Surface-Enhanced Raman Scattering on Hierarchical Porous Cuprous Oxide Nanostructures in Nanoshell and Thin-Film Geometries

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Supporting Information

ABSTRACT: Understanding the mechanism of surface-enhanced Raman scattering (SERS) of molecules on semiconductor nanostructures is directly related to our capabilities of designing and optimizing new SERS-active substrates for broad applications in the field of molecular detection and characterization. Here, we present an exploration of using cuprous oxide nanostructures with hierarchical porosity for enhancing Raman signals of adsorbed probe molecules. Distinct SERS signals were detected on both individual polycrystalline nanoshells and porous thin films composed of cuprous oxide nanocrystals. The observed enhancement of SERS signals can be interpreted as synergistic effects of strong chemical interactions between the probe molecules and cuprous oxide surfaces, localized electromagnetic field enhancement, and the unique hierarchical porosity of the nanostructures. Our work introduced a novel type of semiconductor substrates for high-performance SERS and extended the applications of cuprous oxide nanostructures to spectroscopy-based molecular sensing and characterizations.

SECTION: Nanoparticles and Nanostructures

Since its discovery in the mid 1970s,1−3 surface-enhanced Raman scattering (SERS) has received significant interest, ranging from widespread applications in chemical and biomolecular sensing and fabrication of SERS-active nanostructures to theoretical simulations and aided design of high-performance SERS substrates.4−6 Its high detection sensitivity and unique capability of identifying molecular structures make SERS a powerful analytical tool in a broad range of applications. The past two decades have witnessed significant advances in developing new strategies to construct nanostructured substrates with excellent SERS activity and reproducibility.7−10 While coinage metals and their alloys, either in the form of roughened surfaces or nanoparticle aggregates, have been extensively used for SERS, recent research in this field is more focused on fine-controlled hierarchical nanostructures that exhibit superior SERS performance.11−13 In addition to nanostructures of coinage metals, SERS-active substrates composed of transition metals14 or semiconductor materials15−18 have also emerged, and their enhancement mechanisms have been studied. The emergence of transition-metal and semiconductor nanostructures as SERS-active materials not only advances our fundamental knowledge of Raman enhancement but also expands and facilitates the choice of SERS-active substrates for much broader applications.

Similar to some other semiconductor materials, cuprous oxide (Cu2O) also has the potential to be a SERS-active substrate; however, comprehensive investigations have not been conducted thus far, and there is still a significant lack of sufficient data for further exploration and optimization. Cu2O, a p-type semiconductor with a bulk band gap of 2.2 eV, is an excellent functional material for low-cost photovoltaics,19 high-efficiency photocatalysis20,21 and other energy-related applications.22,23 Cu2O nanostructures of various geometries have been synthesized through bottom-up approaches,24−29 and their unique structure-dependent optical and catalytic properties have been discussed.30−32 For example, it has been recently demonstrated that the light absorption and scattering properties of Cu2O nanoshells can be fine-tuned across the visible and near-infrared spectral regions by tailoring the inner and outer radii of the nanoshells.33 The first example of using Cu2O as SERS substrates was reported by Kudelski and co-workers,34 who observed SERS of pyridine on both Cu2O hydrogel suspensions and Cu2O-coated copper electrodes. It has been recently observed that the Raman signals of 4-mercaptopyridine can be significantly enhanced when the molecules are adsorbed on the surface of Cu2O/Ag nanocomposites.34 However, to the best of our knowledge, there is no report on the direct use of Cu2O nanostructures as active substrates for SERS thus far. The relationship between the optical scattering and the SERS enhancement on Cu2O nanostructures has never been investigated.

In this Letter, we report an exploration of using Cu2O nanostructures with hierarchical porosity to enhance the Raman signals of adsorbed probe molecules. The SERS performance of...
both individual polycrystalline nanoshells and planar thin films composed of Cu$_2$O nanocrystals was evaluated. Strong chemical enhancement for SERS of probe molecules (4-aminothiophenol, 4-ATP) on the surface of the hierarchical Cu$_2$O nanostructures was observed, together with the enhanced Raman signals from dimercaptoazobenzene (DMAB) molecules, which were formed due to a surface dimerization process. In addition, geometry control of Cu$_2$O nanoshells through Ostwald ripening allowed us to observe a correlation between the scattering spectra and the SERS enhancements achievable on individual Cu$_2$O nanoshells. Furthermore, we estimated the electromagnetic contribution to the overall Raman enhancements by performing finite difference time domain (FDTD) simulations on the near-field enhancements of the porous Cu$_2$O hierarchical nanostructures upon optical excitation.

