TiO_2/Ag composite nanowires for a recyclable surface enhanced Raman scattering substrate*

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Multifunctional TiO_2/Ag composite nanowires are fabricated with a hydrothermal method by precipitating Ag nanoparticles (NPs) on the surfaces of TiO_2 nanowires. This hierarchical one-dimensional (1D) nanostructure can be used as a surface enhanced Raman scattering (SERS) substrate with high sensitivity, for detecting the rhodamine 6G (R6G) in a wide range of low concentrations (from 1×10^{-6} M to 1×10^{-12} M). In addition, the substrate can be self-cleaned under the irradiation of ultraviolet (UV) light due to the superior photocatalytic capacity of the TiO_2/Ag composite nanostructure, making the recycled use of SERS substrates closer to reality. With both the evident SERS performance and high efficiency of photocatalytic capacity, such TiO_2/Ag composite nanowires demonstrate considerable potential in the chemical sensing of organic pollutants.

Keywords: surface enhanced Raman scattering, TiO_2, photodegradation, recyclable

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1. Introduction

Surface enhanced Raman scattering (SERS) has been a growing area of interest in recent years due to its potential as a reliable, high-resolution detection technique for extremely minute quantities of target molecules.[1] SERS was proven to have wide applications in biosensing,[2,3] drug delivery,[4] environmental sciences,[5] and detection of chemical warfare agents (homeland security).[6] There are two main mechanisms that contribute to the scattering enhancement observed in SERS: the first is surface plasma resonance generated by the interaction between the laser source and the SERS-active substrate,[7] and the second is chemical enhancement, which primarily originates from the charge transfer mechanism.[8,9]

Noble metals (Au, Ag or Cu) have been used as SERS substrates for decades, because their localized surface plasmon resonances (LSPRs) cover most of the visible and near infrared wavelength range.[10,11] Recently, it has been observed that several semiconductors such as ZnO,[12] TiO_2,[13] SnO_2,[14] CuO,[15] and Fe_2O_3,[16] also exhibit SERS capability, although their enhancement effects are weaker than those of noble metal substrates. In particular, more significant enhancement levels can be obtained by using composites of semiconductors and noble metals, which integrate the advantages of the electromagnetic enhancement with those of chemical enhancement effects.[17–19] Moreover, the photocatalytic efficiency in the decomposition of organic semiconductor compounds, especially TiO_2, can be enhanced by incorporating a plasmonic metal nanostructure into it.[20–22] Therefore, this kind of composite substrate should be suitable for both SERS and photocatalysis applications. Recently, some efforts have been made to fabricate recyclable SERS substrates.[23–25]

In this paper, a typical hierarchical TiO_2/Ag composite nanowire is fabricated through a simple three-step hydrothermal route, with Ag nanoparticles (NPs) grown on the surface Tof iO_2 nanowires. This unique hierarchical semiconductor/metal composite nanostructure can be used as a recyclable SERS-active substrate. The concentration of rhodamine R6G down to 10^{-12} M can be detected and the enhancement factor (EF) is estimated to be 1.94×10^8. The superior performance of this hierarchical nanostructure in SERS and photocatalysis can be attributed to the coexistence of the metal generated plasma oscillations and the semiconductor supplied electron–hole pairs. Furthermore, after performing SERS detection once, the substrate only needs 30 min–40 min to clean itself under UV irradiation.

2. Experimental section

2.1. Synthesis of TiO_2 nanowires

There are two steps in a typical synthesis process. Firstly, 3.75 mmol of P25 (commercial TiO_2 with 75% anatase phase and 25% rutile phase) and 0.3 mol of NaOH were dissolved in 30-mL deionized (DI) water, followed by magnetic stirring for 20 min. The mixed solution was then kept at 180 °C for 24 h in a teflon-lined autoclave. After naturally cooling down to

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room temperature, the reaction product was collected, washed with dilute hydrochloric acid and DI water alternatively, and then dried at 60 °C in air. Secondly, the as-synthesized powder and 3.0-mmol hexadecyl trimethyl ammonium bromide (CTAB) were added into 30-mL DI water and magnetically stirred for 20 min. The mixture was then maintained at 160 °C for 18 h. The final product was collected by centrifugation at 9000 r/min, followed by washing with DI water. Finally, the purified TiO_2 nanowire powder was dried at 60 °C in air for future use.

