Supporting Information:

Role of metal cations in plasmon-catalyzed oxidation: a case study of dimerization of *p*-aminothiophenol

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Supporting Figures

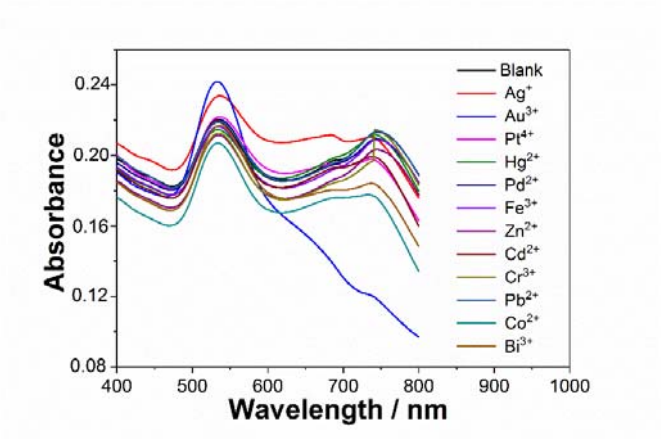

Figure S1 UV-Vis spectra of gold nanoparticles functionalized with PATP at pH 9 in the presence of different metal ions.

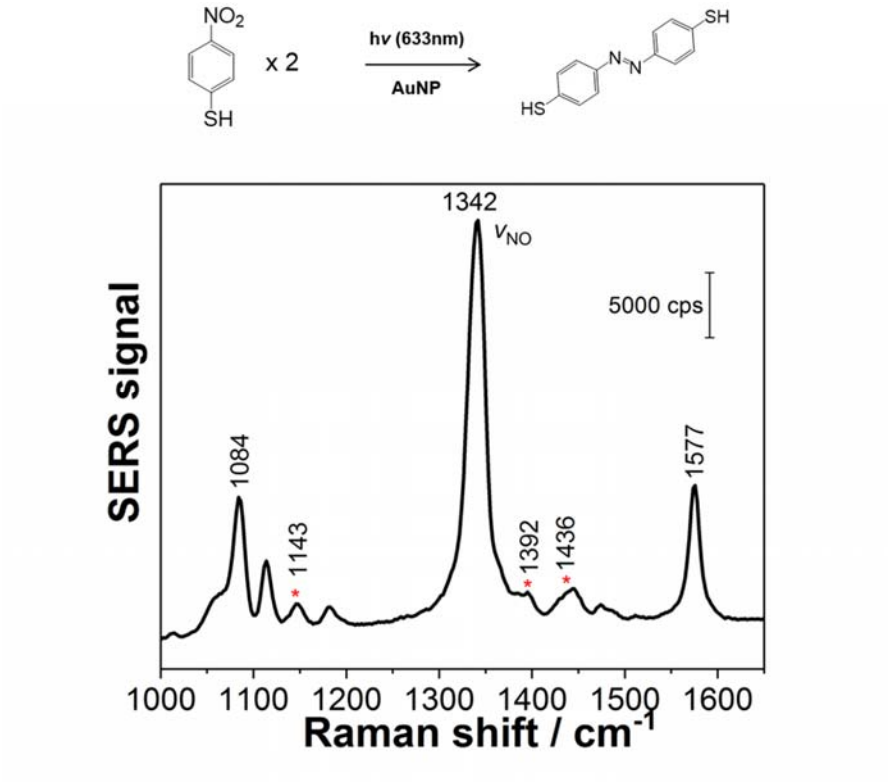

Figure S2 SERS spectra of immobilized gold nanoparticles modified with PNTP after irradiation for 6 s. ($\lambda_{excitation}$ = 633 nm; laser intensity: 500 kW/cm^2). * marked peaks are representative of DMAB.

