Electronic Supplementary Information (ESI):

Self-cleaning porous TiO₂-Ag core-shell nanocomposite material for surface-enhanced Raman scattering

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Experimental Section

Materials: Titanium(IV) *n*-butoxide, ethylene glycol, acetone, ethanol, tin(II) chloride (SnCl₂), silver(I) nitrate (AgNO₃), and 4-mercaptopyridine (4-Mpy) were obtained from Sigma-Aldrich. All the reagents were of analytical grade and used as received without further purification. Deionized water was used throughout the experiments.

Preparation of titanium glycolate microspheres (TGs): The titanium glycolate spheres (TGs) were synthesized at room temperature by following previously reported procedures.^[S1,2] In a typical synthesis, a solution of titanium *n*-butoxide (2 mL) and ethylene glycol (50 mL) was prepared and poured into another solution containing acetone (170 mL) and water (2.7 mL). The solution was stirred at room temperature for 1 h. The solution was then centrifuged to recover a white precipitate, which was washed several times with ethanol and dried in an oven at 60 °C, resulting in TGs.

Preparation of Sn²⁺-grafted titanium glycolate microspheres (Sn²⁺-TGs): The TGs (0.1 g) were dispersed in water (40 mL) containing SnCl₂ (0.1 g). The resulting mixture was stirred at room temperature. After stirring for 30 min, the color of the solid sample turned from white to intense yellow (see Fig. S1 below). The yellow solid sample was harvested by centrifugation, followed by washing with distilled water six times. The obtained product, composed of Sn²⁺-decorated TGs, were labeled as of Sn²⁺-TGs. It is worth noting here that the as-obtained Sn²⁺-TGs were stable enough to be stored in air at room temperature for further characterization/use for a long time.

Detailed discussion on the formation of \operatorname{Sn}^{2+}-TGs: The Sn^{2+} -TGs were prepared by mixing TGs with an aqueous solution of Sn²⁺ ions at room temperature. After stirring for 30 min, the white colored solid sample turned intense yellow (Fig. S1 in ESI⁺).), indicating the successful immobilization of a large number of Sn^{2+} species onto the surfaces of TGs. This obvious color change was in agreement with the change in UV-Vis absorption spectra of TGs after being functionalized with Sn^{2+} ions (Fig. S2 in ESI⁺). The absorption onsets for TGs and Sn²⁺-TGs were observed at ~380 nm and ~500 nm, respectively. The absorption of visible-light by Sn^{2+} -TGs can be attributed to metal-to-metal charge transfer in Ti^{IV}-O-Sn^{II} moieties.^[S3] It should be noted that although the grafting of Sn^{2+} on TGs was achieved in water, the TGs did not undergo hydrolysis and they maintained their structures and composition (see TEM image and IR spectrum in Figs. S3,4 in ESI⁺). To further confirm the presence of Sn²⁺ ions on the TGs and to determine their amount, the Sn²⁺-TGs sample was characterized by X-ray photoelectron spectroscopy (XPS) along with inductively coupled plasma (ICP). Fig. S5 in ESI^{\dagger} show the high resolution XPS spectra for Sn3d and Ti2p of Sn²⁺-TGs. The spectrum for Sn3d exhibited two peaks at 495.4 and 487.0 eV, which were assigned to the $3d_{3/2}$ and $2d_{5/2}$ core level peaks of Sn^{2+} , respectively. The spectrum for

Ti2p showed two peaks at 464.6 and 458.8 eV, which were attributed to the $2p_{1/2}$ and $2p_{3/2}$ core levels, respectively, of Ti⁴⁺ species. A quantitative analysis of the XPS data revealed that the Sn/Ti atomic ratio was ~0.83:1.00, which was indicative of the presence of abundant Sn²⁺ species on the surface of Sn²⁺-TGs. Because XPS is a surface chemical analysis technique, it cannot, however, give the full picture of the Sn/Ti atomic ratio in Sn²⁺-TGs. Therefore, the sample was further analyzed by ICP-AES elemental analysis, which gave a Sn/Ti ratio ~3 mol. %.

Synthesis of porous TiO₂-Ag core-shell nanocomposite (TiO₂-Ag-CSN) material: By using Sn^{2+} -TGs as precursor and by employing different concentrations of aqueous Ag⁺ solutions, porous TiO₂-Ag-CSN materials with different Ag/Ti molar ratio were obtained. As an example, the synthesis of porous TiO₂-Ag-CSN material with Ag/Ti molar ratio of 5% was achieved by *in situ* hydrolysis and condensation of the Sn²⁺-TGs (100 mg) in an aqueous solution (40 mL) containing Ag⁺ ions (6 mg AgNO₃) at 130 °C for 24 h.