Geometry-dependent optical properties and SERS performance of individual Cu$_2$O nanoshells were systematically studied using a combination of dark-field optical microscopy, atomic force microscopy (AFM), and confocal Raman microscopy. Polycrystalline Cu$_2$O nanoshells were synthesized following the method reported recently, and their optical properties could be fine-tuned by varying the time of Ostwald ripening. Cu$_2$O nanoshells obtained after a 30 min Ostwald ripening process were first deposited on a glass substrate and incubated in a 0.8 mM 4-ATP solution for further characterization (see Supporting Information for details). Figure 1a shows the dark-field optical image of Cu$_2$O nanoshells on glass, where isolated nanoshells can be visualized. The AFM image of the same region, as shown in Figure 1b, confirms that these nanoshells are mostly isolated, individual particles without aggregation. The same area of the sample was also studied with confocal Raman microscopy, and a Raman intensity map (1435 cm$^{-1}$ peak) is shown in Figure 1c. We can clearly observe strong Raman signals from individual Cu$_2$O nanoshells, as shown in this Raman map. The Raman intensity on each isolated nanoshell varies, largely due to the slight variation in the overall size, shell thickness, and porosity of these nanoshells.

Raman scattering on Cu$_2$O nanoshells with different Ostwald ripening times was further examined, which allowed exploration over the SERS sensitivity dependence on the structure and optical properties of the nanoshells. Extinction spectra of Cu$_2$O nanoshells with various ripening times are shown in Figure 1d. Due to the mesoscopic overall sizes of these nanoshells, their optical extinctions are dominated by scattering rather than absorption, and complex extinction spectral line-shapes are typically observed primarily due to phase retardation effects. Although these porous nanoshells are polycrystalline and composed of a large number of randomly oriented nanocrystals, the observed extinction line shapes and geometry-dependent tunability are apparently the synergistic optical characteristics of the mesoscopic Cu$_2$O nanoshells rather than the primary Cu$_2$O nanocrystals inside the shells. Detailed studies on such geometrically tunable optical properties of Cu$_2$O nanoshells have been reported elsewhere. Typical TEM images of the nanoshells are shown in Figure S1 in the Supporting Information, which show the progressive increase of shell porosity and the decrease of the shell thickness as the Ostwald ripening proceeds. We have measured SERS spectra of 4-ATP on these individual nanoshells obtained after varying
ripening times. Figures 1e and f show representative SERS spectra and the intensity histograms of the 1435 cm\(^{-1}\) peak, respectively. The SERS spectrum on individual Cu\(_2\)O nanoshells with 5 min of ripening shows very low Raman intensity, while significantly enhanced Raman signals are observed on the nanoshells obtained after 30 min of ripening. Ostwald ripening for 30 min introduced significant changes to the structure of the nanoshells, including decreased shell thickness and increased shell porosity. Such a porosity increase can enhance the adsorption of 4-ATP molecules on the surface of Cu\(_2\)O nanocrystals and may promote a more significant lightning rod effect at the junctions of the nanocrystals. In addition, such a structural change also shifts the Mie scattering resonance frequencies of these mesoscopic particles with respect to the excitation laser wavelength and alternates the profile of the extinction spectrum, resulting in enhanced scattering cross sections at the wavelength of the laser excitation (532 nm). All of these can be major reasons for the increase of the SERS signals.

