Electrical Tuning of the MoOx/Ag Hybrids and Investigation on Their SERS Performance

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Surface enhanced Raman scattering (SERS) technology has become a cutting-edge analytical tool for molecule detections. Nowadays, attractive SERS performance has been achieved on noble metal nanostructures, however these substrates usually suffer from the difficulties of direct adjusting the physical structures to achieve tunable SERS performance. Meanwhile, studies on the semiconductor oxides reveal that attractive SERS performance can be obtained on them, but strategies of engineering material property for SERS performance improvement still pose as a challenge. Here, an electrically programmable SERS substrate is prepared by depositing the hydrothermal synthesized MoOx/Ag hybrids within the electrodes as SERS active region. In the experiment, electrical field is applied on the electrodes to regulate the Ag⁺ ion migration and redeposition in the MoOx solid electrolyte. Through adjusting the leakage current level, the size of Ag NPs in the
MoO$_x$/Ag hybrids is electrically controlled. The SERS performance of the substrate is evaluated by using the rhodamine 6G as the Raman reporter. Results evidence that Raman enhancement factor of $1.13 \times 10^5$, $4.75 \times 10^5$ and $1.04 \times 10^6$ can be obtained by programming the leakage current level to $10^{-7}$, $10^{-5}$ and $10^{-3}$ A, respectively. And maximum detection limit of $10^{-8}$ M is achieved on the $10^{-3}$ A substrate.
Surface enhanced Raman scattering (SERS) technology is renowned for the merits of non-destructive analysis, ultrahigh sensitivity and molecular fingerprint specificity. It has gained extensive research interests for the potential applications in analytical chemistry, biochemical detection and food safety etc.\[^1\] Today, the mechanism understanding of the SERS phenomenon is classified as electromagnetic mechanism (EM) and chemical mechanism (CM).\[^2\] For the EM, the incident light interacts with the noble metals and induces surface plasmon resonances (SPRs). These SPRs bring significantly enhanced surface electromagnetic fields, which produces $10^6$ or higher Raman intensity enhancement.\[^3\] On the other hand, the CM is always triggered by the photo induced charge transfer (PICT) between the adsorbed molecules and the SERS substrate with the help of defect levels in the oxides.\[^4\] As a result, the molecular polarizability is significantly amplified, producing attractive SERS enhancement.

Up to date, noble metals (Au or Ag, etc.) in the form of nanoparticles or nanostructures are used as SERS substrates for the purpose of generating strong SPRs to gain admirable performance.\[^5\] And methods like chemical synthesis or semiconductor fabrication techniques are widely used to prepare these nanoparticles or nanostructures. For example, Hiramatsu et al. reported a versatile and productive method of preparing nearly mono-dispersed gold or silver nanoparticles with adjustable sizes.\[^6\] By modifying the chemical ratio of the tetrachloroauric acid/silver acetate and oleylamineoleylamin, large-scale synthesis of gold (6-21 nm) and silver (8-23 nm) nanoparticles with the relatively low polydispersities of 6.9% could be achieved. Similarly, Lv et al. reported the preparation of gold stars with the core sizes from 26 nm to 50 nm and branches from 7 nm to 10 nm by change the mole ratio of tetrachloroauric acid (HAuCl$_4$), ascorbic acid (AA) and 4-(2-Hydroxyethyl)-1-piperaziny1]-ethanesulfonic acid (HEPES), and each morphology showed distinctive SERS performance, which was ascribed to the change of the localized SPRs frequency.\[^7\]

In the meanwhile, semiconductor fabrication processes of electron-beam-lithography patterning, metal sputtering deposition, selective etching and annealing are alternative ways used to fabricate...
nanostructures for SERS application. However, these approaches always require complex experiment designs and accurate parameter control. Furthermore, the above prepared noble metal nanostructures also hit the obstacle of flexible adjusting the physical structures to achieve tunable SERS performance for the detections of molecules with different SERS activities.

