



Article Polydopamine-Mediated Ag and ZnO as an Active and Recyclable SERS Substrate for Rhodamine B with Significantly Improved Enhancement Factor and Efficient Photocatalytic Degradation

Hsien-Kuo Chin ^{1,2}, Pei-Ying Lin ³, Jyunde Chen ³, Rajendranath Kirankumar ³, Zhi-Hong Wen ⁴, and Shuchen Hsieh ^{3,5,6,*}

- ¹ Division of Cardiovascular Surgery, Department of Surgery, Kaohsiung Armed Forces General Hospital, Kaohsiung 80424, Taiwan; a0868020002@mail.802.org.tw
- ² Institute of Medical Science and Technology, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan
 ³ Department of Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan;
- phoebe00315@yahoo.com.tw (P.-Y.L.); maple4652@hotmail.com (J.C.); r7.kirankumar@gmail.com (R.K.) Department of Marine Biotechnology and Resources, National Sun Yat-Sen University,
- Kaohsiung 80424, Taiwan; wzh@mail.nsysu.edu.tw
- ⁵ Regenerative Medicine and Cell Therapy Research Center, Kaohsiung Medical University, Kaohsiung 80708, Taiwan
- ⁶ School of Pharmacy, College of Pharmacy, Kaohsiung Medical University, Kaohsiung 80708, Taiwan
- Correspondence: shsieh@faculty.nsysu.edu.tw

Abstract: We demonstrate the development of an active multicomponent Ag/PDA/ZnO@GMF surface-enhanced Raman scattering (SERS) substrate via introducing bio-inspired polydopamine (PDA) in between a noble metal (AgNPs) and ZnO nanorods. The insertion of PDA enabled efficient charge redistribution between metal and semiconductor through their aromatic cores. The substrate exhibited a high enhancement factor (EF) of 10¹⁰ for the organic pollutant dye Rhodamine B (RhB). Subsequent exposure of a RhB-loaded substrate to an external UV light source developed an efficient pathway for RhB degradation and replenished the substrate for multiple usage cycles with remarkable photostability. Thus, enhanced performance of the substrate in terms of light-harvesting capability and high charge-separation efficiency was observed. In addition, the much larger surface area of the branched ZnO nanostructures served as a template for PDA assisted synthesis and controlled deposition of AgNPs, which further improved the SERS effect. Our work seeks to understand the contributions of the noble metal and semiconductor components and the synergistic effects of combining them with a facile charge transport medium to enable the fabrication of highly efficient SERS substrates for use in industrial and environmental applications.

Keywords: zinc oxide; polydopamine; surface-enhanced Raman scattering; Rhodamine B; photocatalytic degradation

1. Introduction

The surface-enhanced Raman spectroscopy (SERS) technique has gained worldwide attention for sensitive detection and plasmonic-based catalysis. Usually, the SERS technique utilizes controllable metal nanoparticles (MNPs) and the long-range electromagnetic effect (EM) generates SERS signal. Additionally, a short-range chemical effect, i.e., charge transfer (CT) induced by the presence of a semiconductor (metal oxides) is known to have a significant contribution towards SERS signal enhancement [1,2]. Therefore, SERS substrates that allow the simultaneous occurrence of EM and CT effects are ideally suited for low-level molecular detection and plasmon-based catalysis. Consequently, a multifunctional platform can be efficiently designed using a semiconductor surface embedded with noble MNPs. In recent years, researchers have used



