

Electronic Supplementary Information

Development of Ag nanopolyhedra based fiber-optic probes for high performance SERS detection

Jie Cao,* and Jinzu Wang

Hefei Institutes of Physical Science, Chinese Academy of Sciences,
Anhui, People's Republic of China.

E-mail: candj@mail.ustc.edu.cn.

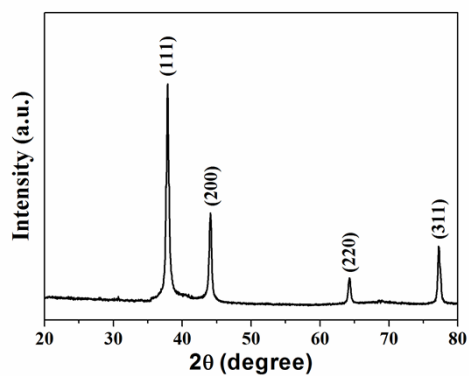


Fig. S1 XRD pattern of the Ag products scraped off from the optical fiber, confirming the formation of fcc silver.

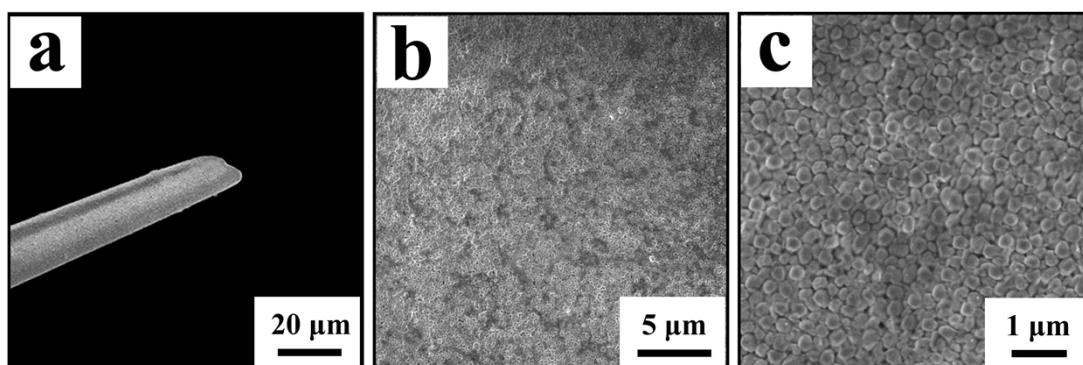


Fig. S2 More SEM images of the fiber SERS probe with different magnifications. (a: The distal tip of the probe was fractured because the reaction condition is in the high-temperature and high-pressure state.)

