

## Electronic Supplementary Information

### From Grignard's Reagents to Well-defined Mg Nanostructures: Distinctive Electrochemical and Solution Phase Routes

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### Experimental

Methyl magnesium chloride 3M in THF, platinum foil, 99.99% (metals basis), and magnesium ribbon (99% metal basis) with approximate dimensions of 3.0 mm were obtained from Alfa Aesar. Naphthalene ( $\geq 99.7\%$ ), anhydrous tetrahydrofuran (THF,  $\geq 99.9\%$ ), and lithium metal (99% trace metals basis) were purchased from Sigma-Aldrich. Ethyl magnesium chloride 2.7 M in THF was obtained from Acros Organics. *n*-Butyl magnesium chloride 3 M in THF and phenyl magnesium chloride 3 M in THF were purchased from Strem. Grignard reagents were used as received.

The Pt foil was cleaned by immersing in nitric acid, followed by flame annealing. The Mg ribbon was mechanically polished and ultrasonicated for 10 min in acetone prior to use. Chemicals were transferred to reaction vessels within an argon-filled glove box and all the experiments were carried out under an argon atmosphere using a glove bag or a Schlenk line.

In a typical electrochemical synthesis, electrocrystallization was induced in constant current mode at a current density of 5 mA/cm<sup>2</sup> using a two-electrode cell constituted from a Pt cathode and a Mg anode. Ethyl magnesium chloride (EtMgCl, 0.5 M) and methyl magnesium chloride (MeMgCl, 0.5 M) dissolved in anhydrous THF were used as the magnesium precursors without the addition of any extraneous electrolytes or metal salts. Current was applied using a programmable Keithley 220 current source operated by a PC with home-built software. Mg nanowires were found to grow on the surface of the Pt electrode and could be readily harvested through ultrasonication.

In a typical reaction for synthesis of Mg nanoparticles through solution-phase reduction, lithium naphthalide was prepared by bath sonicating 2.05 g of naphthalene and 0.112 g of lithium metal in 25 mL of anhydrous THF for 1 h. The mixture was then cannulated under argon to a vigorously stirred solution of 3 mL of 2.7 M EtMgCl, MeMgCl, *n*-butyl MgCl, or phenyl MgCl maintained at 70°C within a three-necked round-bottomed flask connected to a Schlenk apparatus. After 30 min, the gray-colored Mg product was separated by centrifugation, washed with anhydrous THF, and dried under vacuum.

## Characterization

As-synthesized nanostructures were characterized by X-ray diffraction (XRD, Rigaku Ultima IV diffractometer with Cu-K $\alpha$  radiation (1.5418 Å)), scanning electron microscopy (SEM, Hitachi SU-70 instrument operated at an accelerating voltage of 20 kV) and transmission electron microscopy (TEM, JEOL 2010 instrument operated at an accelerating voltage of 200 kV).

Electrochemical characterization was performed using a three-electrode cell consisting of a Mg reference electrode, a Mg counter electrode, and a Pt working electrode. Electrochemical characterization was performed under an argon atmosphere in each case. Cyclic voltammetry plots were recorded using a Princeton Applied Research 263A potentiostat operated using PowerSuite software at a scan rate of 25 mV/s.

## Supplementary Figures

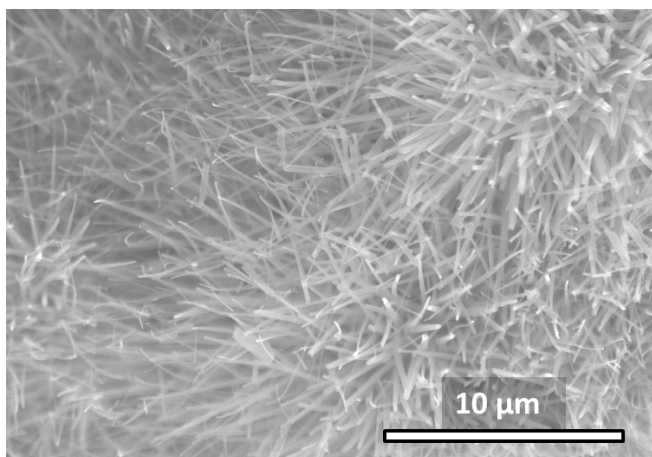


Fig. S1. SEM image of Mg nanowires grown at a current density of 1 mA/cm<sup>2</sup> from a 0.5 M EtMgCl precursor solution.

