, including chloride (Grimmett *et al.*, 1988; Myung and Nobe, 2001), sulphate (Grimmett *et al.*, 1988; Sasaki and Talbot, 1995) and sulphamate (Grimmett *et al.*, 1988, 1990) baths, due to its unique magnetic properties such as low coercivity and low magnetostriction. Most of these studies focus on electrodeposition of iron-nickel at a pH range of 2–4, since at such pH levels the current efficiency is better than that at lower pH values; however, oxidation of iron has proved a problem, therefore a strong oxidation reducer such as L-ascorbic acid has frequently been added to the electrolyte solutions.

In this work, zero-valent iron and iron-nickel thin films and nanowires were electrodeposited from highly acidic chloride baths to efficiently prevent the oxidation of ferrous ions in the electrolyte. Bath compositions consisted of 0–1.5 M FeCl₂ + 0–1.5 M NiCl₂ + 1.0 M CaCl₂ + 0.005 M L-ascorbic acid. The ratio of iron to nickel (Fe²⁺/Ni²⁺) metal ion concentration varied from 0 to 1.5 M, while maintaining a fixed total metal ion concentration of 1.5 M. To prevent oxidation of ferrous to ferric ions, 0.05 M of L-ascorbic acid was added to the deposition bath and solution pH was maintained at 0.3 by the addition of HCl or NaOH; nickel chloride and ferrous chloride were added to electrolyte as metal salts. Compositional and structural variation of electrodeposits with deposition conditions was investigated with thin film deposits. Experiments were performed under galvanostatic mode, at 70°C, with an applied current density of 10 mA/cm² and no agitation. The effects of current density on deposits was performed at 70°C with no agitation where current density was varied from 5 to 20 mA/cm².

![Figure 2](image-url)
Different film compositions of FeNi thin films were acquired by varying the ratio of metal ion concentrations of the bath with fixed current density (10 mA/cm²). Figure 3 shows the variation of the Fe content in deposits with different ratios of metal ion concentrations. As shown in the figure, when the concentration of Fe²⁺ was increased from a pure Ni bath ([Fe²⁺] = 0) to [Fe²⁺]/([Fe²⁺]+[Ni²⁺]) = 0.8, deposit Fe content slightly increased to 20 at.%, and abruptly jumped to 82.8% when Fe²⁺/(Fe²⁺+Ni²⁺) = 0.87. This result was unexpected, because electrodeposition of FeNi alloy is well-known with its anomalous deposition characteristics (Brenner, 1963), which means preferred deposition of Fe compared to Ni, even though the reduction potential of Fe is more negative than that of Ni, when they deposit as an alloy. Unlike other results (Hessami and Tobias, 1989; Gangasingh and Talbot, 1991; Krause et al., 1997; Schlesinger and Paunovic, 2000), deposit Fe content was quite low until [Fe²⁺]/([Fe²⁺]+[Ni²⁺]) approached 0.8. This discrepancy might come from the difference of electrolyte pH. According to the proposed model (Gangasingh and Talbot, 1991), the formation of FeOH and NiOH near the cathode has a critical role in the occurrence of anomalous deposition phenomena. Fe and Ni hydroxides can be easily formed by hydrolysis when operating at a pH range of 2.5–4 (Schlesinger and Paunovic, 2000); however, the FeNi baths used in this work were highly acidic with pH as low as 0.3 in order to prevent generation of hydroxide, and therefore suppressing anomalous characteristics. The effect of current density on compositions of FeNi deposits from baths with Fe²⁺/(Fe²⁺+Ni²⁺) = 0.2 and 0.6 are represented in Figure 4. Deposit Fe content linearly increased as current density changed from 5 to 20 mA/cm². The larger Fe content at higher current density could be caused by a more negative reduction potential of Fe.

Microstructures of FeNi thin films were investigated by x-ray diffraction (XRD) where Figure 5 shows the XRD results of FeNi thin films deposited at 10 mA/cm² and different bath compositions. At metal ion concentrations of 0.3 M Fe and 1.2 M Ni, only face centred cubic (FCC) structures were observed, where FCC(111) and FCC(220) show similar high intensities. As [Fe³⁺] concentration increased, the intensity of FCC(200), (220) and (311) decreased gradually; however, intensity of FCC(111) did not change. Instead, FCC(111) changed to body centred cubic (BCC(110)) at a composition of 0.2 M Ni + 1.3 M Fe. The sudden change in crystal structure is probably due to the similarity in lattice parameter of FCC(111) and BCC(110).

![Figure 3](image-url) **Figure 3** Dependence of deposit Fe content on the ratio of Fe²⁺/(Fe²⁺+Ni²⁺) in electrolytes. The electrodeposition was performed in acid chloride baths at 70°C without agitation.
Fe and FeNi nanowires were fabricated by template-directed electrochemical deposition on anodised alumina templates. Alumina templates with average pore diameters of 200 nm were purchased from Whatman, Inc., whereas alumina nanotemplates with pore diameters of 30 nm were fabricated in-house as previously described. Cu thin films were deposited as a seed layer on one side of the template by sputtering method. Fe and FeNi alloy nanowires were grown through the pores in the template under the same deposition conditions as the thin film process mentioned above. After nanowires’ growth, seed layers and template were removed with 50 mM FeCl$_2$ $+$ 30% HCl and 5 M NaOH, respectively. Finally, the nanowires were suspended in 1 mL of isopropyl alcohol.

