Supporting Information


**Synthesis of Metallic Magnesium Nanoparticles by Sonoelectrochemistry**

Iris Haas and Aharon Gedanken*

## Experimental

## Materials and chemical preparation

The Gringard reagents, ethyl-MgCl as a 2.0M solution in THF (tetrahydrofuran) and buthyl-MgCl as a 1.45M solution in glyme (dibutyldiglyme), and anhydrous aluminum chloride (99.99%) were all obtained from Aldrich and used as received.

Magnesium foils were prepared by machining 99.99% pure magnesium ingots, which were acquired from Alfa. Extra dry tetrahydrofuran (THF) was obtained from Merck, Selectipure, >10 ppm water, as determined by Karl Fischer titration.

In the THF solutions, the concentration of $AlCl_3$ in THF was 0.25 M and the molar ratios of ethyl-MgCl:$AlCl_3$ were 2:1, 1.5:1. In the dibutyldiglyme solutions, the concentration of $AlCl_3$ was x=0.725M and the molar ratio of buthyl-MgCl:$AlCl_3$ was 1:1.

## Electrochemistry

All chemical preparations and electrochemical measurements were carried out under pure argon atmosphere in an M. Braun, Inc. glove box (less than 1 ppm of water and oxygen). Cyclic voltammetry was applied using an EG&G, Inc. 273 potentiostat.

The electrochemical characterizations were performed in one-compartment, three-electrode cells consisting of a magnesium metal counter electrode, a magnesium metal reference electrode, and a Ti sheet working electrode. Cyclic voltammetry (CV)

was typically performed at a rate of 25 mV/s$^{-1}$, starting from the (OCV) open cycle voltammetry (about 1 V *vs*. Mg) to −1 V. All the experiments were performed at room temperature (25 ±2 °C).

**Sonoelectrochemical setup**

All the sonoelectrochemical measurements were carried out under pure argon atmosphere in a glove bag (Aldrich).

An ultrasound horn (ultrasonic liquid processor VC-600, 20 kHz, Sonics & Materials) acts both as the cathode and as the ultrasound emitter[1]. The electroactive part of the sonoelectrode is the planar circular surface, at the bottom of the horn. The immersed cylindrical part is covered by three layers, an isolating plastic jacket, a brass crucible, and another isolating plastic jacket. Potential-step techniques were applied using an EG&G, Inc. 273 potentiostat. This sonoelectrode produces a sonic pulse that is triggered immediately following the current pulse.

**Sonoelectrochemical synthesis of magnesium nanoparticles**

The sonoelectrochemical synthesis was performed in one-compartment, three-electrode cells consisting of a magnesium metal (20 mm X 30 mm) counter electrode, magnesium metal (5 mm X 30 mm) reference electrode, and an ultrasonic tip as a working electrode. In the synthesis, the cathodic current density pulse was 5mA/cm$^2$, and the duration of the current pulse was 600 sec. The off time of the current pulse was 600 ms. The duration of the ultrasonic pulse was 300 ms. The ultrasound power intensity was 76W. The electrolytes were Gringard solutions that were prepared as follows: a. Without AlCl$_3$, 2.0M of a THF solution or 1.45M of a dibutyldiglyme solution. b. Regarding the AlCl$_3$, the molar ratio of the Gringard reagent to the AlCl$_3$ was mentioned above.

## Characterization

The morphology and structure investigations were performed by high-resolution TEM (HRTEM) images that were taken using a JEOL 2010 with a 200 kV accelerating voltage. Samples were prepared by placing one drop of the dispersed nanoparticle solution on a copper/carbon grid (400 mesh), and then drying under argon atmosphere in a glove box. A Scion Image software program was used to measure the distribution of particle size by measuring 150-200 particles from the HRTEM image.

**HRSEM**. The high-resolution scanning electron microscopy (HRSEM) of the product was carried out on a JEOL-JSM 840 scanning electron microscope operating at 15 kV.

**XRD**. The X-ray diffraction pattern of the product was measured with a Bruker AXS D* Advance Powder X-ray diffractometer (using Cu KR = 1.5418 Å radiation). The Mg nanoparticles are air sensitive, and therefore a special air-tight cell for powder x-ray diffraction analysis is necessary[2]. This cell was manipulated under argon atmosphere in a glove box.