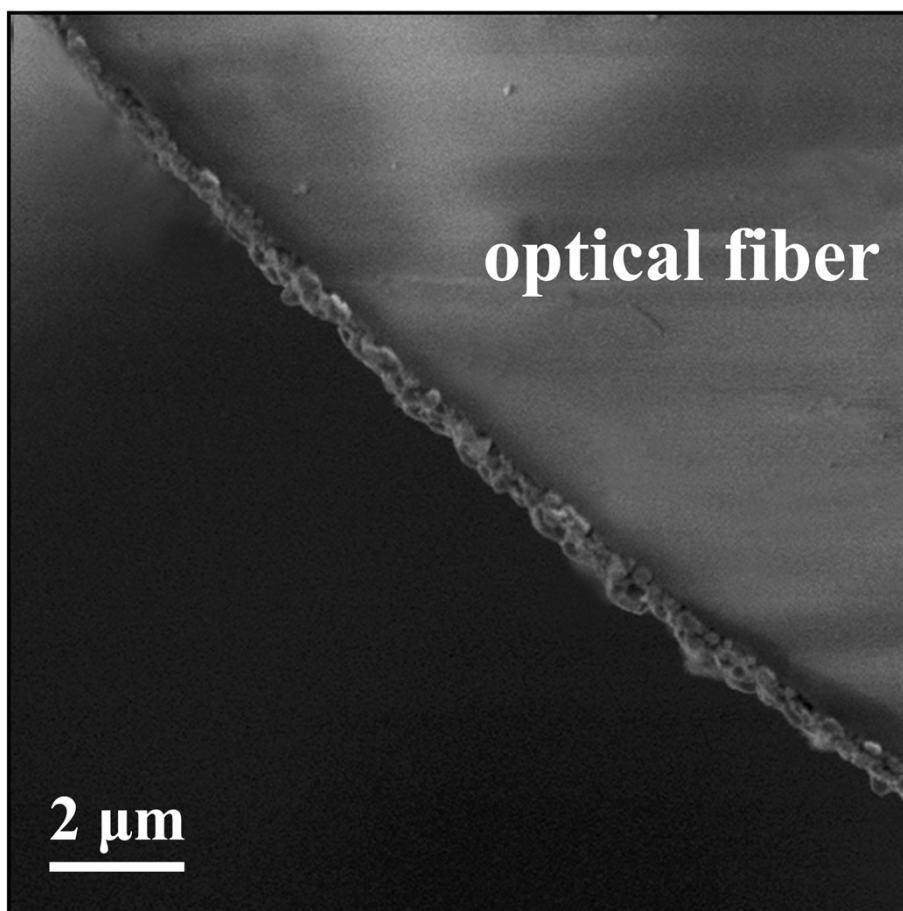


Fig. S3 SEM image of the cross section cut at the tapered portion of fiber SERS probe.

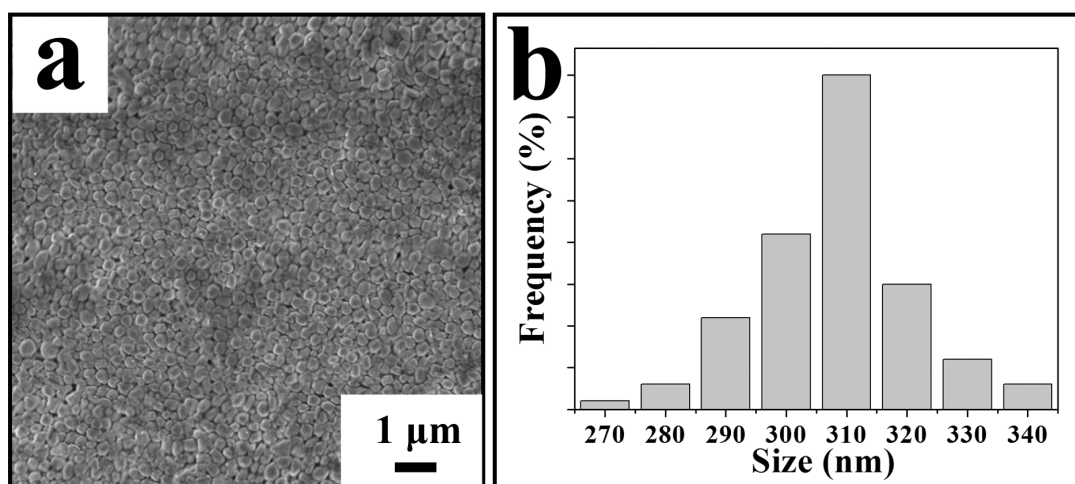


Fig. S4 (a) SEM image of Ag nanopolyhedra integrated onto the surface of the fiber taper, and (b) the corresponding size distribution of the Ag nanopolyhedra.

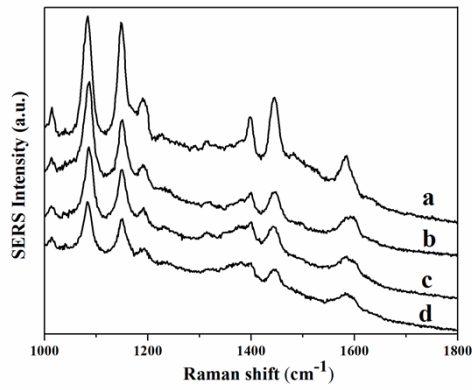


Fig. S5 SERS spectra of 4-ATP (10^{-6} M) measured with the tapered fiber probes with cone angles of (a) 3.8° , (b) 6.1° , (c) 8.6° , and (d) 10.8° .

