Supplementary information for

Continuous Flow Synthesis of Plasmonic Magnesium Nanoparticles with Tunable Optical Properties from Grignard Precursors

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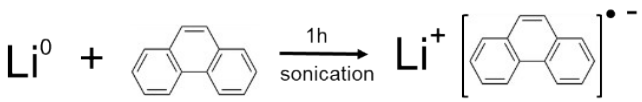
Materials

Lithium disks (99%), phenanthrene, poly(vinylpyrrolidone) (PVP, Mw = 10,000 g/mol), methylmagnesium chloride solution (methyl-MgCl, 3.0 M in THF), n-butylmagnesium chloride solution (n-butyl-MgCl, 2.0 M in THF), iso-butylmagnesium chloride solution (iso-butyl-MgCl, 2.0 M in THF), tert-butylmagnesium chloride solution (t-butyl-MgCl, 1.0M in THF), phenylmagnesium chloride solution (phenyl-MgCl, 2.0 M in THF), benzylmagnesium chloride solution (benzyl-MgCl, 2.0 M in THF), 2-methylallylmagnesium chloride solution (2-methylallyl-MgCl, 0.5 M in THF), anhydrous tetrahydrofuran (THF), anhydrous iso-propanol (IPA), and anhydrous acetone were purchased from Sigma-Aldrich and used as supplied. All glassware, including helical reactors, was washed with aqua 65% nitric acid, thoroughly rinsed DI water and dried overnight at 120°C.

Synthesis of colloidal Mg NPs

The reducing agent is prepared by mixing 0.104 g of lithium disks, 2.680 g of phenanthrene, and 60 mL of anhydrous THF in a 100 mL Schlenk flask under an Ar atmosphere and sonicating for 1 h, producing a dark green solution of Li-phenanthrene (LiPhen) radical anion complex:



(S1)

Note that 0.03 g of PVP is added to reducing agent to act as a capping ligand during Mg NPs synthesis, for a concentration of 0.5 mg/mL in the reducing agent. Mg NPs are then synthesised *via* continuous flow reduction of Grignard reagents with general formula R-Mg-X (where R – alkyl or aryl group; X- halogen) with freshly prepared LiPhen solution. In a typical experiment,

performed at room temperature, a 0.1 M solution of Grignard reagent in THF and a 0.25 M solution of freshly prepared LiPhen complex both in THF are continuously mixed in a T-mixer (inner diameter, i.d. = 0.5 mm), and co-fed at equal flow rates into a glass helical tubular reactor (i.d. = 1.5 mm, length, L = 3.2 m, helical diameter = 10 mm) to produce Mg NPs. The total flow rate is controlled within 2 to 8 mL/min by a Chemyx Fusion 200 syringe pump. The reactor outlet stream is continuously mixed with iso-propanol (IPA) or acetone in another T-mixer to quench unreacted Mg precursor and reducing agent and stop the reaction. Steady-state regime is assumed after the reaction was run for at least 3 times of the mean residence time, after which Mg NP samples are collected in a 2 mL centrifuge tubes. To remove the residual by-products the samples are cleaned by centrifugation and redispersion steps in anhydrous acetone, anhydrous THF and twice in anhydrous IPA.

Characterization of Mg NPs

Ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy was performed using a Thermo Fisher Evolution 220 spectrophotometer with Mg NPs suspended in IPA in polymethyl methacrylate cuvettes at room temperature.

Scanning electron microscopy (SEM) imaging of Mg NPs drop-cast on Si wafers was performed on a Zeiss Gemini SEM 300 operated at 5 kV with in-lens detector for secondary electron imaging. *NP size distributions were obtained by measuring at least 50 NPs with clearly visible edges from SEM images. The sizes measured were the longest dimension, e.g., the distance between opposite corners for a hexagonal platelet or a sphere diameter for faceted spheroids. Reported size polydispersities are the standard deviation of all measurements.*

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images, and STEM electron energy loss spectroscopy (STEM-EELS) maps of samples drop

cast on a Cu-supported lacey ultrathin carbon membrane were acquired at 200 kV on a FEI Osiris STEM with a Gatan Enfinium ER 977 electron spectrometer. STEM-EELS maps of the Mg bulk plasmon were produced by integrating the intensity of the spectrum image from 9.5 to 11.5 eV.

Powder X-ray diffraction (XRD) was performed using a Bruker D8 DAVINCI diffractometer equipped with a Cu Kα source and a position sensitive detector (LynxEye EX) in coupled theta/2theta mode, using a 0.01° step size. Samples were prepared by drop-casting a concentrated colloid of Mg NPs on to the centre of a Bruker Si low background sample holder. The background was subtracted using an automatic fitting and subtraction function in the DIFFRAC.EVA V7.2 software.

Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on Thermo Fisher Scientific iCAP 7400 Duo ICP-OES Analyzer. Prior to the analysis, Mg NPs were digested in an aqueous matrix using dilute nitric acid then diluted to ~1 ppm (mg/L) with deionised water.

Computational Fluid Dynamics

Fluid dynamic simulations of the helical reactor system were carried out using Ansys Fluent 2023 R2 to study diffusion in the THF solvent. The mixing simulations conducted for the fluid consisting of THF solvent containing a tracer at flow rates of 1, 2, 4, and 8 mL/min. The tracer was defined with the same physical properties than the solvent: density of 888 kg/m^3, viscosity of 0.00053 Pa·s, self-diffusion coefficient 3.33e-9 m^2/s, and a molecular weight of 72.11 g/mol. Note, the Mg solid concentration was neglected in the simulation due to its low concentration (<<0.1 M) in the system.

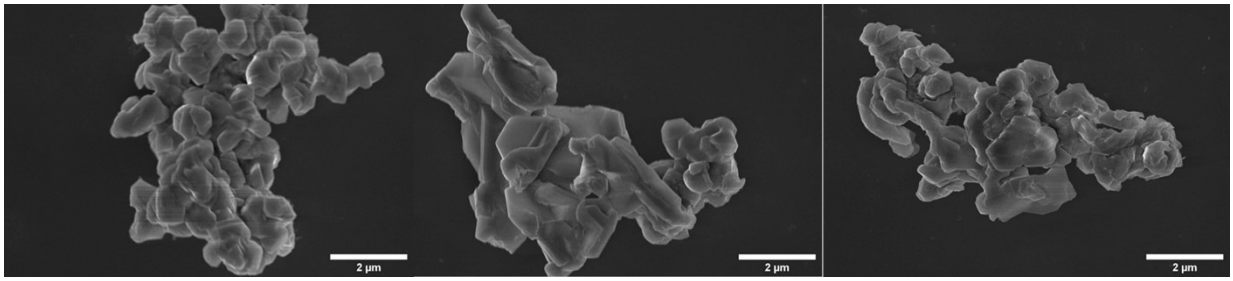


Figure S1. Representative SEM images of Mg particles synthesized by reduction of n-butyl-MgCl (1 mmol) with LiPhen (2.5 mmol) in THF in a batch reactor (reaction volume 12 mL); Reaction time, 5 min.

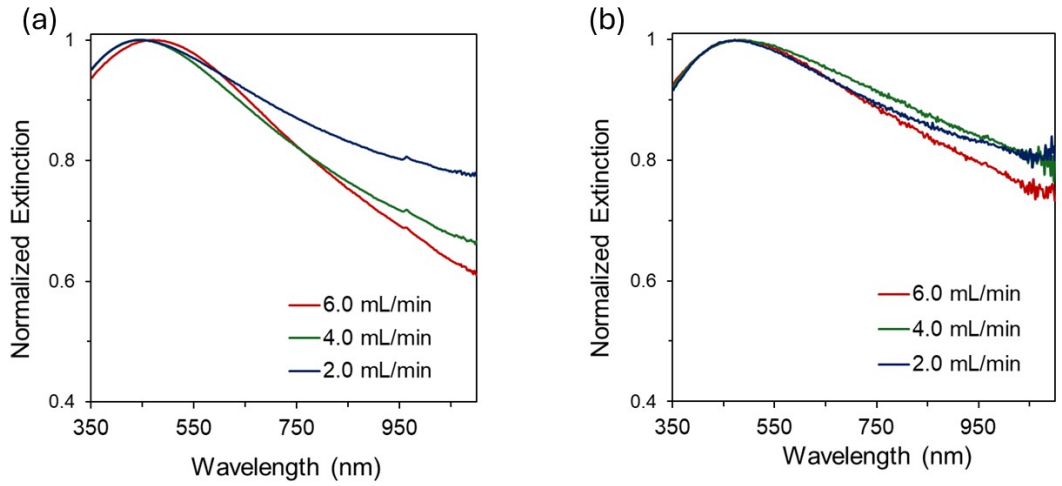


Figure S2. UV-Vis-NIR extinction spectra of Mg NPs produced from (a) n-butyl-MgCl; (b) methyl-MgCl. Solutions of Grignard reagent and LiPhen (in the presence of PVP) are mixed in a T-mixer and co-fed into a 3.2 m long helical microreactor at total flow rates of 6.0, 4.0, and 2.0 mL/min.

