Recyclable Ag-Deposited TiO$_2$ SERS Substrate for Ultrasensitive Malachite Green Detection

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ABSTRACT: An ultrasensitive Ag-deposited TiO$_2$ flower-like nanomaterial (FLNM) surface-enhanced Raman scattering (SERS)-active substrate is synthesized via a hydrothermal method, and Ag nanoparticles (NPs) are deposited through electron beam evaporation. Malachite green (MG), which is widely used in aquaculture, is employed to assess the surface-enhanced Raman scattering (SERS) properties of TiO$_2$/Ag FLNMs. They exhibit ultrasensitivity (limit of detection (LOD) of MG reaches $4.47 \times 10^{-16} \text{ M}$) and high reproducibility (relative standard deviations (RSDs) are less than 13%); more importantly, the TiO$_2$/Ag FLNMs are recyclable, as enabled by their self-cleaning function due to TiO$_2$ photocatalytic degradation. Their recyclability is achieved after three cycles and their potential application is examined in the actual system. Finite difference time domain (FDTD) simulations and the charge-transfer (CT) mechanism further prove that the excellent SERS properties originate from localized surface plasmon resonance (LSPR) of Ag NPs and the coupling field between Ag and TiO$_2$ FLNMs. Therefore, TiO$_2$/Ag FLNMs show promising application in aquaculture.

1. INTRODUCTION

Surface-enhanced Raman scattering (SERS) was accidentally discovered by Fleischmann and co-workers in 1974, which has been rapidly growing over the past 40 years and has now become a valuable technique in the fields of physics, chemistry, medicine, etc. The main drawback of the application of SERS technology is the use of effective substrates, which not only supply high electromagnetic enhancement but also provide stable, uniform, and reproducible performance. Several methods have been successfully utilized to improve the performance of SERS substrates. Many of them are made from noble metals with multiple shapes, such as nanorods, nanoparticles (NPs), nanotriangles, nanocubes, and core–shell nanoparticles. Recently, semiconductor materials have been applied to synthesize semiconductor noble metal SERS substrates that have attracted tremendous attention due to their low cost, high sensitivity, uniformity, and reproducibility.

TiO$_2$ is a significant wide-band-gap semiconductor that has gained wide attention due to its excellent chemical and optical properties. Recently, TiO$_2$ has attracted extensive attention as a suitable candidate as an SERS substrate. It is well-known that Ag NPs provide excellent SERS activity in the visible-light wavelength region and have much lower cost compared with Au NPs, which is very suitable for SERS substrates. Therefore, it is a reasonable attempt to deposit Ag NPs on the surface of TiO$_2$. Combining TiO$_2$ and Ag NPs as a SERS substrate would bring multifunctional SERS activity, which can be applied to detect organic pollutants.

Environmental issues attract increasing attention due to organic pollutants and contaminated food. Malachite green (MG) is a common organic pollutant in aquaculture as an antiseptic, fungicide, and ectoparasiticide due to its efficiency against parasitic and fungal infections in aquatic products. But it is probably teratogenic and mutagenic and even carcinogenic to humans. Therefore, it is banned in aquaculture. However, it is still abused in aquatic products due to its high efficiency and low cost. Therefore, it is necessary to conduct an MG test in aquatic products. The SERS technique is gradually becoming an available tool for detecting environmental pollutants. For its practical application, it is very important to develop SERS-active substrates with low cost and high efficiency. Improvements can be made by the following ways: developing a cheaper technique of fabricating substrates, fabricating a multifunctional SERS substrate, and designing a renewable SERS substrate.
In this paper, a recyclable SERS substrate was made of flower-like TiO2 with deposited Ag NPs. To assess the SERS performance of TiO2/Ag substrates, MG was chosen as a probe molecule. These newly developed SERS substrates showed great advantages in applications: high sensitivity, strong reproducibility, excellent recyclability, and stability in actual application.

2. RESULTS AND DISCUSSION

2.1. Structure and Morphology. Figure S1a,b displays the scanning electron microscopy (SEM) images of TiO2 flower-like nanomaterials (FLNMs), revealing that TiO2 nanomaterials comprise abundant flower-like aggregates and have almost similar morphology. These TiO2 flower-like nanomaterials have sizes in the range of 0.8–1.6 μm (Figure S1e). Figure S1c,d displays the SEM images of TiO2/Ag FLNMs, which are covered with Ag NPs with sizes ranging from 20 to 50 nm (Figure S1f).