The Raman scattering peaks, obtained on these porous Cu\(_2\)O nanoshells, appear at positions of 1004, 1079, 1141, 1189, 1389, 1435, and 1576 cm\(^{-1}\), which are consistent with Raman spectra of adsorbed 4-ATP molecules.\(^{37-39}\) Among them, the peaks at 1141, 1389, and 1435 cm\(^{-1}\) were originally assigned to the \(b_2\) modes due to the photoinduced charge transfer.\(^{17}\) Recently, it has also been reported that these peaks belong to the \(a_g\) modes of the DMAB molecules because of surface chemical transformation.\(^{40,41}\) While the origin of these peaks is still controversial, we observed that the SERS activities of the nanoshells decreased upon further ripening reactions as the extinction maximum was further blue-shifted to be off-resonance with the excitation laser. After Ostwald ripening for 120 min, the nanoshell structures collapsed when a thin-shell limit was reached. Due to the shell collapse, the unique optical tunability of the nanoshells was no longer maintained, and the collapsed shells exhibited extinction spectral features extremely similar to those of primary nanoparticles that are \(\sim 15-30\) nm in size. The SERS intensities obtained on these collapsed nanoshells turned out to be only about 16% of those from nanoshells obtained after 30 min of ripening. This is quite reasonable by considering the facts that the packing density of primary nanocrystals inside of each collapsed nanoshell becomes much lower (see TEM images in Figure S1 in the Supporting Information) and that there is a significant decrease of the scattering cross section at the excitation laser wavelength in comparison to that of the porous nanoshells. It is also possible that some changes in SERS intensities are related to the size of the primary nanoparticles because the size effect was recently reported for SERS enhancement on semiconductor substrates.\(^{16}\) Additional SERS experiments with different laser excitations can further clarify the effects of optical scattering and the particle size on overall SERS enhancement, and the results will be reported and discussed elsewhere.

Although Cu\(_2\)O nanocrystals (\(15-30\) nm in size) have small scattering cross sections at 532 nm (the wavelength of the laser excitation), we figured out that it was still possible to gain great SERS activities by hierarchically assembling Cu\(_2\)O nanocrystals into porous thin films. Here, we demonstrate that SERS-active substrates can be obtained by making porous thin films composed of Cu\(_2\)O nanoparticles via a Meyer rod coating technique. The Cu\(_2\)O nanoparticles were synthesized following a previously reported procedure.\(^{42}\) The as-synthesized Cu\(_2\)O nanoparticles dispersed in methanol give a yellow-orange color, and the extinction spectrum (Figure 2a) shows two peaks at 352 and 452 \(\text{nm}\), which are characteristic features of Cu\(_2\)O nanoparticles with diameters of 15–30 \(\text{nm}\), as reported elsewhere.\(^{32}\) The overall spectral line shape is extremely similar to that of the collapsed nanoshells obtained after Ostwald ripening for 120 min. TEM measurements revealed irregular nanostructures, size distributions, and the agglomeration of Cu\(_2\)O nanoparticles in the porous thin films. As shown in Figure 2b, Cu\(_2\)O nanoparticles with an average size of 22.9 ± 2.6 \(\text{nm}\) were hierarchically assembled into a porous structure with a number of nanometer-sized and even subnanometer-sized gaps. Additional results of TEM and X-ray diffraction (XRD) measurements can be found in the Supporting Information (Figures S2 and S3).

Uniform thin films composed of these nanoparticles with tunable thicknesses can be fabricated on a large scale using the Meyer rod coating method. Figure 2c shows a SEM image, which illustrates the overall morphology of the thin film over an
area of tens of micrometers. It is worth noting that nanoparticle aggregates with sizes around 100 nm are observed, and these local aggregates result in porous structures in the thin films. A higher-magnification SEM image (shown as the inset of Figure 2c) clearly shows that each aggregate subdomain is composed of several primary nanoparticles with diameters in the range of 15–30 nm. Distinct Raman signals of probe molecules could be easily detected when we attached a monolayer of 4-ATP molecules onto the Cu$_2$O nanoparticle thin films. Figure 2d shows an enhanced Raman spectrum of 4-ATP molecules on a Cu$_2$O nanoparticle thin film that was immersed in 0.8 mM 4-ATP for 3 h. The Raman spectrum of bulk 4-ATP powder is also shown for comparison. To ensure a monolayer adsorption of 4-ATP on the substrate, the Cu$_2$O nanoparticle thin-film substrate was washed thoroughly with DI water to remove the excessive 4-ATP molecules and then dried under a nitrogen stream before the Raman study. The enhanced Raman scattering could also be observed when crystal violet was used as the probe molecules (Figures S4 in the Supporting Information).

