Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Precise Control Over the Silica Shell Thickness and Finding the Optimal Thickness for the Peak Heat Diffusion Property of AuNR@SiO_2

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Materials

$HAuCl_4$ (99.99%), $NaBH_4$ (99.9%), cetyltrimethyl ammonium bromide (CTAB; ≥ 99.0%), L-ascorbic acid (≥99.0%), $AgNO_3$ (≥99.0%), and tetraethyl orthosilicate (TEOS; 99.9%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). NaOH (≥97.0%) and isopropyl alcohol (IPA; 99.5%) were purchased from Daejung Chemical & Metal Co., Ltd. (Shiheung, South Korea). The human tongue squamous carcinoma (HSC-3) cell line was purchased from Sigma-Aldrich (St. Louis, MO, USA). Dulbecco's modified Eagle's medium (DMEM) was obtained from HyClone (Waltham, MA, USA). CellTiter 96® AQ_{ueous} One Solution was purchased from Promega (Madison, WI, USA).

Instruments

Transmission electron microscopy (TEM, H-7100, Hitachi, Tokyo, Japan) was used for TEM analysis. The extinction spectra were obtained using a UV-visible spectrometer (SCINCO, South Korea). Bright-field and dark-field images were obtained using a microscope (Olympus IX73, Tokyo, Japan) equipped with a dark-field condenser (NA 0.8–0.92; Tokyo, Japan). The photothermal effects were studied using a continuous-wave (CW) diode 808 nm NIR laser with an output power of 4.8 W (Chang-chun New Industries Optoelectronics, China). A thermometer (YF-160A K type, Tenmars Electronics Co., Ltd., Taiwan) and an infrared thermal imaging camera (FLIR C2, FLIR Systems Inc., USA) were used to measure the temperature and obtain thermal imaging, respectively. X-ray diffraction (XRD) measurements were performed using a X-ray diffractometer (SmartLab, Rigaku, Japan) with a Cu Kα radiation source (45 kV, 200 mA, wavelength : 1.5412 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed using a X-ray photoelectron spectroscope (X-TOOL, ULVAC-PHI, Japan) with a Ar sputter gun (> 5.0 μA, 5 kV). Raman spectra were acquired using an inverted Raman microscope (NOST, South

Korea). An Epoch™ Microplate Spectrophotometer (BioTek Inc., Winooski, USA) was used to assess the cell viability.

