1. Introduction

Label-free biosensors are gaining increased public attention as promising portable and affordable solutions to monitoring food and water for local supplies, as these tools offer analysis of small traces of residues such as drugs, pesticide, pathogens, and toxic substances.\[1\] Considerable endeavors have been devoted to the exploitation of surface-enhanced Raman scattering (SERS)-active substrates due to their fingerprint capability on chemical structure and single-molecule level sensitivity.\[2\] The intriguing applications of SERS-active substrates in surface chemistry and biomolecular sensing are extensively demonstrated based on noble metals, such as Au, Ag, and Pt.\[3\] The high carrier concentrations of noble metals establish the surface plasmon resonance at energies in the visible spectrum,\[4\] which generates the significant enhancement in Raman signals based on electromagnetic enhancement mechanism (EM). The enhancement factors (EFs) are on the order of $10^6$ to $10^{11}$.\[5\] Yet, to apply the aforementioned SERS-active substrates to the practical system, the research community still have to overcome some major obstacles such as high cost, poor biocompatibility, and limited reusability.\[6\]

The rapid growth of nanotechnology has paved the way recently to develop alternative SERS-active substrates using nanostructured metal oxides. The observations of SERS arising from organic molecules adsorbed on some metal-oxide nanoparticles, such as TiO$_2$,\[7\] ZnO,\[8\] Ag$_2$O,\[9\] and W$_{18}$O$_{49}$,\[10\] have been reported with EFs around $10^2$–$10^5$. Especially, metal oxides are endowed with tunable band gap and carrier properties, like wavelength dependence, barrier confinement through introducing impurities, and surface functionalities, which make such system an analytical tool to study SERS mechanism and widen their applications. However, the exploitation of a flat or roughened metal-oxide film as a SERS substrate has so far yielded limited success for the following two reasons.\[11\] First, on metal oxides, the surface plasmons of the conduction band and the vibronic coupling of the conduction and valence bands of Cu$_2$O with the molecular orbital of PATP further enhances the Raman scattering. This study on the combined EM and CT channels on Cu$_2$O nanoplates is promising to identify a new group of SERS-active substrates and advance the fundamental understanding of SERS mechanism, which also opens up a prospect of biocompatible and in situ diagnosis.
valence band occur in the infrared and ultraviolet regions, respectively, which are far from most of Raman scatterings of probe molecules in the visible spectrum, barely enhancing the Raman signals via EM. Second, chemical enhancement mechanism (CM) remains largely unknown, of which complicated interactions of target molecules on metal oxides pose the grand challenge for identifying the SERS mechanism. In fact, the experimental observations of SERS in previous reports merely take place on a certain type of nanostructured metal oxides. Therefore, in our study, we used metal-oxide nanoplate structures to elaborate the geometric effect on EM and the contribution of specific charge-transfer (CT) channels to CM.

Cuprous oxide (Cu$_2$O) is a p-type semiconductor with a direct band gap of 2 eV, which is widely used in photocatalysis and photovoltaics by virtue of superior catalytic activities and optical properties. The first observation of SERS arising from the adsorbed pyridine on Cu$_2$O hydrosol particles and Cu$_2$O-covered Cu was reported by Kudelski et al., showing the potential of adsorbed pyridine on Cu$_2$O hydrosol particles and Cu$_2$O-covered shape-dependent SERS activity of Cu$_2$O nanocrystals associated with Cu$_2$O oxides. Therefore, in our study, we used metal-oxide nanoplate structures to elaborate the geometric effect on EM and the contribution of specific charge-transfer (CT) channels to CM.

Cuprous oxide (Cu$_2$O) is a p-type semiconductor with a direct band gap of 2 eV, which is widely used in photocatalysis and photovoltaics by virtue of superior catalytic activities and optical properties. The first observation of SERS arising from the adsorbed pyridine on Cu$_2$O hydrosol particles and Cu$_2$O-covered Cu was reported by Kudelski et al., showing the potential of Cu$_2$O to be a SERS-active substrate. Recently, the SERS spectra of 4-aminothiophenol (PATP) have been demonstrated on Cu$_2$O nanoparticles and microcrystals. The SERS behaviors were primarily attributed to either hierarchical porosity of nanoparticles or high roughness of etched microcrystals, where the SERS activities were stemmed from adsorbing more analytes on the large surface area and creating Raman hot spots at the rough surface. Nevertheless, the EF observed in these experiments cannot be exclusively attributed to EM, as the interactions between the SERS substrate and probe molecules were significant. A comprehensive and predictive model is still lacking in the SERS mechanism for Cu$_2$O-based nanostructures.

