Supporting Information

Plasmonic-enhanced Raman scattering of graphene on growth substrate and its application in SERS

Yuan Zhao,[a] Guanxiong Chen,[a] Yuanxin Du,[a] Jin Xu,[a] Shuilin Wu,[a] Yan Qu[b] and Yanwu Zhu*[ac]

[a]Department of Materials Science and Engineering & CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei 230026, China

Email: zhuyanwu@ustc.edu.cn

[b]Wuxi Graphene Technologies Co., Ltd, 311 Yanxin Rd, Wuxi 214174, China & Jiangnan Graphene Research Institute, 6 Xiangyun Rd, Changzhou 213149, China

[c]Collaborative Innovation Center of Chemistry for Energy Materials (2011-iChEM), Hefei 230026, China

Calculation of enhancement factor

The SERS enhancement factors (EFs) were estimated by $EF=(I_{SERS}/I_{bulk})\times(N_{bulk}/N_{SERS})$,[1, 2] where I_{SERS} is the peak intensity of the specific Raman band for the probe molecules with 10^{-9} M on the SERS substrate. I_{bulk} is the intensity of the same Raman band from 10^{-2} M analyte. N_{SERS} and N_{bulk} are the number of molecules contributing to I_{SERS} and I_{bulk}. Here, 1649 cm^{-1} Raman peak of RhB and 612 cm^{-1} Raman peak of R6G are selected for EFs calculation. The SERS substrate containing analyte was 4 nm Au/analyte/graphene/Cu foils and the substrate for reference was analyte/graphene/Cu foils, respectively. For two substrates, the analytes were both deposited on the surface of graphene/Cu foils, thus the number of molecules contributing to Raman signals was only related to the concentration of the analyte and $N_{bulk}/N_{SERS}=10^7$. For RhB, the peak intensities I_{SERS} and I_{bulk} at 1649 cm^{-1} were 645 (a.u) and 1255 (a.u). The EF for RhB is estimated to be ~ 5.14×10^6. For R6G, the peak intensities I_{SERS} and I_{bulk} at 612 cm^{-1} were 452 (a.u) and 534 (a.u). The EF for R6G is calculated to be ~ 8.46×10^6. In fact, the EFs should be higher than the values calculated as the Au nanoislands could cover a part of molecules and much less molecules contribute to the Raman intensity I_{SERS}.

The effective diameter of Au nanoislands is estimated as the diameter of a circle surrounding the nanoisland. The average inter-island distance was 18.1 nm, 6.2 nm, 7.0 nm, 9.0 nm, 10.6 nm and 11.3 nm for 2 nm, 4 nm, 6 nm, 8 nm, 10 nm and 18 nm Au, respectively.