Oxide semiconductors have been widely investigated for their admirable light-mater interaction capabilities and tunable optical property. Recently, the out breaking of the material synthesizing and defect engineering methods has brought intensive researches on the oxide semiconductors as the SERS substrate. In the literature, inspiring results have demonstrated that oxide materials like titanium oxides (TiO$_2$), cuprous oxides (Cu$_2$O), zinc oxides (ZnO), reduced graphene oxides (rGO), tungsten oxides (WO$_{3-x}$) and molybdenum oxides (MoO$_x$) show exceptional SERS characteristics, which are ascribed to the defect level assisted PICT and enhancing the CM. Meanwhile, in order to prepare oxide semiconductors with prominent SERS activities, diverse oxide defect engineering strategies have been developed. For example, reductant like NaBH$_4$, dopamine, ascorbic acid (AA), polyethylene glycol (PEG), glucose, ethanol etc. are experimentally used to tune the oxygen vacancy density in the chemical synthesized oxide. In addition, methods like dopant intercalation, dopant implantation, light irradiation, crystal phase manipulating and electrochemical deposition are also extensively used to modify the material properties, introducing abundant defect levels in the band structure of oxides and promoting the PICT. To date, despite the fact that the existing strategies give the widely tunable defect density and consequently the localized surface plasmon resonance (LSPR) properties in the oxides, most of the semiconductor oxides still suffer low SERS enhancement capability. Lately, hybrid SERS substrates prepared by combining both noble-metal materials and oxides have attracted increasing attentions. The SERS performances of oxide/noble metal hybrid structures, for example TiO$_2$-Au, TiO$_2$-Ag, MoO$_x$-Au, graphene oxide/Ag, ZnO/Ag and MoO$_x$-Ag hybrid substrates have been evaluated in the research. Relying on the synergetic effects of EM and CM, attractive SERS improved performance has been achieved. Nevertheless,
it should be mentioned that preparation of metal-oxide/noble metal hybrids always involves multi-
steps of chemical synthesis or extra fabrication process. Additionally, similar as the noble metal
nanostructures, most of these oxide/noble metal hybrids also confront the disadvantages of
unchangeable structures, which impede the tunability of the material optical characteristics.

Herein, we report an electrically programmable SERS substrate prepared by depositing the
hydrothermal synthesized MoO$_x$/Ag hybrids between the Au electrodes with 10-μm space. Then,
electrical field is applied between the electrodes to regulate the Ag$^+$ ion migration and redeposition
dynamics in the MoO$_x$ electrolyte. Through adjusting the leakage current level between the
electrodes, experimental results demonstrate that the size of Ag NPs in the MoO$_x$/Ag hybrids could
be precisely tuned. Moreover, the SERS performance of the prepared substrate is evaluated by using
the rhodamine 6G (R6G) as the Raman reporter. The measured SERS spectra evidence that the
detection capability of the substrate can be promoted when the leakage current increases, and with
the continuous raising of the leakage current level to 10$^{-3}$ A, maximum Raman enhancement factor
of 1.04×10$^6$ and detection limit of 10$^{-8}$ M can be achieved. In all, this novel SERS substrate provides
an attractive way of preparing a dynamically tunable SERS substrate for high sensitivity sensing
applications.

MoO$_x$/Ag hybrids were synthesized by a quick (3 hours) and low temperature (80 °C)
hydrothermal method (see the Material Synthesis in Experimental Section). Scanning electron
microscopy detection was first performed. As shown in the Figure 1(a) and (b), MoO$_x$ nanorods
with the diameter of 250 nm are detected, and sparse Ag NPs randomly anchor on the MoO$_x$
nanorods, indicating that the MoO$_x$ provides good nucleation sites for Ag NPs. Thereafter,
transmission electron microscopy (TEM) analysis in Figure 1(c) discerns that the average size of
the synthesized Ag NPs is about 7.2 nm, while the high resolution TEM (HRTEM) image (inset of
Figure 1(c)) reveals that the lattice space of the synthesized MoO$_x$ nanorode is 3.518 Å, which
corresponds to the (200) face of the monoclinic MoO$_3$. And the lattice space of the Ag NP is 1.139
Å, which reflects the (311) face of Ag metal. Selective area electron diffraction (SEAD) analysis was also performed on the hybrids. The obtained diffraction pattern shown in Figure 1(d) reveals that the (100), (101) and (200) face of the monoclinic crystal phase. Finally, the electron dispersion spectra (EDS) element mapping in the Figure 1(e) further confirms that the MoO$_x$ nanorods surface is covered by Ag NPs.

