Supporting Information

Calculation of the quantum yield of pAuNPs

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Calculation of the quantum yield of pAuNPs

$$\Phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}}$$

The quantum yield (Φ) is defined as the ratio of the number of photons emitted to the number of photons absorbed, which is directly proportional to the ratio of emission cross section and absorption cross section. We estimated the emission cross section of highly polycrystalline AuNPs (pAyNPs) to be 10^{-15} cm^2 by comparing with commercially available CdSe/ZnS Quantum Dots (QDs). The emission intensity of pAuNPs at the single particle level shows an average of ~3000 counts, on the same order of the ~4500 counts emission intensity of CdSe/ZnS QDs, which exhibit an emission cross section on the same order of 10^{-15} cm^2 (ref. 1). While the absorption cross section of ~20 nm AuNPs was well established to be around 10^{-13} cm^2 (ref. 2), based on the ratio of emission cross section and absorption cross section, we roughly estimated the quantum yield of these pAuNPs to be on the order of 10^{-2}.

Supplementary Figures

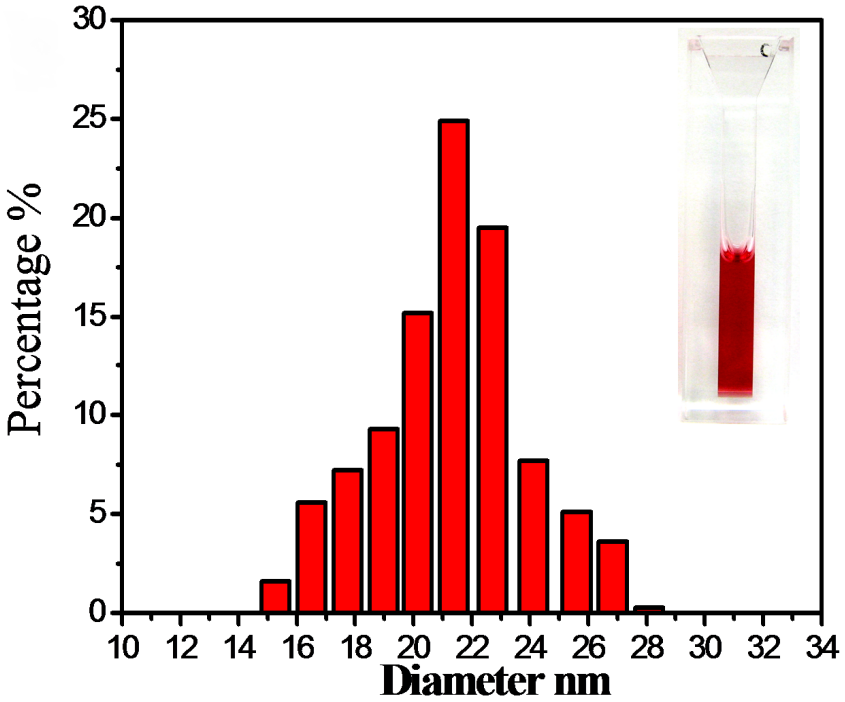

Figure S1. Hydrodynamic diameter distribution of pAuNPs in aqueous solution, showing the hydrodynamic diameter of pAuNPs is 21±1.7 nm in water. Inset is an image of pAuNPs aqueous solution.

