



Atomic layer deposition of iron(III) oxide on zirconia nanoparticles in a fluidized bed reactor using ferrocene and oxygen

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ABSTRACT

Conformal films of amorphous iron(III) oxide and α -Fe₂O₃ have been coated on zirconia nanoparticles (26 nm) in a fluidized bed reactor by atomic layer deposition. Ferrocene and oxygen were alternately dosed into the reactor at temperatures between 367 °C and 534 °C. Self-limiting chemistry was observed via *in situ* mass spectrometry, and by means of induced coupled plasma-atomic emission spectroscopy analysis. Film conformality and uniformity were verified by high resolution transmission electron microscopy, and the growth rate was determined to be 0.15 Å per cycle. Energy dispersive spectroscopy, X-ray diffractometry, and X-ray photoelectron spectroscopy were utilized as a means to determine film composition at each deposition temperature. Over all of the deposition temperatures investigated, films were deposited as amorphous iron(III) oxide. However, after heat treatment at 850 °C in air and N₂ atmospheres, α -Fe₂O₃ was the predominant species.

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1. Introduction

Iron(III) oxide thin films have received significant attention in recent years due to their potential for use in catalytic, optical, electrical and magnetic applications. Iron oxide based Fisher–Tropsch synthesis catalysts, along with cobalt oxide based catalysts, are used industrially to convert synthesis gas to liquids with low H₂/CO ratios and have low CH₄ selectivities [1,2]. Fe₂O₃ is used extensively to catalyze the dehydrogenation of ethylbenzene for styrene synthesis due to the intermediate adsorption strength of Fe³⁺ for ethylbenzene and styrene [3–6]. Iron(III) oxide has a high propensity to transmit visible light while absorbing light in the infrared range, and as such can be used as a solar filter on windows to reduce radiative heat transfer [7,8]. The band gap of iron (III) oxide is 2.0 eV, which allows for the capability of absorbing 38% of the solar spectrum. Relative to TiO₂, which typically only absorbs the ultraviolet portion of the solar spectrum (~5%) it is well suited to help improve the efficiency of photoelectrochemical hydrogen production [9,10]. Additionally, there has been recent extensive research involving iron oxide nanoparticle synthesis, as the nanosized features exhibit different properties than the bulk material and have been used for several important magnetic applications [11–

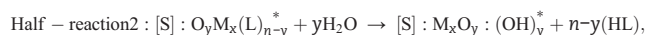
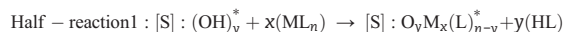
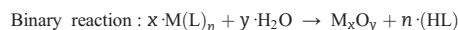
13]. The properties of iron (III) oxide thin films are highly dependent on thickness, morphology and chemical composition, and therefore it is advantageous to have precise control of these properties.

Currently, there are several methods employed for iron oxide thin film deposition, including chemical vapor deposition (CVD), sputtering, arc-plasma spray deposition, and various wet chemistry methods such as sol–gel deposition [7,13–17]. However, there are disadvantages to these methods that limit their ability to precisely control film thickness, morphology and chemical composition. For example, sol–gel methods have the capability to deposit films as thin as 100 nm, but it can be difficult to control its chemical state, and many times films are not uniform and conformal [16–18]. Sputtering is able to deposit thinner films than those of wet chemistry methods, however due to the continuous bombardment of highly energetic species onto the film, the equilibrium state of the deposited oxide is very difficult to control [15,16]. Perhaps the most common technique for iron oxide thin film deposition is CVD. This process involves vapor phase precursors reacting within a deposition chamber on a substrate surface, and as a result there are no geometrical limitations [19]. However, film thickness is difficult to control because this process is not self-limiting, resulting in films that are generally micron-sized or thicker [20]. Films are typically non-conformal and granular due to the fact that excess vapor phase reactants may nucleate and precipitate on the substrate surface. Additionally, film stoichiometry is difficult to control, as the amount of precursor delivered into the deposition chamber is dependent on its vapor pressure [21].

