

Supporting Information

Three-order fluorescent enhancement of perovskite nanocrystals using plasmonic Ag@SiO₂ nanocomposites

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1 Experimental Section

1.1 Materials: Lead chloride (PbCl₂, 99.5%), lead bromide (PbBr₂, 99.0%), caesium carbonate (Cs₂CO₃, 99.9%), ethylene glycol (C₂H₆O₂, 98%), 1-octadecene (C₁₈H₃₆, ≥95.0%), and (3-aminopropyl) triethoxysilane (C₉H₂₃NO₃Si, 99%) were purchased from Macklin. Oleic acid (OA, 85%) and oleylamine (OAm, 80-90%) were obtained from Aladdin. Isopropyl alcohol ((CH₃)₂CHOH, AR), cyclohexane (C₆H₁₂, AR) and silver nitrate (AgNO₃, AR) were purchased from Beijing chemical works. PVP-K40 was obtained from Sigma-aldrich. Tetraethyl orthosilicate (C₈H₂₀O₄Si, AR) and ammonia solution (AR) were purchased from other chemical reagent companies in China. All chemicals were used without any modification.

1.2 Synthesis of Blue Perovskite CsPbX₃ NCs: For the fabrication of perovskite NCs, a mixture of CsCO₃ (0.407g), octadecene (ODE, 20 ml), and oleic acid (OA, 1.25 ml) was added into a 100ml three-neck flask at 120°C, and Cs-precursor was successfully prepared after 1h. The mixture of PbCl₂ (0.0627g) and PbBr₂ (0.0825g) along with ODE (15 ml), OA (1.5 ml), and oleylamine (OAm, 3 ml) was degassed under nitrogen at 130°C for 1h. After complete solubilization of PbX₂ (X= Cl, Br) salts, the reaction temperature was raised to 180°C and kept for another 5 min. Then, Cs-precursor (1 ml) was swiftly injected into above mixture, and reaction mixture was stopped by the ice-water bath after 1min. Finally, the prepared perovskite NCs were collected and redispersed in cyclohexane for further use. The CsPbX₃ NCs with other components can be synthesized through changing halogen components.

1.3 Synthesis of Ag spheres and Ag@SiO₂: Firstly, PVP-K40 (3.3g) and ethylene glycol (20 ml) were put into a 100 ml three-neck flask with the atmosphere protection of nitrogen and the heating temperature to 70°C for 3h to completely dissolve PVP-K40 until the solution is clear and transparent. Then, 0.14g of AgNO₃ was added into the above solution and reacted for 10

min, and further increased the temperature to 130°C for 1h until the solution turned into a viscous silver-gray. After cooling to room temperature, the as-prepared samples were collected by centrifuge and wash with ethanol. Finally, the precipitates were dissolved in 10 ml of ethanol. The as-prepared Ag nanospheres were dispersed into the mixed solution of 6 ml of isopropanol and 2 ml of deionized water. Then, TEOS and APTEs (0.2 ml, 0.3 ml, and 0.6 ml) with different ratios (10:4; 10:1) were added into the above solution. The solutions were stirred for 24h to form Ag@SiO₂. After the reaction, the solutions were transferred to five centrifuge tubes, centrifuged with ethanol, and all the precipitates were dried in at 35°C oven for 8h.

1.4 Synthesis of Ag@SiO₂@NCs:

The dried Ag@SiO₂ materials were added into the same amount of perovskite NCs solution (2 ml), and keeping stirring for 5h. Then, the as-prepared Ag@SiO₂@ perovskite NCs were collected by centrifuge at 5000r/min.

2 Characterization: TEM images were collected by Hitachi H-800 at 200 KV. HRTEM was measured by JEM-2100F at 200KV. Transmittance and absorption spectra were collected with a UV/vis-NIR spectrophotometer (Shimadzu UV-1800). Photoluminescence spectra were recorded on a Shimadzu RF-6000 spectrofluorometer. Atomic Force Microscope (AFM) was conducted with the DI Innova AFM (Bruker). The incident photon conversion efficiency (IPCE) curves were measured with a SolarCellScan 100 measured system (Zolix Instruments). X-Ray Diffraction (XRD) patterns were measured by using a Bruker D8 diffractometer with Cu K_α radiation. FTIR spectra were obtained on a Nicolet Impact 410 FTIR spectrometer by mixing the samples with KBr.