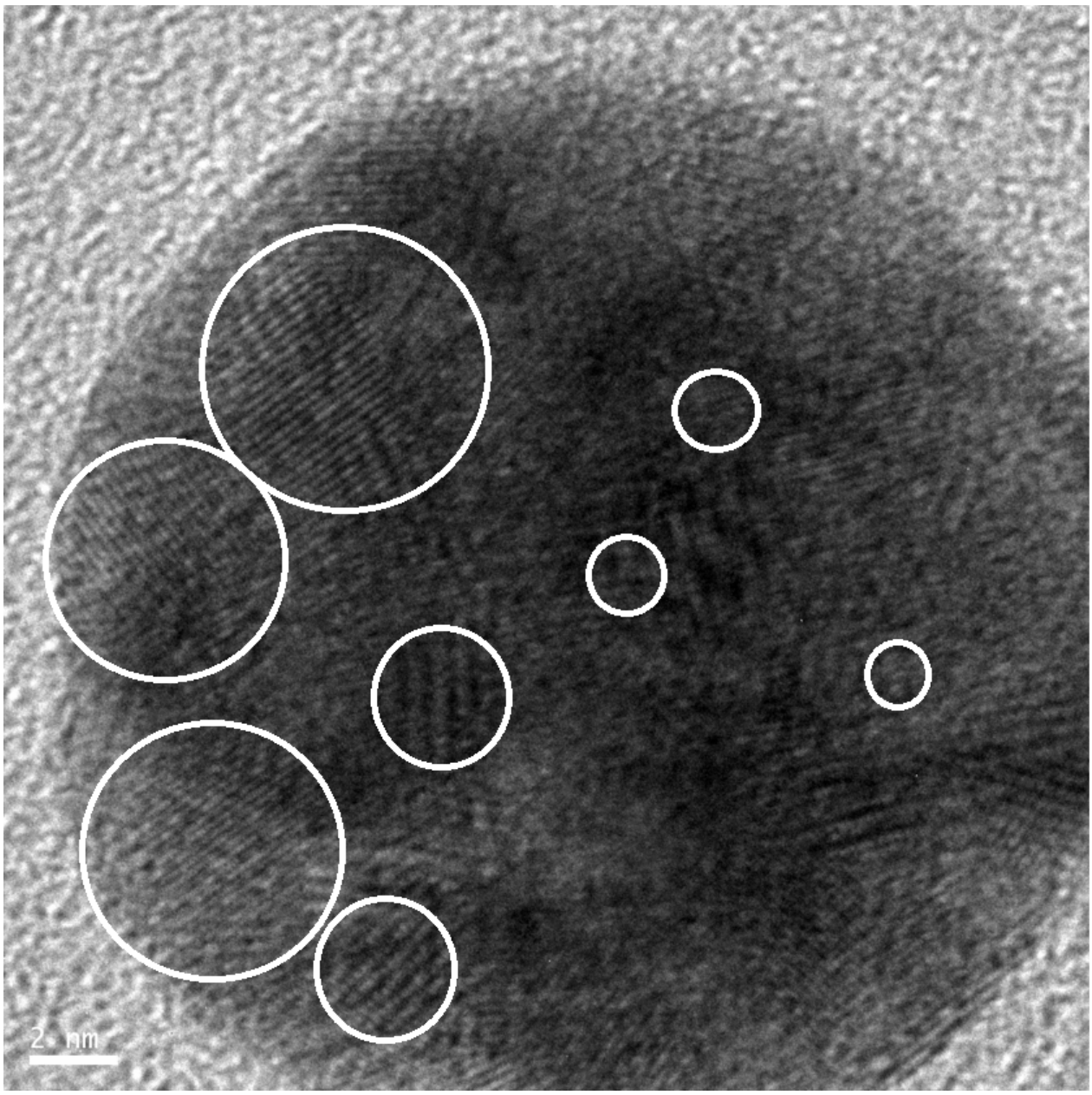

Figure S2. High resolution TEM image of pAuNPs, containing many grains with size down to 1 nm (scale bar: 2 nm). Some of the ~5 nm and ~1 nm representative individual grains are labelled with white circles.

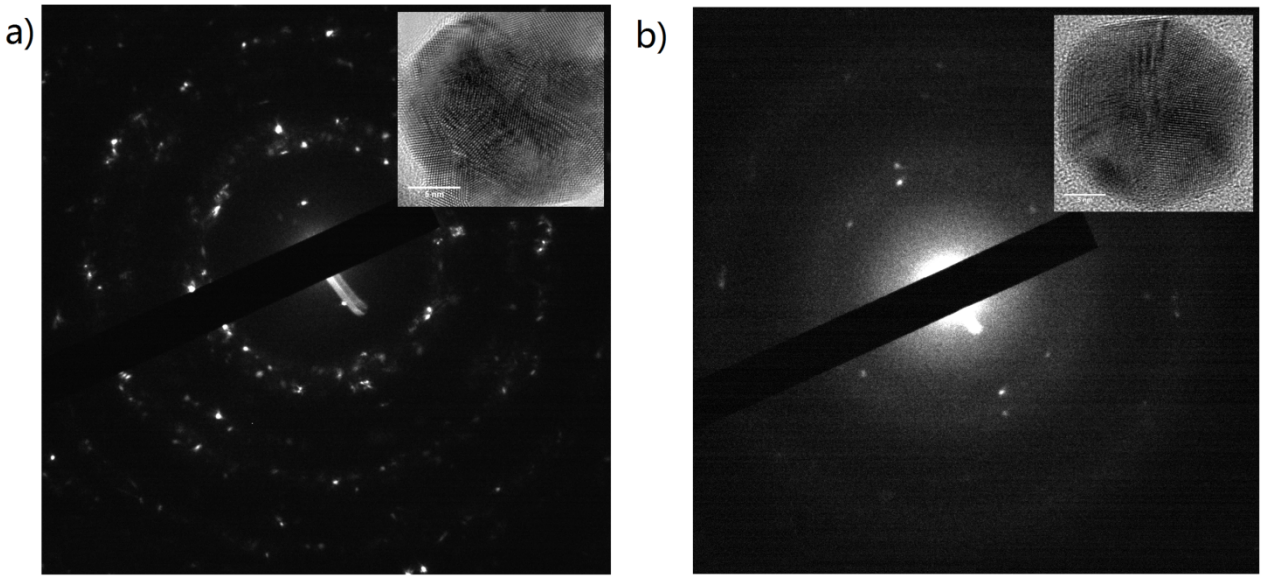

Figure S3. Selected area electron diffraction (SAED) of (a) a typical pAuNP and (b) mAuNP.