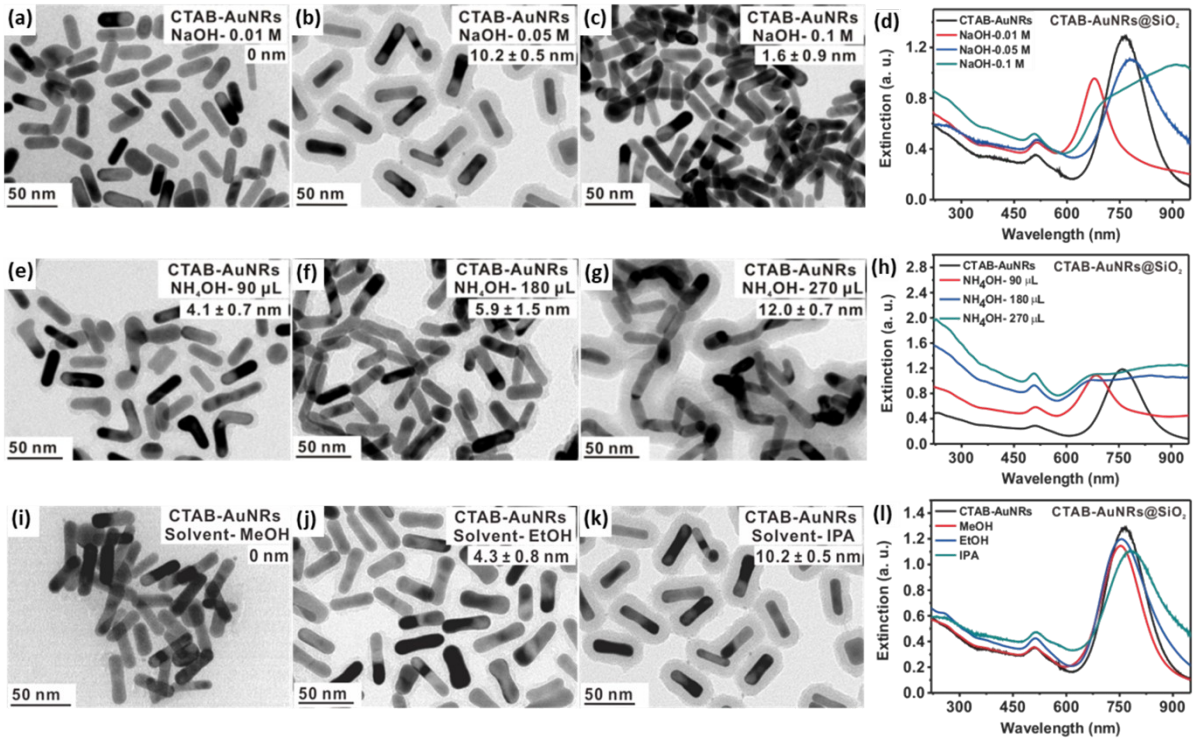


Figure S1. TEM images of CTAB-AuNRs@SiO_2 prepared with (a) 0.01 M, (b) 0.05 M, and (c) 0.1 M NaOH, and (d) UV-Visible spectra. TEM images of CTAB-AuNRs@SiO_2 prepared with (e) 90 µL, (f) 180 µL, and (g) 270 µL of NH_4OH, and (i) UV-Visible spectra. TEM images of the surface of CTAB-AuNRs@SiO_2 prepared using (i) MeOH, (j) EtOH, and (k) IPA, and (l) UV-Visible spectra.

