Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Aligned octahedral core in a nanocage: synthesis, plasmonic, and catalytic properties

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Experimental Details

Chemicals

Gold(III) chloride solution ($HAuCl_4$, 99.99%, 30 wt. % in dilute HCl), sodium borohydrite ($NaBH_4$, 98%, powder), cetylmethylammonium bromide (CTAB, 99.0%, BioUltra, for molecular biology), cetylpyridinium chloride monohydrate (CPC, USP grade), L-ascorbic acid (AA, anhydrous, ACS grade), oxazine (dye content 95%), N,N-Dimethylformamide (DMF, anhydrous, 99.8%) and potassium bicarbonate ($KHCO_3$, 99.7%, ACS grade) were purchased from Sigma-Aldrich. Thiol-terminated polystyrene (M_n=5300g/mol, M_w/M_n=1.10) was purchased from Polymer Source. Carbon paper (Toray) was purchased from Fuel Cell Store. The water used in the syntheses and electrolyte preparation was ultrapure (Millipore, 18.2 MΩ·cm).

Synthesis of Au octahedral seeds

To synthesize 3 nm Au nanoparticles (Figure 1-top, step 1), ice-cold, freshly prepared $NaBH_4$ (10mM 0.6mL) was quickly added into a vigorously stirred mixture of $HAuCl_4$ (15mM, 0.167mL) and CTAB (0.1M, 10.0mL). This solution was stirred for 2 min, then left undisturbed for exactly 2 hours and after that diluted to 50 mL with Milli-Q water. For the synthesis of CTAB-capped Au octahedral seeds (Figure 1-top, step 2), 100mL of 0.2M CTAB, 2.66 mL of 15mM $HAuCl_4$, and 50 mL of 0.12M ascorbic acid were mixed together under mild stirring, the resultant colorless mixture was diluted to 1L. After that, 6 mL of the formerly prepared 3 nm-size Au NPs was immediately added to the vigorously stirred mixture and left undisturbed at room temperature for 12 h. The as-prepared product was concentrated to 5 mL by centrifugation (15 min, 16000 g), and washed with Milli-Q water twice to replace the surfactant-rich solution with deionized water.

Synthesis of Au/Ag core-shell nanocubes

In a typical procedure (Figure 1-top, step 3), 2.5mL of the concentrated Au octahedral seeds and 5mL aqueous solution of CPC (0.3M) were mixed in a 15mL vial. While the solution was heated up to 60°C using thermomixer (1000 rpm mixing rate), 1mL of 10mM $AgNO_3$ and 4mL of 1M ascorbic acid were added consecutively under the vigorous stirring. After 1h of reaction, the vial was cooled down to room temperature. The resulting 30 nm-size NCs were centrifuged at 100g for 10 min to remove AgCl powder (which is formed from unreacted silver nitrate and chloride anion of CPC[1]), then washed at 13000 g for 15 min, and finally re-dispersed in 62.5 mL Milli-Q water.

Synthesis of Au core-cages

0.1 mL of 1mM $HAuCl_4$ was added dropwise (2 ml/min addition rate) into 1 ml of diluted Au/Ag core-shell nanocubes under vigorous stirring (Figure 1-top, step 4). After 10 minutes 0.05 mL of 30% H_2O_2 was injected in the same manner as $HAuCl_4$ (Figure 1-top, step 5). The resulting Au core-cages were washed by centrifugation at first at 16000 g for 15 min and then at 120 for 20 min to remove AgCl powder.

Synthesis of spherical Au nanoparticles

To synthesize nanospheres, we used the following seed-mediated approach[2]. As synthesized Au octahedral seeds were subjected to etching by a mixture of H_2O_2

(0.2mL, 1.0M) and HCl (0.2mL, 1.0M) for 5 min, followed by two washing cycles at 15000 g and replacing the supernatant with 0.1M CPC solution. The obtained Au seeds were used for further Au reduction on their surface, by subsequently adding 15mM $HAuCl_4$ and 0.12M ascorbic acid solutions under stirring at room temperature, which yielded 30 nm-size nanospheres. The nanoparticles were purified by three rounds of centrifugation at 12000 g, and finally redispersed in MilliQ water.