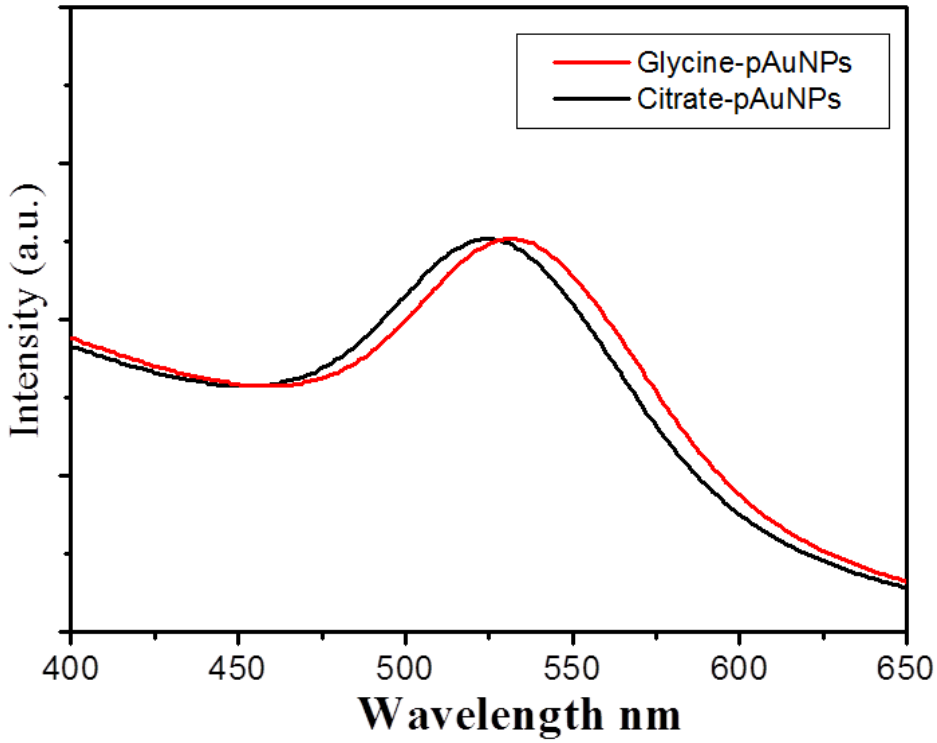

Figure S4. UV-Vis comparison of glycine-pAuNPs and citrate-pAuNPs. After replacing the glycine on pAuNPs by sodium citrate ligand, the surface plasmon absoprtion maximum of pAuNPs was shifted to ~526 nm.

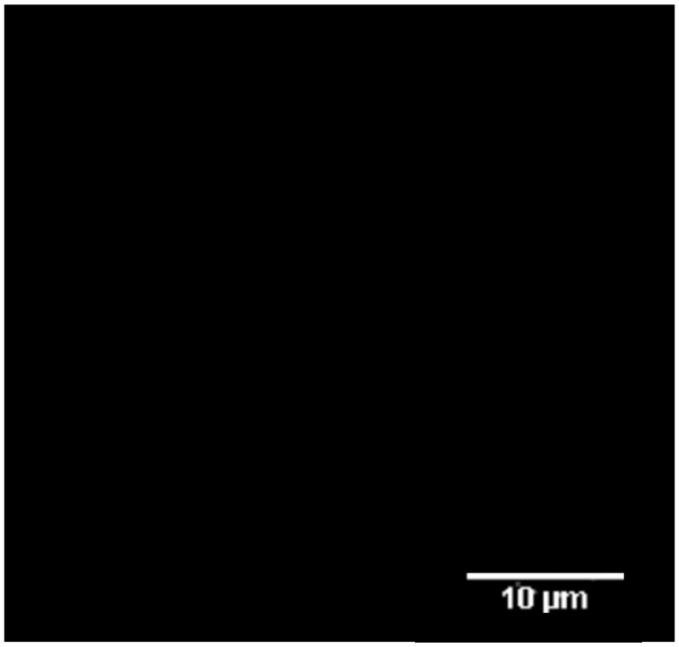

Figure S5. Fluorescence image of individual mAuNPs. Image was obtained from an IX-71 inverted microscope (Olympus) with a 1.3NA 100X oil-immersion objective under Hg-lamp excitation (Ex: 532-587 nm; Em: 605-682 nm; 30 W/cm^2; 0.5 s exposure time) and a Photon Max 512 CCD camera (Princeton Instrument).

