Stability of magnesium based nanoparticles for hydrogen storage
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Hollow MgO Nanoshells: Formation and Stability

High temperature annealing of gas phase synthesized Mg nanoparticles surrounded by an MgO shell leads to formation of hollow MgO nanoshells due to the evaporation assisted Kirkendall effect. Under electron beam exposure in TEM, the (220) MgO surface reduces its high energy by formation of cube facets inside the hollow MgO nanoshell: first a larger surface area is created, which subsequently reduces its size leading to a collapse of the hollow structure within a few minutes. In ambient conditions the hollow nanoshells remain stable for more than a month, but finally they become filled with carbon erasing any identity of MgO. However, keeping the nanoshells in moderate vacuum for more than two months, the formation of only an additional \( \sim 4 \) nm amorphous shell around the MgO nanoshell takes place, while the latter remained stable.

6.1 INTRODUCTION

Currently there is relentless focus on the fabrication of nanoscale materials with controlled shape and size. Particularly, there is strong interest for methods to fabricate hollow nanostructures because of the changes in physical and chemical properties associated with their unique shape making them applicable as high efficiency catalysts and drug delivery systems [1]. Hollow nanostructures can be prepared by various methods like thermal evaporation [2-4], emulsion/water extraction techniques [5], hydrothermal approach [6], and the template method [7,8]. Hollow nanostructure formation using the Kirkendall effect was first demonstrated for Co nanoparticles due to oxidation and sulfidation [9,10]. The Kirkendall effect, a classical phenomenon in metallurgy [9], is associated with the formation of a void in the center of the nanoparticles due to faster outward diffusion of metal ions with simultaneous inward diffusion of vacancies to compensate for the unequal material flow due to the different

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atomic diffusivities. Moreover, low-temperature oxidation of metallic Zn [11], Fe [12], Cu [13], and Al [13], nanoparticles showed the formation of hollow oxide nanoparticles.

Furthermore, MgO is an ionic wide band-gap insulator that is used as a passivation layer in high electron mobility transistors [14], a substrate for thin film growth [15], as MgO nanocrystals providing effective and active absorbents for many toxic chemicals including chemical warfare agents and air pollutants [16-18], and as a catalyst and additives in refractory materials [19,20]. Incorporation of MgO nanorods in superconductors improved performance in their high temperature operation [21]. The control of particle size and specific surface area are of major importance for all previously stated applications. Therefore, major efforts have been taken for the preparation of hollow MgO nanostructures. Hollow MgO nanotubes were prepared by the use of ZnO nanorods as templates [22], while hollow MgO spheres and hexagonal cylinders were prepared by taking Zn as a template material[23,24].

However, many theoretical predictions show that hollow nanospheres are indeed thermodynamically unstable. The reason is that the high surface energy associated with the hollow nanospheres will favor shell shrinkage to form compact nanospheres in order to reduce the surface energy. The explanation for the shrinking process can be given by the diffusion of vacancies from the inner to the outer surface and the corresponding flow of matter from the outer to the inner surface [25,26]. Therefore, in this chapter we show for the first time the formation of hexagonally shaped hollow MgO nanoshells based on the Kirkendall effect, and discuss their structural stability in ambient conditions and under electron beam exposure in TEM.

6.2. EXPERIMENTAL

The Mg nanoparticles were produced by an NC200U nanoparticle source from Oxford Applied Research (http://www.oaresearch.co.uk). The sample chamber was evacuated to a base pressure of ~1x10^{-8} mbar with a partial oxygen pressure of ~10^{-9} mbar. Supersaturated metal vapor is produced by high pressure magnetron sputtering of a magnesium target (99.95% purity obtained from Alpha Aesar) in an inert krypton atmosphere (pressure ~0.25 mbar). The nanoparticles formed in the aggregation volume are removed fast by the use of helium as a drift gas. The nanoparticles were deposited on 25 nm thick silicon-nitride membranes, which were used for HRTEM imaging and
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heating analysis in a JEOL 2010F TEM [27]. In-situ TEM annealing experiments were performed using a Gatan heating holder, where the temperature is accurately controlled with a Gatan model 901 SmartSet Hot Stage Controller. It employs a PID controller which allows accurate control of the temperature within ±0.5 °C. A desired final temperature can be reached with a fast ramp rate without overshoot. The in-situ heating in the TEM was performed without exposing the sample to the electron beam, so that there is no accelerating effect on the Mg evaporation or void formation due to the electron beam. Energy filtered imaging and electron energy loss spectroscopy were performed by using a Gatan GIF model 2000 attached to the JEOL 2010F.

