A Novel SERS Substrate Based on Discarded Oyster Shells for Rapid Detection of Organophosphorus Pesticide

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Abstract: Over the past few years, the concern for green chemistry and sustainable development has risen dramatically. Researchers make an effort to find solutions to difficult challenges using green chemical processes. In this study, we use oyster shells as a green chemical source to prepare calcium oxide nanoparticles (CaO-NPs). Transmission electron microscopy (TEM) results showed the CaO-NPs morphology, which was spherical in shape, 40 ± 5 nm in diameter, with uniform dispersion. We further prepared silver/polydopamine/calcium-oxide (Ag/PDA/CaO) nanocomposites as the surface-enhanced Raman scattering (SERS) substrates and evaluated their enhancement effect using the methyl parathion pesticide. The effective SERS detection limit of this method is 0.9 nM methyl parathion, which is much lower than the safety limits set by the Collaborative International Pesticides Analytical Council for insecticide in fruits. This novel green material is an excellent SERS substrate for future applications and meets the goal of green chemistry and sustainable development.

Keywords: calcium oxide; nanoparticles; surface-enhanced Raman scattering; oyster shells; biocompatible

1. Introduction

The great advantages that surface-enhanced Raman scattering (SERS) spectroscopy offer in detection applications include fingerprint recognition of chemical molecules, non-destructive testing, high sensitivity, rapid detection, quantification, etc. [1]. Therefore, SERS can be applied to a wide range of applications, such as the detection of antibiotic and pesticide residues in agricultural products [2], pathogenic bacteria testing in aquatic environments [3], and identification of plastic particles released from consumer products [4], environmental exhaust fumes, etc. [5]. The significant impact of SERS techniques on molecular detection and plasmon catalysis are quite promising and due to the fact that these materials are of significant interest for a wide range of applications [6]. Since SERS-based techniques rely on the well-organized nanostructures, capable of generating plasmonic events, thus, SERS substrates based on the newly designed and more controlled nanostructures are highly demanded for further advancements. For the efficacy and to obtain the enhanced signals, simultaneous occurrence of a long-range electromagnetic effect (EM) and a short-range chemical effect, i.e., charge transfer (CT), are well needed during SERS measurements [7]. In this context, simultaneous CT can be seen by the use of
semiconductor materials, which predominantly include metal oxides [8]. Therefore, the incorporation of semiconductor materials into SERS substrates would be able to generate a CT mechanism as a dominant contribution to the surface-enhanced Raman signal. To this end, efforts have been made with semiconductor oxide materials, such as ZnO, TiO$_2$ and Cu$_2$O, which are reported to be capable of generating weak and/or strong SERS signals via chemical enhancement [4,9,10]. The versatile application of metal oxides in various areas are well known. As a major drawback, after use, these materials are released to soil and surface water that passes over lakes, rivers, and seas. Nanomaterials, due to their shape and size, are prominent to bind to a wide variety of biomolecules, including proteins, drugs and nucleotides. Therefore, humans become exposed to nanoparticles (NPs) in medical and industrial settings quite commonly. The existence of metal nanoparticles (MNPs) in the ecological system lead to bioaccumulations, causing potential effects on human health and living organisms. Especially the induced toxicity of CuO, ZnO, TiO$_2$, and other metal oxides, which are well known and their adverse effects have been well studied in the past few decades [11–15]. Therefore, it is urgently required to incorporate some non-toxic, biocompatible and ecological friendly metal oxides for the construction of SERS substrates for societal welfare and care.

In our previous work, we reported a simultaneous occurrence of CT and EM mechanisms into a Ag/CuO nanocomposite system at the metal–semiconductor interface [16]. However, realizing the scenario of toxicity, we further present the utilization of non-toxic CaO MNPs into SERS substrates; i.e., a metal-molecular-semiconductor composite system consisting of Ag NPs, PDA and CaO NPs to construct a silver/polydopamine/calcium-oxide (Ag/PDA/CaO) system. For the generation of the SERS substrate, CaO NPs were mainly obtained from a green resource (oyster shells) via a simple chemical process. The strong adhesion of the PDA layer provided a uniform and well-packed composite system [17]. Simultaneously, in-situ preparation of Ag NPs and, thus, effective charge redistributions among Ag NPs and CaO, via a conducting PDA layer to induce a chemical effect during the SERS measurement, was obtained [18]. In our previous work, the Ag/CuO nanocomposite demonstrated an approximately $10^5$ times SERS signal enhancement, mainly through the combination of CT and EM mechanisms [19]. In the present study, such an enhancement factor ($4.7 \times 10^5$) in 10 h with LOD in a nano-regime for 4-aminothiophenol (4-ATP) was obtained for the Ag/CaO nanocomposite and, thus, the incorporation of CaO can be validated. To date, there are no reports demonstrating the incorporation of CaO into a SERS substrate to obtain enhanced SERS signals. Therefore, we believe our study would be able to introduce a newer and non-toxic metal oxide into the process of advancement for newer ecologically friendly SERS substrates and nanomaterials.

