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Supporting Information

Layer-dependent SERS enhancement of TiS₂ prepared by simple electrochemical intercalation

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1 Control electrode experiments

2 In order to simplify the experimental conditions, first of all, only the lithium foil was
3 replaced by one graphite sheet served as the anode and the cathode was unchanged
4 using one copper sheet, and lithium ions were provided by the electrolyte for
5 intercalation. However, although the Raman performance of the obtained few-layer
6 $\text{TiS}_{2(\text{Cu})}$ sample was significantly improved, copper may have an impact on SERS
7 performance. In order to rule out the influence of copper pollution on the SERS property
8 of TiS_2 , control experiments were carried out using a graphite sheet as the cathode
9 instead of the copper sheet to prepare few-layer $\text{TiS}_{2(\text{C})}$. By comparing SERS activity,
10 although the influence of copper was excluded, all following electrochemical
11 experiments were carried out using graphite sheet as cathode.

12 Calculation of Raman enhancement factor

13 The wavelength of the confocal laser used in the experiment was 532 nm, the energy
14 was 0.5 MW, the spot radius was 0.5 μm , and the penetration depth was about 2 μm .
15 The density of R6G powder was 0.99 g/cm^3 and the 10^{-6} M R6G solution of 10 μL was
16 dribbled onto a silicon wafer of 0.5 $\text{cm} \times 0.5$ cm . Taking the peak of 613 cm^{-1} as the
17 calculation, the peak heights of R6G powder, layered bulk TiS_2 and 3- TiS_2 in Fig. S2
18 were 486, 160 and 15000 unit intensities, respectively. The EF calculation of layered
19 bulk TiS_2 and 3- TiS_2 were as follows:

$$20 \quad N_{\text{SERS}} = \frac{N_A \times 0.25\pi \mu\text{m}^2 \times 10 \mu\text{L} \times 10^{-6} \text{mol/L}}{0.25 \text{cm}^2} = 1.89 \times 10^5$$

$$21 \quad N_{\text{normal}} = \frac{N_A \times (0.99 \text{g}/\text{cm}^3 \times 0.25\pi \mu\text{m}^2 \times 2 \mu\text{m})}{479 \text{g}/\text{mol}} = 1.95 \times 10^9$$

$$22 \quad EF_{\text{layered bulk TiS}_2} = \frac{160/1.89 \times 10^5}{486/1.95 \times 10^9} = 3.39 \times 10^3$$

$$23 \quad EF_{3-\text{TiS}_2} = \frac{15000/1.89 \times 10^5}{486/1.95 \times 10^9} = 3.18 \times 10^5$$

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1 **Excitation light wavelength selection and high background signal**

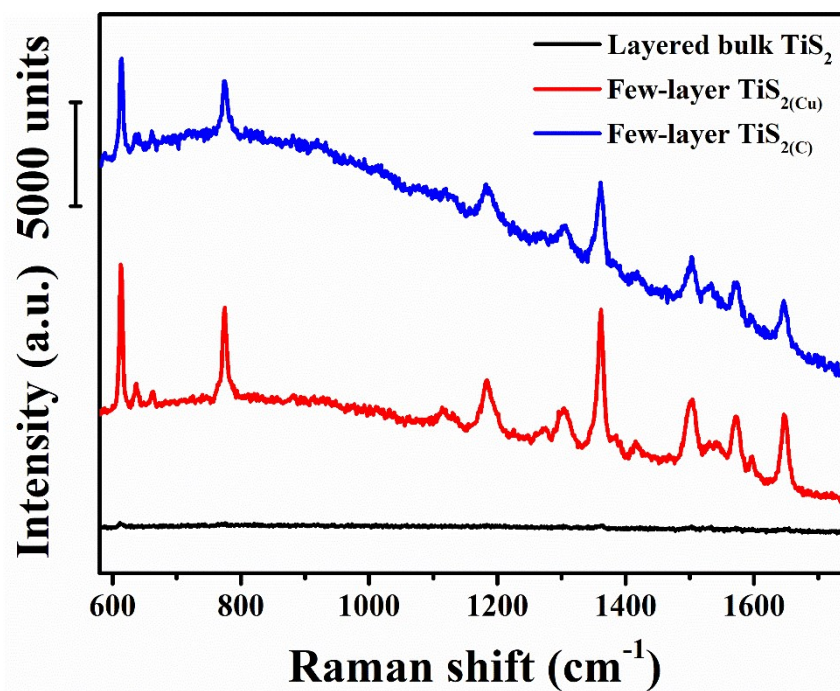
2 In the SERS measurement process, the excitation light source had a great influence on
3 signal enhancement. In order to better choose a suitable excitation light source, the UV-
4 Vis absorption spectra of TiS₂ with different number of layers were shown in Fig. S4a.
5 Few-layer TiS₂ had a weak absorption peak near 601 nm, while the absorption peak of
6 few-layer TiS₂ modified by R6G was near 570 nm (Fig. S4b), which may be due to the
7 charge transfer between R6G and TiS₂. In order to meet the energy required for charge
8 transfer, we considered choosing a 532 nm laser as excitation light source. In the
9 reproduction experiment of SERS spectrum, it was found that the background signal of
10 some spectra was stronger. Few-layer TiS₂ prepared by one centrifugation was used in
11 all control experiments (Fig. 6a and Fig. S1). The certain laser source used in the Raman
12 test may cause the resonance absorption of the molecule, which led to a strong
13 background signal. In addition, the less the average number of TiS₂ layers, the stronger
14 the adsorption capacity for R6G molecules, and the higher the background signal under
15 excitation light. In Fig. 7b, the certain laser source used in the Raman test may cause
16 the resonance absorption of the molecule, which led to a strong background signal for
17 both layered bulk TiS₂ and few-layer TiS₂. Furthermore, the higher the concentration
18 of the probe molecule solution, the greater the background signal under the excitation
19 light, which was the same as previous reports in the literature.^{1,2}

