

# Synthesis of metallic magnesium nanoparticles by sonoelectrochemistry†

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## 4 nm sized metallic magnesium particles were prepared by the sonoelectrochemical method.

In recent years, magnesium has attracted strong interest because of its high performance applications, with hydrogen storage materials<sup>1</sup> being one of the most important. Due to the fact that the storage capacity is limited by material weight, significant attention has been paid to lightweight materials such as magnesium.

Four synthetic techniques have been employed in the preparation of magnesium nanoparticles: cryochemistry,<sup>2</sup> gas-phase synthesis,<sup>3</sup> deposition from ethereal solutions,<sup>4</sup> and deposition from high-temperature molten salts<sup>5</sup> such as MgCl<sub>2</sub>.

Sonoelectrochemistry is a combination of ultrasound waves and electrochemistry. The effects of ultrasound in electrochemistry may be divided into several important branches: (1) ultrasound greatly enhances mass transport, thereby altering the rate, and sometimes the mechanism, of the electrochemical reactions. (2) Ultrasound is known to affect surface morphology through cavitation jets at the electrode–electrolyte interface, usually increasing the surface area. (3) Ultrasound reduces the diffusion layer thickness, and therefore, ion depletion. All these effects are caused by the face-on or side-on geometry of the sonic horn, and the ultrasound is irradiated during the entire experiment. A comprehensive review of the field has recently been published by Compton *et al.*<sup>6</sup> and Pollet and Phull.<sup>7</sup>

Reisse *et al.*<sup>8</sup> have assembled a new setup. This device exposes only the flat circular area at the end of the sonic tip to the electro-deposition solution. The exposed area acts as both cathode and ultrasound emitter, which they term a “sonotrode”. In this process, the electric pulse is followed by an ultrasonic pulse. The ultrasonic irradiation differs in this sonoelectrochemical process from its traditional use as an energy source, because here it serves as a shaking element for the electrode. In other words, its mechanical power is used instead of the chemical energy that is used in sonochemistry. The combination of electrochemistry and sonochemistry is as follows. At the cathode, a pulse of electric current reduces a number of cations, forming a high density of fine metal nuclei.

This short electric pulse is immediately followed by a burst of ultrasonic energy that removes the metal particles from the cathode, cleans the surface of the cathode, and replenishes the double layer with metal cations by stirring the solution. The particles falling from the cathode are nanosized, and they fall to the bottom of the cell.

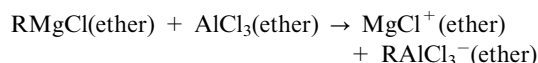
We consider sonoelectrochemistry as a unique method for the preparation of nanometals having a large negative reduction potential, *e.g.*, magnesium and aluminium. This is because the reduction is carried out by the electric current, and metals that cannot be reduced by chemical means will undergo the reduction process because the voltage exceeds the standard reduction potential plus the over-potential. The ultrasonic waves do not play a chemical role here, but rather a mechanical role.

For the preparation of magnesium nanoparticles, one of the major problems was the choice of an appropriate solvent. Most of the commonly-used polar aprotic solvents, such as alkyl carbonates, esters and acetonitrile, are too electrophilic for Grignard reagents, and thus, react with them readily. The only solvents in which stable Grignard solutions can be prepared are ethers. Thus, the Mg deposition was carried out using two different electrolyte solutions based on Grignard reagents in ethers.

The ethers used were tetrahydrofuran (THF) and dibutyl-diglyme (DBDG).

Before starting our sonoelectrochemical experiments we carried out the electrochemistry of the same precursor solution used in the sonoelectrochemistry experiments with the same concentrations. The precursors were the Grignard reagents, EtMgCl and BuMgCl, which were dissolved in THF or DBDG.