2. Materials and Methods

Oyster shells, having a high CaCO$_3$ content, were used as the green source of CaO in our study. After calcination, the CaO content was highest followed by CO$_2$; the percentages of Na$_2$O, MgO, SO$_3$, SiO$_2$, SrO, and H$_2$O were very low [20,21]. The shells were scrubbed to remove sand and salt from the surface and were then placed in an oven to remove moisture and thus to reduce impurities. The agents used in this experiment include dopamine hydrochloride (Sigma-Aldrich, Saint Louis, MO, USA), tris buffer (Sigma-Aldrich, Saint Louis, MO, USA), silver nitrate (Sigma-Aldrich, Saint Louis, MO, USA), sodium hydroxide (Sigma-Aldrich, Saint Louis, MO, USA), ethanol (ECHO Chemical CO., LTD, Kaohsiung, Taiwan), hydrochloric acid (J.T. Baker, Radnor, PA, USA), sodium carbonate (Sigma-Aldrich, Saint Louis, MO, USA), 4-aminothiophenol and methyl parathion (Sigma-Aldrich, Saint Louis, MO, USA). All agents were used directly in the experiment without further purification. The pure water required for samples synthesized and dispensed was obtained from pure water (18.2 MΩ•cm at 25°C) Milli-Q reagent-grade (type I).

Scheme 1 shows the Ag/PDA/CaO NPs preparation process. After the oyster shells were ground at room temperature, 1 M NaOH solution was added and stirred for 2 h. It was then centrifuged and washed with deionized water until neutral. Hydrochloric acid
was added, and the mixture was stirred for 6 h. The filtrate was filtered to obtain a CaCl$_2$ solution. CaCl$_2$ and sodium carbonate were mixed into the water-heating device to heat to 100 °C. After filtering, the powder was placed into a high-temperature furnace heated to 900 °C for 2 h, and spherical calcium oxide nanoparticles (CaO NPs) were synthesized. The reaction mechanism is given by Equation (1):

$$\text{CaCO}_3(s) + 2\text{HCl(aq)} \rightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O(l)}$$  \hspace{1cm} (1)

$$\text{CaCl}_2(aq) + \text{NaCO}_3(s) \rightarrow \text{CaCO}_3(s) + 2\text{NaCl(aq)}$$  \hspace{1cm} (2)

$$\text{CaCO}_3(s) \xrightarrow{\Delta} \text{CaO}(s) + \text{CO}_2(g)$$  \hspace{1cm} (3)

For the PDA and Ag NPs surface modification method of Ag/PDA/CaO NPs, refer to Lin et al. [5]. Utilizing the catechol-amine chemistry of dopamine (DA) as an adhesive layer between CaO NPs and Ag NPs, PDA coating layers were formed on the surface of CaO NPs by oxidative polymerization in an alkaline environment [22]. Surface-exposed PDA functional groups, including catechol, amine, and imine [23] can be used as reducing agents for Ag NPs. We prepared a solution of synthetic PDA, the tris buffer (C$_8$H$_{11}$NO$_2$•HCl) adjusted to pH 8.5 as a solvent and configured the 10 mM dopamine solution. We soaked the synthesized CaO NPs in the dopamine solution and stirred for 12 h. Then, we soaked the PDA-coated CaO NPs in a silver amine solution (Tollen’s reagent), dried it in the oven overnight, and obtained the Ag/PDA/CaO NPs.
2.1. Transmission Electron Microscopy (TEM)

After the nanoparticle powder was dissolved in alcohol, 30 µL of the sample was dripped onto a carbonized copper mesh sheet and dried to complete the test substrate, shooting the image with a transmission electron microscope (JEOL, JEM-2100, Tokyo, Japan). Magnification: 2000–1,500,000×; Resolution: Point image: 0.27 nm and Lattice image: 0.14 nm; Dual tilt bases: X-axis ± 60°; Electron gun: field emission acceleration voltage of 200 kv.

