Electronic Supplementary Information

Colloidal porous gold nanoparticles

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Supplementary text

Synthesis of the PbS nanooctahedrons
PbS nanooctahedrons were grown according to a previously reported method with slight modification.1 Specifically, water (34.26 mL) was added in a 50-mL plastic centrifugation tube, followed by the sequential addition of the aqueous solutions of thioacetamide (2.04 mL, 0.5 M), CTAB (2.57 mL, 0.1 M), lead acetate (2.04 mL, 0.5 M) and acetic acid (4.10 mL, 1 M). Deionized water with a resistivity of 18.1 MΩ cm was used in all preparations. The mixture solution was capped and then left in an 80 °C oven for 8 h.

Synthesis of the colloidal porous Au nanoparticles
The porous Au nanoparticles were synthesized through Au overgrowth on the PbS nanooctahedrons, accompanied by the etching of PbS with the growth solution. The Au growth solution was prepared by the addition of HAuCl4 (0.5 mL, 0.01 M) into CTAC (10 mL, 0.1 M). The as-grown PbS nanooctahedron solutions in different volumes were then injected under vigorous stirring to control the size of the porous Au nanoparticles. After the
injection of the PbS nanoctahedrons, AA (0.5 mL, 0.1 M) was added rapidly under vigorous
stirring. The obtained mixture solution was then left undisturbed for one week. After reaction,
the solution was centrifuged to remove the unreacted species. The product was washed with
HCl acid (0.1 M) once to completely remove the PbS component. In the study of the
surfactant effect, the CTAC solution was changed with CTAB or CTAB–CTAC mixture
solution. In the study of the AA effect, the amount of AA was changed, with the other
conditions kept unchanged.

Characterization
SEM imaging was performed on a Hitachi SU-8020 microscope. TEM imaging and EDX
measurements were carried out on an FEI Tecnai G2 F20 microscope operated at 200 kV.
HAADF-STEM and HRTEM imaging were performed on an FEI Tecnai F20 microscope.
XPS measurements were carried out on a Thermo-VG Scientific ESCALAB 250
spectrometer with Al Kα radiation ($h\nu = 1486.6$ eV). The mass concentrations of Au in the
Au nanoparticles were determined using a PerkinElmer Optima 4300 DV inductively coupled
plasma optical emission spectrometer. Extinction spectra were taken on a Shimadzu UV-3600
ultraviolet/visible/near-infrared spectrophotometer.

Single-particle dark-field scattering measurements
The samples for single-particle dark-field scattering measurements were prepared by drop-
casting the porous Au nanoparticle suspension on conductive ITO-coated glass substrates.
The dropped suspension was kept on the substrate for 1 min and then blown dry with N₂. The
scattering signals from the individual porous Au nanoparticle was measured on a dark-field
microscope (Olympus BX61) that was integrated with a quartz-tungsten-halogen lamp (100
W), a monochromator (Acton SpectraPro 2300i), and a charge-coupled device camera
(Princeton Instruments Pixis 400). The camera was thermoelectrically cooled to -70 °C
during measurements. A dark-field objective (100×, numerical aperture: 0.9) was employed
for exciting and measuring the scattering signals from the individual porous Au nanoparticles.
A pattern-matching method was employed to correlate the geometrical structure of the porous
Au nanoparticles from SEM imaging with the single-particle scattering characterization. The
obtained scattering spectra were calibrated according to our previously reported method.²

Finite-Difference Time-Domain Simulations
All three-dimensional FDTD simulations were performed using FDTD Solutions v8.6 (Lumerical Solutions). During simulations, an electromagnetic pulse from 400 to 1200 nm was launched into a box containing a target nanoparticle. The nanoparticle and its surrounding medium were divided into meshes of 0.5 nm in size. The porous Au nanoparticle was constructed using nanorods with different lengths and radii. Short nanorods were attached randomly on long nanorods to form branches. The branches were then placed in random radial directions to create a porous Au nanoparticle. The size of the porous Au nanoparticle was set according to the average size measured from the TEM images. The radii of the nanorods were also set as the values measured from the TEM images. Since the internal structures of the nanoparticles are different from each other, we employed a trial-and-error method to adjust the number of the branches within the nanoparticles. When the extinction spectrum of the model became very close to the measured one, the model was employed in the further FDTD simulations. For the simulation of the porous Au nanoparticle in water, the refractive index of the surrounding medium was set to 1.33. For the porous Au nanoparticle deposited on the ITO substrate, the refractive index of the medium in the top and side regions was taken to be 1.0 and that in the bottom was set to 1.9 for the ITO-coated glass substrate. The dielectric function of Au was taken from previously measured values.3

