Supporting Information

Low-Cytotoxic Gold-Coated Silver Nanoflowers for Intracellular pH Sensing

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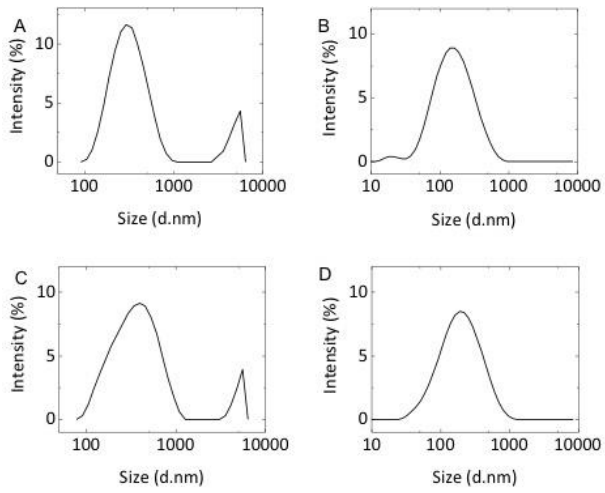

Figure S1. DLS measurements of AgNPs (A, 342.7 nm), AgNFs (B, 131.6 nm), AuAgNPs (C, 357.0 nm) and AuAgNFs (D, 162.7 nm).

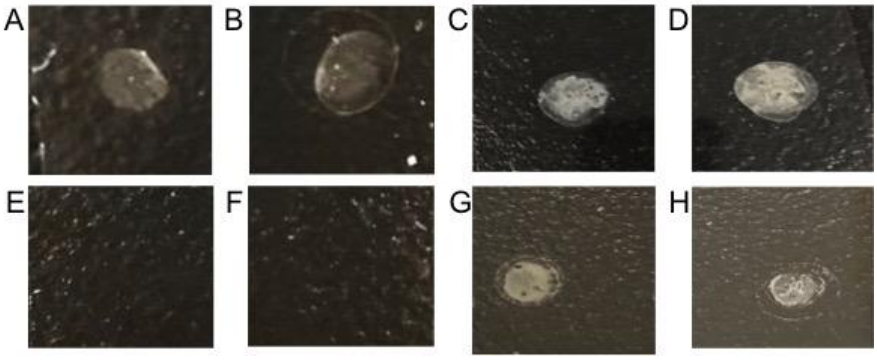

Figure S2. Photographs of AgNPs (A), AgNFs (B), AuAgNPs (C), AuAgNFs (D) on a glass substrate, and AgNPs (E), AgNFs (F), AuAgNPs (G), and AuAgNFs (H) on a glass substrate after treated with 2% of H_2O_2 aqueous solution.

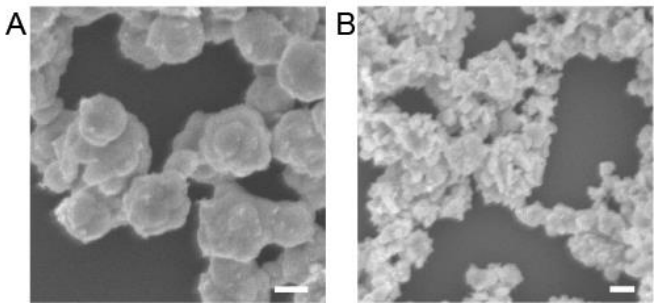

Figure S3. SEM images of AuAgNPs (A), AuAgNFs (B) after treated with 2% of H_2O_2 aqueous.

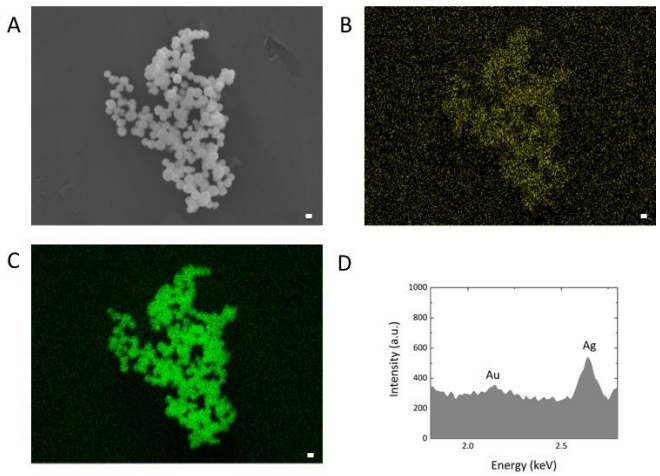

Figure S4. EDX images of AuAgNPs by SEM. SEM image (A), gold elemental mapping (B), silver element mapping (C) and spectrum (D) of EDX elemental analysis. (Scale bar: 200 nm)

