

Supporting Information

Probing the Catalytic Reduction on the Surface of Au Nanoparticles by Second Harmonic Generation and Two-photon Luminescence

Shan Xue^{a,b}, Shun-li Chen^c, Qunhui Yuan^d, Wei Gan^{a,}*

^a Shenzhen Key Laboratory of Flexible Printed Electronics Technology, School of Science, Harbin Institute of Technology (Shenzhen), University Town, Shenzhen 518055, Guangdong; School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, Heilongjiang, China

E-mail: ganwei@hit.edu.cn

^b Institute of Materials Research, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen University Town 518055, China

^c Department of Chemistry and Key Laboratory for Preparation and Application of Ordered Structure Materials of Guangdong Province, Shantou University, Shantou 515063, Guangdong, China

^d Shenzhen Key Laboratory of Flexible Printed Electronics Technology, School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), University Town, Shenzhen 518055, Guangdong, China

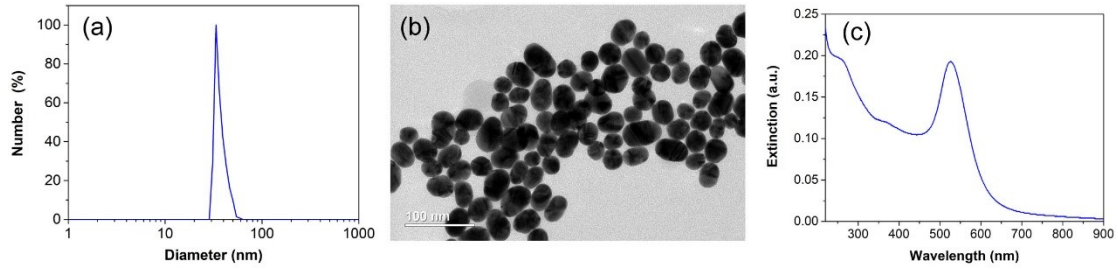


Figure S1. (a) The number-size distributions of the AuNPs obtained by DLS measurements. (b) The TEM image of the AuNPs. (c) Extinction spectra of the AuNPs in colloid.