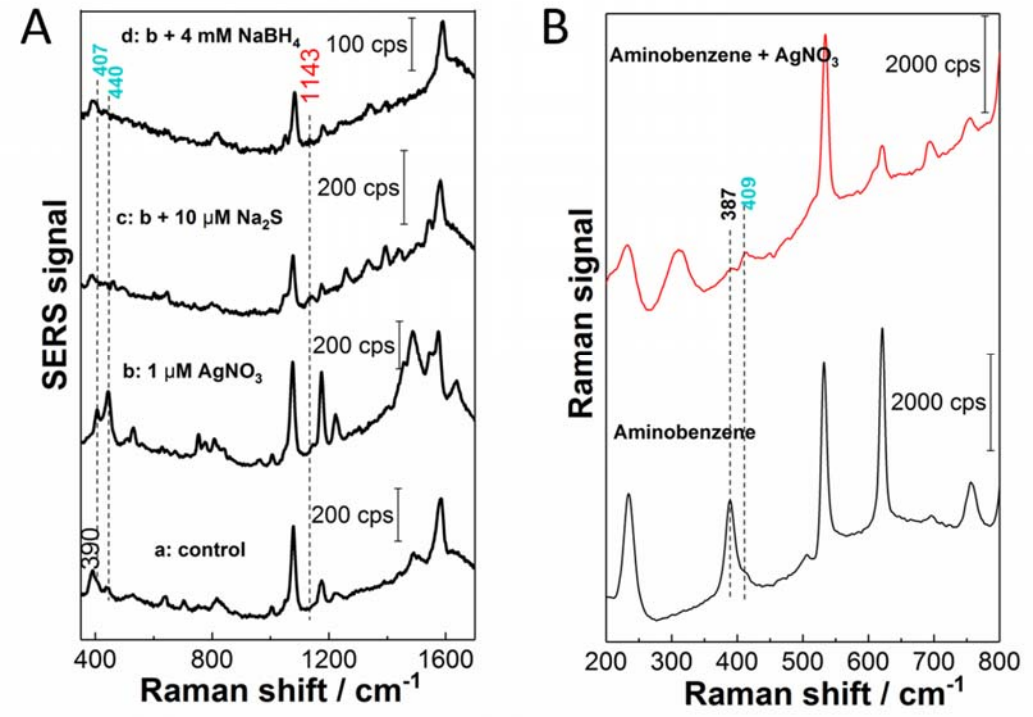

Figure S3 (A) SERS spectra of gold nanoparticles (0.044 nM) with PATP (0.25 μM) at pH 2 (a) before and (b) after incubation with 1.0 μM Ag^+ (control) (c) with further addition of Na_2S, and (d) $NaBH_4$. **(B)** Normal Raman spectra of aminobenzene before (black trace) and after adding $AgNO_3$ (red trace). ($\lambda_{excitation}$ = 633 nm; laser intensity: 500 kW/cm^2)

