Electronic Supplementary Information (ESI)

Localized surface plasmon resonances induced edge effect of gold regular hexagonal nanoplates for reaction progress monitoring

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Materials and Reagents.

Chloroauric acid tetrahydate ($HAuCl_4 \cdot 4H2O$) was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai,China). Polyvinylpyrrolidone (PVP, M.W. 40000) was obtained from Sigma-Aldrich. iron chloride hexahydrate ($FeCl_3 \cdot 6H2O$,99%) and thiourea (TU, 99%) were obtained from Aladdin Reagent Co. (Shanghai, China). All reagents were of analytical grade and were used as received without further purification. Ultrapure water with a resistivity of 18.2 $M\Omega \cdot cm$ was produced from a Milli-Q system (Millipore, Bedford, MA, USA). Glass slides were commercially purchased from Dingguo Changsheng Biotechnology Co., Ltd (Beijing, China).

Apparatus

Light scattering DFM was carried out using a BX51 optical microscope (Olympus, Japan) equipped with a high numerical dark-field condenser (U-DCW, 1.2–1.4). A 100× magnification objective lens was used to collect scattered light and the images were taken using a true-color charge-coupled device (CCD) camera (Olympus, Japan). A monochromator was equipped with a spectrograph (SR303i-B, Andor) and the scattering spectra is obtained using a CCD spectrometer (DU970P-BVF, Andor). The morphology and size of Au nanostructures was characterized by using a Hitachi S-4800 scanning electron microscope (Tokyo, Japan).

Numerical simulations

FDTD simulations were performed using a commercial simulation program (FDTD solutions 8.11.422 by Lumerical Solutions). In the simulation, a total-field scattered-field (TFSF) light source with a wavelength of 400–900 nm was propagated along the z-axis and perpendicular to the x–y plane of the Au nanoplates and a perfectly matched layer (PML) was involved in all boundary conditions. The override mesh cell size used was $2 \times 2 \times 2$ nm^3.

Synthesis of Au nanoplates

Firstly, 0.25g PVP (Alfa Aesar , Mw = 40000) was mixed with 24.5 mL DMF (Shanghai Chemical Co.) in a flask under magnetic stirring (500 rpm), and then the mixture was heated in an oil bath to 140°C and kept there for 4 min. After which 0.7 mL $HAuCl_4$ (24 mM) aqueous solution was injected dropwise into the hot solutions. Stirring and heating was stopped after the reaction was carried out for 40 min.

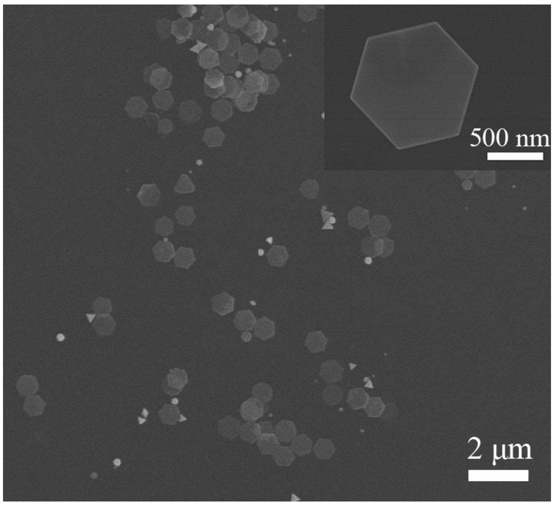


Figure S1. The SEM images of as-prepared gold regular hexagonal nanoplates (AuHNPs). The resulting AuHNPs solution through wet-chemical syntheses in organic media contains a mixture of plate-like nanostructures and pseudospherical nanoparticles. About 40% of the as-prepared AuHNPs are regular according to the statistics of the SEM images by accounting 100 particles.

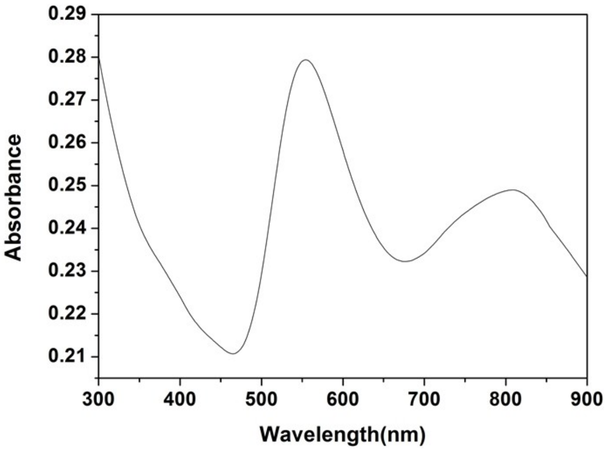


Figure S2. UV-Vis spectra of Au plate-like nanostructures and pseudospherical nanoparticles. The low- and high-energy peaks are attributed to the dipolar resonance of the pseudo-spherical nanoparticles and surface plasmon resonance modes of the AuHNPs that lie within the plane of the nanoplates, respectively.

