Supporting Information

Plasmonic Substrates Comprising Gold Nanostars efficiently regenerate cofactor molecules

Ana Sánchez-Iglesias,^a Javier Barroso,^b Diego M. Solís,^c José M. Taboada,^d Fernando Obelleiro,^c Valery Pavlov, ^b Andrey Chuvilin^{e,f} and Marek Grzelczak^{a,f*}

^a Bionanoplasmonics Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia-San Sebastián, Spain; ^b Biosensing Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia-San Sebastián, Spain; ^c Departamento de Teoría de la Señal y Comunicaciones, University of Vigo, 36301 Vigo, Spain; ^d Departamento de Tecnología de los Computadores y de las Comunicaciones, University of Extremadura, 10003 Cáceres, Spain; ^e CIC nanoGUNE Av. De Tolosa 76, 20018 Donostia-San Sebastián, Spain; ^f Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain.

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1. Characterization of initials nanoparticles



Figure S1. Low Resolution TEM image of the initial (a-c) and Pt-coated (d-f) gold nanoparticles with cubic (a,d), rod-like (b,e) and star-like (c,f) shapes.





Figure S3. HRTEM characterisation and strain analysis of Pt-coated cubes and rods. HRTEM analysis together with lattice spacing analysis confirmed epitaxial growth of Pt on gold surface.

2. Optical Modelling.



Figure S4. Parameterisation of nanoparticles with differently distributed Pt on the gold surface. These models were used for the simulation of the extinction cross section of the particles disperse in colloidal phase. The outcome spectra are presented in Figure 2 in the main manuscript.

3. Photochemistry



Figure S5. Time dependent NADH photoregeneration on plasmonic substrates containing nanoparticles of different shapes.



Figure S6. UV-vis-NIR spectra of the solution containing Pt-coated gold nanoparticles of different shapes in water (black) and in TEAOH (red) showing blueshift of the LSPB.

4. Photoelectrochemistry.



Figure S7. Low-resolution SEM images showing fragment of working electrodes covered with Ptcoated nanoparticles of different shapes, (a) cubes, (b) rods, (c) stars. In all samples the particles formed coffee ring, bright regions visible on the left part of the images. Scale bars in the left panel is 100 µm while in right is 500 nm.



Figure S8. I-t curves obtained from the electrode coated with bare nanoparticles. The electrodes were immersed in a solution containing TEAOH (1M), phosphate buffer (pH8) and irradiated with light (400-1200 nm, 150 mW/cm²) at 0 V at 25 °C. Each electrode contained the same amount of nanoparticles in term of metallic gold.



Figure S9. I-t curve obtained from an empty electrode. The electrode was immersed in the solution containing TEAOH (1M), phosphate buffer (pH8) and irradiated with light (400-1200 nm, 150 mW/cm^2) at 0 V at 25 °C.



Figure S10. SEM images of the electrode after photoelectrochemical characterisation, showing morphological stability of the nanoparticles.

5. XPS analysis of the plasmonic substrates.



Figure S11. XPS spectra showing the presence of Au $4f_{7/2}$ and Pt $4f_{7/2}$ peaks in all samples. The ration between these two peaks served to estiamte the relative amoutn of the Pt on the particles surface.

6. SEM characterisation of substrates covered with gold nanorods and nanostars.



Figure S12. SEM image of plasmonic substrate containing gold nanorods (upper) and gold nanostars (lower).