

Hydrogenated Black TiO₂ Nanowires Decorated by Ag Nanoparticles as Highly-Improved Sensitive and Reusable SERS Substrates

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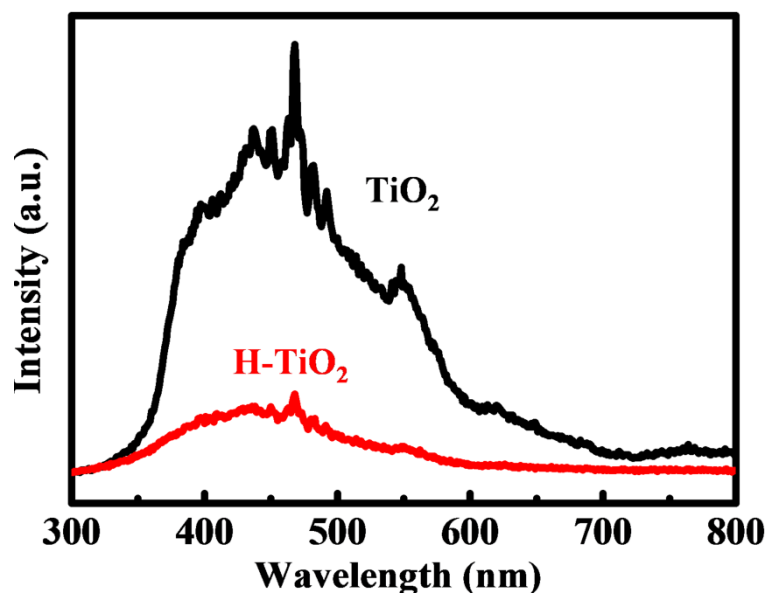


Fig. S1. Photoluminescent spectra of TiO₂ NWs and H-TiO₂ NWs, respectively. Excitation wavelength: 310 nm

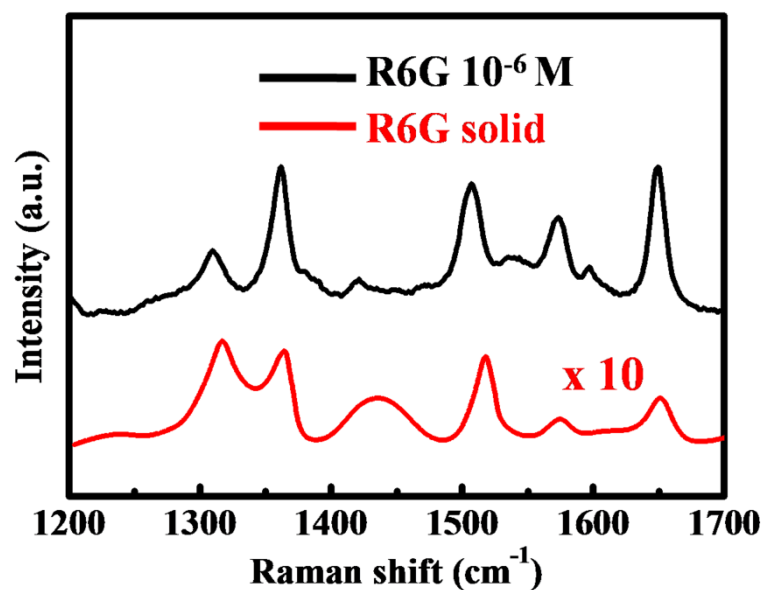


Fig. S2. Normal Raman spectra of solid R6G and SERS spectra of 10^{-6} M R6G adsorbed on Ag/H-TiO₂ NWs. For better comparison, the intensity of solid R6G Raman spectra is multiplied by 10.

