

Electronic Supplementary Information (ESI)

Liquid Metal Assisted Sonocatalytic Degradation of Organic Azo Dyes to Solid Carbon

Experimental Section

Material synthesis and preparation

Gallium and Galinstan (GalInSn fluid 4 N) were purchased from ThermoFisher Scientific Australia Pty Ltd. Methyl orange was obtained from May & Baker Ltd. Dagenham, England. Congo red was obtained from Edward Gurr, Ltd. Sulfuric acid (H₂SO₄, 98 %) was obtained from MERCK Pty Ltd. N,N-Dimethyl-p-phenylenediamine (97 %, 5g), and 1,4 – Benzoquinone (≥99.5 % (HPLC grade)), Eriochrome black T (ACS reagent, indicator grade) were purchased from Sigma Aldrich PTY LTD. Analytic grade EDTA disodium salt (AR (≥98.5 %)) was purchased from Asia Pacific Speciality Chemicals Limited. Ethanol (100 % undenatured) was purchased from Chem-Supply Pty Ltd. Deionized water (DIW, resistivity of 18.2 MΩ.cm at 25 °C) was prepared and purified in-house by the use of a Milli-Q reagent deionizer (Millipore).

Sonocatalysis degradation of methyl orange

In the preliminary investigation, sonocatalytic degradation of organic dye with LM (galinstan) was performed, various concentration of methyl orange was prepared from a stock solution of 100 ppm, then, a drop of galinstan (~ 199 mg) was fully immersed in the reaction vial. In each case, 5 mL of methyl orange was used in a bath sonicator (Soniclean Pty Ltd Soniclean 750HT, 220/240 V AC, 50/60 Hz, 380 W) and 10 mL was used with the probe sonicator (Branson Sonic Power Sonifier B-12, 220/240 V AC, 40 Hz, 150 W). The solution media was acidified by the addition of 10 µL [0.1 mM] sulphuric acid. The vials were then subjected to sonication at room temperature at varying durations of time depending on the sonicator configuration. After that, the colloidal suspension was allowed to settle and reform the liquid metal or centrifuged using a ThermoFisher Scientific Heraeus™ Multifuge™ X1 Centrifuge Series coupled with a ThermoFisher Scientific Fiberlite™ F15-8 x 50cy Fixed Angle Rotor at 8000 rpm for 20 minutes. The supernatant and any pellets were then separated using decantation technique. Investigations involving the use of liquid metal gallium were carried out at a temperature slightly above room temperature in an analogous fashion.

Materials characterization

Field emission SEM using in-lens secondary electron detector (FESEM, Zeiss Sigma VP equipped with an Oxford XMax 50 mm² Silicon Drift energy dispersive X-ray (EDX) detector) was used for SEM analysis. The samples' morphology and EDX results were obtained using a JEOL 7001F at an operating voltage of 3 KV and 20 KV, respectively. Transmission electron microscopy (TEM) images were obtained using a JEOL 2100 TEM at 200 keV, which is equipped with a silicon drift EDX detector (Oxford XMax 80 mm²) for compositional analysis and TVIPS TemCam F-Series camera for imaging. For X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., Manchester, U.K.) samples were cast on a clean glass substrate. A monochromatic Al Kα X-ray source (1486.7

eV) with 90° take-off angle (normal to the analyzer) was employed at 15 mA emission current, and wide scan with step size of 1.0 eV for 120s at pass energies of 200 - 1500 eV. The XPS data were analyzed using CasaXPS software version 2.3.19PR1.0, and the binding energy was calibrated to the standard adventitious carbon at 284.6 eV. Chemical composition and physical state of some materials were analyzed using Attenuated Total Reflectance, Fourier Transform Infrared Spectroscopy (ATR-FTIR, BRUKER, USA). The analysis was carried out in the range of 4000 – 375 cm^{-1} at resolution of 4 cm^{-1} and scanning frequency of 24. A HPLC Series 1100 with Column Heater and Fluorescence Detector (Hewlett Packard, Model 1100) was used for chromatography analysis. A Cary 60 UV-Visible spectrophotometer (Agilent Technologies) was used for UV-Vis spectroscopy. Raman spectra were collected using an Olympus BHSM microscope, equipped with 10 and 50× objectives and part of a Renishaw 1000 Raman microscope system that is also equipped with a monochromator, a filter system, and a charge-coupled device (CCD). Raman spectra were excited by a He-Ne laser (785 nm) in the range between 100 and 3200 cm^{-1} . Several acquisitions were used to improve the signal-to-noise ratio. Atomic force microscopy (AFM) images were taken using a Bruker Dimension Icon AFM powered by Nanoscope III in PeakForce mode configured to ScanAsyst in air while simultaneously collecting the height and phase data. NanoScope Analysis version 2.0 was used to treat images and analyse all material thickness. The sample was dispersed in filtered deionized water and drop-casted on clean mica wafer. In an LCMS experiment, each diluted sample was infused into the ESI source of the mass spectrometer following chromatographic separation of a 10 μL injection volume. The samples were analysed in full-scan mode (m/z 100-500), with a solvent blank (water) injected between samples. A detailed description of the instrument parameters can be found in reference [1]. Using a continuous flow injection of the MO standard into a 1:1 mixture of mobile phases A and B, the ESI source and mass spectrometer were first tuned to maximise the signal for MO (m/z 304.0761, $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_3\text{S}^-$). For this analysis, the sample was injected at 0.01 mL min^{-1} and the solvent flow was set to 0.3 mL min^{-1} .