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Atomic layer deposition (ALD) is a self-limiting technique that is capable of depositing highly conformal films one molecular layer at a time [22–25]. Deposition is based upon the principle of splitting a binary reaction (typical of CVD) into two half-reactions and alternating the exposure of gas phase precursors of each half-reaction to a surface, as shown below:



where M represents the metal species, n is the number of ligands (L), $x:y$ is the metal to oxide ratio, [S] represents a surface site, and * represents an active surface species [26]. Operating conditions are controlled in such a way that the precursors of one half-reaction react only with the precursors of the other. This ensures atomic level control, since there is at most one sub-monolayer of added species per half-reaction [27].

Iron oxide ALD has been demonstrated on a wide array of crystalline surfaces using $\text{Fe}(\text{thd})_3$ and $\text{Fe}(\text{acac})_3$ as precursors [28,29]. Recently, $\text{Fe}(\text{C}_5\text{H}_5)_2$ (ferrocene) and oxygen have been used to deposit iron oxide films onto Si(100) and anodic aluminum [30]. The growth rates on Si(100) and anodic aluminum were 0.14 nm and 0.06 nm per cycle, respectively. At deposition temperatures below 500 °C a mixture of hematite and an unidentified phase was present. In this work, ALD of iron oxide on zirconia nanoparticles using ferrocene and oxygen is investigated. Films are deposited in a fluidized bed reactor (FBR) at temperatures ranging from 367 °C to 534 °C. They are shown to be highly conformal and uniform and can be controlled with angstrom level precision. As-deposited, the films are amorphous iron(III) oxide, but with heat treatment can be crystallized into $\alpha\text{-Fe}_2\text{O}_3$.

2. Experimental details

2.1. Material preparation

A schematic representation of the FBR is shown in Fig. 1. The reactor is 3.5 cm in diameter and includes a porous stainless steel (SS)

distributor plate and filter at the inlet and outlet, respectively. These are used to prevent particles from leaving the reactor, while allowing gas to pass through freely. The details of this reactor configuration have been described elsewhere [26]. Product gases were measured using a Stanford Research Systems QMS series mass spectrometer.

Fluidization was accomplished at reduced pressure in conjunction with a mechanical vibration platform, as shown in Fig. 1. Mechanical vibration has been shown to aid in overcoming interparticle forces present between nanoparticles, resulting in smaller aggregate sizes and a decreased minimum fluidization velocity [30]. The pressure drop across the bed was measured as a function of gas flow rate in order to maintain fluidization throughout the ALD cycle.

The ALD cycle consisted of dosing ferrocene (99% purity acquired from Alfa Aesar®) and high purity oxygen (99.9%) in alternate doses into the reactor at temperatures ranging from 367 °C to 534 °C. Ferrocene was delivered into the reactor using a 200 cc bubbler (Precision Fabricators Ltd.) heated to 60 °C and nitrogen was employed as a carrier gas. The reactor was then purged with nitrogen in order to remove any excess ferrocene and by-products. Once purged, oxygen was dosed, followed by another nitrogen purge. All lines were heated to 65 °C in order to prevent any ferrocene vapor from depositing. A three factor central composite experimental design, shown in Fig. 2, was carried out with temperature, ferrocene dosing time, and oxygen dosing time all varying accordingly.

