Supplementary Information

Single-shot laser treatment provides quasi–three-dimensional paper-based substrates for SERS with attomolar sensitivity

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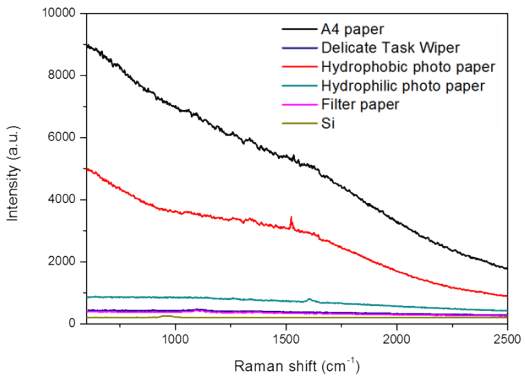

Fig. S1 Background Raman signals of common paper substrates. The filter paper provided the lowest background signals, similar to those of Si.

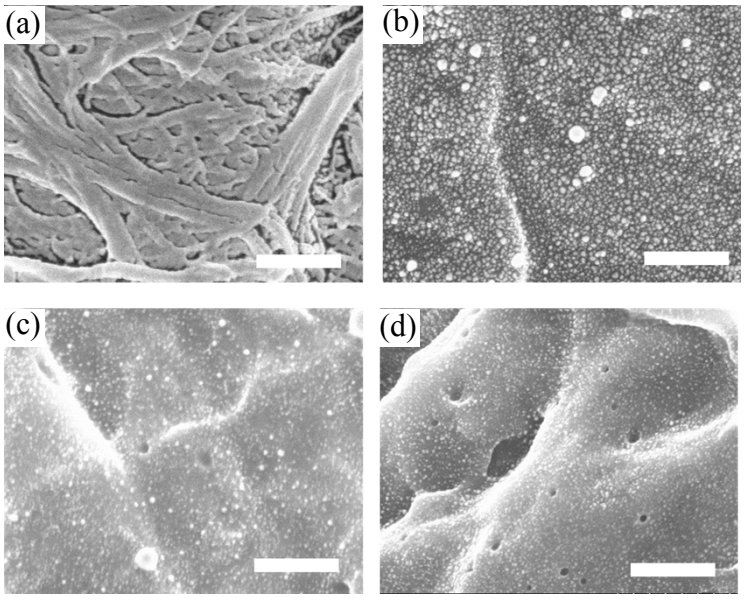

Fig. S2 SEM images revealing the distributions of Au NPs formed on filter paper after (a) 0, (b) 1, (c) 3, and (d) 5 shots of KrF laser illumination. Scale bars: 500 nm.

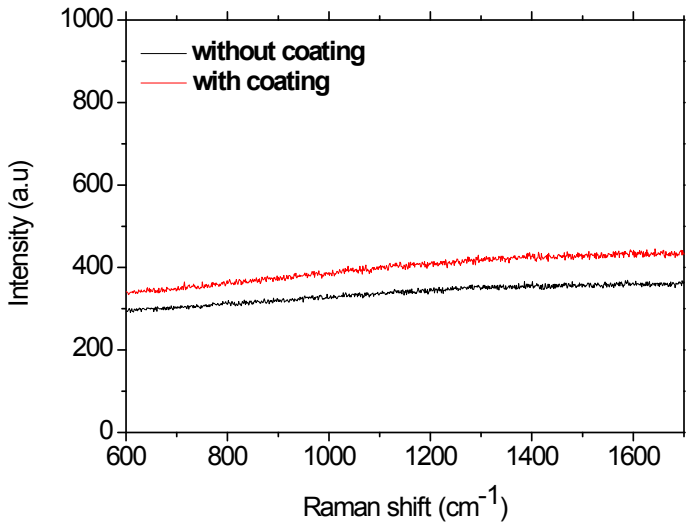

Fig. S3 Background Raman signals of filter papers before and after coated with a perfluorooctyltrichlorosilane monolayer. The perfluorooctyltrichlorosilane monolayer did not perform any noise peak in the spectrum.

