Electronic Supplementary Information:

Synthesis of the magnetic Fe$_3$O$_4$-Au hybrids for sensitive SERS detection of cancer cells at low abundance

Yanchun Qiu, Dan Deng, Ping Wu,* Hui Zhang, and Chenxin Cai*

Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, National and Local Joint Engineering Research Center of Biomedical Functional Materials, College of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210097, P. R. China.

* Corresponding author, E-mail: wuping@njnu.edu.cn (P. Wu); excai@njnu.edu.cn (C. Cai)
Fig. S1 (A) Typical TEM image of the prepared Au NPs. (B) Size distribution of the prepared Au NPs.

Fig. S2 Size distribution of the Fe\textsubscript{3}O\textsubscript{4} (A) and Fe\textsubscript{3}O\textsubscript{4}-Au NPs (B).
**Fig. S3** UV–vis spectrum of the prepared Au NPs.
**Fig. S4** Fluorescence spectra of the free 4-ATP (0.01 μM, a) and supernatant of the 4-ATP/Fe₃O₄-Au NPs nanostructures after centrifugation (b). The fluorescence spectra were obtained under excitation at 295 nm.

To check the adsorption stability on the Fe₃O₄-Au NPs, we dispersed the 4-ATP/Fe₃O₄-Au NPs (2 mg) into water (1 mL) and stirred for 2 h at 250 rpm, and then the suspension was centrifuged at 10000 rpm. The supernatant was collected and its fluorescence spectrum was recorded. As shown in curve (b), no fluorescence signal of 4-ATP was detected, indicating that almost no 4-ATP molecule was desorbed from the surface of Fe₃O₄-Au NPs. These results demonstrate that the adsorption of 4-ATP on the Fe₃O₄-Au NPs is stable.
**Fig. S5** SERS spectra of 4-ATP labeled at the surface of Fe$_3$O$_4$-Au NPs before (a) and after (b) the nanostructures were conjugated with the anti-CEA.

**Fig. S6** SERS spectra for the 8 independent measurements of A549 cells ($1\times10^5$ cells mL$^{-1}$) after binding of the anti-CEA/4-ATP/Fe$_3$O$_4$-Au tags and anti-CEA/Au substrates.