The optical properties of the MoO$_x$/Ag hybrids were investigated as well. The $UV$-$vis$ absorption spectra of the MoO$_x$/Ag hybrids and pure MoO$_x$ are shown in the Figure 2(a). The spectra measured on MoO$_x$/Ag hybrids display a strong absorption peak near 210 nm, which is induced by the light absorption of the tetrahedral MoO$_x$. In the meanwhile, two weak and relatively broad absorption humps appear near 236 and 275 nm (band 1 and 2), which are contributed by the Mo$^{6+}$ in an octahedral structure. While the fourth weak absorption peak near 330 nm is ascribed to be the interaction between the Ag NPs and incident light (band 3). On the other hand, the $UV$-$vis$ absorption spectra measured on MoO$_x$ only show the band gap absorption edge (wavelength < 350 nm), and the absorption induced by the defects at the long wavelength (wavelength > 500 nm) is very weak, indicating the MoO$_x$ prepared in this work is defect deficiency.\textsuperscript{[15]} The Raman spectra of the MoO$_x$/Ag hybrids were collected and shown in Figure 2(b). It can be observed that the spectra are comprised by complex Raman vibrational modes. The characteristic peaks at 366 cm$^{-1}$ can be assigned to the vibrational modes of $\sigma$ (Mo=O), and peaks at 596 and 63 cm$^{-1}$ are attributed to the $\gamma$ (Mo-O-Ag) vibrational mode, indicating the formation of the Ag-O bond during the reduction process. In addition, the peak at 870 cm$^{-1}$ is assigned to $\nu$ (Mo-O-Mo) vibrational mode, whereas peaks at 910 and 938 cm$^{-1}$ are ascribed to the $\nu$ (Mo=O) vibrational modes.\textsuperscript{[16]}

To realize the electrical tuning of the MoO$_x$/Ag hybrids, in the subsequent steps, the MoO$_x$/Ag hybrids (wt%: 2.5%) were dissolved in H$_2$O and ethanol (5:3) mixed solution again, sonicated for 10 min, and then spin coated on the Si wafer with prefabricated 100-nm thickness of paired Au electrodes. The prepared substrate was annealed at 80 °C for 0.5 h in the air to improve the
adhesion. Figure 3(a)-(c) shows the optical image, schematic structure and SEM image of the prepared SERS substrate. It can be found that the spin-coated MoO₃/Ag hybrids remain the nanorods morphology and form thin film on the wafer surface with 92-nm physical thickness (Figure 3(d)). More specifically, the MoO₃/Ag hybrids in the space between the Au electrodes with the dimension of 10×10 μm² composes the SERS active region, while the two electrodes are used to electrically program the active region.

