Electronic Supplementary Information (ESI)

One pot aqueous synthesis of nanoporous Au₈₅Pt₁₅ materials with surface bound Pt islands: An efficient methanol tolerant ORR catalyst

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Materials used:

High purity analar grade of silver nitrate, tetrachloroaurate trihydrate, trisodium citrate decahydrate, sulphuric acid, methanol were purchased from SISCO Research Laboratories Pvt. Ltd., India. Potassium tetrachloroplatinate (II) hexahydrate (99.9%) (K₂PtCl₄.6H₂O), sodium borohydride (99.9%) (NaBH₄), Nafion[®] 117 solution in low aliphatic alcohols (5% solution) and Nafion[®] 117 membrane were procured from Sigma-Aldrich Pvt. Ltd., India. Gas diffusion layer (GDL) sheets were purchased from SAI Energy Solutions Pvt. Ltd, India. Vulcan XC-72 carbon and HiSPECTM Platinum (20 wt% Pt) supported on carbon and HiSPECTM Platinum–Ruthenium (20 wt%) supported on carbon were purchased from Alfa Aesar Pvt. Ltd., India. Oxygen (99.9%) (O₂) and Nitrogen (99.9%) (N₂) were supplied by Indian Oxygen limited, India. All glass wares were cleaned using aqua regia. Millipore water was used for all the preparative work.

Characterization of nanoparticles:

Optical SPR spectra of $Au_{100-x}Ag_{2x}$ and $Au_{100-x}Pt_x$ aqueous sols were recorded using an Agilent diode array spectrophotometer (model 8543). Alloy compositions of NPs were determined by using inductively coupled plasma-mass spectrometry (ICP-MS)

Thermo Fisher ICPMS-series-2. Powder x-ray diffraction (PXRD) patterns of NPs were recorded by employing a advanced Bruker X-ray diffractometer (model D8) with Cu K-alpha radiation (λ =1.5406Å). Low angle x-ray diffraction (LAXRD) patterns were measured using Rigaku RU 300 X-ray diffractometer with a goniometer radius of 217.5 mm. X-ray photoelectron spectroscopy analysis of the NPs were studied by a Multilab 2000 (Thermo Fisher scientific) X-ray photoelectron spectrometer, fitted with a twin anode X-ray source using Mg K-alpha radiation (1253.6 eV). The size and morphology of the NPs were studied using transmission electron microscopy (TEM) with the aid of FEI Tecnai G2 20 (200keV). HAADF-STEM images and elemental mapping of NPs were imaged by employing JEOL-2100F (200 keV) field emission electron microscope. CV and LSV studies of nanoporous catalysts were performed using an Autolab potentiostat galvanostat (model PGSTAT-30) along with rotating disk electrode (RDE) setup. Meticulously polished glassy carbon electrode (BAS; geometric area: 0.007 cm²) and GC RDE (Metrohm; geometric area: 0.0314 cm²) were used as working electrode for CV and ORR studies. Platinum wire served as the counter electrode and mercury/mercurous sulphate (1.0 N H₂SO₄) (MMS) is used reference electrode. The background electrolyte was aqueous solution of 1.0 N H₂SO₄.For CV and MOR studies, the electrolyte were purged with pure N₂ in order to remove all the dissolved oxygen. In contrast, the oxygen purged electrolyte was used for ORR and in addition, the electrolyte was spiked with required amount of methanol for methanol tolerant ORR studies.

Sample preparation for ICP-MS:

The $Au_{100-x}Ag_{2x}$ and $Au_{100-x}Pt_x$ NPs were dissolved in aqua regia. After evaporating the excess acid, the resulting contents were dissolved in dilute HNO₃ and analysed by ICP-MS. The values of 'x' as calculated from ICP-MS data were found to be proportional to the concentrations used in the preparative steps.

Synthesis of Au_{100-x} Ag_{2x}/C and Au_{100-x}Pt_x/C materials:

Vulcan XC-72 carbon (10 mgs) was added to each of the centrifuged $Au_{100-x}Ag_{2x}$ and $Au_{100-x}Pt_x$ suspensions, and vigorously stirred for one hour. A nearly transparent supernatant solution indicates the complete adsorption of NPs on carbon matrix. The resulting $Au_{100-x}Ag_{2x}/C$ and $Au_{100-x}Pt_x/C$ solutions was centrifuged, thoroughly washed with water and dried in vacuum oven at room temperature for further analysis like PXRD, XPS, CV, LSV etc.