Furthermore, three different control experiments or samples were synthesized for comparative studies. (1) The first control experiment involved the synthesis of materials without Ag^+ ions in the above synthetic procedure. This resulted in only porous TiO₂ microspheres, with no Ag nanoparticles, as expected (see TEM image in Fig. S7 in ESI[†]), and (2) Pure TGs without Sn²⁺ (instead of Sn²⁺-TGs) were used as precursor under identical reaction conditions; however, the synthesis resulted in a mixture of porous TiO₂ microspheres and Ag nanoparticles, instead of porous TiO₂-Ag core-shell structure (see TEM image in Fig. S8 in ESI[†]). (3) An additional porous TiO₂-Ag composite, labeled as TiO₂-Ag, with Ag/Ti = 1 mol % and containing discrete Ag nanoparticles on the surface of porous TiO₂ (see TEM image, Figure S16 in ESI[†]) was also prepared by decreasing the amount of Ag⁺ in the solution (1.2 mg).

General Characterization: The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 X-ray diffractometer with Cu K α radiation (λ = 1.5418 Å). The scanning electron microscopic (SEM) images were taken on a JEOL JSM 6700F electron microscope. The TEM images were obtained with a Topcon 002B TEM microscope, whereas the HRTEM image was obtained with a JEOL JSM-3010 TEM microscope. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatized X-ray source (Al K α *hv* = 1486.6 eV). The energy scale of the spectrometer was calibrated using Au 4f_{7/2}, Cu 2p_{3/2}, and Ag 3d_{5/2} peak positions. The standard deviation for the binding energy (BE) values is 0.1 eV. The UV-Vis diffuse reflectance spectra were recorded on a Lambda 950 spectrophotometer (PerkinElmer). The nitrogen adsorption and desorption isotherms were measured using a Micromeritics ASAP 2020M system. The ICP elemental analyses were performed on a Perkin-Elmer Optima 3300DV ICP spectrometer.

Surface-enhanced Raman scattering (SERS) measurements: Raman and SERS spectra were obtained at room temperature with a micro-Raman instrument (Renishaw 1000, Gloucestershire, U.K.) equipped with a He/Ne laser (633 nm) and a CCD detector. The laser power at the sample position was typically 2.0 mW. An integration time of 1 s was used for both Raman and SERS spectra. All of the Raman spectra presented in this work consisted of an average of five spectra, which were collected at five different positions over the samples. In this study 4-mercaptopyridine (4-Mpy) was chosen as a model analyte to investigate the performance of the as-prepared TiO₂-Ag-CSN substrate for SERS detection. In a typical experiment, 5 mg of powdered TiO₂-Ag-CSN was placed on a glass slide (see SEM image of the SERS substrate in Fig. S13 in ESI⁺), and then 100 μ L of 1 x 10⁻⁵ or 1 x 10⁻⁶ M ethanol solution of 4-Mpy was drop-casted on it. After the solvent was allowed to dry, the resulting sample was directly used as a SERS substrate for the SERS analysis. For reference, the normal Raman spectrum of 100 μ L of 5 x 10⁻² M ethanol solution of 4-Mpy with 5 mg of pure porous TiO_2 was also recorded in the same way. Raman enhancement factor (EF) can be estimated from the experiments as follows:

 $EF = (I_{SERS}/I_{Raman}) (N_{bulk}/N_{ads})$

where I_{SERS} and I_{Raman} are the Raman intensity of the same Raman band under SERS and normal Raman conditions, respectively. N_{bulk} is the number of 4-Mpy molecules drop-casted on the pure porous TiO₂, and N_{ads} is the number of 4-Mpy molecules placed on the porous Ag-TiO₂-CS material. Here, the strongest Raman band at 1100 cm⁻¹ was selected to calculate the EF value. During the experiment, the Raman measurement parameters including the laser power were kept constant. The I_{SERS} was obtained from 10^{-5} M 4-Mpy solution on the porous Ag-TiO₂-CS material, and the I_{Raman} was obtained from 5 x 10^{-2} M 4-Mpy solution on the pure porous TiO₂ sample. For both experiments, the laser focal volume was kept constant (1 \Box m diameter). To determine EF value, we assumed that all of the 4-Mpymolecules used in the SERS experiment were adsorbed on the silver surface. Thus, the EF value we obtained was an underestimated value, and the real EF value could actually be some orders of magnitude higher.

