Gold Nanoparticles and g-C$_3$N$_4$-Intercalated Graphene Oxide Membrane for Recyclable Surface Enhanced Raman Scattering

Lulu Qu,* Na Wang, Hui Xu, Weipeng Wang, Yang Liu, Lidia Kuo, T. P. Yadav, Jingjie Wu, Jarin Joyner, Yanhua Song, Haitao Li, Jun Lou, Robert Vajtai, and Pulickel M. Ajayan*

Toxic organic pollutants in the aquatic environment cause severe threats to both humans and the global environment. Thus, the development of robust strategies for detection and removal of these organic pollutants is essential. For this purpose, a multifunctional and recyclable membrane by intercalating gold nanoparticles and graphitic carbon nitride into graphene oxide (GNPs/g-C$_3$N$_4$/GO) is fabricated. The membranes exhibit not only superior surface enhanced Raman scattering (SERS) activity attributed to high preconcentration ability to analytes through π–π and electrostatic interactions, but also excellent catalytic activity due to the enhanced electron–hole separation efficiency. These outstanding properties allow the membrane to be used for highly sensitive detection of rhodamine 6G with a limit of detection of $5.0 \times 10^{-14} \text{M}$ and self-cleaning by photocatalytic degradation of the adsorbed analytes into inorganic small molecules, thus achieving recyclable SERS application. Furthermore, the excellent SERS activity of the membrane is demonstrated by detection of 4-chlorophenol at less than nanomolar level and no significant SERS or catalytic activity loss was observed when reusability is tested. These results suggest that the GNPs/g-C$_3$N$_4$/GO membrane provides a new strategy for eliminating traditional, single-use SERS substrates, and expands practical SERS application to simultaneous detection and removal of environmental pollutants.

1. Introduction

Due to rapid global population growth and subsequently increased agricultural and industrial activities, the concentration of organic pollutants released into aquatic environments has increased substantially[1,2]. These various organic pollutants pose a significant environmental and health concern[3]. Therefore, global efforts on developing robust technologies to detect and remove pollutants effectively from water is a vital focus of research[4]. Among these technologies, graphene-based membrane separation has become one of the prominent methods for solving environmental challenges[5,6]. These graphene-based materials, specifically graphene oxide (GO) nanosheets, can assemble into few-layered laminates through filtration, dip coating, or spin coating, forming selective 2D pathways that can quickly transport small molecules[7,8]. Sub-micrometer-thick GO membranes, as found by Geim and co-workers, do not allow gases, vapors, or liquids to penetrate through but allow water to permeate unimpeded[9]. Since then, the assembled GO membranes have been successfully applied to water purification and removal of organic pollutants from the aquatic environments[10–15]. However, the concentration of pollutants in water needs to be evaluated using a combination of techniques, and the GO membrane itself exhibits weak reusability due to the saturated adsorption of pollutants. Thus, it is necessary to fabricate GO-based membrane with multifunctionality such as detection, self-cleaning, and recyclability.

Surface-enhanced Raman scattering (SERS) is an ultrasensitive analytical technique for identification of chemicals and biological species owing to its considerable molecular recognition ability[16–19]. The SERS phenomenon is mainly attributed to the local amplification of electromagnetic field originated from the interaction of incident light with noble metal nanostructures[20–22]. Therefore, a main method of exploiting SERS-based analytical platforms is the development of SERS-active nanostructures. Generally, Raman enhancement can be achieved
using metallic nanoparticles (Au, Ag, and Cu) with different shapes and architectures,[23–26] but they are lacking stability and reproducibility. Nanoscale lithography techniques such as electron beam lithography,[27] nanosphere lithography,[28] and focused ion beam,[29] are efficient methods to improve the yield of highly stable and reproducible SERS substrates, although these techniques are expensive and technologically demanding. Considering these problems, we fabricated graphene-based membranes as SERS substrates by a facile filtering process in previous work, which exhibited superior enrichment ability and high reproducibility, and avoided sophisticated fabrication methods.[30] However, the membranes are single-use due to the saturated adsorption of pollutants and cross-contamination. Therefore, practical applications of graphene-based membrane in SERS detection can be further broadened by developing renewable membranes that are cost-effective, extremely sensitive, and reproducible.