Nanoparticles characterization

UV-Vis spectra were recorded using Cary 5000 UV-Vis-NIR spectrophotometer and Ocean Optics Flame UV-Vis spectrometer. Scanning and transmission electron microscopy images were recorded using Hitachi S5200 STEM (SEM and bright field TEM images, recorded at 10-30 kV accelerating voltage) and Hitachi HD2000 STEM (bright and dark field TEM images, 200 kV accelerating voltage).

SERS Experiments

A Raman reporter, oxazine 720, was introduced into the solution of core-cages functionalized with thiol-terminated polystyrene (PS-SH); this surface functionalization was used to render solvent compatibility between the reporter and the nanoparticles. PS-SH-functionalized core-cages were obtained using previously reported ligand exchange procedure[2]. Briefly, 0.2 mL of ~50 times concentrated solution of nanoparticles in water was rapidly injected under sonication into thiol-terminated polystyrene (M_n=5300g/mol, M_w/M_n=1.10) solution in dimethylformamide (10 ml, 0.1mg/ml). After subsequent removal of free PS-SH from the core-cages solution via multiple centrifugation, oxazine 720 was added to the solution of nanocages (to have a final oxazine concentration of 20 μM). The resultant solution was incubated for 2 hours; then, a droplet of the core-cage solution sample was deposited onto a microscope slide. Core-cages concentration in this solution was determined to be 0.75 nM (as Au octahedral cores were quantitatively converted into Ag/Au core-shell nanocubes and subsequently into Au core-frames, the final Au core-frames concentration was determined from UV-vis spectral analysis of Au octahedral cores, according to their average size from TEM image analysis and corresponding extinction coefficient[3]).

Raman spectra were recorded using Horiba HR800 spectrometer equipped with an upright microscope with a 20× (0.35 NA) objective lens, and two interchangeable excitation sources, 785 nm and 532 nm (both set to the same laser power of 23 mW). The Raman spectra were baseline corrected to remove the background signal from the substrate.

Numerical Calculations

The optical response of the core-cage nanostructure was numerically investigated using finite difference time domain (FDTD) method from Lumerical Inc. The dielectric constant of gold was modeled using the experimental data from Ref [4]. A perfectly matched layer was used to terminate the simulation domain to minimize reflections. The various cross-sections were calculated using the formalism of total field scattered field in the FDTD method. Figure S5 shows the results of a simple gold cage without surface perforations and core for comparison. The cage structure shows a single resonance at 630 nm and the resonance is comparatively narrow. The maximum field intensity enhancement is about three times larger compared to the core-cage structure but this enhancement exists for a narrow band of frequencies.

Details of the estimation of the normalized E-field intensity around and within the core-cage surface as a function of the incident light wavelength (Fig. 4j, k, l, main text): we calculated the average value of $|E/E_0|^2$ in the volume defined as a 36×36×36 nm^3 cube with a centered core-cage of 30 nm side-length within, minus the metal region (i. e., the core-cage structure itself). The cube size was selected to include the region around the core-cage up to 3 nm away from its surface in all directions, as E-field enhancement dissipates quickly with increasing the distance from the outer surface (4d-i, main text), and is negligible further away from the core-cage surface.

Photoelectrochemistry

Experiment was performed using a three-electrode system connected to an electrochemical workstation (BioLogic SP-300 High-End Potentiostat). Ag/AgCl (with saturated KCl as the filling solution) and platinum mesh were used as reference and counter electrodes, respectively. Carbon paper (Toray TGP-H-060, purchased from Fuel Cell Store) was used as a substrate (0.75 cm^2) for working electrode preparation. Au core-cages and spherical Au aqueous NP solutions concentration were adjusted to the same optical density of 0.4 at 530 nm, and 200 μL of the solutions were drop-casted onto carbon paper substrates (working area 0.5 cm^2) and dried at room temperature. The electrolyte (0.5 M $KHCO_3$) was saturated with CO_2 for at least 30 min prior to acquiring the electrochemical data.