In order to increase the ionic conductivity of the ether-based Grignard solutions, AlCl<sub>3</sub> was added to the solution according to the following reaction:<sup>9</sup>

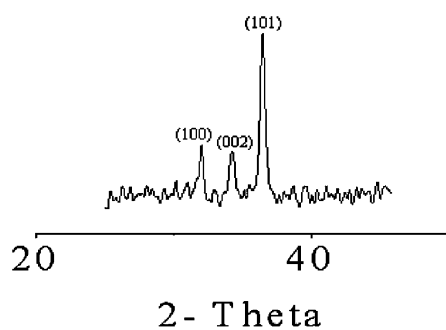


The MgCl<sup>+</sup> formed in this reaction was an electrochemically-active species. Ref. 9 indicates that the Mg deposition–dissolution is not a simple two-electron process of Mg ions, but is in fact more complicated.

The material that was found deposited on the cathode was characterized as magnesium by XRD measurements. The ICP results revealed only Mg, and no Cl or any other impurity was detected. The deposition of Mg on the electrode was observed for both electrolytes. The electrochemical experiments paved the way for the sonoelectrochemical measurements that were

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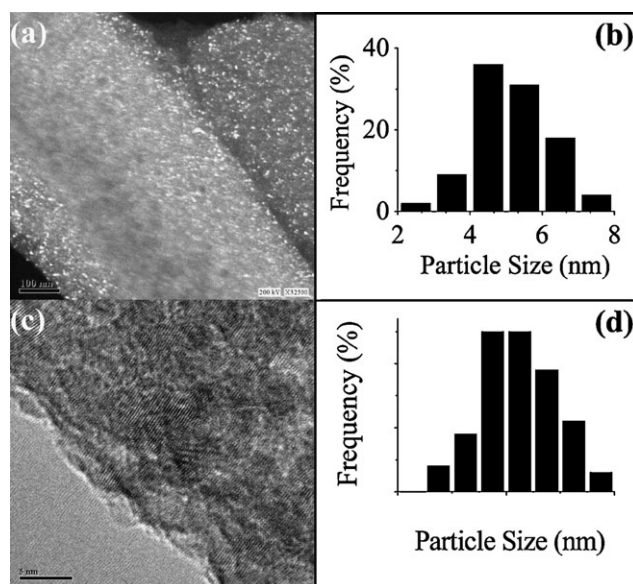
**Fig. 1** XRD pattern of an  $\text{Mg}^0$  nanoparticle produced by the sonoelectrochemical process.

planned for the fabrication of nanosized Mg. The electrochemical results (Fig. S1) are presented in the ESI.†

The same electrolytes were used to prepare magnesium nanoparticles by the sonoelectrochemistry procedure. The XRD of the deposited product obtained sonoelectrochemically is presented in Fig. 1, and shows the presence of crystalline Mg. All the diffraction peaks could be indexed to the hexagonal phase of magnesium (JCPDS 035-0821). The major peaks are  $2\theta = 32.1, 34.4$  and  $36.6^\circ$ , and are assigned to the (100), (002) and (101) Mg planes, respectively. A first indication of the presence of small particles was observed from the width of the diffraction peaks. The application of the Debye–Scherrer formula to the diffraction peaks at  $32.1, 34.4$  and  $36.6^\circ$  indeed led to calculated sizes of  $29.0, 20.9$  and  $22.7$  nm, respectively. The ICP results revealed only Mg, and no Cl or any other impurity was detected.

Further support for the identification of the product as magnesium was obtained from HRSEM (Fig. 2), HRTEM (Fig. 3, and Fig. S4 in ESI†) and SAED (Fig. S3 in ESI†) measurements. Fig. 2 depicts a gradual magnification ( $\times 4000, \times 40\,000, \times 120\,000$ ) of  $2\text{-}\mu\text{m}$  size particles, demonstrating that the aggregated particles are composed of very small particles. However, due to the limited magnification of the instrument the smallest particles identified by SEM are  $68 \pm 8$  nm, which can be further resolved to smaller particles with a better SEM. The SEM measurements lead to the conclusion that the Mg nanoparticles are aggregated and it is not easy to separate them.