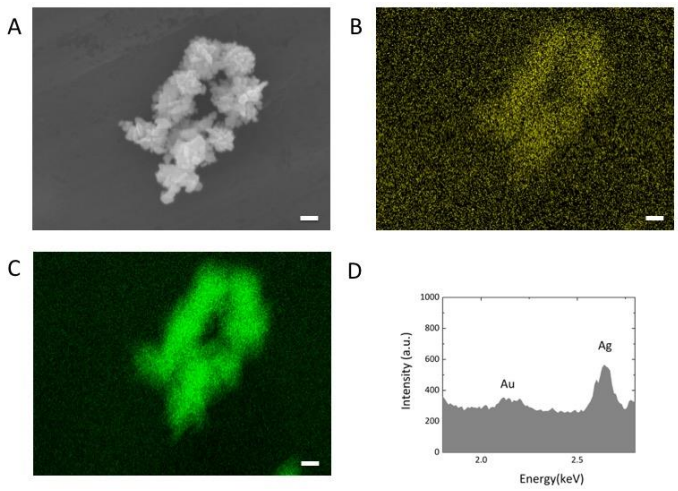

Figure S5. EDX images of AuAgNFs by SEM. SEM image (A), gold elemental mapping (B), silver element mapping (C) and spectrum (D) of EDX elemental analysis. (Scale bar: 200 nm)

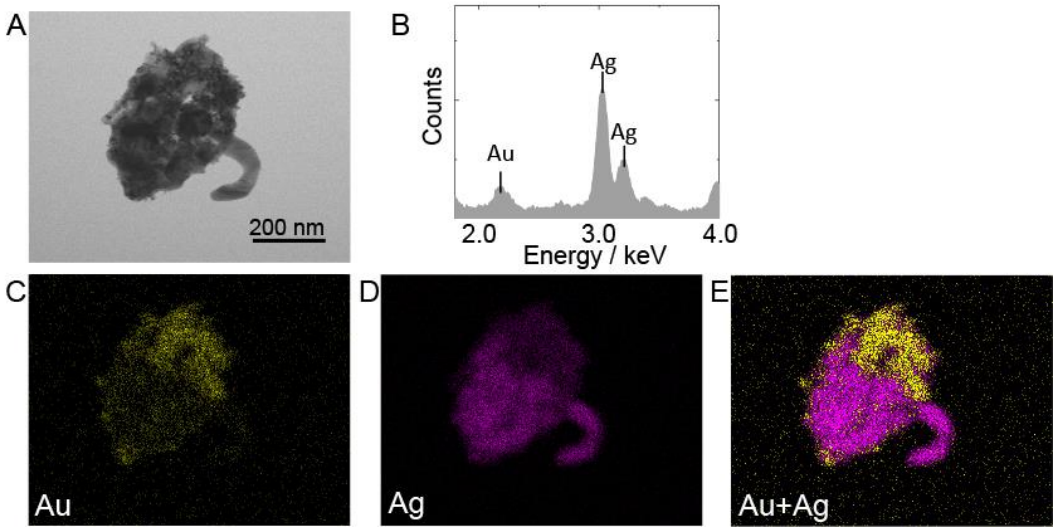

Figure S6. EDX images of AuAgNPs by STEM. STEM image (A), spectrum (B), gold elemental mapping (C), silver element mapping (D) and merged image of individual gold and silver mapping (E).