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). SERS-based analyte detection and surface plasmons to assist or induce catalytic action to derive a variety of chemical conversions with the additional advantage of confirming reaction products [3,4]. Several efforts have been made to construct a SERS substrate with MNPs and metal-oxide semiconductors such as ZnO, CuO, Cu₂O, and TiO₂ [5–10]. Among them, ZnO nanostructures are the most commonly used, due to the use of their wide bandgap (3.37 eV) in several applications [11,12] and SERS techniques [13–16]. Additionally, their different crystal facets generated through different optimized conditions are quite fascinating and have different applications [17,18]. Several attempts in the past few decades were directed toward the development of SERS substrates that were specifically composed of one or two noble metals directly deposited onto hierarchical ZnO structures (Table 1) [15–30]. However, the fabrication of a SERS active substrate having a significant enhancement factor (EF) by utilizing noble metals and semiconductors is still challenging. The incorporation of an adhesive layer consisting of a long-range π conjugated segment such as polydopamine (PDA) may be beneficial in this sense because the strong adhesion of a PDA layer is able to bind together the noble metal and metal oxide and provide a uniform and well-packed substrate for effective charge redistribution [31]. The synergistically improved charge transfer through an active charge transport layer of PDA and the increased number of adsorption sites due to branched nanostructures of ZnO are highly effective in that they produce a large enhancement of SERS activity. In addition, ZnO nanostructures may contribute to the chemical effect (CE) and their high refractive index promotes strong light confinement. Thus, a PDA layer in between a noble metal and the branched nanostructures of ZnO, owing to the unique organic semiconductor nature, is highly beneficial for overall SERS enhancement. Developing the as mentioned SERS substrates to realize improved SERS effects is thus essential.

Table 1. ZnO based SERS sub	ostrates developed	in the past	few years
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SERS Substrate Based on ZnO	SERS Reporters	EF	Ref.
Ag/ZnO nano arrays	benzenethiol, Rhodamine 6 G, adenine	$10^{10} - 10^{11}$	[19]
Au/ZnO Nano Rods/Graphite	Rhodamine 6 G	$2.3 imes10^6$	[20]
Si/ZnO nanotrees	Rhodamine 6 G	10^{6}	[21]
Ag@ZnO Nanorods	Rhodamine 6 G	$1.6 imes10^6$	[22]
Ag/ZnO/Si	Rhodamine 6 G	$8.7 imes10^7$	[23]
Au/ZnO	phenanthrene	10^{6}	[24]
Ag/ZnO-nanorods	4-aminothiophenol	$3.5 imes10^7$	[25]
ZnO/graphene/Ag	Rhodamine 6 G	$0.95 imes 10^{12}$	[26]
Mg/ZnO heterostructure	4-MPY	$1.36 imes10^7$	[27]
Au/ZnO nanorods	Dopamine	$1.2 imes10^4$	[28]
$ZnO/ZnS/MoS_2$	Rhodamine 6 G	$1.4 imes10^8$	[29]
ZnO/Au Nanoarrays	Rhodamine 6 G	$1.2 imes 10^7$	[30]
Ag/PDA/ZnO@GMF	Rhodamine B	10 ¹⁰	Our substrate

The SERS-based label-free trace detection of organic molecules from a highly dilute solution and the visualization of their degradation on a designed substrate is quite attractive and promising to monitor pollutants for a clean and safe environment [32]. Consequently, the SERS technique has been widely used by research groups for the trace detection of various organic dyes, pesticides, and biomolecules down to the single-molecule level. Among them, organic dye molecules are highly colored. A trace amount below 1 ppm of dye is clearly visible and can influence the water environment considerably. Therefore, removal of dye molecules from wastewater by using sensitive techniques is important. Combining the strong local surface plasmon resonance (LSPR) between noble metal and nanostructures of ZnO via an active charge transport layer of a conducting PDA to create a substrate that exhibits strong SERS activity and is photocatalytic can provide a substrate that is ideally suited for both detection and remediation of organic pollutants.

In this scenario, we constructed a multicomponent Ag/PDA/ZnO@GMF SERS substrate by introducing a facile charge transport channel of PDA in between AgNPs and ZnO nanorods. Additionally, the ZnO nanostructures formed multibranched clusters which increased active site density and thereby further improved the SERS effects and photocatalytic activity. The main advantages of PDA in our system are summarized as follows: (1) A large number of PDA functional groups, including catechol, amine, and imine, served as both reducing agent and as the anchor for homogeneous and controlled distribution of grown AgNPs onto ZnO nanostructures: (2) The excellent stability of PDA conferred durability as well as excellent biocompatibility to the substrate; (3) The remarkable mechanical reinforcement of PDA, as strong adhesion prevented leakage of AgNPs and ZnO segments and thus excellent recyclability of the substrate was observed; (4) Efficient charge redistribution between Ag and ZnO through the plentiful π electrons of PDA improved the SERS effect. Overall, these factors and a mode of easy charge transport between Ag and ZnO played an essential role in achieving an improved plasmon sensitivity (EF: 10¹⁰) for a model organic pollutant dye (Rhodamine B, RhB) molecule. The substrate possesses high stability and UV light-induced self-cleaning and further can be reused even after six cycles. Due to the enhanced SERS sensitivity and to the other stated advantages that this hybrid SERS system demonstrates, this model may provide new strategies for developing highly sensitive and stable SERS technology.