2.2. X-ray Diffraction (XRD)

The samples were prepared by drying and grinding calcium oxide nanoparticles into a uniform powder. The powder was flattened on a test substrate for X-ray diffraction. The diffraction pattern of the calcium oxide nanoparticles was used to identify the crystal grid parameters. We measured calcium oxide and calcium carbonate powder samples at room temperature using an X-ray powder diffractometer (Bruker D8 Advance, Karlsruhe, Germany). The Cu Kα1 with a wavelength of 1.5418 Å and energy of 8.05 KeV was used as the X-ray source and the X-ray tube was a Cu target. The operating voltage was 40 kV and the operating current was 40 mA. The detector is a high-speed, high-sensitivity PSD detector with the best resolution of -0.03° (FWHM). The 2θ angle was scanned at a scanning speed of 0.5 s at each pitch from 20 °C to 80 °C, and the spacing was 0.1°.

2.3. X-ray Photoelectron Spectroscopy (XPS)

Samples were prepared for analysis using X-ray photoelectron spectroscopy (XPS) by depositing an aliquot of the sample solution onto clean silicon wafer at room temperature and drying in air. XPS spectra were acquired using a JAMP-9500F (JEOL, Tokyo, Japan) equipped with a monochromatic Mg Kα X-ray (1253.6 eV) radiation source. The spectra were calibrated using the C 1s peak at 285 eV from adventitious surface carbon as an internal reference. The Cu and Ag peak curve fitting was performed with a Gaussian/Lorentzian ratio of 0.7 using peak fitting software by JEOL SpecSurf XPS (version 1.7.3.9), after a Shirley-type background subtraction.

2.4. Raman Spectroscopy

The modified metal/polymer/CaO NPs were deposited on a silicon substrate (1 cm × 1 cm) as a SERS substrate. Next, 5 µL 4-ATP and methyl parathion at different concentrations were dropped on the surface of SERS substrate, and its SERS enhancement effect was detected by Raman spectroscopy (WITec alpha300R, WITec, Ulm, Germany) at a laser wavelength of 532 nm and an intensity of 30.5 µW, and further detected the representative pesticide in water.

3. Results and Discussion

The surface morphologies of the composites were observed using transmission electron microscopy (TEM), as shown in Figure 1a,d, showing that CaO NPs, 40 ± 5 nm in diameter, were synthesized successfully with a spherical shape. Figure 1b and e demonstrate that after synthesizing the PDA onto CaO NPs, its surface became rough, and a coating was observed. The inset in Figure 1d and e shows high-resolution TEM (HRTEM) images of CaO NPs and PDA/CaO nanocomposites. The lattice spacings were 0.24 and 0.27 nm through calculation, corresponding to the crystal plane of (200) and (111), which proves a calcium oxide composition [24]. Figure 1c,f show that Ag NPs were successfully deposited on each calcium oxide nanoparticle. The inset in Figure 1f shows the HRTEM result. The spacing of Ag (111) was 0.237 nm [25], which confirms that Ag NPs were reduced on the surface of the CaO NPs by about 12 ± 5 nm.
Figure 1. TEM images of various nanoparticles: (a,d) CaO NPs at different magnifications; (b,e) PDA/CaO nanocomposites at different magnifications; the insets in (d) and (e) are HRTEM images of random CaO nanoparticles and PDA/CaO nanocomposites, showing lattice spacing between CaO (111) and (200) planes. (c,f) Ag/PDA/CaO nanocomposites at different magnifications; the inset in (f) is an HRTEM image of a random Ag/PDA/CaO nanocomposite showing lattice spacing between Ag (111) and CaO (200) planes as well.

The X-ray diffraction (XRD) results of the synthesized composites are shown in Figure 2. In addition to the CaO signal, the Ag/PDA/CaO (blue line) also had Ag (111) and (200) signals, in accordance with the standard diffraction pattern of Ag NPs (JCPDS: 04-0783) [26]. These results prove that we successfully synthesized Ag NPs on CaO NPs.