2.2. Material characterization

Visual inspection of the films was carried out using a 200 kV JEOL 2010F Schottky field emission high resolution transmission electron microscope (HRTEM). Film composition was determined via energy dispersive spectroscopy (EDS), X-ray diffraction (XRD, Scintag PAD5 Powder Diffractometer, $\text{CuK}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$), and X-ray photoelectron spectroscopy (XPS, PHI 5600, Physical Electronics Inc., Al $\text{K}\alpha$). EDS results were obtained from a spectrometer that was coupled with the Schottky field emission TEM. XRD analysis was performed using a scan rate of $2^\circ/\text{min}$ and step size of 0.2° . A pass energy of 58.7 eV and step size of 0.2 eV were used during XPS analysis. The resulting scans were internally calibrated by shifting the C 1s peak to 285.0 eV. Induced coupled plasma-atomic emission

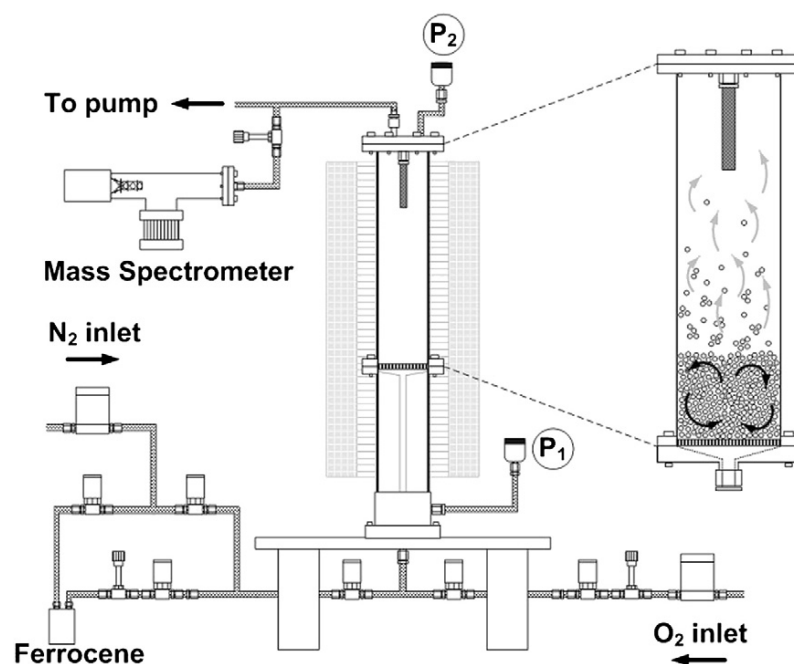


Fig. 1. Schematic diagram of the ALD fluidized bed reactor.

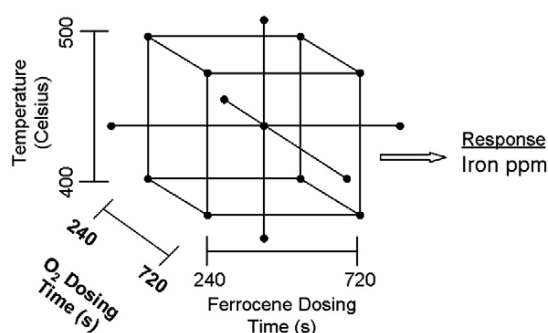


Fig. 2. Experimental design used to study factors affecting iron oxide growth rate.

spectroscopy (ICP-AES) was used as means to quantify the mass percent of iron in the film.

3. Results and discussion

3.1. Fluidization

The main advantage of an FBR compared to other reactor configurations is the benefit of constant particle recirculation, resulting in excellent fluid–solid contact and increased heat and mass transfer coefficients [22,31]. In an ALD reactor, this would result in the active surface sites reacting quickly with the reactant due to continuous exposure to the gas phase precursors. Therefore, it is imperative that the particles remain in a fluidized state during the entire ALD process. In order to ensure this, a fluidization curve was generated to verify that the particles could be fluidized, and to determine the appropriate superficial gas velocity used throughout the reaction. Incipient fluidization occurs when the pressure drop as a function of superficial fluid velocity remains constant [32]. The fluidization curve shown in Fig. 3 verifies that the particles become fluidized at a superficial gas velocity of 0.015 cm/s.