6.3. RESULTS AND DISCUSSION
Mg nanoparticles with sizes 10-80 nm, after annealed at 400 °C for 10 minutes inside a TEM (5x10^{-7} mbar), showed the formation of hollow MgO nanoshells. Figure 6.1 a shows that they have an MgO shell of (~ 3 nm thick) around an Mg core. This shell is a result of oxidation during nanoparticle formation taking place in an aggregation volume after magnetron sputtering [27]. When the Mg nanoparticles are annealed at 400 °C, the Mg core is completely evaporated and only a crystalline MgO shell remains as Figure 6.1 b indicates. As a matter of fact, during annealing the Mg nanoparticles start to form a void at the Mg/MgO interface and at corners where adjacent facets meet. The void grows further until a completely hollow MgO shell is formed.

The void formation process can be attributed to the so-called Kirkendall effect. The latter generally occurs with processes like oxidation, nitridation and sulfidation. Basically it refers to a faster outward diffusion of cations compared to an inward diffusion of anions, where the amount of outward material flow is compensated with an inward flow of vacancies, which subsequently cluster to form a void. In our case we observe a similar Kirkendall effect, but it is now predominantly associated with Mg.
Figure 6.1. (a) Mg nanoparticles with sizes in the range 10-80 nm having an outer MgO shell of (~3 nm) thick prepared by gas phase synthesis. (b) The same set of nanoparticles after annealing at 400 °C for 10 minutes forming hollow MgO nanoshells without any change in shape and size.

evaporation. Oxidation during the vacuum annealing inside the TEM has a negligible effect since thickening of the preexisting crystalline MgO shell is not observed.

The vapor pressure ($P_v$) of nanoparticles with a highly curved surface is significantly higher than that for a flat surface ($P_{v0}$) following the Kelvin equation: [28,29].

$$\frac{P_v}{P_{v0}} = \exp \left(\frac{4\gamma M}{\rho_p RT d} \right)$$  \hfill (6.1)
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Figure 6.2. (a) A set of Mg nanoparticles prior to annealing at 400 °C. (b) The same set of nanoparticles after 10 min. annealing at 400 °C, where some of them do not form a complete hollow MgO nanoshell. (c) An Mg nanoparticle with a size of 40 nm prior to annealing at 300 °C. (d) The same nanoparticle as in (c) after one hour of annealing at 300 °C with the MgO shell trying to follow the Mg core once the vacancies are created at the Mg/MgO interface.

with γ the surface energy, M the molecular weight, $\rho_p$ the density of the particle, $R$ the gas constant, $T$ the temperature, and $d$ the particle size. The driving force for the evaporation is very fast at 400 °C forming a hollow MgO nanoshell within approximately 10 minutes of annealing for all Mg particles in the size range 10 – 80 nm. In contrast, our observation for the same set of Mg nanoparticles at 300 °C indicated a clear size effect on evaporation [30]. Irrespective of particle size, very few Mg nanoparticles do not form a complete hollow Mg core when annealed at 400 °C. The reason can be the quality of the MgO shell formed by nanoparticle oxidation during deposition under high pressure...
magnetron sputtering. Apparently, these very few nanoparticles have a high quality dense MgO shell preventing any Mg evaporation.