For HRTEM analysis, the as-prepared product was dispersed on a copper grid coated with carbon. Fig. 3 presents the results of HRTEM measurements of the products obtained in THF and DBDG without  $\text{AlCl}_3$ . The images clearly show the

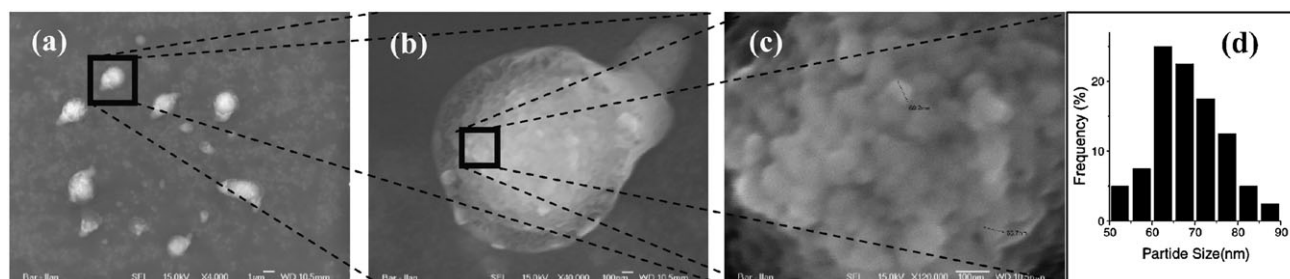


**Fig. 3** HRTEM image of magnesium nanoparticles. (a) Bright field image of BuMgCl in a DBDG solution (1.45 M) without  $\text{AlCl}_3$ . (b) A histogram of the size of magnesium nanoparticles. (c) Magnesium nanoparticles produced sonoelectrochemically from BuMgCl in a 1.45 M DBDG solution, without  $\text{AlCl}_3$ . (d) A histogram of the size of individual magnesium nanoparticles.

formation of small, well-dispersed particles in the range of  $4.5 \pm 0.5$  nm.

The identification of the white particles as magnesium nanoparticles in Fig. 3(a) originates from the fringes detected in Fig. 3(c). The interplanar distance in Fig. 3(c) was  $0.247$  nm, which fits very well with the  $d$  value of the (101) plane of Mg ( $0.245$  nm according to PDF file number 035-0821). MgO nanoparticles could also be found among the Mg particles, and they were also characterized by their fringes. The selected-area electron diffraction analysis (SAED) also showed diffractions related to Mg, as well as to MgO nanoparticles (Fig. S3 in ESI†). The reason for obtaining MgO as a by-product is due to a technical problem in that transferring the grid from the glove-box to the HRTEM machine causes their exposure to air, and although this is a short exposure,  $< 10$  s, the Mg particles are easily oxidized during this period. Additional identification and structural data are presented (Fig. S2–S5) in the ESI.†

In conclusion, a unique technique is presented herein for the preparation of metallic nanoparticles. This is demonstrated for



**Fig. 2** SEM images of magnesium nanoparticles produced sonoelectrochemically from BuMgCl in a 1.45 M dibutyldiglyme solution, without  $\text{AlCl}_3$ . (a)–(c): Images are from low magnification to high magnification. (d) A histogram of the size of individual magnesium nanoparticles (image (c)).

a very reactive metal, Mg, whose standard reduction potential is  $-2.356$  V. No active reducing agents are known to reduce such an active metal. The only way to chemically reduce Mg ions is to use another metal with a more negative reduction potential, such as Na or Li. It is therefore clear that only electrolytic methods could lead to the reduction of Mg ions. Sonoelectrochemistry is such a technique, which, in addition, produces the metal as a powder composed of nanoparticles. Moreover, the present method is considered a promising technique for the fabrication of a large amount of nanometal particles. In the case of reactive metals, avoiding oxidation is a major task. However, this paper shows that using a plastic bag is sufficient for this purpose. Our paper demonstrates the application of this method for the preparation of 4-nm size particles.

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