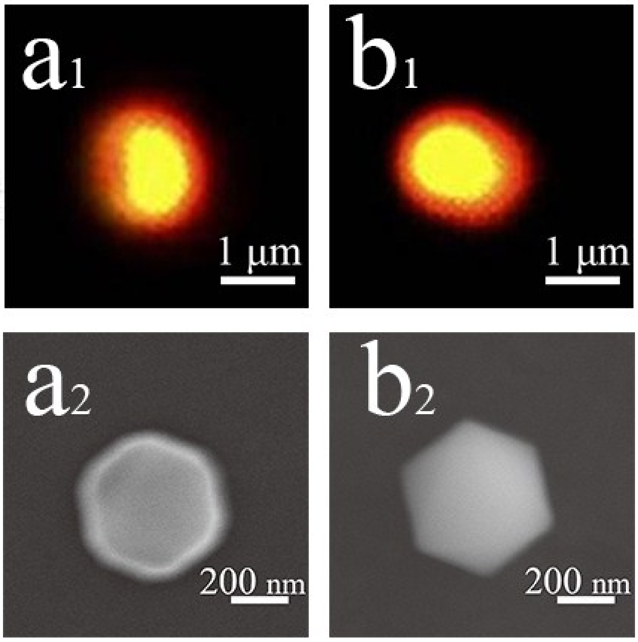


Figure S3. DFM image of AuHNPs smaller than 500 nm. (a1-b1) and their corresponding SEM images (a2-b2). The scattering images exhibit elongated solid bright spot.