3 Finite-difference time-domain simulations: The electric field distribution was calculated using commercial software with a frequency domain solver based on the 3D FDTD method. The FDTD method is an explicit time marching algorithm used to solve Maxwell's curl equations on a discretized spatial grid. The absorbing boundary conditions of perfectly matched layer were obtained in different directions. An electric pulse was launched into the boundary to simulate the distribution of electric field. The size of Ag nanosphere in the mesh range (300 nm × 300 nm × 300 nm) was fixed when calculating the electric field distribution of Ag@SiO₂ with different SiO₂ thickness with mesh size of 0.5 nm.

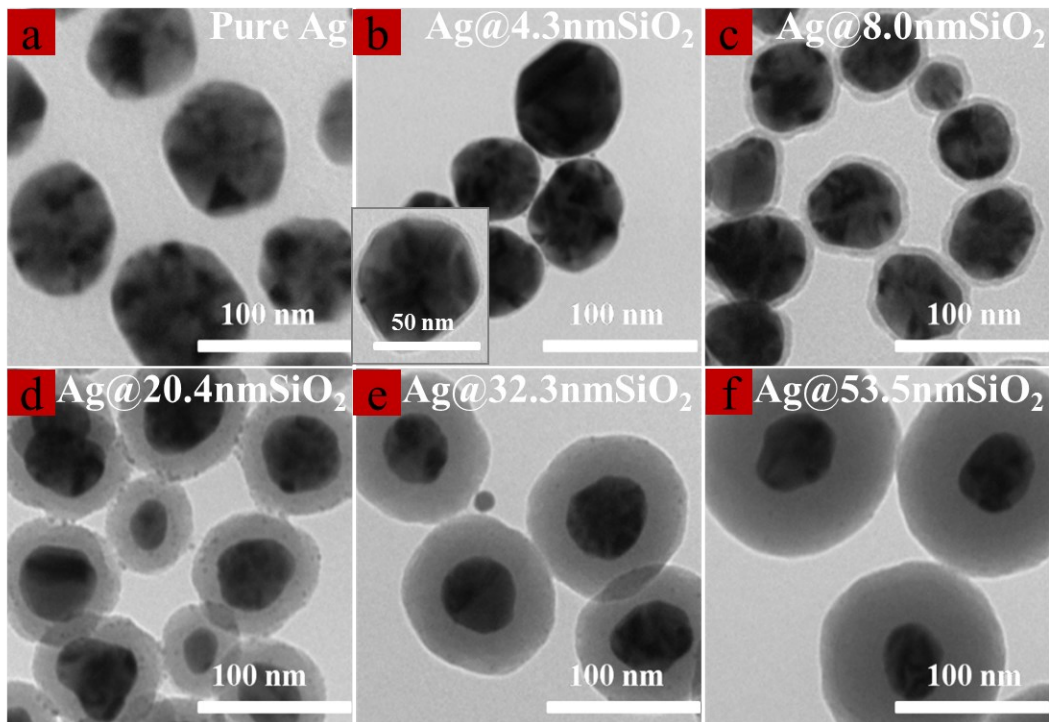


Figure S1. TEM images of pure Ag spheres (a) and Ag@SiO₂ nanostructures with different SiO₂ thickness of 4.3 nm (b), 8.0 nm (c), 20.4 nm (d), 32.3 nm (e) and 53.5 nm (f).

