

Supporting Information

Experimental Section

Synthesis of GO: The method due to Hummers and Offeman was adopted to prepare GO from graphite powder (10–20 micron) supplied by Graphite India Limited, Bangalore, India. One gram of graphite powder was added to 23 ml of cooled (0°C) concentrated H₂SO₄. Three grams of KMnO₄ was added gradually with stirring and cooling, so that the temperature of the mixture was maintained below 20 °C. The mixture was then stirred at 35 °C for 30 min. Forty six millilitres of distilled water was slowly added to cause an increase in temperature to 98°C and the mixture was maintained at that temperature for 15 min. The reaction was terminated by adding 140 ml of distilled water followed by 10 ml of 30% H₂O₂ solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulphate could not be detected with BaCl₂, then washed 3–4 times with acetone and dried in an air oven at 65°C overnight.

Synthesis GO-platinum intermediate: 10 mg of GO was dispersed in 50 ml of toluene by sonication. To this GO dispersion, 30 mg of chloroplatinic acid, 400 µl of oleylamine and 200 µl of oleic acid were added and the mixture was stirred and refluxed for an hour.

Synthesis of Ru intermediate: 25 mg of Ru chloride and 200 µl of oleylamine was added to 25 ml of toluene and stirred at 60 °C for 1 hour. At the end of one hour, a dark green solution is obtained.

Synthesis of G/Pt and G/PtRu nanoparticle composite: To 50 ml of GO – platinum intermediate solution, 50 mg of sodium borohydride dissolved in 50 ml of methanol is added with stirring. The black solid that precipitates at the end of the reaction was repeatedly washed with acetone and dried at room temperature. This results in G/Pt nanoparticle composite. To 50 ml of GO – platinum intermediate solution, 10.1 ml of the Ru-intermediate solution is added with stirring and continued stirring for one hour. At the end of one hour 144 mg of sodium borohydride dissolved in 50 ml of methanol is added with stirring. The black solid is processed as explained above. This results in G/PtRu nanoparticle composite.

Characterization and electrochemical measurements: All the samples were characterized by powder X-ray diffraction (pXRD) using a Philips X'pert Pro diffractometer (Cu K α radiation, secondary graphite monochromator, 2° 2 θ per min), infrared (IR) spectroscopy uses a Nicolet IR200 FTIR spectrometer (KBr pellets, 4 cm⁻¹ resolution), thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). XPS data were collected in a ThermoScientific Multilab 2000 instrument, and the binding energies are with respect to

graphitic carbon C1s at 284.5 eV. The binding energy is accurate to within ± 0.1 eV. Transmission Electron Microscopy (TEM) images were recorded with FEI Tecnai T20 at an accelerating voltage of 200kV which is equipped with an Energy Dispersive X-ray Spectrometer. The electrochemical characterisation of G/Pt and G/PtRu nanoparticle composite is carried out using cyclic voltammetry (CV) in a conventional three electrode system (PG26250, Techno Science Instrument) where SCE (saturated calomel electrode) is used as the reference electrode, and a platinum foil is used as the counter electrode.

Electrochemical preparation: 10 mg of graphene-nanoparticle composite is mixed with 20 mg of nafion, isopropyl alcohol is added to the mixture followed by sonication for 15 minutes to make a catalyst ink. The catalyst ink is coated on a 0.5 cm x 0.5 cm area on a graphite sheet. The electrodes are dried and weighed after drying. For gravimetric analysis, we have calculated the platinum content in the nanocomposites.

Electrochemical measurements: A conventional cell with a three electrode configuration was used for all experiments. A glass cell of about 70 mL capacity with suitable ground-glass joints to introduce a working electrode, Pt foil auxiliary electrodes, and a saturated calomel electrode (SCE) as reference was used for electrochemical studies. All solutions were prepared using doubly distilled water. Potential values are reported against SCE. Electrochemically active surface area (ECSA) of Pt nanoparticles was calculated from hydrogen electrosorption curve, which was recorded between 0 and +1.2 V in 1 M H₂SO₄ solution. To measure methanol electrooxidation reaction activity, cyclic voltammetry was performed between -0.2 and +1.0 V in a mixing solution containing 2 M CH₃OH and 1 M H₂SO₄. The scan rate was set at 40 mV s⁻¹.

