Electronic Supplementary Information

Uptake of silver nanoparticles by DHA-treated cancer cells examined through surface enhanced Raman spectroscopy in a microfluidic chip

Zhiming Zhai[1,2], Fengqiu Zhang[1,2,3], Xiangyu Chen[2], Jie Zhong[1,2], Gang Liu[2], Yangchao Tian[2], Qing Huang[1,2,*]

[1]*Institute of Technical Biology and Agriculture Engineering, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China*

[2] *University of Science and Technology of China, Hefei 230026, China*

[3] *School of Physical Engineering, Zhengzhou University, Zhengzhou, China*

* Corresponding author: huangq@ipp.ac.cn

Contents

1. Morphology and size of the Ag@CD NPs

2. TEM images of Ag@CD@p-ATP NPs

3. Enhancement factor (EF) of the Ag@CD NPs

4. SERS sensitivity of the Ag@CD NPs

5. FTIR spectra of the NPs

6. Zeta potential of the NPs

7. Raman signal of PDMS

8. SERS intensity of the Ag@CD@p-ATP@FA NPs

9. Cytotoxicity of the beta-cyclodextrin

10. Cytotoxicity of the Ag@CD and Ag@CD@p-ATP@FA NPs at higher concentration

1. Morphology and size of the Ag@CD NPs

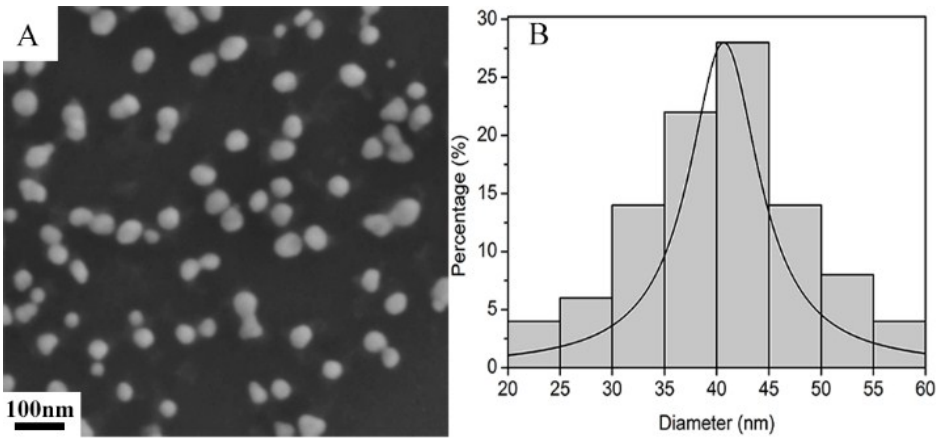

Figure S1. SEM image (A) of the and the size diameter distribution (B) of the Ag@CD NPs

2. TEM images of Ag@CD@p-ATP NPs

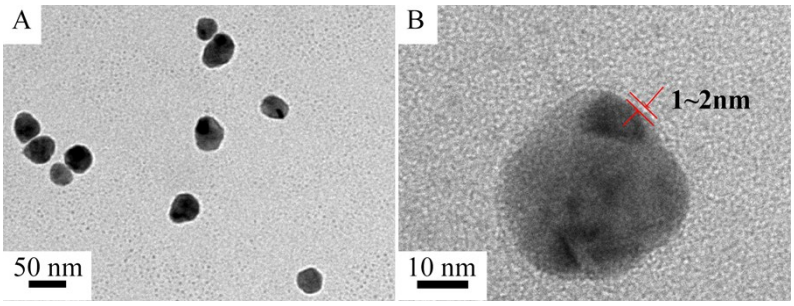

Figure S2. TEM images of Ag@CD@p-ATP NPs

3. Enhancement factor (EF) of Ag@CD NPs

We employed the Raman peak intensity at 1076 cm^{-1} of p-ATP molecules to evaluate the average SERS EF of the Ag@CD NPs. The average SERS EF can be calculated by the following formula given by the literature.[1]

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{RS}/N_{RS}}$$

Where I_{SERS} and I_{RS} represent the intensities of the same peak of the SERS spectra acquired on the Ag@CD substrate and the normal Raman spectra on the quartz plate

respectively, and N_{SERS} and N_{RS} represent the number of p-ATP molecules on the substrates and quartz plate within the laser focus spot respectively. Since the measurement conditions such as laser power, laser wavelength, and acquiring time are identical, the above formula can be rewritten as:

$$\mathrm{EF} = \frac{I_{SERS}}{I_{RS}} \cdot \frac{S_{SERS} V_{RS} C_{RS}}{S_{RS} V_{SERS} C_{SERS}}$$

For the SERS measurement, 10 μL of 10^{-8} M p-ATP ethanol solution was dripped and dispersed on the Ag@CD substrate, and the area of solution was about 25mm^2; 10 μL of 10^{-2} M p-ATP ethanol solution was dispersed on the quartz plate, and the area of solution was about 9 mm^2. Figure S3 shows representative SERS and Raman signal from the Ag@CD NPs and the quartz plate. The intensities of the (C-C and C-S stretching) at 1076 cm^{-1} band was used to calculate the EF, and the I_{SERS} and I_{RS} are 4692 and 328, respectively. The EF is calculated to be 4×10^7.

