Supporting information

Size Dependent Two-photon Excitation Photoluminescence Enhancement in Coupled Noble Metal Nanoparticles

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1. Extinction spectra of coupled Au nanospheres

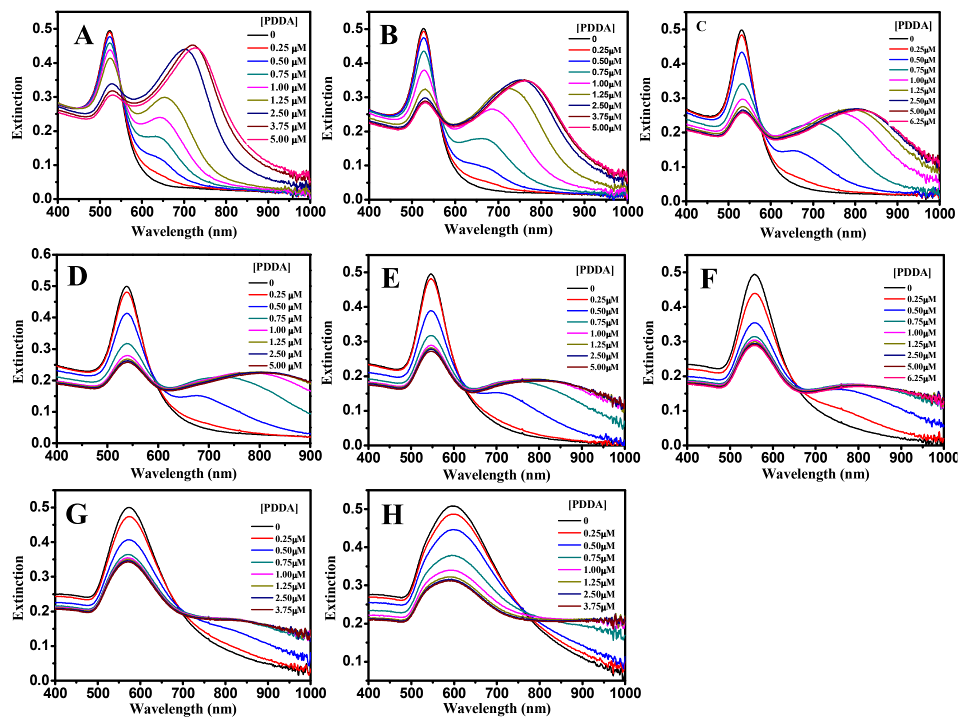

Figure S1. UV-Vis extinction spectra of (A) 20 nm, (B) 30 nm, (C) 40 nm, (D) 55 nm, (E) 80 nm, (F) 95 nm, (G) 110 nm and (H) 120 nm Au NSs in the presence of different amounts of PDDA.

2. Extinction spectra of coupled Ag nanospheres

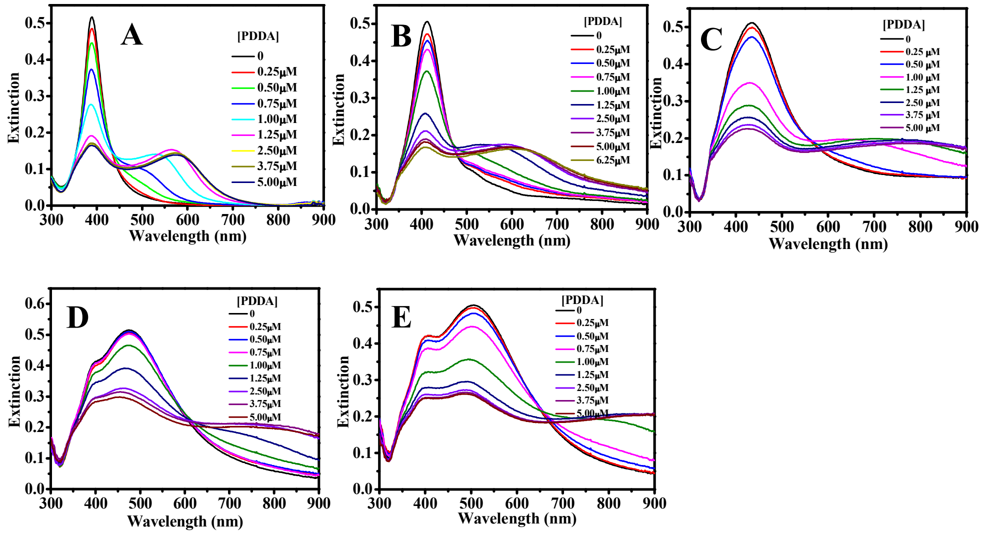

Figure S2. UV-Vis extinction spectra of (A) 15 nm, (B) 30 nm, (C) 50 nm, (D) 75 nm and (E) 100 nm Ag NSs in the presence of different amounts of PDDA.

