Supporting Information

Ag-decorated TiO₂ nanograss for 3D SERS-active substrate with visible light self-cleaning and reactivation

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Figure S1. The transmission spectrum of the 400 nm longpass filter (FGL400M) mentioned in our experiments, measured with UV/VIS/NIR spectrophotometer (SHIMADZU UV-3600).



Figure S2. Exponential decay of the SERS signals intensity depending on the experimental time.

In the six hours SERS mapping image as shown in the insert of Figure S2, nine lines paralleling to the X axes at equal distance were chosen, the average intensity of nine points at equal distance on each line was estimated and regarded as the SERS signal intensity of the middle points of each line. The SERS signals intensity depending on the experimental time is shown in Figure S2, the

nonlinear fitting of the data obeys the exponential decay character as the following equation:

$$I = Ae^{-Bt}$$

where the I is the SERS signals intensities and t is the collecting time of the corresponding signal.

The parameters of A, B are given in Figure S2.



Figure S3. Coefficients of SERS signal variation (the ratio of the standard deviation and the mean of SERS signals).

As the SERS signals intensity depends on the experimental time due to the photocatalytic degradation of Rhodamine 6G (R6G) by Ag decorated rutile TiO_2 film, the coefficients of variation were estimated separately within each line selected in the insert of Figure S2 which was collected in adjacent time. The standard deviation and the mean of SERS signals corresponding to every line were calculated based on the intensities of the nine points on each line as mentioned above. Most of the coefficients of variation are less than 20 %, indicating that the Ag-decorated TiO_2 substrate has a comparative uniform spatial enhancement.



Figure S4. Absorption spectra of the Ti foil, rutile TiO₂ film as-prepared and that after 40 min Ag evaporation (UV/VIS/NIR spectrophotometer (SHIMADZU UV-3600)).



Figure S5. Time evolution of photocatalytic degradation of R6G by Ag decorated rutile TiO₂ film.

The Ag decorated rutile TiO_2 film (1 cm²) was soaked in 3 mL R6G (5 × 10⁻⁶ M) aqueous solution contained in a quartz glass tube. Then the film (kept in the solution) was illuminated with visible light (as mentioned in the experimental section) for 2 hours. The initial R6G aqueous and that after 1 and 2 hours illumination were used for UV-Vis absorption measurements. The result shows that the absorption spectra of R6G gradually decrease with increasing illuminating time and almost disappear after 2 hours visible light illumination, indicating the Ag decorated rutile TiO₂ film can degrade R6G under visible light.



Figure S6. SERS spectra of R6G (2×10^{-8} M) over Ag-decorated TiO₂ substrates of the as-prepared and that re-detecting of the self-cleaned substrate with fresh R6G after visible light irradiating for 1 hour, the integration time is 5 s.



Figure S7. SERS spectra of R6G (2×10^{-8} M) over four Ag-decorated TiO₂ substrates under different treatment conditions, the integration time is 5 s. Curve (1) detecting directly, (2) rinsing with water for about 5 seconds, (3) irradiating with visible light for 5 minutes, (4) irradiating with visible light for 5 minutes and following water rinsing for about 5 seconds, (5) rinsing with deionized water for about 5 seconds before irradiating with visible light for 5 min, followed rinsing with deionized water for about 5 seconds again. The results indicate that the R6G can be photocatalytic degraded to other molecules by the Ag-decorated TiO₂ substrates under visible light (see curve 3) and the followed water rinsing can help to removing the residual ions (see curve 4). The former water rinsing can enhance the photocatalytic degradation in aqueous condition (see curve 5).



Figure S8. SERS spectra of 4-ATP (2×10^{-8} M) over the Ag-decorated TiO₂ substrate of the as-prepared and that after visible light self-cleaning, the integration time is 5 s.