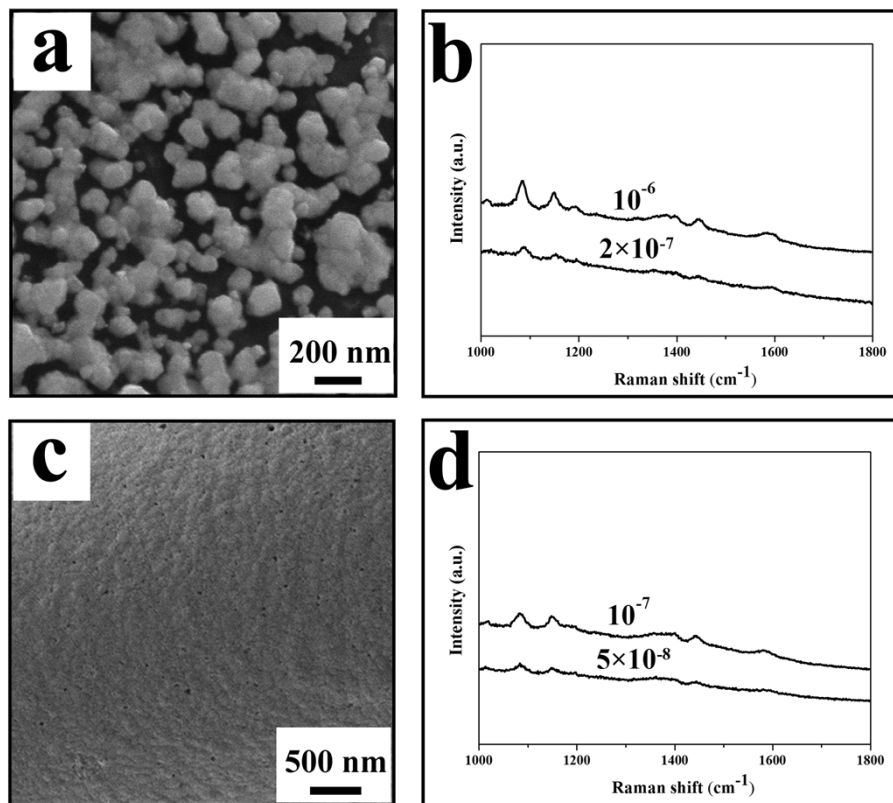


Fig. S6 (a) SEM images of the 3.8° tapered fiber probes based on Ag nanoparticles achieved by laser-induced deposition method, and (b) the corresponding SERS spectra of different concentrations of 4-ATP. (c) SEM image of the 3.8° tapered fiber probes based on Ag film formed by evaporation method, and (d) the corresponding

SERS spectra of different concentrations of 4-ATP.

Since 4-ATP is well-known for its distinct Raman features and strong affinity for noble metal surface via thiol bonding, SERS has been a predominant approach for the detection of trace amounts of 4-ATP molecules. Prior works of planar SERS substrate demonstrated the limit of detection (LOD) of 4-ATP was usually between 10^{-6} and 10^{-9} M.¹ Besides, using Ag spherical aggregates on a Si wafer, the LOD of 4-ATP was reported to be as low as 10^{-10} M.² For the silver–gold microtubes on the indium tin oxide substrates, the LOD of 4-ATP was shown down to 6.0×10^{-12} M.¹ However, it is worth pointing out that the quantitative comparison between the planar SERS substrate and the fiber SERS probe is not possible because of variations in the two optics systems. For example, the planar SERS substrates are front excited, and the SERS signal from analyte adsorbed onto the SERS material is directly collected by the Raman spectrometer. Nevertheless, fiber SERS probes are backexcited by the laser beam which propagates through the fiber and then interacts with the SERS material and the analyte. Meanwhile, part of the resulting SERS signal is coupled back into the probe and then collected by the Raman spectrometer. In this regard, unlike the measurement carried by the planar SERS substrate, the fiber SERS probe may find potential applications in real-time, in situ, and remote detection. Additionally, it is difficult to make direct comparison of LOD based on the literature since the data were acquired with different instruments, experimental parameters, and environmental conditions. For comparison, the other 3.8° tapered fiber probes based

on silver nanoparticles (achieved by laser-induced deposition method)³ and silver film (formed by noble metal evaporation method)⁴ were prepared according to the methods as previously described.^{3,4} The surfaces of the fiber SERS probes were characterized by SEM, and the corresponding SEM images of Ag nanoparticles and Ag film on the optical fiber are shown in Fig. S6a and c (ESI†). The SERS activities of these two types of fiber probes were also tested under the same measurement conditions, and the detection limits for 4-ATP molecule were found to be 2×10^{-7} and 5×10^{-8} M, as shown in Fig. S6b and d (ESI†). We note that our detection limit of 4-ATP is one or two orders of magnitude higher than those achieved by using the tapered probes based on Ag film and Ag nanoparticles, respectively. The better SERS activity may be derived from the unique morphological characteristics of this polyhedron-like structure.⁵ As mentioned in the introduction, the sharp corners/edges on polyhedral shapes could serve as hot spots with extremely large electromagnetic field for the generation of high SERS enhancement.^{5,6}