3. Two-photon excitation photoluminescence spectra of coupled Au nanospheres

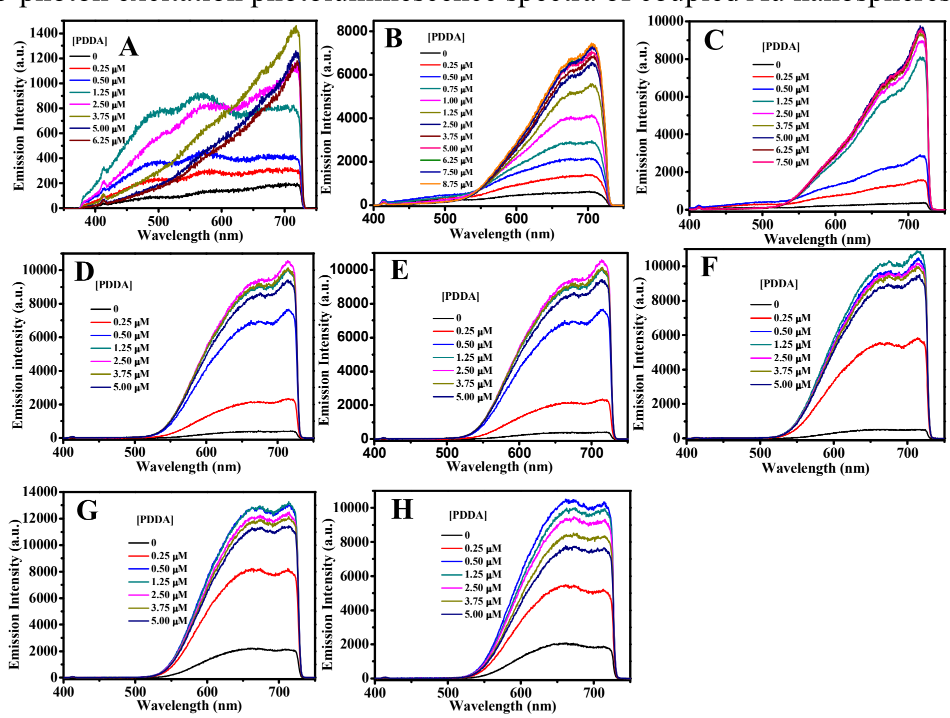

Figure S3. TPPL spectra of (a) 20 nm, (b) 30 nm, (c) 40 nm, (d) 55 nm, (e) 80 nm, (f) 95 nm, (g) 110 nm and (h) 120nm Au NSs in the presence of different amounts of PDDA.

4. Two-photon excitation photoluminescence spectra of coupled Ag nanospheres

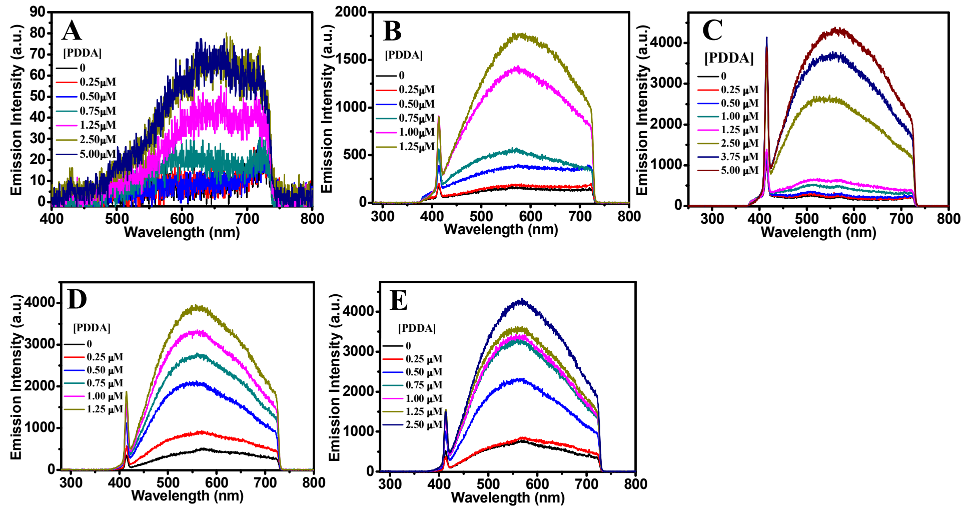

Figure S4. TPPL spectra of (a) 15 nm, (b) 30 nm, (c) 50 nm, (d) 75 nm and (e) 100 nm Ag NSs in presence of different amounts of PDDA.

5. Two-photon action cross section calculation method and procedure

The two-photon action cross section of coupled metal nanoparticles was calculated according to equation 1:

$$\varphi_{2p(sample)} = \varphi_{2p(ref)} \frac{I_{sample} C_{ref} n_{sample}^2 P_{ref}^2}{I_{ref} C_{sample} n_{ref}^2 P_{sample}^2} \quad (1),$$

where φ_{2p} is the two-photon action cross section, I is the integrated TPE intensity, C is the concentration, n is the refractive index and P is the incident power on the sample of the samples and reference.