Electrode potentials were converted to the reversible hydrogen electrode (RHE) reference scale using the following equation: $E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + 0.197\ \mathrm{V} + 0.0591 \times \mathrm{pH}$. Linear sweep voltammetry (LSV) was performed at a scan rate of 50 mV/s from 0.0 V to -0.8 V vs RHE in dark and under visible light (400-800 nm) illumination (Plasma Light Source Thorlabs HPLS345). The electrochemical cell was thermostated at 25^0C for all experiments.

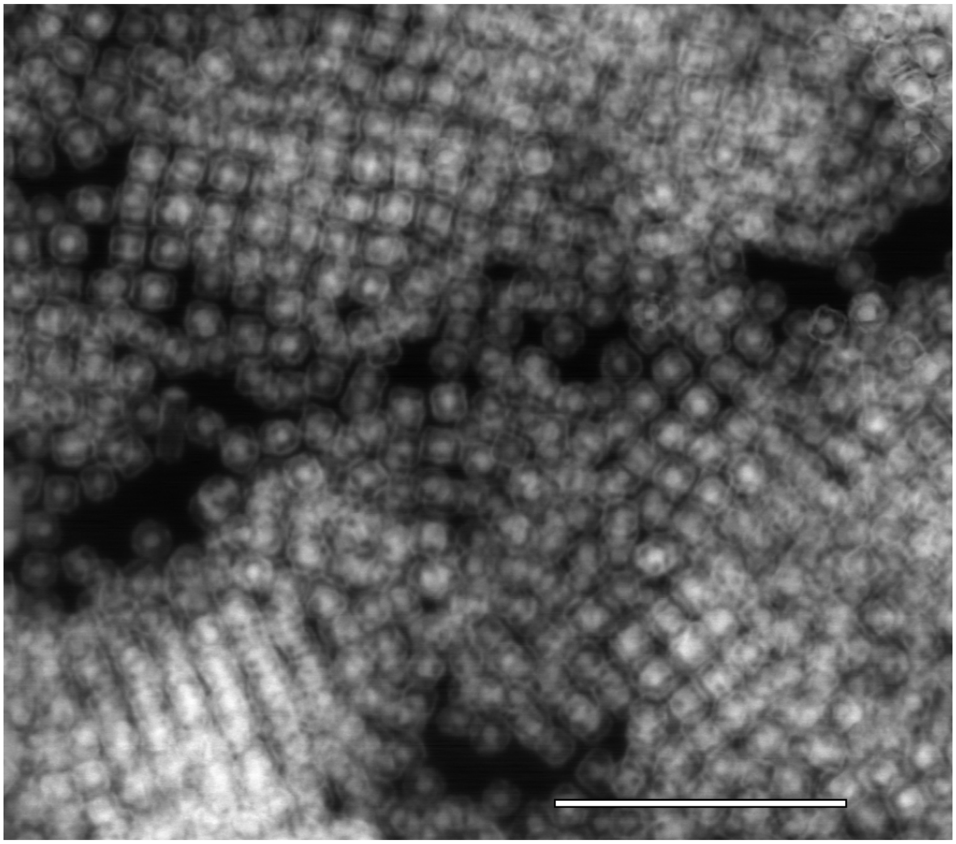

Figure S1. Low magnification dark field TEM images of core-cages obtained using standard protocol; scale bar is 300 nm.