Electro-catalyst ink preparation for CV and LSV studies:

The Au_{100-x}Pt_x electrocatalyst for both GC and GC-RDE was prepared by mixing 250 ml of H₂O and 50 μ l of Nafion (5 wt %) to 2.0 mg of Au_{100-x}Pt_x catalyst. The mixture was ultrasonicated for 10 minutes and a 10 μ l of catalyst ink was coated on GC. The modified GC containing the electrocatalyst was allowed to dry in vacuum at room temperature for three hours. This GC was used as working electrode for CV and LSV studies.

Membrane electrode assembly (MEA) for full cell studies:

HiSPEC Pt-Ru/C (0.5 mg/cm²) was used as anode material and Nanoporous $Au_{85}Pt_{15}/C$ catalyst (1.0 mg/cm²) was used as cathode material. The ink was prepared using adequate amount of the catalysts with NAFION solution in Isopropanol: Ethanol mixture (1:1) and sonicated well to get a stable suspension. The catalyst ink was coated on commercial GDL sheets by brush coating and dried. Then GDL sheets (anode and cathode) were placed on either side of the Nafion membrane, hot pressed at 90°C for 3 minutes and assembled in a prototype fuel cell for testing the performance.

Table S1: X-ray diffraction data for $Au_{100-x}Ag_{2x}$ and $Au_{100-x}Pt_x$ nanomaterials showing the crystallite size and lattice constant values.

Compositions	$Au_{100-x}Ag_{2x}$ nano-alloys		$Au_{100\text{-}x}Pt_x$ nanomaterials	
	Crystallite Size (nm)	Lattice constant values	Crystallite Size (nm)	Lattice constant values
X=5	6.14	4.050	5.54	4.062
X=10	5.54	4.053	5.17	4.061
X=15	4.60	4.066	5.16	4.046
X=20	4.35	4.068	5.10	4.041

$Au_{100-x}Ag_{2x}$	Total	no. of	No. of S	lurface	Pt atoms	Relative ECSA	
nano-alloys	atoms		atoms		required to		
					replace Ag		
	Au	Ag	Au	Ag		Au	Pt
x=5	9115	959	1775	187	480	0.73	0.27
x=10	8242	1832	1605	357	916	0.49	0.51
x=15	7446	2628	1450	512	1314	0.43	0.57
x=20	6716	3358	1308	654	1679	0.41	0.59

Table S2: Number of atoms calculations for $Au_{100-x}Ag_{2x}$ and $Au_{100-x}Pt_x$ nanomaterials with their relative ECSA values.



Figure S3. (a) SPR spectra for $Au_{100-x} Ag_{4x}$ (x=15) alloy nanoparticles, (b) SPR of the same ($Au_{85}Ag_{60}$ alloy NPs) after replacement with x moles equivalent of H₂PtCl₆ solution, (c) SPR of $Au_{85}Ag_{60}$ alloy NPs after Br₂ etching.



Figure S4. SPR spectra of porous Au nanoparticles formed by Br_2 etching from $Au_{100-x} Ag_{2x}$ alloy NPs (a-d) at x= 20, 15, 10, 5 respectively.



Figure S5. (A) TEM image, (B) selected area electron diffraction (SAED) pattern, (C) simulated SAED pattern and (D) SAED intensity profiles showing the d-values of $Au_{85}Ag_{30}$ alloy NPs.



Figure S6. (A) TEM image, (B) selected area electron diffraction (SAED) pattern, (C) simulated SAED pattern and (D) SAED intensity profiles showing the d-values of nanoporous $Au_{85}Pt_{15}$ materials.



Figure S7. TEM image of $Au_{85}Pt_{15}/C$ catalyst showing the dispersion of nanomaterials on Vulcan XC-72 carbon.



Figure S8. LSV studies showing the ORR graphs of $Au_{85}Pt_{15}/C$ catalyst coated on GC-RDE at different rpms (100, 200, 400, 800, 1600 (a-e)) under O₂ saturated conditions in 1.0 N H₂SO₄ electrolyte.



Figure S9. Polarization curves showing the steady state performance with its current and power densities using nanoporous $Au_{85}Pt_{15}/C$ as cathode material and Commercial PtRu/C as anode material at different temperatures under Methanol (2M) and air (300 ml/min).