Au nanorods (NRs) with average aspect ratio of 4 were used as the reference. The refractive index and the incident power are same for Au and Ag NSs samples and the Au NRs reference. Equation 1 can be simplified to equation 2:

$$\varphi_{2p(sample)} = \varphi_{2p(ref)} \frac{I_{sample} C_{ref}}{I_{ref} C_{sample}} \quad (2)$$

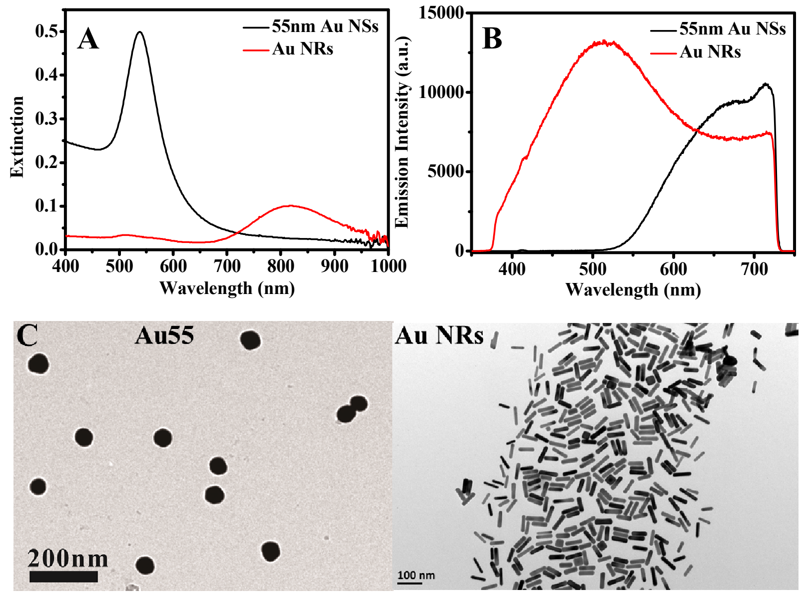

Figure S6. (a) UV-Vis extinction spectra, (b) TPPL spectra of 14.5 pM 55nm Au NSs and 20.4 pM Au NRs (average aspect ratio of 4); (c) TEM images of 55nm Au NSs and Au NRs

Concentrations of the undiluted Au and Ag NPs samples and Au NRs reference (C_0) were calculated from ICP elemental analysis and their average sizes were obtained from the TEM images. In details, the concentration of metal nanoparticles (C_0) can be calculated by using equation 3:

$$C_0 = \frac{C_m}{\rho V} \quad (3),$$

where C_m is the concentration of metal from elemental analysis in ppm, ρ is density of metal, V is the volume of single particle, subscript 'm' stands for metal (Au or Ag, ρ_{Au}=19.3 g • cm^{-3}, ρ_{Ag}=10.5 g • cm^{-3}). The volume of a single nanosphere can be calculated from equation 4:

$$V_{NS} = \rho \frac{4}{3}\pi R^3 \quad (4),$$

where R is the radius of Au or Ag NSs. The volume of a single gold nanorod can be obtained from equation 5:

$$V_{Au\ NR} = \frac{4}{3}\pi R^3 + \pi R^2 (L - 2R) \quad (5),$$

where R is half of the width of single gold nanorod and L is the length of single gold nanorod.

The integrated TPPL intensity can be obtained from TPPL spectra. We understand that there are some uncertainties in the calculated two-photon action cross section (underestimated by up to 50%) due to the cutoff of the TPPL spectra. However, as all the values are underestimated by the same factor, the overall trend will remain unchanged. The two-photon action cross section of Au NRs is φ_{2p}=30 000 GM (at 820nm, 1 GM=10^{-50}cm^4 • s/photon), according to *Zijlstra, P. et al.*[1] Therefore, the two-photon action cross section can be calculated according to equation 2.

The calculation of two-photon action cross section of 55nm Au NSs is illustrated as an example: Based on elemental analysis, Au concentration of 55nm Au NSs (C_m) is 170.68 ppm; the Au concentration of Au NRs (48nm ×12nm) is 23.58 ppm. According to Eq. 3 to 5 and taking dilution into consideration, the concentration of 55nm Au NSs (C_{Au55nm}) and Au NRs (C_{ref}) are 14.5 and 20.4 pM, respectively. The integrated TPE intensity of 55nm Au NSs (I_{Au55nm}) and Au NRs (I_{ref}) are 1251568 and 3070406, respectively. According to equation 2, the two-photon action cross section of 55nm Au NSs are calculated to be 1.7×10^4 GM per particle.

Reference

(1) Zijlstra, P.; Chon, J. W. M.; Gu, M. *Nature* **2009**, *459*, 410-413.