For the maneuverable synthesis of nanocrystals, we have reported cyclic scanning electrodeposition (CSE) method to fabricate metal and metal-oxide nanocrystals with various morphologies. In this work, the CSE was extended to synthesize Cu$_2$O hexagonal nanoplates, which became the building blocks to construct a 3D Cu$_2$O network. It is worthwhile noting that an impressive SERS activity and reproducible measurements were achieved on Cu$_2$O nanoplates, opening up the way for a systematic investigation of the SERS mechanism, and broadening the application of Cu$_2$O nanocrystals. Particularly, the shape-dependent SERS activity of Cu$_2$O nanocrystals associated with EM was studied using finite-difference time-domain (FDTD) simulation. Meanwhile, the dominant contribution of chemical-bonding and photo-induced charge-transfer (PICT) enhancements to SERS activity was methodically studied by applying density functional theory (DFT) calculation. The research proposes a promising route to design a high-performance SERS-active substrate based on the electrochemical synthesis of nanocrystals. Most importantly, our results shed light on the SERS mechanism by elaborating the contributions of EM and CM on the SERS activity of Cu$_2$O.

2. Results and Discussion

2.1. Synthesis of Cu$_2$O Nanoplates

The Cu$_2$O nanoplates were synthesized via CSE. A thin Cu film with a thickness of about 200 nm was electroplated on a conductive substrate, which was then subjected to cyclic voltammetry in a NaNO$_3$ electrolyte with the pH value of 9. Figure 1a presents the current–potential response of CSE, by which the dependence of the growth habit on electrochemical overpotential is recorded. The first anodic peak occurring in the forward scan is associated with the anodic dissolution of Cu to Cu$^{2+}$ ions. The second anodic peak at more positive potential is the oxidation of OH$^-$ to O$_2$. A high concentration of Cu$^{2+}$ ions was generated after the anodic scan and readily captured by excess OH$^-$ ions in the alkaline medium, leading to the precipitation of Cu$^{2+}$ in the form of Cu(OH)$_2$ near the interface. In the reverse cathodic scan, two cathodic peaks represent the seed formation and the crystal growth of Cu$_2$O nanocrystals, respectively. The onset potential (≈0.1 V vs Ag/AgCl) regarding the reduction of Cu$^{2+}$ is in conformity to the previous results in the literature. Scanning electron microscope (SEM) images at different endpoints (≈−0.2 and −0.75 V) of the reverse scan illustrate the growth of Cu$_2$O from incipient crystals to the 3D network of Cu$_2$O nanoplates (Figure 1b). At a potential of −0.2 V, plentiful crystal seeds and scattered Cu$_2$O nanoplates were observed (Figure 1b1). The overpotential was small at the initial stage of the reaction; the nucleation proceeded with a slow reaction rate. Meanwhile, the adions supply was sluggish due to the precipitation of Cu(OH)$_2$. Besides, NO$_3^-$ ions were speculated to selectively adsorb on {111} facets to efficiently hinder the growth of Cu$_2$O nanocrystals along the [111] direction, leading to the formation of 2D hexagonal nanoplates, where the top and bottom planes were bounded by [111] planes and the side planes were enclosed by a mixture of {100} and {111} planes. Generally, the stacking faults were present in the plate-like nanocrystals, where the adions were preferentially deposited on these high-energy sites of the existing nanocrystals. As the potential was scanned to a more negative region, the nucleation and growth of Cu$_2$O became prospering under a high overpotential. A large second cathodic peak corresponds to fast growth of branched nanoplates on the substrate and active sites of the formed nanocrystals (Figure 1b2), resulting in full coverage of Cu$_2$O nanoplates. The hyperlinked Cu$_2$O network structure is composed of massive Cu$_2$O hexagonal nanoplates with a thickness of single piece about 20 nm and a diameter of about 1 μm. The crystal structure of Cu$_2$O nanoplates was characterized by transmission electron microscopy (TEM) and selective area electron diffraction (SAED). Figure 1c shows the intercrossed structure of the Cu$_2$O nanoplates, in which one individual nanoplate had a hexagonal shape consistent with the observation in SEM images. Two sets of spots in the SAED pattern can be identified: (110) Bragg reflections (d-spacing, 3.0 Å), and (220) Bragg reflections (d-spacing, 1.5 Å) of Cu$_2$O single crystal, respectively (Figure 1c1). The entire synthesis of Cu$_2$O nanoplates was completed within 10 min at ≈25 °C, and high production yield was guaranteed. Such a synthesis has many advantages including fast production, low temperature, and economical manufacture compared with the previously reported shape-controlled synthesis of Cu$_2$O.