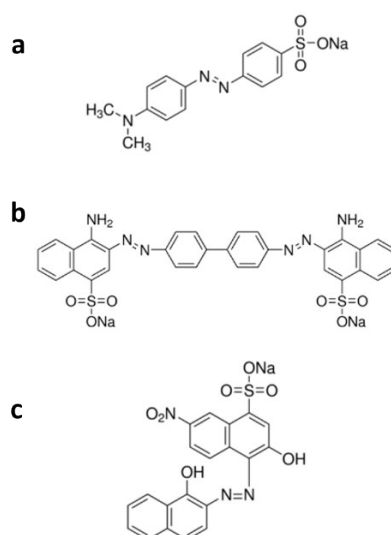


Figure S1. Chemical structures of (a) methyl orange, (b) congo red and (c) eriochrome black T.

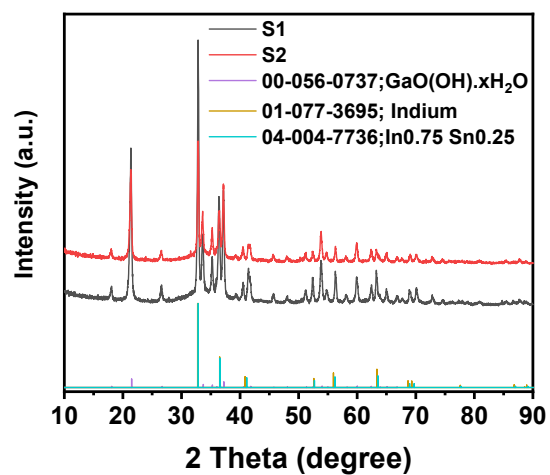


Figure S2. XRD patterns of the residue obtained from sonocatalytic degradation of methyl orange with liquid metal galinstan in acidified media after multiple runs.

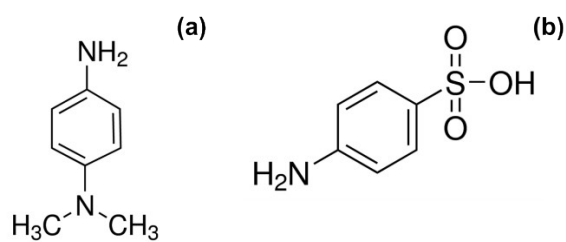


Figure S3. Chemical structure of (a) *N,N*-Dimethyl-*p*-phenylenediamine (DMPD), and (b) 4-aminobenzenesulfonate.