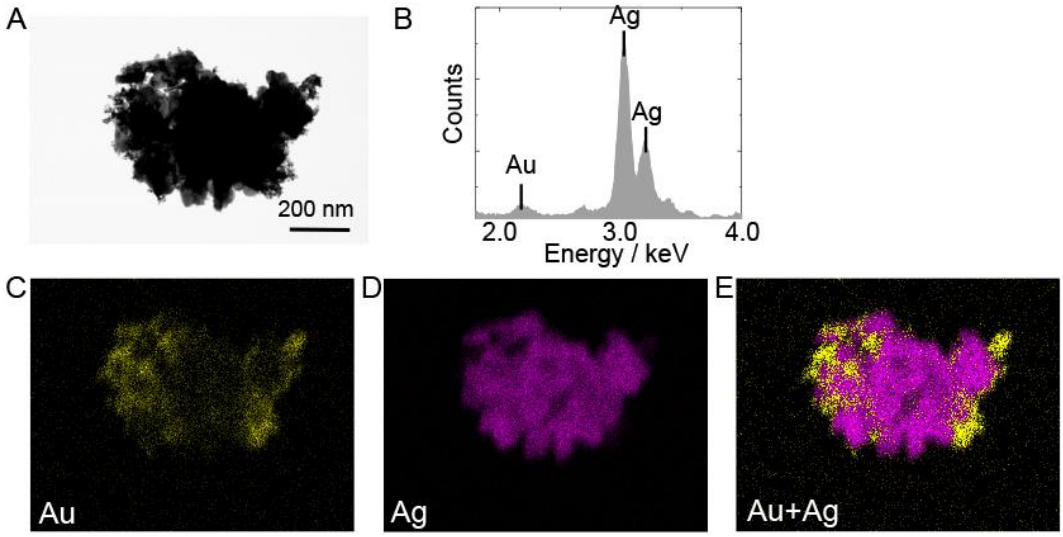

Figure S7. EDX images of AuAgNFs by STEM. STEM image (A), spectrum (B), gold elemental mapping (C), silver element mapping (D) and merged image of individual gold and silver mapping (E).

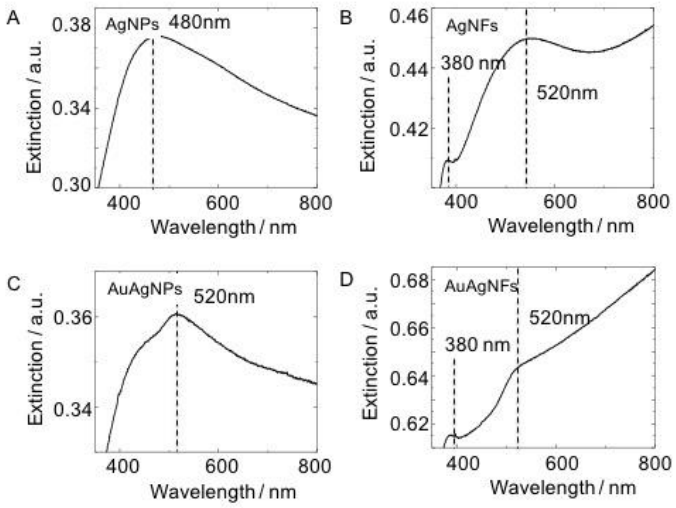

Figure S8. Extinction spectra of AgNPs (A), AgNFs (B), AuAgNPs (C), and AuAgNFs (D) dispersed in water.

SERS measurements of 4-MBA

The pH response from 4-MBA-AuAgNFs or 4-MBA-AuAgNPs was investigated separately by recording SERS spectra in acidic to basic pH levels in PBS buffer solution. SERS spectra at each pH in PBS buffer solution were acquired after immersion of the sample for 10 min.

The intense bands at 1078 cm^{-1} and 1587 cm^{-1} correspond to ν(C–C) benzene ring breathing mode of 4-MBA. Both of them were shifted compared to the normal Raman spectrum due to the charge transfer between 4-MBA and metal.[1]

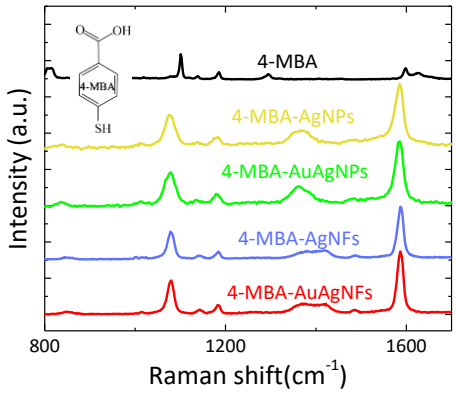

Figure S9. SERS activities of AuAgNFs, AgNFs, AuAgNPs and AgNPs with excitation of 532 nm laser.