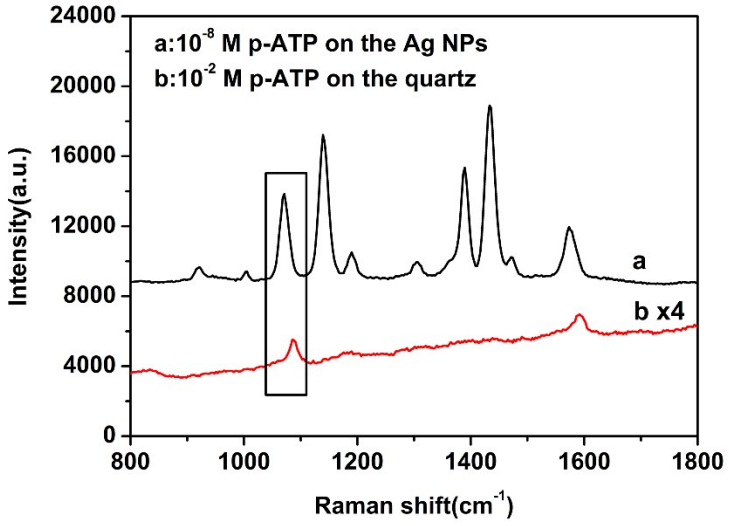

Figure S3. The SERS spectra of 10^{-8} M p-ATP in ethanol solution dispersed on the Ag@CD NPs (a) (black line), and the Raman spectrum of p-ATP on the quartz (b) (red line).

4. SERS sensitivity of the Ag@CD NPs

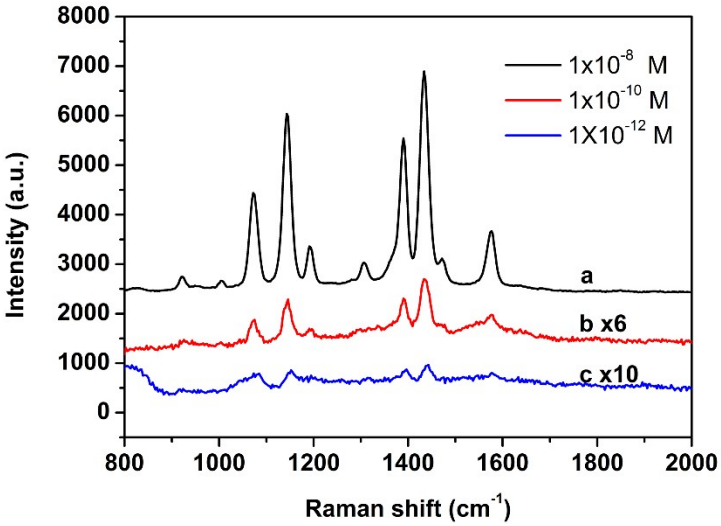

Figure S4. SERS spectra of p-ATP with different concentrations detected by the Ag@CD NPs. The Raman signal at low concentration of 10^{12} M of p-ATP can be identified clearly.

5. FTIR spectra of the NPs

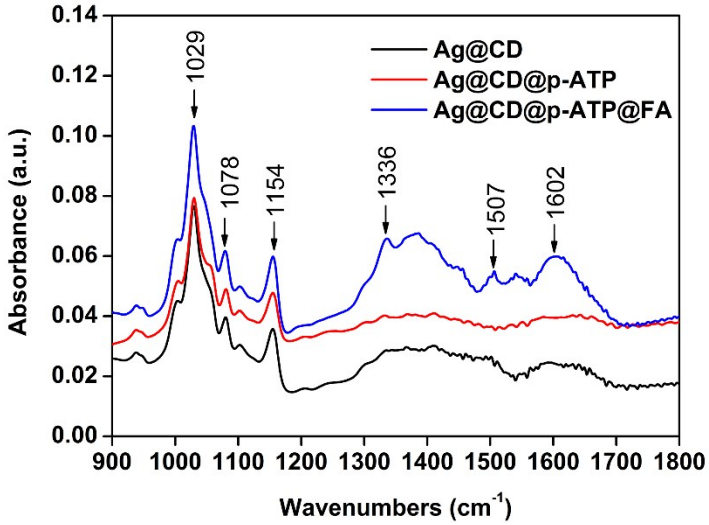

Figure S5. The FTIR spectra of as-synthesized Ag@CD, Ag@CD@p-ATP and Ag@CD@p-ATP@FA, respectively.