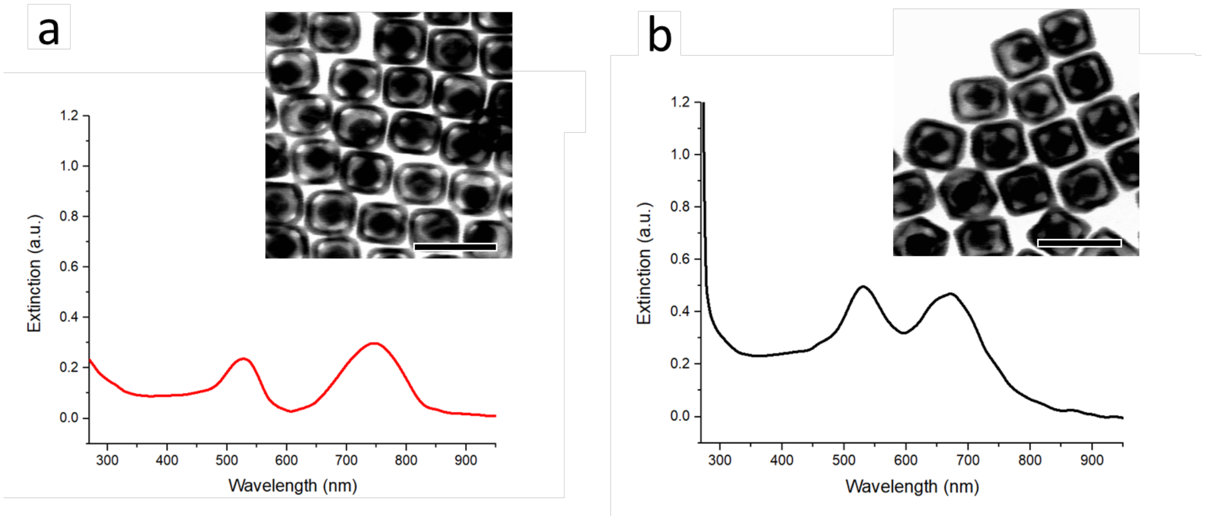

Figure S2. Extinction spectra of core-frames obtained with larger amounts of $HAuCl_4$ added at the step 4 of the synthesis (Figure 1), resulting in the thicker frame thickness compared to the original synthesis: wall thickness in (a) 4.0±0.4 nm, (b) 5.3±0.9nm. Insets show representative bright field TEM images of obtained particles; scale bars are 50 nm.

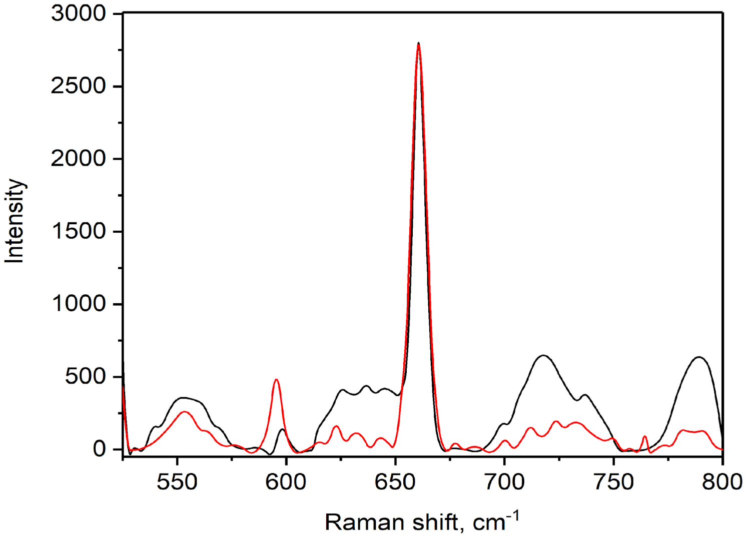

Figure S3. SERS spectra of 0.75 nM PS-stabilized Au core-cages in the presence of 20 μM oxazine in DMF acquired at 532 nm excitation wavelength. The molecular weight of PS ligands was 5000 g/mol. Raman spectra of the control with no nanocages (gray line) and with nanocages (red line). Fluorescence background correction function of the Raman microscope was employed to minimize minor fluorescence contribution to the SERS spectra.