Electrical tuning of the MoO₃/Ag hybrids in our work was conducted by using a Keithley 4200-SCS semiconductor parameter analyzer. As an electro-active material, the anodic dissolution rate of the silver metal under the electrical field can reach 35.6 nm·s⁻¹.[17] In the experiment, when the electrical bias was applied on the electrodes, the Ag anodically dissolved and Ag⁺ ions migrated along the electrical field towards the cathode in the MoO₃ oxide electrolyte. During the migration process, the Ag⁺ ions were reduced when they met the electrons from the cathodes, and redeposited near the cathodes side again.[18] Relying on the above electro-migration mechanism, the dissolution rate of Ag⁺ ions were controlled through adjusting the current level between the electrodes during the programing period, and consequently the size of the redeposited Ag NPs were regulated within the oxide electrolyte. Therefore, in our experiment, the current level through the SERS active region was controlled by setting the current compliance during the voltage sweep on the two electrodes (Figure 4(a)). Typically, three similar SERS substrates with the designated leakage current level (10⁻⁷, 10⁻⁵ and 10⁻³ A) were programmed, respectively. At this stage, it was worth noting that, for the purpose of preventing catastrophic breakdown of the MoO₃/Ag hybrids when the voltage exceeded a certain threshold voltage (>100 V), our voltage sweeps were carried out in multi-steps. In the first step, when the MoO₃/Ag hybrids was in the pristine state, the current compliance was set to 10⁻⁷ A. When the sweep voltage climbed, the leakage current simultaneously increased until it reached the first compliance of 10⁻⁷ A, then the sweep voltage was stopped. Thereafter, for the device needed to be programmed to higher leakage current, the current compliance was tuned to 10⁻
On the other hand, the leakage current increase to $10^{-3}$ A, respectively, and the voltage sweep was applied again until the leakage current finally reached the specific level. At this moment, it could be found from the I-V curve in Figure 4(a) that, below the threshold voltage, all three devices own relatively low leakage current ($<1 \times 10^{-10}$ A@1V). This indicates that, although Ag NPs are stationed on the MoO$_x$ nanorods, the density of the Ag NPs is relatively low, and thus they are not connected with each other to form the current path. However, only after the voltage sweep, the migration of Ag$^+$ ions and gradual increase of the Ag NPs size forms the current path, resulting in the rising of the device leakage current.

The SERS performance was evaluated by using the rhodamine 6G (R6G) as the probe molecules. During the measurement, a 532-nm semiconductor laser was used as the excitation source, and the spot diameter of the laser on the substrate was 12.5 um (100× objective lens), which could cover the SERS active area. The Raman spectra were collected under a laser power of 1 mW with an integration time of 10 s. The measured Raman spectra were shown in Figure 4(b). It can be found that no detectable Raman peak can be observed on the silicon substrate when the concentration of R6G is $10^{-4}$ M. On the other hand, relatively faint Raman peaks originate from R6G were observed on the pristine MoO$_x$ substrate and pristine MoO$_x$/Ag hybrids device, which can be ascribed to the weak Raman signal enhancement of these two substrates (see Figure S1 in the Supporting Information). Furthermore, when the leakage current increase to $10^{-3}$ A, the fingerprint peaks of R6G are enhanced remarkably, indicating the SERS performance of the MoO$_x$/Ag hybrids is improved through the electrical programing. In detail, prominent Raman peaks of R6G at 609, 769, 1193, 1355, 1471, 1538, 1605 and 1646 cm$^{-1}$ are observed on the collected SERS spectra. The peaks located at 609 cm$^{-1}$ is due to the C-C-C ring in-plane bending, and 769 cm$^{-1}$ is assigned to out-of-plane bending of the C-H atom on the xanthene’s skeleton. Moreover, peak at 1193 cm$^{-1}$ arises from the C-H in-plane bending. And the peaks from 1355 to 1646 cm$^{-1}$ belong to aromatic C-C stretching vibration modes. In addition to that, the Raman signals intensities on substrates with the $10^{-5}$ A and $10^{-7}$ A programmed leakage current were also collected and shown in Figure 4(b). Impressively, the
measured Raman intensity decreases with the reducing of the leakage, revealing that the change of MoO$_x$/Ag hybrids SERS property is closely related to the leakage level and the Raman enhancement capability of the substrate can be electrically programmed by fine control of the voltage sweep. The enhancement factors (EFs) of the three substrates with 10$^{-7}$, 10$^{-5}$ and 10$^{-3}$ A leakage current are calculated by integrating the Raman peak at 1355 cm$^{-1}$ (see the Supporting Information). Through the calculation, EFs of 1.13×10$^5$ (10$^{-7}$ A), 4.76×10$^5$ (10$^{-5}$ A) and 1.04×10$^6$ (10$^{-3}$ A) are achieved for the respective leakage current level, which further verifies the tunable SERS performance (Figure 4(c)). The detection limit of the substrate with 10$^{-3}$ A is also accessed by detecting the R6G solutions with different concentrations. It shows in Figure 4(d) that the intensities of the characteristic peaks coincidentally drop with the decrease of the R6G concentration, and the minimum detectable concentration of 10$^{-8}$ M can be achieved when the substrate leakage is 10$^{-3}$ A.