2. Materials and Methods

2.1. Preparation of Zinc Oxide Substrate (ZnO@GMF)

Equimolar solutions (0.025 M) of Zinc nitrate (Zn(NO₃)₂·6H₂O) and C₆H₁₂N₄ were prepared separately with ultrapure water up to a final volume of 40 mL. Equal volumes of both the solutions were then mixed. Next, the filter paper (GMF) was immersed into the mixed solution and heated at 90 °C while stirring continuously for 1 h. After that, GMF was taken out of the solution, thoroughly washed with ultrapure water, and dried in an oven at 60 °C to obtain the zinc oxide substrate ZnO@GMF.

2.2. Preparation of PDA-Reduced Silver on Zinc Oxide Substrate (Ag/PDA/ZnO@GMF)

A dose of 2 mg/mL dopamine was taken into 1 M Tris-HCl buffer (pH adjusted at 8.5). The prepared zinc oxide substrate (ZnO@GMF) was immersed into this dopaminecontaining buffered solution and stirred for 24 h at room temperature. After that, the substrate was washed and dried to obtain the polydopamine (PDA) deposited ZnO@GMF substrate, i.e., PDA/ZnO@GMF. A separate solution of AgNO₃ (0.1 M) was prepared with liquid ammonia and the resulting substrate PDA/ZnO@GMF was immersed into this solution for 2, 4, 6, 8, 10, and 12 h while stirring continuously at room temperature for deposition of AgNPs. The resulting substrates were thoroughly washed with ultrapure water and alcohol and then vacuum-dried to obtain the substrates Ag/PDA/ZnO@GMF.

2.3. Preparation of Polydopamine-Reduced Silver Nanoparticles in Glass Fiber Filter Paper (*Ag*/PDA@GMF)

The basic procedure was the same as that of Ag/PDA/ZnO@GMF, except that the AgNPs were directly reduced on PDA@GMF.

2.4. Surface-Enhanced Raman Spectroscopy for Detection Limit Test

Different concentrations $(10^{-3} \text{ M}-10^{-10} \text{ M})$ of RhB solutions were prepared. The SERS substrates Ag/PDA/ZnO@GMF, having different deposition times, were then used to investigate effective SERS enhancement by adding 10 µL aliquots from each RhB solution. The SERS signal of RhB on each substrate was recorded and compared. The laser wavelength used in this experiment was 532 nm.

2.5. Surface-Enhanced Raman Spectroscopy for Monitoring the Reaction Degradation of Rhodamine B

An aliquot of 10 μ L from 10⁻³ M RhB solution was added onto the prepared SERS substrates (Ag/PDA/ZnO@GMF) and the SERS signals of RhB were recorded immediately. All the substrates were then irradiated with 254 nm UV light and modified signals of RhB were recorded every 10 min until the end of reaction when no RhB signal was found. The same 532 nm laser was used here.

2.6. ICP-MS Sample Preparation

First, we cut the samples into 1 cm², then dissolved in 5 mL of 1 M nitric acid solution and heated at 80 °C for 1 h. The ICP-MS data were taken after the samples had equilibrated to room temperature.

3. Results

A number of groups have attempted to develop ZnO based SERS substrates over the past few years. The details are shown below in Table 1. Most efforts were mainly focused on the direct deposition of noble metals onto the hierarchical nanostructures of ZnO.