2.2. Raman Spectra of PATP Adsorbed on Cu$_2$O Nanoplates

To evaluate the performance of Cu$_2$O nanoplates as a SERS-active substrate, the PATP was used as the probe molecule. The
Cu₂O nanoplate substrates were immersed in PATP solutions with different concentrations and then thoroughly washed with ethanol and DI water, so the PATP molecules were deposited on Cu₂O nanplates for Raman characterization. As shown in Figure 2a, the Raman spectra of bulk PATP (in the form of compacted powders) and 0.8 × 10⁻³ m PATP molecules adsorbed on the bare substrate (made of stainless steel), and Cu₂O nanplates are significantly distinct. No Raman signal of the PATP molecule was detected on the bare substrate, ruling out the effect of the stainless steel for Raman enhancement.

For bulk PATP, three primary characteristic Raman peaks locating at 1079, 1187, and 1578 cm⁻¹ are observed, which are allocated with the C–S stretching, the C–H stretching, and the C–C stretching of PATP molecule, respectively. [23] The Raman spectrum shows the specificity toward the totally symmetric a₁ vibration mode and consists well with the Raman spectrum of the previously reported PATP in solid state. [23a] Using Cu₂O nanplates, the Raman signal intensity of 0.8 × 10⁻³ m PATP is obviously enhanced, and there is an appearance of new vibrational bands, which are ascribed to the nontotally symmetric b₂ vibration mode.
vibration mode of the PATP molecule. Specifically, the peak at 1143 cm\(^{-1}\) is assigned to the C–H bending, and the peaks at 1392 and 1437 cm\(^{-1}\) correspond to two vibration assignments of the combined C–C stretching and C–H bending,\(^{[23a]}\) suggesting that charge-transfer processes occur between PATP molecules and Cu\(_2\)O nanoplates.\(^ {[24]}\)

Figure 2b reveals the Raman spectra of PATP molecules with different concentrations varying from \(8 \times 10^{-5}\) to \(1 \times 10^{-3}\) M. The Raman intensities of PATP increase with rising concentration. Besides, the Raman spectrum of PATP can be evidently detected on Cu\(_2\)O nanoplates with the concentration as low as \(8 \times 10^{-5}\) M. The detailed investigation of Raman peaks was conducted by comparing the Raman signal of bulk PATP with the SERS signal of PATP at different concentrations. The Raman intensity ratios of \(I_{\text{SERS}}/I_{\text{bulk}}\) at six characteristic Raman peaks increase near-linearly when increasing probe molecule concentration from \(10^{-5}\) to \(10^{-3}\) M (Figure 2c), while the intensity ratios of Raman peaks associated with \(b_2\) vibrations are much higher than those of \(a_1\) vibrations. For \(1 \times 10^{-3}\) M PATP, the Raman intensity ratio of 26.7 is obtained at 1436 cm\(^{-1}\), whereas the ratio at 1580 cm\(^{-1}\) is only 2.4, indicating a selective enhancement of nontotally symmetric \(b_2\) vibration mode. Since the bulk material contributes exclusively to the \(a_1\) vibration mode, the dependence of \(I_{\text{SERS}}/I_{\text{bulk}}\) on the vibration mode is a clear indication for the CM to the SERS activity on Cu\(_2\)O nanoplates. It is rational to anticipate that the increased active CT processes are established to enhance the Raman intensities at peaks 1143, 1392, and 1578 cm\(^{-1}\). In addition, the magnitude of the EF was estimated based on the Raman intensity ratio. The sample volumes were determined by the area of the laser spot and the penetration depth of the focused laser. To simplify the calculation for a rough surface, we assumed that the volumes of bulk PATP and adsorbed PATP molecules under the laser spots were identical.\(^{[14a]}\) The EF could then be estimated as \(\approx 10^5\) at 1143, 1392, and 1578 cm\(^{-1}\) (Note S1, Supporting Information), which are exceptionally higher than that of the majority of metal oxides reported.\(^ {[6,25]}\)