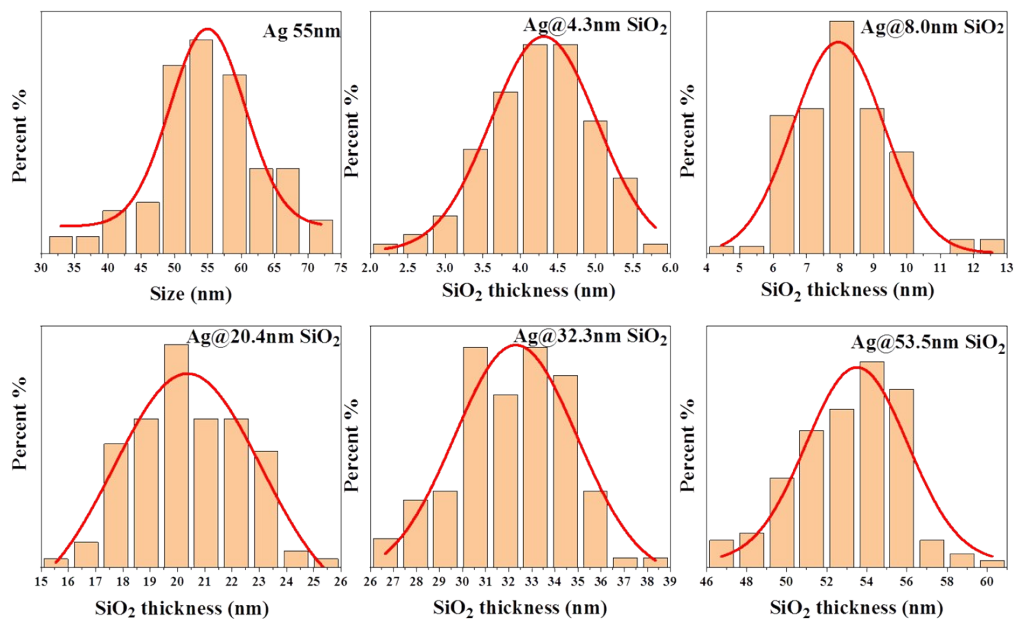


Figure S2. Diameter distribution of Ag spheres, and SiO₂ thickness statistics analysis distributions corresponding to Figure S1.

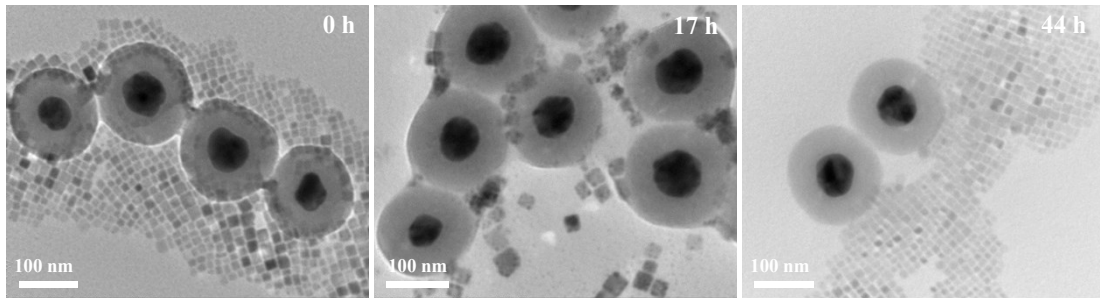


Figure S3. TEM images of Ag@SiO₂@NCs as a function of time.