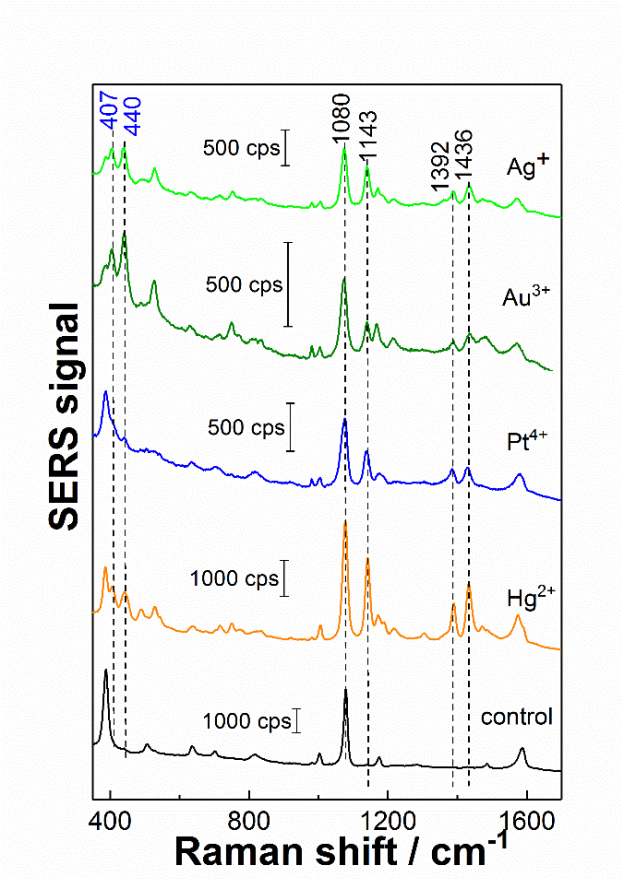

Figure S4 SERS spectra (averages of 10 measurements) of gold nanoparticles with PATP at pH 9 before and after incubation with 1 µM Ag^{+}, 2 µM Au^{3+}, 5 µM Pt^{4+} and 10 µM Hg^{2+} ions. (λ_{exc} = 785 nm; laser intensity: 1.84 ×10^{6} W/cm^{2}, acquisition time 1 s).

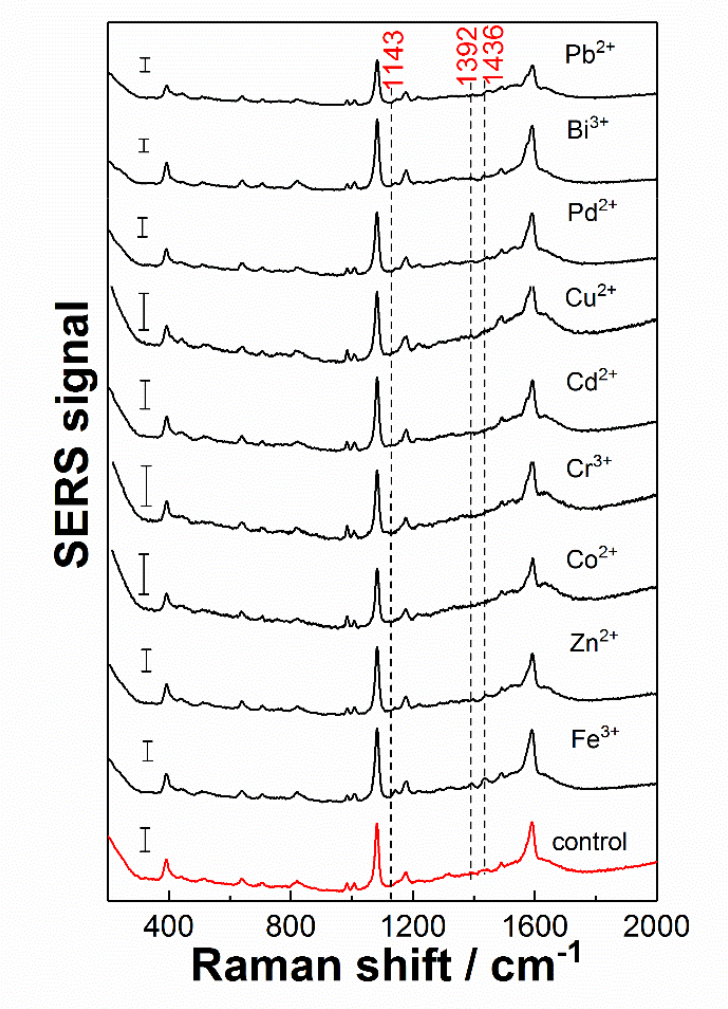

Figure S5 SERS spectra (averages of 10 measurements) of gold nanoparticles with PATP at pH 9 before and after incubation with different metal ions for 10 min at room temperature. ($\lambda_{excitation}$ = 633 nm; laser intensity: 500 kW/cm^2, acquisition time 1s) Scale bars: 200 cps.

