

## Supporting Information

# Dark Field Scattering Spectroelectrochemistry Analysis of Hydrazine Oxidation at Au NPs Modified Transparent Electrodes

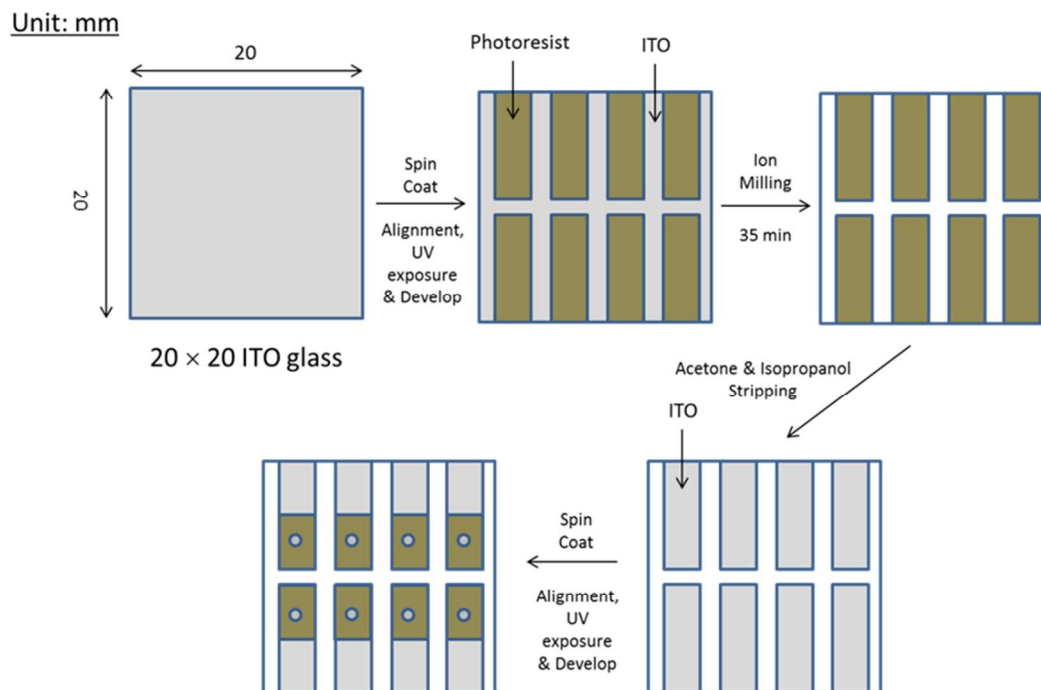
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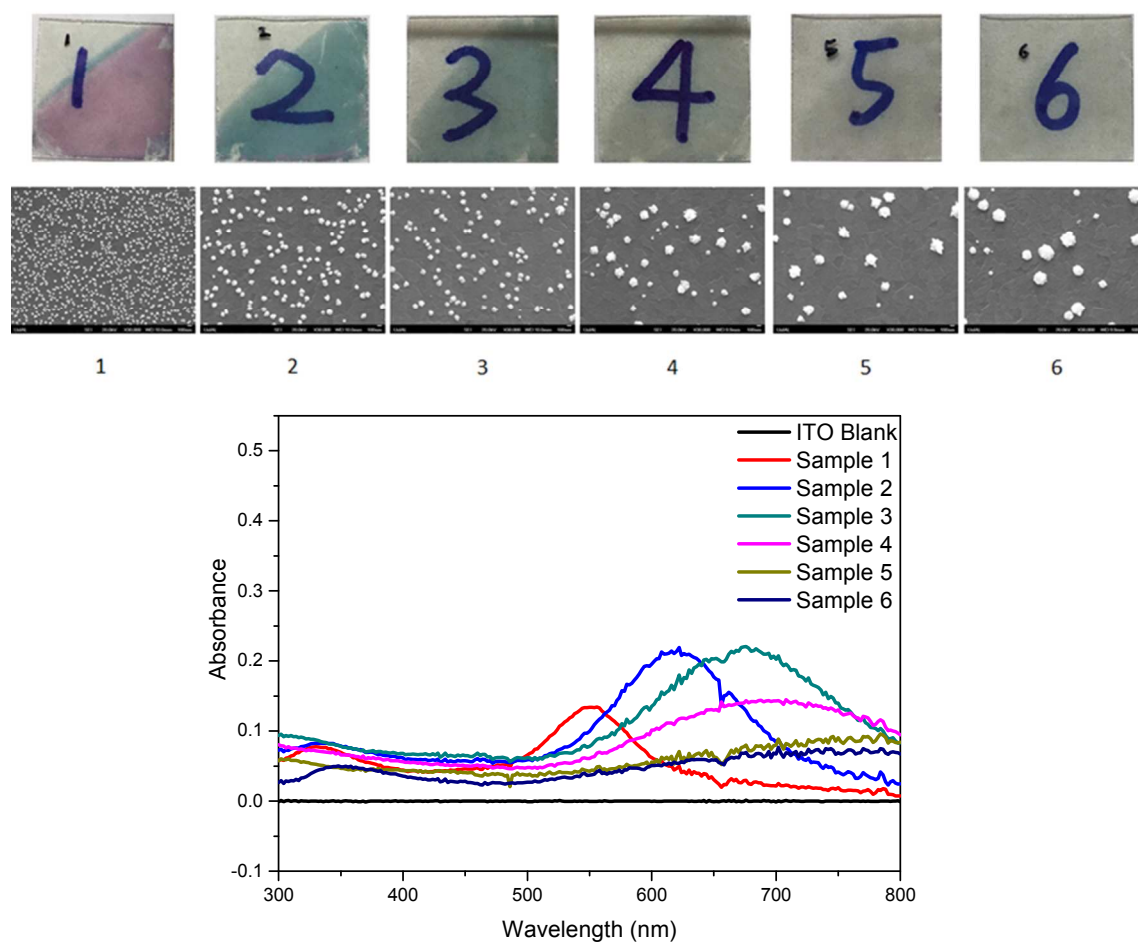
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Figure S1