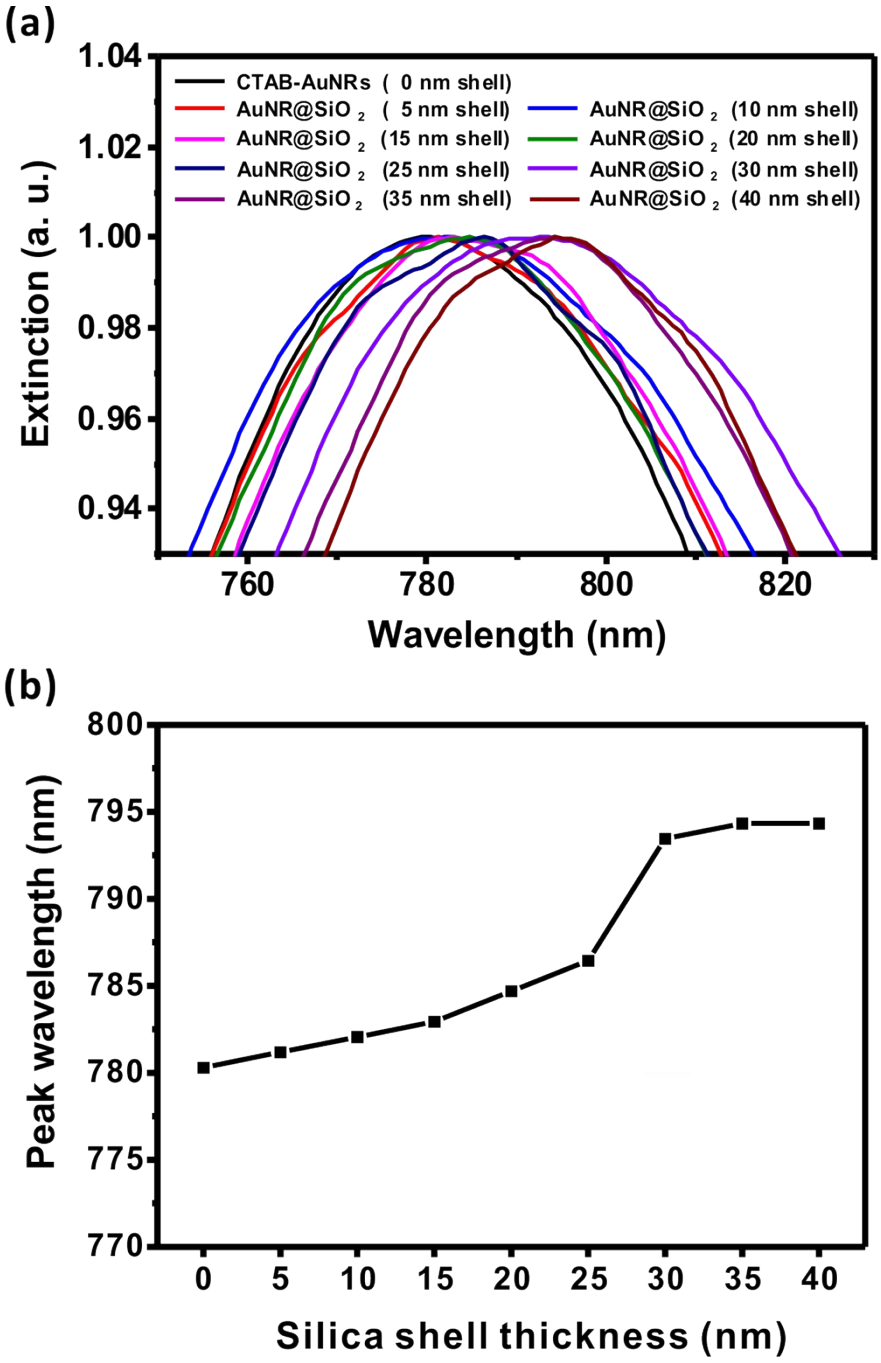


Figure S2. (a) UV spectra of CTAB-AuNRs and AuNR@SiO_2 with 5, 10, 15, 20, 25, 30, 35, and 40 nm SiO_2 shells, (b) changes of λ_{max} of the CTAB-AuNRs and AuNR@SiO_2 with 5, 10, 15, 20, 25, 30, 35, and 40 nm SiO_2 shells.

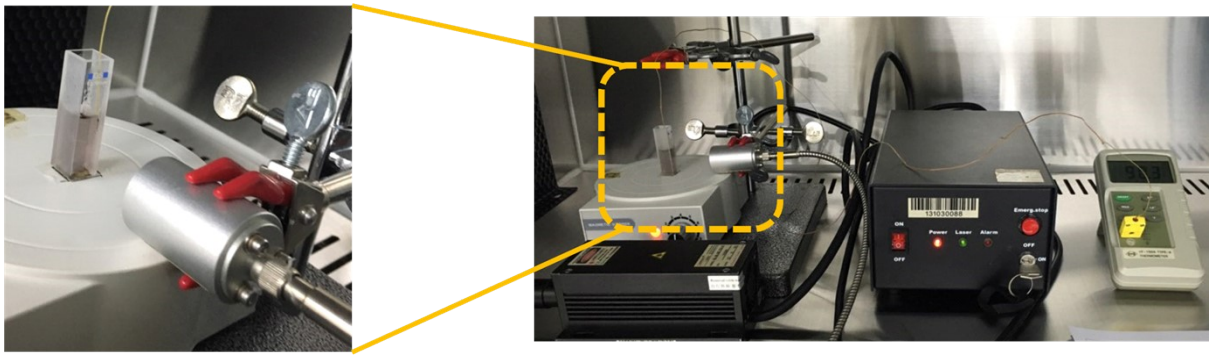


Figure S3. Experimental setup of the 808 nm CW laser at a power density of 1.25 W/cm^2.