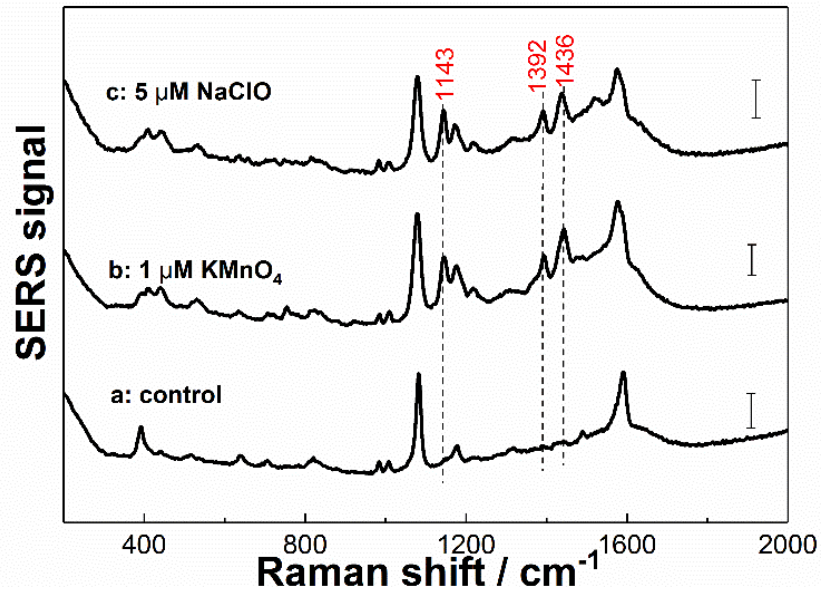

Figure S6 SERS spectra of gold nanoparticles with PATP at pH 9 before and after incubation with 1.0 μM KMO_4 and 5 μM NaClO for 10 min at room temperature. (λ_{exc} = 633 nm; laser intensity: 500 kW/cm^2, acquisition time 1 s). Scale bars: 200 cps