In this study, we demonstrate a PDA mediated deposition of AgNPs onto the nanostructures of ZnO for the development of a multicomponent Ag/PDA/ZnO@GMF SERS substrate. We used GMF because of its commercially availability, low-cost, and its superior physical adsorption capability over silicon wafers. Furthermore, the 3D steric-construction structure of GMF offers a high surface area for immobilizing MNPs. The SERS substrate Ag/PDA/ZnO@GMF was prepared by the deposition of ZnO on GMF, followed by the incorporation of PDA layer on ZnO@GMF, and finally, in-situ formation of AgNPs. The substrate morphology was characterized using scanning electron microscopy (SEM). We found that GMF existed as long tubular fibers with a relatively smooth surface. Rod-like structures were formed after being coated by ZnO and heated to a temperature of 90 °C (Figure 1). Following application of the PDA film, the in-situ chemical reduction of silver ions over PDA/ZnO@GMF formed AgNPs that decorated the PDA/ZnO structures as shown in Figure A2.



Figure 1. SEM images of ZnO@GMF substrates at different resolutions (a) 2 µm, (b) 1 µm, (c) 500 nm, respectively.

Additionally, we confirmed the ZnO deposition at room temperature. However, under such conditions, ZnO revealed a decreased crystallinity and formed cluster-like aggregates of irregular shapes (Figure A1). We further investigated the optimum time for AgNP deposition between 2 and 12 h on the PDA/ZnO@GMF substrates. As shown in Figure A2, there were no AgNPs observed to form on ZnO surfaces for deposition times of 2 h and 4 h. This indicates that the particle size of the AgNPs was quite small during that reaction time. When the deposition time was increased to 6 h, relatively uneven distributions of AgNPs on ZnO were observed. At a deposition time of 8 h, the particle distribution was relatively uniform, and the average particle size was 28 ± 7 nm. The average size of the AgNPs was estimated from the SEM image shown in Figure A2d using the image J software program (version Java 1.8.0). Finally, at a deposition time of 12 h, the AgNPs aggregated, nearly covering the original ZnO crystal structures. We therefore conclude that the optimal time for AgNP deposition on PDA coated ZnO was 8 h.

We next used Xray Photoelectron Spectroscopy (XPS) to confirm the chemical composition of the Ag/PDA/ZnO@GMF substrates. First, we performed XPS measurements to detect silver on the substrate (Ag-8h/PDA/ZnO@GMF) where Ag ions were directly reduced on PDA/ZnO@GMF. We observed signal peaks at 368.6 and 374.6 eVs, which were assigned to the Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, indicating the presence of AgNPs on the substrate. Next, XPS spectra of the Zn $2p_{3/2}$ transition was collected and compared from substrates with and without adsorbed AgNPs. As shown in Figure 2, the XPS spectrum of ZnO@GMF revealed a distinct peak at 1023.9 eV, which corresponds to the binding energy of zinc oxide. The introduction of PDA reduced the binding energy to 1023.7 eV. The consequent addition and in-situ generation of AgNPs on PDA/ZnO@GMF further reduced the binding energy to 1022.7 eV. Such peak shifts for Ag and ZnO can be attributed to the CT effect between them, where PDA played the role of conducting layer for charge redistribution.



Figure 2. X-ray photoelectron spectroscopy of (**a**) Zn $2p_{3/2}$, (**b**) Ag $3d_{5/2}$ and Ag $3d_{3/2}$ -(i) glass fiber filter paper, (ii) zinc oxide substrate, (iii) polydopamine deposited on zinc oxide substrate, (iv) polydopamine reduced silver nanoparticles on zinc oxide substrate.

The CT effect from the metal-molecule-semiconductor interface is illustrated by the energy band diagram of zinc oxide and silver shown in Figure 3. In general, the electrons within solid materials require more energy relative to the vacuum level to overcome lattice adsorption forces to become free electrons [33,34]. The combination of a semiconductor and a metal induces electron flow from higher to lower Fermi level—bringing the two Fermi levels to a new equilibrium. The work functions of zinc oxide and silver are 5.3 eV and 4.1 eV, respectively. Therefore, when these two materials combine, the electrons flow from the AgNPs to ZnO. Hence, the electron density of the silver is reduced. Moreover, we can observe that the XPS signal of Ag 3d shifted towards higher binding energy, and the Zn 2p signal shifted towards lower binding energy—indicating that there is a tendency for electrons to move from the AgNPs to ZnO. Since ZnO and AgNPs were separated by

a PDA film, the resonance structure of the PDA served as a bridge for electron transfer between these two. In addition, PDA itself promoted the process of electron transport and thereby contributed to the signal enhancement.