SERS Measurements
In the SERS measurements in aqueous solutions, the porous Au nanoparticles and a gold nanosphere sample with the particle concentration of 0.46 nM were incubated in an aqueous solution containing $10^{-5}$ M CV for 8 h. The solution was then transferred to a cuvette for the SERS measurements. In the substrate-based ensemble SERS measurements, the substrate samples for the porous Au nanoparticles and the Au nanospheres were prepared by drying 50 μL of the nanoparticle dispersion with the particle concentration of 4.1 nM on clean Si wafers (1 cm × 1 cm). In a typical procedure, 25 μL of an aqueous CV solution ($10^{-6}$ M) was dropped and dried on each treated Si substrate in dark. The substrate was then washed with water for three times. For the single-particle SERS measurements, the substrate was prepared by dropping 100 μL of the porous Au nanoparticle suspension on a clean Si wafer. The dropped suspension was kept on the substrate for 1 min and then blown dry with N$_2$. The resultant substrate was then immersed in an aqueous CV solution ($10^{-6}$ M) overnight for the adsorption of the Raman probe molecules. The substrate was finally rinsed with water to remove unbound CV molecules and dried in flowing N$_2$. All SERS spectra and SERS mapping images were acquired on a Renishaw inVia Reflex Raman microscope and
A 532-nm laser was employed for excitation. The excitation laser light was focused on the sample through an air objective (50×, numerical aperture: 0.75). The laser power was 0.5 mW in all SERS measurements. The signal acquisition time was fixed at 20, 1 and 20 s for the solution, substrate ensemble and substrate single-particle SERS measurements, respectively. The signals for the SERS mapping on the single nanoparticles were collected at 1617 cm⁻¹. A code for automated mapping was used to control the movement of the stage in a step of 0.1 μm during the mapping measurements. The enhancement factors (EFs) were estimated according to the single-particle measurement results using the expression \( \text{EF} = \frac{I_{\text{surface}}}{I_{\text{solution}}} \times \frac{N_{\text{solution}}}{N_{\text{surface}}} \), where \( N_{\text{solution}} \) and \( N_{\text{surface}} \) represent the numbers of CV molecules probed in a standard solution and on the nanoparticle, \( I_{\text{solution}} \) and \( I_{\text{surface}} \) represent the normal and SERS signal intensities, respectively. \( I_{\text{solution}} \) and \( I_{\text{surface}} \) were measured using an identical laser power. \( N_{\text{solution}} \) and \( N_{\text{surface}} \) were determined according to the previously reported method.

**Electrochemical Measurements**

Electrochemical measurements were carried out using an electrochemical workstation (CHI660E). The standard three-electrode configuration was employed. A glassy carbon electrode deposited with the porous Au nanoparticles or the Au nanospheres was used as the working electrode, a saturated calomel electrode as the reference electrode and the counter electrode was a Pt wire. A 0.5 M KOH solution was used as the electrolyte. The working electrode was prepared by drop-casting 5 μL of the porous Au nanoparticle or the Au nanosphere suspension with the Au mass concentration of 0.2 mg mL⁻¹ on the glassy carbon electrode surface. The electrode was dried in air for 1 h at room temperature before use.

** Supplementary figures**
**Fig. S1**  SEM image of the PbS nanoctahedrons. The PbS nanoctahedron sample was used to synthesize the porous Au nanoparticles.

**Fig. S2**  Effect of the surfactant. Shown are the SEM images of the Au nanoparticles prepared using CTAB and CTAC at different molar ratios. (a) 0.10 M CTAB only. (b) 0.08 M CTAB and 0.02 M CTAC. (c) 0.06 M CTAB and 0.04 M CTAC. (d) 0.05 M CTAB and 0.05 M CTAC. (e) 0.04 M CTAB and 0.06 M CTAC. (f) 0.02 M CTAB and 0.08 M CTAC. (g) 0.10 M CTAC only.
**Fig. S3**  TEM image of the colloidal porous Au nanoparticle sample. This large-area TEM image shows the high purity and high size uniformity of the nanoparticle sample.

**Fig. S4**  Effect of the AA amount. Shown are the TEM images of the nanoparticles produced by adding AA in different volumes, which are indicated above the TEM images. The concentration of AA is 0.1 M. The molar ratios between AA and HAuCl₄ are also provided. The reaction time is fixed at 8 h. For 50-μL AA, the etching is nonuniform. Some PbS nanoparticles are almost completely etched, while the etching of some other PbS nanoparticles is difficult to be observed.
Fig. S5  Growth process. The TEM images were taken for the products obtained for different periods of the reaction time, as indicated above the TEM images.