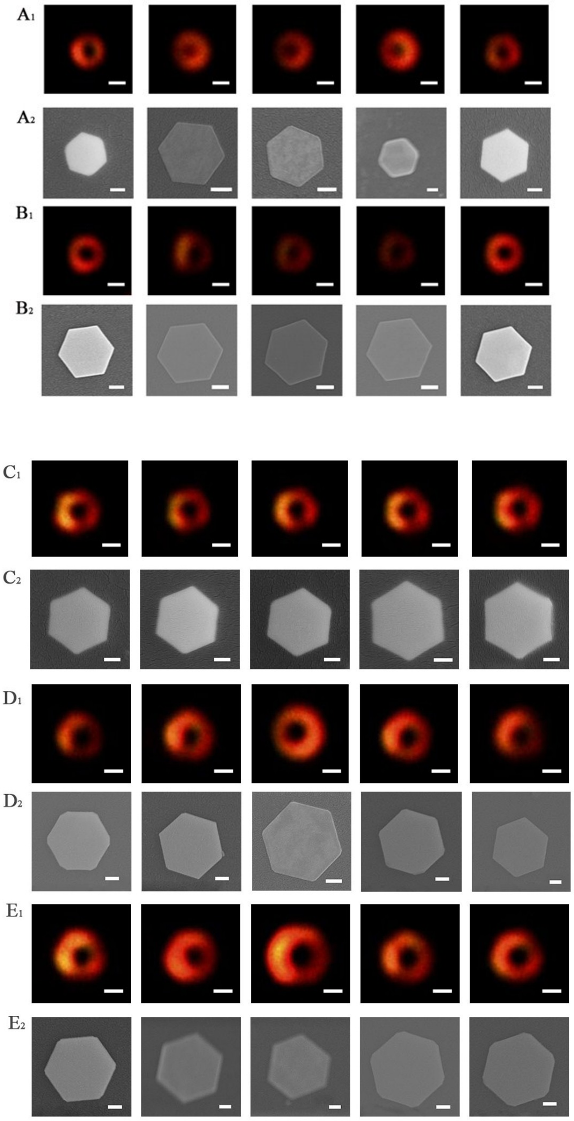
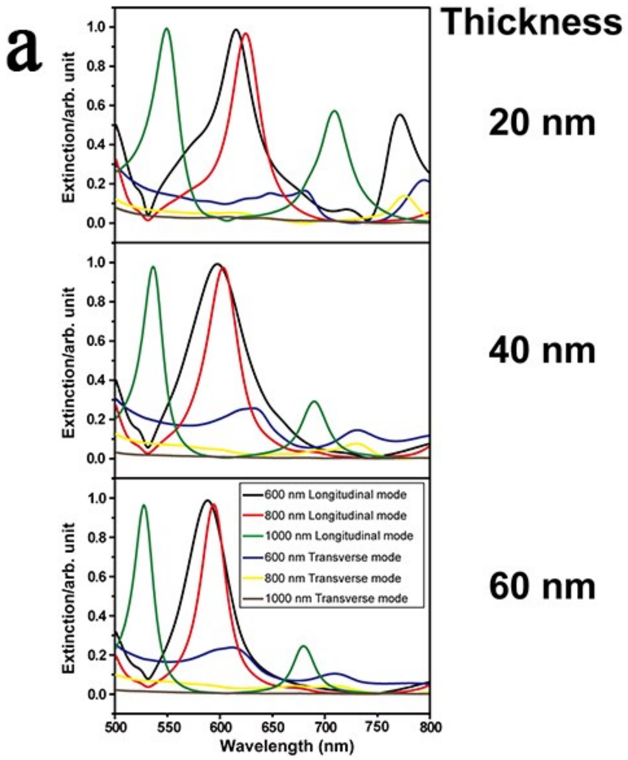
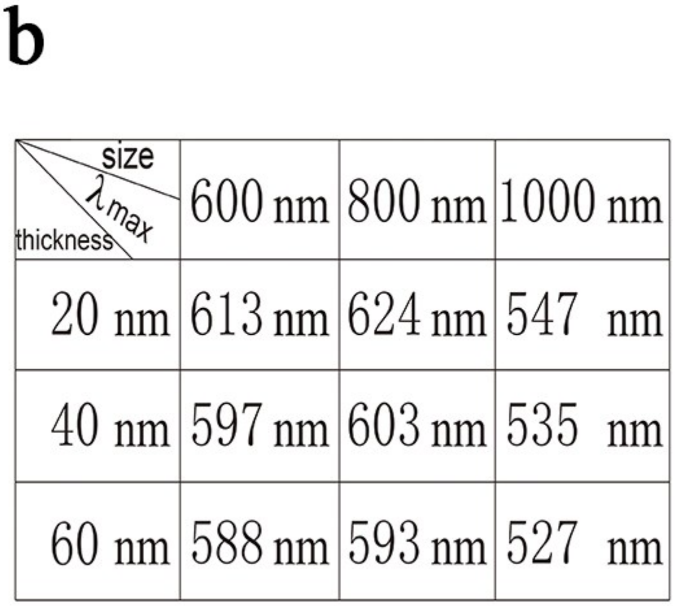


Figure S4. Doughnut-shaped far-field scattering patterns (DNSPs) of representative regular AuHNPs in the range of 500-1000 nm. (A1–E1) DFM images (the scale bar is 500 nm); (A2–E2) the corresponding SEM images (the scale bar is 200 nm). It can be seen that the DFM images exhibit similar DNSPs in spite of different sizes.





thickness \ λmax \ size	600 nm	800 nm	1000 nm
20 nm	613 nm	624 nm	547 nm
40 nm	597 nm	603 nm	535 nm
60 nm	588 nm	593 nm	527 nm

Figure S5. FDTD simulations of the hexagonal Au nanoplates. (a) Simulated extinction spectra for the longitudinal mode and transverse mode of individual regular Au hexagonal nanoplates with different sizes of 600 nm, 800 nm and 1000 nm and with a thickness of 20 nm, 40 nm and 60 nm. This suggests that the LSPR peaks can be assigned to the longitudinal mode. (b) The main LSPR peaks wavelength of AuHNPs with different sizes of 600 nm ,800 nm and 1000 nm and with a thickness of 20 nm, 40 nm and 60 nm. It can be seen that for the same size, the LSPR peak (λmax) is gradually blueshifted with the increasing thicknesses, while for the same thickness, the LSPR peak(λmax) is redshifted and then blueshifted with the increasing sizes.