2.2. Synthesis of TiO_2/Ag composite nanowires

Decorating Ag NPs was obtained through a glucose-assisted method reducing small-sized Ag NPs. In typical synthesis conditions, 2.0-mmol TiO_2 nanowires and 1-g glucose were successively dissolved in 40-mL DI water. The mixture was heated to 60 °C in 10 min under magnetic stirring, then 0.002-mol $AgNO_3$ dissolved in 5-mL DI water was quickly injected into the mixture under stirring. The reaction was further carried out at 90 °C for 1 h with stirring to ensure its homogeneous deposition. After treatment, the reactants were cooled down to room temperature naturally and washed thoroughly with DI water and ethanol by centrifugation at 9000 r/min. The gray precipitates were collected and air-dried at 60 °C for 6 h.

2.3. SERS detection and self-cleaning cycles

We dissolved a small quantity of TiO_2/Ag composite nanowires into 5-mL DI water and ultrasonicated the mixture to make the nanowires uniformly dispersed in the solution. The 20-μL nanowire suspension was then dropped onto the surfaces of a series of small silicon squares, and the substrates were dried at 60 °C for 30 min. For each test, 20-μL R6G solutions with different concentrations (10^{-6} M $\sim$ 10^{-12} M) were then dropped onto the as-prepared substrates and dried under room temperature. After samples were studied for SERS with a 632.8-nm excitation laser, the photocatalytic self-cleaning experiments were performed by irradiating the substrates with a UV lamp (PLS-SXE300/300UV, 340 nm–400 nm) at room temperature for a certain time. The distance between the lamp and substrate was 10 cm. After each 10-min UV irradiation, Raman spectra were detected to check the states of degradation on the SERS substrates. For recyclability characterization, the "detection–cleaning" process was repeated 10 times.

2.4. Characterization

X-ray diffraction (XRD) measurements were carried out using an XD3 diffractometer. The scanning electron microscopy (SEM) images were recorded by using a Hitachi S-4800 field emission scanning electron microscope with an accelerating voltage of 15.0 kV. The transmission electron microscopy (TEM) images were obtained by a JEM-2100 microscope at 200 kV. Raman spectra were obtained using a LabRAM HR800 model confocal microscopy Raman spectrometer.

3. Results and disscussion

Figure 1 illustrates the XRD patterns of the TiO_2/Ag composite nanowires, TiO_2 nanowires, and Ag NPs. As shown in Figs. 1(a) and 1(b), TiO_2/Ag composite nanowires and TiO_2 nanowires both display the diffraction peaks of anatase phase (JCPDS no. 21-1272). However, four characteristic peaks of Ag, which can be distinguished and indexed as the (111), (200), (220), and (311) planes, are displayed in the pattern of TiO_2/Ag composites. Figure 1(c) shows the XRD pattern obtained in a comparative experiment with only Ag NPs produced using the same hydrothermal method, confirming that the TiO_2/Ag composite includes high-purity face-centered Ag crystal.

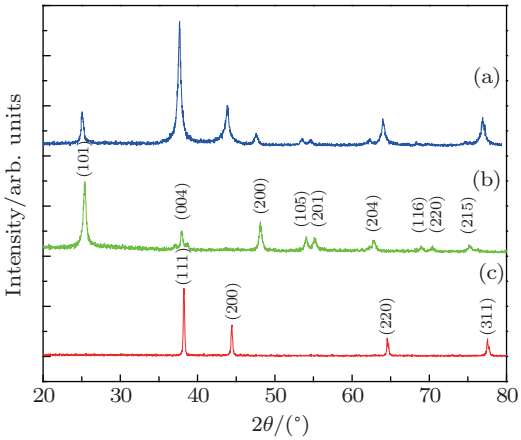


Fig. 1. (color online) XRD patterns of (a) TiO_2/Ag composite nanowires, (b) TiO_2 nanowires, and (c) Ag nanoparticles.