We analyzed each step of the Ag/PDA/CaO SERS substrate formation by using high-resolution X-ray photo-electron spectroscopy (XPS). The Ag 3D XPS spectra in Figure 3a for Ag NPs exhibited peaks at 368.1 eV and 371.2 eV, which are assigned to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. As shown in Figure 3b, the high-resolution XPS of the Ca 2p revealed a signal of calcium oxide at 350.8 eV and 354.4 eV. Moreover, dopamine molecules were polymerized on the CaO NP surfaces, and the Ca 2p signal shifted 0.4 eV from 350.8 eV to the lower binding energy of 350.4 eV. These results indicate that the push electron effects of PDA resulted in a shift in Ca 2p signal to a lower binding energy because the chemical environment around Ca changed. After the PDA reduced the Ag NPs on the calcium oxide, the signal of Ca 2p shifted to a lower binding energy, from 350.4 eV to 350.1 eV. According to the literature, when semiconductors combine with metals, electrons flow from higher to lower Fermi levels, allowing both Fermi levels to reach a new equilibrium [27–29]. Because the work function is 1.69 eV of calcium oxide and 4.1 eV of silver [30], the electrons transferred from calcium oxide to silver when they were combined, as shown in Figure 3c.
To evaluate the SERS activity of the Ag/PDA/CaO substrate, we selected 4-ATP as model probe molecules and configured 4-ATP using ethanol to $10^{-3}$ M. We examined pure 4-ATP $10^{-2}$ M on a silicon substrate as normal Raman spectra (Figure 4a). The labeled peaks in the normal Raman spectra correspond well to those reported for pure 4-ATP in earlier reports. The peaks at 1154, 1200, and 1448 cm$^{-1}$ are assigned to the $\delta$(C−H) stretching vibration. The peaks at 1088, 1154, 1400, and 1588 cm$^{-1}$ are assigned to the $\nu$(C−S), $\delta$(C−H), $[\nu$(C−C) + $\delta$(C−H)], and $\nu$(C−C) stretching vibration, respectively. We used different Ag NP deposition times of 2, 4, 6, 8, 10, and 24 h to prepare the SERS substrates and analyzed 4-ATP, in order to find the most suitable preparation condition. Figure A1 in the Appendix A shows significant enhancement in intensity, beginning 2 h after deposition. We calculated the effective enhancement factors (EFs) by comparing the SERS peak intensity at 1448 cm$^{-1}$ of 4-ATP on Ag/PDA/CaO nanocomposites to that of 4-ATP on CaO NPs, according to the formula $I_{\text{SERS}}/I_{\text{substrate}} \times $ (concentration factor) $^{[31,32]}$. $I_{\text{SERS}}$ is the Raman intensity of the probe molecule on the Ag/PDA/CaO substrate, $I_{\text{substrate}}$ is the Raman intensity of the probe molecule on the silicon substrate. The concentration factor is the corresponding concentration of the different concentrations of the probe molecule in ethanol. The calculated EFs were $3.8 \times 10^5$, $5.1 \times 10^5$, $5.2 \times 10^5$, $3.2 \times 10^5$, $4.7 \times 10^5$, and $4.6 \times 10^5$ at 2, 4, 6, 8, 10, and 24 h respectively. The results indicate that EF reached
5.1 × 10^5 after 4 h of deposition. Therefore, we found that 4 h of deposition time for Ag NPs is the most appropriate for preparing a Ag/PDA/CaO nanocomposite as the SERS substrate for detecting 4-ATP. Under these conditions, less deposition time was needed for the best EF result.

We further investigated the detection limit of 4-ATP with the Ag/PDA/CaO-4h substrate. We formulated 4-ATP to 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7} and 10^{-8} M in ethanol. As shown in Figure 4, CaO and Ag/PDA materials showed no SERS effects; however, after detection of the Ag/PDA/CaO-4 h substrates, an obvious SERS effect was observed. The calculated EFs were 1.1 × 10^6, 7.8 × 10^6, 3.6 × 10^7, 1.0 × 10^8, 9.6 × 10^8, and 6.5 × 10^9, for 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7} and 10^{-8} M, respectively, and the detection limit reached ~10^{-8} M.