The Raman enhancement capability of Cu$_2$O nanoparticle thin films was also investigated via a combination of optical microscopy and confocal Raman map. Figures 2e and f reveal a dark-field optical image and a confocal Raman map of the 4-ATP-coated Cu$_2$O nanoparticle thin film, respectively. The thin film exhibits excellent uniformity and shows greenish-blue color under the dark-field microscopy. The confocal Raman map was utilized to obtain a SERS intensity distribution in the same area (100 × 100 µm, red box in the optical image). The Raman map is based on the intensity of 4-ATP peaks ranging from 890 to 1753 cm$^{-1}$. It is clearly revealed that the prescratched area showed almost no Raman signal, and uniform Raman intensity was observed from the area that was covered with Cu$_2$O nanoparticles. As shown in Figure 2f inset, SERS from the Cu$_2$O-nanoparticle-covered region has a normal distribution for their peak intensity with a relative standard deviation of 25%. We assume that such intensity deviation might be attributed to the various nanogaps between Cu$_2$O nanocrystals, which were observed in the SEM and TEM investigations.

A detailed evaluation of the SERS performance of Cu$_2$O porous thin films involves careful examinations of several important factors, such as the effects of film thickness on the overall SERS intensities, the concentration effects of the probe molecules, and the reproducibility of Raman enhancements at different sites on the films. The Meyer rod coating method provides a convenient approach to fabricating large-area nanostructured thin films with tunable thickness and excellent uniformity. As shown in Figure 3a, the extinction spectra of Cu$_2$O nanoparticle thin films shows an increased extinction with an increased deposition via the Meyer rod coating. With the increase of the extinction due to thickness increase, the line shape and peak positions of the extinction spectra are quite identical, indicating a uniform increase of film thickness while well-preserving the optical characteristics of the thin-film structures. Figure 3b shows the Raman spectra of 4-ATP adsorbed on the Cu$_2$O porous thin films with different thicknesses under green light (532 nm, 0.88 mW) excitation. All of the peaks shown in the enhanced Raman spectra of 4-ATP are consistent with those in literature reports. The inset plot shows the relationship between the intensity of the Raman peak at 1435 cm$^{-1}$ and the intensity of extinction at 352 nm of the thin films. It is clear that the Raman intensity increases dramatically with the increase of the Cu$_2$O film thickness. The curve fitting indicates that as the layer increases, the Raman intensity increases exponentially. The increase of the Raman intensity might be due to the increasing number and/or area of SERS “hot spots” in the nanoscale interparticle gaps as a consequence of the thicker layer of Cu$_2$O nanoparticle thin films. The Raman intensities for the porous thin films are quite uniform, as discussed previously in the confocal Raman scanning experiments.

We have further investigated Raman spectra of the probe molecules adsorbed on Cu$_2$O nanoparticle thin films that were immersed into 4-ATP solutions with different concentrations. The overall uniform SERS intensity on Cu$_2$O thin films allows a detailed exploration on adsorption of the probe molecules, which could be very critical for small molecules such as 4-ATP. Figure 3c shows the Raman spectra from the thin films with 4-ATP concentrations varied from 8 × 10$^{-7}$ to 8 × 10$^{-4}$ M. The Raman intensities are mostly linear when the 4-ATP concentrations are low, and the Raman intensities are saturated when the solution concentrations are high. This result agrees with the model of Langmuir adsorption that has been discussed in detail by others. We could clearly observe 4-ATP Raman signals when a solution with a concentration as low as 8 µM was used.

We estimated the SERS enhancement factor (EF) on the porous Cu$_2$O nanoparticle thin films to be around 35 000 based on the known method. The SERS EF on nanoshells with a 30 min ripening process is estimated to be about an order of
due to adsorption of 4-ATP to Cu
electromagnetic field enhancement and chemical enhancement
Raman enhancement to a combination of scattering-induced
due to their structural and optical similarity. We attribute the
nanoshells and those on the collapsed nanoshells are similar
da result of the lightning rod effect, which was found to
be very significant for hierarchically assembled porous
nanostructures in comparison to that of individual solid
particles. As shown in Figure 4c and d, the porous Cu$_2$O
nanoparticle cluster has multiple spots with high EM intensity
due to the porous structures and nanoscale interparticle gaps.
The maximum EM intensity achievable inside of the porous
nanoparticle aggregate (Figure 4d) is 16.37, which is more than
double as compared to that of a solid Cu$_2$O sphere with a
similar overall size (Figure 4c). We have constructed 10 porous
nanoparticle aggregates and found that the simulated results
were quite reproducible (Figure 4e).