Morphologies of resulting suspended nanowires were investigated with scanning electron microscopy (SEM) where their composition was measured using energy dispersive spectroscopy (EDS). Figure 6(A) shows the SEM images of randomly distributed FeNi nanowires. The inset image clearly shows the diameter of FeNi nanowires to be 30 nm. Even though the same deposition condition for depositing thin films of 20Fe80Ni was adopted, composition of nanowire was of lower Fe content, 10Fe90Ni from EDS analysis.

![Figure 4](image.png) Dependence of deposit Fe content on the applied current density

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![Figure 5](image.png) XRD analysis of FeNi alloy deposits from various bath compositions: A, 1.2 M Ni $+$ 0.3 M Fe; B, 0.9 M Ni $+$ 0.6 M Fe; C, 0.3 M Ni $+$ 1.2 M Fe; D, 0.2 M Ni $+$ 1.3 M Fe
Such a compositional discrepancy might be due to the difference of local metal ion concentration at the cathode surfaces. Owing to high aspect ratio (>1,300:1) of pores in the template, the mass transfer phenomena at the bottom of pores could be different from that of thin film surface.

**Electrodeposition of iron-palladium thin films and nanowires**

FePd was mainly studied as an alternative material of high coercivity, rarely studied with electrodeposition. Standard reduction potential of Pd$^{2+}$ is 0.915 V, which is more positive than that of Fe$^{2+}$ ($E^0 = -0.447$ V); therefore it is difficult to co-deposit Fe and Pd in the ionic state from the same electrolyte. Amine was added as a complexer in order to reduce the difference in reduction potentials of the two ions by reducing the standard redox potential of Pd ions (Schlesinger and Paunovic, 2000).

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Pd(NH_3)_2^{2+}(aq) + 2e^- \rightarrow Pd(s) + 4NH_3, \quad E^0 = 0.0 \text{ V}
\]

Furthermore, FePd thin films were electrodeposited from an ammonium citrate complex bath and the effect of current density on composition and material properties was systematically analysed. The electrolyte composition consists of 0.002 M PdCl$_2$ +0.018 M FeCl$_2$·4H$_2$O + 0.2 M citric acid-diammonium, where the pH was kept constant at 9 by adjusting with HCl or NH$_4$OH. FePd thin films were electrodeposited galvanostatically on to gold sputtered Si wafers with surface areas of 2.0 cm$^2$. Inert platinum-coated titanium electrodes were used as insoluble anodes. All experiments were performed at room temperature, with agitation at 200 rpm, using an EG&G Princeton Applied Research Potention/Galvanostat, model 173. The current density was varied from 1 to 25 mA cm$^{-2}$. Composition of the thin films was determined by using an Atomic Absorption Spectrometer (AAnalyst 800, Perkin Elmer Instruments).

To study the effects of current density on thin film composition, FePd thin films were deposited at current densities of 1, 2.5, 5, 10 and 25 mA cm$^{-2}$. Figure 7 shows the dependence of deposit palladium content (wt. %) in the electrodeposits as a function of current density. Deposit palladium content decreased from ~90 wt. % to ~37 wt. % when increasing the current density from 1 mA cm$^{-2}$ to 10 mA cm$^{-2}$; however, at higher current densities palladium content increased from ~37 wt. % to ~45 wt. % as the current density was increased from 10 mA cm$^{-2}$ to 25 mA cm$^{-2}$. Juzikis et al. electrodeposited, under pulse plating conditions, FePd thin films from different sulphate baths and studied the effects of current density on deposits. The range studied was 3–30 mA cm$^{-2}$, and they found that palladium content decreased from ~70 wt. % to ~30 wt. % with an increase in current density from ~5 to ~12 mA cm$^{-2}$, then the palladium content increased with increased current density, showing that the general relationship between palladium content and current density is in agreement (Juzikis et al., 1994).

![Figure 6(B)](image_url)

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**Figure 6** SEM image and EDS result of 30 nm FeNi nanowires
Based on thin film studies, nanowires were electrodeposited. Nanowires were deposited galvanostatically with the template as a cathode and a platinum-coated titanium sheet as the anode using a multichannel EG&G PAR VMP2 potentiogalvanostat. Experiments were performed under the same conditions as thin film experiments with an applied current density of 2.5 mA cm$^{-2}$ and deposited for 15 h. Figure 8(A) shows an SEM image of FePd nanowires with diameters of 200 nm and average lengths of 9 μm. The diameter of FePd nanowires was uniform with a slight variation of length. EDS analysis shows the composition of nanowire of 14 wt% Fe with 86 wt% of Pd (Figure 8(B)).

**Conclusions**

Zero-valent iron, iron-nickel, iron-palladium thin films and nanowires were electrodeposited from aqueous electrolyte using template-directed electrodeposition methods. Alumina nanotemplates were prepared for synthesis of nanowires. Anodisation was performed in sulphuric acid, resulting in pore size as ~30 nm with 40 micron long. Prior to electrodeposition of nanowires, thin films of iron, iron-nickel, iron-palladium were electrodeposited to characterise the composition and microstructures. Composition of iron-nickel alloys varied slowly when concentration of iron was low, but abruptly increased at Fe$^{2+}$/(Fe$^{2+}$ + Ni$^{2+}$) = 0.8. As deposited iron content in iron-nickel alloys increased, FCC dominant structures changed to BCC structures. Thin films and nanowires of iron-palladium alloys were also obtained with electrodeposition from citrate-ammonium complex bath. Composition of iron-palladium nanowires was verified with EDS, which was 14Fe86Pd.
Acknowledgements

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References