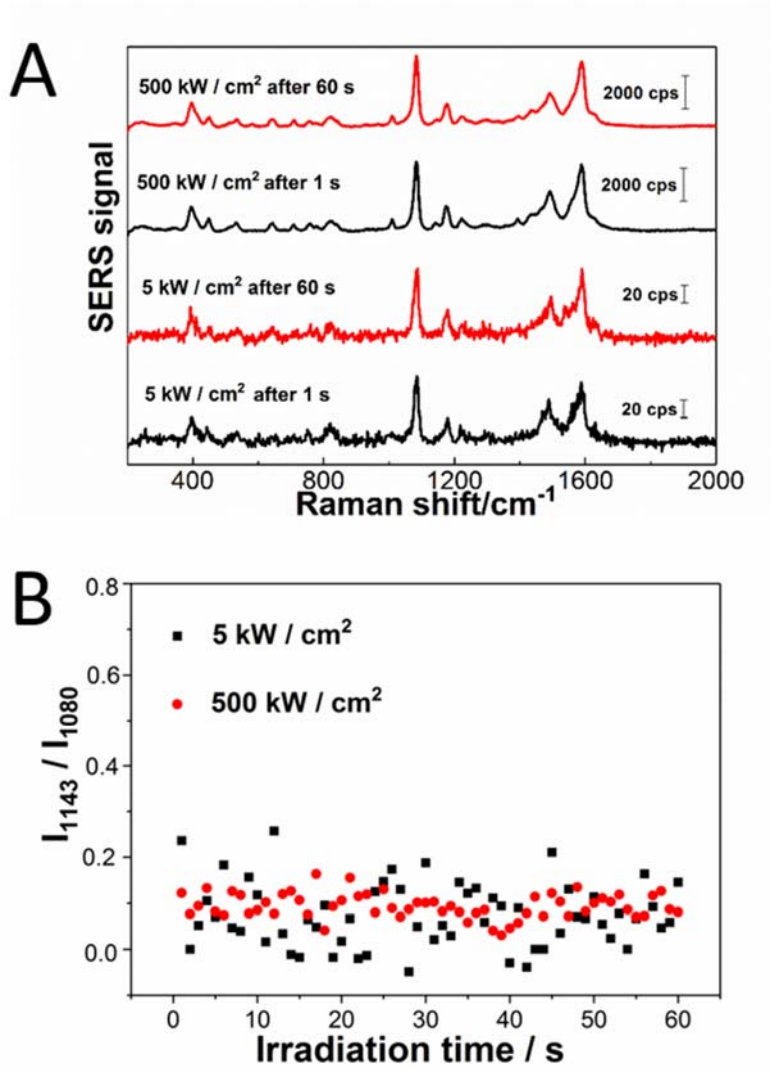

Figure S7 (A) SERS spectra of gold nanoparticles with PATP obtained after irradiation with a laser intensity of 5 kW/cm^2 and 500 kW/cm^2 after 1 s (black traces) and 60 s (red traces), respectively. **(B)** Signal intensity ratio I_{1143}/I_{1080} in the SERS spectra of gold nanoparticles with PATP in the absence of Ag^+ at pH 9 as a function of irradiation time using an intensity of 5 kW/cm^2 (black squares) and 500 kW/cm^2 (red dots). ($\lambda_{excitation}$ = 633 nm, acquisition time: 1 s) Spectra were excited with the same laser intensity as that used for irradiation.