20 **Notes and references**

- 21 1 I. Geiman, M. Leona and J. R. Lombardi, *J. Forensic Sci.*, 2009, **54**, 947-952.
22 2 Y. Y. Huang, C. M. Beal, W. W. Cai, R. S. Ruoff and E. M. Terentjev, *Biotechnol.*
23 *Bioeng.*, 2010, **105**, 889-898.

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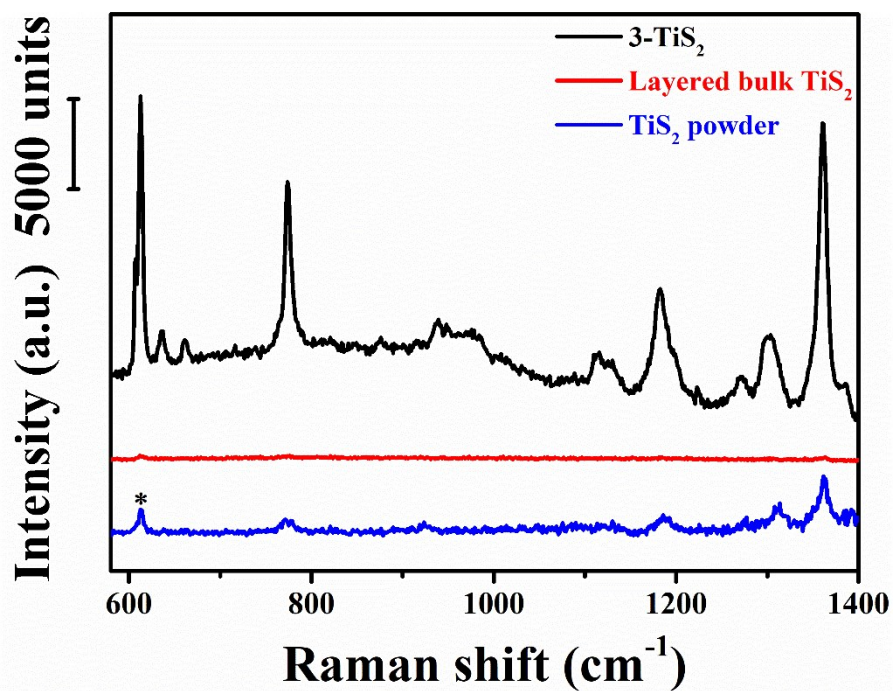


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3 **Fig. S1** SERS spectra of 10^{-6} M R6G on layered bulk TiS_2 , few-layer $\text{TiS}_2(\text{Cu})$ and few-
4 layer $\text{TiS}_2(\text{C})$.

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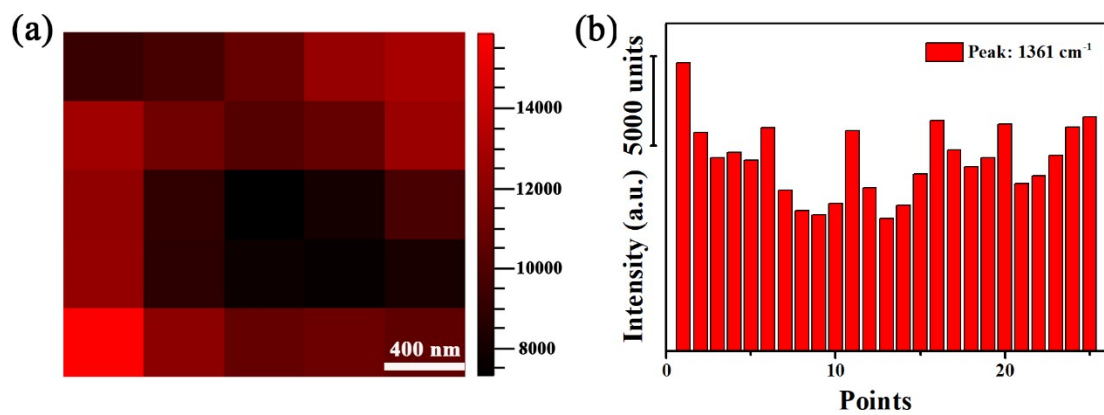
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3 **Fig. S2** SERS spectra of 10^{-6} M R6G on 3-TiS₂, layered bulk TiS₂ and TiS₂ powder. *

4 represents the contrast peak of Raman EF calculation.