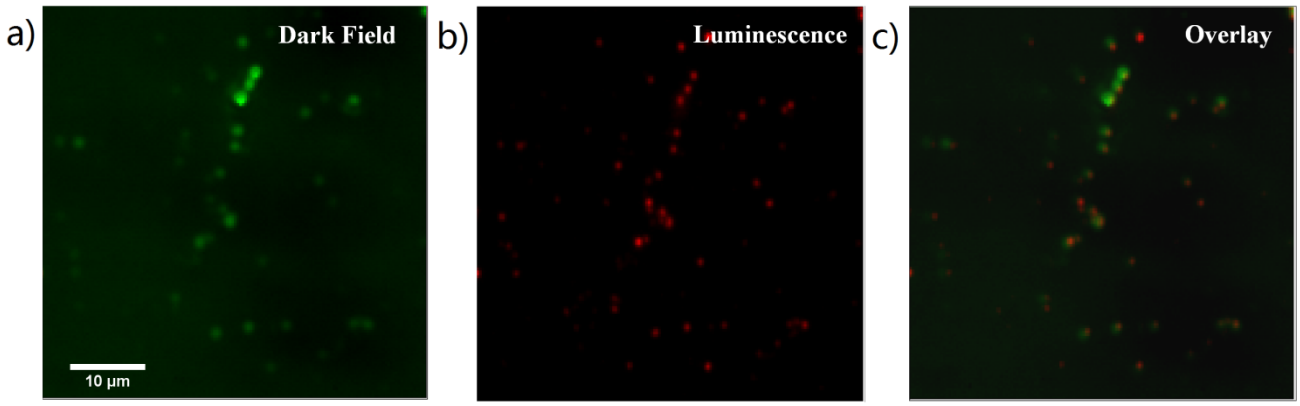

Figure S6. Dark-field (a), luminescence (b), and overlay (c) images of the pAuNPs. Co-locatization of scattering particles and luminescent particles indicates that surface plasmon and luminescence indeed arise from the same particle.

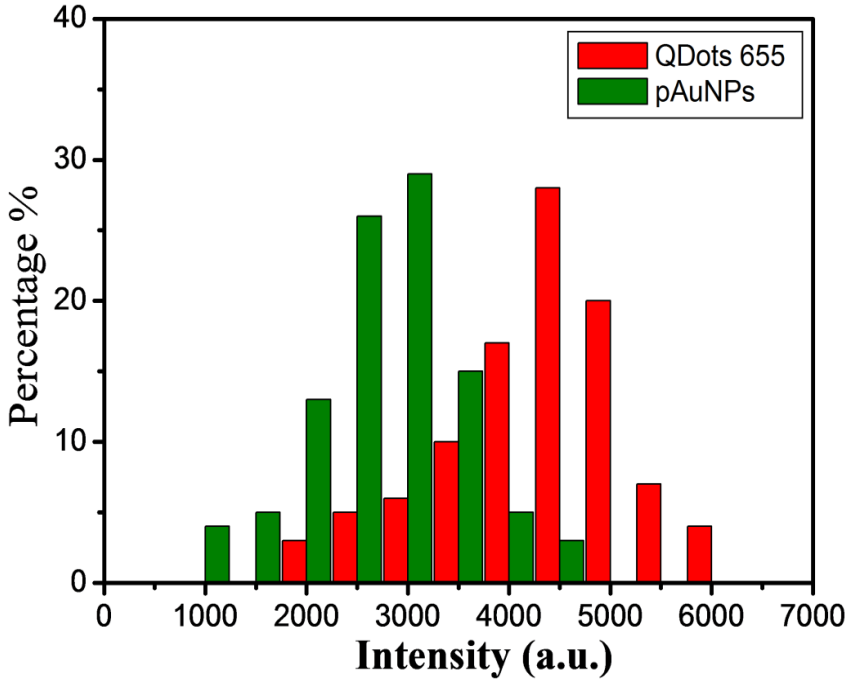

Figure S7. Fluorescence intensity comparison between pAuNPs and commercially available QD655s at the single particle level. Fluorescence images of nanoparticles were taken under Hg-lamp excitation (QDots: Excitation: 400-440 nm; Emission: 540 nm LP, 0.5 s exposure time, pAuNPs: Excitation: 532-587 nm; Emission: 605-682 nm 0.5 s exposure time). Emission intensity distributions were plugged by counting ~150 pAuNPs and QD655s.

