Supporting Information for

Direct Coating of Mesoporous Titania on CTAB-capped Gold Nanorods

Junwei Zhao,[1,2] Pengyu Xu,[1] Yue Li,[1] Jian Wu,[1] Junfei Xue,[1] Qiannan Zhu,[1] Xuxing Lu,[1] Weihai Ni*,[1]

1. Division of *i*-Lab & Key Laboratory for Nano-Bio Interface Research, Suzhou Institute of Nano-Tech & Nano-Bionics, Chinese Academy of Sciences, Suzhou, Jiangsu, 215123, China
2. Materials Science and Engineering School, Luoyang Institute of Science and Technology, Luoyang, Henan, 471023, China

1. Chemicals. Hydrogen tetrachloroaurate (III) trihydrate, silver nitrate, L-ascorbic acid, cetyltrimethylammonium bromide (CTAB), absolute methanol (MeOH), Titanium diisopropoxide bis(acetylacetonate) (TDAA), and 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) were purchased from Sigma-Aldrich. Sodium borohydride ($NaBH_4$), hydrochloric acid (HCl), sodium hydroxide (NaOH), and hydrogen peroxide (H_2O_2) were purchased from Sinopharm Chemical Reagent Co. Ltd. All of these reagents were used without any further purification. Solutions were prepared with deionized (DI) water (18.2 MΩ).

2. Experimental Section

2.1 Preparation of AuNRs with Different LSPRs.

Five AuNR samples with decreasing LSPR wavelength (LSPRW) were prepared. The longest one, possessing an ensemble LSPR peak at 730 nm, was prepared in aqueous solutions using a seed-mediated method. Specifically, the seed solution was made by adding $HAuCl_4$ (0.25 mL, 0.01 M) into CTAB solution (9.75 mL, 0.1 M) in a plastic tube. After the solution was mixed by inversion, a freshly prepared, ice-cold $NaBH_4$ solution (0.6 mL, 0.01 M) was added all at once, followed by rapid inversion mixing for 2 min. The resultant CTAB-stabilized Au nanoparticle seed solution was kept at room temperature for 2−4 hr before use. The growth solution was made by mixing $HAuCl_4$ (20 mL, 0.01 M) and $AgNO_3$ (4 mL, 0.01 M) with CTAB (400 mL, 0.1 M) in a glass bottle. HCl solution (8 mL, 1.0 M) was then added, followed by the addition of a freshly prepared ascorbic acid solution (3.2 mL, 0.1 M). The resultant solution was mixed and then the seed solution (0.15 mL) was added. The reaction mixture was agitated by gentle inversion for 10 sec and left undisturbed at least overnight. The as-synthesized AuNRs possess average dimension 85.5±4.7×29.0±2.6 nm and aspect ratio 3.0±0.3.

The other four AuNR samples were prepared by oxidation shortening. The AuNR sample with a LSPRW of 730 nm was used as the starting one for the oxidation, and hydrogen peroxide was used as the oxidation agent. Typically, 10 mL of as-synthesized AuNR solution was added with 0.2 mL of H_2O_2 solution. After that, the longitudinal plasmonic peak of the AuNR sample performed blue shift at a rate of ~2 nm per min. The oxidation reaction was arrested at controlled periods of time by centrifugation, and the AuNRs were redispersed into DI water. Four AuNR samples with ensemble LSPR at 698, 675, 637, and 597 nm were obtained after the oxidation.

2.2 Preparation of the AuNR@mTiO$_2$ nanostructures.

TDAA was used as the TiO_2 precursor. Typically, 10 mL of the AuNR solution was washed twice by centrifugation to remove excess CTAB surfactant, and then the AuNRs were redispersed into 6.47 mL of DI water. An appropriate volume of 0.01 M CTAB solution was added to the AuNR solution to achieve 0.18 mM CTAB concentration. The pH of the solution was adjusted to around 10.5 by adding 0.1 M NaOH solution. To the reaction solution, different volume (100, 130, 180, 250, and 300 μL) of TDAA methanol solution (V_{TDAA}: V_{MeOH} = 1: 100) was added step by step (every 0.5−1 hr, 10−15 μL at a time) under vigorous stirring. After the mixture solution was stirred for 2 hr at room temperature, the product was washed twice by centrifugation and redispersed in 10 mL of DI water before further use. To investigate the effect of CTAB on the $mTiO_2$ shell, the CTAB concentration was controlled at 0.005, 0.061, 0.122, 0.18, 0.24, 0.3, 0.5, 1, 1.5, and 2 mM, while keeping the other conditions unchanged in the reaction solution.