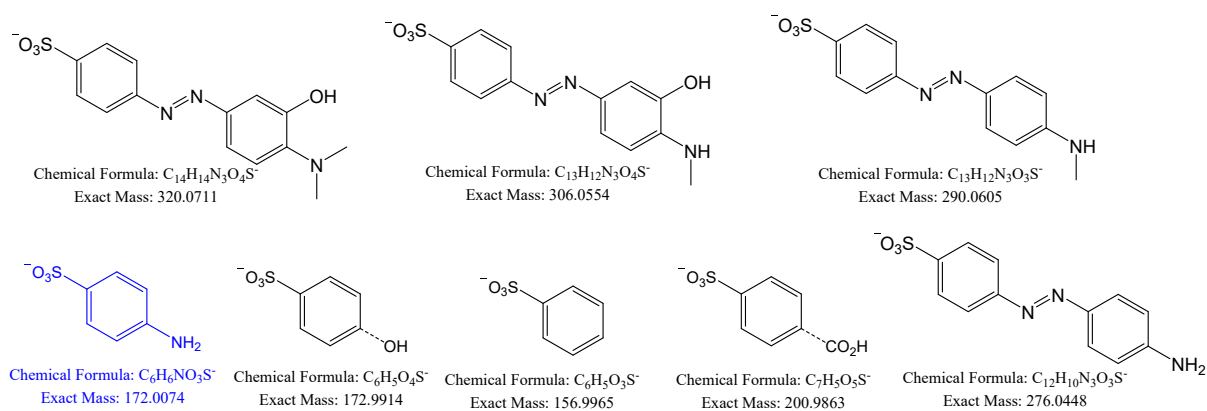
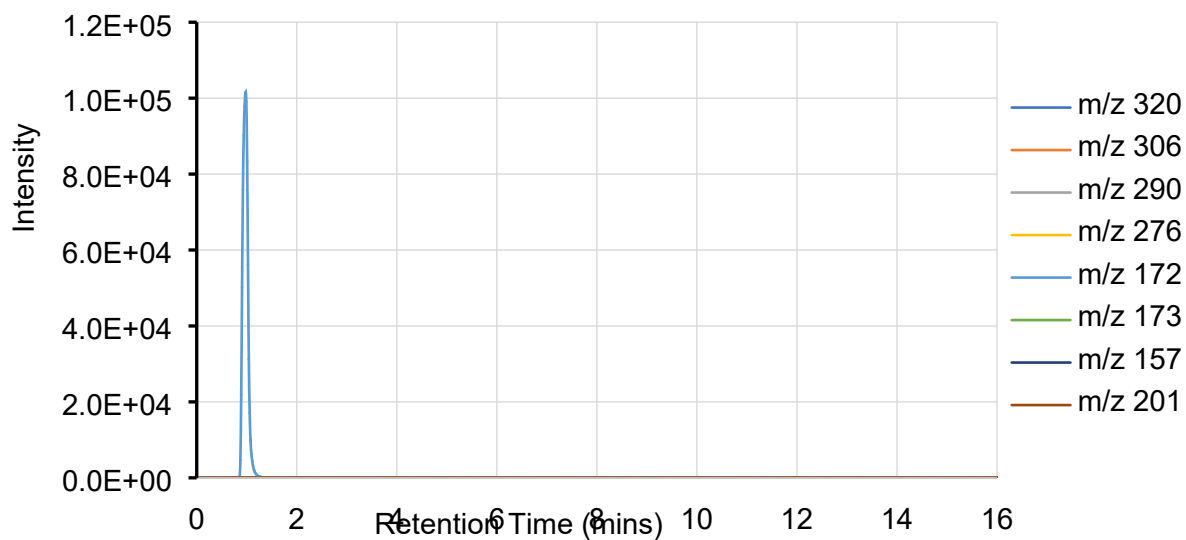


Figure S4: Extracted ion chromatograms of product ions in treated MO (75 ppm) where a series of degradation products were considered as discussed in reference 1.

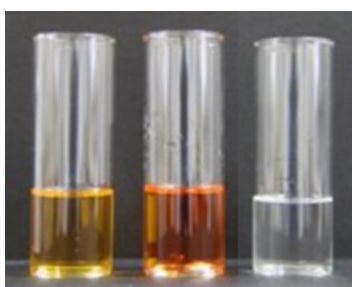


Figure S5. Digital images of solutions of 12.4 mg/L of MO and CR prior to catalysis and after sonocatalysis with liquid Ga (liquid catalyst was removed).

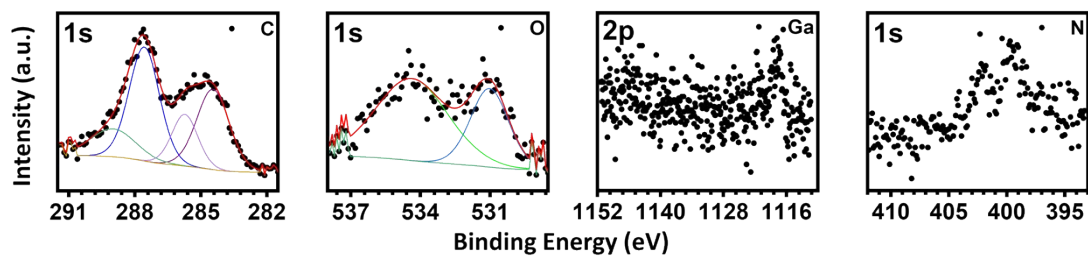


Figure S6. XPS spectra for C, O, Ga, and N after etching the sample.

