

## **Supplementary Information**

**Electro-catalytically active Au@Pt nanoparticles for Hydrogen evolution reaction: An insight into Tryptophan mediated supramolecular interface towards a universal core-shell synthesis approach.**

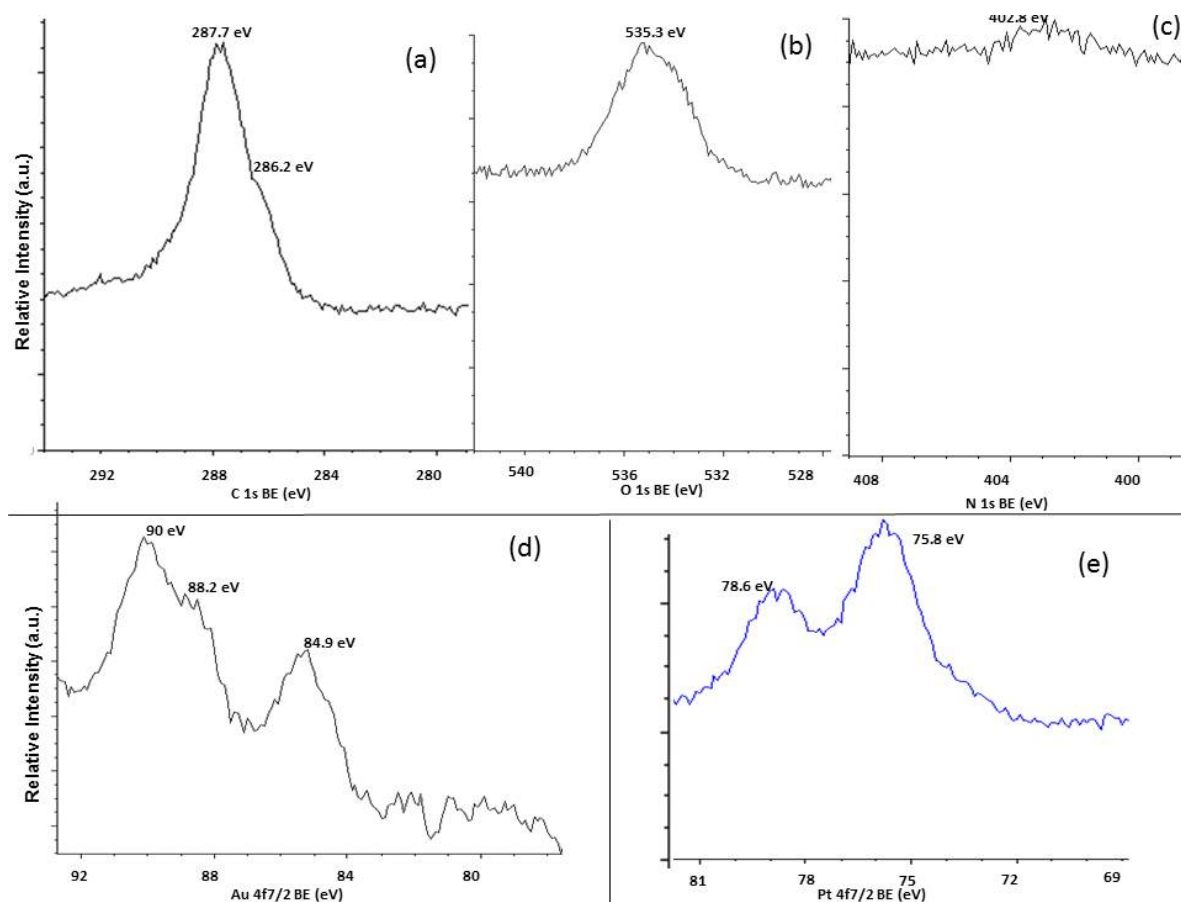
**Sarvesh Kumar Srivastava<sup>a</sup>, Jonathan Sabaté del Río<sup>b</sup>, Ciara K. O'Sullivan<sup>b,†</sup>, Chiaki Ogino<sup>a</sup>, Akihiko Kondo<sup>\*a</sup>**

<sup>a</sup> Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada, Kobe, 657-8501, Japan; E-mail: [akondo@kobe-u.ac.jp](mailto:akondo@kobe-u.ac.jp); Tel & Fax: +81-78-803-6196.