Reusability of SERS substrates can be usually achieved by combining semiconductors with photocatalytic ability such as TiO2 and ZnO.[31–35] For example, an Au-coated TiO2 nanotube array was prepared for recyclable SERS detection, achieving self-cleaning of the adsorbed analytes through a photocatalytic degradation process.[36] However, these semiconductor catalyst-based SERS substrates exhibit some disadvantages such as low sensitivity and solar spectrum mismatch. Hence, fabricating efficient visible-light-driven photocatalytic SERS substrates is a challenging, although promising, task. Graphitic carbon nitride (g-C3N4) was recently reported to demonstrate unique efficiency visible-light-driven photocatalytic SERS substrates based on the electrostatic, π–π stacking, and hydrogen-bonding interactions.[41,42] GNPs with a size of 30 nm in diameter (Figure S2, Supporting Information) were then modified on the surface of g-C3N4/GO nanosheets and the potential for high SERS activity. The combination of g-C3N4 with GO is effective for decreasing the recombination rate of photogenerated electron–hole pairs, thus improving visible-light utilization efficiency.[40] Inspired by these excellent properties, a multifunctional membrane was prepared by intercalating gold nanoparticles and bilayer g-C3N4 into GO nanosheets (GNPs/g-C3N4/GO) as an ultra-sensitive and highly reproducible SERS substrate. The prepared GNPs/g-C3N4/GO membranes exhibit superior SERS activity originated from π–π and electrostatic interactions. Moreover, because of their excellent catalytic properties, the GNPs/g-C3N4/GO membranes can self-clean by photocatalytic degradation of adsorbates under illumination of visible light into inorganic small molecules, so that recycling can be achieved. The outstanding properties of GNPs/g-C3N4/GO membranes were further demonstrated by preconcentration, SERS identification, removal, and recyclable SERS detection of 4-chlorophenol, which suggest that they hold great promise for highly reproducible, portable, and cost-effective applications as SERS substrates with visible-light-cleanable features.

2. Results and Discussion

2.1. Preparation and Characterization of the Multifunctional GNPs/g-C3N4/GO Membrane

The multistep preparation of multifunctional GNPs/g-C3N4/GO membranes is displayed in Figure 1. A dispersion, which contains negatively charged GO sheets about 1–3 µm in size with a 0.78 nm thickness and positively charged g-C3N4 consisting of a larger percent of bilayers with the representative thickness across the sheet of 1.33 nm (Figure S1, Supporting Information), was initially prepared to construct g-C3N4-functionalized GO nanosheets (g-C3N4/GO) based on the electrostatic, π–π stacking, and hydrogen-bonding interactions.[31,42] FNPs with a thickness of 3.9 µm were then modified on the surface of g-C3N4/GO nanosheets (Figure S3, Supporting Information). After, the GNPs/g-C3N4/GO membrane was assembled by vacuum filtration of the above dispersion of GNPs and g-C3N4/GO on a porous PC membrane. As formed, the g-C3N4/GO nanosheets interlocked parallelly, forming lamellar structures. Since the lateral size of the GO nanosheets is larger than that of g-C3N4 and GNPs, the GO nanosheets can sandwich g-C3N4 and GNPs. To address stability, hydrazine was added to the prepared GNPs/g-C3N4/GO, partially reducing the membrane at room temperature. Once the GNPs/g-C3N4/GO membrane was dried, it was used for sample filtration. During filtration, the water passed through the pores but the organic pollutants were enriched on the surface of the membrane by π–π stacking or other interactions, stimulating the highly sensitive SERS detection of analytes in polluted water. When SERS detection was achieved, the GNPs/g-C3N4/GO membrane could be cleaned by photocatalytic decomposition of adsorbates under the visible light irradiation, thus resulting in recyclable SERS substrates.