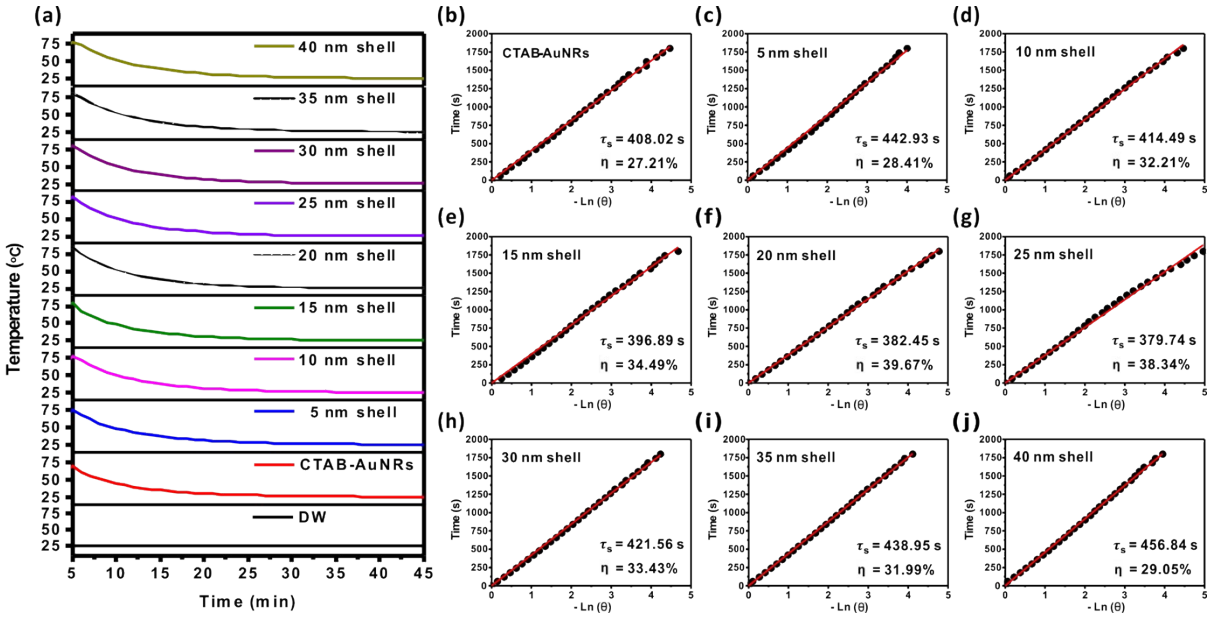
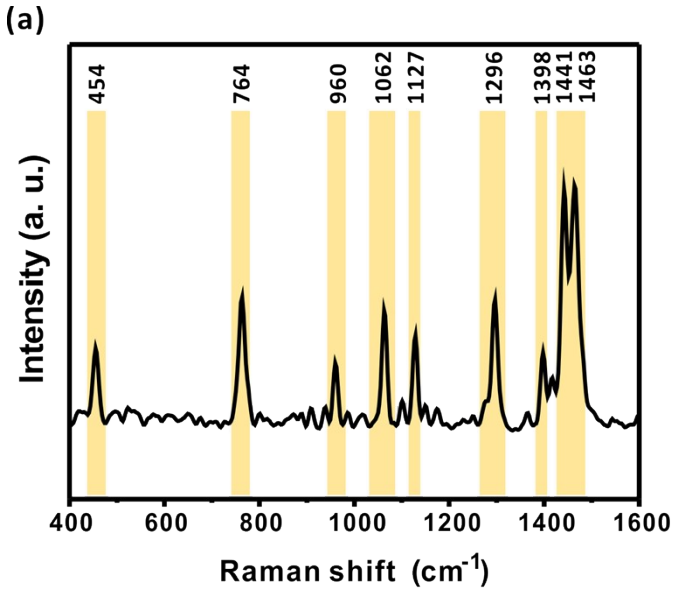
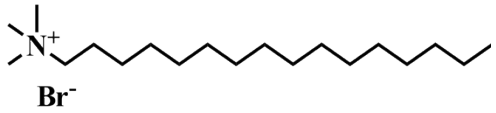


Figure S4. (a) Cooling curves of DW, CTAB-AuNRs, and AuNR@SiO_2. Time constants (τ_s) and photothermal conversion efficiencies (η) of (b) CTAB-AuNRs and AuNR@SiO_2 ((c) 5, (d) 10, (e) 15, (f) 20, (g) 25, (h) 30, (i) 35, and (j) 40 nm) for heat transfer from the system.