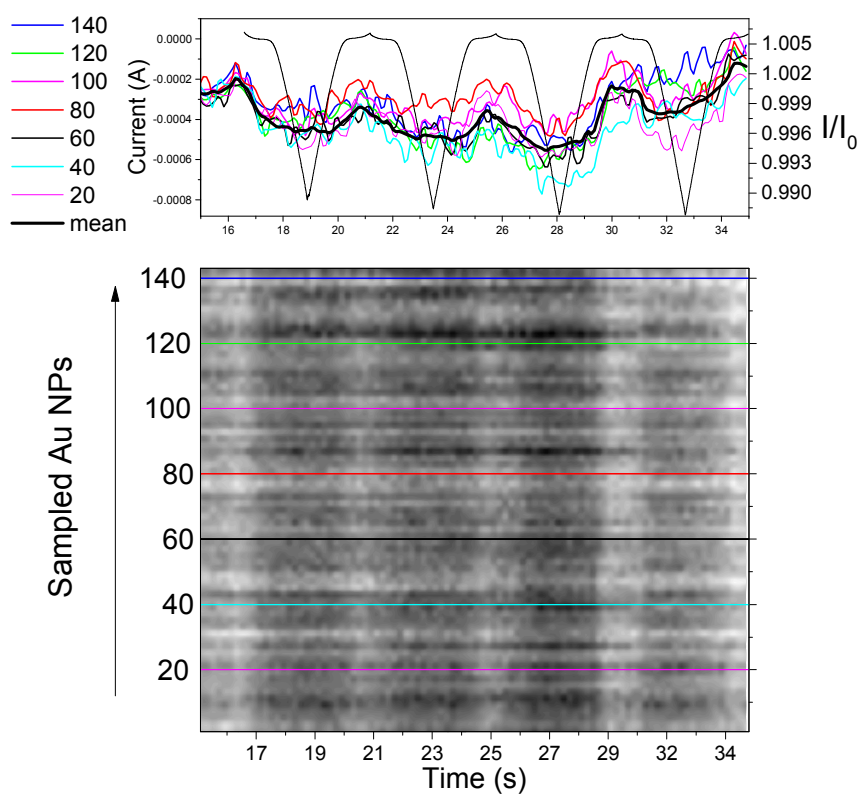
**Figure S1.** Schematic diagram of ITO UME fabrication