We compared these results with those reported in other studies. Sun et al. [33] used a silver nanoparticle colloidal solution to enhance the 4-ATP molecular signal, and the detection limit was ~10^{-7} M. Recently, scientists have used different substrates to reduce the silver nanoparticles to further enhance the 4-ATP signal, with a detection limit of ~10^{-7} M for a single molecule [34–36]. In our study, Ag/PDA/CaO nanocomposites synthesized through simple steps successfully enhanced the SERS effect and improved the detection limit to ~10^{-8} M for 4-ATP single-molecule detection. The SERS intensity is determined by several factors, such as particle size and shape and the nature of the aggregate [37,38]. In our results, the self-assembled Ag/PDA/CaO nanocomposites had uniform particle sizes and shapes of Ag NPs. This characteristic, resulting in the formation of numerous “hot spots”, offers great signal improvement in SERS through strong electromagnetic enhancement.

The spectra of methyl parathion of differing concentrations (5 µL of 10 mM, 1 mM, 0.1 mM, 0.01 mM, 1 µM, 0.01 µM, 1 nM, and 0.9 nM) on the Ag/PDA/CaO nanocomposites are shown in Figure 5. The major characteristic bands in the SERS spectra of the methyl parathion could be identified at 1353 and 1596 cm^{-1}, which correspond with the variation in the C–H bending and phenyl stretching, respectively [39]. The calibration curve of 1353 cm^{-1} peak intensity and the corresponding concentration displayed a good linear relationship, ranging from 0.01 M to 0.9 nM, showing a linear correlation coefficient R^2 of 0.96 for methyl parathion (Figure 5c). The detection limit was 0.9 nM, which is much lower.
than the safety limits set by the Collaborative International Pesticides Analytical Council (CIPAC) for insecticide in fruits.

![Figure 5](image_url)

**Figure 5.** (a) SERS spectra of methyl parathion at different concentrations. (b) A zoomed-in view of the rectangle in (a), showing the intensity signal of $9 \times 10^{-10}$ M methyl parathion. (c) Linear calibration plot between the SERS intensity (peak at 1353 cm$^{-1}$) and methyl parathion concentration.

In addition, Table 1 compares the analytical performances of various SERS nanocomposites for the detection of methyl parathion, which is comparable or even superior to the other SERS nanocomposites reported in the literature. The above results demonstrate that Ag/PDA/CaO nanocomposites have the potential for the highly sensitive detection and quantitative analysis of methyl parathion residue.
Table 1. Comparison of various SERS substrates in methyl parathion detection.

| Materials / Methods | Method | Chemicals      | Detection Limit (nM) | References |
|---------------------|--------|----------------|----------------------|------------|
| AgNPs-Ge/Si         | Raman  | Methyl Parathion | 100                  | [39]       |
| Au-Ag alloy         | Raman  | Methyl Parathion | 5                    | [40]       |
| Au/nanosphere/AI2O3-layer/Ag-nanoparticles | Raman  | Methyl Parathion | 1                    | [41]       |
| Ag NPs on 3D PDMS nanotentacle array | Raman  | Methyl Parathion | 78                   | [42]       |
| Silver nanoparticles/graphene | Raman  | Methyl Parathion | 600                  | [43]       |
| Ag/AuNWs/PDMS      | Raman  | Methyl Parathion | 3.8                  | [44]       |
| polyaniline nanoparticles | Raman  | Methyl Parathion | 11.3                 | [45]       |
| triangular gold nanoparticles | Raman  | Methyl Parathion | 500                  | [46]       |
| Ag/PDA/CaO         | Raman  | Methyl Parathion | 0.9                  | This work  |

4. Conclusions

A SERS substrate was successfully designed, constructed, and established by utilizing non-toxic CaO as a semiconductor material for the first time, over other toxic, traditionally used metal oxides (CuO, Cu2O, ZnO, Fe2O3, etc.). The construction process involved the construction of CaO NPs from green resource oyster shells, followed by PDA coating on CaO NPs and further in-situ construction of Ag NPs onto a PDA/CaO support. The obtained LOD in the nanomolar regime and significant enhancement factor in SERS signals for sensing methyl parathion with the constructed substrate demonstrate the effectiveness of the SERS-constructed substrate by using CaO.

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Conflicts of Interest: The authors declare no conflict of interest.
Appendix A

![Figure A1. SERS spectra of 4-ATP acquired on Ag/PDA/CaO substrates prepared under different Ag-NPs deposition times (0, 2, 4, 6, 8, 10 and 24 h).](image)

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