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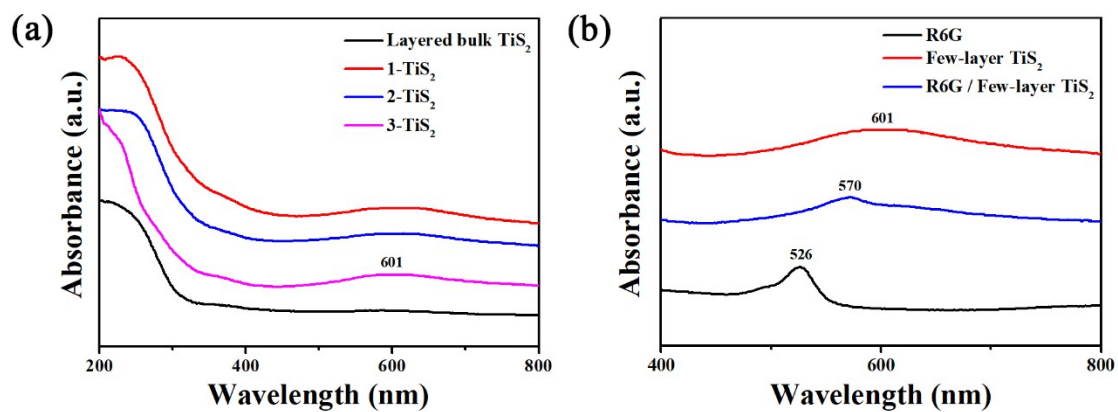
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2 **Fig. S3** (a) Raman mapping of 10^{-6} M R6G absorbed on few-layer TiS_2 sample at the
 3 1361 cm^{-1} peak. (b) Columnar statistics of 25 sampling points of 1361 cm^{-1}
 4 characteristic peak intensity.

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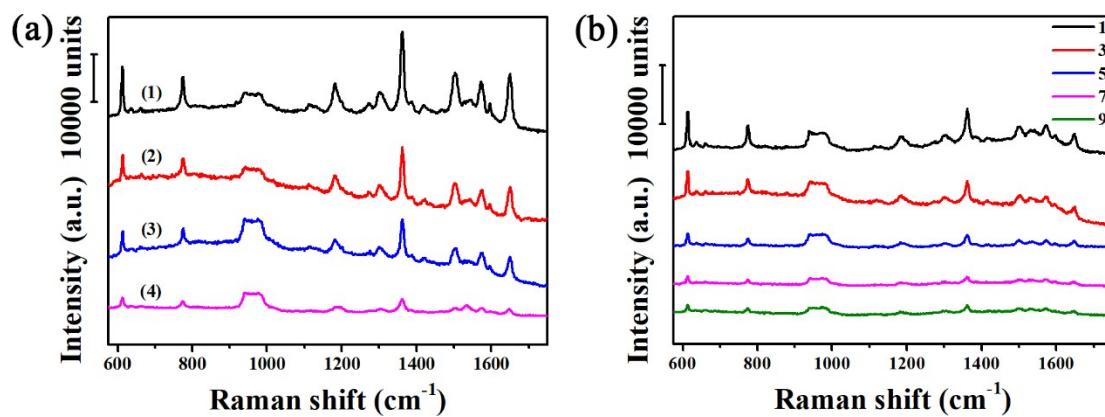
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2 **Fig. S4** (a) UV-Vis absorption spectra of layered bulk TiS_2 , 1- TiS_2 , 2- TiS_2 and 3- TiS_2 .

3 (b) UV-Vis absorption spectra of R6G, few-layer TiS_2 and few-layer TiS_2 modified

4 with R6G molecules.

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1
 2 **Fig. S5** (a) SERS spectra of 10^{-6} M R6G with few-layer TiS_2 placed at (1) room
 3 temperature, (2) $40\text{ }^\circ\text{C}$, (3) $60\text{ }^\circ\text{C}$ and (4) $80\text{ }^\circ\text{C}$ for 12 hours. (b) SERS spectra of 10^{-6} M
 4 R6G with few-layer TiS_2 stored in aqueous solution for 1, 3, 5, 7 and 9 days.