Selection of excitation wavelength for SERS measurements: It is generally accepted that the SERS spectra are strongly related to surface plasmon excitation of SERS substrate, especially for the electromagnetic enhancement mechanism.^[S7,8] Thus, the SERS spectrum of 4-Mpy (10^{-5} M) was measured first at 514 nm because the strongest surface plasmon absorption of TiO₂-Ag-CSN was around 500 nm (Fig. S12 in ESI[†]). For comparison, the SERS spectrum of 4-Mpy (10^{-5} M) was also measured at 633 nm, which would lead to a relatively low-efficiency plasmonic excitation. However, the results (Fig. S14 in ESI[†]) demonstrated that SERS signals obtained at 633 nm were higher than those obtained at 514 nm.

In order to explain why the SERS enhancement at 633 nm excitation was higher than 514 nm excitation, two important points were considered. 1) Nanocomposite materials such as our TiO₂-Ag-CSN, which combine TiO₂ with Ag nanoparticles in one system, generally exhibit quite different SERS properties compared with the metal (or Ag) nanostructures in pure forms.^[S8] 2) For pure Ag nanostructures, their SERS spectra are strongly related to the surface plasmon absorption spectra of the Ag nanoparticles. However, the plasmonic excitation of Ag nanoparticles in materials such as TiO₂-Ag-CSN under very strong laser irradiation (*i.e.*, at 514 nm excitation wavelength) may lead to the electron-transfer from Ag to TiO₂, forming efficiently-separated electron-hole pairs, although this process is generally less efficient. It is worth noting that the laser light source had a very high intensity (about 2500 W/cm^2 in our case) to do this. This may be why, we still think, the SERS at 633 nm excitation was lower than the one at 514 nm despite the plasmon absorption was higher at 514 nm than 633 nm. In other words, these energy-rich electron-hole pairs generated by the plasmonic excitation of Ag nanoparticles may oxidize/decompose the organic molecules absorbed on Ag surfaces, thereby resulting in a lower SERS signals at higher excitation energy (514 nm versus 633 nm). In some previous reports, Ag nanoparticles-based composite materials have been shown to possess visible-light-induced oxidation activity at a certain extent due to the plasmon excitation.^[S9,10] For example, Ag/AgCl composite material is active for the decoloration of organic dye,^[S9] and montmorillonite-supported Ag/TiO₂ composite can be act as a bacteria photodegradation material.^[S10] Obviously, further investigation of the excitation wavelength-dependent SERS for a Ag-based composite system is highly needed, but it is beyond the scope of this paper. Thus, in this communication the SERS/Raman spectra were all measured at 633 nm.

Light-induced regeneration of TiO₂-Ag-CS SERS substrate: UV-irradiation of the TiO₂-Ag-CSN sample after SERS test was performed in a water-cooled quartz cylindrical cell which was illuminated from an internal light source with about 1 cm optical path length. The UV-light source was a 125 W high-pressure mercury lamp, and the irradiation intensity of the UV-light was ~90 mW/cm². Typically, the TiO₂-Ag-CS sample after SERS test was dispersed in O₂-saturated water (40 mL) and then exposed to the UV-light irradiation for 3 h. After the irradiation, the solid sample was harvested and dried in air for further SERS test.

It is well known that TiO₂ is a UV-responsive (< 400 nm) semiconductor material and a highly active photocatalyst, whereas Ag nanoparticle, is not a photocatalyst but a visible-light-responsive (> 400 nm) material due to its plasmon absorption.^[S11] However, in TiO₂-Ag-CSN nanocomposite material, there are two possibilities for its self-cleaning activity in the presence of SERS-active Ag nanoparticles under irradiation. 1) Under UV light, the TiO₂ core of TiO₂-Ag-CSN can be excited to directly generate highly active oxidative species (such as \cdot O₂⁻, \cdot OH) on TiO₂ or Ag surfaces due to the charge-transfer from TiO₂ to Ag (see possible photocatalysis mechanisms, Fig. S17a,b).^[S11] These active oxidative species can lead to the decomposition of the 4-Mpy molecules adsorbed on the surfaces of TiO₂-Ag-CSN microspheres. It should be noted that the highly active oxidative species generated on TiO₂ surfaces (Fig. S17a in ESI[†]), which are not in contact with Ag nanoparticles, can diffuse into the solution, and react also with the organic compounds present on the Ag surfaces.^[S11] 2) Under visible light, the Ag nanoparticles shell of TiO₂-Ag-CSN can also been excited due to plasmon absorption. The resulting photogenerated electrons may transfer from the Ag nanoparticles to TiO₂'s conduction band, resulting in the efficient electron-hole separation and possible oxidation reactions on the Ag surfaces (see the corresponding mechanism, Fig. S17c in ESI[†]).^[S9,10] It should also be noted that the charge-transfer form Ag to TiO₂ under visible-light irradiation is much lower than that from TiO₂ to Ag under UV-light irradiation.