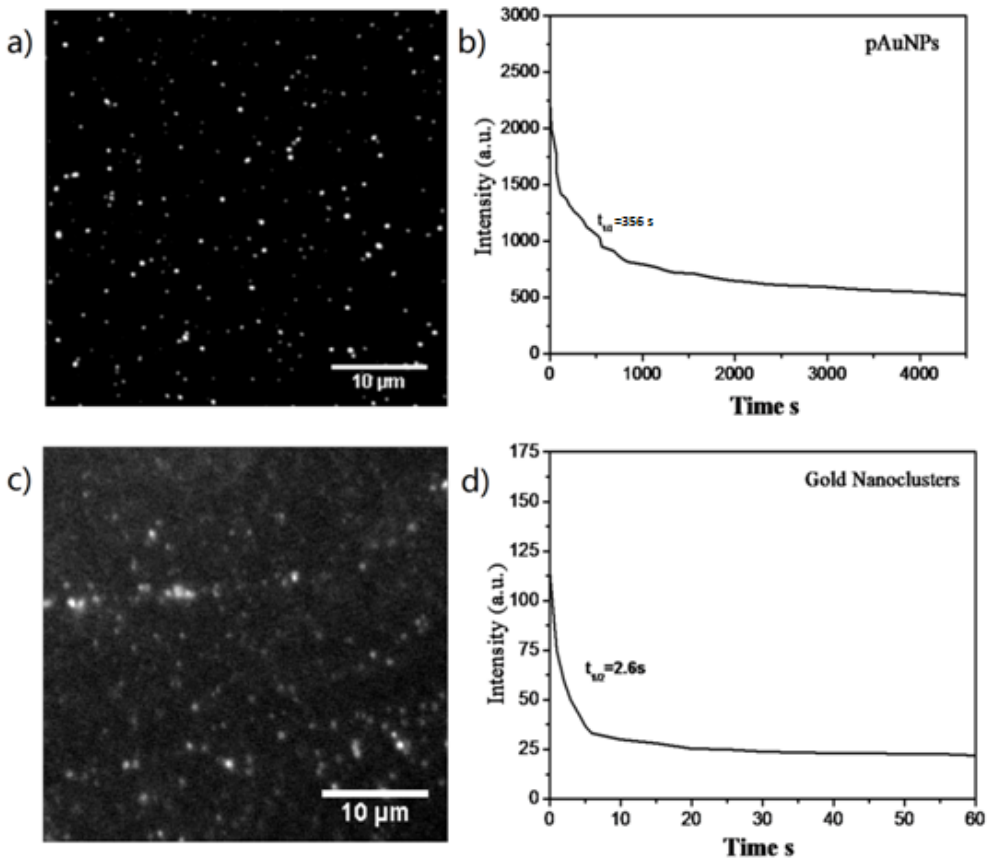

Figure S8. Brightness and photostability comparison of pAuNPs and luminescent ~2 nm gold nanoparticles at the single particle level. (a) fluorescence image of pAuNPs at the single particle level. (b) photostability of 50 pAuNPs as a function of time. (c) luminescence image of 1~2 nm gold nanoparticles at the single particle level. (d) photostability of 50 ~2 nm gold nanoparticles as a function of time. Photobleaching half lifetime was defined as the time point when the total intensity was reduced to the half of the original value, which was 356 s for pAuNPs and 2.6 s for small gold nanoparticles, respectively. (Excitation: 532-587 nm; Emission: 605-682 nm; 0.5 s exposure time)

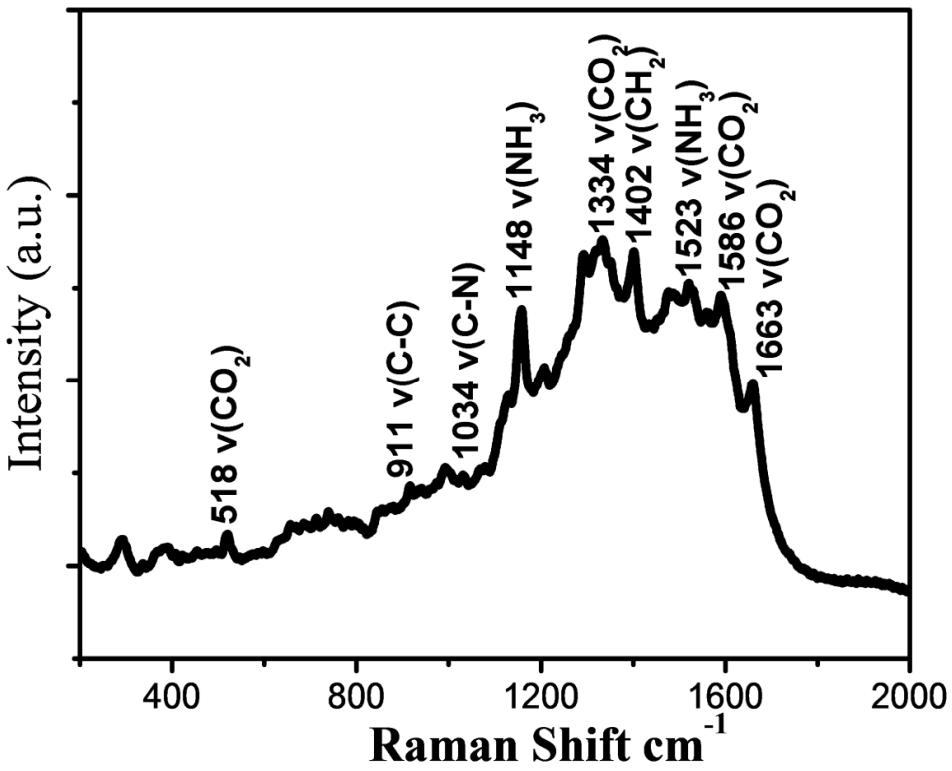

Figure S9. Surface enhanced Raman scattering (SERS) spectrum of pAuNPs coated by glycine. The observed Raman spectrum shows specific Raman lines at 518 cm^{-1}, 911 cm^{-1}, 1034 cm^{-1}, 1148 cm^{-1}, 1334 cm^{-1}, 1402 cm^{-1}, 1586 cm^{-1} and 1663 cm^{-1}, which can be assigned to previously reported glycine SERS lines[(Ref)]. For examples, the lines at 518 cm^{-1}, 1334 cm^{-1}, 1402 cm^{-1} and 1663 cm^{-1} of the nanoparticles can be assigned to COO^- bending and stretching. The line at 911 cm^{-1} is close to previously reported C-C stretching vibration lines at 901 cm^{-1}. The line observed at 1034 cm^{-1} is due to C-N vibration line. The lines observed at 1148 cm^{-1} and 1523 cm^{-1} most likely result from NH_3^+ vibrations.

