Supporting Information for

TiN Nanorods as Effective Substrate for Surface-Enhanced Raman Scattering

Fengtong Zhao, Xiaotian Xue, Wangyang Fu, Yuehua Liu, Yunhan Ling and Zhengjun Zhang*



Figure S1. HR-TEM image of the as-prepared TiN nanorods



Figure S2. The simulated *EF* of samples with different rod lengths



Figure S3. The reflectivity of TiN nanorods with different rod length. For the 396nm, 437nm and 586nm TiN nanorods samples, they also has a valley between the two valleys.



Figure S4. (a) the raw data of R6G in different concentrations (the raw data of Figure 5(a)) (b) the raw data of MB in different concentrations (the raw data of Figure 5(b))



Figure S5. The SERS map of the TiN nanorods sample in 532 nm laser excitation, the integration time for each point is one second.

Here, the SERS map of TiN nanorods samples was displayed in Figure S5. The Rhodamine 6G (R6G) solution with 10^{-5} M concentration was used to showed the reproducibility and the integration time was 1 second for each point. As shown in the figure, the intensity is mainly distributed among 850~1150, which indicates a good reproducibility for TiN nanorods samples.



Figure S6. (a) The SERS spectra and the normal Raman spectra with crystal violent (CV) molecule in 532 nm laser excitation (b) The SERS spectra and the normal Raman spectra with crystal violent (CV) molecule in 633 nm laser excitation

We measured the normal Raman spectra and the SERS spectra of crystal violent (CV). The integration time is 5 seconds for both of them. We calculated the enhancement factor using formula (1): [1]

$$EF = \frac{I_{SERS}}{I_{NR}} \times \frac{N_{Vol}}{N_{Surf}}$$
(1)

In 532 nm laser excitation, the *EF* is ca. 2.6×10^3 using the Raman peak at 1176 cm⁻¹ (ca. 6×10^3 using the Raman peak at 1372 cm⁻¹). In 633 nm laser excitation, the EF is ca. 5.1×10^3 using the Raman peak at 1176 cm⁻¹ (ca. 8.1×10^3 using the Raman peak at 1372 cm⁻¹).



Figure S7. (a) The SERS spectra of CV in different concentrations varying from 10^{-4} M to 10^{-6} M with 532 nm laser (b) The SERS spectrum of CV in 10^{-6} M concentration with 532 nm laser (c) The SERS spectra of CV in different concentrations varying from 10^{-4} M to 10^{-6} M with 633 nm laser (b) The SERS spectrum of CV in 10^{-6} M concentration with 633 nm laser



Figure S8. The SERS spectra at different time in heating-soaking cycles for (a) R6G probe molecule, (b) MB probe molecule and (c) CV probe molecule. (d) The peak intensity variations with heatingsoaking cycles. (e) The Raman spectra of CV probe molecule before and after corrosion. (f) The SEM image of TiN nanorods substrate before corrosion. (g) The SEM image of TiN nanorods after corroding 3 hours in hydrochloric acid solution. (h) The SEM image of TiN nanorods after corroding 3 hours in sodium hydroxide solution.

Figure S8(a-c) gave the Raman spectra for heating-soaking cycles. In a typical cycle, the TiN nanorods substrate was soaked in solution for 10 min and then heated at 300 °C for 10 min with three probe molecules. All of the solution concentration was 5×10^{-5} M. Figure S8(a-c) successively gave the SERS spectra of R6G, MB and CV. Figure S8(d) displayed the peak variations with heating-soaking cycles of three molecules. The intensities didn't decrease dramatically after 5 cycles at 300 °C for 50 min. Then, the corrosion influence for SERS property of TiN nanorods was carried out by hydrochloric acid solution and sodium hydroxide solution with 1 M concentration for 3 hours. The probe molecule was CV and the soaking time was 30 min in 10⁻⁵ M concentration solution. The Raman spectra before and after corrosion was shown in Figure S8(e). Compared to the vacuity contrast group, the SERS spectra had little change after corroding, which was also confirmed by the almost unchangeable morphology images before and after corrosion in Figure S8(f-h). Therefore, the TiN substrate can be used in actual harsh environment.



Figure S9. The normalized Raman intensity and the SERS effect by simulation in different rod length with 473nm incident laser (the Raman peak is1176 cm⁻¹ of crystal violent molecule)

Reference:

[1] Ru, E. C. L.; Blackie, E. J.; Meyer, M.; Etchegoin, P. G., Surface Enhanced Raman Scattering Enhancement Factors: A Comprehensive Study. *Journal of Physical Chemistry C* 2007, *111*, 13794-13803.