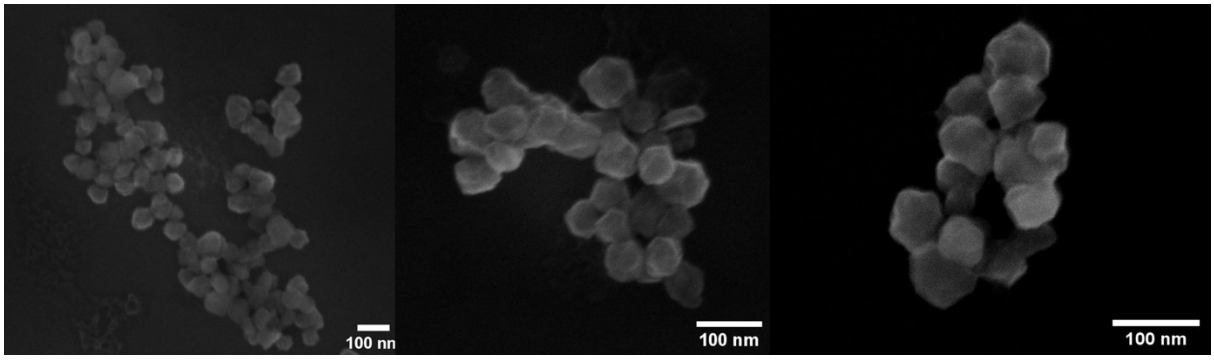


Figure S3. Representative SEM images of Mg NPs produced from Phenyl-MgCl. Solutions of Grignard reagent and LiPhen (in the presence of PVP) are mixed in a T-mixer and co-fed into a 3.2 m long helical microreactor at total rate of 6 mL/min with a 55 s residence time.

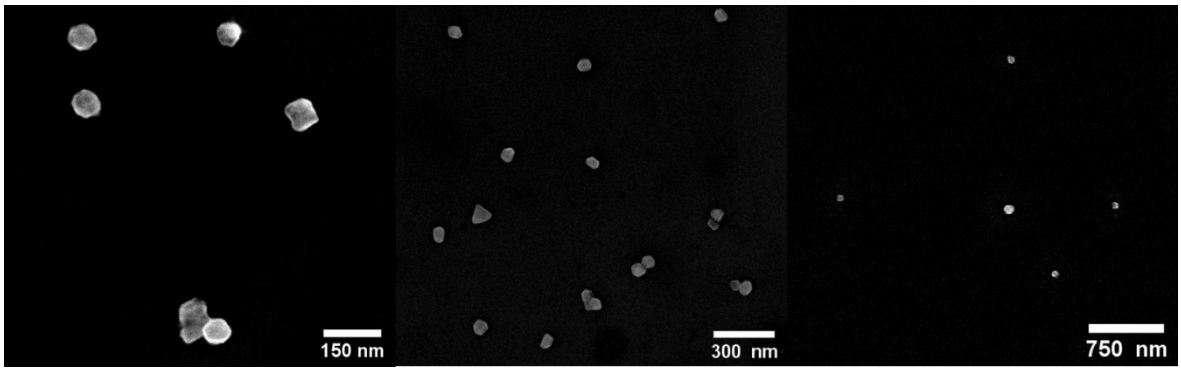


Figure S4. Representative SEM images of Mg NPs produced from Phenyl-MgCl and quenched with acetone. Solutions of Grignard reagent and LiPhen (in the presence of PVP) are mixed in a T-mixer and co-fed into a 3.2 m long helical microreactor at total rate of 2 mL/min with a 170 s residence time.

Table S1. Effects of flow rate and residence time on Mg yield synthesised in a 3.2 m long continuous flow microreactor with 6.0 mmol of phenyl-MgCl.

Flow rate, mL/min	Residence time, s	Yield, %
4	85	56
6	55	43
8	27	36

Table S2. Effect of the reactor length and total flowrate on the values of Dean and Reynolds numbers.

Reactor length, m	Flow rate, mL/min	Re	De
Reaction time 55 s			
3.2	6.0	134	76
2.0	3.75	83	83
0.65	1.22	32	18
Reaction time8 s			
3.2	4.0	89	50
2.0	2.5	55	31
0.65	0.8	21	12
Reaction time 170 s			
3.2	2.0	45	25
2.0	1.25	28	16
0.65	0.4	11	6