2.3 Calcination of AuNR@mTiO$_2$ nanostructures

The AuNR@mTiO$_2$ nanostructures were deposited on 0.7 × 4 cm quartz substrates by drop-casting and evaporation of the solution to form uniform films. The amount of nanostructures deposited on the substrates was controlled at 0.1 mg. The nanostructures on the quartz slide were then placed in a tube furnace in air ambiance at 450 ℃ for 2 hr with a ramp rate of 10 ℃/min. The substrate samples were allowed to cool down to room temperature. Extinction spectra were obtained from the AuNR@mTiO$_2$ nanostructure films after the calcination.

2.4 Preparation of the hollow TiO$_2$ nanostructures

The hollow TiO_2 nanostructures were obtained by etching the Au cores of the AuNR@mTiO$_2$ nanostructures. Typically, 10 mL of the nanostructures was precipitated by centrifugation and redispersed in 10 mL of 0.1M CTAB solution. Then, 200 μL of 1 M HCl and 350 μL of H_2O_2 (30 wt %) solutions were added. The solution mixture was kept at 45 ℃ for ~1 hr to allow for the complete etching of the AuNR cores. The resultant hollow TiO_2 nanostructures were washed by centrifugation with water before further use.

2.5 Generation of $^1O_2$ using the AuNR@mTiO$_2$ nanostructures.

The generation of $^1O_2$ using ABDA as probe molecules with the procedure is described below. 2 mL of as-synthesized AuNR@mTiO$_2$ nanostructures was firstly precipitated by centrifugation. The supernatant was removed, and the precipitation was redispersed in 2 mL of 0.1 mM ABDA aqueous solution in a quartz cuvette. To exclude ABDA absorption decrease due to adsorption, the solution mixture was placed in the dark for 4−6 hr to reach an adsorption equilibrium before irradiation. A semiconductor diode laser (L808P200, 808 nm, 210 mW) from Thorlabs was used for irradiation. The laser beam was introduced horizontally from the side surface into the solution. The optical path was 1 cm. The distance between the cuvette and the laser was adjusted to obtain a spot size 4×8 mm and an average power density 656 mW/cm^2. During the irradiation, the solution was under vigorous stirring. Every 1 hr, 0.1 mL of the solution was taken out and measured in a quartz cuvette with 1 cm optical path by a UV-vis spectrophotometer after removing the nanostructures by centrifugation. The reaction was monitored for 8 hr. The apparent quantum efficiency is defined as (number of reacted ABDAs)/(number of incident photons) × 100%.

3. Characterizations

The morphology of the samples was characterized by field emission scanning electron microscopy (FESEM, Hitachi, S-4800). TEM imaging was performed on an FEI Tecnai Spirit microscope operating at 200 kV. The extinction and absorption spectra of solution samples were measured on a Cary 60 UV−vis spectrophotometer with cuvettes of 0.5 or 1.0-cm optical path length. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer at a scanning rate of 4° min^{-1}, using Cu-Kα radiation (λ=1.54056 Å). Faced-centered-cubic structure of Au (JCPDS 1-1172) and the anatase phase of TiO_2 (JCPDS 21-1272) were used to analyze the XRD patterns.