The SEM images of the TiO_2 and TiO_2/Ag nanowires are shown in Fig. 2. Three typical SEM images of congregated and individual pure TiO_2 nanowires are shown in Figs. 2(a)–2(c). It is observed that the products after a two-step hydrothermal process have wire-like morphologies with diameters ranging from 200 nm to 400 nm, with lengths of up to 8 μm, exhibiting a high aspect ratio (up to 1:20). The surface of the TiO_2 nanowire is not smooth but has some NP tubercle-like structures. Figures 2(d)–2(f) show the SEM images of the synthesized TiO_2/Ag composite nanowires. They reveal that the Ag NPs with an average size of 20 nm are uniformly decorated on the surface of TiO_2 nanowires. After the third hydrothermal treatment, TiO_2/Ag composite nanowires retain the primitive mophologies of TiO_2 nanowires.

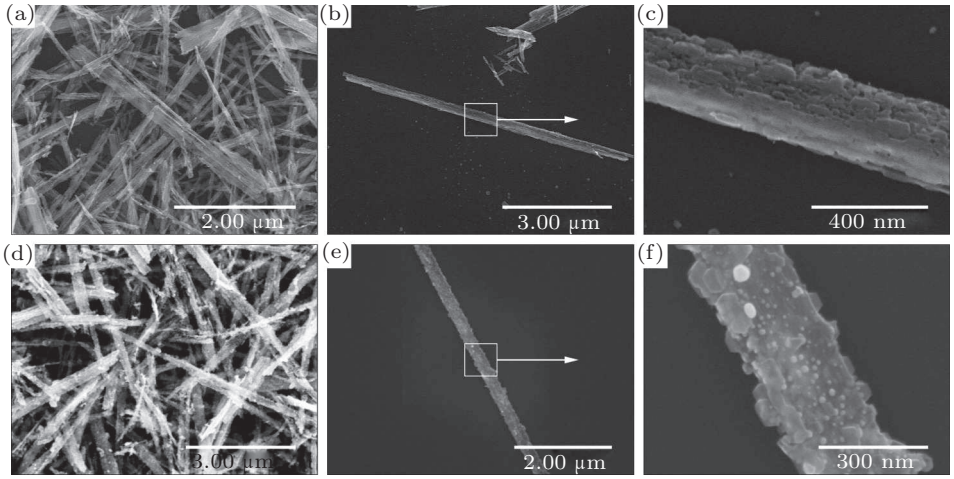


Fig. 2. (a) SEM images of TiO_2 nanowires. (b) and (c) SEM images of a single nanowire at different magnifications. (d) SEM image of TiO_2/Ag composite nanowires. (e) and (f) SEM images of single TiO_2/Ag composite nanowire at different magnifications.

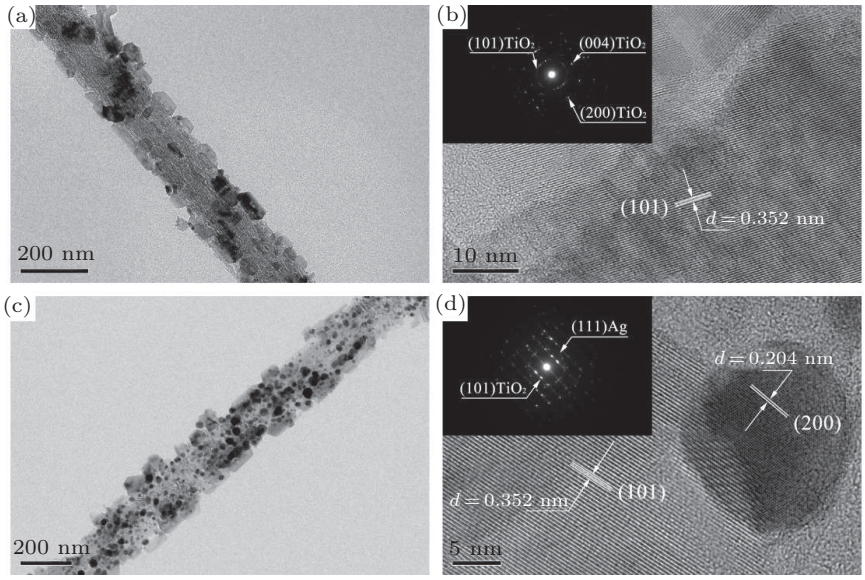


Fig. 3. (a) TEM image of single TiO_2 nanowire. (b) HRTEM image of a TiO_2 nanowire, with the inset showing the corresponding SAED patterns. (c) TEM image of a single TiO_2/Ag composite nanowire. (d) HRTEM image of a TiO_2/Ag composite nanowire, with the inset showing the corresponding SAED patterns.