To determine whether visible-light irradiation through direct excitation of Ag nanoparticles can clean the TiO₂-Ag-CSN SERS substrate, a cutoff filter ($\lambda > 400$ nm) which can remove the light with a wavelength shorter than 400 nm was used to ensure that only Ag shell was excited by visible light during the photo-treatment process (the intensity of visible light is about 10 mW/cm²), whereas TiO₂ core did not absorb the visible light in this region. With the use of the cutoff filter, no observable change in SERS spectrum was observed after 3 h visible-light irradiation of the sample. This observation indicates that the photoexcitation of Ag shell under visible light is not efficient for the regeneration of TiO₂-Ag-CSN SERS substrate. Thus, to evaluate or to achieve the self-cleaning property of TiO₂-Ag-CSN, UV-light had to be employed to excite the TiO₂ core as TiO₂ was found to be predominantly responsible for the self-cleaning activity of the TiO₂-Ag-CSN system.

It should be emphasized that the laser light used for excitation during the SERS measurement is a light source with a very high intensity (the light intensity is about 2500 W/cm², in our case), whereas the light source for photodegradation of 4-Mpy under visible light is a low-intensity mercury lamp (light intensity is about 0.01 W/cm² under visible light ($\lambda > 400$ nm)). This means, the intensity of laser is about 250,000 times as high as that of the mercury lamp ($\lambda > 400$ nm). This is why the decomposition of 4-Mpy under SERS measurements occurred upon the SERS irradiation, but not under the visible light irradiation with ordinary mercury lamp because the lamp's power in the latter case was not sufficient to do so.

Typically, the TiO₂-Ag-CSN sample after SERS test was dispersed in O₂-saturated water and then exposed to the UV-light irradiation for 3 h. After the irradiation, the solid sample was collected and dried in air for further use as SERS substrate or SERS evaluation. For comparison, the solid-powder substrate was also directly irradiated by UV light. The results showed only 15% decrease of SERS signals in the case of solid-powder substrate after direct UV-irradiation, indicating the presence of a large proportion of the organic molecules still adsorbed on this material. On the other hand, complete disappearance of the SERS signals was observed for solid-powder sample dispersed in O₂-saturated water for 3 h. This clearly indicates that the later method was more effective for self-cleaning the organic molecules (4-Mpy) off the TiO₂-Ag-CSN mocrospheres than the solid sample irradiated directly.

This may be because the interaction of UV light with the solid-powder sample in water allows highly active oxidative species (such as $\cdot O_2^-$, $\cdot OH$) to form easily, diffuse more smoothly, and become more accessible for degrading the organic molecules on the material.^[S11]

In addition, it should be noted that the self-cleaning property of TiO_2 -Ag-CSN must be associated with TiO_2 's well-known inherent photocatalytic activity towards oxidation of organic compounds (the general reaction is shown as below). Thus, for such reactions, it is not unusual that an O₂-saturated environment is beneficial to the reaction or allows fast oxidation or degradation of the organic compound (*i.e.*, 4-Mpy in this case), as also demonstrated for other organic compounds in previously reported photocatalysis studies.^[S11]

$$2C_5H_5NS + 33/2 O_2 + UV \rightarrow 10CO_2 + 5H_2O + 2NO_2 + 2SO_2$$



Fig. S1. Photographs of the TGs sample and the Sn^{2+} -TGs sample.



Fig. S2. UV-Vis absorption spectra of the TGs sample and the Sn^{2+} -TGs sample.



Fig. S3. TEM images of the Sn²⁺-TGs sample.



Fig. S4. IR spectrum of the Sn^{2+} -TGs sample. The Sn^{2+} -TGs sample maintained the IR absorption bands of organic components in TGs,^[S1,2] indicating that during the grafting of Sn^{2+} on TGs in water at room temperature, TGs did not undergo the transformation of TGs to TiO₂ through losing the organic component in TGs.



