Electronic Supplementary Information

Enzymatic Etching of Gold Nanorods by Horseradish Peroxidase and its Application to Blood Glucose Detection

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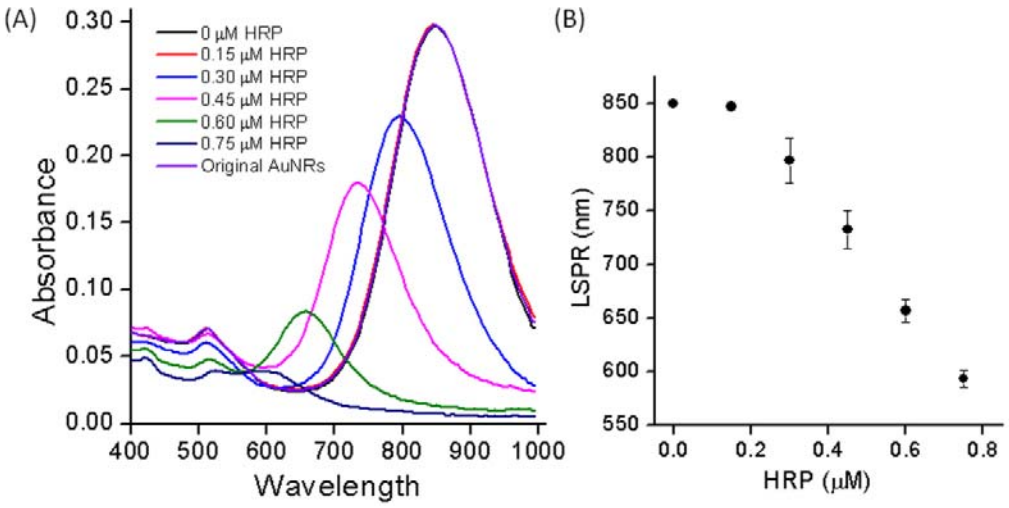

Figure S1. Effect of HRP concentration on etching of AuNRs. (A) Absorbance spectra of the AuNRs after incubation in the presence of H_2O_2 (0.1 mM) and different concentrations of HRP for 15 min. (B) Shift of the LSPR maximum as a function of HRP concentration.

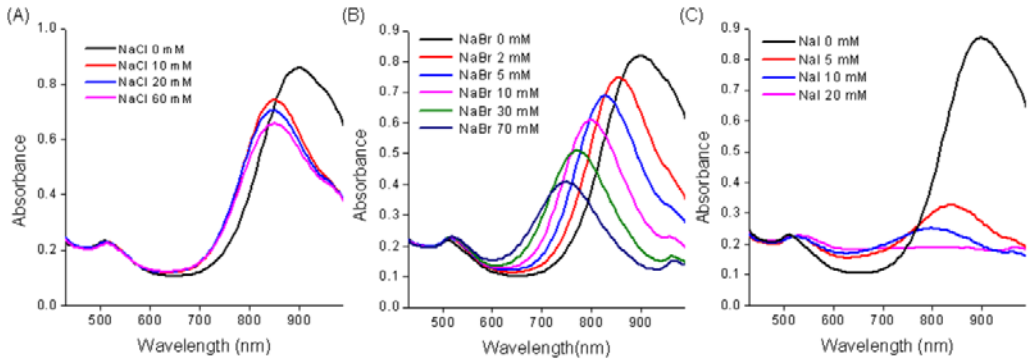

Figure S2. Halide effect on the enzymatic etching of AuNRs. Absorption spectra of the AuNRs solution (Au0 = 0.29 mM) after incubation in the presence of HRP (1.5 µM), H_2O_2 (176 µM) and different concentrations of: (A) NaCl, (B) NaBr and (C) NaI. Note that in the case of NaCl the initial shift of the band (NaCl 10 mM) may be due to the presence of Br^- ions in the solution. All spectra were normalized at 400nm.

Table S1. Redox potential for gold halides.

$AuX_4^- + 2e^- \leftrightarrow AuX_2^- + 2X^-$	
Halide	**E (v)**
Cl^-	**0.926**
Br^-	**0.802**
I^-	**0.550**
$AuX_2^- + e^- \leftrightarrow Au + 2X^-$	
Halide	**E (v)**
Cl-	**1.154**
Br-	**0.959**
I-	**0.578**