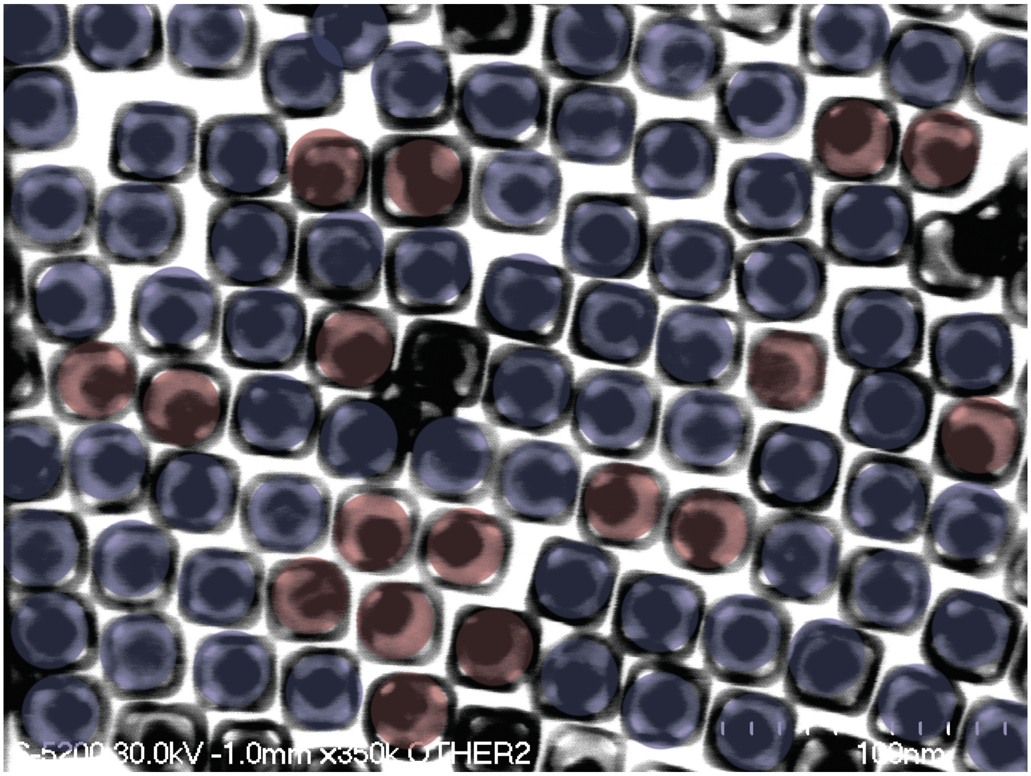

Figure S4. An example of TEM image analysis to determine the populations of centered vs cornered core position assessment: analysis of 1000+ cages showed 80% predominance of centered core-frames (marked in blue) vs 20% of core-frames with cornered core (marked in red).

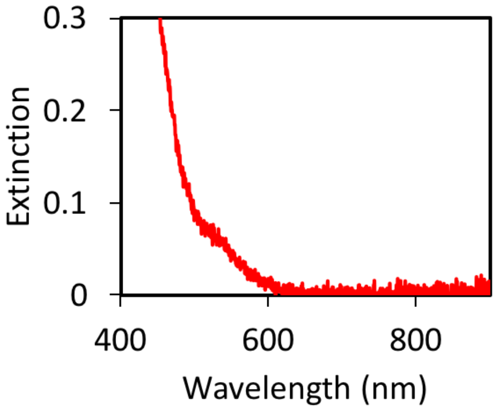

Figure S5. Extinction spectrum of the gold seeds obtained in the step 1 of the core-cage synthesis (refer to Figure 1 of the main text). The shoulder peak is characteristic of gold nanoparticles with very small size (diameter < 3 nm)[5].