Figure S2



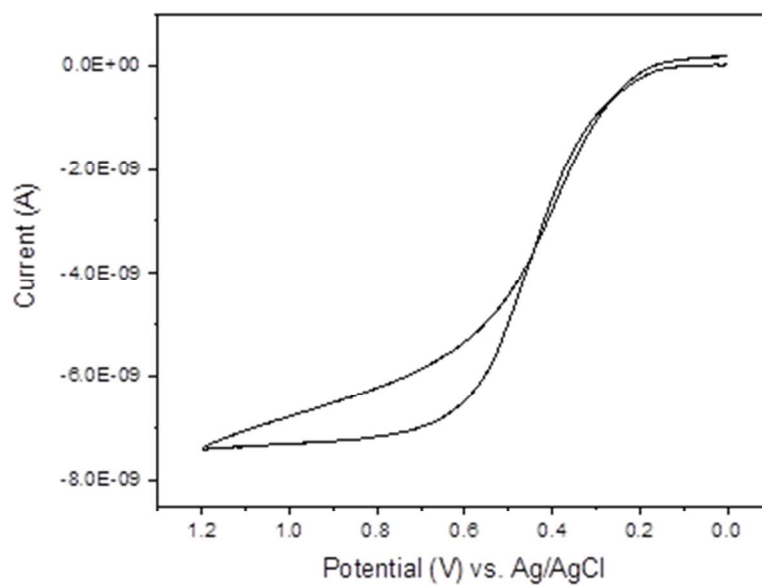
**Figure S2.** UV-Vis absorption spectra of Au NPs modified bare ITO with different coverage

Figure S3



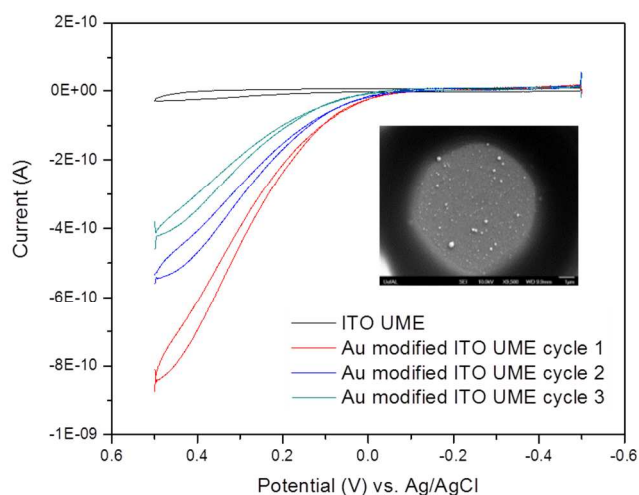
**Figure S3.** (top) Time evolutions of light scattering intensity relative to initial light intensity  $I/I_0$  of seven selected single Au NP and average variation of scattering intensity  $I/I_0$  of the total 150 Au NPs when the electrode potential was cycled linearly from -0.4 V to 0.75 V and then back to -0.4 V (vs. Ag Ag/AgCl) for four cycles at a scan rate of 0.5 V/s; (bottom) Time evolutions of  $I/I_0$  of all 150 Au NPs in DFS frame shown in inset Figure when the electrode potential was cycled linearly from -0.4 V to 0.75 V and then back to -0.4 V (vs. Ag Ag/AgCl) for four cycles at a scan rate of 0.5 V/s.