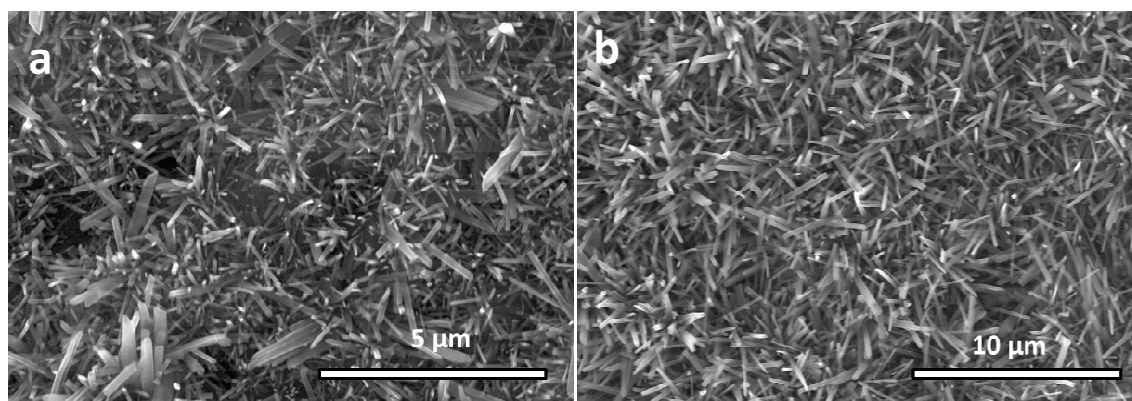


Fig. S2. SEM images of Mg nanowires grown on (a) carbon steel and (b) Ni using MeMgCl as the precursor.

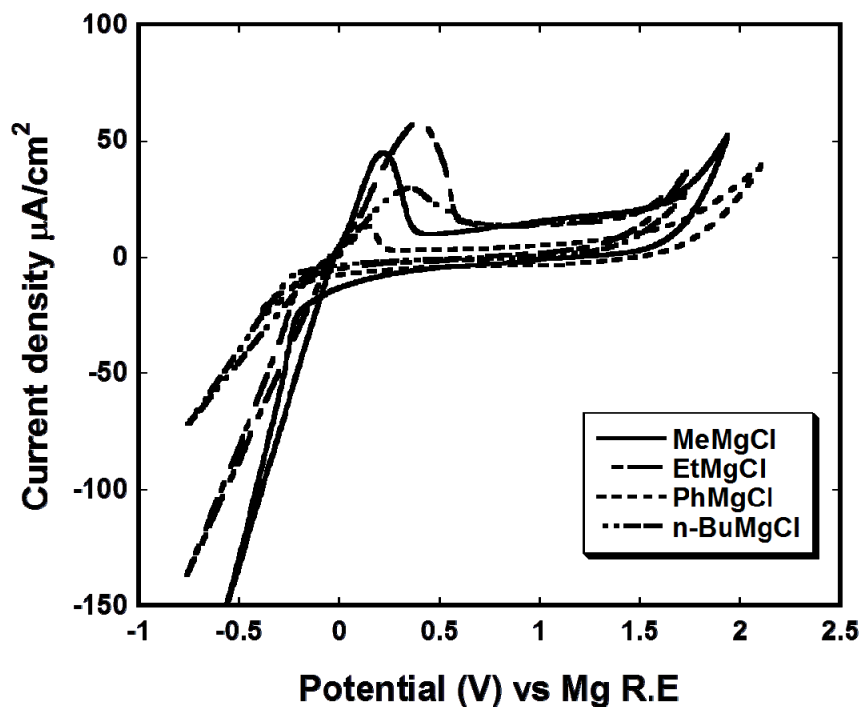


Fig. S3. Cyclic voltammetry of 0.5 M solutions of Grignard reagents (MeMgCl, EtMgCl, phenylMgCl, and *n*-butylMgCl) in anhydrous THF. The scan rate is 25 mV/s. The cathodic portion clearly indicates a lower deposition rate for the *n*-butylMgCl and phenylMgCl precursors, which can be attributed to their lower ionic conductivities.