3.2. In situ mass spectroscopy

Residual gas analysis (RGA), which has been shown to be an effective method to observe the termination of ALD half reactions on various substrates, was used to observe the ALD reaction *in situ* [23,26]. The RGA plot of one complete cycle is shown in Fig. 4 at a temperature of 450 °C. Each half-reaction was clearly observed and indicated that the chemistry was self-limiting. When ferrocene was dosed into the reactor ('Ferrocene Dose'), there was an increase in the partial pressure of CO₂. Soon after,

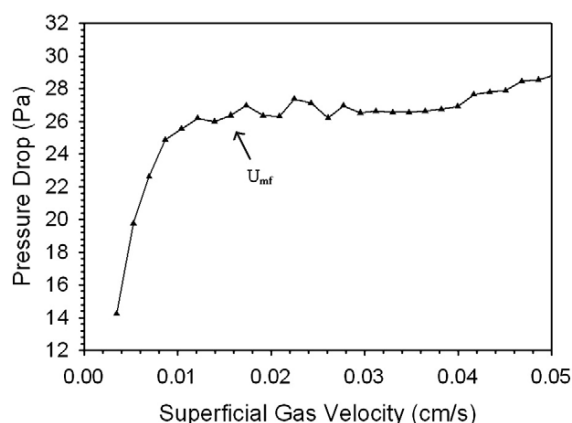


Fig. 3. Pressure drop across the bed as a function of superficial gas velocity. Incipient fluidization occurs at 0.015 cm/s.

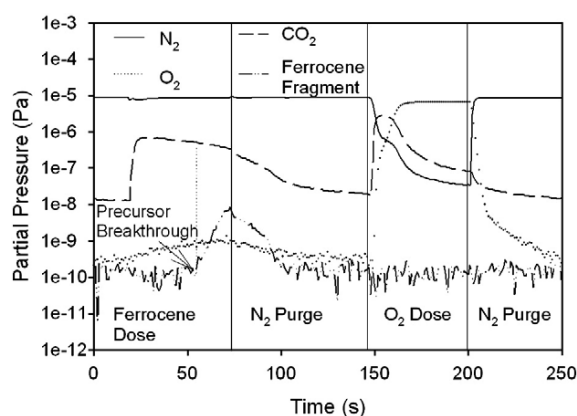


Fig. 4. In situ mass spectroscopy results during one complete ALD cycle.

the partial pressure of ferrocene began to increase, which signified precursor breakthrough, and eventually reached a maximum. The CO₂ subsequently decreased, which indicated that the surface was saturated and the reaction had reached completion. After the reactor was purged, oxygen was dosed ('O₂ Dose') and the partial pressure of both CO₂ and oxygen increased. As oxygen continued to be dosed, the reaction product began to decrease, which signifying that the reaction was approaching completion. In the first half reaction, CO₂ is attributed to chemisorbed oxygen reacting with ferrocene ligands adsorbed on the surface. As O₂ is dosed in the second half reaction, it reacts with the remaining chemisorbed ferrocene ligands to evolve CO₂, and oxidizes the iron. This mechanism has been observed during ALD of metals and metal oxides using metallocene precursors with oxygen, such as for Ru and RuO₂ using Ru(C₅H₅)₂ [33,34].

3.3. Film characterization

HRTEM images after 200 coating cycles at 450 °C are shown in Fig. 5a and b. These images clearly indicate that the films are conformal and uniform around the particles. From visual inspection, the films are about 3 nm thick, corresponding to a growth rate of 0.15 Å per cycle, which is comparable to other metal oxide ALD growth rates [29,35,36]. Additionally, there is a clear differentiation between films around individual particles. This is observed in Fig. 5b, where films around two individual particles can be observed, indicating that particles have not been glued together. EDS results, shown in Fig. 5c, confirm the presence of iron. C and Cu peaks result from the grid that particles were analyzed on and are not representative of the particle surfaces. The only remaining peaks were Zr, Fe and O, which clearly indicated that iron had been deposited on the ZrO₂ particle substrates.