Figure 1 shows the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of TiO2/Ag FLNMs. The microstructure of flower-like TiO2/Ag FLNMs is further observed. Figure 1b shows the HRTEM image of TiO2 with lattice fringes of 0.35 Å, which corresponds to the (100) plane of hexagonal Ag. Figure 1c shows the HRTEM image of TiO2 with lattice fringes of 0.35 nm, which corresponds to the (101) plane of anatase TiO2. The SEM and TEM images demonstrate that Ag NPs are successfully deposited on the TiO2 FLNMs.

Figure S2 portrays the X-ray diffraction (XRD) patterns of TiO2 FLNMs and TiO2/Ag FLNMs. TiO2 FLNMs exhibit the pure anatase phase due to characteristic diffraction peaks at 2θ = 25.28° (101), 37.80° (004), 48.05° (200), 53.89° (105), 55.06° (211), 62.88° (204), 68.76° (116), 70.31° (220), and 75.03° (215). The results can be introduced to anatase TiO2 (ICDD (International Center of Diffraction Data) No. 21-1272). The red line belongs to TiO2/Ag FLNMs. It shows no Ag signals, as the thickness of deposited Ag particles is only 6 nm.

2.2. X-ray Photoelectron Spectroscopy (XPS) Spectrum. To check the chemical valence states and chemical composition of TiO2/Ag FLNMs, XPS measurements were carried out (Figure S3). C 1s at 284.8 eV is selected as the calibration peak. Figure S3a shows the full-scan XPS spectrum. It is observed that TiO2/Ag FLNMs are composed of Ti, O, C, F, and Ag elements. F element is the residual of hydrofluoric acid (HF) from the hydrothermal reaction, and the peak at 684.7 eV indicates that F− is absorbed on the surface of TiO2.20 Figure S3b illustrates the XPS band of Ag 3d. Peaks at 367.8 and 373.8 eV are attributed to Ag 3d3/2 and Ag 3d5/2, respectively, indicating that Ag is deposited on the TiO2 nanomaterials. Figure S3c shows XPS bands for the Ti 2p region; peaks at 458.9 and 464.7 eV are attributed to Ti 2p3/2 and Ti 2p1/2, respectively, indicating the presence of Ti4+ ions.21 Figure S3d shows the XPS band of O 1s. The characteristic peak of O 1s is composed of two peaks fitted by the Gaussian equation (Avantage, Thermo Fisher Scientific). The peak at 530.8 eV originates from the O–Ti bonding, and the peak at 532.8 eV is attributed to O2 adsorption. The XPS results verify that TiO2/Ag FLNMs are successfully obtained.

2.3. SERS Applications. Illegally used aquaculture drugs cause severe problems in aquatic food products due to their negative effects on the environment and public health. MG is a triphenyl methane dye that has been abused used over the past few decades in aquaculture, with high fungicidal efficiency even at very low concentrations.22 However, MG can enter the food cycle easily and cause carcinogenic, mutagenic, and teratogenic abnormalities in humans.23 Thus, a fast, facile, low-cost, and sensitive analytical technique is urgently needed for detecting MG in aquatic products. The SERS technique provides a new way to fulfill this demand. The SERS properties of TiO2/Ag FLNMs, including sensitivity, reproducibility, and recyclability, and actual application are demonstrated through a series of experiments.

2.3.1. Sensitivity. The SERS performance of TiO2 FLNMs, Ag NPs, and TiO2/Ag FLNMs is demonstrated in Figure 2a–c, respectively. It is obvious that TiO2/Ag FLNMs exhibit the best SERS performance. The fingerprint Raman peaks of MG are still visible even at 10−15 M (Figure 2c). Peaks at 917, 1179, and 1215 cm−1 originate from the out-of-plane C–H bending, the in-plane modes of C–H bending, and C–H rocking, respectively; peaks at 1294 and 1368 cm−1 belong to in-plane aromatic C–H bending vibration and N-phenyl stretching, respectively; and peaks at 1491, 1594, and 1619 cm−1 originate from ring C–C stretching.24–26 All peaks are consistent with the characteristic peaks of MG.

It is noted that the minimum concentration of MG on TiO2/Ag FLNMs reached 1.0 × 10−15 M and the limit of detection (LOD)27 is another prominent parameter for SERS performance that is meaningful for practical application. The intensity of the peak at 1619 cm−1 versus the logarithmic concentration of MG for TiO2/Ag FLNMs is illustrated in Figure 2d. The corresponding LOD is 4.47 × 10−16 M.