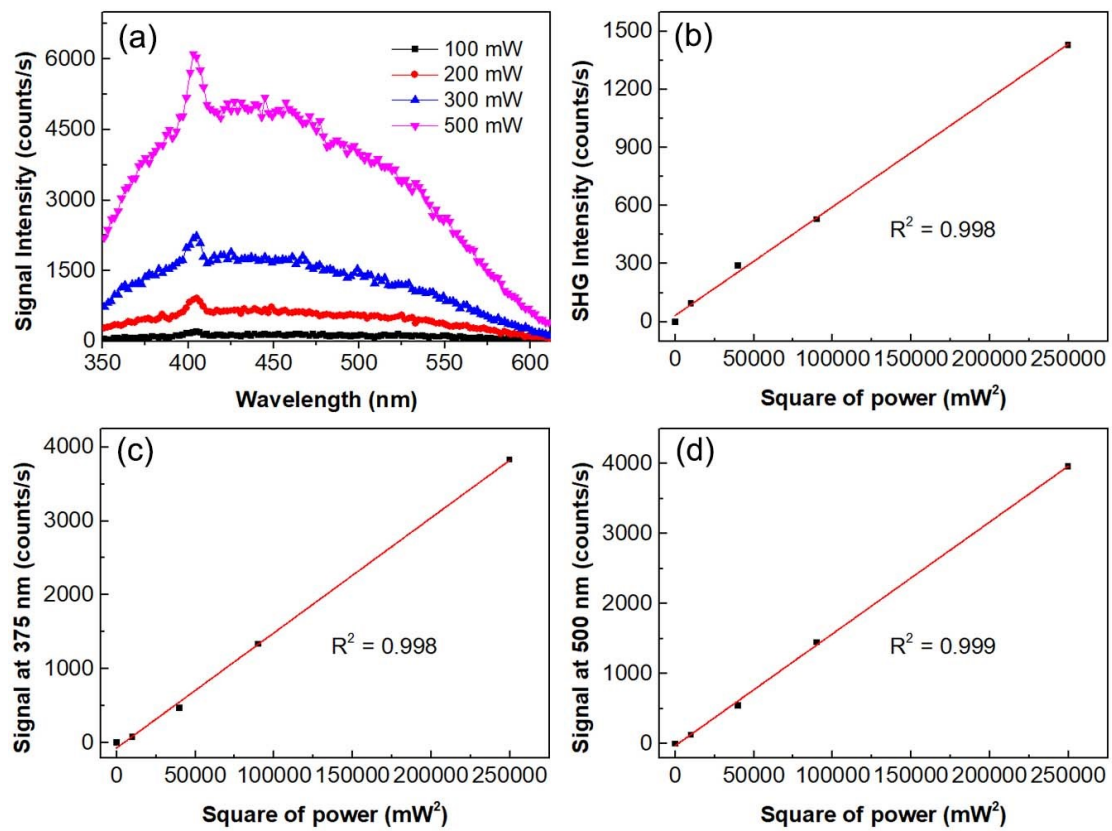


Figure S2. (a) Emission spectra of 37 nm colloidal AuNPs excited by 810 nm laser with different powers. (b–d) The relationship between the signal intensity at wavelength of 405 nm (b), 375 nm (c) and 500 nm (d) and the square of laser power. The lines in the figures are linear fitting curves.

Table S1. The size and zeta potential of AuNPs mixed with different concentrations of NaBH₄ obtained by DLS.

Sample	AuNPs	AuNPs+0.1 mM NaBH ₄	AuNPs+0.5mM NaBH ₄	AuNPs+1 mM NaBH ₄	AuNPs+2 mM NaBH ₄
Number mean diameter (nm)	36.9±1.9	36.9±2.2	33.7±1.7	34.7±1.4	43.9±4.2
Zeta-potential (mV)	-34.8±5.6	-20.9±5.8	-13.6±5.0	-10.9±2.5	-10.6±2.2

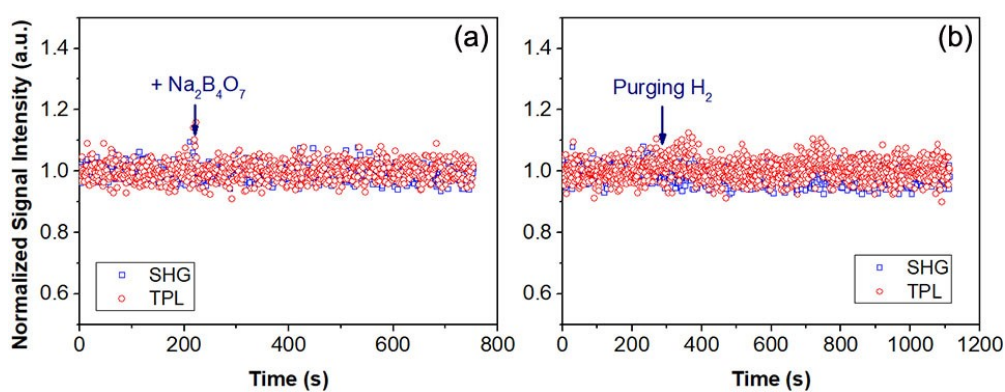


Figure S3. (a) Normalized time-dependent SHG and TPL intensities of citrate-stabilized AuNPs after the addition of 1 mM sodium borate. (b) Time-dependent SHG and TPL intensity of citrate-stabilized AuNPs after H₂ purging.

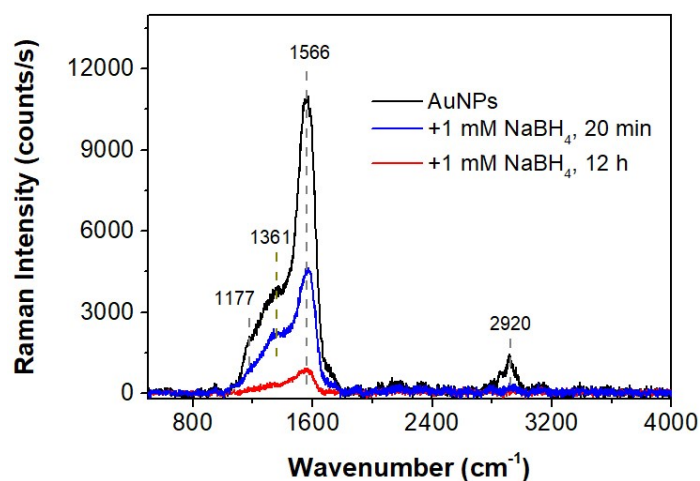


Figure S4. The Raman spectra of citrate-stabilized AuNPs colloids and after mixed with 1mM NaBH₄ at different time. The Raman peaks in the figure belong to the carboxyl or methylene group of citrate on the surface of nanoparticle¹.