Two properties intrinsic to ALD, self-limiting chemistry and linear growth rate, are confirmed in Figs. 6 and 7 by measuring iron mass percent as a function of ferrocene dosing time and number of ALD cycles at 450 °C, respectively. As ferrocene dosing time was increased from 67 s to 480 s, the iron mass percent in the film increased from about 1% to 11%. However, as the dosing time was increased to 883 s, the amount of iron in the film did not significantly increase, confirming that ferrocene does not continue to react once all of the surface sites are saturated. Nearly linear growth is observed in Fig. 7 as the number of ALD cycles is increased from 50 to 200. The discrepancy between iron mass percent in Fig. 6 and that of Fig. 7 is due to the fact that zirconia nanoparticles were not used to study the growth of the films as a function of number of ALD cycles, but rather zirconia particles that had a mean diameter of 110 μm.

Contour plots shown in Fig. 8 summarize how the mass percent of iron in the film varies with ferrocene dosing time, oxygen dosing time, and temperature. Each graphic depicts one factor (e.g. dosing time) as a function of another while holding the third factor constant at its

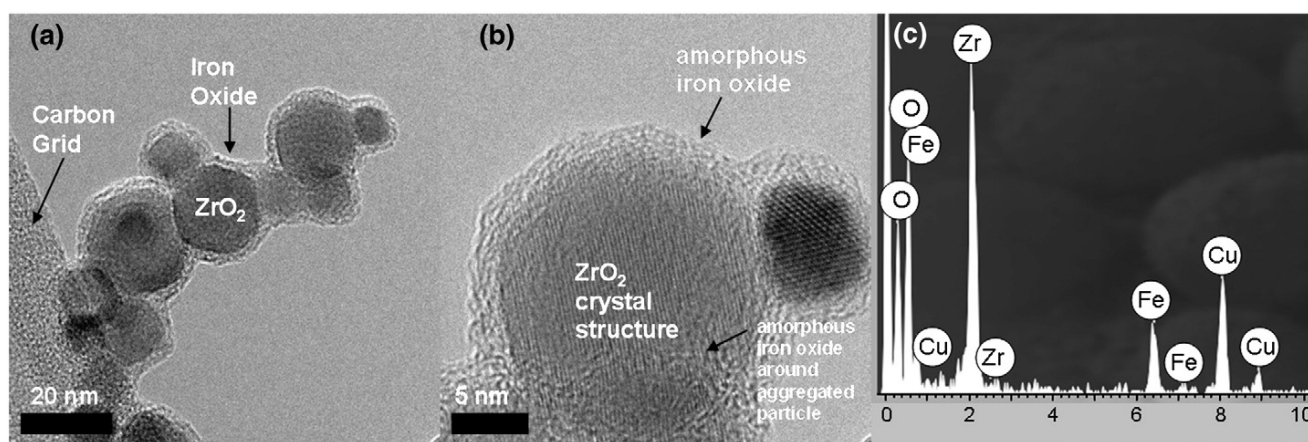


Fig. 5. a) and b) HRTEM micrographs after 200 coating cycles. c) EDS spectrum confirms the presence of iron.

center point (refer to Fig. 2 for a schematic of the experimental design). Because the majority of change in iron mass percent was observed at short dosing times, each of these axes is shown only up to their center point. As seen in Fig. 8a and b, the amount of iron in the film began to decrease as the temperature was raised beyond 500 °C. This is likely due to the thermal desorption of ferrocene, which has been shown to desorb molecularly intact [37]. Additionally, a greater dependence was observed for ferrocene dosing time than that of oxygen on the final iron mass percent in the films. As seen in Fig. 8a, as ferrocene dosing time decreased below 200 s, the amount of iron in the film decreased rather dramatically, whereas the change was not nearly as significant for oxygen dosing time (Fig. 8b). This was further corroborated in Fig. 8c, where large changes in iron content were attainable even at very low oxygen dosing times. This can be explained by the fact that ferrocene was dosed into the reactor with the aid of a carrier gas (N_2) because of its low vapor pressure. Therefore, the mass of ferrocene available to react with the fluid bed per unit time was much smaller than that for oxygen.