Transmission electron microscopy was used to further investigate the prepared crystals and composite nanostructures. In Fig. 3(a), a typical micrograph of a single TiO_2 nanowire is presented. Distinct NPS on the TiO_2 nanowire surface, with sizes ranging from 60 nm to 100 nm, can be observed. Figure 3(b) shows an HRTEM image of a TiO_2 nanowire and its corresponding selected area electron diffraction (SAED) pattern (insert). From the distance between the adjacent fringes, the lattice spacing of $d = 0.352$ nm can be indexed to (101) plane of TiO_2. The concentric circles which can be seen in the inserted SAED pattern are indexed to the (101), (004), (200) planes of TiO_2, respectively. The representative TEM image of a single TiO_2/Ag composite nanowire is shown in Fig. 3(c). It can be seen that Ag NPs uniformly grow on the surface of TiO_2 nanowire. A local HRTEM image in Fig. 3(d) indicates that Ag NPs are spherical and the lattice spacing can be measured to be $d = 0.206$ nm, which corresponds to the (200) plane of metallic Ag with an fcc structure. The inserted SAED pattern includes both TiO_2 (101) and Ag (111) planes, which further confirms that Ag NPs grow on the TiO_2 crystal.

As shown in Fig. 4(a), the SERS activities of TiO_2/Ag composite nanowires, TiO_2 nanowires, and Ag NPs were measured by using R6G as probe molecule with a 632.8-nm laser excitation line. R6G dye is often employed as a criterion to judge the enhancement competence of a given substrate due to its obvious increase in Raman spectrum response intensity on SERS substrates. The strong and medium-strong Raman bands at 1648, 1575, 1510, 1361, 1310, 1187, 774, and

611 cm^{-1} are assigned to the xanthene ring stretch, ethylamine group wag, and carbon–oxygen stretch of R6G.[26] Comparing these Raman spectra, it is obvious that the TiO_2/Ag composite nanowires exhibit the highest SERS enhancement ability. Figure 4(b) shows the SERS spectra collected from TiO_2/Ag composite nanowires, with different concentrations (from 10^{-6} M to 10^{-12} M) of R6G solution dropped onto them. The spectrum band intensities show a significant downward trend with the decline of the concentration of the analyzed target. The change of SERS intensity is attributed to the difference in coverage of R6G molecules on the surfaces of TiO_2/Ag composite nanowires prepared under different concentrations of R6G solution. Owing to the hierarchical nanostructure of Ag NPs decorating the surfaces of TiO_2 nanowires, the integration of the electromagnetic enhancement effect arising from the surface plasma resonance of Ag NPs with the chemical enhancement properties of the TiO_2 nanowires could extend the detection limit of substrates to 10^{-12} M.

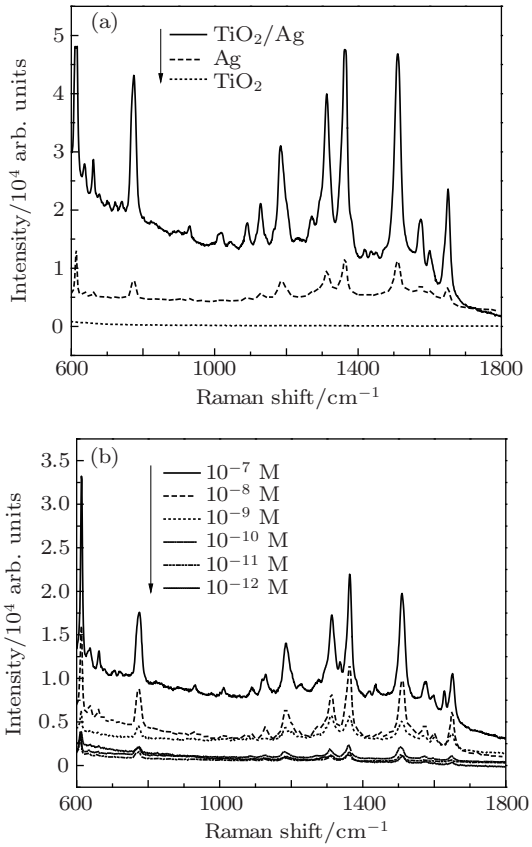


Fig. 4. (a) Raman spectra of R6G with a concentration of 10^{-6} M, acquired from TiO_2/Ag composite nanowires, Ag NPs and TiO_2 nanowires. (b) Raman spectra of R6G at six different concentrations on TiO_2/Ag composite nanowires.

