

Generation of Catalytically Active Materials from a Liquid Metal Precursor

Faegheh Hoshyargar,^a Husnaa Khan,^a Kourosh Kalantar-zadeh,^b and Anthony P. O'Mullane^{*a}

^a School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia

^b School of Electrical and Computer Engineering, RMIT University, GPO Box 2476, Melbourne, VIC 3001, Australia

* Email: anthony.omullane@qut.edu.au.

Electronic Supplementary Information

Experimental:

Materials and chemicals

Potassium hexacyanoferrate (III) (potassium ferricyanide, $K_3Fe(CN)_6$, 99%), anhydrous sodium thiosulphate ($Na_2S_2O_3$, 98%), p-Nitrophenol (4-Nitrophenol, $O_2NC_6H_5OH$, 99%), sodium borohydride ($NaBH_4$, 99.99%), potassium dichromate ($K_2Cr_2O_7$, 99%), formic acid (CH_2O_2 , 95%), anhydrous sodium hydroxide (NaOH, 98%) and Gallium(III) chloride ($GaCl_3$, 99.999%) were all purchased from Sigma-Aldrich. Galinstan (Galinstan fluid 4N) was purchased from Geratherm Medical AG. All aqueous solutions were prepared using deionised water (resistivity of 18.2 M Ω .cm at 25°C) purified by use of a Milli-Q reagent deioniser (Millipore). Tin doped indium oxide (ITO) glasses (Corning® alkaline earth boro-aluminosilicate glass, 25×25×1.1 mm³, indium tin oxide coated one surface, $R_s = 5 - 15 \Omega$) were purchased from Delta Technologies, Ltd.

Preparation of the catalyst

The catalyst was prepared by dispersing galinstan in aqueous solutions in a sonication bath (Soniclean Pty. Ltd. Soniclean 750HT, 220/240V ac, 50/60Hz, 380W) for controlled durations. The mass of galinstan, the pH of the solution and the sonication time were systematically altered to achieve the fastest reaction rate for ferricyanide reduction with thiosulphate ions using concentrations of 0.1 M sodium thiosulphate and 1 mM potassium ferricyanide at $(25 \pm 2)^\circ C$ in a total reaction volume of 3 ml.

Surface characterisation

The catalyst was investigated by a Zeiss Sigma VP Field Emission Scanning Electron Microscope (FESEM) at an operating voltage of 20 kV under high-vacuum conditions equipped with an Oxford XMax 50 Silicon Drift (SDD) EDS detector. Dispersions of galinstan were drop casted onto cleaned

Si wafer and immobilised by solvent evaporation. Successive drop casting/wiping of DIW was employed to remove any NaOH residues.

Catalytic reactions

For the optimised ferricyanide reduction reaction 0.1 ml of the catalyst (prepared via sonicating 0.3 g of galinstan in 0.1 M NaOH for 30 min) was injected in the UV-vis cuvette containing 3 ml of the reaction solution (1 mM ferricyanide, 0.1 M thiosulphate and 0.1 M NaOH) and the reaction progress was successively measured by UV-vis spectroscopy using an Agilent Cary® 50 UV-Visible spectrophotometer.

The design of catalysts based on galinstan was also extended and optimised to other charge transfer reactions such as 4-Nitrophenol reduction. 5 ml of deionised water (DIW) was added into a glass vial containing 200 mg galinstan and the mixture was sonicated for 30 min. 0.1 ml of the resulting dispersion was injected into the reaction mixtures with a total volume of 3 ml (containing 0.1 mM 4-Nitrophenol and 0.1 M sodium borohydride or 0.2 mM potassium dichromate and 0.1 M formic acid) in quartz cuvette at $(25 \pm 2)^\circ\text{C}$ and the catalytic activity was monitored by UV-vis spectroscopy.

The control experiment with sodium gallate was achieved by using 0.02 M GaCl_3 made up in 0.1 M NaOH to generate $\text{NaGa}(\text{OH})_4$.

Electrochemical experiments

The immobilised galinstan electrode was prepared by drop casting the galinstan dispersion in DIW onto a cleaned ITO substrate at 200°C . Ag/AgCl and Platinum were used as reference and counter electrodes, respectively. The electrochemical experiment was carried out using a Biologic VSP-300 potentiostat. The galinstan coated ITO glass working electrode was immersed into a 0.1 M NaOH solution immediately before running the open circuit potential (OCP) *versus* time experiment. The OCP was run for 30 min to be consistent with the sonication time used in the preparation of the catalyst.