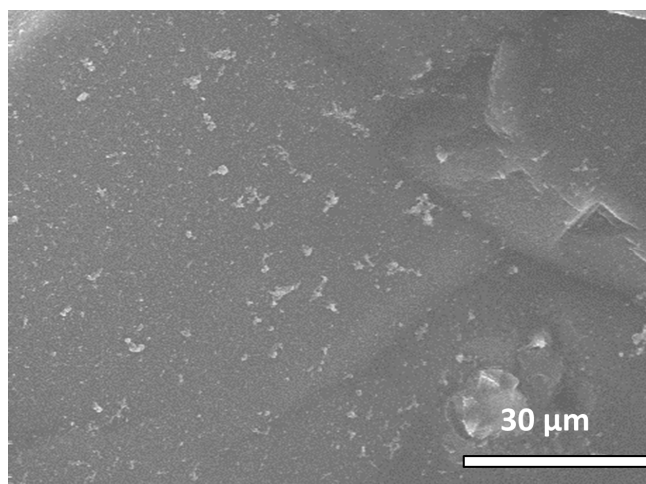


Fig. S4. Representative SEM image of Mg thin films obtained on the Pt electrode using *n*-butylMgCl as the precursor.

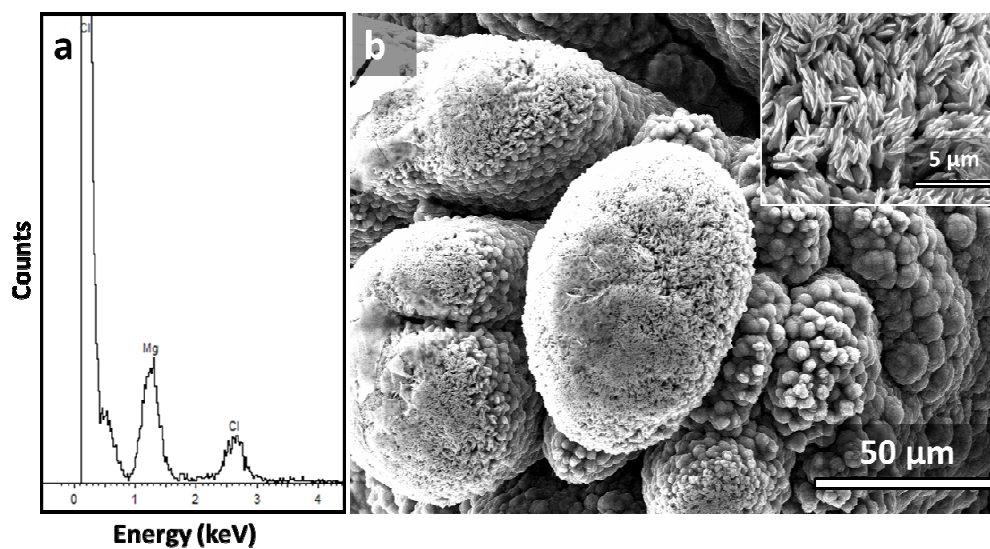


Fig. S5. (a) EDX spectrum and (b) SEM image of Mg nanostructures grown from a 0.5 M MeMgCl solution with the addition of 0.25M AlCl<sub>3</sub> in THF at a current density of 5 mA/cm<sup>2</sup>.

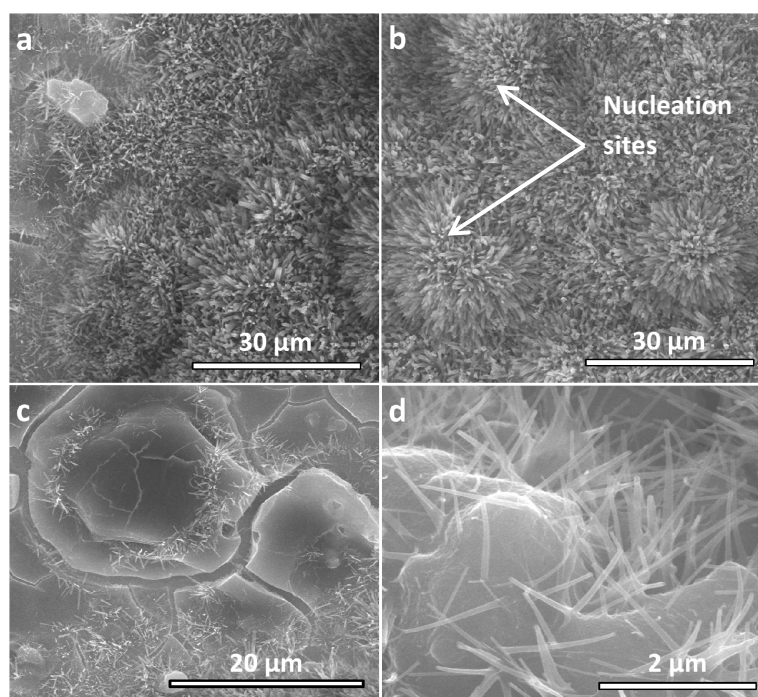


Fig. S6. SEM images indicating initiation of nucleation of Mg nanowires upon electrocrystallization from a 0.5 M THF solution of MeMgCl. Panels (c) and (d) indicate that nanowire growth is initiated at the edges of cracks in the deposited Mg film.