Figure S4

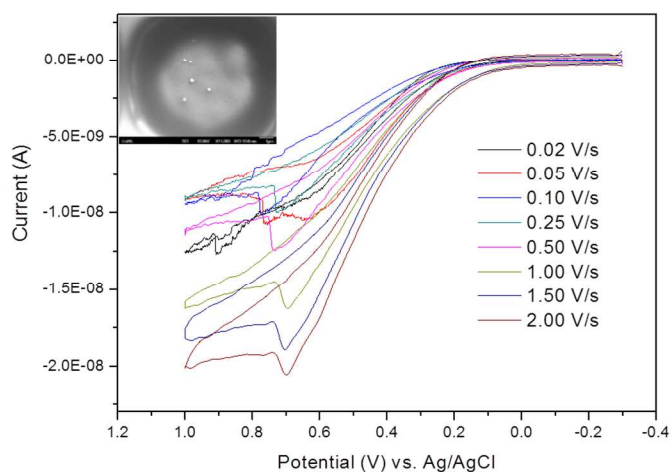


**Figure S4.** 10 mM ferrocyanide oxidation on 10  $\mu$ m ITO UME

Figure S5



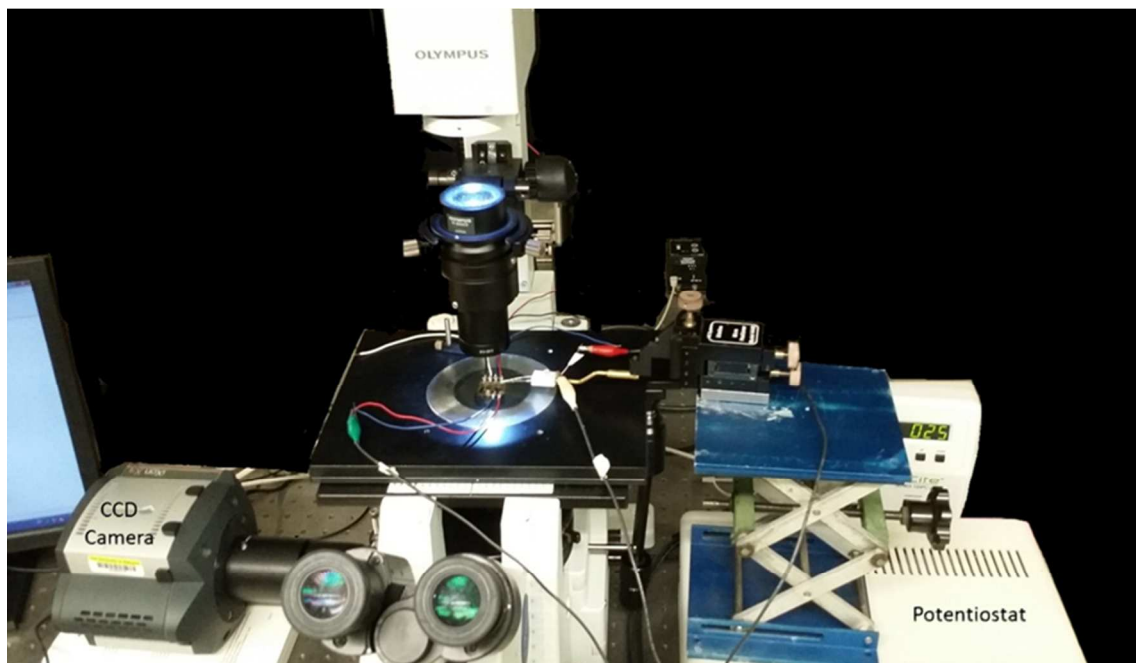
(A)



(B)

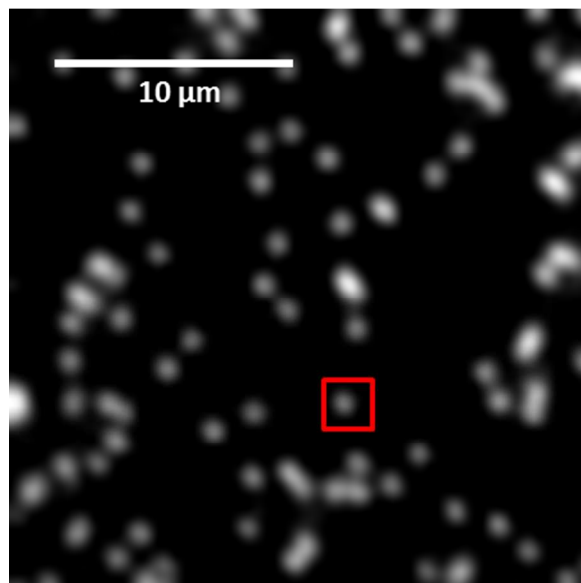
**Figure S5.** (A) three consecutive CVs of a few Au NPs modified ITO UME (colored) in 50 mM hydrazine in contrast to sluggish reaction at bare ITO UME (black). Inset: SEM image of the Au NPs-modified ITO UME; (B) CV of hydrazine oxidation in 50 mM hydrazine at a 10  $\mu\text{m}$  Au disk UME; (C) CVs of hydrazine oxidation and scan rate dependence in 1.0 M hydrazine solution at a few Au NPs modified ITO UME. Inset: SEM image of the Au NPs-modified ITO UME.