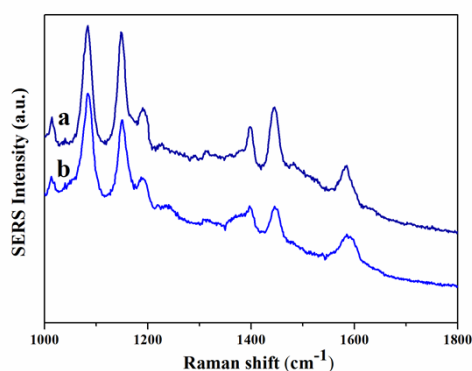


Fig. S7 SERS spectra of 4-ATP (10^{-6} M) measured in (a) the “dip-and-dry” detection mode, and (b) the in situ detection mode.

In addition to the “dip-and-dry” mode of detection cited above, the fiber SERS probe offers the possibility of in situ measurement. Fig. S7 (ESI†) demonstrates the SERS spectra of 4-ATP (10^{-6} M) in the “dip-and-dry” (a) and in situ (b) modes of detection. The in situ spectrum was recorded before removing the probe and allowing it to dry for the “dip-and-dry” spectrum acquisition. The 1084 cm^{-1} band intensity for in situ measurement is approximately 15 % lower than that shown for the “dip-and-dry” mode. This phenomenon may be attributed to refractive index changes from aqueous ($n \approx 1.33$) solutions to air ($n \approx 1$). The higher refractive index of the surrounding medium probably results in a higher loss of light at the probe-solution interface (in comparison to probe-air interface) with a consequent lower intensity of the scattered light going back to the Raman spectrometer through the optical fiber.⁷

Characterization

The characterization of crystal phase was carried out using X-ray diffraction (XRD) (Philips X’pert-PRO, Cu $K\alpha$ radiation). SEM images were captured using an FEI Quanta 200 FEG field-emission scanning electron microscopy. Optical micrographs were taken using digital optical microscope (DOM) (model XHC-MV2). Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy dispersive X-ray spectrum (EDS) studies were performed with a JEOL-2010 microscope operated at an accelerating voltage of 200 Kv. For the DOM and SEM examinations, measurements were directly carried out on the fiber SERS probes. For TEM and XRD analyses, the samples were scraped off from the optical fiber and

collected for characterization. For the detection experiments of 4-ATP, the 4-ATP was dissolved in deionized water to a 10^{-6} M concentration. This solution was used to prepare other diluted solutions (such as 10^{-7} , 10^{-8} , and 10^{-9} M) by successive dilutions with deionized water. The Raman spectra were recorded on a commercial Raman spectrometer (B&W TEK Opto-electronics, MiniRam).

References

- 1 T. Wang, X. G. Hu, and S. J. Dong, *Small*, 2008, **4**, 781.
- 2 Y. Y. Liu, Y. X. Zhang, H. L. Ding, S. C. Xu, M. Li, F. Y. Kong, Y. Y. Luo, and G. H. Li, *J. Mater. Chem. A*, 2013, **1**, 3362.
- 3 M. Li, and C. Yang, *Chin. Phys. Lett.*, 2010, **27**, 044202.
- 4 C. Viets and W. Hill, *J. Mol. Struct.*, 2001, **563**, 163.
- 5 Y. X. Li and Z. F. Ma, *Nanotechnology*, 2013, **24**, 275605.
- 6 J. W. Hong, S. Lee, Y. W. Lee and S. W. Han, *J. Am. Chem. Soc.*, 2012, **134**, 4565.
- 7 A. Pesapane, A. Lucotti, and G. Zerbi, *J. Raman Spectrosc.*, 2010, **41**, 256.