Supporting figures

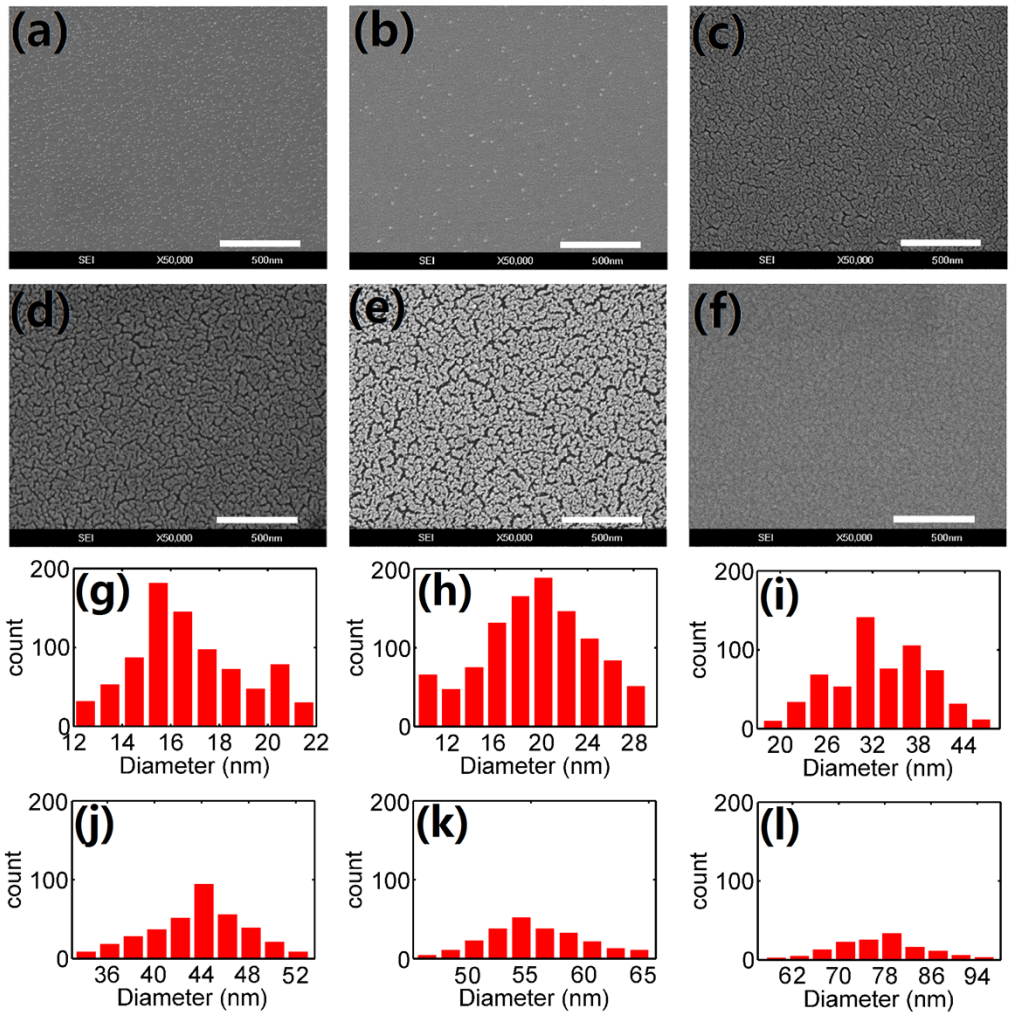

Fig. S1 SEM images for (a) 2 nm, (b) 4 nm, (c) 6 nm, (d) 8 nm, (e) 10 nm and (f) 18 nm Au on graphene/Cu substrates, giving an effective diameter of (g) ~15.5 nm and a particle density of 828/μm^2 for 2 nm Au, (h) ~24.2 nm and a particle density of 1071/μm^2 for 4 nm Au, (i) ~32.7 nm and a particle density of 604/μm^2 for 6 nm Au, (j) ~44.1 nm and a particle density of 357/μm^2 for 8 nm Au, (k) ~55.6 nm and a particle density of 225/μm^2 for 10 nm Au, (l) ~78.3 nm and a particle density of 127/μm^2 for 18 nm Au, respectively. The scale bar in (a-f) is 500 nm.

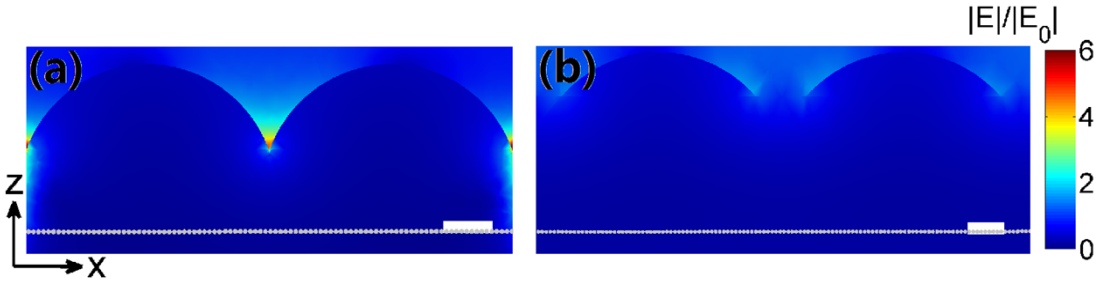

Fig. S2 Simulated electric field intensity distribution of Au/graphene/Cu hybrid system at 1100 nm in the x-z plane for Au particle diameter *d* and period *p* to be (a) *d*=70 nm, *p*=60 nm and (b) *d*=80 nm, *p*=60 nm. The gray dot lines are 1 nm-thick graphene. The scale bar is 10 nm.

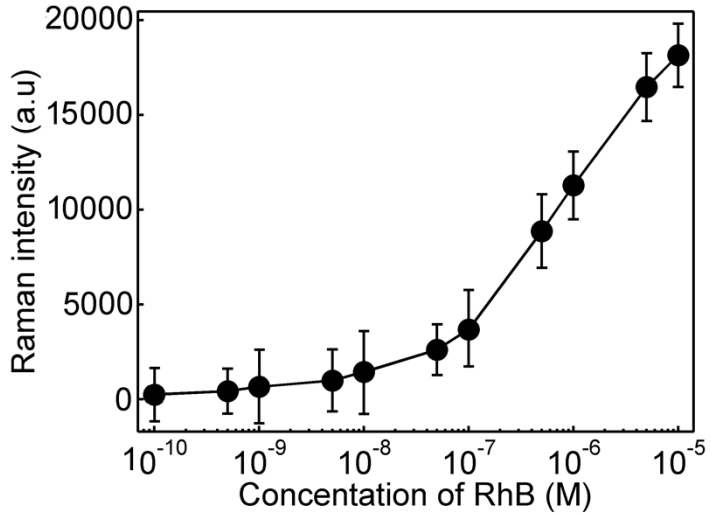

Fig. S3 The intensity of SERS signal at 1649 cm^{-1} versus 11 different molecule concentration of RhB.