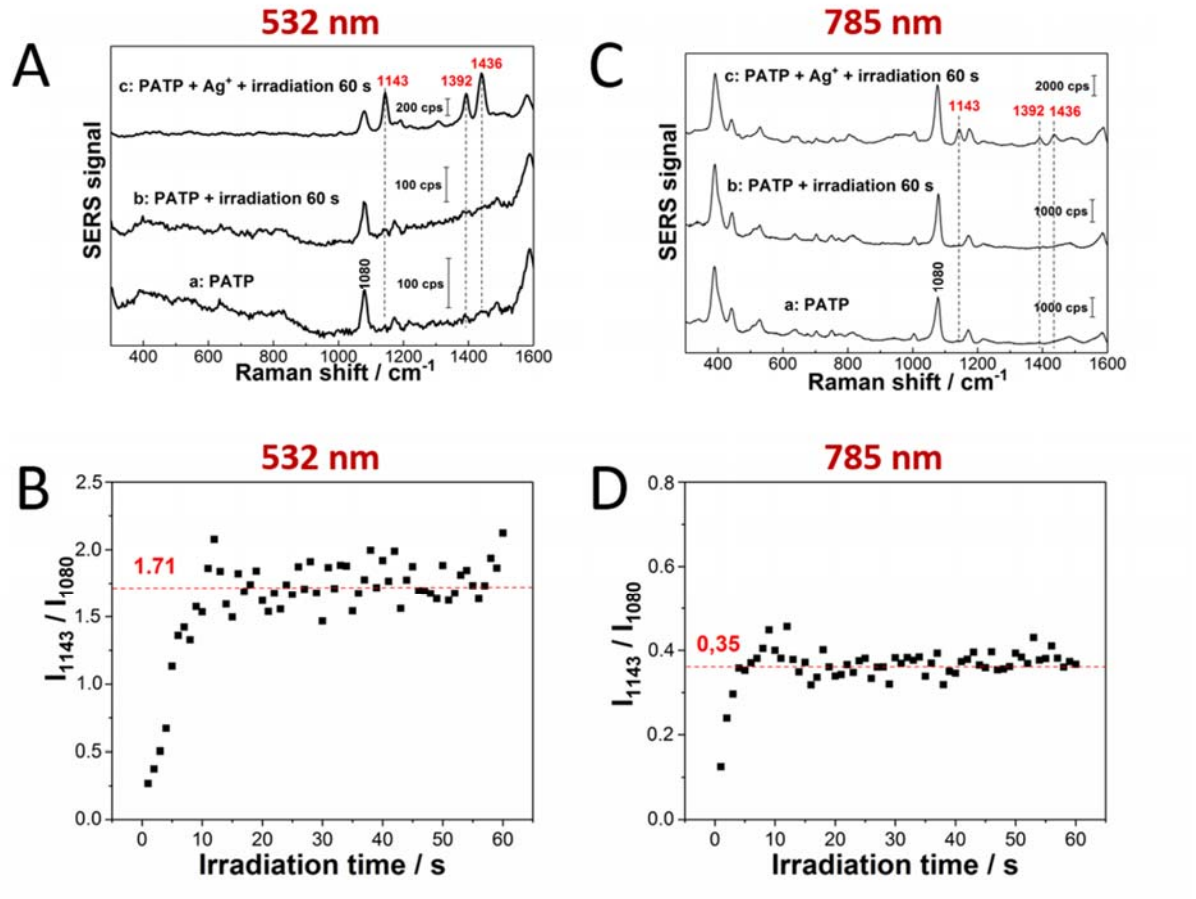

Figure S8 SERS spectra of gold nanoparticles with PATP in the absence and presence of Ag^+ before and after irradiation for 60 s using **(A)** an excitation laser at 532 nm with an intensity of 1.4×10^6 W/cm^2 and **(C)** an excitation laser at 785 nm with an intensity of 4.6×10^5 W/cm^2 **(B) and (D)** Signal intensity ratio I_{1143}/I_{1080} determined from SERS spectra obtained in the presence of Ag^+ as a function of irradiation time with the two laser wavelengths, respectively.