<sup>b</sup> Nanobiotechnology & Bioanalysis Group, Department of Chemical Engineering, Universitat Rovira i Virgili, Avinguda Països Catalans, 26, Tarragona 43007. Spain

<sup>†</sup> ICREA, Passeig Lluís Companys 23, 08010 Barcelona, Spain

E-mail: [ciara.osullivan@urv.cat](mailto:ciara.osullivan@urv.cat) Tel: +03-49-775-5840



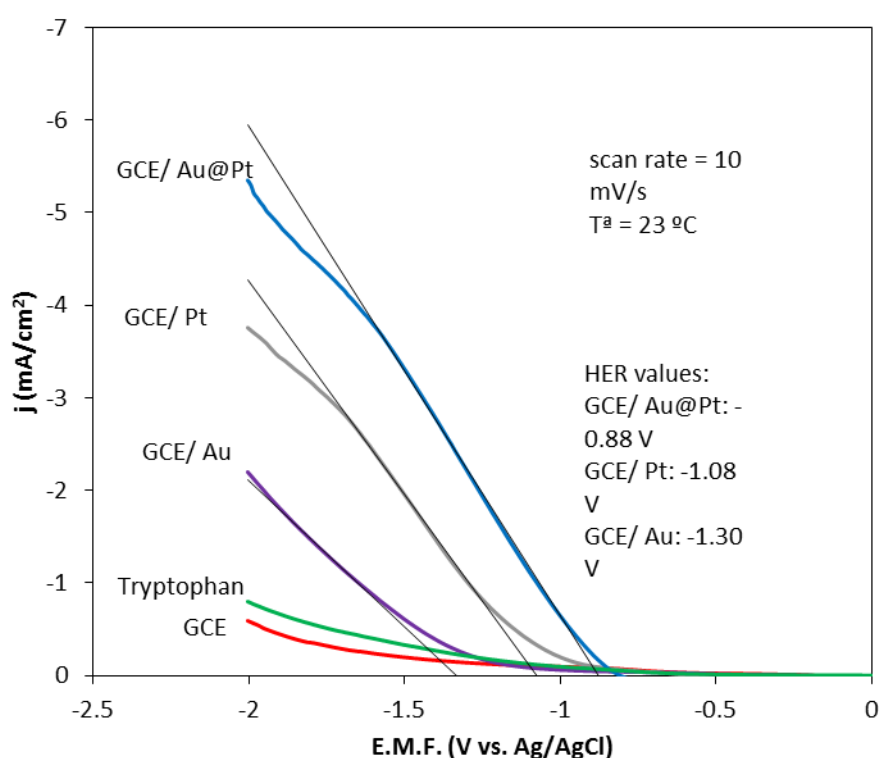
**Figure S1.** XPs spectra of (a) C1s, (b) O1s, (c) N1s, (d) Au 4f, (e) Pt 4f

Surface analysis for Au@Pt bimetallic NPs was also carried out using X-ray photoelectron spectroscopy (XPS) obtained from JEOL JPS9010 MC photoelectron spectrometer operating at 10 kV and 30 mA to generate (Al)K $\alpha$  radiation. The results obtained were analyzed by SpecSurf ver. 1.7.3.9 software.

Resulting Au@Pt nanoparticles were subjected to XPS analysis (figure S2) to confirm the underlying surface composition. Au core was denoted at 88.2 eV and 84.9 eV representing Au 4f 5/2 and Au4f 7/2 component respectively confirming bulk metal (Au) in the reaction mixture. Also, a prominent peak for Au at 90 eV was observed which can be attributed to the electrostatic charging around the metallic cluster due to the polymerizing action of Trp. Metallic shell of Pt was observed at 78.6 eV and 75.8 eV. Since, Trp was the only active chemical agent used in this reaction, interesting observation was made when C1s, O1s and