Figure 3. Charge transfer scheme from Ag to ZnO.

Next, we performed SERS measurements of RhB on the designed substrates-GMF, Ag/ZnO@GMF, ZnO@GMF, Ag/PDA@GMF, and Ag/PDA/ZnO@GMF, to determine the contribution of the CT effect on SERS signal enhancement. Figure 4 shows that no RhB signal could be observed on GMF nor on ZnO@GMF substrates, suggesting that neither GMF nor ZnO@GMF exhibit SERS activity. On the ZnO@GMF substrate, however, ZnO directly reduces the AgNPs, and a relatively weak SERS signals was detected. Next, we observed that the AgNPs on PDA in the absence of ZnO exhibit SERS activity, but the enhancement is limited. Finally, we tested the SERS signal of the Ag/PDA/ZnO@GMF substrate and observed a very strong signal intensity. Therefore, as we hypothesized, the combination of zinc oxide and AgNPs, when combined with PDA, can significantly enhance the SERS effect, even greater than the enhancement effect of AgNPs themselves. Moreover, we believe that the catechol functional groups of PDA can further undergo oxidation to form orthoquinone functional group. This property further allowed PDA to release electrons during the oxidation process and act as an efficient electron contributor [35]. Therefore, zinc oxide was more exposed to electrons, and the energy required to excite electrons was reduced. It is worth noting that the conjugated aromatic core of PDA helped in efficient electron transport.

Next, we measured the SERS enhancement on Ag/PDA/ZnO@GMF at different AgNP deposition times (2, 4, 6, 8, 10, and 12 h). As the AgNP deposition time increased from 2 to 8 hours, the detectable concentration of RhB gradually decreased from 10^{-4} , 10^{-6} , 10^{-7} , to 10^{-9} M, respectively. However, for longer deposition times, the detectable concentration of RhB increased for 10^{-6} M at 10 h and 10^{-5} M at 12 h. These results indicated that the optimum deposition time of 8 h exhibited the largest SERS enhancement effect with the lowest detection limit of RhB (Figure 5).

In order to clearly define the extent of SERS enhancement, we further calculated the EF for the substrate Ag/PDA/ZnO@GMF using the following equation [36]:

$$EF = I_{SERS} / I_{bulk} \times (concentration factor)$$

where I_{SERS} represents the SERS signal intensity of the RhB peak on the Ag/PDA/ZnO@GMF substrate at 1364 cm⁻¹, and I_{bulk} represents the original Raman signal intensity of RhB solution on the top of a silicon wafer under otherwise identical conditions. According to the calculated process [37], the EF has already excluded the possibility of electronic transitions of the RhB molecules themselves. These results are presented in Table A1. We can see that there is a minimum detection limit of 10^{-9} M for an 8 h AgNP deposition time and the enhancement factor is 10^{10} . Previous reports of RhB EF were in the range of $10^6 \sim 10^9$ [38,39]. This result shows an effective SERS enhancement, which can efficiently improve the SERS sensitivity and perform as a SERS substrate.



Figure 4. SERS spectra of RhB on GMF, Ag/ZnO@GMF, ZnO@GMF, Ag/PDA@GMF, and Ag/PDA/ZnO@GMF.

Raman Shift (cm⁻¹)

Apart from the sensitive SERS signals of RhB, the catalytic behavior of the substrate can also be exploited by taking advantage of plasmon effect. Plasmons provide more electrons (collective oscillations) to accelerate the rate of a chemical reaction. Moreover, plasmons serve as an efficient catalyst through "hot electrons", which are transferred to the excited state of molecules on the metallic surface and thus the required activation energy to initiate a chemical reaction is provided. Based on this assumption, we tested the photocatalytic activity of all the designed Ag/PDA/ZnO@GMF substrates by UV-induced degradation of RhB. We measured the SERS intensity under UV radiation and observed a gradual decrease in RhB intensities with increasing time of irradiation over all the substrates. However, among them, the requirement of a minimal irradiation time was observed for the substrate Ag-8h/PDA/ZnO@GMF. Therefore, the CT effect well contributed to the catalytic degradation of RhB upon UV radiation on Ag-8h/PDA/ZnO@GMF (Figure 6).