Figure 2A is an optical image of the free-standing GNPs/g-C3N4/GO membrane. The membrane can be bent randomly without breaking, demonstrating excellent flexibility (Figure 2B,C). The microstructure of the GNPs/g-C3N4/GO membrane was analyzed using scanning electron microscopy (SEM) images. As shown in Figure 2D, corrugations constructed by GO and g-C3N4 could be clearly observed. In addition, GNPs or their clusters were dispersed uniformly on the surface of GNPs/g-C3N4/GO membrane (Figure 2E; Figure S4, Supporting Information), indicating the homogeneous intercalation of GNPs between the lamellar structures of g-C3N4/GO nanosheets and the potential for high SERS activity. The thickness of this membrane is about 3.1 µm, which was confirmed by the cross-sectional SEM image (Figure 2F). After a short treatment of GNPs/g-C3N4/GO membrane with hydrazine, the corrugated nanostructured surface and uniform distribution of GNPs remained, but the interlayer distance between GO layer sheets increased with a final membrane thickness of 3.9 µm. Interestingly, the water penetrability of the GNPs/g-C3N4/GO membrane increases significantly with the hydrazine treatment time, accompanied with an obvious decrease in Rhodamine 6G (R6G) rejection rate (Figure S5, Supporting Information). These variations may be attributed to the formation of defect and ripple structure in the GNPs/g-C3N4/GO membrane, induced by the strong reducing agent. To investigate the defects within GNPs/g-C3N4/GO membranes, Raman spectroscopy was employed. For graphene-based materials, the in-plane vibration of sp2-bonded carbon atoms correlates with the G peak intensity while the degree of disorder or defects correlates with the D peak intensity.[41] The D to G peak ratio (I_d / I_g), which is used to evaluate the degree of disorder in graphene-based materials, slightly increases with the
hydrazine treatment, confirming the formation of structural defects and the small amount of GO sheets reduction during the hydrazine treatment process (Figure S6, Supporting Information). Undoubtedly, these structural defects or larger ripples within hydrazine-treated GNPs/g-C$_3$N$_4$/GO membranes enable water and other molecules to permeate the membrane easily, dramatically affecting the water flux and the rejection rate of the GNPs/g-C$_3$N$_4$/GO membranes. This is not anticipated for the construction of the membranes having excellent preconcentration ability. Therefore, a 20 min hydrazine treatment was chosen to ideally fabricate the GNPs/g-C$_3$N$_4$/GO membranes. The results further indicated that the hydrazine treatment procedure not only improved the stability and robustness of GNPs/g-C$_3$N$_4$/GO membrane but also increased water flux, thus reducing filtration time.

2.2. Multifunctional GNPs/g-C$_3$N$_4$/GO Membrane: SERS and Catalytic Properties

The multifunctional properties of the GNPs/g-C$_3$N$_4$/GO membrane including SERS and catalytic activity were investigated through a series of experiments using R6G as a target molecule, which can adsorb onto the GNPs/g-C$_3$N$_4$/GO membrane by strong electrostatic and $\pi-\pi$ stacking interactions. Figure S7 (Supporting Information) shows SERS spectra obtained from pure g-C$_3$N$_4$, GO, GNPs, and GNPs/g-C$_3$N$_4$/GO membranes treated with $1.0 \times 10^{-9}$ m R6G under 532 nm excitation. No obvious Raman bands were observed from GO and g-C$_3$N$_4$, and the intensity of SERS signals acquired from GNPs/g-C$_3$N$_4$/GO membrane was about 12 times stronger than that from GNPs, suggesting that the prepared GNPs/g-C$_3$N$_4$/GO membrane was highly SERS active. Such observed behavior can be explained by the random formation of localized plasmons or “hot spots” at intercalated GNPs junctions in GNPs/g-C$_3$N$_4$/GO membranes, thus giving rise to large Raman enhancement ability.