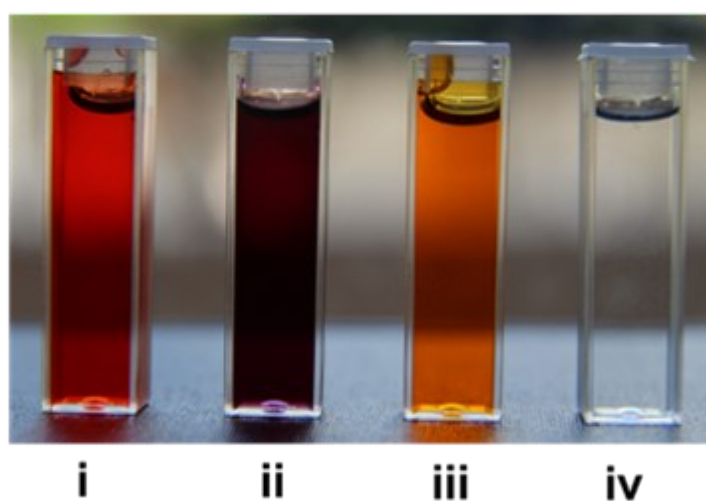


Figure S7. Digital images of 100 ppm (i) congo red, (ii) eriochrome black T, (iii) methyl orange and (iv) representative image of the supernatant obtained after sonication degradation.

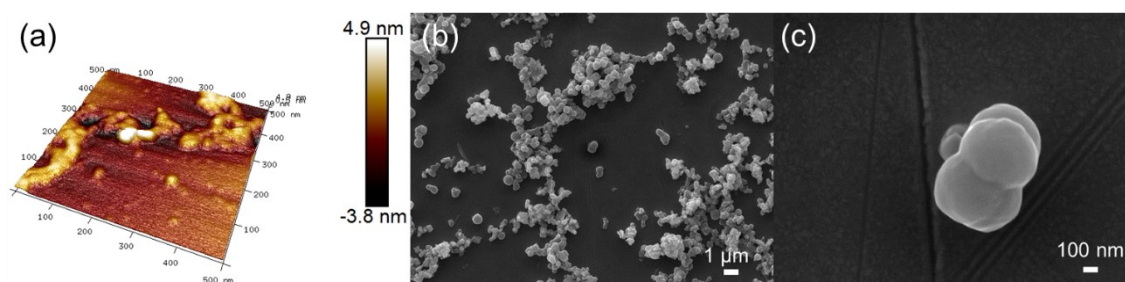


Figure S8. (a) AFM image and (b-c) SEM images of carbon particles obtained from sonocatalytic degradation of 100 mg/L of methyl orange.