In addition, we were interested to investigate whether a combination of Ag and ZnO was required to achieve efficient photocatalytic degradation of RhB, or if AgNPs alone on the PDA@GMF support was sufficient. For this purpose, Ag/PDA/ZnO@GMF and Ag/PDA@GMF were employed for the SERS signal measurements. The green line in Figure 7 is the substrate without ZnO and with an 8 h AgNP deposition time. For

(a) 2 h

Ag-8h/PDA@GMF, we observed a significant SERS signal for RhB. However, the signal intensities were unaffected by UV radiation even after 40 min—indicating that the pure silver nanoparticle does not have catalytic degradation activity for RhB. The presence of ZnO led to a significant decrease in the SERS intensity under the same irradiation conditions (blue line). Therefore, from the controlled experiments, we confirmed that the presence of ZnO is required to drive the catalytic degradation of RhB.

Next, we examined the reaction kinetics. For this purpose, we took the natural logarithm of intensities and plotted it against the reaction time. The samples with different deposition times were analyzed as regression curves, as shown in Figure A3a–f. The rate law by the first-order reaction can be written as below:

$$(I_t/I_0)_{1364} = -kt$$

where I_0 and I_t are the SERS intensities before and after UV irradiation and k is the reaction rate constant for the degradation. We observed that an oblique line can be fitted at each deposition time. Further, we tried to determine the order of the degradation reaction. The reaction rate constant k value was calculated from the slope of each oblique line.

(c) 6 h





(b) 4 h



Figure 6. SERS monitoring of photocatalytic degradation of Rhodamine B (10^{-3} M), substrate at different AgNP deposition times—(**a**) 2 h, (**b**) 4 h, (**c**) 6 h, (**d**) 8 h, (**e**) 10 h, and (**f**) 12 h.



Figure 7. $(I_t/I_0)_{1364}$ vs. reaction time. Both samples had 8 h deposition time of Ag. The blue and green lines are with and without ZnO respectively.

The rate constants and R squared values are listed in Table A2. We observed that the substrate with a deposition time of 8 h had the largest linear slope, i.e., the maximum reaction rate constant (0.0391 min^{-1}). The maximum rate constant for the catalytic degradation

of RhB on the Ag-8h/PDA/ZnO@GMF can be attributed to the significant charge transfer between semiconductor and metal via the aromatic conjugated core of PDA. However, further increased deposition time (10 h and 12 h) of AgNPs on PDA/ZnO@GMF suppressed the rate constants of RhB degradation, because excessive AgNPs accumulated on ZnO nanorods and suppressed the UV-induced electron transport—resulting in decreased photocatalytic activity. Therefore, the deposition time of 8 h was sufficient to drive efficient catalytic degradation of RhB.

We further measured the elemental content of the AgNPs and ZnO using inductively coupled plasma mass spectrometry (ICP-MS) for different AgNP deposition times on PDA/ZnO@GMF. Table 2 shows the Zn and Ag content of the substrate at 0, 2, 4, 6, 8, 10, and 12 h deposition times as measured by ICP-MS (unit: micrograms of element per milliliter of nitric acid). It can be clearly observed that the amount of AgNPs increased with deposition time. This result further confirms our assumption that the amount of AgNPs increased with deposition time and that excessive deposition leads to AgNP accumulation on the ZnO nanorods (deposition time of 10 h and 12 h) and hinders electron transfer between Ag and ZnO—leading to reduced photocatalytic activity.

Table 2. ICP-MS of substrates with different silver-nanoparticle deposition times.

Sample	Zn (µg/mL)	Ag (µg/mL)
Blank	$5.12 imes 10^{-4}$	$0.07 imes 10^{-4}$
0 h	42.5	$1.86 imes10^{-4}$
2 h	34.5	2.00
4 h	44.9	4.49
6 h	41.8	7.46
8 h	41.1	10.2
10 h	37.8	10.8
12 h	39.3	12.8

After confirming strong SERS activity and photocatalytic degradation of RhB on the constructed SERS substrate, we wanted to check whether repeated cycles with simultaneous removal of RhB can generate better SERS substrates. The optimum substrate with 8 h AgNP deposition time was chosen to test sustainability over repeated cycling of catalytic degradation of RhB. We examined the RhB photocatalytic degradation reaction cycle five times and plotted the number of cycles by photocatalytic degradation efficiency, as shown in Figure 8. We observed that the degradation reaction efficiency reduced below 80% by the third cycle and was about 70% by the fifth cycle. This is due to the accumulation of material in the process of repeated experiments, thereby reducing the surface area of the catalyst and thus the overall catalytic activity. This result indicates that there is still considerable photocatalytic activity after repeated testing and thus considerable potential and prospect for the development of recyclable sensing materials.