Generally, for an ideal SERS substrate, quantitative SERS detection is expected to be achieved through the change in the analyte concentration. To evaluate the quantitative detection property of the GNPs/g-C$_3$N$_4$/GO membrane, R6G molecules at the concentrations ranging from $5.0 \times 10^{-14}$ to $1.0 \times 10^{-6}$ m was measured by filtrating 2 mL R6G solution through the membrane, as shown in Figure 3A. The systematic results demonstrated that the GNPs/g-C$_3$N$_4$/GO membrane can achieve quantitative detection in R6G concentrations ranging from $4.0 \times 10^{-13}$ to $1.0 \times 10^{-9}$ m (Figure 3B). Within this concentration range, the SERS intensity was at 613 and 1360 cm$^{-1}$, which assign the C–C–C ring in-plane stretching, aromatic C–C stretching vibrations of R6G,[44] can be expressed quantitatively by the following equations, $I_{613} = 144.3097 \log[c] + 1832.89$ and $I_{1362} = 220.1445 \log[c] + 2829.621$, respectively, where $I$ is the SERS signal intensity and $c$ is the molar concentration of R6G (Figure 3C). The quantitative detection ability down to...
Figure 3. A) Schematic showing the experimental procedures for the preconcentration and SERS detection of analytes. B) SERS spectra for different concentrations of R6G adsorbed onto the GNPs/g-C3N4/GO membrane: a) $5.0 \times 10^{-14}$ M, b) $4.0 \times 10^{-13}$ M, c) $3.0 \times 10^{-12}$ M, d) $2.0 \times 10^{-11}$ M, e) $1.0 \times 10^{-10}$ M, f) $1.0 \times 10^{-9}$ M, g) $1.0 \times 10^{-8}$ M, h) $1.0 \times 10^{-7}$ M, i) $5.0 \times 10^{-7}$ M, j) $1.0 \times 10^{-6}$ M. C) Plots of SERS intensity versus logarithmic R6G concentration at the bands of 613 and 1360 cm$^{-1}$. D) UV–vis spectra of R6G with GNPs/g-C3N4/GO membrane after illumination for different intervals. E) Process of photocatalytic degradation of R6G under visible light illumination in the presence of a) GNPs, b) GO, c) g-C3N4, d) GNPs/g-C3N4/GO membrane, e) g-C3N4/GO, and f) GNPs/g-C3N4/GO mixture. The initial concentration of R6G was $1.0 \times 10^{-5}$ M. F) The electron transfer mechanism and the photocatalytic degradation of organic pollutants with GNPs/g-C3N4/GO membrane under visible light irradiation.
1.0 × 10⁻⁹ m is three orders of magnitude, which is comparable to that of the highly sensitive screen printed substrates[44] and lower than that of the other reported SERS-active nanostructures without analyte enrichment capability.[45–47] When the R6G concentration is higher than 1.0 × 10⁻⁹ m, SERS “hot spots” in the GNPs/g-C3N4/GO membrane will be occupied almost completely by the analyte molecules, which leads to weak fluctuations in SERS signal intensities. However, only very few molecules located under the laser spot area as the R6G concentration are lower than 5.0 × 10⁻¹⁴ m, and therefore, no SERS signals were observed. In fact, the detection ability of the GNPs/g-C3N4/GO membrane can be greatly improved by increasing the initial volume of the analyte solution, which has been demonstrated by detection of R6G molecules at 1.0 × 10⁻¹⁴ m using the 20 mL R6G solution (Figure S8, Supporting Information). The above results demonstrate the excellent SERS activity and quantitative analysis ability of the GNPs/g-C3N4/GO membrane.

Apart from the SERS detection ability, the GNPs/g-C3N4/GO membrane also exhibits high photocatalytic activity. To investigate this behavior, the photocatalytic activity of the GNPs/g-C3N4/GO membrane, as well as the pure g-C3N4, GO, GNPs, g-C3N4/GO, and GNPs/g-C3N4/GO mixtures, were assessed by decomposing R6G solutions under visible light illumination. The degradation process was recorded by monitoring the change in the absorbance maximum of R6G. Dark adsorption was initially performed for 30 min to achieve saturated adsorption and check for self-degradation. The absorbance remained nearly unchanged for g-C3N4, GO, GNPs, and other nanocomposites, implying weak adsorption and self-degradation in the dark. The subsequent visible light irradiation results show no change was obtained from the absorption spectrum of the R6G solution in the absence of g-C3N4 (Figure 3E-a,b). However, the absorption intensity of R6G decreases significantly with a prolonged illumination time for the existence of g-C3N4, g-C3N4/GO, the GNPs/g-C3N4/GO mixture, and the GNPs/g-C3N4/GO membrane, indicating that the g-C3N4 and g-C3N4/containing nanocomposites indeed possess photocatalytic functions (Figure 3D,E). It can be observed that the dye was degraded almost completely after 60 min by g-C3N4/GO and GNPs/g-C3N4/GO mixture, which is twice as fast as that of g-C3N4 alone (>130 min). After forming the GNPs/g-C3N4/GO membrane by a filtration procedure, the degradation time increased to 100 min due to the decreased specific surface area, but was 1.3 times faster than that of g-C3N4 alone, suggesting excellent catalytic activity of the prepared GNPs/g-C3N4/GO membrane. This enhanced and efficient photocatalytic performance is mainly ascribed to the enormous improvement of charge separation efficiency. Under visible light irradiation, the g-C3N4 was excited and the photogenerated electrons from g-C3N4 (~3.38 eV) easily transferred to the GO sheet (~4.4 eV) due to their suitable energy levels,[40] reducing electron–hole recombination and enhanced separation efficiency. These electrons were captured and utilized for the reduction of oxygen to radical species, which oxidize dye molecules to CO₂ and H₂O and are responsible for excellent catalytic activity of GNPs/g-C3N4/GO membranes. The above results illustrate that the GNPs/g-C3N4/GO membranes have multifunctionality including effective preconcentration, excellent SERS detection ability, and high catalytic activity.