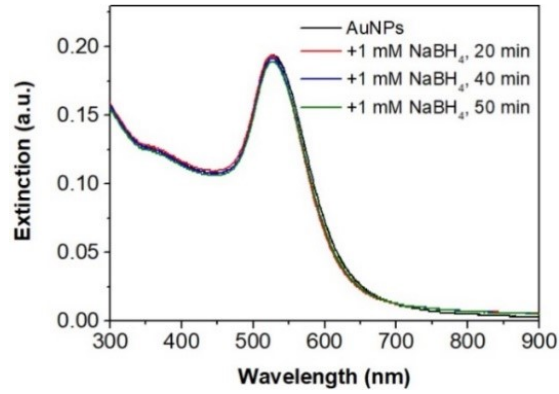


Figure S5. The UV-vis extinction spectra of citrate-stabilized AuNPs after the addition of 1 mM NaBH_4 .

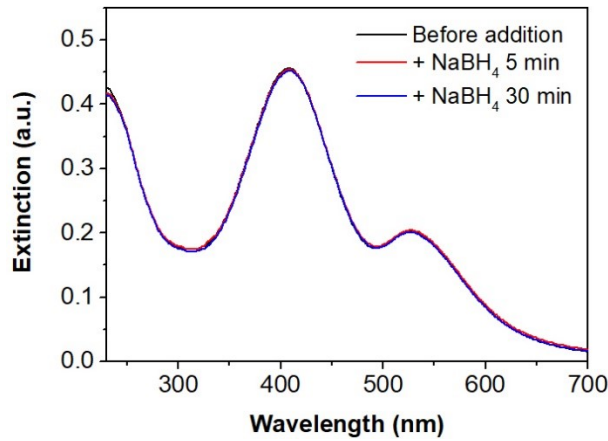


Figure S6. The UV-vis spectra after the addition of 1 mM NaBH_4 to the mixed solution of AuNPs and 4-NTP

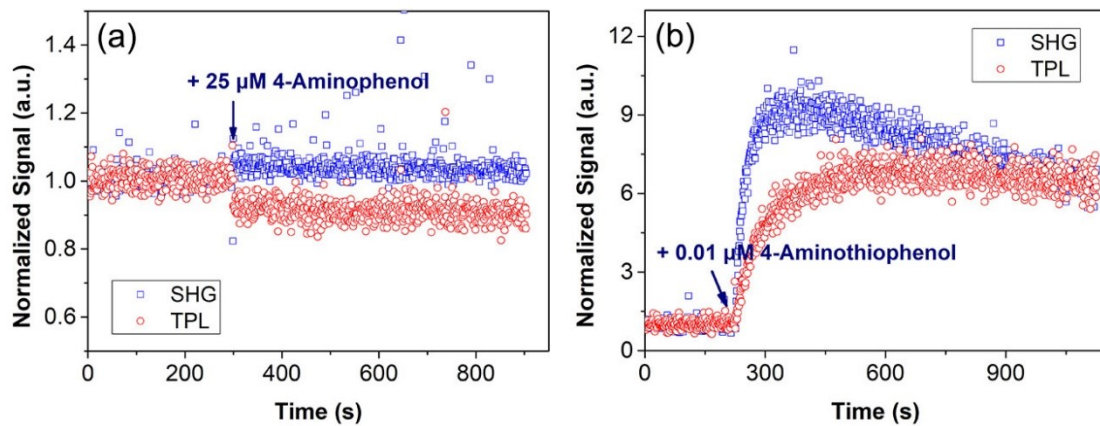


Figure S7. Normalized time-dependent SHG and TPL signals from AuNPs after the addition of 25 μM 4-aminophenol (a) and 0.01 μM 4-aminothiophenol (b), respectively. The curves have been corrected using UV-vis absorption spectra.

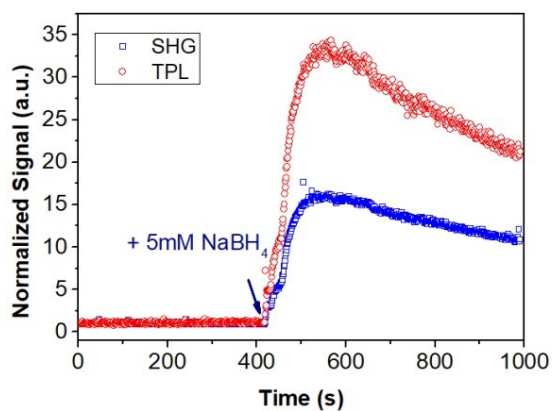


Figure S8. Time-dependent SHG and TPL signals of AuNPs colloid after the addition of 5 mM NaBH₄.

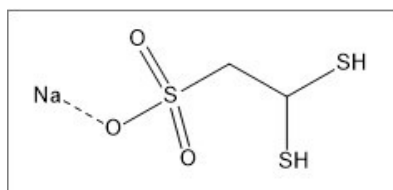


Figure S9. The chemical structure of 2,3-dimercapto-1-propanesulfonic acid sodium (DMPS).