Figures 6.2 c & d show that during annealing at a lower temperature of 300 °C, once the vacancies are created at the Mg/MgO interface due to the outward diffusion of the Mg, the MgO shell around the Mg {1010} facet attempts to follow the Mg core in order to stay in contact with it. This is triggered by the fact that the shell can remain more stable by preserving its contact with the Mg core than when a void with its additional interfaces is formed. This drives an inward curving of the MgO (220) surface to a larger length scale, where the possibility of pore/hole formation within the particle is suppressed. The inward curving of the MgO ceases once the void is formed due to vacancy clustering. The faster void formation by annealing at 400 °C, when compared with that of 300 °C, indicates that the MgO shell does not have sufficient response time to follow the Mg Core. This is a plausible reason why the MgO shells before and after annealing at 400 °C appear identical in contrast to the observations at 300 °C, where the shells change as a result of void formation.

The HRTEM images in Figure 6.3 show the collapse of a hollow MgO nanoshell by a process of inward faceting within a period of a few minutes after exposure to the TEM electron beam. Since the (220) surface of the MgO is highly unstable because of its high energy, and transforms into the less energetic (200) and (020) by inward faceting under the TEM electron beam. By contrast to our previous studies the Mg nanoparticles with an MgO shell underwent outward faceting of (220) surfaces, while thereafter the faceting was terminated [27]. However, here, with a hollow MgO shell faceting proceeds inwards in the hollow area and continuous until the particle completely shrinks. There are two mechanisms responsible for the collapse of the hollow MgO nanoshells: (i) Faceting of a high energy surface at the expense of creating a larger surface area. (ii) Reduction of the total surface area by a shrinkage process. First MgO (220) transforms to the more stable lower energy (200) and (020) surfaces by inward faceting under the influence of the electron beam creating a larger surface area. Subsequently, a reduction of the surface area occurs by a faceting process that progresses inwards until there is a complete collapse of the hollow nanoshell by shrinkage forming a more compact structure. Furthermore, it is important to analyze the stability of hollow MgO nanoshells in ambient conditions if to
be used for a successful practical application. In this respect, the same sample with hollow nanoshells when kept for 68 days in ambient conditions shows completely collapsed structures.

**Figure 6.3.** HRTEM images of a part of a hollow MgO nanoshell with the inset showing the whole MgO nanoshell before and after the initiation & progress of the collapse (a) The initial ~3 nm thick MgO nanoshell has {220} inner and outer facets, (b) The same shell in the final stage of collapse after 2 minutes of exposure to the Tem electron beam.
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In fact, after such a prolonged exposure to ambient conditions any identity of the MgO nanoshell becomes absent. Figure 6.4 shows that the hollow MgO becomes filled with other material. In order to investigate further this point, we used energy-filtered imaging in the TEM and the results confirmed that the filling material is carbon. The bright field TEM image in figure 6.4 b also confirms that the carbon only reacts with the hollow MgO nanoshell and not with the surrounding amorphous silicon nitride membrane on which the Mg nanoparticles are deposited.

Within the same framework, it is worth to investigate the time span the hollow MgO nanoshells can be stable in ambient conditions and how fast they undergo changes.

Figure 6.4. (a) Hollow MgO nanoshell after 68 days in ambient condition have become completely filled with carbon. (b) Hollow MgO nanoshell during the process of filling with carbon.
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The bright field TEM image in figure 6.5 a show the hollow MgO nanoshells, kept for 44 days in ambient conditions, remained stable. In comparison with figure 6.4 it is clear that additional twenty four days will lead to unstable MgO shells we also examined also MgO nanoshells kept for prolonged periods of time in vacuum. In this case, fresh hollow MgO nanoshells were kept in vacuum (pressure $\sim 10^{-2}$ mbar) for 72 days. After 58 days only an amorphous shell ($\sim$ 4nm thick) was formed around the crystalline MgO and it remained unchanged for the rest of the testing period figure 6.5 b).