In the end, to explore the physical mechanism of the improved SERS performance of the MoO$_x$/Ag hybrids after electrical programming, the optical and SEM image were first investigated and shown in Figure 5(a) and (b). It can be observed in the optical image that discernible change of the MoO$_x$/Ag hybrids happens near the cathodes. In the meanwhile, from the SEM detection on the electrically programmed substrate (Figure 5(b)), it further illustrates that the size of Ag NPs (average size: 38.97 nm) significantly grows up as compared to that (average size: 7.25 nm) in the pristine state, which can be ascribed to the Ag$^+$ ion electro-deposition on the initial Ag NPs during the voltage sweep step. Moreover, it also can be observed on the SEM image that the MoO$_x$ changes from monoclinic phase (nanorods) to orthorhombic phase (nanoflakes), resulting from the thermal effect during the programing phase.$^{[19]}$ On this basis, it is observed that Ag NPs and MoO$_x$ forms more robust heterojunction after electrical programing, however, band edge alignment between Ag NPs and MoO$_x$ reveals that they form ohmic contact kind of heterojunction, resulting in little help on promoting the charge transfer (see Figure S2 in the see the Supporting Information)$^{[20]}$. In the meanwhile, as shown in the Figure S1, the chemical enhancement from the
pure MoO$_x$ is also insignificant when compared to the total SERS enhancement, thus it can be inferred that SERS enhancement of the MoO$_x$/Ag NPs hybrids is mainly contributed by the EM from Ag NPs. Therefore, finite-difference time-domain (FDTD) simulation is performed to investigate the Ag NPs’ surface electromagnetic field. The MoO$_x$/Ag hybrids before and after electrical programming were modeled based on the SEM detection images (see Figure S3 in the Supporting Information), and the surface electromagnetic fields were extracted. As it is shown in Figure 5(c) and (d) that LSPR are generated on both MoO$_x$/Ag hybrids under the light irradiation. However, it also can be clearly found that much stronger surface electromagnetic field exists on the Ag NPs with larger size compared to that on the pristine Ag NPs with relatively smaller size, which consequently boosts the SERS performance significantly.

To summarize, an electrical programmable SERS substrate prepared by the MoO$_x$/Ag hybrids is demonstrated. Through controlling the leakage current level, the size of Ag NPs in the MoO$_x$/Ag hybrids can be precisely controlled. The SERS performance with different programmed leakage levels is evaluated by using the $R6G$ as the Raman reporter. Experimental results show that tunable Raman enhancement factor of $1.13\times10^5$ ($10^{-7}$ A), $4.75\times10^5$ ($10^{-5}$ A) and $1.04\times10^6$ ($10^{-3}$ A) can be obtained. And maximum detection limit of $10^{-8}$ M can be achieved on the $10^{-3}$ A substrate. In the end, physical simulation reveals that the increase of Ag NPs size after electrical programming shifts the LSPR frequency towards the 532-nm laser excitation source, which significantly promotes surface electromagnetic field of Ag NPs and enhances the SERS performance.

Experimental Section

*Materials:* Glucose (99%) was purchased from Macklin; ammonium heptamolybdate (AHM, >99%), silver nitrate (AgNO$_3$, 99.8%), ethanol (99.7 %) and nitric acid (HNO$_3$, wt%: 68%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. In all the experiments, deionized water (resistivity of 18.2 MΩ · cm) was used to prepare the solutions.