AuNR Sample	Initial LSPRW (nm)	Initial AuNR length (nm)	Initial AuNR width (nm)	Initial AuNR aspect ratio	TiO_2 Thickness (nm)	LSPRW after TiO2 coating (nm)	Plasmon shift due to TiO_2 (nm)
1	730	85.5(4.7)	29.0(2.6)	3.0(0.3)	11	784	54
2	698	83.0(6.2)	29.6(2.1)	2.8(0.2)	14	740	42
3	675	77.5(5.3)	30.9(2.5)	2.5(0.3)	18	714	39
4	637	66.6(6.6)	30.2(2.4)	2.2(0.3)	20	677	40
5	597	47.0(8.8)	27.0(2.5)	1.7(0.3)	28	634	37

Table S1. Dimension and LSPRW of AuNR samples before and after TiO_2 coating

AuNR Sample	AuNR length after calcin. (nm)	AuNR width after calcin. (nm)	AuNR Aspect ratio after calcin.	LSPRW after calcin. (nm)	Plasmon shift due to calcin. (nm)
1	74.1(8.8)	32.8(2.5)	2.3(0.4)	751	-33
2	71.4(9.2)	34.6(2.9)	2.1(0.3)	703	-37
3	65.1(6.9)	36.7(2.3)	1.8(0.2)	696	-18
4	56.8(3.6)	33.3(1.9)	1.7(0.2)	680	3
5	42.9(4.7)	32.4(2.1)	1.3(0.2)	657	23

Table S2. Dimension of AuNRs and LSPRW of AuNR@mTiO_2 samples after calcination.

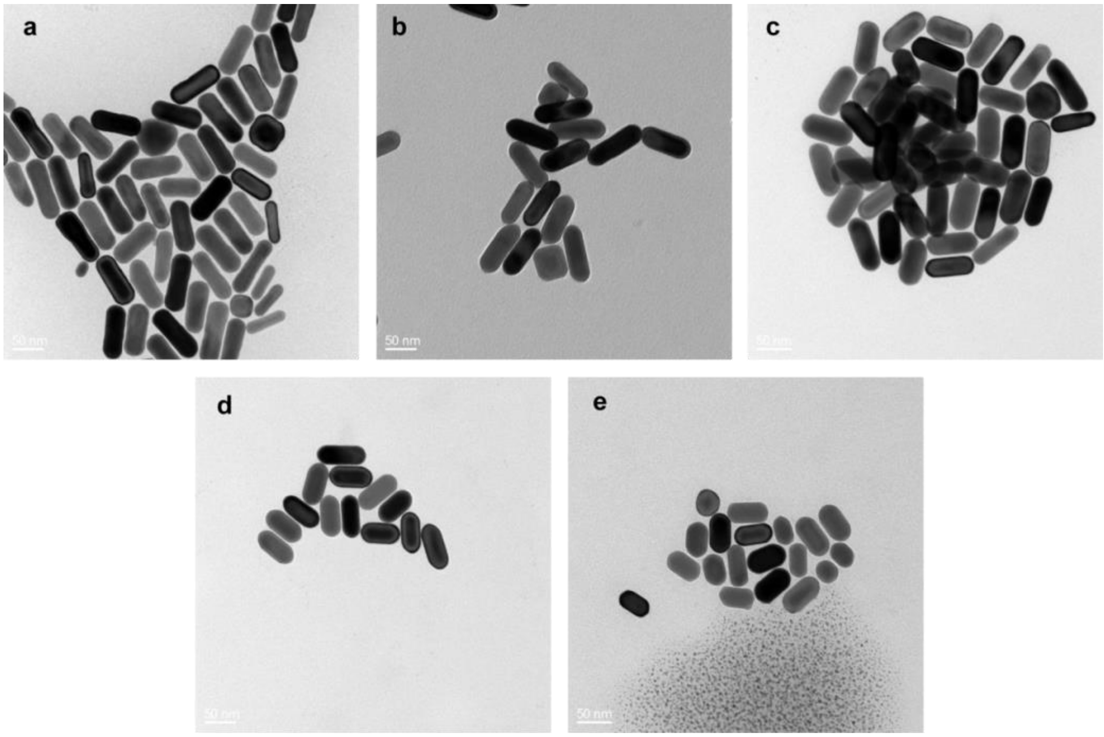

Figure S1. (a−e) TEM images of the five AuNR samples with LSPR at 730, 698, 675, 637, and 597 nm, respectively.