The uniformity of nanocrystals and the reproducibility of SERS activity are crucial for a SERS-active substrate. To assess the Cu\(_2\)O nanoplates in this regard, the patterned Cu\(_2\)O nanoplate array was fabricated by conducting the CSE in a photosresist template, on which a metallic Cu dot array was electroplated in advance (Figure S1, Supporting Information), and subsequently converted into Cu\(_2\)O nanoplate array via CSE process in NaNO\(_2\) electrolyte. Each individual Cu\(_2\)O cluster was constituted by a number of Cu\(_2\)O nanoplates. The fabrication process is illustrated in Figure S2 (Supporting Information). Figure 3 shows SEM images of the Cu\(_2\)O nanoplate array, exhibiting that Cu dots were uniformly converted into nanoplate clusters across the substrate. The reproducibility of SERS activity was examined on 10 random Cu\(_2\)O nanoplate clusters across the entire sample. The Raman spectra of PATP are shown in Figure 4a, revealing the nearly identical spectral profiles. Also, Figure 4b presents the intensity histogram of six PATP characteristic Raman peaks, where the average relative standard deviation of six Raman peaks is less than 7.7, indicating the good reproducibility of SERS activity across the Cu\(_2\)O nanoplate array. Moreover, the SERS activity of Cu\(_2\)O nanoplates and the reproducibility were concurrently displayed on the Raman mapping of the patterned Cu\(_2\)O nanoplate substrate. Figure 4c is the optical image of the as-prepared substrate, in which a 30 µm \(\times\) 26 µm area was selected for Raman mapping including four Cu\(_2\)O clusters. Figure 4d1–d3 shows the mappings for different Raman peaks at 1143, 1347 (\(b_2\) vibration mode), and 1578 cm\(^{-1}\) (\(a_1\) vibration mode), respectively. Figure 4d4 shows a synthetical Raman mapping for the three characteristic Raman
peaks. Obviously, the high Raman intensities of PATP were generated on the locations with Cu$_2$O nanoplates, in contrast to the scarcely acquired Raman signal on the bare substrate. Also, the Raman intensities of PATP molecules on individual Cu$_2$O clusters are approximately identical. Good reproducibility of the Raman signals attained on the SERS-active Cu$_2$O is attributed to the uniformly dense and shaped Cu$_2$O nanoplates synthesized via the CSE method.

Supplementing to Cu$_2$O nanoplates, we report the synthesis of Cu$_2$O nanofibers for the first time via the CSE method. A square-wave potential was applied in the reversed cathodic scan instead of the linear-sweep voltammetry to carry out the shape-controlled synthesis of the nanofibers. The Cu$_2$O nanofiber possesses an aspect ratio of 100. The morphology and interior structure of Cu$_2$O nanofibers were characterized by SEM and TEM (Figures S3 and S4, Supporting Information). Notably, a remarkable SERS activity with an EF of $\approx 10^5$ was acquired by constructing 3D nanostructures on the substrate with the high-density Cu$_2$O nanofibers. (Note S2 and Figures S5–S7, Supporting Information).

2.3. Elaboration of SERS Mechanisms

Two enhancement mechanisms were taken into account in our model to interpret the SERS activity of Cu$_2$O nanofibers. First, the shape-dependent SERS activity of Cu$_2$O nanofibers associated with EM was studied by applying the FDTD simulation. Since the surface plasmon resonance frequency of Cu$_2$O locates in the infrared wavelength region, which is far from the wavelength of the excitation laser used for the Raman measurement, the EM occurring on Cu$_2$O nanocrystals is ascribed to a purely geometric factor, also known as the lightning rod effect, where the local electromagnetic field tends to concentrate at the vicinity of protrusions. To simplify the analysis of the local electromagnetic intensity correlated with the geometry, the
FDTD computations were carried out on three models, where the dimensions of Cu$_2$O nanoplates were determined based on the SEM observations. Figure 5a depicts the shape effect of Cu$_2$O nanoplates on the enhancement of the local electromagnetic field. There is a larger local electromagnetic field (1.71× enhancement) around the hexagonal nanoplate than a circular nanoplate (1.51× enhancement), particularly at six corners of the hexagonal nanoplate. As shown in Figure 5b, the interparticle gap is also a crucial parameter to concentrate the electromagnetic field. Under a polarized electromagnetic wave perpendicular to the interparticle gap, the local electromagnetic field rises apparently with the decreased distance between two hexagonal nanoplates, while the local electromagnetic field barely increases if the electromagnetic wave is polarized parallelly to the gap. In addition, the orientation of nanoplates was studied using the model constituting two intercrossed nanoplates with an inclined angle of 60° (Figure 5c). The local electromagnetic field was intensively enhanced (2.72× enhancement) at the valley between two nanoplates. We can conclude that the local electromagnetic field was magnified by both designing hexagonal geometry and constructing a hyperlinked network structure, and consequently to contribute to enhanced Raman signal intensity.[26,27] Since the EF of SERS was roughly proportional to $|E|^4$, the enhanced Raman scattering of PATP on Cu$_2$O stemming from EM only contributes a small portion of SERS activity.[28]