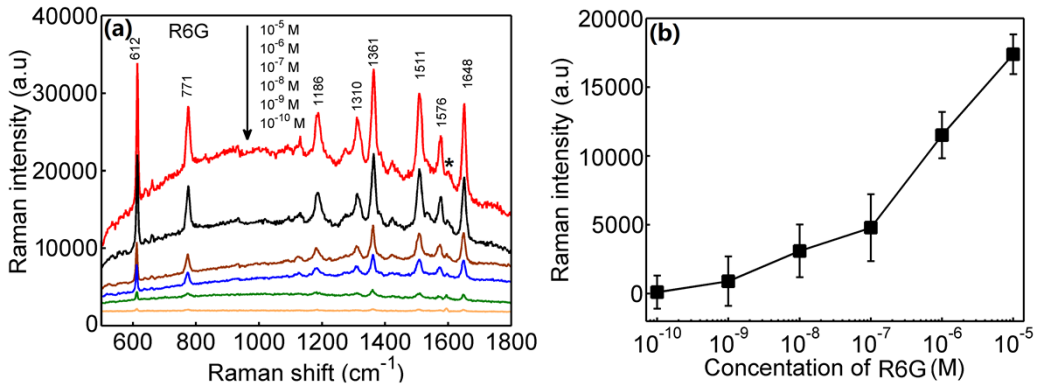

Fig. S4 (a) SERS spectra of R6G (4 nm Au/R6G/graphene/Cu) with six different molecular concentrations. * marks the G band of graphene. (b) The intensity of SERS signal at 612 cm^{-1} versus the concentration of R6G.

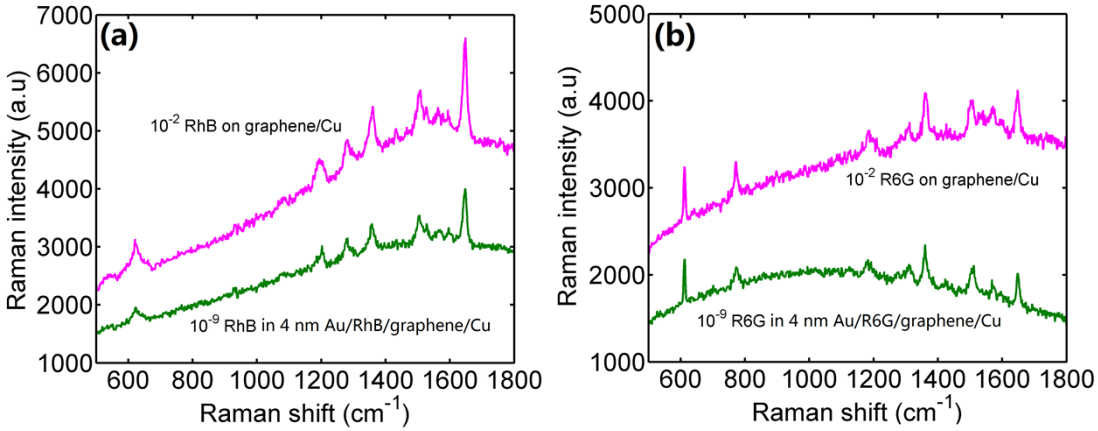

Fig. S5 Raman spectra of (a) RhB and (b) R6G on different substrates with different concentrations. Raman spectra of 10^{-9} M in 4 nm Au/analyte/graphene/Cu structure (dark green lines) and 10^{-2} M on graphene/Cu substrate (rose lines), respectively.

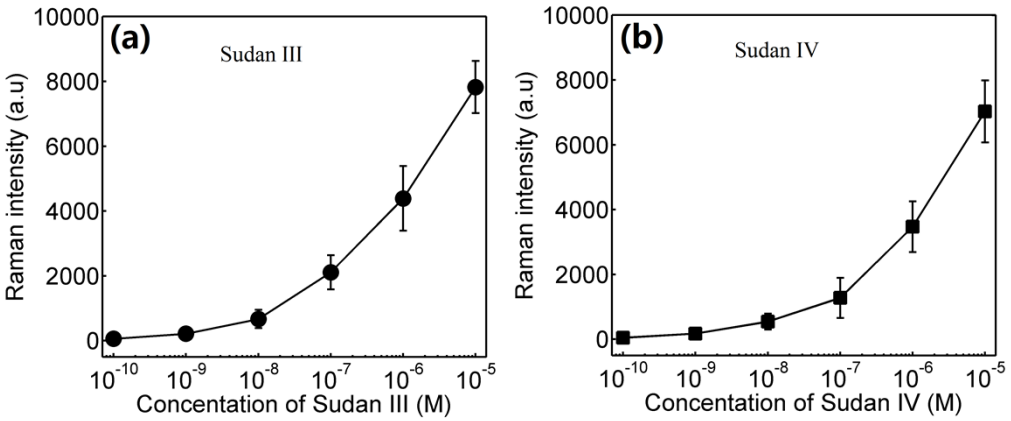

Fig. S6 The intensity of SERS signal versus the concentration of (a) Sudan III at 1345 cm^{-1} and (b) Sudan IV at 1344 cm^{-1}.

Notes and references

1. L. Zhang, C. Jiang and Z. Zhang, *Nanoscale*, 2013, 5, 3773-3779.
2. W. Fan, Y. H. Lee, S. Pedireddy, Q. Zhang, T. Liu and X. Y. Ling, *Nanoscale*, 2014, 6, 4843-4851.