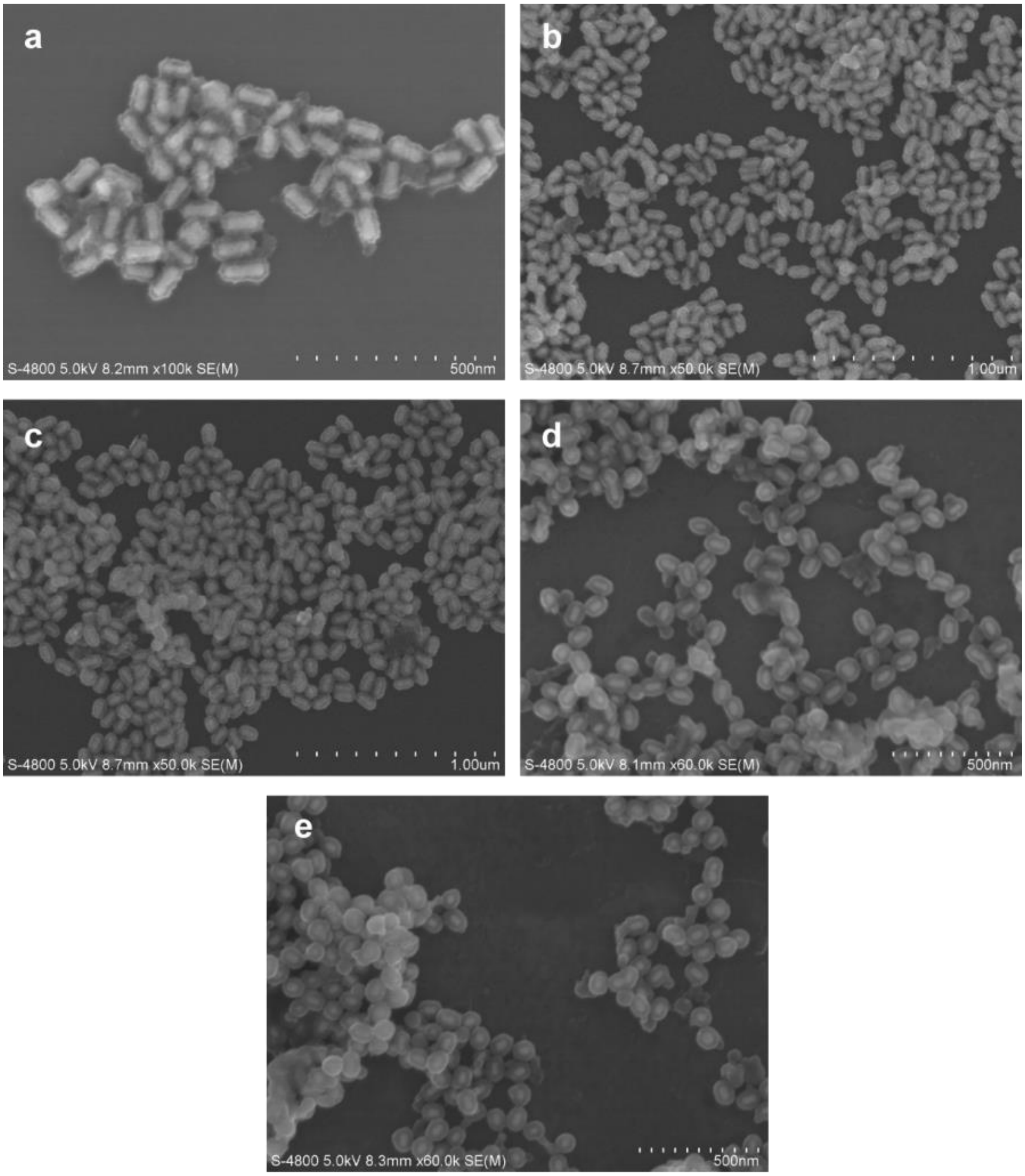

Figure S2. (a−e) SEM images of the five AuNR@mTiO$_2$ nanostructure samples with decreasing AuNR aspect ratios.