(b)



(c)

Raman shift (cm^{-1})	Chemical structure	Vibration mode	Raman scattering activity
451	CCC, CNC	Bending	Strong
761	CH_2	Rocking	Very strong
960	CN, CC	Stretching	Strong
	CH_3	Rocking	
1062	CC	Stretching	Very strong
	CH_3	Rocking	
1127	CH_3, CH_2	Wagging	Strong
	CH_3	Rocking	
1295	CH_2	Twisting	Very strong
1398	CH_3	Bending	Medium
1441	CH_2	Scissoring	Very strong
1464	CH_2	Scissoring	Very strong

Figure S5. (a) Raman spectrum, (b) chemical structure, and (c) vibration modes of CTAB.[1]

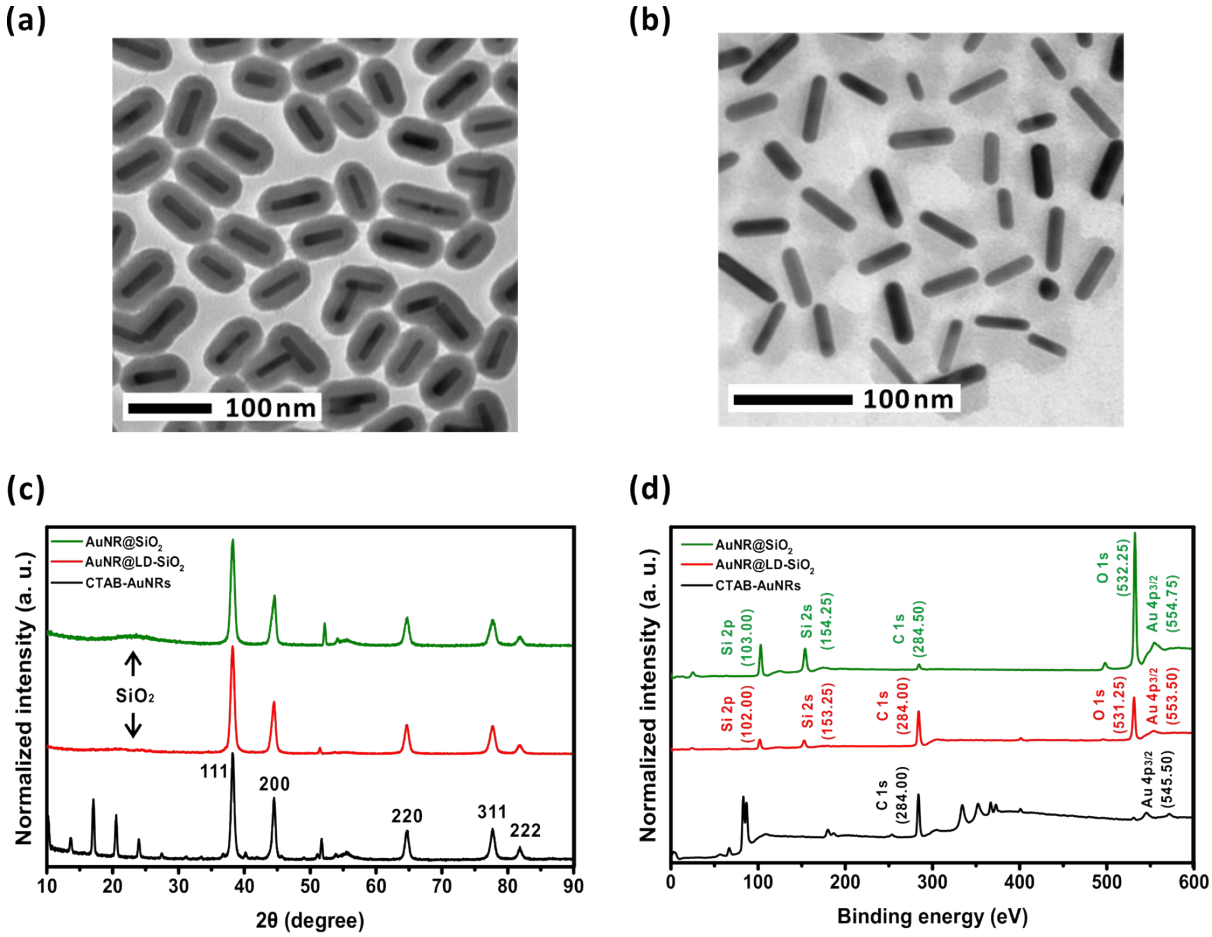


Figure S6. TEM images of the as-prepared (a) AuNR@SiO_2 and (b) AuNR@LD-SiO_2; (c) X-ray diffraction patterns and (d) X-ray photoelectron spectroscopy spectra of the CTAB-AuNRs (black line), AuNR@LD-SiO_2 (red line), and AuNR@SiO_2 (green line).