EDS results confirm the presence of iron but do not give any information regarding the oxidation state or crystalline nature of the films. Therefore, powder XRD was utilized in an effort to further understand the crystallinity of the film. XRD results of uncoated and coated particles after 200 cycles are shown in Fig. 9. For both samples, only peaks representative of the ZrO_2 nanoparticles were evident, which

suggests that the films were likely amorphous as deposited. After 200 cycles it was apparent that the peaks were less sharp than uncoated particles, but the angle and relative intensity of the peaks remained unchanged. This can be observed visually in the high resolution TEM image in Fig. 4b, where the crystalline and ordered nature can be clearly observed in the ZrO_2 particle, but not in the deposited film.

Because the coated film was amorphous, samples were thermally annealed in both air and an inert environment at 850 °C for 4 h in an effort to crystallize the film and to help determine whether iron metal or amorphous iron oxide was deposited. At 850 °C in air, $\alpha-Fe_2O_3$ is the thermodynamically favored state of iron oxide. In an inert environment, however, $\alpha-Fe_2O_3$ would only be expected if the deposited film was amorphous iron(III) oxide, as it was not exposed to an oxidizing atmosphere during heat treatment. As seen in Fig. 10, there are peaks representative of $\alpha-Fe_2O_3$ for the sample heat-treated in air, which were not present in the sample measured in the as-deposited state. The crystal structure of the sample that was heat-treated in an inert environment was nearly identical to that of the sample thermally annealed in air, which indicated that amorphous iron(III) oxide was deposited on the particle surfaces by ALD using ferrocene and O_2 at a temperature of 450 °C.

In order to verify that the sample heat treated in an N_2 atmosphere was not oxidized from iron(II,III) oxide to iron(III) oxide due to oxygen or water adsorbed on its surface, XPS measurements were conducted for

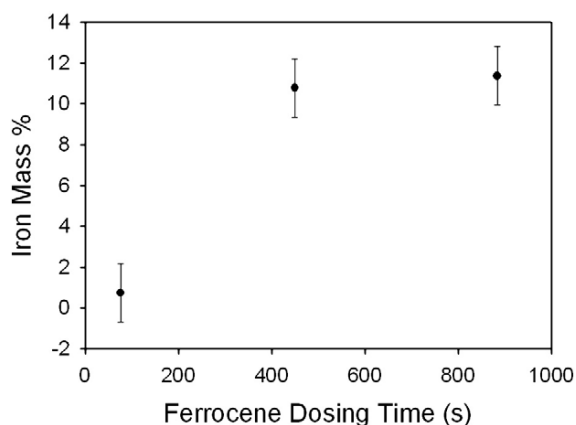


Fig. 6. ICP-AES iron mass percent in the film as a function of ferrocene dosing time. Self-limiting chemistry is confirmed.

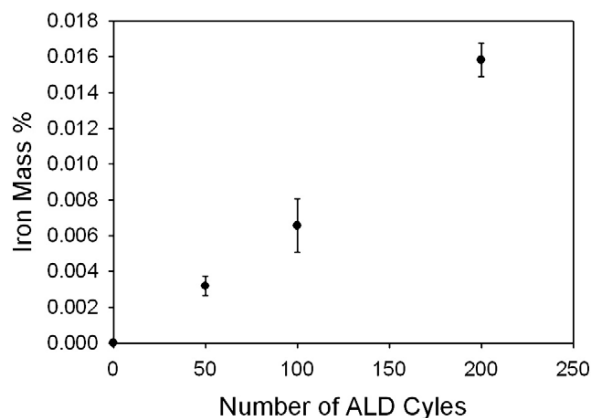


Fig. 7. ICP-AES iron mass percent in the film as a function of the number of ALD cycles. Nearly linear growth is observed.