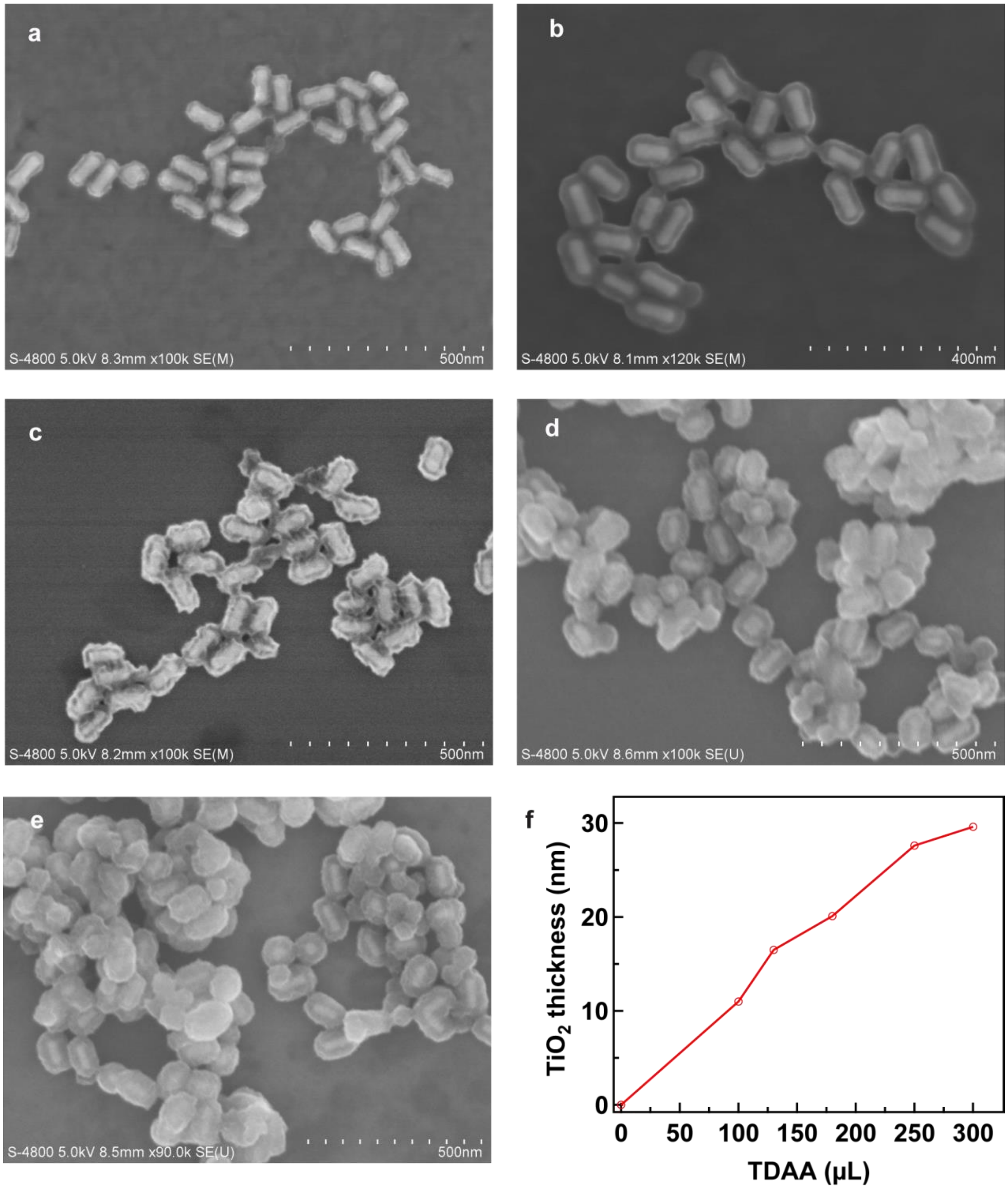

Figure S3. (a−e) SEM images of AuNR@mTiO$_2$ samples with various TiO$_2$ thicknesses. 100, 130, 180, 250, and 300 μL of TDAA solutions were added to the reaction solution, respectively. The coating of TiO$_2$ was performed on as-synthesized AuNRs. (f) TiO$_2$ thickness as a function of TDAA volume.