**ICP**. To analyze the Mg content on the electrode after the electrochemical deposition, we washed the metal with an acidic solution (HCl, pH=1). This solution was determined with an inductively-coupled plasma (ICP) spectrometer (Ultima 2, Jobin Yvon Horiba).

**UV-Visible**. The UV-Visible absorption spectra were recorded on a Perkin Elmer UV-Visible spectrophotometer.

## 1. Electrochemical Experiments.

The cyclic voltammograms are illustrated in Figure 1. We have observed different current densities in the two solvents, and in THF the current was 10 times larger than in dibutyldiglyme. We attribute this difference to the viscosity of the solutions; dibutyldiglyme is a more viscous solvent than THF. Since the electrochemical route is a diffusion control process, the higher the viscosity of the solvent, the lower is the solution's ionic conductivity. This is the reason why higher currents were observed in the THF solution.
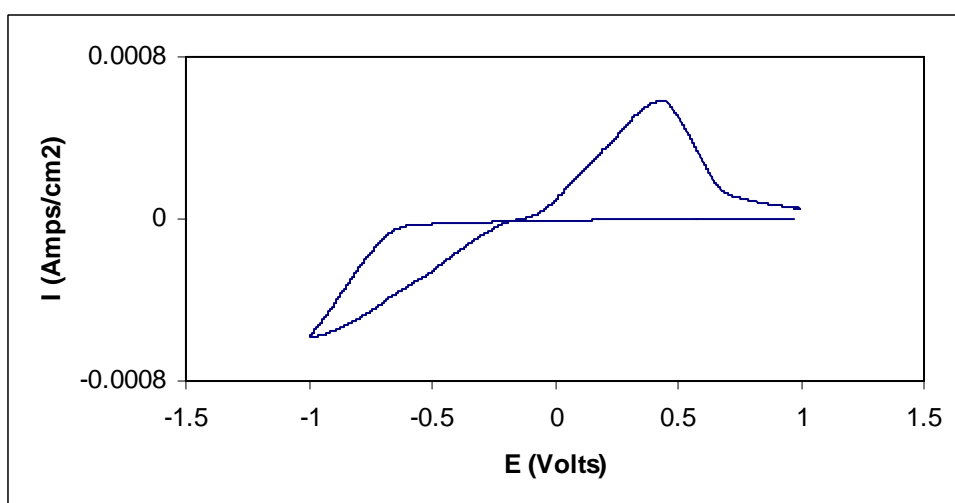
a.
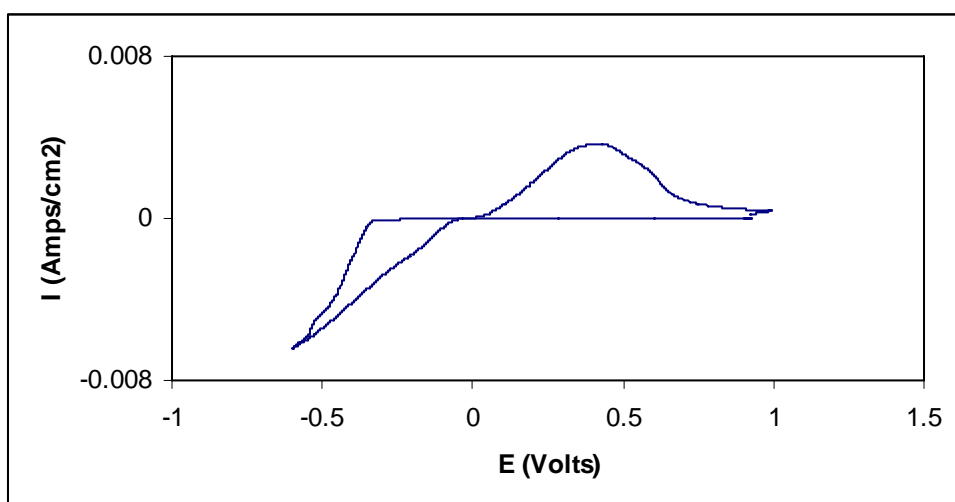


b.