Fig. S6  Size control. (a–e) SEM images of the porous Au nanoparticle samples obtained by adding different amounts of the PbS nanoctahedrons. The added volumes of the PbS nanoctahedron solution are 50, 60, 70, 80 and 90 μL, and the average sizes of the corresponding nanoparticle samples are 168 ± 9, 145 ± 7, 136 ± 8, 123 ± 10 and 119 ± 9 nm, respectively. (f) Extinction spectra of the five porous Au nanoparticle samples.
Fig. S7  Dark-field scattering spectra. Twenty scattering spectra were measured on the individual porous Au nanoparticles. There are two scattering peaks. The average wavelengths of the high- and low-energy peaks are 451 ± 6 and 686 ± 14 nm, respectively.

Fig. S8  FDTD simulations. The porous Au nanoparticle is supported on the ITO substrate. (a) Schematics of the two excitation polarizations. (b) Simulated scattering spectra under the two excitation polarizations. The diameter of the porous Au nanoparticle used in the simulation is 168 nm.
Fig. S9  SERS measurements. The SERS spectra were recorded from the solutions containing the porous Au nanoparticles and CV, with the concentration of CV varied. The concentrations of CV are labeled on the corresponding spectra. When the CV concentration is $10^{-10}$ M, no Raman signal can be detected from CV.
Fig. S10  Individual porous Au nanoparticles. (a) SEM image of the region for SERS mapping. (b) SEM images of the imaged individual porous Au nanoparticles.
**Fig. S11**  SERS of the individual Au nanospheres. (a) SEM image of the region for SERS mapping. (b) SERS mapping image. The Raman signal of CV for imaging was detected at 1617 cm\(^{-1}\). (c) SEM images of the imaged individual Au nanospheres.

**Fig. S12**  Single-particle SERS measurements. The SERS spectra of CV were recorded on a single porous Au nanoparticle (p-Au NP), on a single Au nanosphere (Au NS) and on a Si substrate without any metal nanoparticles. All of the substrates were treated with CV.
**Fig. S13** Electric field intensity enhancements. The enhancements of the porous Au nanoparticle were simulated at the wavelength of 532 nm. (a) Under in-plane polarized excitation. (b) Under out-of-plane polarized excitation.

**Fig. S14** Stability of the porous Au nanoparticles. (a) Cyclic voltammetric response of the freshly prepared porous Au nanoparticles and the porous Au nanoparticles stored after a half year, respectively, in 0.5 M KOH with methanol. (b) Chronoamperograms of the electrodes made of the porous Au nanoparticles (p-Au NPs) and the Au nanospheres (Au NSs) at their corresponding peak oxidation potentials. The oxidation peak of the porous Au nanoparticles stored after a half year exhibits a slight negative shift, with slight reduction of the peak current. Such changes might arise from the difference during the preparation of the working electrodes. The long-term storage therefore has a minor effect on the catalytic activity. The current for methanol oxidation shows a rapid decay in the beginning and then gradually reaches a steady state. The rapid decay of the current in the beginning can be attributed to the accumulation of poisonous intermediate species. After the reaction lasts for 3 h, the oxidation
current of the porous Au nanoparticles is 12.2 μA/μg, indicating that the porous Au nanoparticles have relatively good durability during methanol oxidation.

**Supplementary table**

**Table S1**  Typical Raman enhancement factors (EFs) of colloidal plasmonic nanoparticles arranged in the order of decreasing EFs

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>EF</th>
<th>Excitation wavelength</th>
<th>Reference</th>
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<tr>
<td>Starlike Au nanoparticles (on Au films)</td>
<td>~10^{12}</td>
<td>830 nm</td>
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<td>Ag–Au bimetallic nanodendrites</td>
<td>~10^{11}</td>
<td>633 nm</td>
<td>7</td>
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<td>Au nanostars (on Au substrates)</td>
<td>~10^{10}</td>
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<td>AuAg alloy nanomurchins</td>
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<td>633 nm</td>
<td>9</td>
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<tr>
<td>Au nanostars (on Au films)</td>
<td>~10^9</td>
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<td>10</td>
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<td>----------------------------</td>
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<tr>
<td>Au nanoparticles with 1-nm gap</td>
<td>(1–50) × 10^8</td>
<td>633 nm</td>
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<td>Nanoporous Au disks</td>
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<td>Mesoscopic Au meatball particles</td>
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<tr>
<td>Porous Au nanoparticles</td>
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<td>This work</td>
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<td>Au nanostars</td>
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<td>Holey AuAg alloy nanoplates</td>
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<td>Porous Au nanoparticles</td>
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<td>Coarse Au nanoparticles</td>
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<td>Porous AuAg alloy nanoparticles</td>
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<td>Self-assembled plasmonic vesicles</td>
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**Supplementary references**