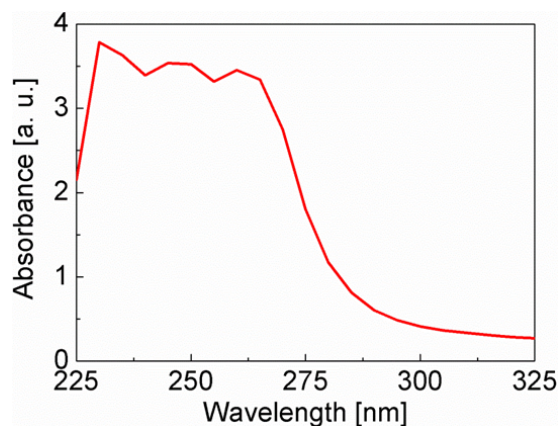


Figure S1. UV-vis spectrum of the catalyst prepared in 0.1 M NaOH via 30 min of sonication.

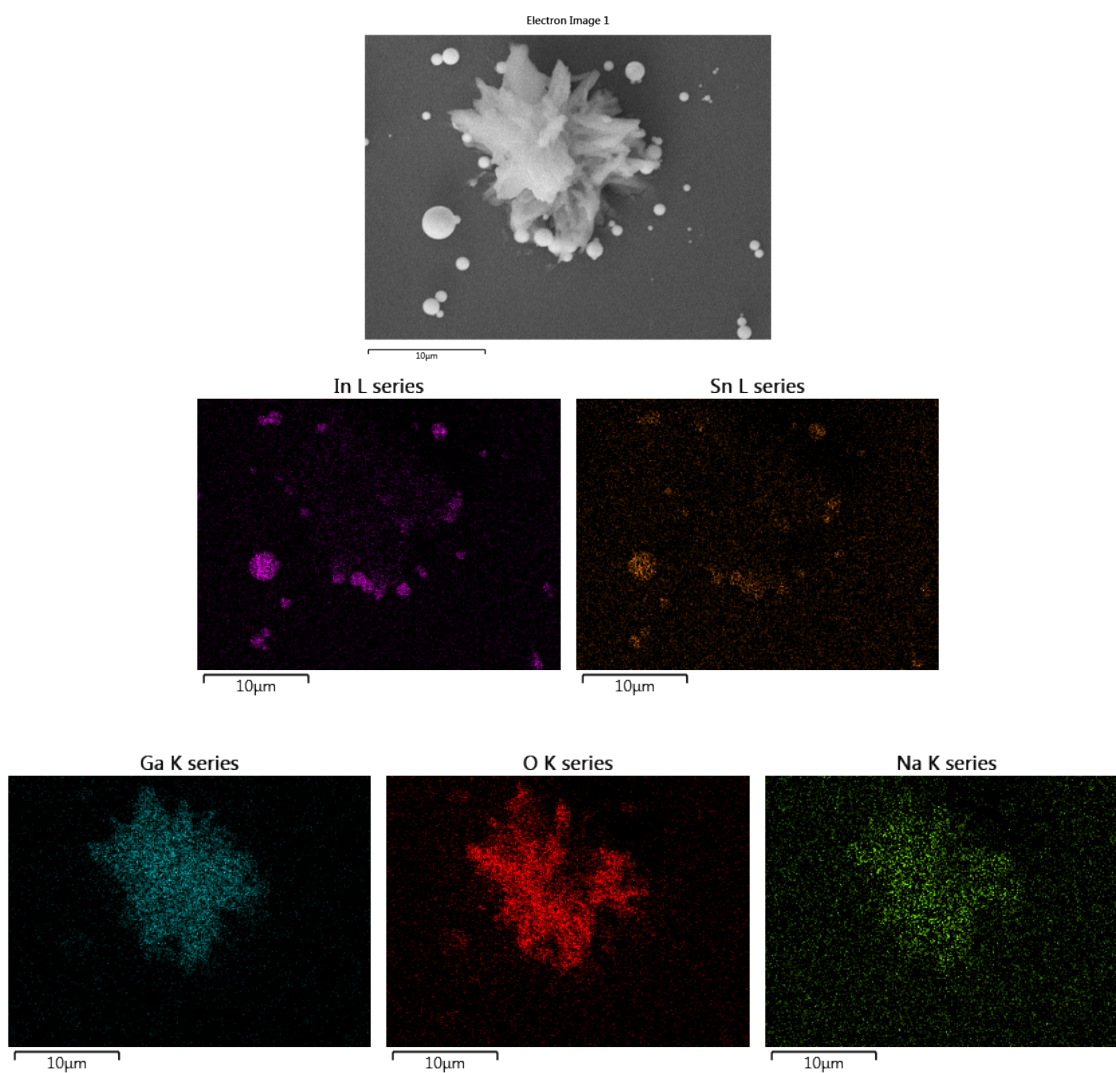


Figure S2. FESEM image and EDX mapping of the catalyst (prepared via sonicating 0.3 g of galinstan in 0.1 M NaOH) drop casted onto cleaned Si wafer.

It can be seen that the spherical microstructures are In:Sn whereas the central area consists of Na, Ga and O which indicates the crystallisation of $\text{NaGa}(\text{OH})_4$ from the drop casting procedure and solvent evaporation.