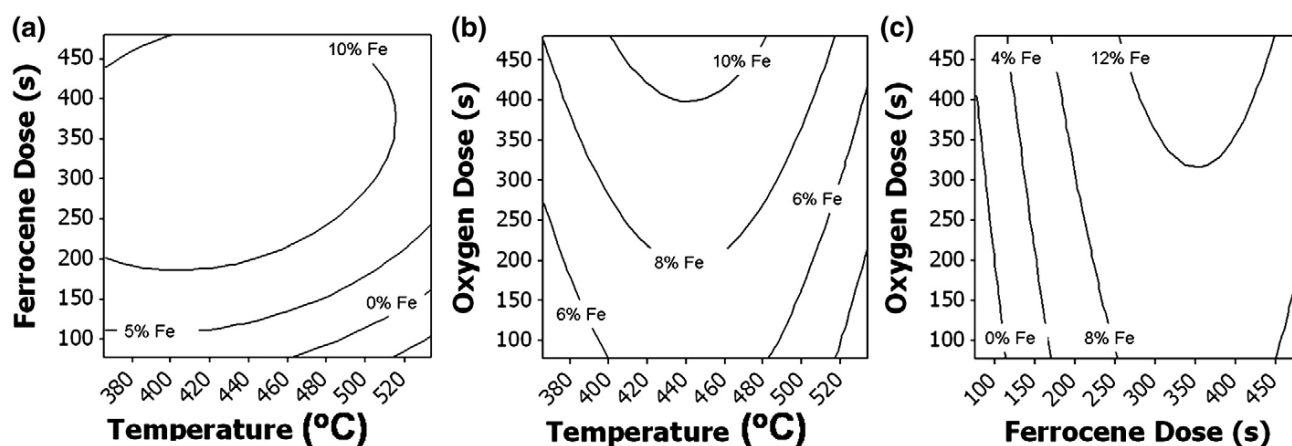


Fig. 8. Contour plots of a) ferrocene dosing time vs. temperature at a constant O_2 dosing time of 480 s, b) O_2 dosing time vs. temperature at a constant ferrocene dosing time of 480 s, and c) O_2 dosing time vs. ferrocene dosing time at a constant temperature of 450 °C.

both the amorphous and heat-treated samples. These results confirmed that iron(III) oxide was deposited, as shown in Figs. 11 and 12. The binding energy associated with electrons residing in the $Fe\ 2p_{3/2}$ orbitals in both the amorphous and heat-treated samples was approximately 711.0 eV, which is in good agreement with previously reported literature values [38,39]. Because the difference in binding energy between these orbitals for the Fe^{2+} and Fe^{3+} oxidation states is very small, it can be difficult to determine the relative amount of Fe^{2+} and Fe^{3+} in the sample

[40]. Therefore, Gaussian curves centered around Fe^{2+} (709.2 eV–709.8 eV) and Fe^{3+} (710.6 eV–711.2 eV) were added and fit to the data using a sum of least squares approximation. The binding energy of metallic iron (707 eV) was not considered as it falls considerably away from the center of the $Fe\ 2p_{3/2}$ peak. As seen in Figs. 11 and 12, a majority of the contribution to the best fit line was due to the Fe^{3+} peak, while that of the Fe^{2+} was much smaller. Therefore it can be concluded that most of the iron was in the Fe^{3+} oxidation state, similar to the XRD results, but the presence of the Fe^{2+} state, albeit to a significantly lower degree, cannot be excluded.