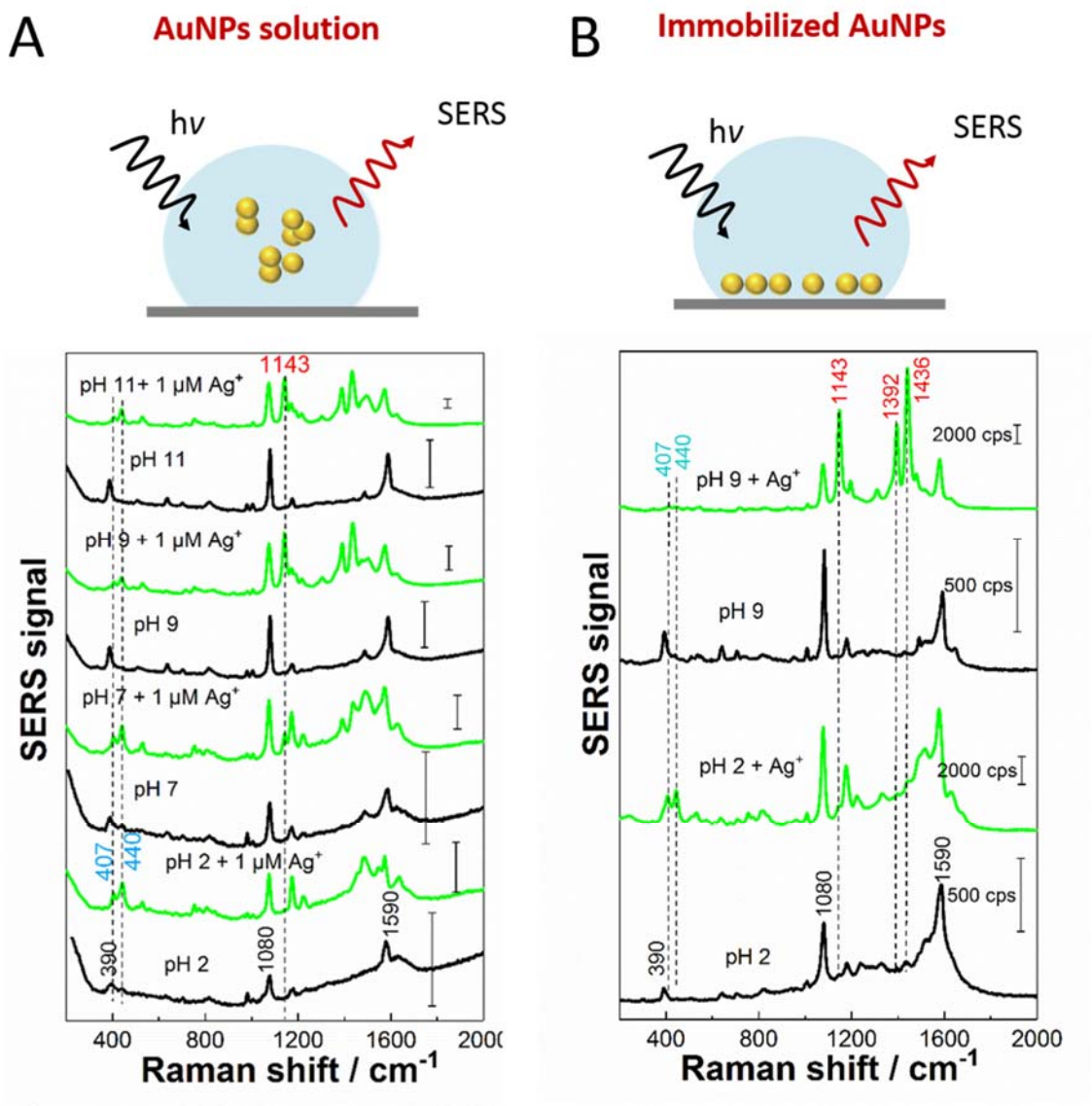

Figure S9 (A) SERS spectra of gold nanoparticles with PATP in the absence and presence of Ag^+ at pH 2, pH 7, pH 9, and pH 11, respectively ($\lambda_{excitation}$ = 633 nm; laser intensity: 500 kW/cm^2, acquisition time 1s). Scale bars: 200 cps. **(B)** SERS spectra of immobilized gold nanoparticles functionalized with PATP on a glass slide before and after incubation with Ag^+ at pH 2 and pH 9 (($\lambda_{excitation}$ = 633 nm, laser intensity 50 W/cm^2, acquisition time: 1 s).

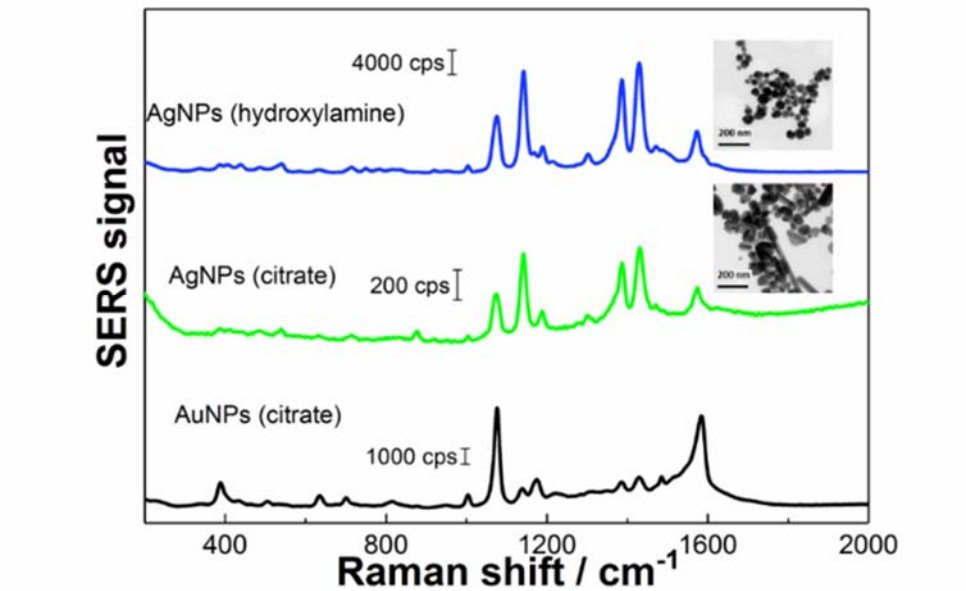

Figure S10 SERS spectra of citrate reduced gold nanoparticles, citrate reduced[1] silver nanoparticles, and hydroxylamine reduced[2] silver nanoparticles with PATP. Insets: TEM images of citrate reduced and hydroxylamine reduced silver nanoparticles. ($\lambda_{excitation}$ = 633 nm; laser intensity: 500 kW/cm^2, acquisition time 1 s).

References

(1) Lee, P.; Meisel, D. *J. Phys. Chem.* **1982,** *86*, 3391-3395.
(2) Leopold, N.; Lendl, B. *J. Phys. Chem. B* **2003,** *107*, 5723-5727.