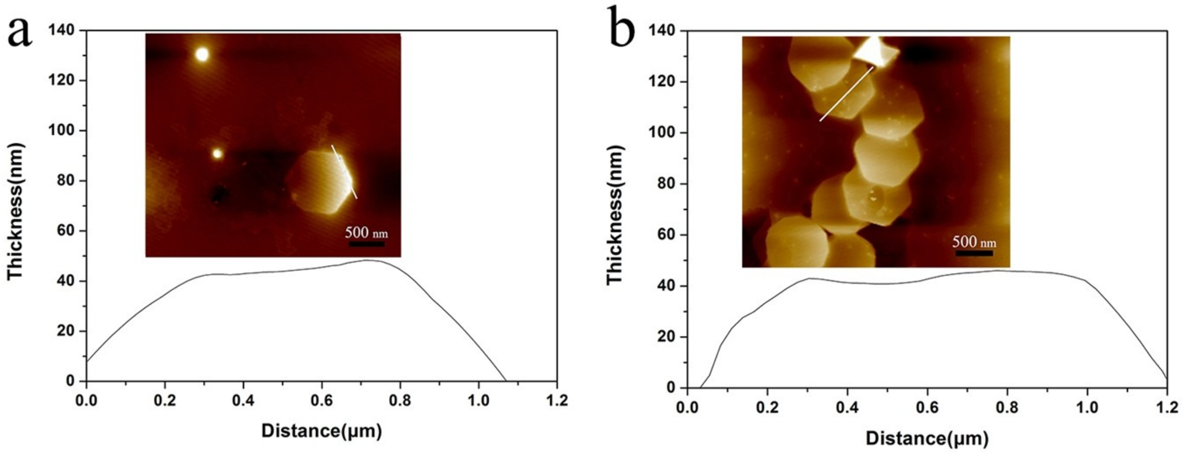


Figure S6. AFM images and height profiles of AuHNPs.

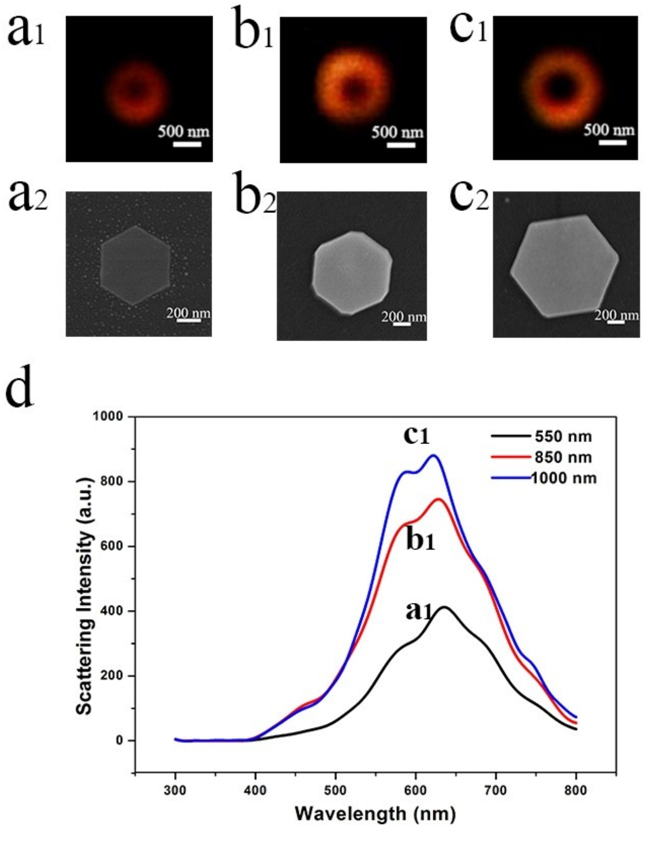


Figure S7. DFM images of AuHNPs with 550 nm, 850 nm, 1000 nm. (a1-c1), their SEM images (a2-c2), and their corresponding scattering spectra (d). Light scattering spectra of different sizes exhibited similar peak position but different scattering intensity. It can be concluded that the appearance of edge effect of different sizes is independent of scattering spectra.

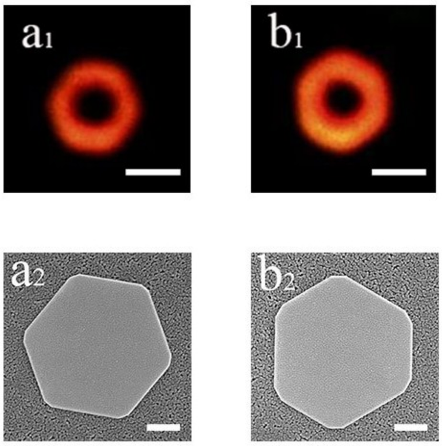


Figure S8. DFM images of AuHNPs larger than 1000 nm (a1-b1, scale bar is 1μm) and their corresponding SEM images (a2-b2, scale bar is 300 nm). The shapes of scattering images present obvious hexagonal profile in DFM, whose orientations are in the agreement with authentic external contour obtained by SEM.