Figure 8. Five repeated photocatalytic degradation reactions on the Ag-8h/PDA/ZnO@GMF substrate.

4. Conclusions

We have successfully constructed an active Ag/PDA/ZnO@GMF SERS substrate utilizing the combination of AgNPs, ZnO nanostructures, and PDA, on a GMF scaffold. This material exhibits both electromagnetic (EM) and charge transfer (CT) effects and has a strong SERS enhancement factor (EF) while also demonstrating efficient catalytic degradation of RhB under UV radiation. We further validated our findings by comparison to Ag/PDA@GMF and ZnO@GMF. The facile construction of the substrate may be attributed to the incorporation of PDA, because the additional oxidation process of catechol functional groups in PDA released electrons to ZnO and thereby lowered the excitation energy. Moreover, the long-range conjugated aromatic core of PDA served as an efficient electron transport or charge redistribution layer between AgNPs and ZnO. Additionally, the 3D steric-construction structure of GMFs offered a high surface area for immobilizing metal NPs. To our knowledge, this is the first report using PDA as an adhesive layer between a noble metal and semiconductor to achieve a significant SERS enhancement factor (of the order of 10^{10}) on a xanthene dye RhB. In addition, SERS-based platforms are desirable to achieve high sensitivity for detection of very small trace amounts of dye, because in conventional methods, the dye takes a long time to produce and grow to the detectable range. SERS-based label-free detection of trace organic molecules in a dilute solution and visualization of their degradation on the designed substrate is an attractive and promising platform for use in monitoring pollutant concentrations in water, thus contributing to a clean and safe environment.

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Appendix A



Figure A1. SEM images of a low-crystalline zinc oxide substrate at different resolutions (a) 2 μm, (b) 1 μm, (c) 500 nm.



Figure A2. SEM images of substrates with different silver nanoparticle deposition times: (**a**) 2 h, (**b**) 4 h, (**c**) 6 h, (**d**) 8 h, (**e**) 10 h, and (**f**) 12 h.



Figure A3. $\ln(I_t/I_0)_{1364}$ plotted against reaction time, substrate at different silver nanoparticle deposition times: (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, (e) 10 h, and (f) 12 h.

	2 h	4 h	6 h	8 h	10 h	12 h
$10^{-3} { m M}$	$4.72 imes 10^4$	$5.36 imes 10^4$	$7.14 imes10^4$	$8.94 imes10^4$	$6.42 imes 10^4$	$6.67 imes10^4$
$10^{-4} { m M}$	$2.50 imes 10^5$	$4.69 imes 10^5$	7.21×10^5	$7.30 imes 10^5$	4.51×10^5	$6.46 imes 10^5$
$10^{-5} { m M}$		$2.86 imes 10^6$	$6.11 imes 10^6$	$6.41 imes 10^6$	$3.64 imes10^6$	$5.63 imes 10^6$
$10^{-6} {\rm M}$			$4.75 imes10^7$	$5.71 imes 10^7$	$1.64 imes10^7$	$3.43 imes10^7$
$10^{-7} { m M}$			$2.39 imes 10^8$	$5.02 imes 10^8$		
$10^{-8} { m M}$				$2.31 imes 10^9$		
$10^{-9} { m M}$				$1.95 imes 10^{10}$		

Table A1. The enhancement factor calculated for the substrate with different silver nanoparticle deposition times.

Table A2. Reaction rate constants and R-squared values calculated for substrates with different silver nanoparticle deposition times.

Time (h)	Reaction Rate Constant (min^{-1})	R Squared	
2	0.0134	0.9866	
4	0.0187	0.9637	
6	0.0251	0.9796	
8	0.0391	0.9680	
10	0.0316	0.9813	
12	0.0294	0.9717	

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