Figure S6



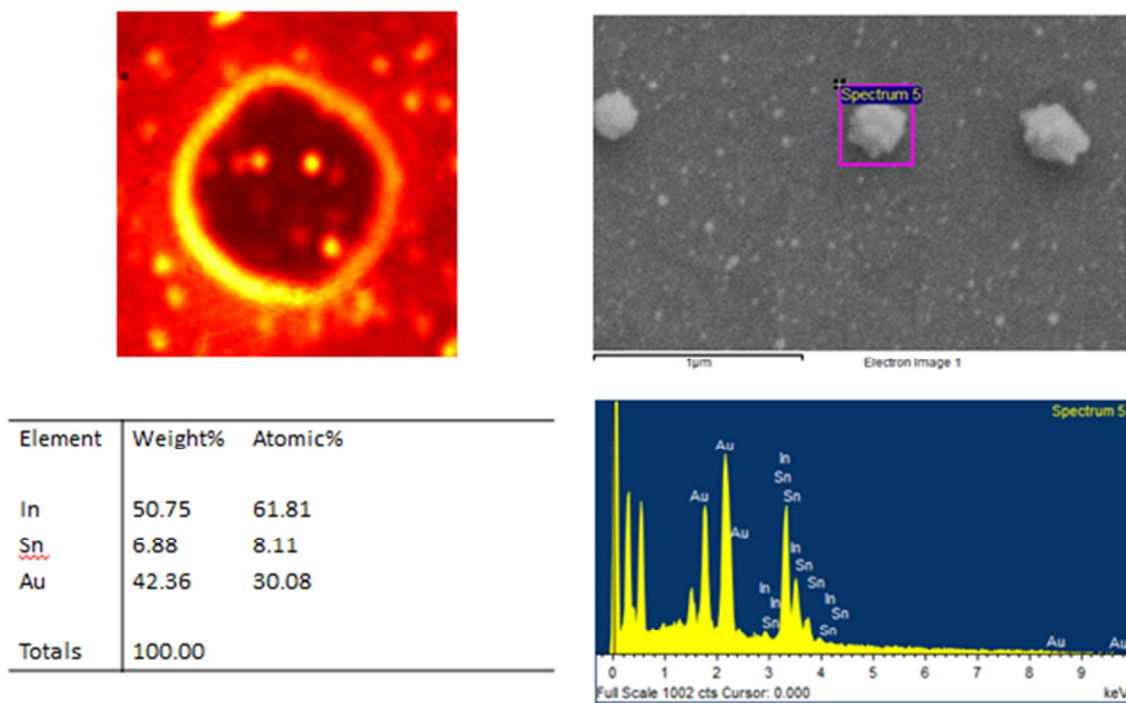
**Figure S6.** Experimental setup for hydrazine oxidation reaction with combined electrochemical and optical detection methods