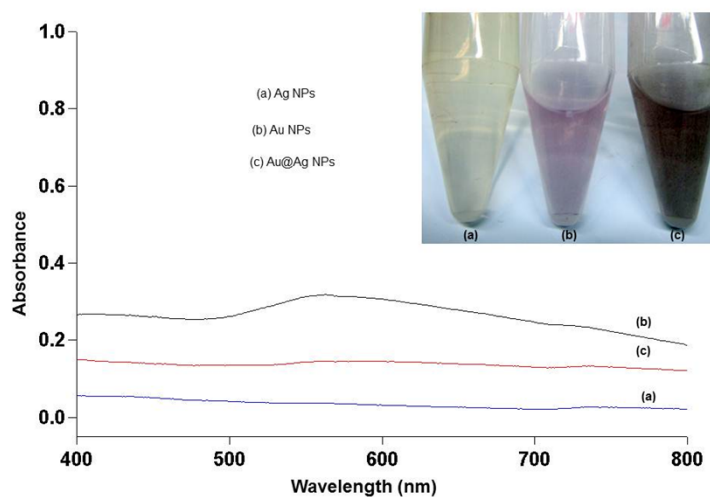
N1s XPS spectra of Au@Pt were observed (amino and carboxyl ends). C1s spectra doublet showed the presence of carboxyl group at 286.2 eV along with probable presence of amine carboxyl (NH-C=O) peak at 287.7 eV.

Also, N1s spectra showed remarkable presence of NH<sub>4</sub>Cl (402.3 eV) in the reaction mixture. Peak shifting and broadening can be attributed to the prominent presence of oxygenated groups at 535.3 eV as is the case in carbonyl, carboxyl and oxygenated metallic species.

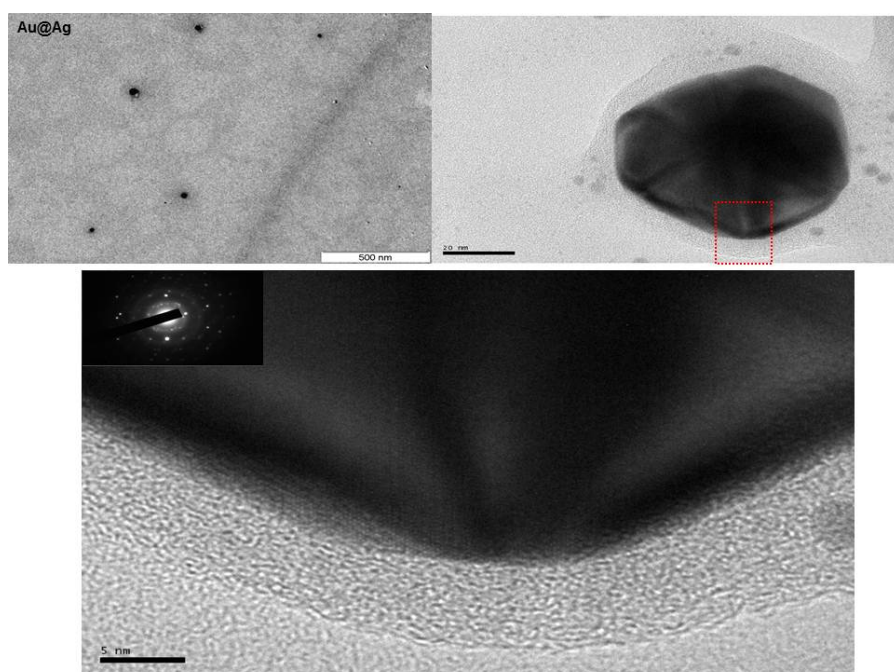


**Figure S2.** Polarization curves for the hydrogen evolution reaction on GCE, free Trp, Au NPs, Pt NPs and Au@Pt NPs between 0 V and -2 V vs Ag/AgCl at a scan rate of 10 mV/s in 90 mM Tris-HCl buffer, pH 8.0