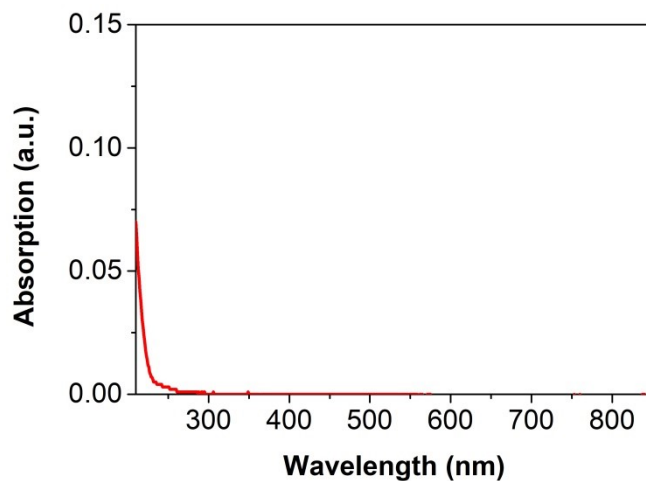


Figure S10. UV-vis absorption spectra of 10 μM DMPS aqueous solution.

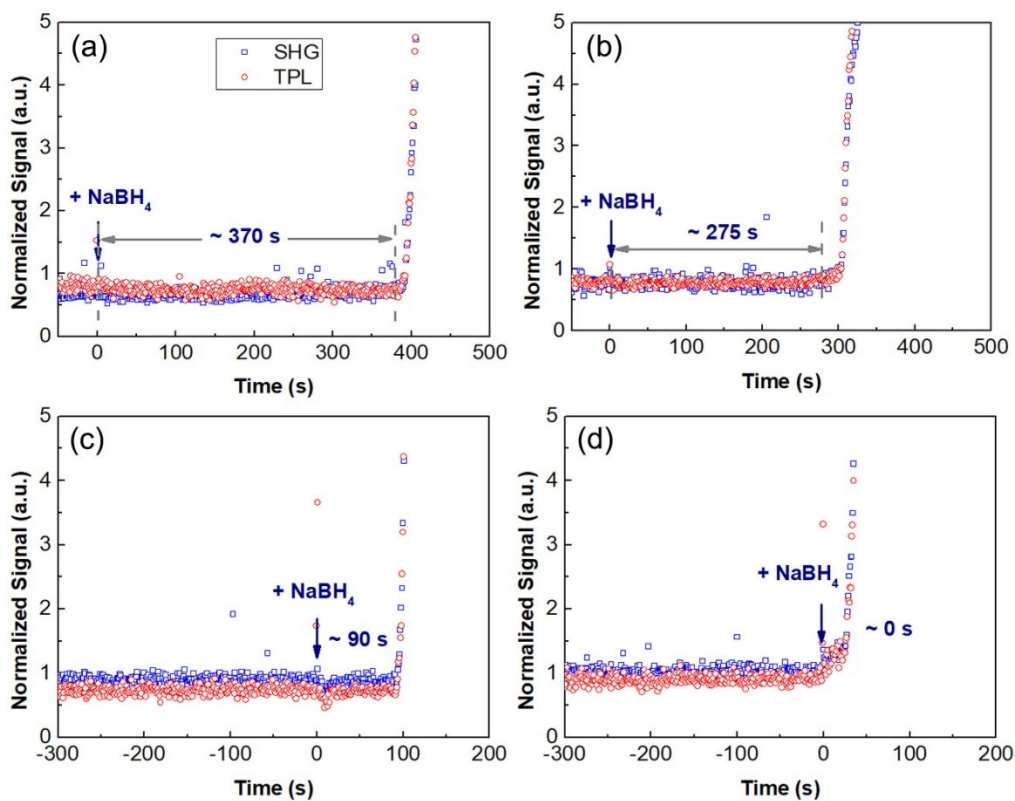


Figure S11. Time-dependent SHG and TPL signals before and after the addition of 5 mM NaBH₄ to solutions containing the same amount of AuNPs and different amount of 4-nitrothiophenol. The concentrations of 4-nitrothiophenol in (a), (b), (c), (d) are 25, 10, 5, and 0.5 μ M, respectively. NaBH₄ was added at $t = 0$ s.

Refs:

1. Park, J.-W.; Shumaker-Parry, J. S., Structural study of citrate layers on gold nanoparticles: role of intermolecular interactions in stabilizing nanoparticles. *J. Am. Chem. Soc.* **2014**, *136* (5), 1907-1921.