2.3. Self-Cleaning and Recyclability of GNPs/g-C3N4/GO Membrane

If a SERS substrate can clean itself fully after adsorbing target analytes, it is potentially recyclable and can be used for further removal and SERS detection. Recyclable application of the GNPs/g-C3N4/GO membrane can be attributed to its multifunctional ability, SERS detection, and catalytic activity. Thus, we investigated the self-cleaning and recyclability of the GNPs/g-C3N4/GO membrane. The target analytes were initially enriched by GNPs/g-C3N4/GO membrane (Figure S9A, Supporting Information), and SERS measurement was performed to evaluate the amount or concentration of R6G (Figure S9B, Supporting Information). Subsequently, the GNPs/g-C3N4/GO membrane was immersed into deionized water under visible light illumination and washed with deionized water at least three times for the purpose of removing any remaining ions and molecules. Figure 4A shows Raman spectra of the GNPs/g-C3N4/GO membrane after the visible irradiation at different intervals. It can be observed that the Raman intensity decreases with the extension of illumination time, further indicating excellent photocatalytic performance of GNPs/g-C3N4/GO membrane, which is consistent with UV results in Figure 2D. After 130 min, no SERS signals were acquired from the GNPs/g-C3N4/GO membrane, illustrating that R6G molecules were cleaned by a photodegraded process. Figure 4C shows the recyclability of the GNPs/g-C3N4/GO membrane. A fully recovered SERS signal was observed following filtration of the R6G solution using the GNPs/g-C3N4/GO membrane, indicating that the membrane preserved its SERS functionality. After 130 min of the visible light illumination, the SERS signal of R6G completely vanished. In addition, the results are reproducible after repeating the “detection-cleaning” procedure five times (Figure 4D). The above results demonstrate the general reversibility of this highly sensitive GNPs/g-C3N4/GO membrane.

2.4. Reproducibility of GNPs/g-C3N4/GO Membrane

In addition to high sensitivity and excellent recyclability, the reproducibility of Raman signals from SERS substrates is another important parameter to consider. Generally, nanoparticle aggregates can form “hot spots,” thus giving rise to large Raman enhancement, but random distribution of “hot spots” will result in poor reproducibility, which is not ideal for practical application. To test the spot-to-spot reproducibility, the GNPs/g-C3N4/GO membranes were used to enrich 1.0 × 10⁻⁸ m R6G and Raman-mapped from 4 random-selected zones under identical experimental conditions. Figure 5 plotted the intensity of the 1360 cm⁻¹ band from R6G before and after visible light degradation, which demonstrated uniformity across the entire GNPs/g-C3N4/GO membrane. Furthermore, to evaluate the membrane-to-membrane homogeneity, SERS signals of R6G before degradation at sixteen arbitrarily chosen positions were
taken from four GNPs/g-C3N4/GO membranes. To obtain a statistically significant result, the relative standard deviation of the intensity at the 1360 cm\(^{-1}\) band of R6G was calculated to be 14.1\%, which further indicated the uniform structure and surface properties of our GNPs/g-C3N4/GO membranes.