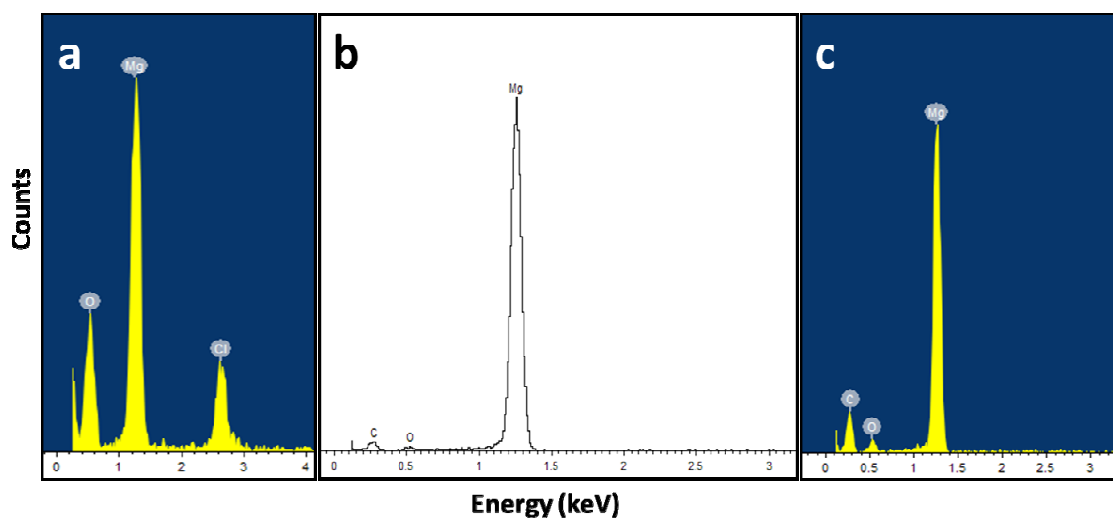


Fig. S7. EDX data of (a) as-prepared Mg nanowires (derived from MeMgCl) showing the presence of chlorine; (b) after washing with copious amounts of anhydrous THF, the Cl concentration is diminished below detectable limits. (c) EDX spectrum acquired for Mg nanoparticles prepared from EtMgCl by lithium naphthalide reduction. Trace amount of oxygen detected by EDX might come from surface oxides formed during sample preparation. Samples were carbon coated in order to obtain better contrast images in the SEM. The observed carbon peak is derived primarily from the carbon coating.

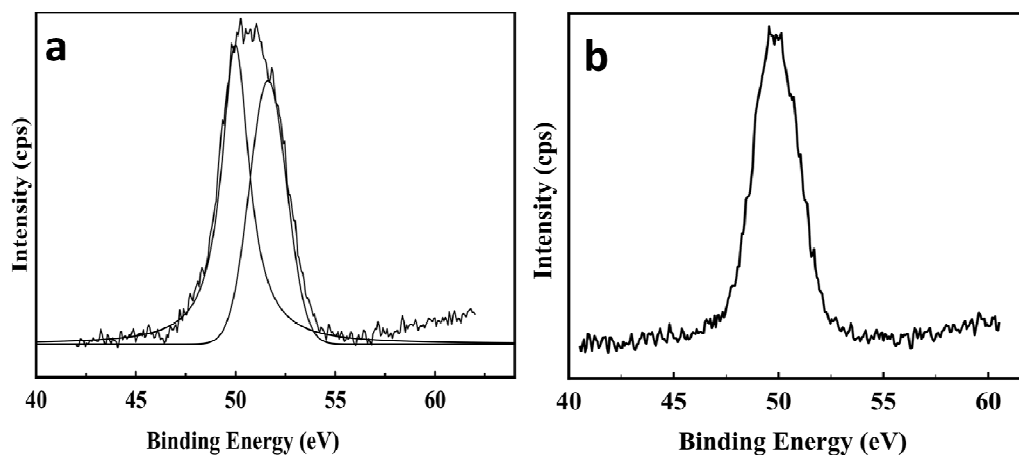


Fig. S8. XPS spectra of Mg nanowires. (a) High-resolution Mg 2p spectrum of as-prepared Mg nanowires showing two distinctive features at 49.9 and 51.7 eV, which correspond to metallic Mg and Mg<sup>2+</sup>, respectively. (b) after washing with copious amounts of THF, only one sharp peak characteristic of metallic Mg centered at 49.9 eV is observed.