*Figure S1. Typical cyclic voltammograms measured using a. a THF solution with ethyl-MgCl:AlCl$_3$, molar ratio 1.5:1, the concentration of AlCl$_3$ in THF is 0.25M. and b. a dibutyl-diglyme solution with buthyl-MgCl:AlCl$_3$, molar ratio 1:1. The concentration of AlCl$_3$ in dibutyl-diglyme is 0.725M.*

## 2. Sonoelectrochemical experiments.

Figure 2 shows the absorption spectrum of the dispersed magnesium nanoparticles after the SONOEL process. We observed an absorption band peaked at 260 nm, which is due to the surface plasmon band of Mg. Creighton *et al*. observed a similar absorbance value for magnesium nanoparticles prepared by chemical methods[3] .
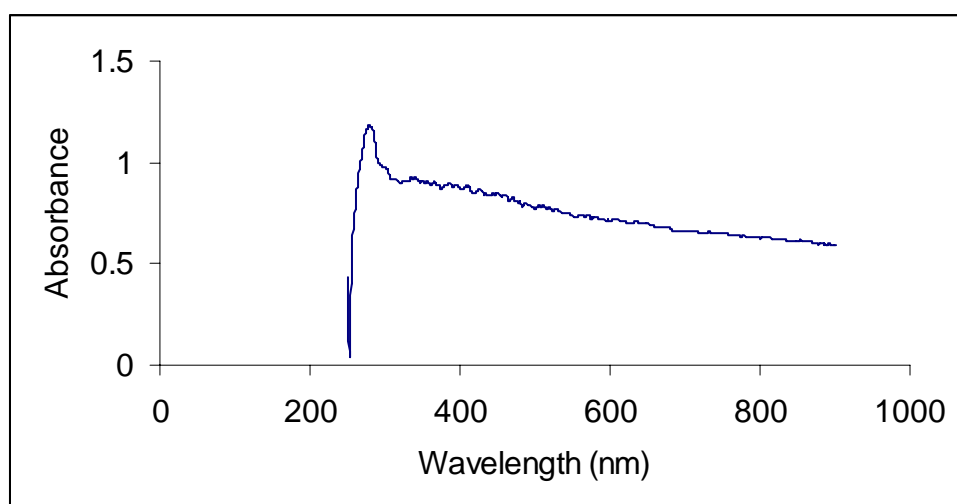


Figure S2. UV-Visible absorption spectra of magnesium nanoparticles

**Product efficiencies of the sonoelectrochemistry process:**

The product efficiencies in the sonoelectrochemical process of the Gringard reagent in THF or in a dibutyldiglyme solution were 41.35% and 33.08%, respectively. These efficiency measurements were conducted in the absence of $AlCl_3$. We assign the different product efficiencies to the solution viscosity. The efficiency is higher in the less viscous solvent. Adding $AlCl_3$ to the Gringard solution increased the efficiency dramatically, raising it to 82.70% and 51.69% in THF or dibutyldiglyme, respectively. Again it can be seen that the product efficiency is higher in a THF solution. The product efficiency (82.70%) was found to be independent of the concentration of the $AlCl_3$, and varying the molar ratio of ethyl-MgCl:$AlCl_3$ (in a THF solution) from 2:1, to 1.5:1 (the concentration of $AlCl_3$ in THF is 0.25M) did not change the product's efficiency. When the molar ratio was raised to 1:1, a precipitate of an Al salt was observed. The product efficiency is defined as the weight of the product in relation to the number of Coulombs that have passed through the solution.

**SAED analysis:**

ED results shows clearly the presence of metallic Mg. Since part of the Mg was oxidized by air exposure it shows also MgO. The inner circle fits with the *d* value of the (101) plane of Mg (0.245 nm according to PDF file number 035-0821).
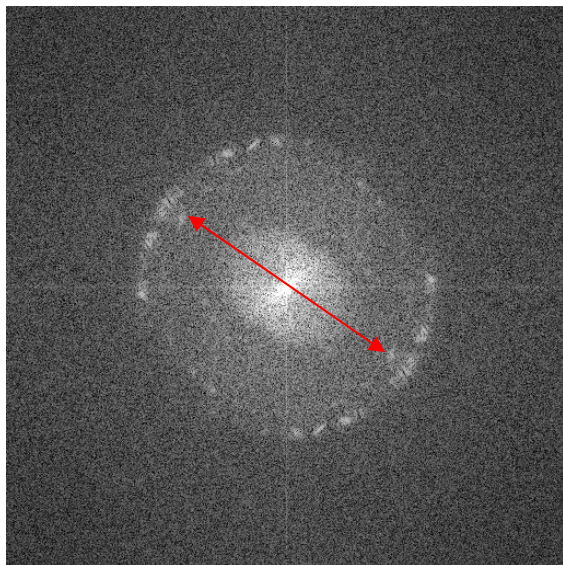