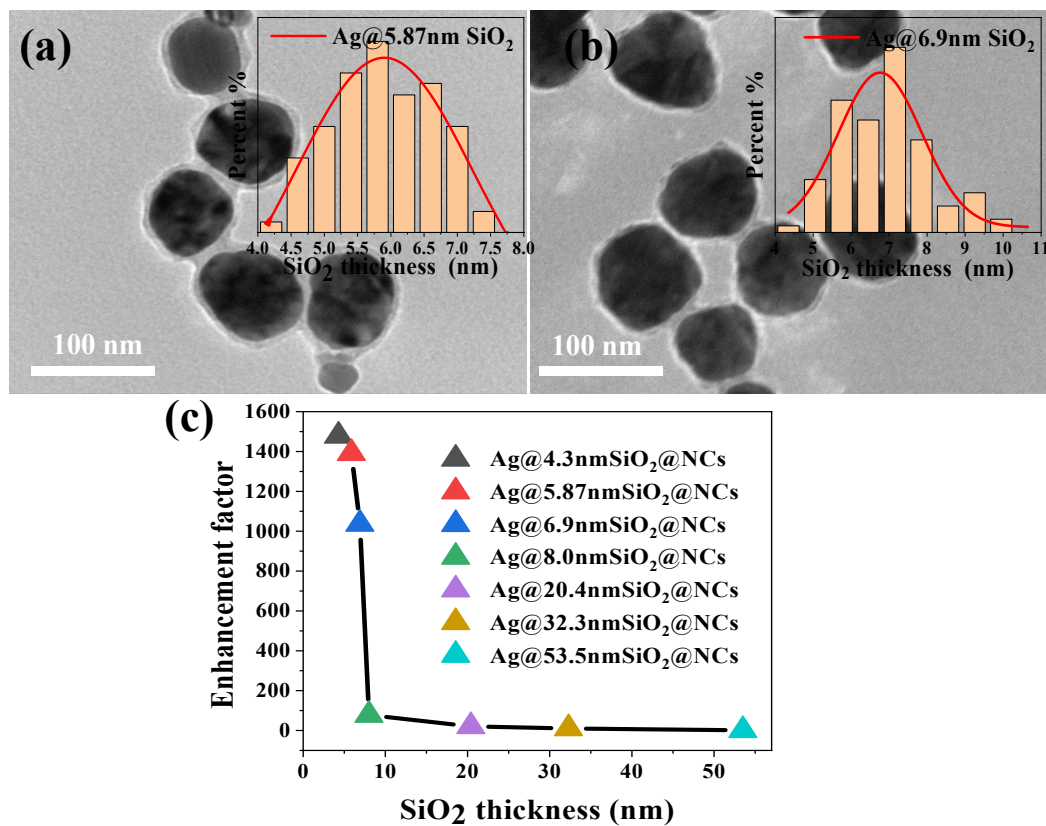


Figure S4. TEM images of Ag@SiO₂ with the SiO₂ average thickness of (a) 5.9 nm and (b) 6.9 nm; (c) PL intensity enhancement factor of Ag@SiO₂@CsPbCl_{1.5}Br_{1.5} NCs with different SiO₂ thickness under 410 nm wavelength.

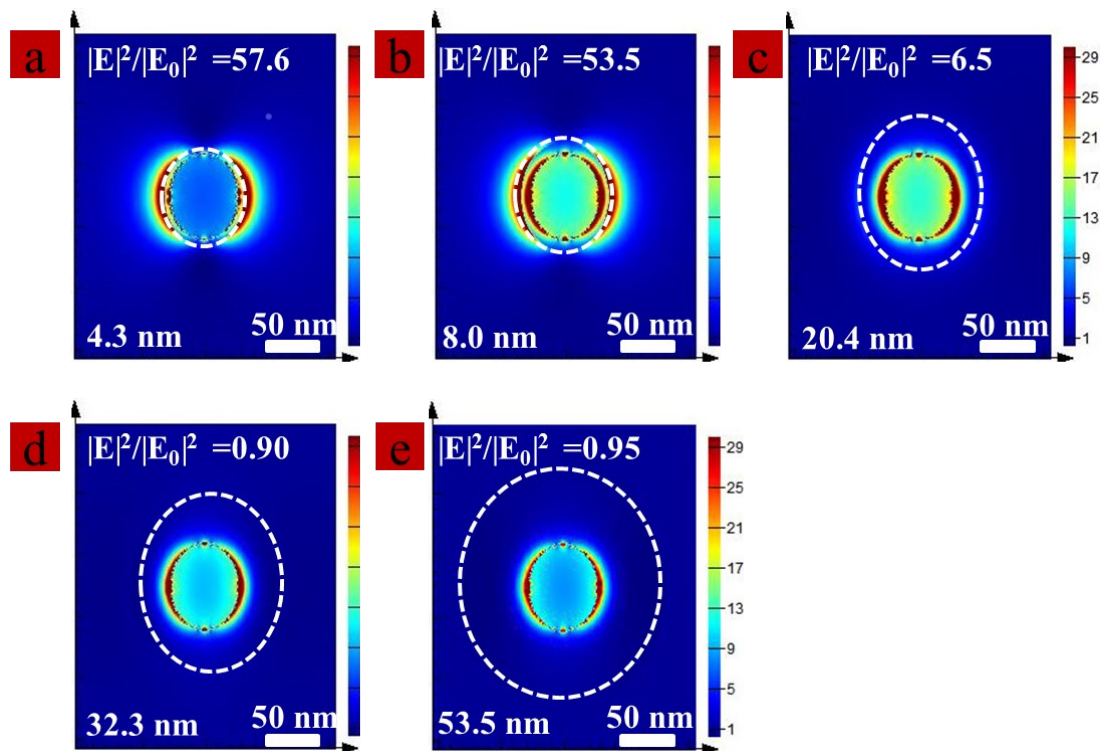


Figure S5. Simulated electric field intensity distributions of Ag@SiO₂ with the SiO₂ thickness of 4.3 nm (a), 8.0 nm (b), 20.4 nm (c), 32.3 nm (d) and 53.5 nm (e) at 410 nm. Dashed circles highlight the periphery of the silica shells surfaces.