The enhancement factor (EF) is another significant parameter for SERS. To assess the EF of TiO2/Ag FLNMs, the peak at 1619 cm−1 for MG is employed to evaluate the EF according to the following equation:28

\[
\text{EF} = \frac{I_{\text{SERS}}}{I_{\text{RS}}}C_{\text{RS}}C_{\text{SERS}}
\]

where \(I_{\text{SERS}}\) and \(I_{\text{RS}}\) represent the Raman intensities of the probe molecules adsorbed on SERS substrates and bare substrates, respectively. \(C_{\text{SERS}}\) and \(C_{\text{RS}}\) are the concentrations of probe molecules on SERS substrates and bare substrates, respectively. All of the testing conditions are consistent. A high SERS EF of 3.49 × 1011 is obtained when using a \(C_{\text{SERS}}\) of 10−15 M and a \(C_{\text{RS}}\) of 10−4 M. Compared with other substrates, different SERS substrates used for MG detection with their enhancement factor (EF) and LOD (M) are listed in Table S1.

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27272
This reveals that TiO$_2$/Ag FLNMs achieve ultrasensitive detection.

2.3.2. Reproducibility. The reproducibility of SERS signals is determined under consistent testing conditions; the signals from multiple tests are within a certain error range that is no more than 20%.$^{29}$ Three-dimensional (3D) Raman signals of MG at $1.0 \times 10^{-13} \text{ M}$ are acquired from 30 random spots (Figure 3a) and 3D mapping (Figure S4), which show that excellent reproducibility is achieved. The relative standard deviations (RSDs) of the characteristic peaks at 1179, 1368, and $1619 \text{ cm}^{-1}$ are 9.61, 12.34, and 4.26%, respectively (Figure 3b–d). All RSDs are less than 13%, indicating that TiO$_2$/Ag FLNM substrates have high reproducibility. The reasons for the high reproducibility of TiO$_2$/Ag can be summarized as follows: first, TiO$_2$/Ag FLNMs are uniform and Ag NPs are equally spread on the surface of FLNMs. Furthermore, MG molecules are completely adsorbed before testing, making the concentration of Mg consistent on the surface of TiO$_2$/Ag FLNMs. Therefore, TiO$_2$/Ag FLNMs would be a promising substrate for practical applications.

2.3.3. Recyclability. Due to the photocatalytic degradation of TiO$_2$, the clear advantage of TiO$_2$/Ag FLNMs is its recyclability.$^{30}$ For recyclable SERS performance, Figure 4a displays the typical process: after SERS measurements, the substrates are soaked in deionized water and irradiated with a UV lamp (<400 nm) for 1 h at room temperature, and then the substrates are placed 2 cm away from the UV lamp with the nanostructures facing the UV light. To check if the photocatalytic degradation is completed, SERS detection is used to check that the substrates are clean. In recyclable processes, the photocatalytic reaction of MG is$^{31}$

$$\begin{align*}
\text{C}_{35}\text{H}_{54}\text{N}_{12}\text{O}_{12} & \xrightarrow{\text{TiO}_2/\text{Ag, \text{hv}}} \text{CO}_2 + \text{H}_2\text{O} + \text{HNO}_3 + \text{(small molecules)} \\
R^2 &= 0.9774 \\
\text{LOD} &= 4.47 \times 10^{-16} \text{ M} \\
1619 \text{ cm}^{-1}
\end{align*}$$

The advantage of photocatalytic degradation is that it decomposes MG molecules to CO$_2$, H$_2$O, HNO$_3$, and small molecules, which endows the SERS substrates with the self-cleaning function. The process is repeated three times to ensure its recyclability (Figure 4b), indicating that TiO$_2$/Ag FLNMs are suitable for use as a recyclable SERS substrate.