On the basis of both the experimental and computational
results, the observed Raman enhancement of the probe
molecules on the hierarchical porous Cu$_2$O nanostructures
can be most reasonably described as a result of the synergistic
effect of strong chemical interactions between molecules and
cuprous oxide surfaces, localized electromagnetic field enhance-
ment, and the unique hierarchical porosity of the nanostruc-
tures. With the recent study of SERS on semiconductor
substrates, there are plenty of reports on the strong chemical
interactions between probe molecules and semiconductors.$^{46}$
Because the thiol groups have strong affinity for transition
metals, we believe that in our case, 4-ATP can be strongly
adsorbed on Cu$_2$O nanoparticles. Such adsorption will possibly
induce charge transfer between the 4-ATP molecules and Cu$_2$O
nanoparticles and consequently enhance the Raman signals. On
the other hand, Cu$_2$O can also act as a surface catalyst that
promotes the molecular dimerization of 4-ATP to form DMAB,
which has a larger Raman cross section and a different way of
interacting with the Cu$_2$O surface to generate even stronger
Raman signals. In either mechanism, the chemical enhancement
of 4-ATP on the surface of Cu$_2$O nanocrystals is undoubtedly

Figure 4. FDTD simulations of the scattering-enhanced electric field: (a) electric field intensity as a function of the size of Cu$_2$O nanoparticles; (inset) electric field intensity of individual Cu$_2$O nanoparticles of 20 and 40 nm; (b) gap dependence of the intensities of the electric field enhanced by two nanocrystals; (inset) two Cu$_2$O nanoparticles (20 nm in diameter) with a gap of 2 nm; (c) FDTD simulation of a solid Cu$_2$O nanosphere; (d) FDTD simulation of a porous Cu$_2$O nanoparticle; (e) variation of the electric field intensity maximum in porous nanoparticle aggregates. The scale bars are 40 nm for all of the panels.

magnitude higher than that achievable on porous thin films if
we assume that the SERS enhancements on the porous Cu$_2$O
nanoshells and those on the collapsed nanoshells are similar
due to their structural and optical similarity. We attribute the
Raman enhancement to a combination of scattering-induced
electromagnetic field enhancement and chemical enhancement
due to adsorption of 4-ATP to Cu$_2$O nanostructures. We have
also assembled Cu$_2$O micrometer-sized polyhedral particles
into thin films. Under similar condition (8 × 10$^{-4}$ M 4-ATP
solution treatment), however, we detected extremely weak
Raman scattering from the thin films of micrometer-sized
particles (Figures S5 in the Supporting Information). It is
highly likely that micrometer-sized Cu$_2$O particles have a
relatively small surface area available for the adsorption of 4-
ATP and lack the porous hierarchical structures possessing a
large number of nanoscale interparticle gaps that may be crucial
for the local electromagnetic field enhancement.

Our experimental results can be further understood when
 correlated with a FDTD simulation. FDTD is one of the
primary available computational electrodynamic modeling
techniques, which can be applied to predicting near-field
electromagnetic (EM) distributions in the vicinity of an optical
scatter. We have conducted a series of computations to
understand the effects of hierarchical assembly of Cu$_2$O
nanoparticle clusters on the local EM field enhancement.
Figure 4a shows the size effect of Cu$_2$O nanoparticles on the
enhancement of the localized electromagnetic field. To more
quantitatively illustrate the local EM enhancement inside of the
nanoscale interparticle junctions, we performed FDTD
simulation on Cu$_2$O nanoparticle homodimers that are
composed of two identical nanospheres in close proximity to
each other. As shown in Figure 4b, the local EM field is
significantly enhanced when the interparticle gap is small in
comparison to the particle size. A total EM enhancement of
around 22 can be obtained for the hot spot between the 20 nm
particles with a gap of 2 nm (Figure 4b, inset). For 40 nm
particles, the electric field enhancements can be as high as 56.
Because Cu$_2$O is a semiconductor and its plasmon resonances
are not in the visible region, we believe such EM enhancement
can be a result of the lightning rod effect, which was found to
be very significant for hierarchically assembled porous
nanostructures in comparison to that of individual solid
particles. As shown in Figure 4c and d, the porous Cu$_2$O
nanoparticle cluster has multiple spots with high EM intensity
due to the porous structures and nanoscale interparticle gaps.
The maximum EM intensity achievable inside of the porous
nanoparticle aggregate (Figure 4d) is 16.37, which is more than
double as compared to that of a solid Cu$_2$O sphere with a
similar overall size (Figure 4c). We have constructed 10 porous
nanoparticle aggregates and found that the simulated results
were quite reproducible (Figure 4e).
demonstrated. Besides the chemical enhancement, electromagnetic enhancement can be another major reason for the strong Raman enhancements. Our preliminary FDTD simulation indicates that the local EM is easily enhanced by 4–8 times near individual Cu₂O nanoparticles with a size of 20–100 nm, while hot spots with much higher EM intensity can be obtained on hierarchically assembled nanoparticle aggregates. Although larger particles can result in a stronger local EM field, as predicted by FDTD calculations, we did not observe strong Raman EFs on the order of 10⁶−10⁸ as predicted by FDTD calculations, we did not observe strong Raman EFs on the order of 10⁶−10⁸. Our work presents, for the first time, a systematic study of the Raman enhancement on hierarchical porous Cu₂O nanostructures and opens up new opportunities of probing interesting physical and chemical processes that may occur on Cu₂O surfaces by SERS.