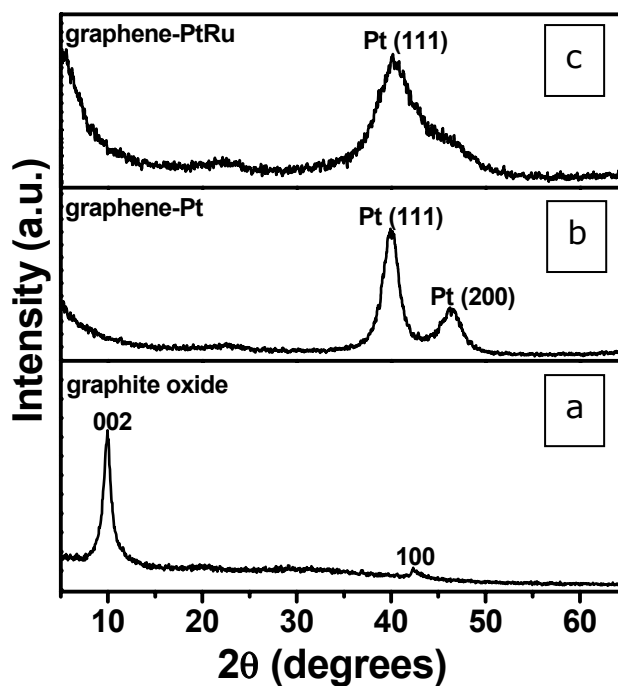


Figure S1 XRD patterns of pristine GO (a), graphene –Pt (b) and graphene – PtRu (c) nanocomposite.

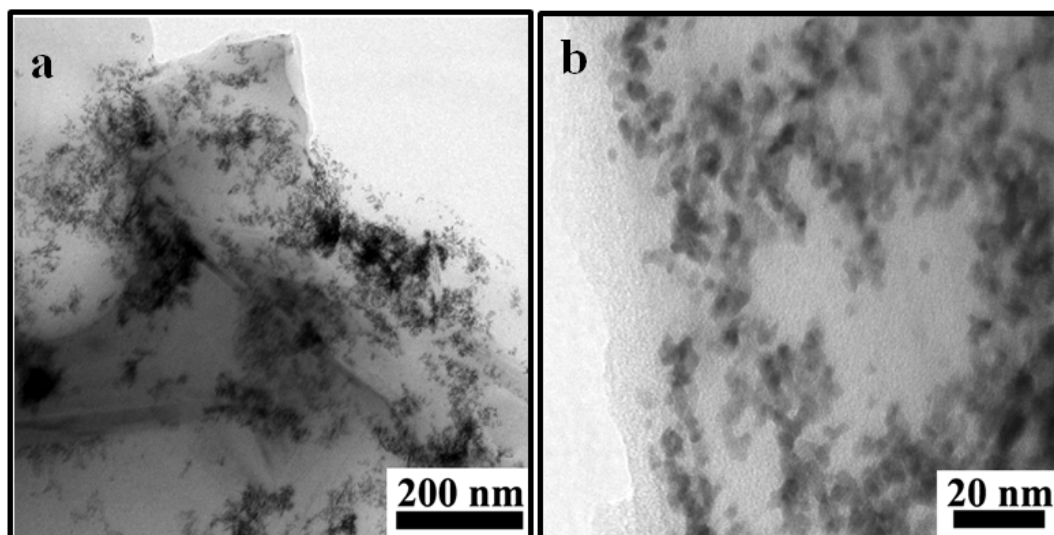


Figure S2 (a) Low and (b) high magnification bright-field TEM images of Pt nanoparticles on graphite sheets.