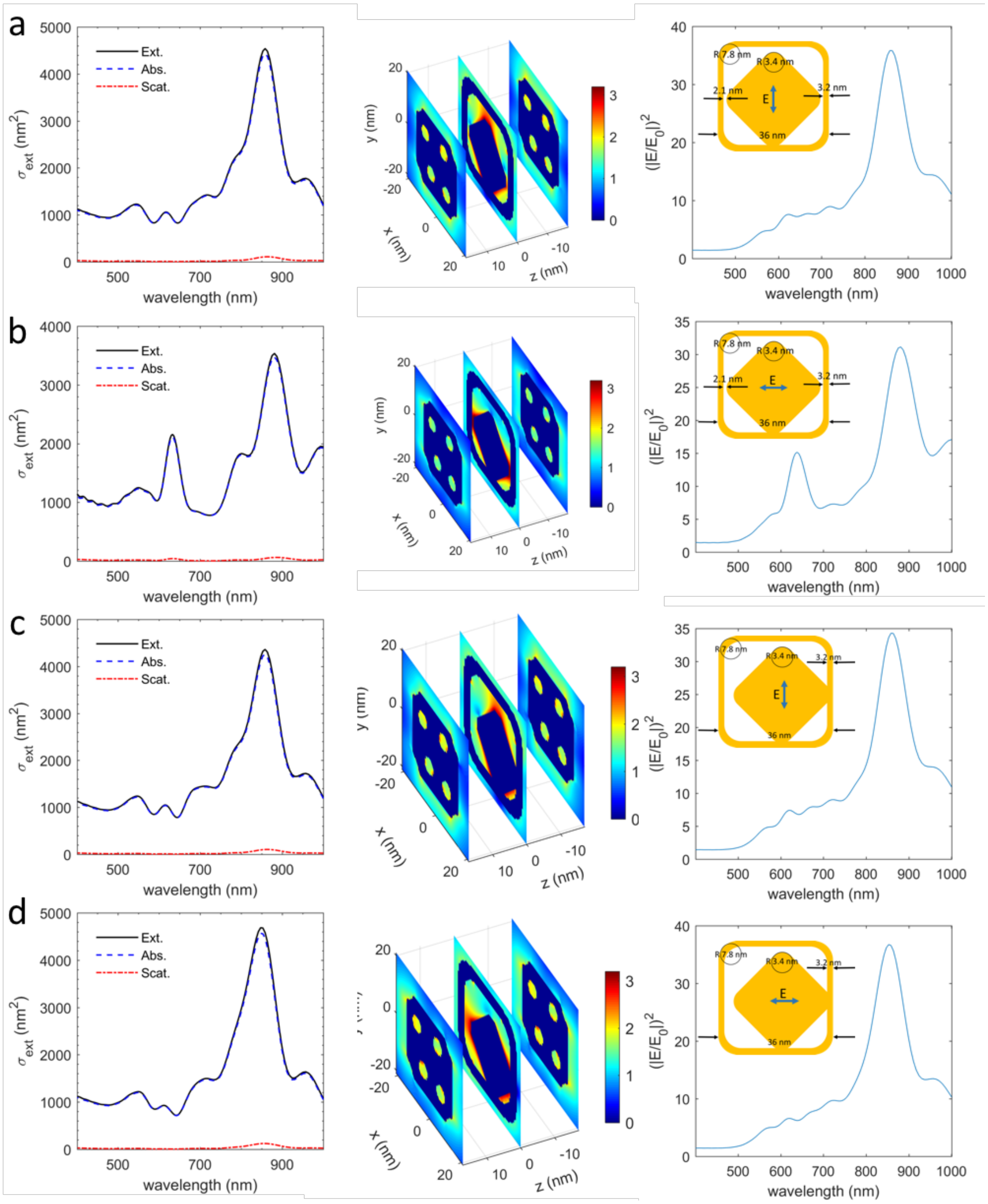

Figure S6. FDTD simulations of core-cage nanostructures with the core attached to one (a, b) and two (c, d) faces of the cage, while being aligned (all vertices facing the walls of the cubic cage). Left graphs show extinction, absorption and scattering cross-sections, central figures show normalized electric field intensity profiles at corresponding extinction maxima, and right graphs show average field intensity enhancement. The feature sizes and polarization are shown in the corresponding cartoon insets on the right.