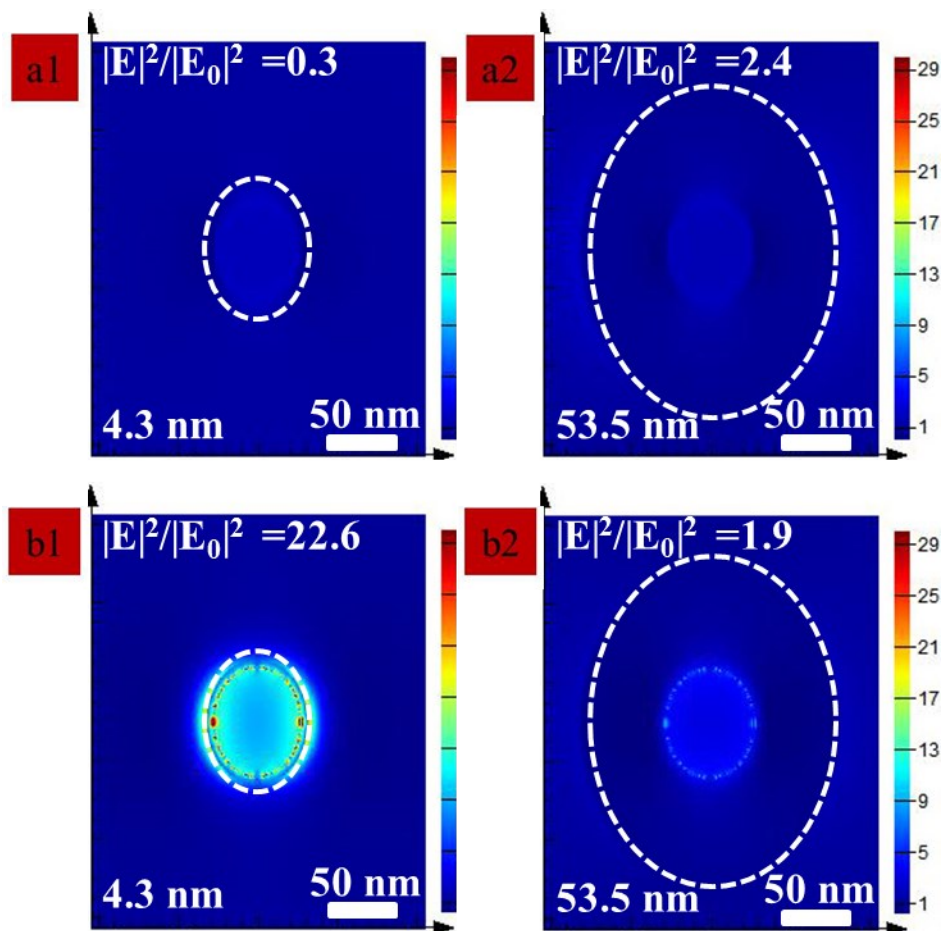


Figure S6. Simulated electric field intensity distributions of Ag@SiO₂ with the SiO₂ thickness of 4.3 and 53.5 nm: a1, a2) at 330 nm, b1, b2) at 365 nm.

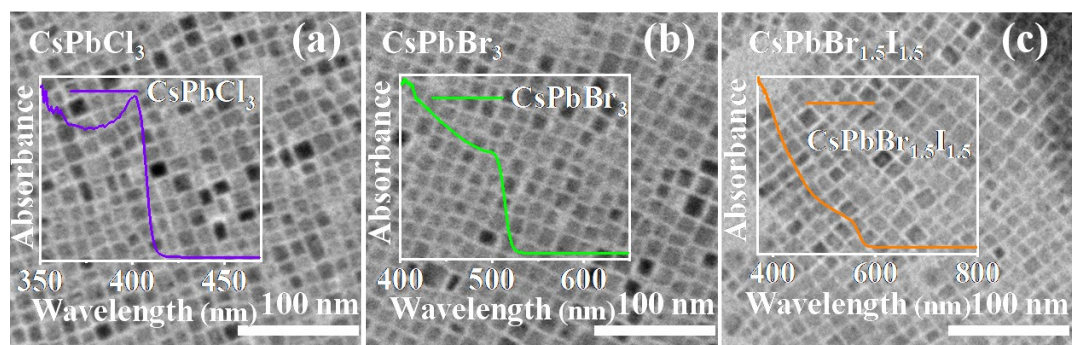


Figure S7. TEM images and UV-vis absorption spectra (insets) of (a) CsPbCl₃, (b) CsPbBr₃ and (c) CsPbBr_{1.5}I_{1.5} perovskite NCs.