Fig. S5. XPS spectra of (left) Sn3d and (right) Ti2p for the Sn²⁺-TGs sample.



Fig. S6. (a) The scanning transmission electron microscope (STEM) image of porous TiO_2 -Ag-CSN material, and (b) the corresponding energy-dispersive spectroscopy (EDS) line profile (elemental mapping) (green arrow).



Fig. S7. TEM image of pure porous TiO₂.



Fig. S8. TEM images of a mixture of porous TiO₂ and Ag nanoparticles.



Fig. S9. (a) N_2 adsorption/desorption isotherms and (b) the corresponding pore size distribution of porous TiO₂-Ag-CSN material.



Fig. S10. XRD patterns of pure porous TiO₂ (black line) and porous TiO₂-Ag-CSN material (orange line). A and R denote anatase and rutile TiO₂, respectively. The XRD pattern of TiO₂-Ag-CSN showed that the core of TiO₂-Ag-CSN was composed of a mixture of anatase and rutile TiO₂. Moreover, the presence of a small XRD peak for metallic Ag confirmed that the shell of the TiO₂-Ag-CSN was composed of Ag nanocrystals. The mol ratio of anatase/rutile in the TiO₂-Ag-CSN material is about 1:1, which is calculated from the relative peak intensities of anatase (101) and rutile (110).^[S4] In contrast, porous TiO₂ (a control sample) was identified as pure anatase TiO₂. This is probably because for the TiO₂-Ag-CSN material, the incorporation of Sn⁴⁺ in TiO₂ promoted the anatase to rutile transformation. Similar phenomena were also reported previously.^[S5]



Fig. S11. XPS spectra of Ag3d (a) Sn3d (b) and Ti2p (c) for the TiO₂-Ag-CSN sample; (d) Comparison of XPS spectra of Sn3d for the Sn²⁺-TGs sample (black line) and the TiO₂-Ag-CSN sample (red line). The XPS spectrum for Ag3d (Fig. S11a) showed two peaks at 368.1 and 374.1 eV, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ core levels, respectively, of metallic Ag.^[S6] The spectra for Ti2p and Sn3d (Fig. S11b,c) indicated that the Ti and Sn species in TiO₂-Ag-CSN were Ti⁴⁺ and Sn⁴⁺, respectively. It should be pointed out that in comparison with Sn²⁺-TGs (Figure S11d), TiO₂-Ag-CSN exhibited two $3d_{3/2}$ (495.7 eV) and $2d_{5/2}$ (487.3 eV) peaks at higher binding energies, indicating the changes of Sn species from 2+ in Sn²⁺-TGs to 4+ in TiO₂-Ag-CSN. In addition, a quantitative analysis of the XPS data revealed that the Sn/Ti atomic ratio in TiO₂-Ag-CSN was ~0.84:1.00, which is similar to the value (0.83:1.00) obtained in Sn²⁺-TGs.



Fig. S12. Solid state diffuse reflectance UV-Vis spectrum of porous TiO_2 -Ag core-shell composite material. For comparison, the UV-Vis extinction spectrum of pure porous TiO_2 sample is also shown in this figure. Unlike pure TiO_2 , TiO_2 -Ag-CSN showed strong visible light absorption with an absorption maximum at ~500 nm, which was mainly attributed to the surface plasmon absorption band of Ag nanoparticles.



Fig. S13. SEM image of the TiO_2 -Ag-CSN SERS substrate. The SEM image shows that the SERS substrate was composed of multi-layered aggregates of TiO_2 -Ag-CSN.



Fig. S14. Comparison of SERS spectra of 4-Mpy (10^{-5} M) that was drop-casted and dried on TiO₂-Ag-CSN. The excitation wavelengths for the SERS measurements were 514 and 633 nm, respectively.



Fig. S15. Normal Raman spectrum of 4-Mpy (5 x 10^{-2} M) that was drop-casted and dried on pure porous TiO₂.



Fig. S16. Porous TiO₂-Ag composite (TiO₂-Ag, Ag/Ti = 1 mol. %) with discrete Ag nanoparticles on the surface of porous TiO₂.



Fig. S17. Photocatalysis mechanisms of (a) pure TiO_2 under UV-light irradiation, (b) TiO_2 -Ag composite under UV-light irradiation, and (c) TiO_2 -Ag composite under visible-light irradiation.



Fig. S18. SERS spectrum of remained 4-Mpy for the TiO_2 -Ag-CSN substrate (10⁻⁵ M) washed by water six times.

Supporting Information References

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