ASSOCIATED CONTENT

Supporting Information
Experimental details including syntheses of Cu₂O nanoparticles and the fabrication of porous Cu₂O thin films, additional sample characterizations, SERS spectra of crystal violet, SEM image of Cu₂O microcarpets, and details for FDTD simulation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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656


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Supporting Information

Methods

Syntheses of Cu₂O nanoparticles: The Cu₂O nanoparticles were synthesized according to a previously reported method.¹ All chemicals reagents for nanocrystal syntheses were analytical grade and were used without any further purification. In a typical synthesis, 3.333 g polyvinylpyrrolidone (PVP, Mw=1,300,000, Alfa) was dissolved in CuCl₂ (0.01mol/L, 100 ml) aqueous solution. Then, 10 mL NaOH (2.0 mol/L) solution was added dropwise into above transparent light green solution. During this process, the color of the solution was changed to turbid blue-green, and then to dark brown. After stirring for 0.5 h., an ascorbic solution (10 mL, 0.60 mol/L) was added dropwise into the dark brown solution. The mixture was aged at room temperature under constant stirring for three hours and the final solution changed to orange-yellow. After the reaction, centrifugation was used for several times to remove the residual inorganic ions and polymer. The final product was dispersed in methanol with a volume of 40
mL. Some products after purification were dried in vacuum at 50 °C for further characterization. For the synthesis of Cu₂O micro particles, we have followed a method reported elsewhere and D-glucose was used in the reaction. The size of Cu₂O particles was determined by SEM measurements and the products have been repeated several times in our experiments.

**Thin film preparation:** The Meyer rod coating was employed to fabricate scalable and uniform Cu₂O nanoparticle thin films. The glass substrate is put on a flat plate and a Meyer rod was pulled over the ink and substrate, which leaves a uniform layer of Cu₂O nanoparticles. The thicknesses of the thin films can be controlled by repeating the coating process. For enhanced Raman measurements, the well prepared Cu₂O nanoparticle thin films were incubated in 4-aminothiophenol (4-ATP) and crystal violet (CV) solutions for three hours, respectively, a similar procedure as being reported by others. The samples were then thoroughly washed using ethanol. This typical incubate-wash treatment could assure to get rid of the excess molecules on the surface. The Cu₂O thin films were then washed thoroughly using DI-water and dried under N₂ before the spectroscopic study.

**Characterization:** X-Ray powder diffraction (XRD, Rigaku Ultima IV diffractometer) was employed for crystal structure determination. Absorbance spectra were carried out on a Cary 50 UV-Vis spectrophotometer. Furthermore, the microstructures were analyzed by using transmission electron microscopy (TEM) on a FEI Tecnai electron microscope with an acceleration voltage of 120 kV. Scanning electron microscopy (SEM) was used for the examination of the morphologies of Cu₂O nanoparticle thin films. SEM micrographs were obtained on a Zeiss Supra40VP variable-pressure field-emission SEM. All SERS spectra and confocal Raman images were collected on an Aramis confocal microscope (Horiba Jobin Yvon, Edison, NJ) equipped with a diode-pump solid state (DSPP) laser (532 nm). The laser, with an intensity of 0.88 mW, was focused using a 50× objective (NA 0.75) onto the samples on the glass slides, which were mounted onto a 200×200×200 μm piezo scanner. The Raman signals were collected with the same objective under a 180° back-scattering configuration and passed through an edge filter into a monochrometer and electric-cooled charge-coupled devices (CCD) camera. To obtain a Raman map, an array of Raman spectra was collected when the laser was raster scanned across a selected area of the sample. The Raman spectra were acquired for 1 s at each pixel. The spectra were then mathematically processed, and the intensity distribution for the Raman peaks of interest can be revealed.
Experimental results