Figure S7



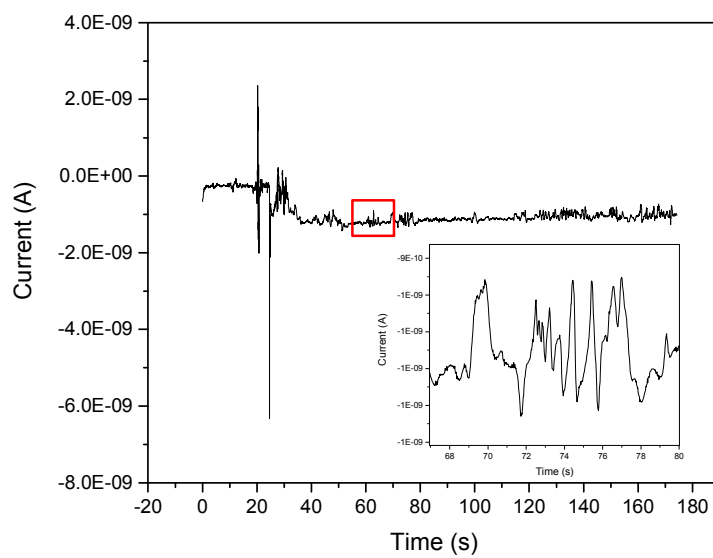
**Figure S7.** DFS image of Au modified bare ITO under hydrazine oxidation. The particle inside the red square is the particle selected for analysis.

Figure S8



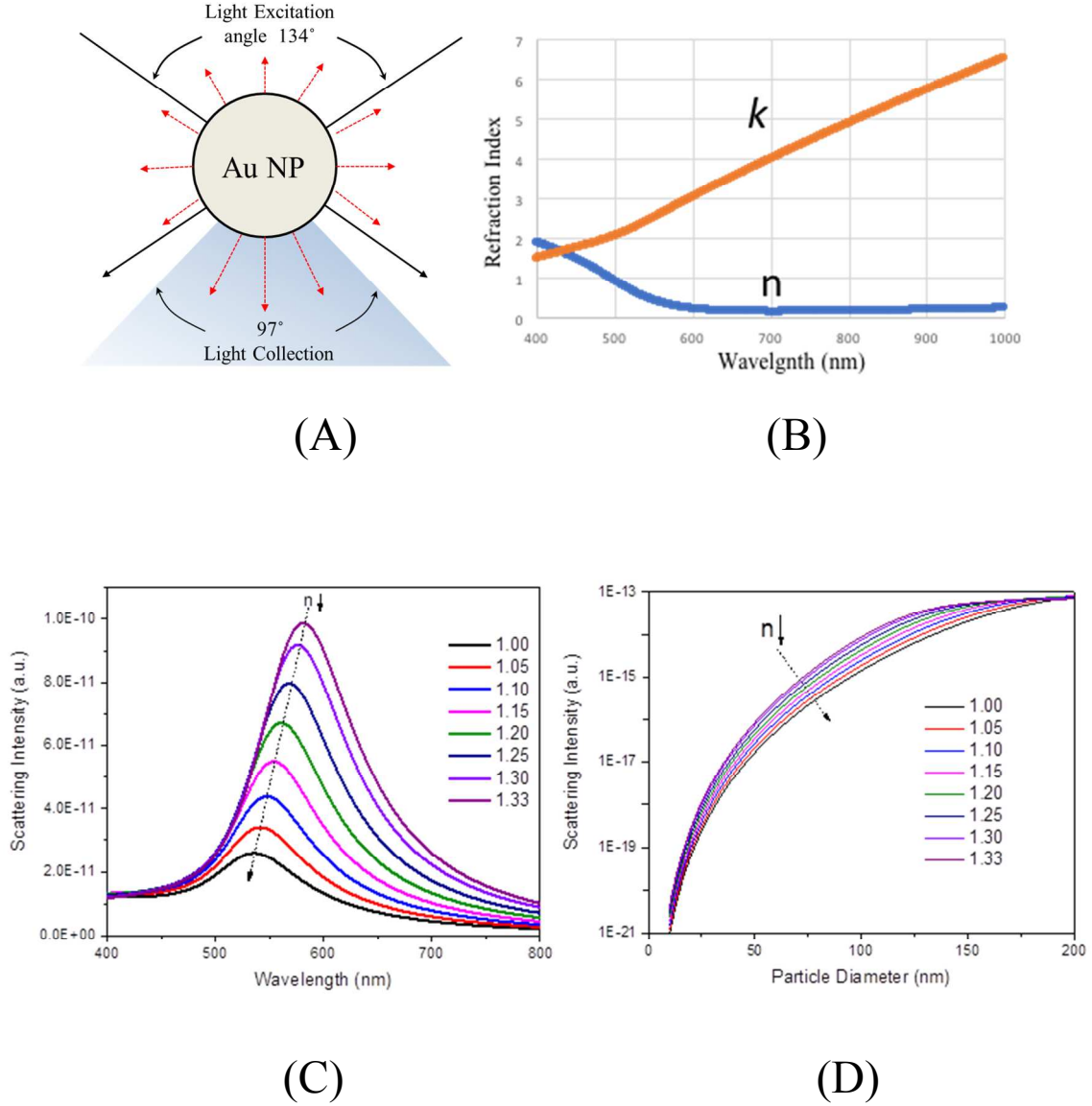
**Figure S8.** EDS result of Au NPs modified ITO UME. DFS image (top left) and high resolution SEM image (top right) show the size and shape of UME. EDS spectra (bottom right) indicates the element formation and abundance.