6. Zeta potential of the NPs

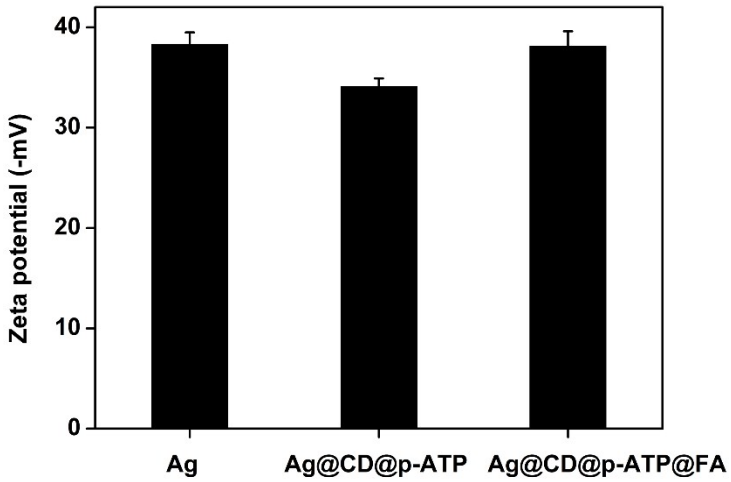

Figure S6. Zeta potential measurements for Ag@CD, Ag@CD@p-ATP and Ag@CD@p-ATP@FA NPs, respectively.

7 Raman signal of PDMS

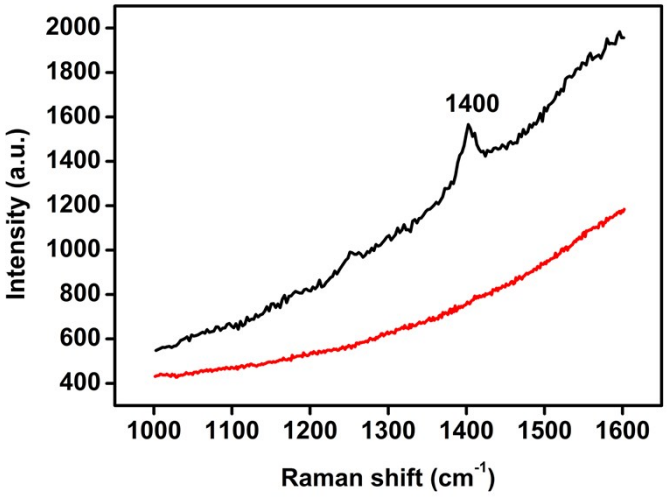

Figure S7. The red line represents the Raman spectrum taken with laser focused on the cells inside the microfluidic channel; the black line represents the Raman spectrum taken with laser focused on the PDMS on top of the microfluidic chip.