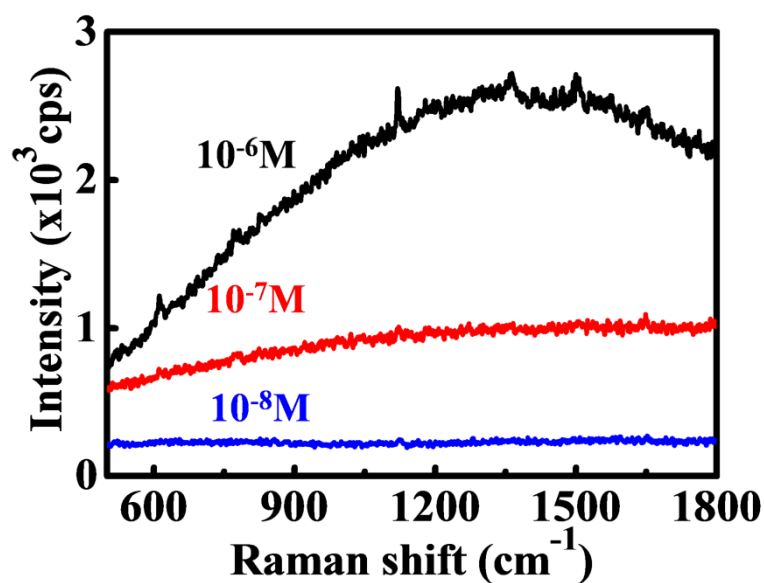
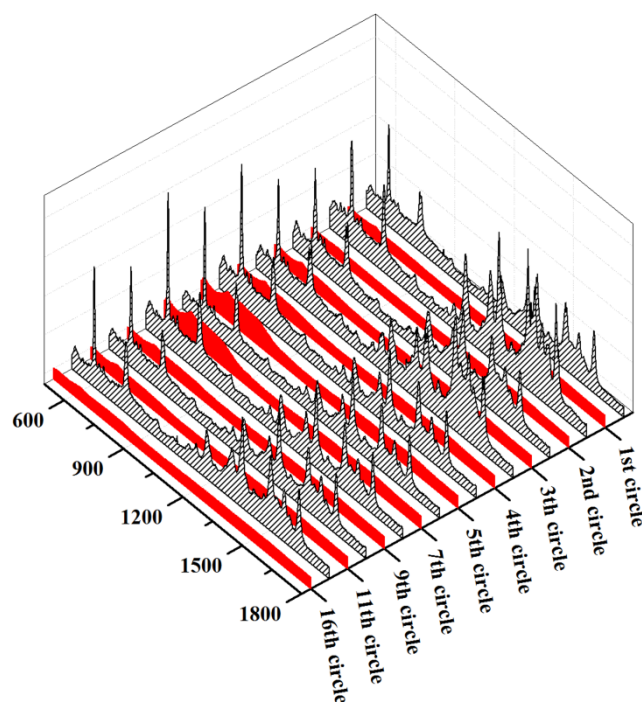


Fig. S3. SERS spectra collected on Ag/TiO₂ NWs exposed to different R6G concentrations. For 10^{-6} M to 10^{-9} M: excitation, 514 nm; power, ~ 0.3 mW; data collection, 10 s.

(a)



(b)

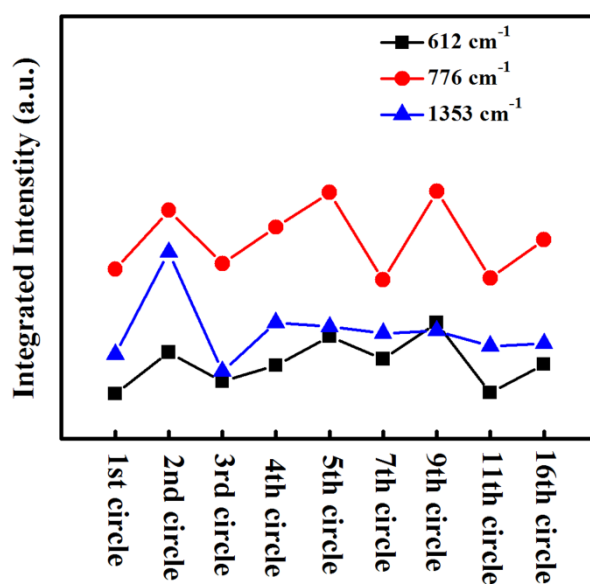


Fig. S4. (a) Raman spectra of R6G molecules recorded over 16 cycles of recycling. (b) The calculated integrated intensity of main peaks at 612 cm⁻¹, 776 cm⁻¹ and 1353 cm⁻¹ of R6G Raman spectra collected in various circle. For the sake of clarity and brevity, some circles of recycling were not given.