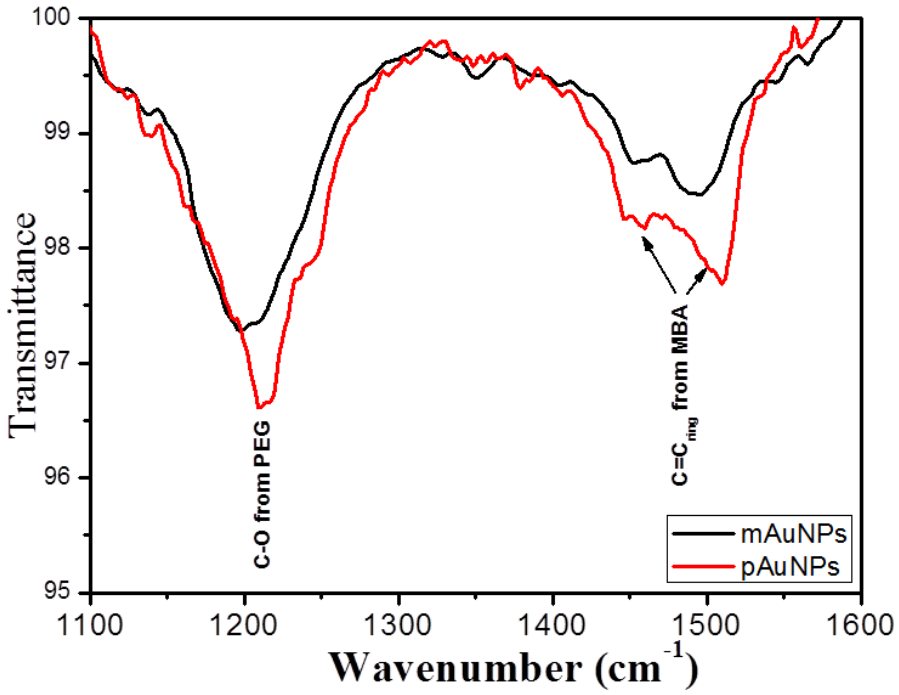

Figure S10. IR spectra of MBA-mAuNPs and MBA-pAuNPs. The C-O band at 1200 cm^{-1} is assigned to the coated PEG ligand, and the C=C bands at 1450 and 1500 cm^{-1} are assigned to the benzene ring vibration of coated MBA ligand.

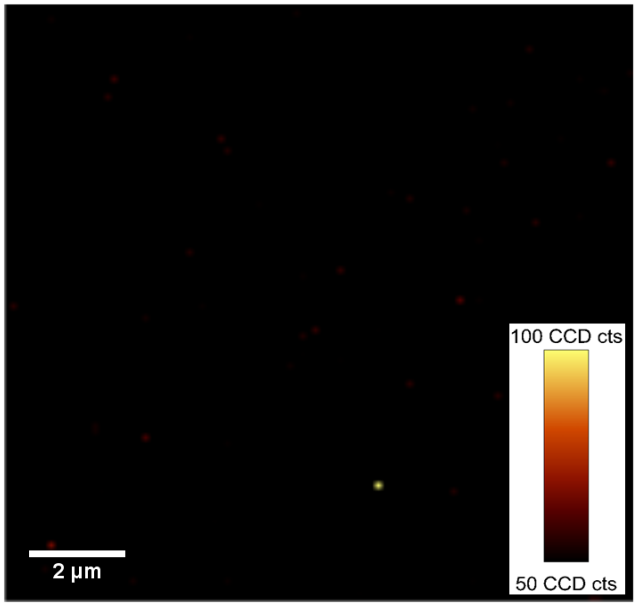

Figure S11. Raman image of individual MBA-mAuNPs. The image was taken under 781 nm laser excitation with 0.1 s integration time and constructed based on the Raman vibration peak at 1579±10 cm^{-1}.