TEM images of polycrystalline nanoshells are shown in Figure S1, where the porosity changes during the Ostwald ripening process can be clearly observed. This result is consistent with what has been reported previously.⁵

![TEM images of nanoshells](image)

**Figure S1.** TEM images of nanoshells obtained after Ostwald ripening for (a) 5 minutes; (b) 30 minutes; (c) 60 minutes; and (d) 120 minutes.

TEM measurements of Cu₂O nanoparticles revealed irregular nanoscale structures, size distributions, and the agglomeration of Cu₂O nanoparticles. As shown in Figure S2a, the Cu₂O
nanoparticles with size below 40 nm were aggregated in a porous manner, which is very similar to that of SEM observations. The size distribution of nanoparticles was obtained as shown in the inset of Figure S2a where about 150 nanoparticles were measured and the histogram shows a normal distribution with an average size of $22.9 \pm 2.6$ nm. Figure S2b gives a HRTEM image of a Cu$_2$O nanoparticle which clearly indicates the crystal lattice structure. The lattice plane distance is 3.0 Å, which can be assigned to the d space of (110) planes for cubic phase Cu$_2$O crystals. The corresponding fast Fourier transform pattern of the HRTEM image is shown in the Figure S2b inset, indicating a highly crystalline quality of Cu$_2$O nanoparticles.

**Figure S2.** a. TEM micrograph of Cu$_2$O nanoparticle aggregations, inset: size distribution of Cu$_2$O nanoparticles; b. HRTEM image of a Cu$_2$O nanoparticle with high crystallinity, inset: corresponding fast Fourier transfer image.

The Cu$_2$O crystal structure was further confirmed by X-ray powder diffraction (XRD) and Raman spectroscopy. Figure S3a exhibits the XRD pattern of as-prepared Cu$_2$O nanoparticles. We notice that all of the peaks have well agreed with Bragg reflections of the standard cubic cuprite structure (Pn3m a = 4.267 Å PDF card No.078-2076). Such XRD results confirmed the purity of our Cu$_2$O crystalline structures and indicated that there are no detectable crystalline structures of any contaminations. The Cu$_2$O nanoparticle crystal structure was further confirmed by Raman spectroscopy (Figure S3b). Three shape Raman shift peaks at 96, 151, 220 cm$^{-1}$ can be observed, and these peaks match perfectly with literature reports.}

\[^6\]
**Figure S3.** a, XRD pattern of the as-synthesized Cu$_2$O nanoparticles; b, typical Raman spectrum of Cu$_2$O nanoparticle thin film.

**Figure S4.** Enhanced Raman spectra of crystal violet (CV) obtained on Cu$_2$O nanoparticle thin films that were incubated with CV solutions of different concentrations.
**Figure S5.** a, Raman spectra of 4-ATP in the same concentration (0.8 mM) with different substrates, Cu$_2$O nanoparticle thin film and Cu$_2$O micro particle thin film; b, SEM image of the Cu$_2$O micro particle used in the Raman measurement in a.

**FDTD simulation**

Theoretical simulation of the near-field electro-magnetic intensity was conducted via a Finite-difference time-domain (FDTD) approach by using EM Explorer software. The optical constants of cuprous oxide ($n = 3.113$, $k = 0.232$, with an irradiation of 532 nm light) are obtained from SOPRA N&K Database. A 128 nm grid size and 1.0 nm Yee cell were used in our calculations for single Cu$_2$O particle simulation. The porous nanoparticle aggregates in the simulations were constructed by 200 Cu$_2$O nanocrystals (20 nm in diameter) randomly distributed within a large sphere of 114 nm (the average size of particle aggregations). 256 nm grid size and 1.0 nm Yee cell were used in the simulation. We have done multiple simulations on porous nanoparticle aggregates and two examples are shown in Figure S6. The results were processed with ParaView software for visualization.
Figure S6. Typical two examples of porous nanoparticle aggregates that were simulated. The red color on the small particles is generated during the three dimensional construction rather than represent the EM intensity.

References