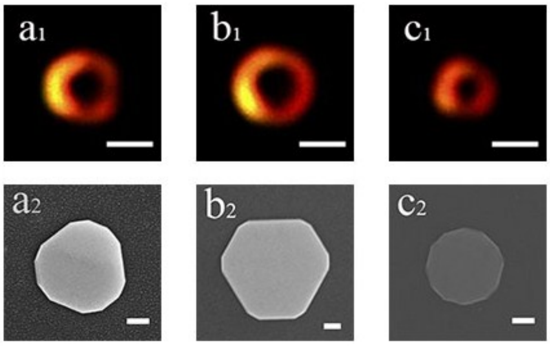


Figure S9. DFM images of irregular Au nanoplates (a1-c1, scale bar is 1 μm) and their corresponding SEM images (a2-c2, scale bar is 300 nm). Different shapes of nanoplates also show similar edge effect if the size is beyond diffraction limit (about 200 nm).

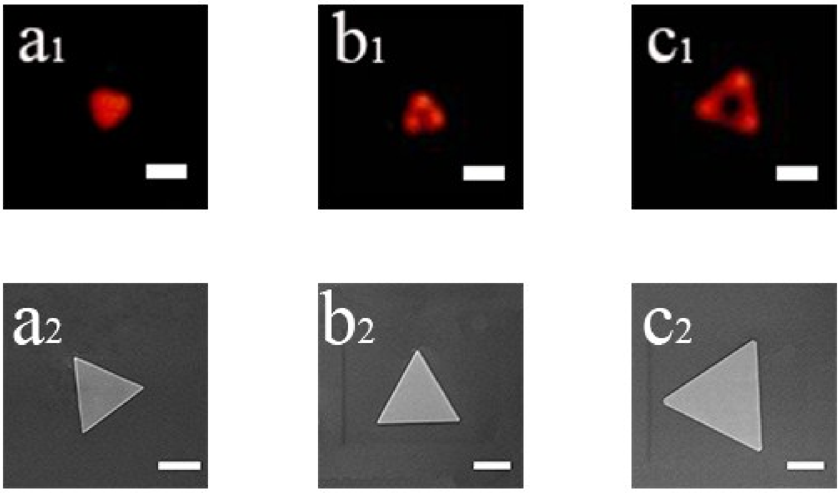


Figure S10. Characterization of different sizes of triangular Au nanoplates.
(a1-c1) dark-field light scattering image of the prepared Au nanoplates (scale bar: 500 nm) and SEM images (scale bar:500 nm) with edge lengths of 880 nm (a2),1100 nm (b2), 1500 nm (c2). The scattering intensity of the vertices are quite apparent in the entire scattering images. The Au triangular nanoplates contain three sharp vertices or ‘‘tips’’ that contribute significantly to their optical and electronic properties.