Please note that the b$_2$ vibration mode shows higher Raman intensity ratio ($I_{SERS}/I_{bulk}$) than that of a$_1$ vibration mode, indicating that the CM is dominant to the enhancement of the Raman scattering of the PATP on Cu$_2$O nanoplates. The PATP molecule has a thiol group and generally attaches to the substrate by a nucleophilic substitution reaction at 90 °C for a few hours. Otherwise, simple physisorption is more likely to take place.[29] To investigate chemical states of the PATP molecule on Cu$_2$O sample, we conducted surface characterization with X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum presents the existence of Cu and S in the as-prepared sample (Figure 6a). Figure 6b,c shows the high-resolution spectra of the Cu 2p, where two separate peaks are observed at the binding energies of 932.8 and 952.6 eV, belonging to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ of Cu(I), respectively. There are no “shake-up” satellite peaks appearing in the higher binding energy range, ruling out the presence of Cu(II) in the sample.[30] The S 2p spectrum has a doublet structure due to the existence of S 2p$_{3/2}$ and S 2p$_{1/2}$ peaks, which are fitted using a 2:1 peak area ratio and a 1.2 eV splitting (Figure 6d). The S 2p$_{3/2}$ signal is centered at 162.6 eV, while the S 2p$_{1/2}$ signal is located at 163.7 eV, exhibiting the bound thiol on Cu$_2$O. Moreover, there are no unbound thiol molecules on Cu$_2$O because no detectable intensities are present in the binding energies of 165 eV for S 2p$_{3/2}$ and 163.5 eV for S 2p$_{1/2}$.[31] Thus, the covalent bonding between PATP molecules and Cu$_2$O nanoplates is affirmatively established through the Cu–S linkage. The presence of high-density stacking faults in Cu$_2$O nanoplates leads to the surface state energy level and consequently to facilitate the chemisorption of PATP molecules without high-temperature treatment.[32] Meanwhile, such chemisorption could magnify the Raman scattering cross-section of PATP molecules and conduce to the occurrence of SERS on the Cu$_2$O nanoplates.[33]
On the other hand, the emergence of the covalent bonding promotes the molecular resonance of PATP molecules and the PICT process between PATP molecules and Cu$_2$O nanoplates. The ab initio calculation was carried out to study the ground-state properties, and electronic transitions of the PATP and the PATP adsorbed on Cu$_2$O. The geometry of the PATP molecule was fully relaxed, and the PATP adsorbed on Cu$_2$O was optimized via the Cu$-$S bonding as verified in XPS results. The DFT calculation was implemented using the VASP code, in which an energy cutoff 800 eV was adopted.[33] The on-site repulsion $U$ and the exchange correction parameter $J$ were introduced to improve the accuracy of the DFT calculation, since the presence of d-orbit electrons in the Cu atom generally leads to the significant underestimation of the band gap of Cu$_2$O in a standard DFT calculation.[35] Additionally, the behaviors of valence electrons and the internal shells in the Cu$_2$O system (Cu 3p$^6$, 3d$^{10}$, and 4s$^1$; O 2s$^2$ and 2p$^4$) were taken into account by using plane-wave-based projector augmented wave pseudopotential.[36] Figure 7 presents the molecular orbital of the PATP molecule, exhibiting an energy difference between highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level of 3.24 eV so that the frequency of the incident light ($\omega_0$ 2.33 eV) was far from the molecular resonance frequency of the PATP molecule ($\omega_{IK}$). Therefore, both the molecular resonance from the ground state $|I\rangle$ to excited state $|K\rangle$ of the PATP molecule and the PICT process between PATP and Cu$_2$O were thermodynamically prohibited. Also, the energy level of molecular orbitals significantly shifted and the HOMO–LUMO gap was reduced to 0.95 eV when the covalent bonding was formed between PATP and Cu$_2$O nanoplates. Figure 7 reveals HOMO and LUMO of the PATP adsorbed on Cu$_2$O nanoplates, where the electrons in the HOMO were distributed across the PATP molecule and Cu$_2$O, while the electrons in the LUMO were localized on the Cu$_2$O, implying that the change of electron density distribution of the PATP molecule occurs via Cu$-$S bonding. The molecular resonance of the PATP molecule became thermodynamically feasible ($\omega_0 > \omega_{IK}$), and the PICT process between PATP and Cu$_2$O nanoplates was promoted based on the Herzberg–Teller selection rules.[37] The Raman scattering of the PATP was intensively enhanced by virtue of the vibronic coupling of the conduction band $|S\rangle$ and valence band $|S'\rangle$ of Cu$_2$O with the molecular ground state $|I\rangle$ and excited state $|K\rangle$ of PATP. During the PICT from Cu$_2$O to PATP, the electrons in the valence band of the Cu$_2$O were stimulated by the incident light, generating the electrons in the conducting band and leaving the holes in the valence band. Thereafter, the excited electrons can transfer favorably to the matching energy level of the LUMO of the PATP through resonant tunneling,[7,29a] which eventually transited back to the valence band of the Cu$_2$O and recombine with the holes, radiating Raman photons at some vibrationally states.[7] On the other hand, the electrons occupying the ground state of the PATP were excited from HOMO to LUMO, which then transferred to the matching energy level above the conducting band of the Cu$_2$O via resonant tunneling. The Raman photons were radiated when the excited electrons transmitted back to the
Cu2O nanoplates associated with EM was studied by applying of SERS mechanism. The shape-dependent SERS activity of plates, which paved the way for a comprehensive investigation of the dominant contribution of chemical-boding and PICT enhancements to the occurrence of SERS. Owing to several tunable features inclusive of tunable band gap and carrier properties via introducing impurities and surface functionalities, the design of metal-oxide nanocrystal-based SERS-active substrates is beyond expanding the SERS to nonnoble metals and is promising for the biocompatible and in situ diagnosis for broad biological and biomedical applications.