Calculating the SERS enhancement factor (EF) is a classical approach to evaluating the SERS performance. The EF is estimated according to the following standard equation:

$$\mathrm{EF} = \left(\frac{I_{\mathrm{SERS}}}{I_{\mathrm{bulk}}}\right)\left(\frac{N_{\mathrm{bulk}}}{N_{\mathrm{SERS}}}\right), \quad (1)$$

where I_{SERS} and I_{bulk} refer to integrated intensities of the adsorbed 10^{-6}-M R6G molecules on the surface of TiO_2/Ag composite nanowires and 10^{-3}-M R6G on the silicon wafer; N_{SERS} and N_{bulk} represent the corresponding number of 10^{-6}-M R6G and 10^{-3}-M R6G molecules contributing to the Raman signals, respectively. We obtained a laser spot size of 1 μm^2 by using a 100× objective lens. Assuming that the R6G molecules are dispersed on the substrate uniformly and the area of a single R6G molecule is about 1×10^4 nm^2,[27] the EF of a TiO_2/Ag composite nanoflower was calculated to be approximately 1.94×10^8.

When a Ag particle contacts an n-type semiconductor particle such as TiO_2, there occurs a flow of electrons between Ag and TiO_2 readjusting for the equilibration of the Fermi level between the two particles. The work function of Ag is larger than that of TiO_2,[28] which results in the elevation of the Ag Fermi level and the formation of a Schottky barrier (depletion layer) in the junction region.[29] As shown in Fig. 5, the introduction of an R6G molecule into the TiO_2/Ag composite nanowires makes it possible to build a complete charge transfer (CT) system of "donor-bridge-acceptor", because the Ag Fermi level is obviously lower than the surface state energy level of TiO_2.[30] Besides this dynamic CT, intrinsic TiO_2-to-R6G and R6G-to-Ag CT could also occur when the energy levels of the system match the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of R6G under excitation. Moreover, it should be mentioned that the electromagnetic enhancement mainly generated by Ag NPs and chemical enhancement induced by the CT process would both improve the SERS performances of TiO_2/Ag composit nanowires.

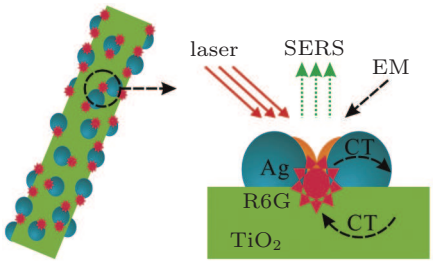


Fig. 5. (color online) Schematic illustration of the SERS mechanism in TiO_2/Ag composite nanowires.

Compared with other fabricated SERS substrates, TiO_2/Ag composite nanowires have one main advantage, i.e., they are recyclable. TiO_2 is regarded as the most efficient and environmentally benign photocatalyst, and it has been most widely used for the photodegradation of various pollutants.[31,32] A Ag–TiO_2 nanocatalyst enhances the photocatalytic activity due to a better separation of photogenerated charge carriers and improves the oxygen reduction in-

ducing a higher extent of degradation of atoms.[33] The photocatalytic capability of TiO_2/Ag composite nanowires could be employed to degrade the molecules after performing SERS analysis once, and then substrates can be carried out with a new detection cycle. Figures 6(a) and 6(b) show the SERS spectra of the UV-induced photodegradation of 10^{-6}-M R6G dispersed on the TiO_2/Ag composite nanowires in different environments. Monitoring the change of SERS spectra at the main peak of 1510 cm^{-1}, it can be observed that the water-assisted photodegradation is a little more efficient compared with anhydrous photodegradation. It takes 40 min to complete self-cleaning in a dry environment while 30 min to achieve the same effect in water-assisted photodgradation. The general photocatalytic mechanism of a semiconductor/metal composite nanostructure is based on electro–hole pairs generated by UV irradiation and local surface plasma resonance assisted charge separation, which react with both oxygen and water molecules to yield strongly oxidizing radical species, which in turn stimulate the degradation of organic molecules.[34] Therefore, the existence of water can increase the number of effective oxidizing radical species, and improve the photocatalytic effectiveness of fabricated TiO_2/Ag composite SERS substrates.