8. SERS intensity of the Ag@CD@p-ATP@FA NPs

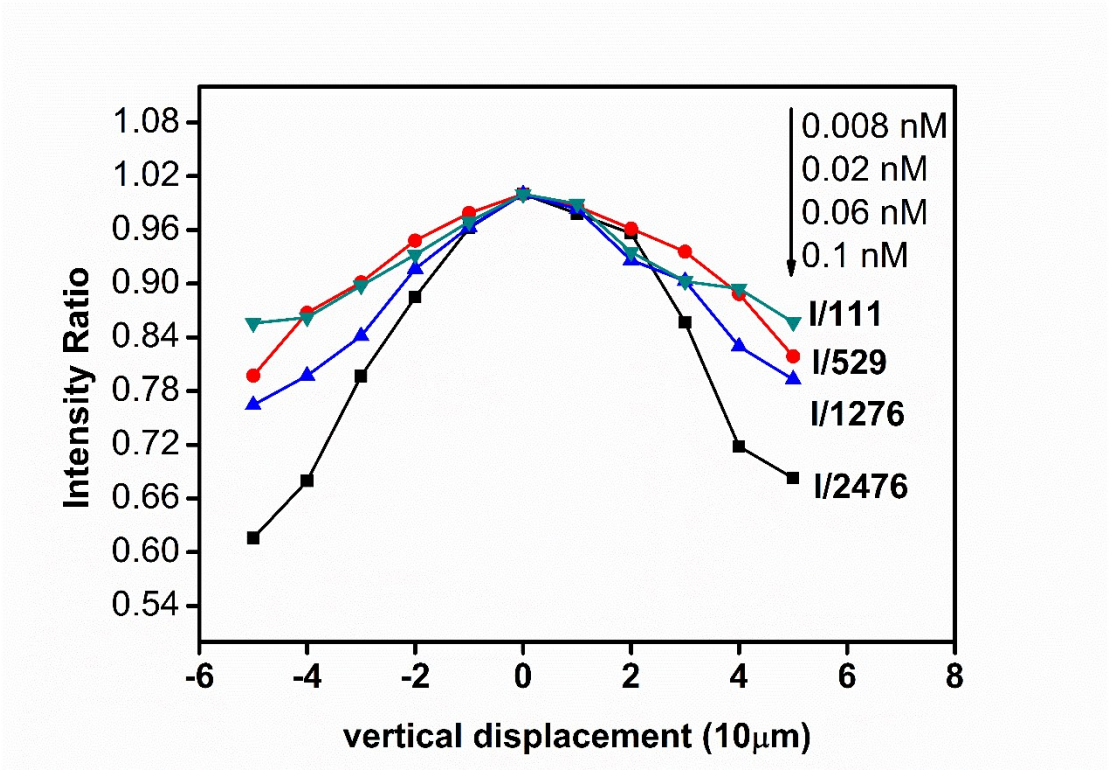

Figure S8. The SERS intensities of Ag@CD@p-ATP@FA depend on its vertical displacement on z-platform. We selected 4 different concentrations of Ag@CDp-ATP@FA in the test.

9. Cytotoxicity of the beta-cyclodextrin

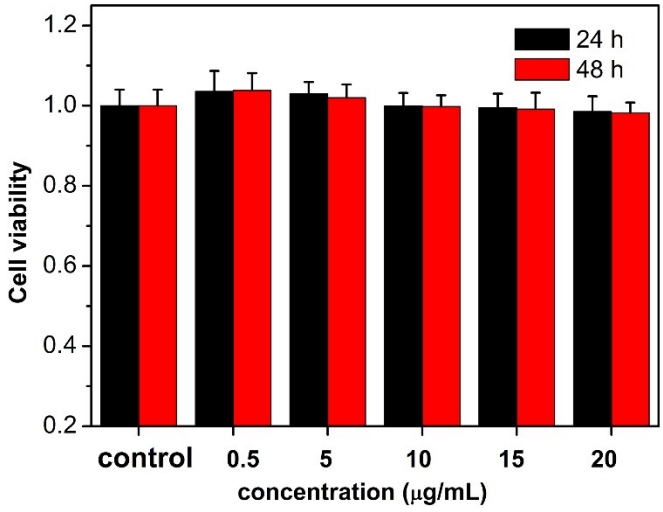

Figure S9. Cell viability of HeLa cells incubated with beta-cyclodextrin of different concentrations (0, 0.5, 5, 10, 15, 20 μg/mL) after 24 h and 48 h, respectively.

10. Cytotoxicity of the Ag@CD and Ag@CD@p-ATP@FA NPs at higher concentration

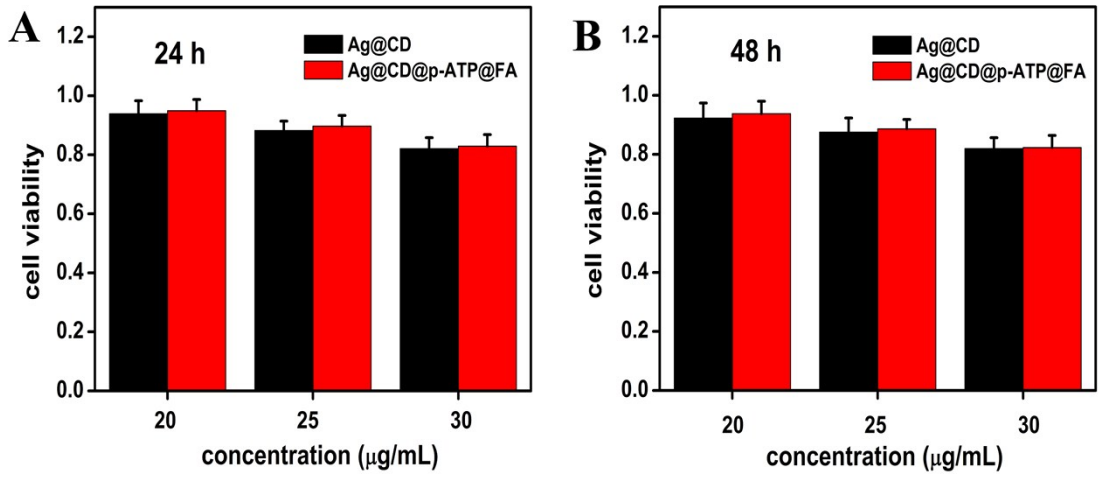

Figure S10. The cell viability test for the HeLa cells incubated with Ag@CD and Ag@CD@p-ATP@FA NPs at different concentrations for 24 h (A) and 48 h (B), respectively.

Notes and references

1 S. E. Hunyadi and C. J. Murphy, *J. Mater. Chem.*, 2006, 16, 3929-3935.