Figure S3. SAED of Mg nanoparticles
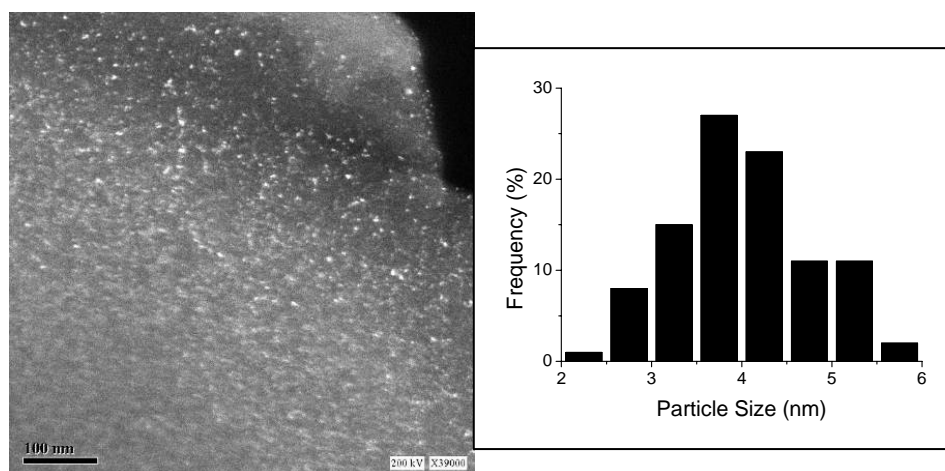
## HRTEM analysis:



Figure S4. HRTEM image of magnesium nanoparticles: Bright field image of ethyl-MgCl in a THF solution (2.0 M) without $AlCl_3$ and a histogram of the size of magnesium nanoparticles.
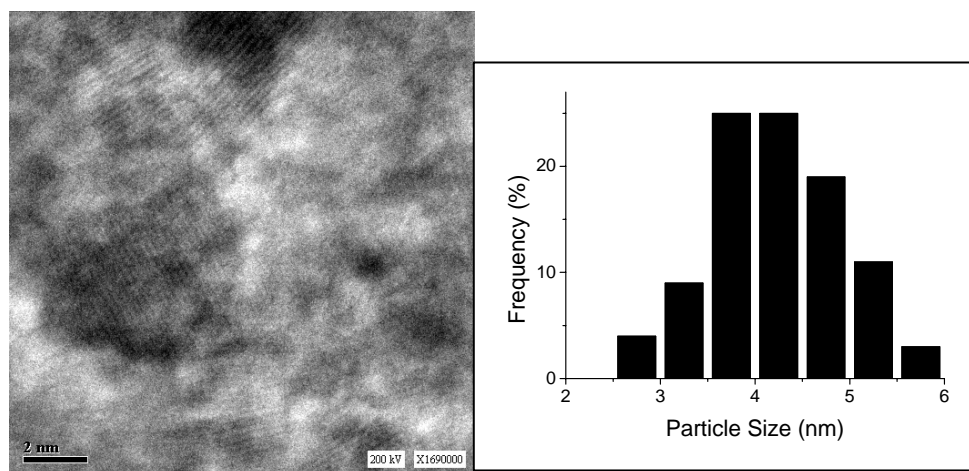


Figure S5. HRTEM image of magnesium nanoparticles produced sonoelectrochemically from buthyl-MgCl in a 1.45M dibutyldiglyme solution, without $AlCl_3$ and a histogram of the size of individual magnesium nanoparticles.

## Reference

1. (a) Haas, I.; Gedanken, A.Chemistry of Materials 2006, **18**, 1184. (b) Haas, I.; Shanmugam, S.; Gedanken, A. Journal of Physical Chemistry B 2006, **110**, 16947.

2. Palchik, O.; Gedanken, A.; Rubinstein, Y. Rev. Sci.Instr. **2003**, 74, 3175-3176.

3. Creighton, J.A.; Eadon, D.G. J. Chem. Soc. Faraday Trans., **1991**, 87(24), 3881-3891.