2.5. Application of GNPs/g-C3N4/GO Membrane for Recyclable Detection of Organic Pollutants

4-Chlorophenol is one of the phenolic compounds with high toxicity in industrial wastewaters that can result in adverse effects on digestive, nervous, and respiratory system, and even cancer.\[^{48,49}\] Therefore, developing an effective method to detect and remove 4-chlorophenol from polluted water is urgent. Next, the GNPs/g-C3N4/GO membranes were used for 4-chlorophenol detection to further expand its practical application. The Raman spectrum of solid 4-chlorophenol and the SERS spectrum of 4-chlorophenol solution were collected, as shown in Figure S10 (Supporting Information). The SERS bands at 1092 and 1590 cm\(^{-1}\) are resulted from the C=O bonds stretching and C=C ring stretching vibration, respectively.\[^{36}\] The band at 815 cm\(^{-1}\) is attributed to C–C ring in-plane bending modes. Comparing the Raman spectra, no obvious changes in Raman shifts and relative intensity were observed. This result may be due to the adsorption of most of the molecules onto the surfaces of GO or g-C3N4 by π–π stacking and hydrogen bonding interactions, inhibiting strong polarization of molecules caused by direct contact with GNPs.\[^{50,51}\]

Figure 6A shows SERS spectra of different concentrations of 4-chlorophenol varying from 5.0 \(\times\) 10\(^{-5}\) to 2.0 \(\times\) 10\(^{-10}\) M. The intensity of typical Raman bands decreases obviously with the reduced 4-chlorophenol concentration, and most bands are clearly visible even the 4-chlorophenol concentration in solution is as low as 2.0 \(\times\) 10\(^{-10}\) M. In addition, the quantitative detection for 4-chlorophenol has also been achieved in the range from 2.0 \(\times\) 10\(^{-10}\) to 1.2 \(\times\) 10\(^{-7}\) M. This illustrated that, as SERS substrates, GNPs/g-C3N4/GO membranes are highly active, further indicating that the GNPs/g-C3N4/GO membrane is promising for detection of various other pollutants.

Furthermore, the GNPs/g-C3N4/GO membrane can self-clean 4-chlorophenol by photocatalysis under visible light irradiation. This process was monitored by SERS, as displayed in Figure 6C. After 150 min visible illumination, 4-chlorophenol (1.2 \(\times\) 10\(^{-7}\) M) enriched on the GNPs/g-C3N4/GO membrane was removed completely, suggesting excellent photocatalytic activity of GNPs/g-C3N4/GO membrane. The advantage of the photocatalytic process is that the main degradation products are CO\(_2\), H\(_2\)O, and HCl (Figure S11, Supporting Information), all of which are relatively clean for the GNPs/g-C3N4/GO membrane.

Finally, we investigated the recyclability of the GNPs/g-C3N4/GO membrane for SERS detection and catalytic activity. SERS responses for 4-chlorophenol after the preconcentration and self-cleaning treatment were displayed in Figure 6E. For all recyclability tests, the GNPs/g-C3N4/GO membrane was initially used to filter the 4-chlorophenol solution, then...
characterized by SERS, and soaked into deionized water under the visible light irradiation for about 150 min. Subsequently, the membrane was washed with deionized water three times for the removal of any remaining ions and molecules and then submitted to SERS detection. No characteristic Raman bands of 4-chlorophenol were observed under this circumstance and its Raman spectrum is similar to that of a new one. This observation is due to the decomposition of adsorbed 4-chlorophenol on the GNPs/g-C₃N₄/GO membrane into some ions and small molecules, which were removed from the membrane by a simple and easy washing process. After the GNPs/g-C₃N₄/GO membrane became clean, it was repeated for preconcentration, SERS detection, and self-cleaning of 4-chlorophenol solution with the same concentration four times. The results suggest that the SERS signal intensity remained similar at per recyclable detection before or after degradation, indicating that the GNPs/g-C₃N₄/GO membrane is effective for recyclable SERS application and can be extended for in situ environmental pollutants monitoring and removing.