2.3.4. Application in the Actual System. To further verify the actual system of TiO$_2$/Ag FLNMs, various water samples from the Fuxian Lake and the Dian Lake are selected as actual water samples without any purification. Before SERS measurements, 0.0927 g of MG is dissolved in 10 mL of Fuxian Lake and Dian Lake water samples, separately. Then, they are diluted to different concentrations. Figure 5a displays the SERS spectra of MG on TiO$_2$/Ag FLNM substrates from different water samples at a concentration of $1.0 \times 10^{-10} \text{ M}$. It is found that all of the water samples show high SERS performance, and the minimal detectable concentration of MG with the Fuxian Lake water sample is $1.0 \times 10^{-12} \text{ M}$ (Figure 5b) and the minimal detectable concentration of MG with the Dian Lake is $1.0 \times 10^{-11} \text{ M}$ (Figure 5c). They are lower than the minimum value found in aquatic products (2 μg/kg).$^{32}$ This proves that TiO$_2$/Ag FLNMs possess potential applicability in actual water systems.
2.4. Mechanism. It is commonly recognized that there are two interacting mechanisms for the SERS effect: the electromagnetic (EM) mechanism and the charge-transfer (CT) mechanism. The EM mechanism involves the enhancement of optical fields and requires the excitation of the localized surface plasmon resonance (LSPR) originating from the substrate. The EM model does not require specific bonds between the adsorbate and the substrate, which is a long-range effect and is mainly contributed by noble metals. The CT mechanism is mainly contributed by semiconductor substrates, which involves the CT between the adsorbate and the substrate and is a short-range effect. A direct bond between the adsorbate and the substrate is required for the CT enhancement. The SERS enhancement mechanism of TiO₂/Ag FLNMs is the combined contribution of the EM effect of surface-deposited Ag NPs and the CT effect between TiO₂ and probe molecules.

To verify the EM mechanism contribution of TiO₂/Ag FLNMs, the finite difference time domain (FDTD) method was applied to simulate the EM field distribution of Ag NPs and Ag NPs deposited on TiO₂ FLNMs. In this simulation, the diameter of Ag NPs was set to 20 nm, the separation distance of the adjacent Ag NPs was 5 nm, the thickness of TiO₂ layer was 20 nm, and the laser wavelength was 532 nm. The FDTD simulation results are shown in Figure 6, which reveals that the strong EM field is distributed in the space between Ag NPs (Figure 6a) and the interface between Ag NPs and the TiO₂ layer (Figure 6b). This tiny gap was called a hot spot that played a decisive role in SERS enhancement. With more hot spots, it was easier to obtain high-intensity SERS signals.
Compared with Figure 6a, the EM field was more stronger, as shown in Figure 6b, which would achieve high SERS performance. From the FDTD results, TiO$_2$/Ag FLNM substrates supplied more hot spots and high EM, which led to improve the SERS performance.

According to the previous work,$^{40}$ the SERS enhancement mechanism of a semiconductor substrate depends on the chemical adsorption between the SERS substrate and probe molecules. The probe molecules can be adsorbed to the substrate, and its Raman signals can be enhanced by the CT mechanism, even at ultralow concentrations. Therefore, the semiconductor substrate shows ultrasensitive detection properties at ultralow concentrations.$^{41}$

It is obvious that the enhancement on TiO$_2$/Ag substrates must be from the synergistic effect of Ag and TiO$_2$ including the EM enhancement of Ag and the CT enhancement of TiO$_2$. The combined SERS enhancement on the TiO$_2$/Ag substrates can be described as follows

$$I_{\text{SERS}} = I_{\text{EM}(\text{Ag})} + I_{\text{EM}(\text{TiO}_2 - \text{Ag})} + I_{\text{CT}(\text{TiO}_2 - \text{Ag})} + I_{\text{CT}(\text{TiO}_2 - \text{MG})} + I_{\text{CT}(\text{Ag} - \text{MG})}$$

Here, $I_{\text{EM}(\text{Ag})}$ and $I_{\text{EM}(\text{TiO}_2 - \text{Ag})}$ represent the EM enhancements of deposited Ag NPs and the interface between Ag NPs and CT. Therefore, the semiconductor substrate shows ultrasensitive detection properties at ultralow concentrations.$^{41}$
and TiO₂ FLNMs, respectively. The other three terms in the expression originate from the CT enhancement between Ag NPs, TiO₂, and MG molecules. The deposited Ag NPs on the surface of TiO₂ can be excited by localized surface plasmon resonance (LSPR), and photoexcited electrons can be injected into the conduction band (CB) of TiO₂ after the transfer to the lowest unoccupied molecular orbital (LUMO) of the MG molecules adsorbed on TiO₂. All these items contribute to the combined TiO₂/Ag substrate enhancement together. Therefore, it is not surprising to observe that TiO₂/Ag FLNMs exhibit high SERS enhancement in our present experiment.