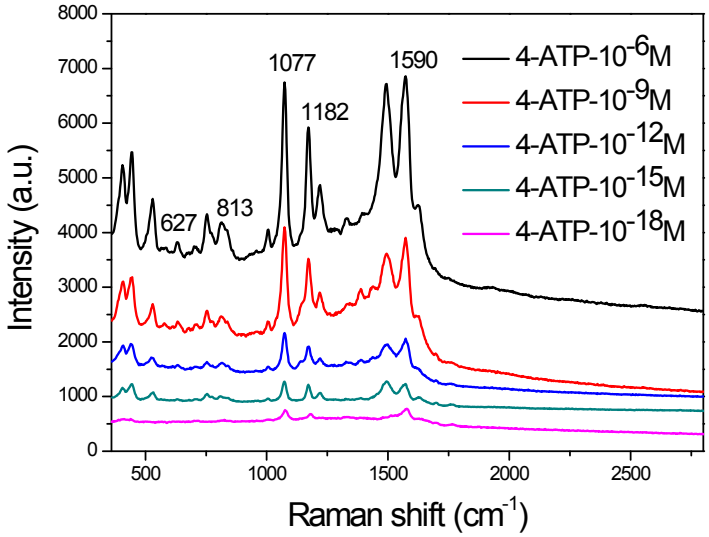

Fig. S4 SERS spectra of various concentrations of 4-ATP dried on Au NP–containing SERS filter paper, demonstrating attomolar detection ability.

Note that the SERS spectra of 4-ATP on the Au NP–containing SERS filter paper is slightly different from that on the Ag NP–containing SERS filter paper (Fig. 7b). We suspect the difference may be due to the following reasons. While Au or Ag are natural catalysts for many kinds of oxidation/reduction reactions, various chemical interactions (even reactions) might occur on the Au and Ag NPs. For example, chemical adsorption-induced vibrations, charge transfer between the metal and molecules, photo-induced damage and metal-catalyzed side reactions would all

disturb the SERS spectra of analytes.[1, 2] As a result, the information from a SERS spectrum is always mixed with substrate-induced disturbances (due to metal–molecule or substrate–molecule interactions) and would no longer clearly dependent on the primary structure of analytes. The different SERS spectra of 4-ATP on Au and Ag NP–containing SERS filter paper might originate from the above interactions accordingly. This phenomena were commonly seen in many previous studies. The SERS spectra of 4-ATP on Ag SERS substrates [3-6] were different from that on Au SERS substrates.[7-10] Therefore, we only compare the intensities of main 4-ATP Raman fingerprints throughout the study, and ignore the side-reaction-induced noise peaks.

Reference:

1. W. Xu, X. Ling, J. Xiao, M. S. Dresselhaus, J. Kong, H. Xu, Z. Liu, J. Zhang, *Proc. Natl. Acad. Sci. USA*, 2012, **109**, 9281–9286.

2. W. Xu, N. Mao, J. Zhang, *Small*, 2013, **9**, 1206–1224.

3. X. Zhao, B. Zhang, K. Ai, G. Zhang, L. Cao, X. Liu, H. Sun, H. Wang, L. Lu, *J. Mater. Chem.*, 2009, **19**, 5547–5553.

4. N. M. S. Sirimuthu, C. D. Syme, J. M. Cooper, *Chem. Commun*., 2011, **47**, 4099–4101.

5. J. Zheng, Y. Zhou, X. Li, Y. Ji, T. Lu, R. Gu, *Langmuir* 2003, **19**, 632-636.

6. Z. Zhang, F. Xu, W. Yang, M. Guo, X. Wang, B. Zhang, J. Tang, *Chem. Commun.*, 2011, **47**, 6440–6442.

7. Y. H. Ngo, D. Li, G. P. Simon, G. Garnier, *Langmuir* 2012, **28**, 8782−8790.

8. L. Sun, D. Zhao, M. Ding, H. Zhao, Z. Zhang, B. Li, D. Shen, *J. Mater. Sci. Technol.*, 2013, **29**, 613-618.

9. Y. Li, Z. Ma, *Nanotechnology* 2013, **24**, 275605-1-275605-7.

10. X. Hu, W. Cheng, T. Wang, Y. Wang, E. Wang, S. Dong, *J. Phys. Chem. B* 2005, **109**, 19385-19389.