**Au@Ag NPs**

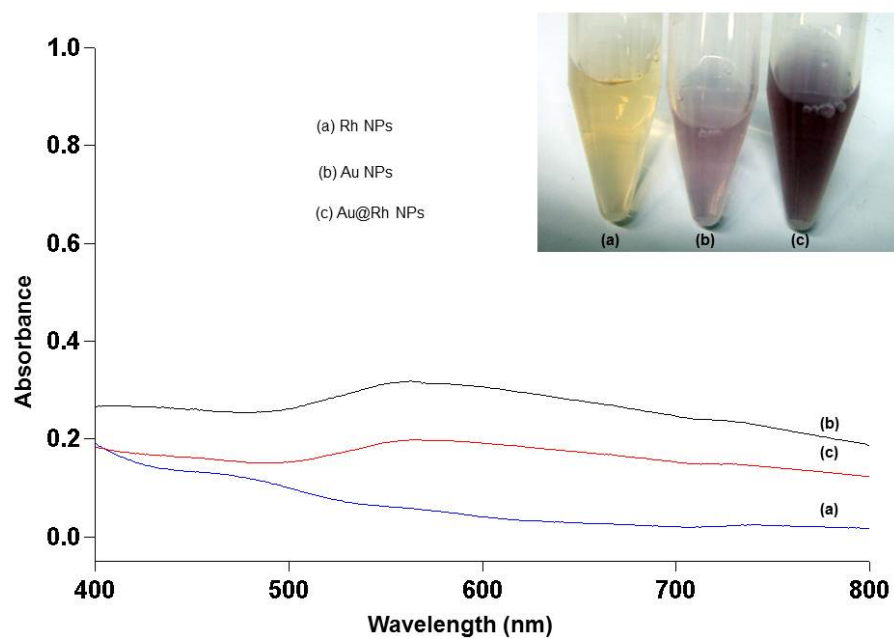


**Figure S3.** Visible spectra of Au, Ag and Au@Ag nanoparticles. Inset image depicting observed color in each of the above mentioned reaction mixture.

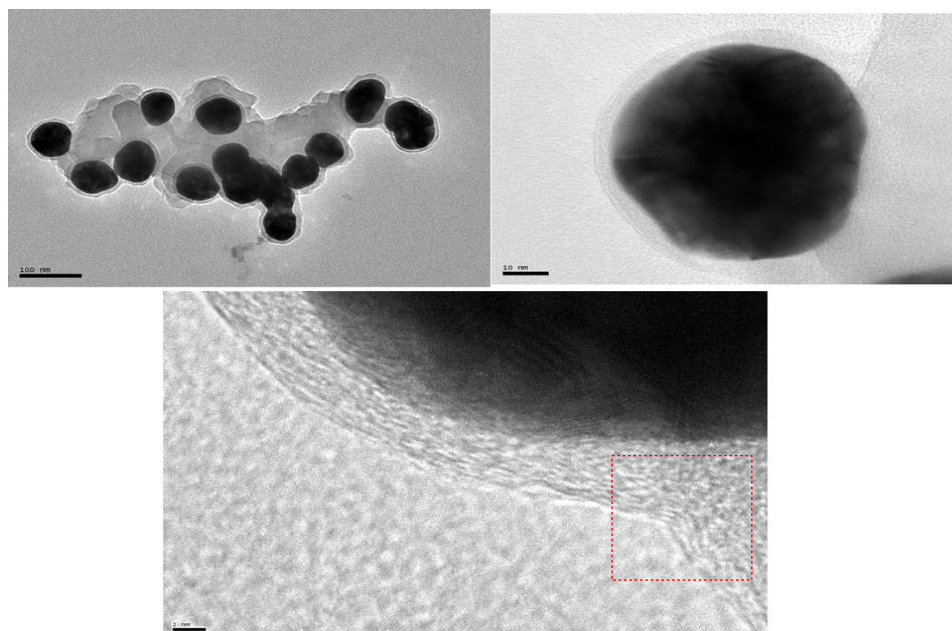


**Figure S4.** TEM images of Au@Ag NPs clearly depicting the core-shell boundary interface. Inset image confirms the crystalline Au (111) core.

**Au@Rh NPs**



**Figure S5.** Visible spectra of Au, Rh and Au@Rh nanoparticles. Inset image depicting observed color in each of the above mentioned reaction mixture.



**Figure S6.** TEM images of Au@Rh NPs. Highlighted area of the boundary interface clearly depicts Au (111) lattice fringes.