4. Experimental Section

Materials: Copper (II) sulfate pentahydrate (CuSO4·5H2O), sulfuric acid (H2SO4), hydrochloric acid (HCl), sodium nitrite (NaNO2), and 4-aminothiophenol (PATP) were purchased from Sigma-Aldrich. Copper plating additive and leveler were obtained from Atotech Asia Pacific Ltd. All reagents were used as received without further purification. The solutions were prepared with deionized water (18.2 MΩ).

Synthesis of Cu2O Nanocrystals: The electrochemical synthesis of Cu2O nanocrystals was performed using a Reference 600 Potentiostat (Gamry Instrument) in a standard three-electrode system. The Pt wire, saturated Ag/AgCl, and stainless steel substrate were used as the counter electrode, reference electrode, and working electrode, respectively. The stainless steel substrates were grinded and polished to a roughness less than 30 nm before the electrodeposition. In the Cu electrolyte consisting of 0.3 v CuSO4, 10% v/v H2SO4, 60 ppm HCl, 0.5 mL L−1 copper plating additive, and 20 mL L−1 copper plating leveler, a Cu thin layer was electroplated on the substrate using the linear-sweep voltammetry from 0 to −1 V along with a cathodic potential of −0.3 V for 45 s. Then, the Cu-coated substrate was subjected to CSE at a scan rate of 10 mV s−1 in 0.412 NaNO2 to produce Cu2O nanocrystals. The anodic scan started from −0.75 and paused at 1.45 V, and subsequently an immediate cathodic scan from 1.45 to −0.75 V was carried out. Similarly, the Cu2O nanofibers were synthesized via CSE in the same electrolyte, while the linear-sweep and square-wave forms were applied. The anodic scan from −0.75 to 1.45 V was performed on the Cu-coated substrate, which was then subjected to a constant nucleation step at the potential of −1.8 V for 45 s. Thereafter, the square-wave form was applied (Eoff = 0 V, Eon = −0.3 V; 10 cycles per sec) for 10 min.