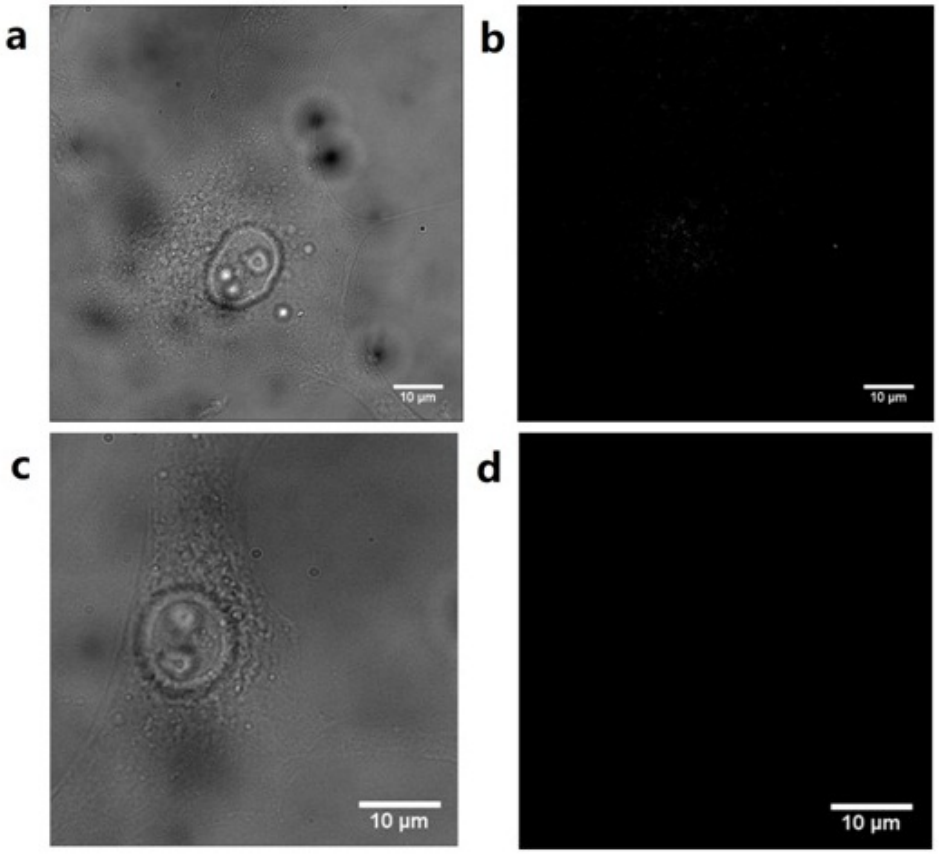

Figure S12. Control experiments of fixed human glioblastoma U87MG cell labeling with pAuNPs under different conditions. Bright field (a) and fluorescence (b) images of fixed human glioblastoma U87MG cell stained with MBA-pAuNPs. Bright field (c) and fluorescence (d) images of fixed human glioblastoma U87MG cell stained with MBA-pAuNPs-cRGD after saturated the surface integrin $\alpha_v\beta_3$ receptor by incubating cells with 1 mM cRGD solution before labeling. The fluorescence images were taken under Hg-lamp excitation (Ex: 532-587 nm; Em: 605-682 nm, 30 W/cm^2, 0.5 s exposure time).

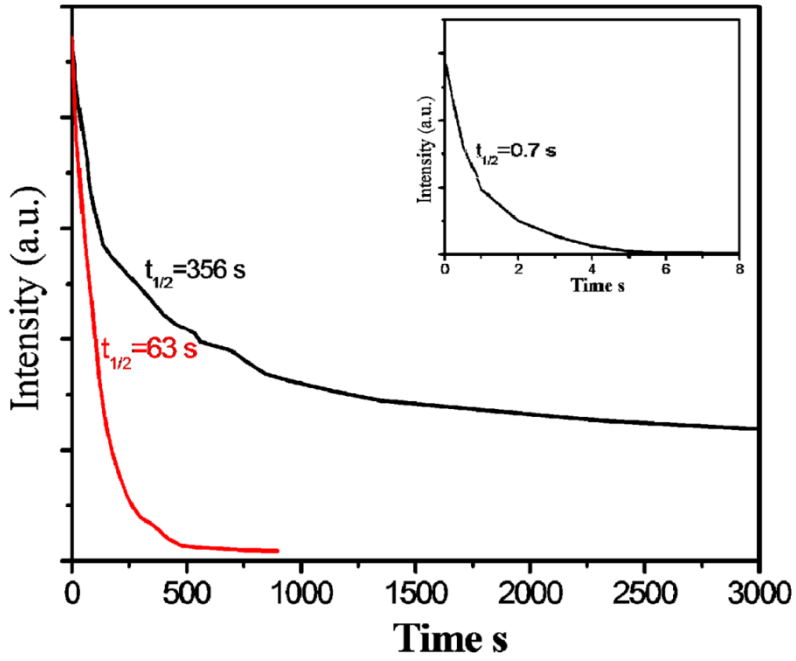

Figure S13. Photostability comparison of pAuNPs, QD655s and FITC. Photobleaching halftimes were determined to be 356 s (pAuNPs, black), 63 s (QD655s, red) and 0.7 s (FITC, inset), respectively.