![Figure 6.5](image_url)

**Figure 6.5** (a) Hollow MgO nanoparticles after 44 days in ambient condition without any size and shape change (b) Hollow MgO nanoparticles after 72 days in vacuum. On all the particles an outer 4 nm thick amorphous shell is formed.
Finally, we will compare our results for Mg nanoparticles with Al nanoparticles, which is another candidate for making nanoshells. As it was discussed in the Ref. 13, Al nanoparticles below 8 nm in size will always form a hollow core with low temperature oxidation. Similarly Mg nanoparticles (prepared by gas phase synthesis) below 15 nm in size during the gas phase deposition will form a hollow Mg core with a surrounding oxide shell (due to the Kirkendall effect associated with oxidation) while the rest of the Mg nanoparticles (sizes > 15 nm and < 100 nm) with MgO shell will form a hollow MgO nanoshell by an evaporation process during high temperature annealing, e.g. at 400 °C.

6.4. CONCLUSIONS
We demonstrated for the first time the formation process of hollow MgO nanoshells due to the Kirkendall effect (associated with Mg evaporation) starting from gas phase synthesized Mg nanoparticles. Inwards faceting of the MgO shell takes place by exposure to the TEM electron beam. The unstable (220) surface of MgO reduces its high energy by inward faceting into (200) and (020) faces, with the hollow MgO shell collapsing in a period of a few minutes. The nanoshells remain stable for up to one and a half month in ambient conditions, and further they become filled with carbon erasing the identity of MgO. However, keeping the nanoshells in moderate low vacuum (for more than two months) the formation of only an additional (a few nanometers thick) amorphous shell around each MgO nanoshell takes place, strongly enhancing the stability of the nanoshells. These results indicate that MgO nanoshells can remain stable for extended periods of time, and that they have potential in applications as for example in catalysis and drug delivery.
REFERENCES


Chapter 6


SUMMARY

The present thesis aims to provide understanding on the applicability of nanoparticles for hydrogen storage. In particular we are interested in Mg nanoparticles which are known as one of the promising candidates for hydrogen storage. Our main motivation was to analyze the structural details and the changes that can occur within the nanoparticles during hydrogen absorption/desorption and heating treatments.

In the course of the investigation we were confronted with the problem associated with the thermal stability of magnesium nanoparticles. Mg nanoparticles with sizes in-between 10-50 nm showed the formation of voids and hollow Mg cores due to oxidation and evaporation. Only the (∼3 nm) MgO shell remains after heating at 300 °C for a few hours (under various conditions). A crucial aspect is that size reduction is favoring the evaporation of the Mg, because a higher vapor pressure is associated with smaller nanoparticles, e.g. nanoparticles with sizes of 15-20 nm develop a hollow core within 1-2 hours of annealing at 300 °C, whereas nanoparticles larger than 50 nm did not show any observable Mg evaporation.

Therefore in order to overcome these limitations, different strategies have been investigated that can help to alleviate the thermal stability limitations of Mg nanoparticles (NPs). (i) Addition of Cu prevents void formation during NP production and reduces the fast evaporation/voiding of Mg during annealing; (ii) Alloying can prevent Mg evaporation: e.g. Mg with Ni forms a thermally stable core/shell (MgNi2/Ni) preventing Mg evaporation during annealing. (iii) Covering a layer of Mg NPs with a Ti film leads to suppression of Mg evaporation during subsequent vacuum annealing.

In addition we also discovered how the presence of oxygen and the MgO shell around the Mg core is crucial for the stability of the Mg nanoparticles. The addition of Ti to the Mg target shifts the Mg-nanoparticle sizes distribution to smaller sizes in the range 5-20 nm and leads to less protective Mg-oxide shells for nanoparticles below 15 nm. This in return accelerates the evaporation of Mg that leads to hollow Mg cores. The presence of oxygen plays a dual role in forming MgO protected stable Mg nanoparticles above a critical size (∼15 nm), and hollow ones below this size both due to evaporation and oxidation associated Kirkendall effects. Along with this, the Kirkendall effect associated
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with evaporation was used to produce hollow MgO nanoshells by annealing Mg nanoparticles at 400 °C for 10 min. Under electron beam exposure in a TEM, the (220) MgO facets reduce their high surface energy by forming cube (200) facets, although this initially increases the total surface area of the nanoshells. However, this change in facets is quickly followed by nanoshell size reduction and collapse of the shell into a densified structure within a few minutes.