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Material Synthesizing: MoOx/Ag hybrids were prepared by a low temperature chemical synthesis reaction. Basically, AHM (882.7 mg) was used as molybdenum source and dissolved into deionized water (25 ml), then the mixed solution was stirred slowly (8000 rpm) at 80 °C. Thereafter, glucose solution (20 ml, wt%: 2.57%) was slowly added into the above mixed solution and stirred for 10 minutes. After that, HNO₃ (150 ul, wt%: 68%) was added into the mixed solution. After one-hour reaction, the mixed solution turned dark blue, and then AgNO₃ solution (25 ml, wt%: 1.94%) was slowly added to the above solution, and the stirring rate was accelerated to 15000 rpm for two hours. After the reaction was completed, the product was centrifuged, washed with acetonitrile, ethanol and deionized water, respectively, and finally dried in the oven at 80 °C for 8 hours.

Characterization: Voltage sweep and leakage current measurements were performed using a Keithley 4200-SCS semiconductor parameter analyzer system (Tektronix, US). The SEM images of the substrates were acquired by a Hitachi SU-70 system (Hitachi, Japan) under an accelerating voltage of 5 kV. The TEM images were obtained on a JEM-2100F transmission electron microscope (JEOL, Japan). The UV-vis spectra were collected with a spectrometer (TU1901, P-General, Samutprakarn, Thailand). SERS measurements were made by a Raman microscope equipped with a spectrometer (QE Pro, Ocean Optics, USA). A 532-nm semiconductor laser was used as the excitation source, and the diameter of the spot size of the laser on the substrate is 12.5 μm (100x objective lens). The Raman spectra were collected under a laser power of 1mW, and an integration time of 10 s.

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.

References


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Figure 1. a) and b) The SEM images of the MoO$_x$/Ag hybrids with different magnifications. c) The TEM image of the MoO$_x$/Ag hybrids. The inset in (b) shows the lattice space of MoO$_x$ and Ag, respectively. d) The SEAD pattern of the MoO$_x$/Ag hybrids. e) The EDS mapping images of the Mo, Ag and O element on the MoO$_x$/Ag hybrids.
Figure 2. a) The UV-vis absorption spectra of the MoO$_x$/Ag hybrids and pure MoO$_x$. The inset in (a) shows the optical image of the MoO$_x$/Ag hybrids solution. b) The Raman spectra of the MoO$_x$/Ag hybrids.
Figure 3. a) The optical image of the pristine substrate. b) The schematic structure of the SERS substrate. c) The SEM image of the pristine substrate. d) The SEM cross-section image of the substrate.
Figure 4. a) The $I-V$ curves obtained during the electrical programming. b) The SERS spectra measured on different substrates. The concentration of R6G is $10^{-4}$ M. c) The calculated enhancement factor of the substrate with $10^{-7}$, $10^{-3}$ and $10^{-3}$ A leakage current. d) The detection limited of the substrate with $10^{-3}$ A leakage current.
Figure 5. a) The optical images of the SERS substrates before and after electrical programming. b) The SEM surface image of the SERS substrate after electrical programming. c) The simulated surface electromagnetic field of the SERS substrate before electrical programming. d) The simulated surface electromagnetic field of the SERS substrate after electrical programming.
An electrically programmable SERS substrate prepared by depositing the hydrothermal synthesized MoO$_x$/Ag hybrids is presented. By using the rhodamine 6G as the Raman reporter, tunable SERS performance with the Raman enhancement factor of $1.13 \times 10^5$, $4.75 \times 10^5$ and $1.04 \times 10^6$ can be obtained by programming the leakage current level to $10^{-7}$, $10^{-5}$ and $10^{-3}$ A, respectively.

**Keywords:** surface enhanced Raman scattering; electrical programming; molybdenum oxide/Ag NP hybrids; electromagnetic enhancement

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