Figure S9



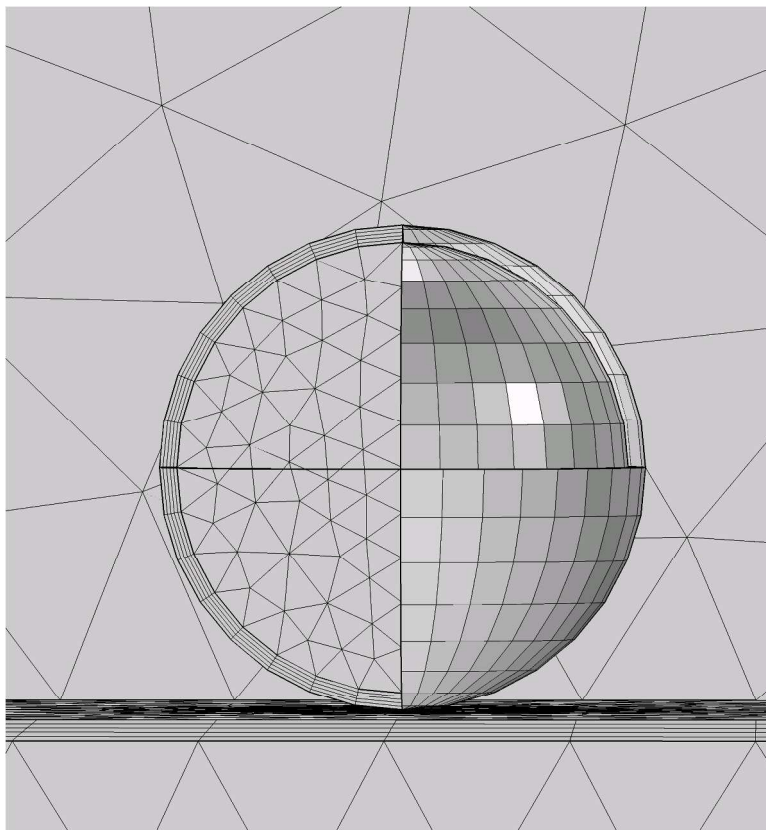
**Figure S9.** Au nanoparticle collision experiment on 10  $\mu\text{m}$  ITO UME under 0.3 V vs. Ag QRE. Inset is the zoom in of the red rectangular area.

Figure S10



**Figure S10.** (A) DFS light collection and incident light geometry that is used in DFS-EC equipment for calculating light scattering intensity with Mie theory; (B) Simulated light scattering spectrum of a single 100 nm (in diam.) Au NP in media with various refractive index from 1.33 to 1.00; (C) Mie simulation of light scattering intensity in dependences of medium refractive index. (D) Simulated light scattering intensity as a function of Au NP size (in diam.)

Figure S11



**Figure S11.** Example of meshing employed for the scattering calculations carried out using the RF Module of COMSOL Multiphysics. The  $\text{Au}_2\text{O}_3$  shell was represented as a mapped mesh with  $\geq 5$  layers in all cases. This example is for an Au core radius of 48 nm and an  $\text{Au}_2\text{O}_3$  shell thickness of 3.7 nm.