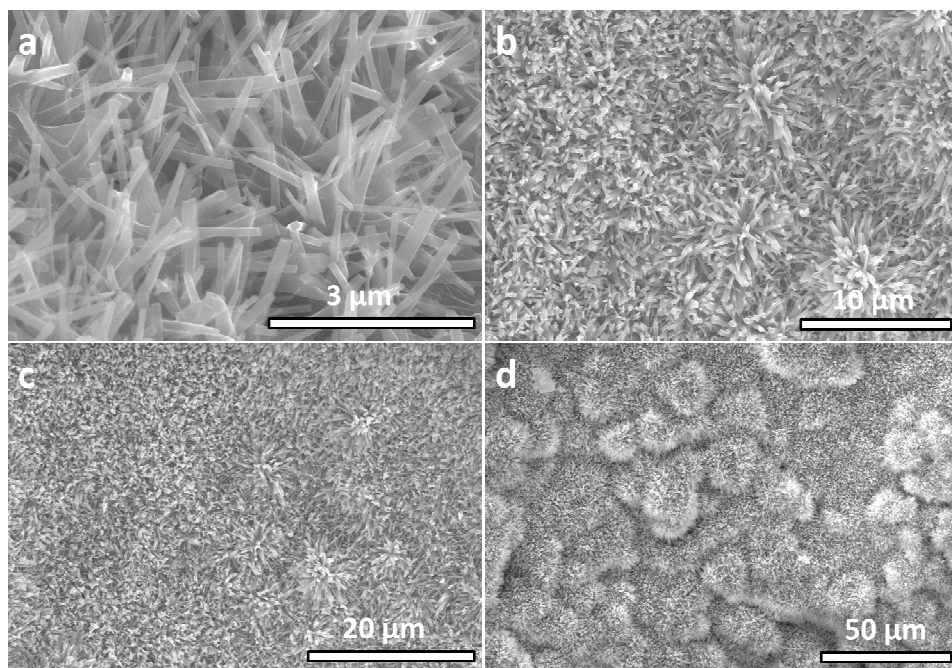


Fig S9. SEM images of samples collected after 1 h of deposition showing complete coverage of the electrode surface with Mg nanowires; (a)-(d) high to low magnification panoramic SEM images.

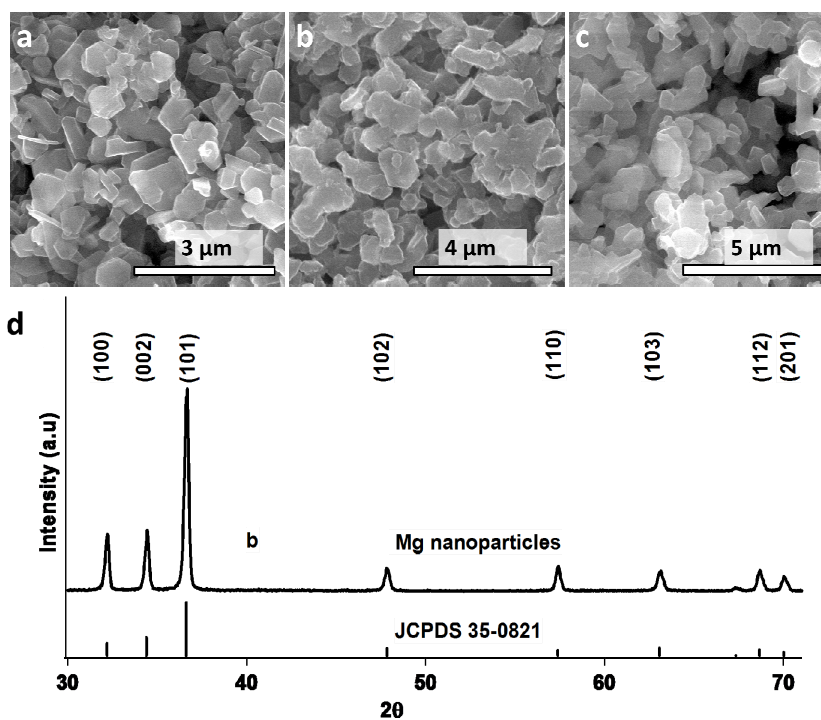


Fig. S10. SEM images of Mg nanostructures obtained *via* solution-phase lithium naphthalide reduction from (a) EtMgCl, (b) *n*-butylMgCl, and (c) phenylMgCl. (d) XRD pattern confirming phase identification for Mg nanoparticles grown using *n*-butylMgCl as the precursor.