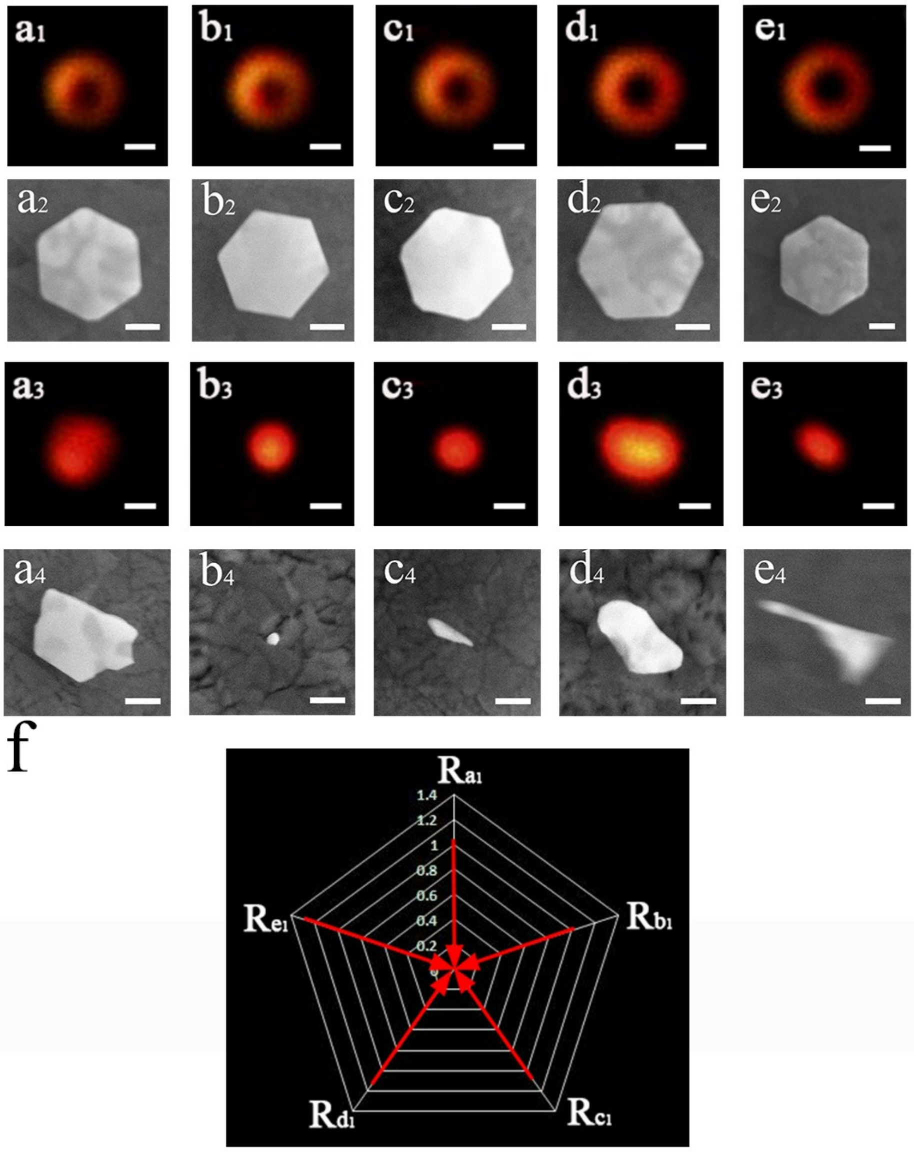


Figure S11. DFM images before (a1-e1) and after (a3-e3) the etching reaction. SEM images of the same AuHNPs before (a2-e2) and after (a4-e4) the reaction with sizes of 850 nm (a2), 880 nm (b2),900 nm (c2), 990 nm (d2), 1000 nm (e2) respectively. The scale bar under DFM is 500 nm, while that under SEM is 300 nm. (f) variation of R-values against size of the nanoplates during the etching process corresponding to the above five AuHNPs. The arrows indicate the reduced trend of R-values.

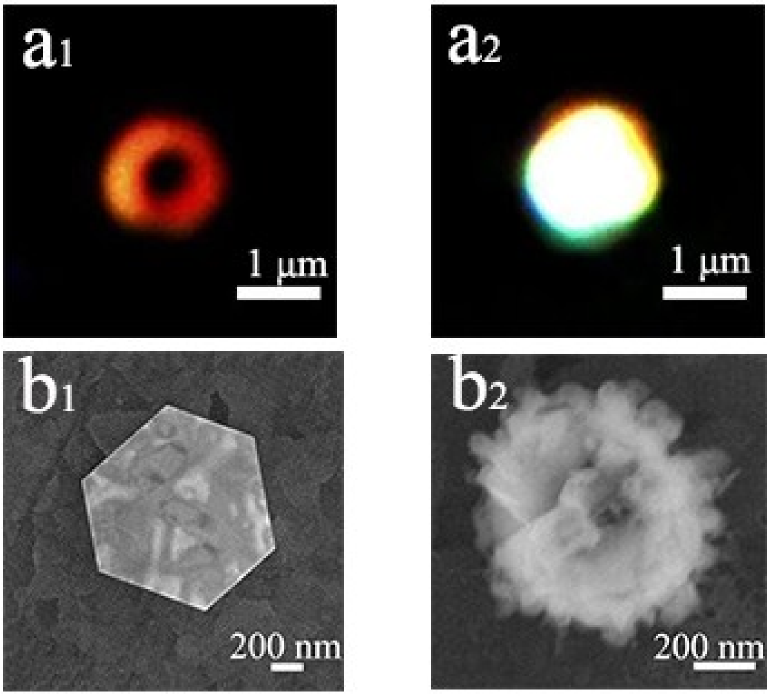


Figure S12. (a1, b1) DFM images of AuHNPs before and after their interaction with Hg^0. (a2, b2) SEM images of the same nanoplate. The edge effect disappears and strong white light spot appears subsequently after direct exposure of AuHNPs to liquid Hg^0 generated by reducing Hg^{2+} with ascorbic acid.