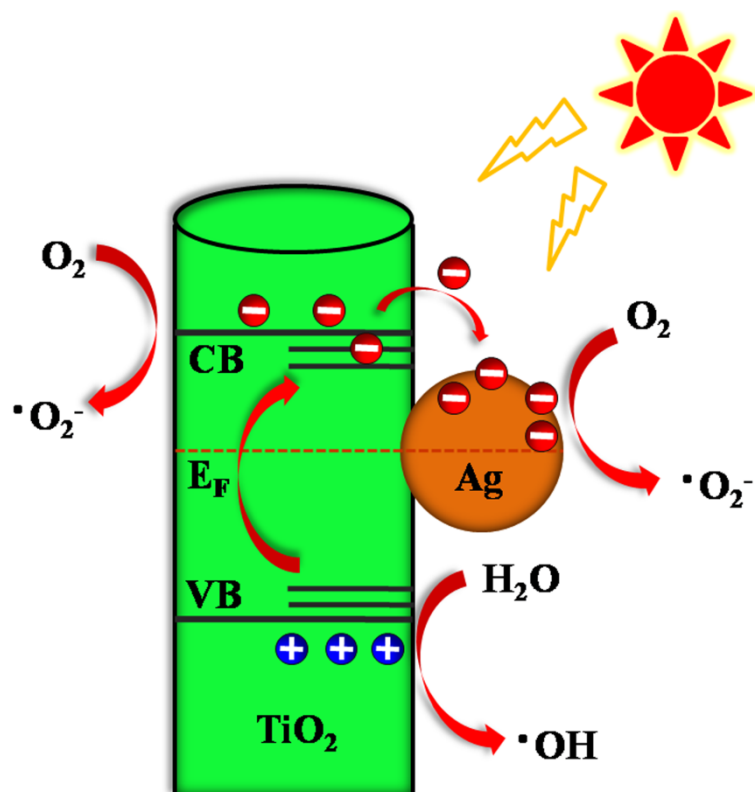


Fig. S5. Schematic diagram of the photocatalytic mechanism occurring within Ag/H-TiO₂ NWs.

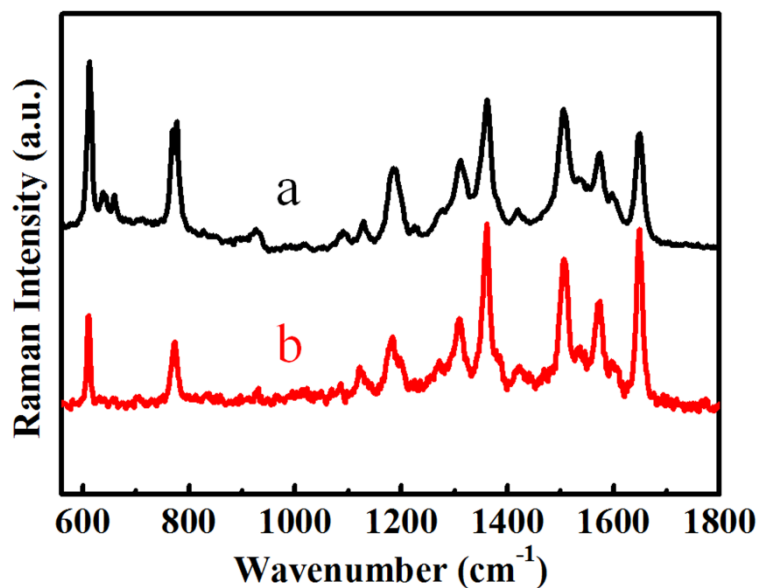


Fig. S6. The SERS spectra of 10⁻⁶ M R6G molecules obtained from (a) the substrate of Ag/H-TiO₂ prepared at least 6 months ago and (b) the freshly prepared substrate.

EF Calculation Method

The Raman enhancement factor (EF) can be estimated based on Fig. S2 by the

formula as followed:¹

$$EF = \left(\frac{I_{SERS}}{I_{bulk}} \right) \left(\frac{M_{bulk}}{M_{SERS}} \right)$$

I_{SERS} and I_{bulk} refer to integrated intensities of the same R6G Raman peak collected on solid R6G and the Ag/H-TiO₂ NWs substrate with 10⁻⁶ M R6G molecules adsorbed on the surface. M_{SERS} and M_{bulk} are the number of adsorbed molecules and molecules in solid phase, and they are calculated based on the estimated concentration of surface R6G. Here, Raman peak at 1650 cm⁻¹ are chosen to calculate the EF. Taking the volume of laser spot and the density of solid R6G (0.79 g/cm³) into account, the EF is estimated to be $\sim 1 \times 10^8$.

1 Y. Peng, L. Qiu, C. Pan, C. Wang, S. Shang and F. Yan, *Electrochimica Acta*, 2012, **75**, 399-405.