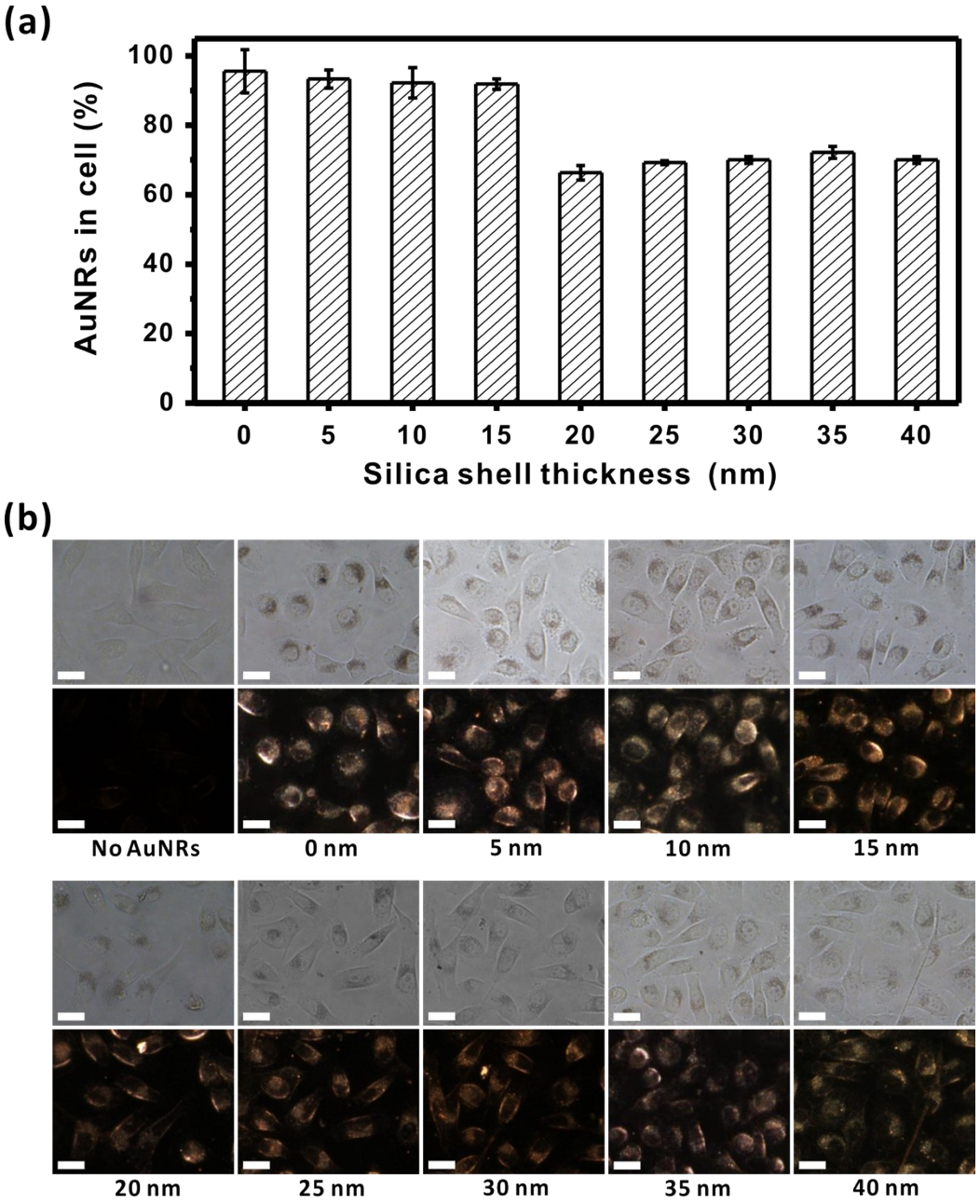


Figure S7. (a) Content of the AuNRs (OD = 1.5) in the cells measured at 780 nm and (b) bright-field and dark-field images of cells incubated with CTAB-AuNRs and AuNR@SiO_2 with defined silica shell thicknesses (5, 10, 15, 20, 25, 30, 35, and 40 nm).

REFERENCES

1. H. Gokce, S. Bahceli, *Opt. Spectrosc.*, 2013**, 115**, 632-644.