3. Conclusion

For the purpose of detection and removal of organic pollutants, a multifunctional membrane, with functionalities including SERS activity and photocatalysis, was successfully constructed by intercalating g-C₃N₄ and GNPs into GO nanosheets (GNPs/g-C₃N₄/GO). The membranes were highly SERS active, which allowed highly sensitive detection of R6G as low as $5.0 \times 10^{-14}$ M due to excellent preconcentration ability by $\pi-\pi$ and electrostatic interactions. In addition, the membrane exhibited high catalytic activity due to the enhanced electron separation efficiency, which reduced electron–hole recombination. Because of these outstanding properties, the GNPs/g-C₃N₄/GO membrane can be used for highly sensitive and recyclable detection and monitoring.
4. Experimental Section

Reagents: All the chemicals were of analytical grade and used as received without further modification. R6G, chloroauric acid (HAuCl₄·3H₂O), melamine, sodium citrate, 4-chlorophenol, and cetyltrimethylammonium bromide (CTAB) were bought from Sigma-Aldrich (St. Louis, MO).

Characterization: A Bruker Multimode 8 atomic force microscopy was employed to characterize the thickness of GO and g-C₃N₄ by coating samples onto a mica substrate. Transmission electron microscopy characterizations were done on a JEOL 2010 with an acceleration voltage of 200 kV. The samples were prepared by drop coating the solution onto lacy carbon-coated copper grids. SEM images were taken using FEI Quanta 400 ESEM FEG. The UV–vis absorption spectra were collected using a NanoDrop 2000c (Thermo Fisher Scientific) spectrophotometer. SERS measurements were performed using a microscopic confocal Renishaw RM2000 spectrometer at 532 nm line.

Synthesis of GO Dispersions: Starting with a natural graphite powder, the GO was prepared using a modified Hummer’s method.[25] Graphite powder (0.18 g) was dispersed in a mixture of concentrated H₂SO₄ (2 mL), K₂S₂O₇ (0.625 g), and P₂O₅ (0.625 g), and was kept at 80 °C for 4.5 h under continuous stirring. The obtained product was then filtered and washed three times for the removal of any remaining acid. Fluffy effective degradation of 4-chlorophenol simultaneously. All the results demonstrated that the GNPs/g-C₃N₄/GO membrane can potentially be used as SERS active substrates, ultimately allowing cost-effective, reproducible, and recyclable SERS applications.

Figure 6. A) SERS spectra for different concentrations of 4-chlorophenol enriched onto the GNPs/g-C₃N₄/GO membrane: a) 2.0 × 10⁻¹⁰ M, b) 1.0 × 10⁻⁹ M, c) 5.0 × 10⁻⁹ M, d) 2.5 × 10⁻⁸ M, e) 1.2 × 10⁻⁷ M, f) 6.0 × 10⁻⁷ M, g) 3.0 × 10⁻⁶ M, h) 1.0 × 10⁻⁵ M, i) 5.0 × 10⁻⁵ M. B) Plots of SERS intensity versus logarithmic 4-chlorophenol concentration at the bands of 813 and 1092 cm⁻¹. C) Raman spectra monitoring photocatalytic degradation of 4-chlorophenol on the GNPs/g-C₃N₄/GO membrane. D) The curve intensity of 4-chlorophenol versus photocatalytic time at 813 and 1092 cm⁻¹. E,F) The recyclability test of the photocatalytic decomposition of 4-chlorophenol using GNPs/g-C₃N₄/GO membrane. The exposure time is 1 s and the laser power of 5 mW.
graphite was collected and left to dry all night. Then, the dried sample was placed into concentrated H₂SO₄ (30 mL) at 0 °C while stirring, followed by a slow and careful addition of KMnO₄ (3.75 g). The reaction mixture was kept at 35 °C for 2 h, diluted with 60 mL of deionized water, and set aside for additional 2 h. After further diluting with deionized water (175 mL), 5 mL of 30% H₂O₂ was added. The solution color became bright yellow, accompanied by immediate bubbling. The mixture was washed with 10% hydrochloric acid solution and deionized water to completely ensure the removal of residual metal ions and acid, and then kept for 2 d of drying (60 °C). Finally, by sonicing the dried GO in deionized water for 2 h, a homogeneous and brownish GO suspension with the concentration of 2.5 mg mL⁻¹ was obtained.

Fabrication of Bilayer Carbon Nitride (g-C₃N₄): The bulk g-C₃N₄ was prepared using melamine as the precursor in the muffle furnace with the chimney connecting to the atmosphere. Initially, melamine (2 g) was calcined at 550 °C for 4 h where the furnace was preheated at a constant rate of 2 °C min⁻¹. The brilliant yellow bulk g-C₃N₄ was obtained. Subsequently, 500 mg bulk g-C₃N₄ was ground into powder and heated at 550 °C for 1 h (ramp rate, 5 °C min⁻¹). The prepared sample was light yellow. Then, it was maintained at 550 °C for another 1 h with a heating rate of 2 °C min⁻¹. The final obtained sample was white and denoted as the g-C₃N₄ bilayer.