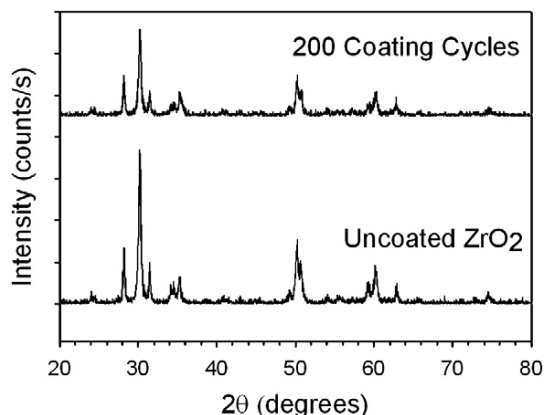


Fig. 9. XRD spectrum of uncoated and coated ZrO_2 nanoparticles after 200 ALD cycles.

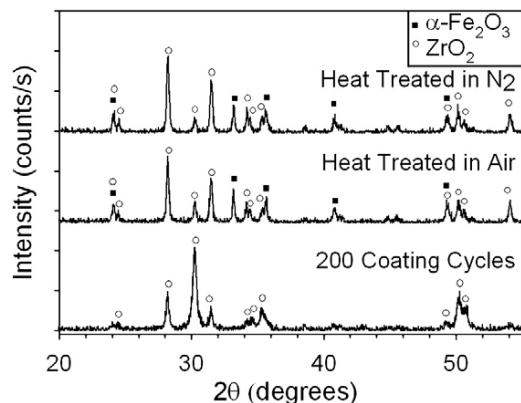


Fig. 10. XRD spectrum of as-deposited and heat-treated samples after 200 ALD coating cycles.

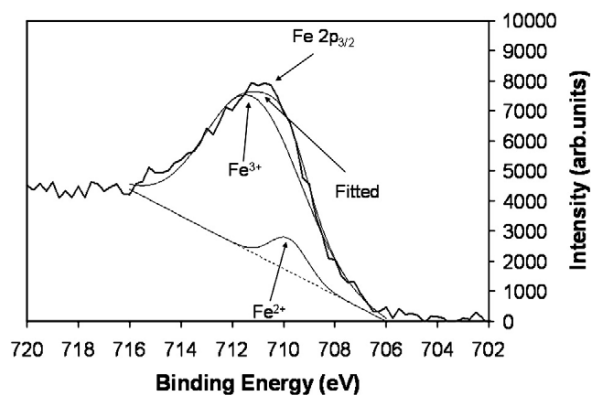


Fig. 11. XPS spectrum of $Fe\ 2p$ of amorphous iron oxide film.

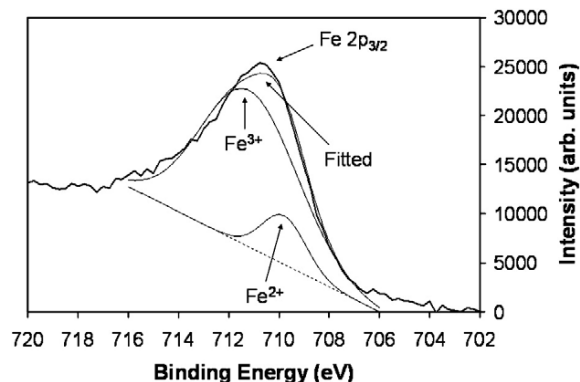


Fig. 12. XPS spectrum of $Fe\ 2p$ of iron oxide film heat treated at 850 °C.

4. Conclusions

ALD chemistry that combined ferrocene and oxygen as precursors was used to deposit ultrathin amorphous iron oxide layers on zirconia nanoparticles in a fluidized bed reactor. Self-limiting chemistry, characteristic of ALD, was observed via *in situ* mass spectrometry and ICP-AES studies. HRTEM images were used to show the conformal and uniform nature of the films on individual nanoparticles. XRD and XPS analyses established that essentially all of the iron oxide that was deposited was amorphous and in the +3 oxidation state. After heat treatment at 850 °C, it was shown that the films could be crystallized to form α -Fe₂O₃, even on the high radius of curvature substrates used here.

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