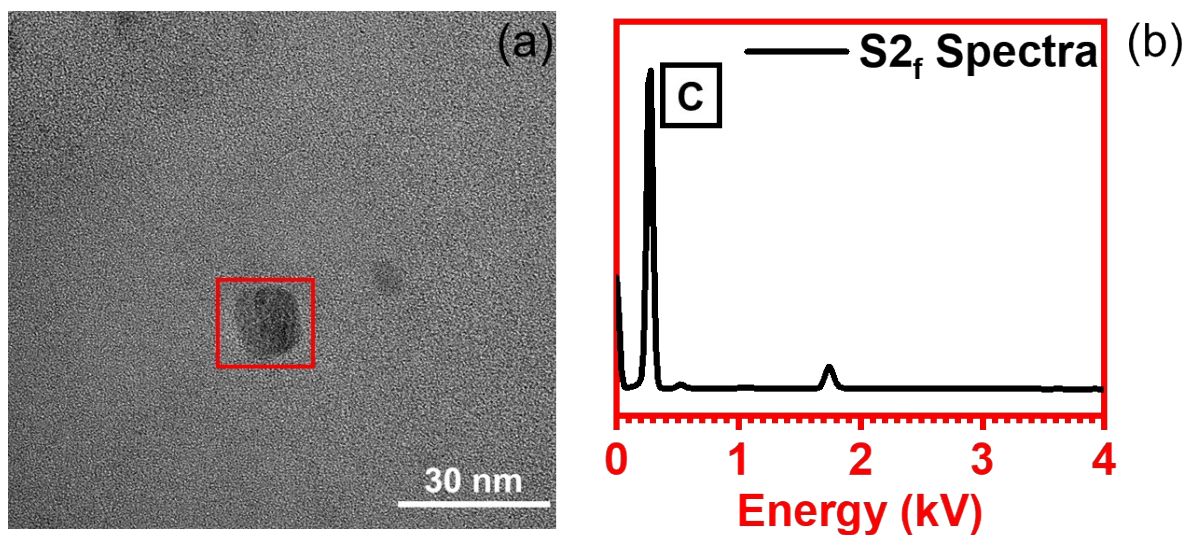


Figure S9. (a) TEM image for the 12.4 ppm MO-GaInSn degradation product, and (b) EDS analysis of the area marked red in (a).

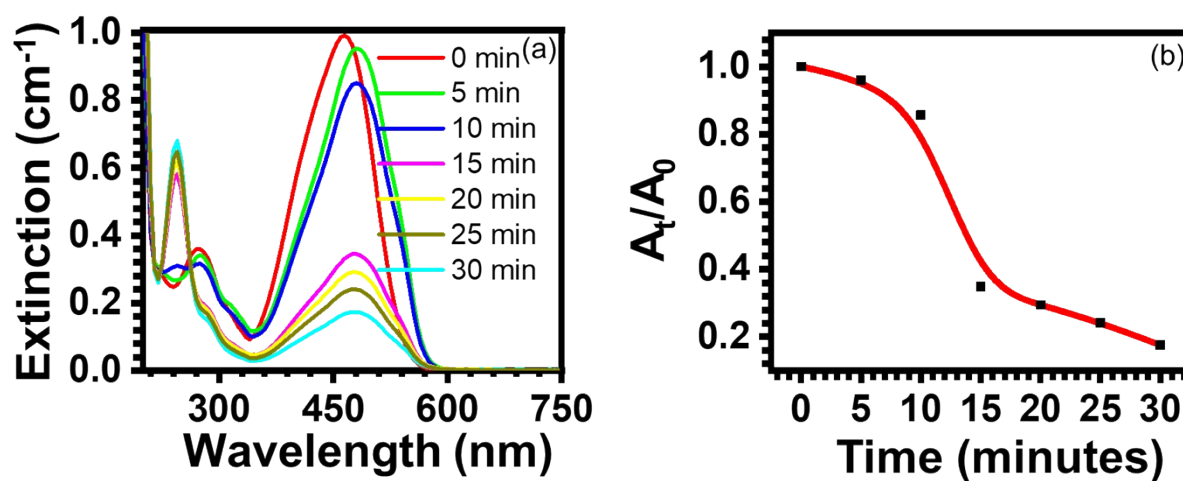


Figure S10. (a) UV-Vis spectra of 12.4 ppm MO recorded as a function of sonication time, and (b) plot of (A_t/A_0) versus time.

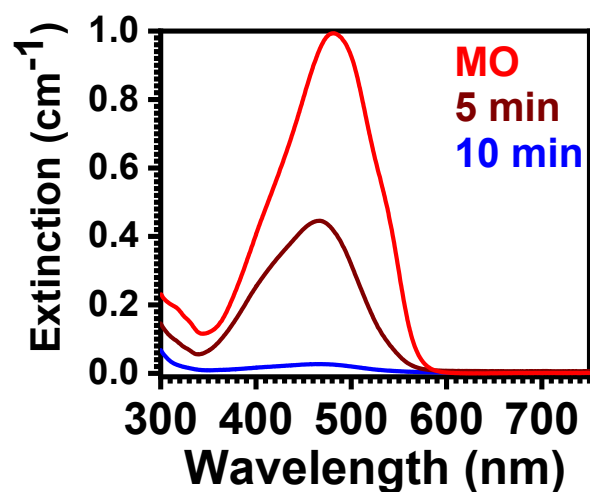


Figure S11. UV-Vis spectra of 12.4 ppm MO when a pre dispersed liquid metal catalyst was used for the reaction showing the absorbance of the solution after 5 and 10 min of sonication.

Table S1. Raman shift position and Intensity ratio (I_D/I_G) of the sample.

Sample	D-band (Lorentzian fit)		G-band (Lorentzian fit)		I_D/I_G
	Position cm^{-1}	FWHM cm^{-1}	Position cm^{-1}	FWHM cm^{-1}	
S2 _f	1361.82	155.77	1583.9	88.05	0.61

References

1. T. Chen, et al., J. Am. Soc. Mass. Spectrom., 2008, 10, 997.