Estimation of SERS enhancement factor (EF)

EF was estimated based on the following equation. $EF = (I_{SERS}/N_{SERS})/(I_{bulk}/N_{bulk})$, where I_{SERS} and I_{bulk} are the SERS intensity of 4-MBA on the surface of metal nanoparticles and that of normal Raman scattering from 4-MBA, respectively. N_{SERS} and N_{bulk} are the number of 4-MBA molecules. Assuming full coverage of 4-MBA monolayers on the metal nanoparticles with 0.8 x 0.8 nm^2 spacing per molecule and the diameter of AgNFs and AgNPs were estimated to be 200 x 10^{-9} m. The number of 4-MBA molecules N_{bulk} was 6.07 x 10^8, and the number of 4-MBA molecules N_{SERS} was 4.9 x 10^5. Considering the laser power, EF was calculated for AgNFs: 5.7 x 10^5, AuAgNFs: 2.7 x 10^5, AgNPs: 1.7 x 10^5, AuAgNPs: 1.4 x 10^5.

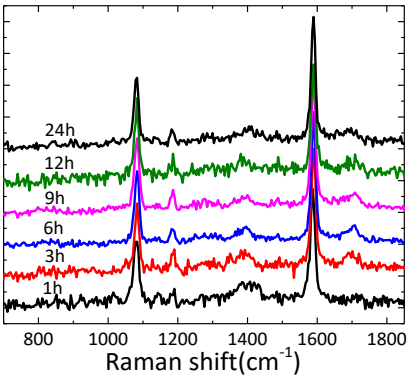

Figure S10. Typical SERS spectra at different time points measured with 4-MBA-AuAgNFs inside A549 cells.

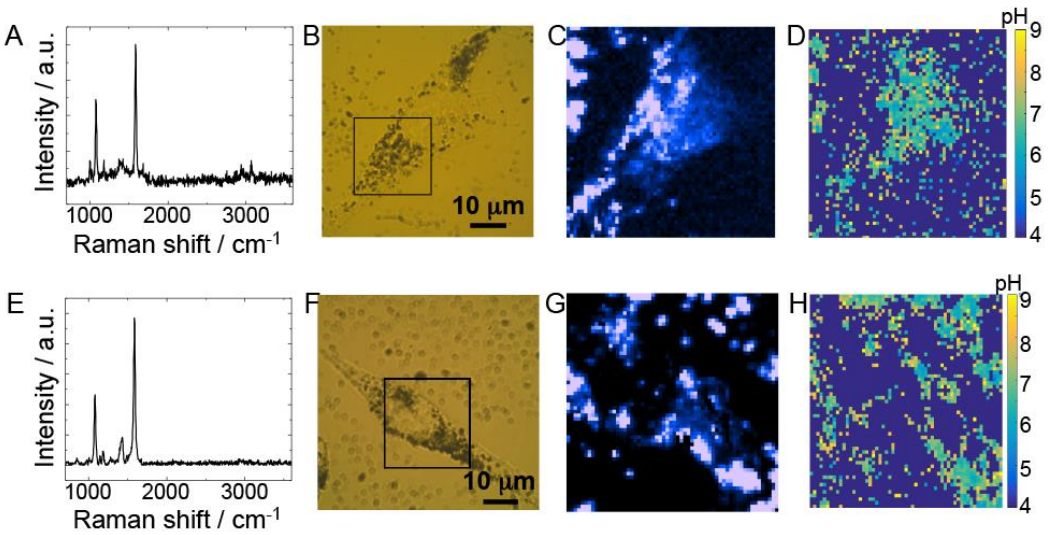

Figure S11. Two set of pH imaging inside single A549 cell. A549 cells incubated with 0.1 mg / mL of AuAgNFs for 24 h. (A) (E) Typical SERS spectra of 4-MBA-AuAgNFs inside single A549 cell. (B) (F) Optica transmission images of cells with 4-MBA-AuAgNFs. (C)(G) SERS mappings constracted with the peak intensity at 1078 cm^{-1}, whcih were scanned marked by black square area in the transmission images in (A) (E). (D), (H) the corresponding pH mapping reconstructed using the peak around 1440 cm^{-1}.

REFERENCES

(1) Capocefalo, A.; Mammucari, D.; Brasili, F.; Fasolato, C.; Bordi, F.; Postorino, P.; Domenici, F. Exploring the Potentiality of a SERS-Active pH Nano-Biosensor. *Front. Chem.* **2019,** *7* (413).