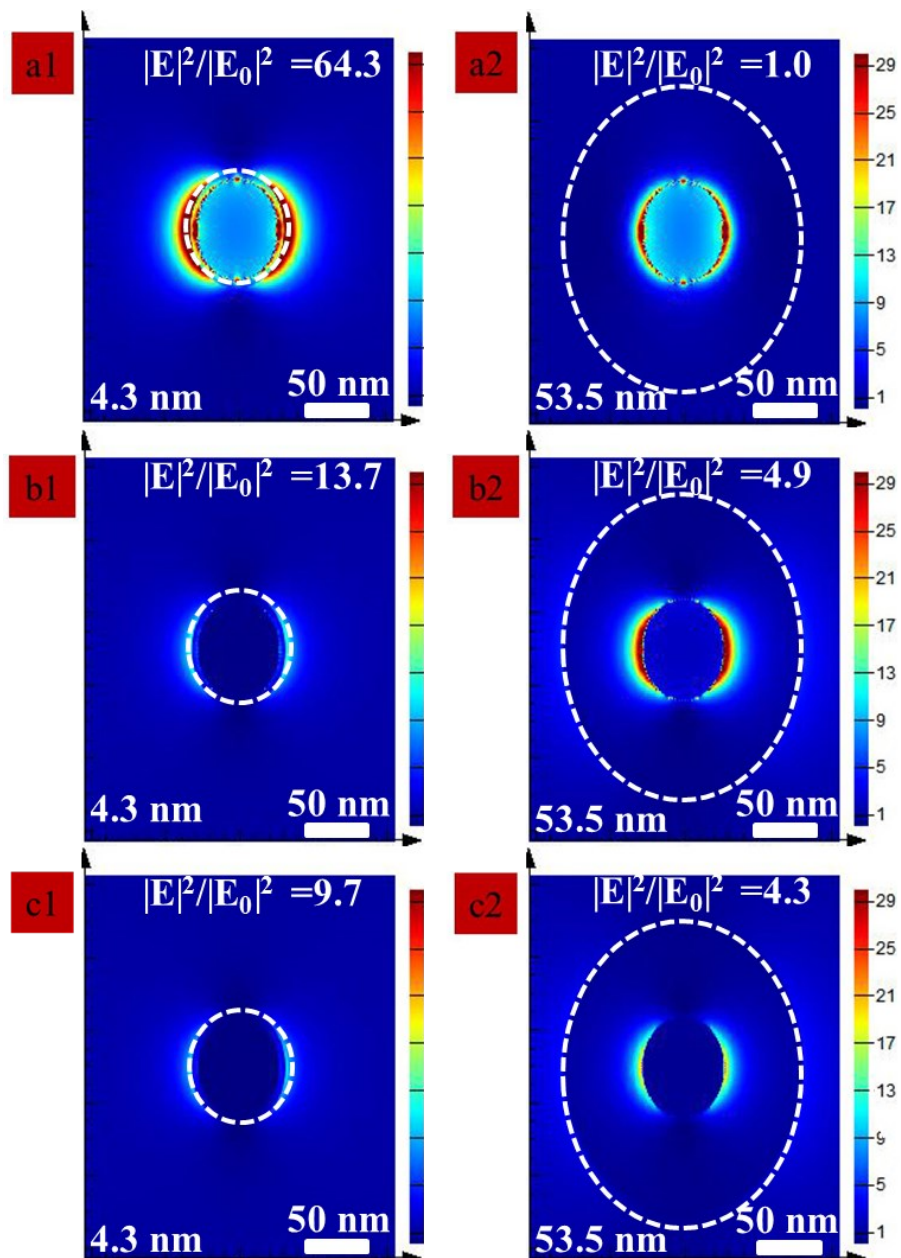


Figure S8. Simulated electric field intensity distributions of Ag@SiO₂ with the SiO₂ thickness of 4.3 and 53.5 nm: a1, a2) at 407 nm, b1, b2) at 519 nm, c1, c2) at 579 nm. Dashed circles highlight the periphery of the silica shells surfaces.