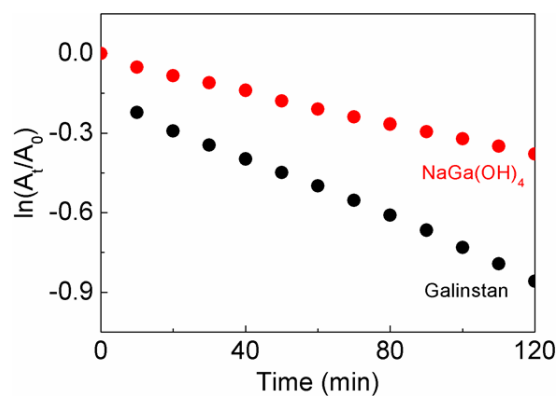


Figure S3. Plot of $\ln(A_t/A_0)$ versus time of the reduction of 1 mM $[\text{Fe}(\text{CN})_6]^{3-}$ with 0.1 M $\text{S}_2\text{O}_3^{2-}$ in the presence of soluble $\text{NaGa}(\text{OH})_4$ compared to the corresponding plot for galinstan.

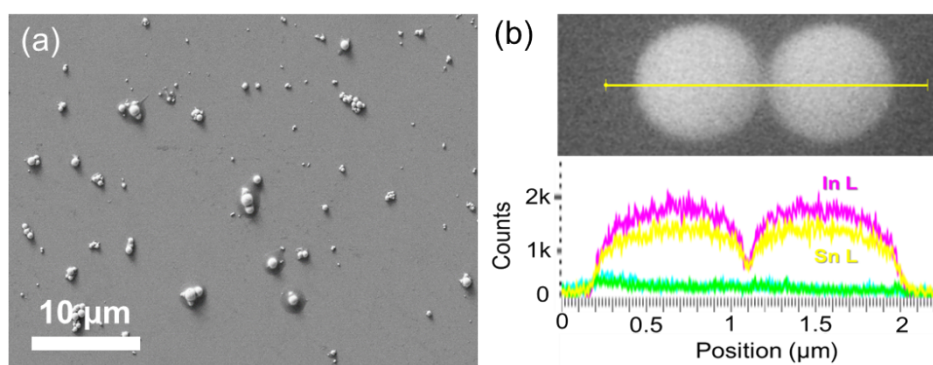


Figure S4. (a) FESEM image and (b) EDX profile across the microstructures shown in the high resolution SEM image of galinstan based microstructures created in 0.1 M NaBH_4 .

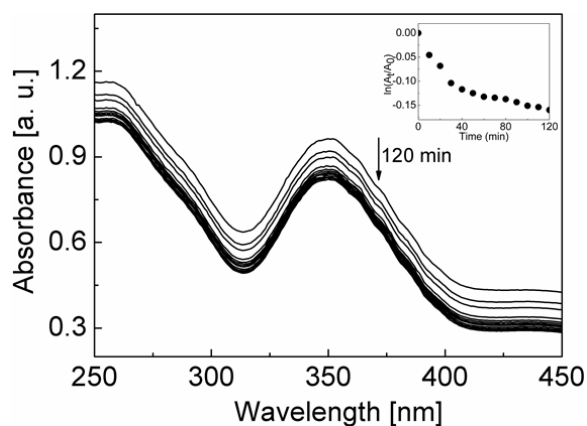


Figure S5. Time dependent UV-vis absorption spectra of the reduction of dichromate in the presence of galinstan based catalyst (inset: plot of $\ln(A_t/A_0)$ versus time).

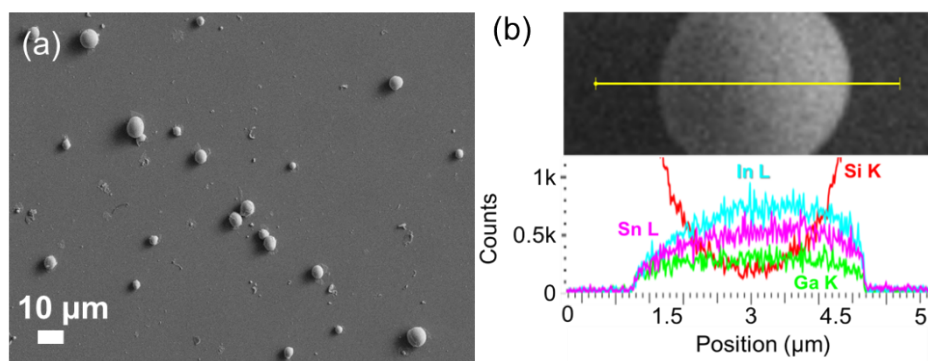


Figure S6. (a) FESEM image and (b) EDX profile across the microstructures shown in the high resolution SEM image of galinstan based microstructures created in 0.1 M formic acid.