3. Conclusions

In summary, a new type of SERS-active substrate was developed based on the shape-controlled synthesis of Cu2O nanocrystals. A substantially enhanced Raman intensity of analytes and a good reproducibility were achieved on Cu2O hexagonal nanoplates, which paved the way for a comprehensive investigation of SERS mechanism. The shape-dependent SERS activity of Cu2O nanoplates associated with EM was studied by applying FDTD simulation. Meanwhile, the SERS activity correlated with CM was studied via the DFT calculation, advancing our understanding of the dominant contribution of chemical-boding and PICT enhancements to the occurrence of SERS. Owing to several tunable features inclusive of tunable band gap and carrier properties via introducing impurities and surface functionalities, the design of metal-oxide nanocrystal-based SERS-active substrates is beyond expanding the SERS to nonnoble metals and is promising for the biocompatible and in situ diagnosis for broad biological and biomedical applications.
A photolithography technique was applied for the fabrication of patterned Cu₂O nanoplate array. The stainless steel substrate was cleaned by ultrasonication in isopropanol and DI water for 20 min and dried with compressed air. AZ 1500 (Clariant, Switzerland) was spin-coated at 4000 rpm for 60 s and baked on a hotplate at 110 °C for 60 s. The photoresist was exposed using a URE-2000/35 UV mask aligner (Chinese Academy of Sciences, China) and it was developed in the AZ 3135 developer for 60 s. Thereafter, a complete CSE process was conducted on the as-prepared photoresist template to produce metallic Cu dot array, which was subsequently converted into Cu₂O nanoplate array. The photoresist was removed by rinsing with acetone and DI water after CSE.

Characterization: Field-emission scanning electron microscopy (SEM) images of Cu₂O nanocrystals were recorded by a Hitachi S-4800. Transmission electron microscopy (TEM) was carried out using a JEOL JEM 2010F. The binding energies of Cu and S were characterized using X-ray photoelectron spectroscopy (PHI VersaProbe II Scanning XPS Microprobe).

All Raman spectra were obtained by a confocal Raman microscope (LabRAM HR Evolution, Horiba Jobin Yvon) equipped with a diode-pump solid-state (DSPP) laser (532 nm) and a diode laser (785 nm), where the neutral-density filter (ND filter) was applied, and the laser was focused using a 100× objective (NA = 0.9). The number of gratings in the Raman microscope was 1800 groove mm⁻¹. The acquisition time of a single Raman spectrum was 3 s, while the acquisition time of the Raman map was 1 s for each pixel in the selected area of samples. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer.

Before Raman study, the as-prepared Cu₂O nanocrystals on the stainless steel substrate were immersed in PATP solutions with different concentrations for 3 h. The substrate was then washed thoroughly by DI water and dried with compressed air. AZ 1500 (Clariant, Switzerland) was used for Cu₂O nanocrystals under laser irradiation of 532 nm.[11] DFT analysis was implemented using the VASP code, in which an energy index with a real part of 3.133 and an imaginary part of 0.232 was basically predicts the electromagnetic field distribution by numerically solving Maxwell’s differential equations.[11] The complex refractive index with a real part of 3.133 and an imaginary part of 0.232 was used for Cu₂O nanocrystals under laser irradiation of 532 nm.[11] DFT analysis was implemented using the VASP code, in which an energy cutoff 800 eV was adopted.[11] The on-site repulsion U (7.5 eV) and the exchange correction parameter J (0.98 eV) were introduced to calculate the band gap of Cu₂O.

Supporting Information

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

Acknowledgements

S.P.F. and C.L. acknowledge the financial support from the General Research Fund of the Research Grants Council of Hong Kong Special Administrative Region, China (Award No. 17206518). N.X.F and C.L. acknowledge a seed project from MIT Energy Initiative and Institute for Technology (MIT). The authors would like to thank Gang Chen for sharing the Raman spectroscopy facility.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

chemical enhancement, Cu₂O nanopoltes, electromagnetic enhancement, shape-controlled synthesis, surface-enhanced Raman scattering

Received: March 25, 2019
Revised: May 22, 2019
Published online: July 3, 2019

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