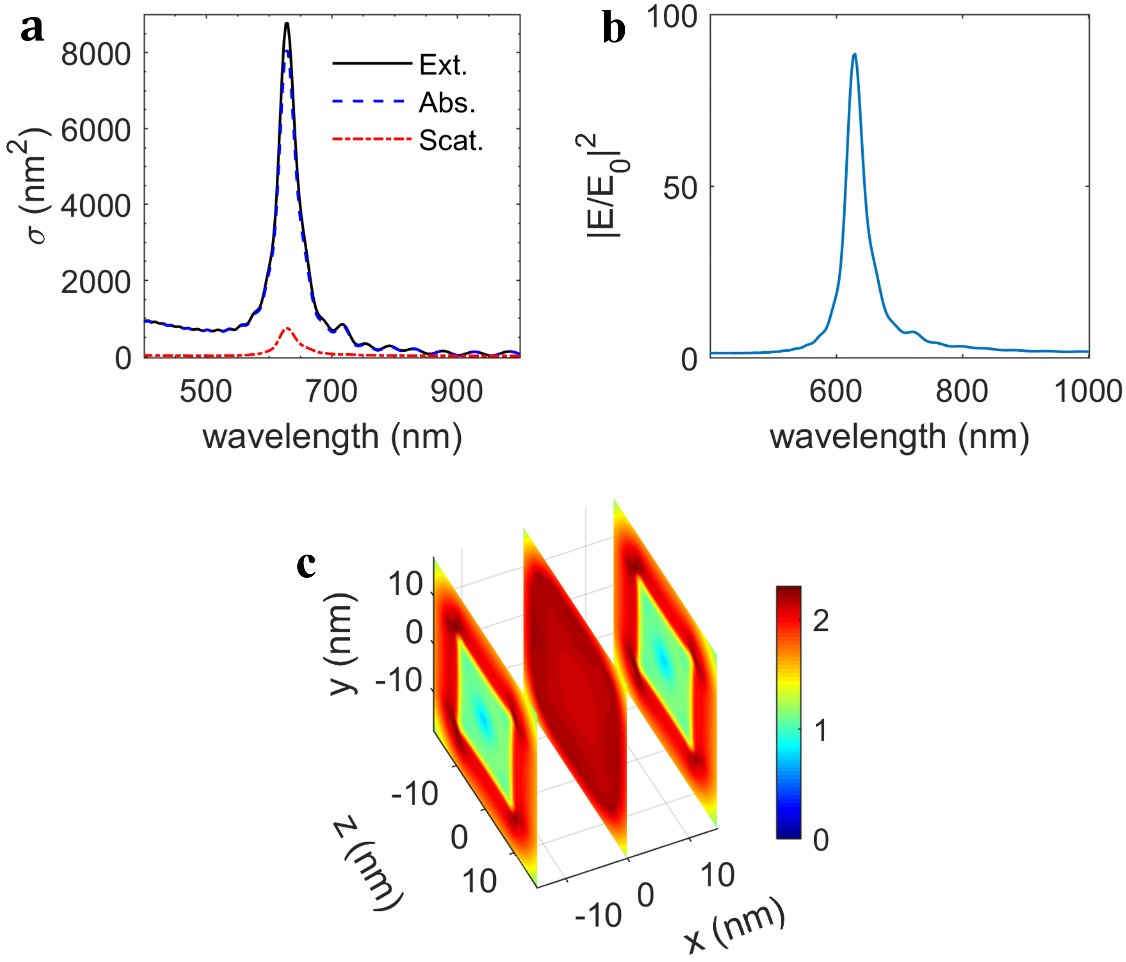

Figure S7. FDTD simulations of (a) extinction, absorption and scattering cross-sections, (b) average field intensity enhancement, and (c) field intensity profile at 630 nm of a hollow gold cage structure with edge length of 30nm.

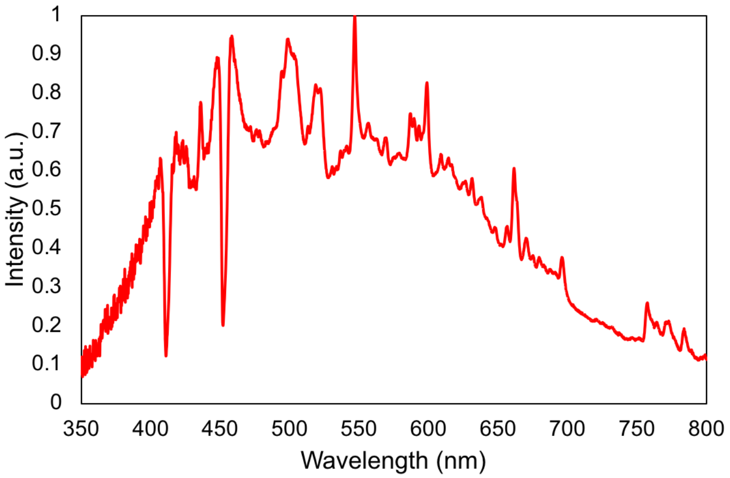

Figure S8. Emission spectrum of the light source used in the photoelectrochemical tests.

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