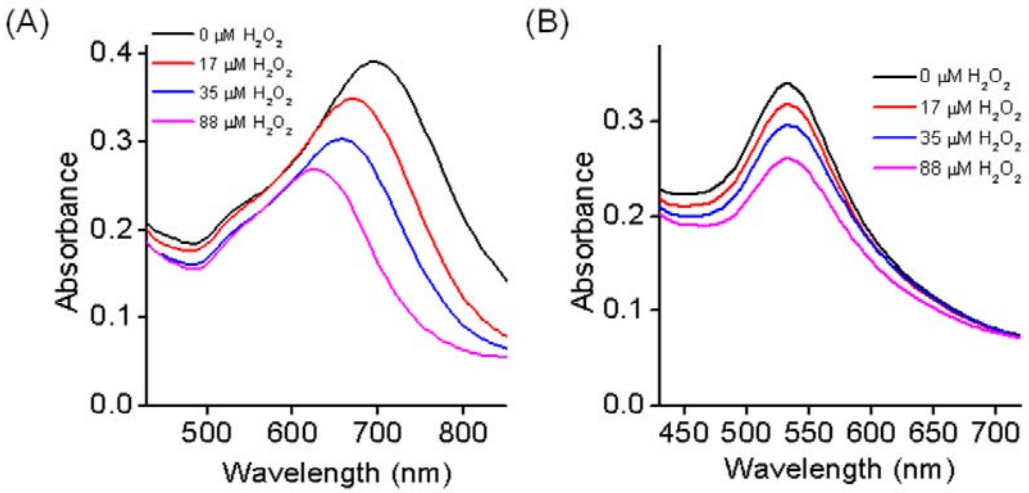

Figure S3. Enzymatic oxidation of gold nanoparticles (A) Absorbance spectra of polyvinylpyrrolidone coated gold nanostars (AuNs@PVP; 0.26 mM), after incubation in the presence of HRP (1 μM), NaBr (25mM) and different concentrations of H_2O_2 for 15 min (B) Absorbance spectra of spherical citrate gold nanoparticles (AuNS@citrate; 0.35 mM) after incubation in the presence of HRP (1 μM), NaBr (25 mM) and different concentrations of H_2O_2. Note that the rates of oxidation are different than in the case of AuNRs due to the use of a lower concentration of HRP in all cases.

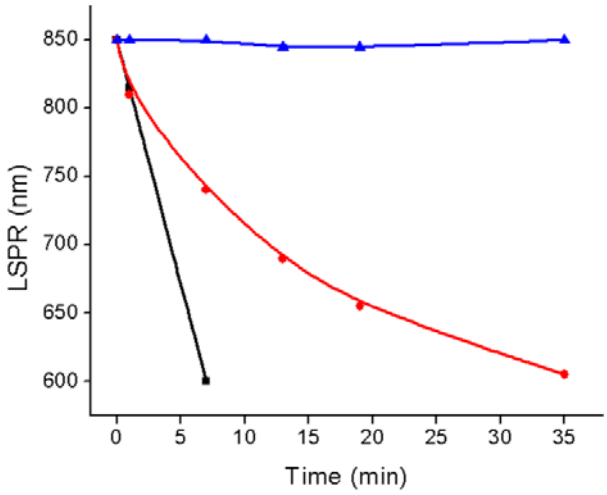

Figure S4. Variation of LSPR maxima with time during the oxidation etching of AuNRs by HRP 1.5 µM and H_2O_2 0.1 mM (black squares), Fenton reagent 0.25 mM and H_2O_2 0.1 mM (red circles), and only H_2O_2 0.1 mM (blue triangles).

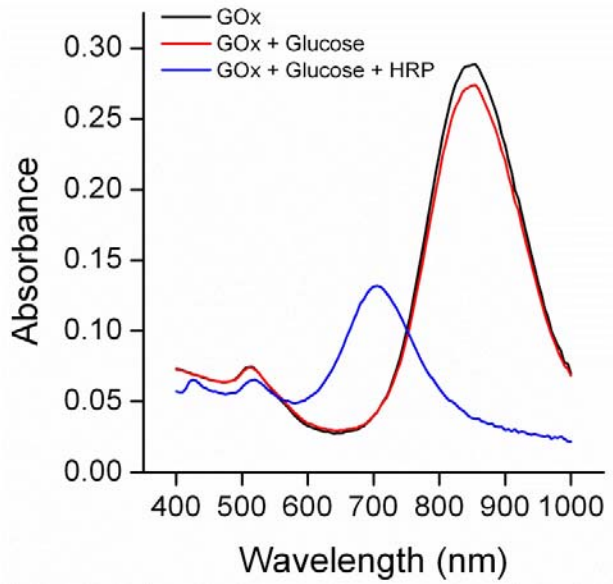

Figure S5. Control experiments showing the importance of HRP in the etching of AuNRs. AuNRs were incubated with GOx (50 nM) and Glucose (0.1 mM) in the presence (Blue line) or absence (red line) of HRP (1.5 µM), or only in the presence of GOx (50 nM) (black line) for 20 min.