3. CONCLUSIONS

In summary, a novel strategy for a multifunctional SERS substrate based on the Ag-deposited TiO₂ FLNM substrate is proposed with excellent sensitivity, reproducibility, and recyclability. The developed TiO₂ FLNM substrate has been used for the detection of MG, which is a universal organic pollutant in aquaculture. Raman measurements indicate that TiO₂/Ag FLNMs have high sensitivity (the LOD of MG reaches 4.47 × 10⁻¹⁶ M), reproducibility (RSDs are less than 13%), and recyclability (it can be repeated for three cycles) and exhibit a promising application in an actual system. Furthermore, the FDTD simulation results reveal that TiO₂/Ag FLNM substrates give rise to more hot spots, and the CT process of metal-semiconductor-molecular system synergetically contributes to its high SERS performance. Thus, we firmly believe that TiO₂/Ag FLNM substrates have potential to be used in aquatic products.

4. EXPERIMENTAL SECTION

4.1. Reagents and Instruments. A Ti film (99.999% purity) was supplied by Haiyuan Aluminum Corporation, hydrofluoric acid (HF, 40 wt %) was purchased from Tianjin Fengchuan Chemical Reagent Corporation, and malachite green (MG) was purchased from Maklin Corporation. Deionized water of 18.2 MΩ was used in all experiments. All reagents were used as received without any refinement.

Surface morphology structural properties were characterized by scanning electron microscopy (SEM, Quanta FEG 250, FEI). The microstructures of the substrates were further studied by transmission electron microscopy (TEM, JEOL 2010, Japan). X-ray diffraction (XRD) data were measured using an Ultima IV Rigaku (Japan) to verify the phase of the substrates. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) was performed to check the chemical valence states and chemical composition. SERS spectra were recorded using a confocal Raman spectrometer (Andor, England).

4.2. Preparation of TiO₂ FLNMs (Flower-like TiO₂ Nanomaterials). TiO₂ flower-like nanomaterials were synthesized by a one-step sol hydrothermal method between the Ti film and the HF solution according to the precious work. First (Figure 8a), a mixed solution of 10 mmol of hydrofluoric acid (HF) and 60 mL of 3 cm Ti films was put into a 100 mL stainless steel Teflon autoclave at 110 °C for 6 h. The chemical processes were as follows:

\[ \text{Ti} + 6\text{HF} \rightarrow \text{H}_2\text{TiF}_6 + 2\text{H}_2 \]
\[ \text{H}_2\text{TiF}_6 + 4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 + 6\text{HF} \]
\[ \text{Ti(OH)}_4 \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} \]

After natural cooling, the product was rinsed with deionized water and dried at 80 °C for 6 h. The chemical processes were as follows. TiO₂ FLNMs were obtained.

4.3. Preparation of Hybrid TiO₂/Ag FLNMs. After the abovementioned processing, Ag NPs were deposited on films by electron beam evaporation (Chinese Academy of Sciences Instrument Corporation, China). The evaporation rate was 0.1 Å/s and the thickness was 6 nm, Finally, TiO₂/Ag FLNMs were obtained (Figure 8b,c).

4.4. SERS Measurements. In the traditional method, probe molecules were first dropped onto the substrate and dried, which greatly increased the detection time. Moreover, during the drying process, the coffee ring distributed the probe molecules nonuniformly, which led to lower reproducibility. To overcome this shortcoming, promoting detection efficiency and signal stability, SERS measurements were conducted in the aqueous environment in this paper. First, TiO₂/Ag FLNM substrates were soaked in solution for 3 h to achieve adsorption equilibrium. Then, the substrates were transferred...
to a custom-made quartz slot (15 mm × 15 mm × 1 mm), which was covered with the cover glass (Figure S5). The Raman signals were recorded using a confocal microscopy Raman spectrometer system with an excitation laser wavelength of 532 nm. A microscope objective of 50× was used, 1200 (L/mm) grating was selected, acquisition time was adjusted to 10 s, and the accumulation number was three times for each test.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04082.

- SEM images of TiO₂ FLNMs and TiO₂/Ag FLNMs (Figure S1);
- XRD pattern of TiO₂ FLNMs and TiO₂/Ag FLNMs (Figure S2);
- XPS analysis of TiO₂/Ag FLNMs (Figure S3);
- schematic of the custom-made quartz slot (Figure S4);
- and different SERS substrates used for MG detection with their enhancement factor (EF) and LOD (M) (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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