Preparation of Gold Nanoparticles: GNPs were synthesized using sodium citrate reduction of HAuCl₄·3H₂O.[53,54] A solution of HAuCl₄ (100 mL, 0.05 wt%) in Milli-Q water was heated to boiling point, followed by dropwise addition of sodium citrate (10 mL, 34 × 10⁻³ M) under continuous stirring. The reaction mixture was maintained at boiling for 15 min and left to cool down to room temperature. The concentrated GNPs solution was obtained by centrifuging the synthesized colloidal nanoparticles at 8000 rpm for 10 min and redispersing in water with 1% of the initial volume.

Preparation of GNPs/g-C₃N₄/GO Membrane: Bilayer carbon nitride (g-C₃N₄) was initially functionalized using positively charged CTAB. Briefly, g-C₃N₄ (10 mg) was suspended in deionized water (20 mL) by ultrasonication in the presence of CTAB (0.01 wt%) for 2 h. After the suspension was washed three times, it was redispersed in 10 mL of deionized water to yield a stable dispersion of g-C₃N₄ (1.0 mg mL⁻¹).

Next, 2 mL of GO aqueous solution was mixed with 2 mL of g-C₃N₄ solution, stirred for 1 h, and sonicated for 1 h. Then, 2 mL of concentrated GNPs were put into the mixture and sonicated for another 1 h. Following sonication, the mixture was filtered with a PC (Whatman) membrane (0.2 mm pore size, 10% porosity, 2.83 cm² effective filtration area). After the product was dried in a vacuum oven (40 °C, 30 min), the GNPs/g-C₃N₄/GO was peeled from the PC membrane and treated with hydrazine in ethanol (15 × 10⁻³ M) for 20 min.

Photocatalytic Activity Measurements: The photocatalytic experiments of pure g-C₃N₄, GO, GNPs, g-C₃N₄/GO, and GNPs/g-C₃N₄/GO solution were carried out by degradation of R6G. Each of the samples were immersed in R6G solution (1.0 × 10⁻³ M, 10 mL) and kept in the dark for 30 min to ensure the adsorption equilibrium was reached. Subsequently, the above suspension was irradiated under a 500 W xenon lamp (Philips) with a 400 nm cutoff filter. All the beakers were placed 5 cm away from the visible light source to ensure that they were illuminated uniformly. The R6G concentration was monitored using a UV–vis spectrophotometer by recording the absorbance (525 nm) at different intervals.

Batch Sorption Experiments and SERS Detection: To evaluate the adsorption of R6G onto the GNPs/g-C₃N₄/GO membranes, batch experiments were carried out. To prepare standard solutions of various concentrations, the stock solution was diluted with deionized water. Next, 2 mL of the R6G solution was filtered through the GNPs/g-C₃N₄/GO membrane on a PC membrane at room temperature. Once the solution passed through the GO membrane, Raman measurements were conducted to evaluate the concentration of the analytes in the retentate. To prevent laser irradiation-induced catalytic and photochemical decomposition, the laser power and the exposure time at the membrane position was set as 1 mW and 0.1 s, respectively. The presented spectra were the average of five different positions of the membrane. In addition, the adsorption and SERS detection protocol of different concentrations of 4-chlorophenol in deionized water was similar to that of R6G, unless otherwise stated.

Recyclable SERS Detection: After the GNPs/g-C₃N₄/GO membrane was investigated by SERS measurements, it was soaked into deionized water and illuminated using a 500 W xenon lamp for ten minute intervals. To ensure the removal of any remaining ions and small molecules, the membrane was subsequently rinsed with deionized water several times. The amount of the residual analytes on the GNPs/g-C₃N₄/GO membrane was monitored by SERS measurements. Once the GNPs/g-C₃N₄/GO membrane was self-cleaned by this facile photodegraded process, it was washed several times, and vacuum dried for subsequent recyclable SERS detection.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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