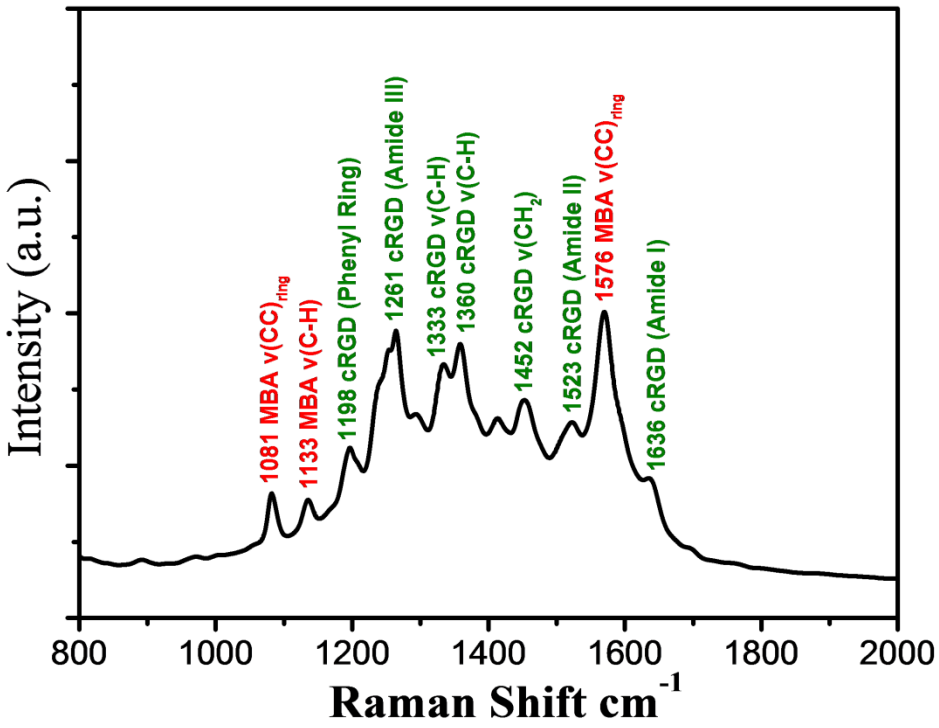

Figure S14. Surface enhanced Raman spectrum of MBA-pAuNPs-cRGD on labeled U87 Cells. The obtained Raman spectrum shows specific Raman lines from MBA at 1081 cm^{-1} (C-C ring), 1133 cm^{-1} (C-H vibration), and 1576 cm^{-1} (C-C ring), and Raman signal from cRGD at 1198 cm^{-1} (Phenyl ring), 1261 cm^{-1} (Amide III), 1333 cm^{-1} and 1360 cm^{-1} (C-H vibration), 1452 cm^{-1}(CH_2 vibration), 1523 cm^{-1} (Amide II) and 1636 cm^{-1} (Amide I).

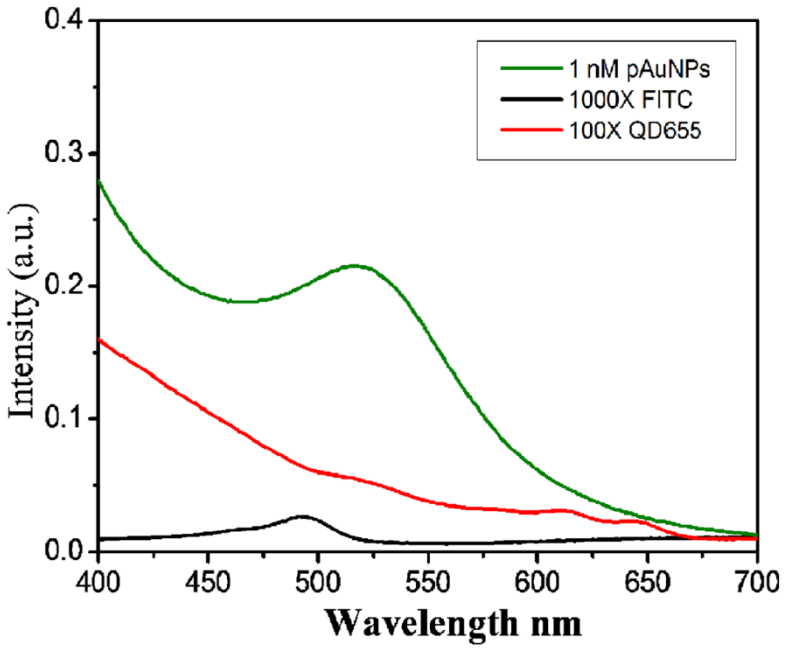

Figure S15. The absorption comparison of pAuNPs, QD655s and FITC. By assuming the absorption and concentration follows a linear relationship in the experimental range, the surface plasmon absorption of pAuNPs is more than 300 times and ~10^4 times larger than the QDs and FITC at the same concentrations in the visible range, respectively.

References

1. S. M. Iftiquar, Y. Wijaya, R. Dumke, *Opt. Photonics. Lett.*, 2011, **4**, 1.

2. P. K. Jain, K. S. Lee, I. H. El-Sayed and M. A. El-Sayed, *J. Phys. Chem. B.,* 2006, **110**, 7238.