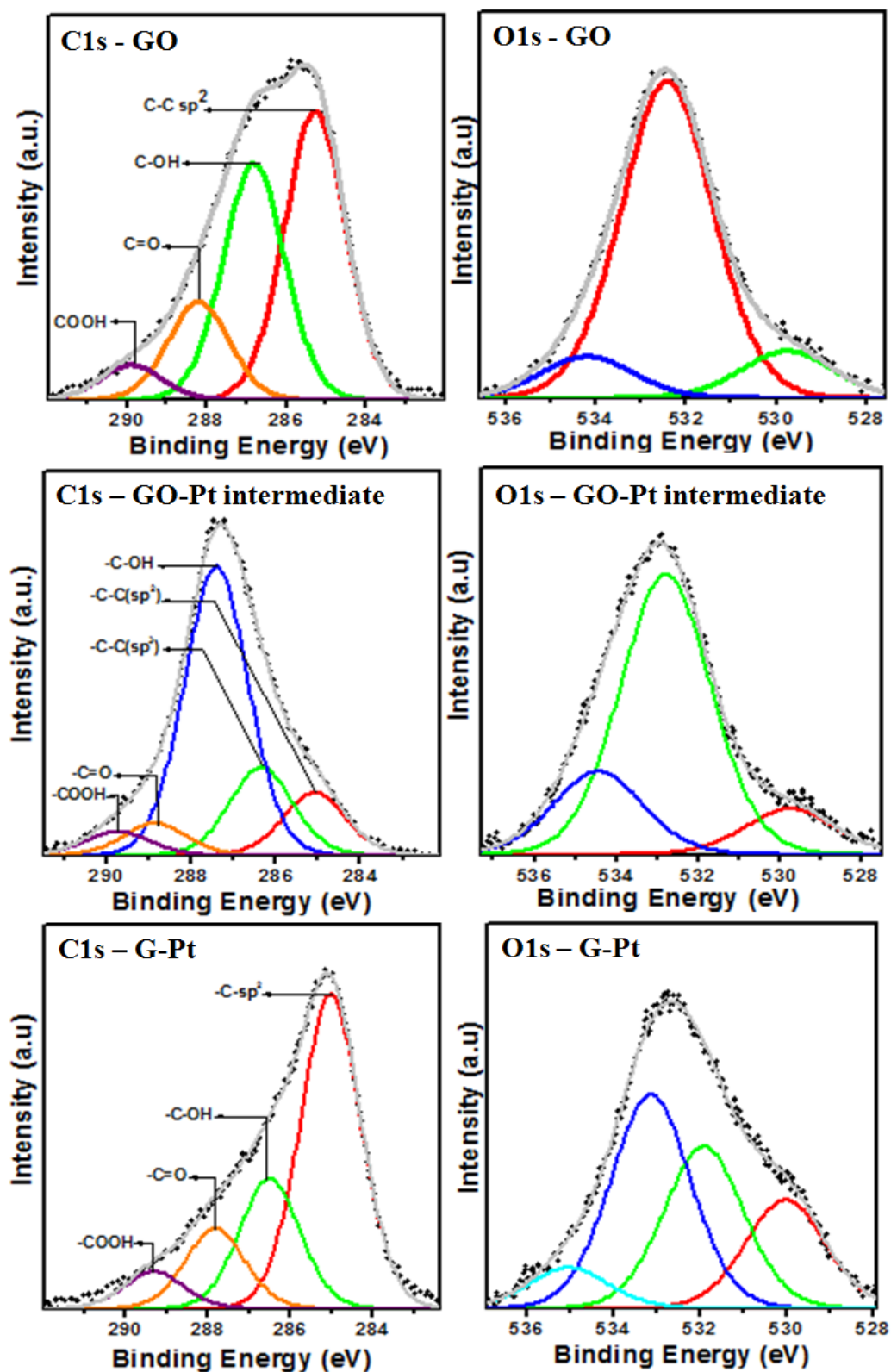


Figure S3 C1s and O1s core level XPS spectra of pristine GO, GO-Pt intermediate and G-Pt.

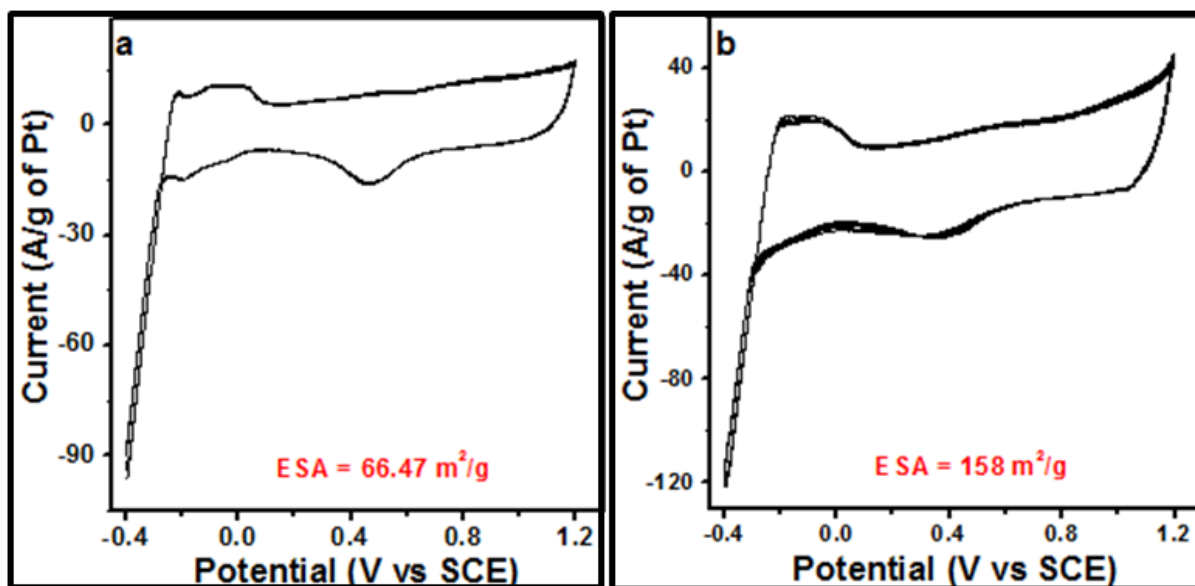


Figure S4 The ECSA of G-Pt (a) and G-PtRu (b) was measured from cyclic voltammograms in 1 M H₂SO₄ with a scan rate of 40 mV s⁻¹.