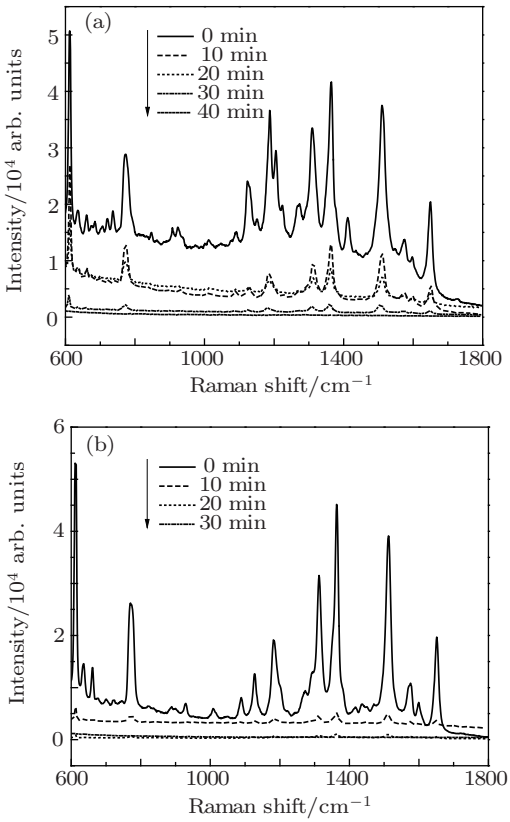


Fig. 6. Photodegradation of R6G under UV irradiation from the primitive concentration 10^{-6}-M SERS spectra showing (a) R6G degradation in a dry environment, (b) water-assisted R6G degradation.

As shown in Fig. 7, the cycle of "detection–cleaning" was conducted 10 times. It is clear that the intensities of characteristic peaks remain at the same level when the analyte is live but is completely eliminated after UV irradiation. These results indicate that it is feasible for TiO_2/Ag composite nanowires to be used as recyclable SERS substrates to detect the organic pollutants.

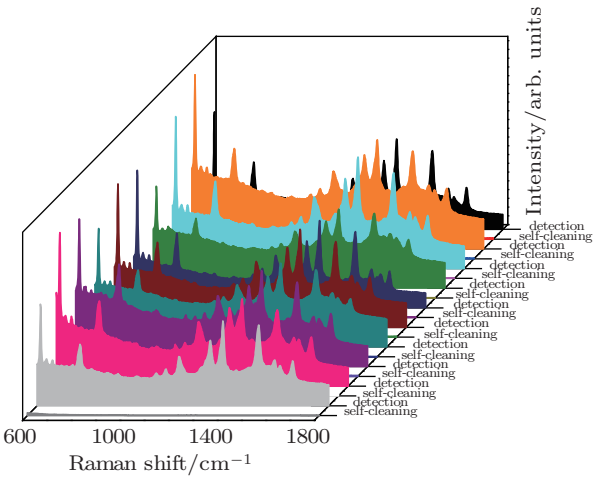


Fig. 7. (color online) Raman spectra of ten adsorption/UV cleaning cycles of R6G 10^{-6} M. Each cycle consists of the adsorption of R6G solution followed by UV irradiation for 40 min in a dry environment. The graphs show the Raman spectra before and after cleaning.

4. Conclusions

In this study, we demonstrate a facile and novel strategy for the fabrication of a recyclable SERS-active substrate composed of TiO_2/Ag composite nanowires. One-dimensional (1D) TiO_2 nanowires are prepared through a simple, two-step hydrothermal route, and SERS-active substrates are obtained through the decoration of silver nanoparticles by a third hydrothermal route. Raman measurements show that the composite nanowires can indeed develop both strong SERS activity and efficient phoytogradation. The enhancement factor of the TiO_2/Ag is approximately 1.94×10^8 with R6G as the probe molecule and characteristic peaks can be identified to be as low as 10^{-12} M. In particular, the substrate demonstrates its rapid self-cleaning capacity under UV irradiation regardless of whether it is assisted by water or not. Raman measurements show that the composite nanowires can indeed be recycled at least 10 times and maintain unwavering SERS capacity. Such as-prepared TiO_2/Ag composite nanowires make an opportunity to expand the application of semiconductor/metal composite nanostructures in the SERS field.

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