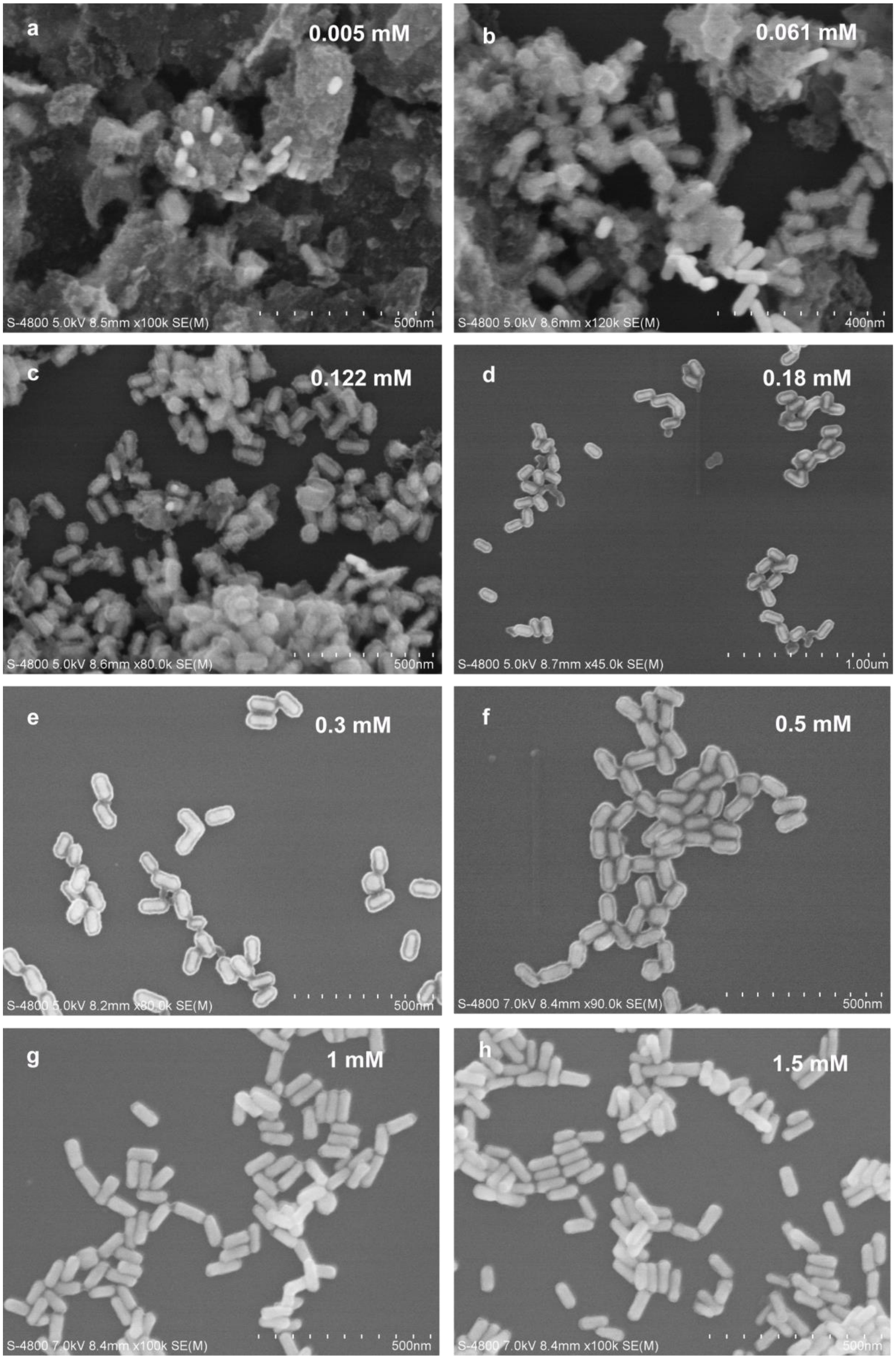

Figure S4. (a−h) SEM images of AuNR@mTiO$_2$ samples prepared with various CTAB concentrations. The CTAB concentrations are labeled on the SEM images.

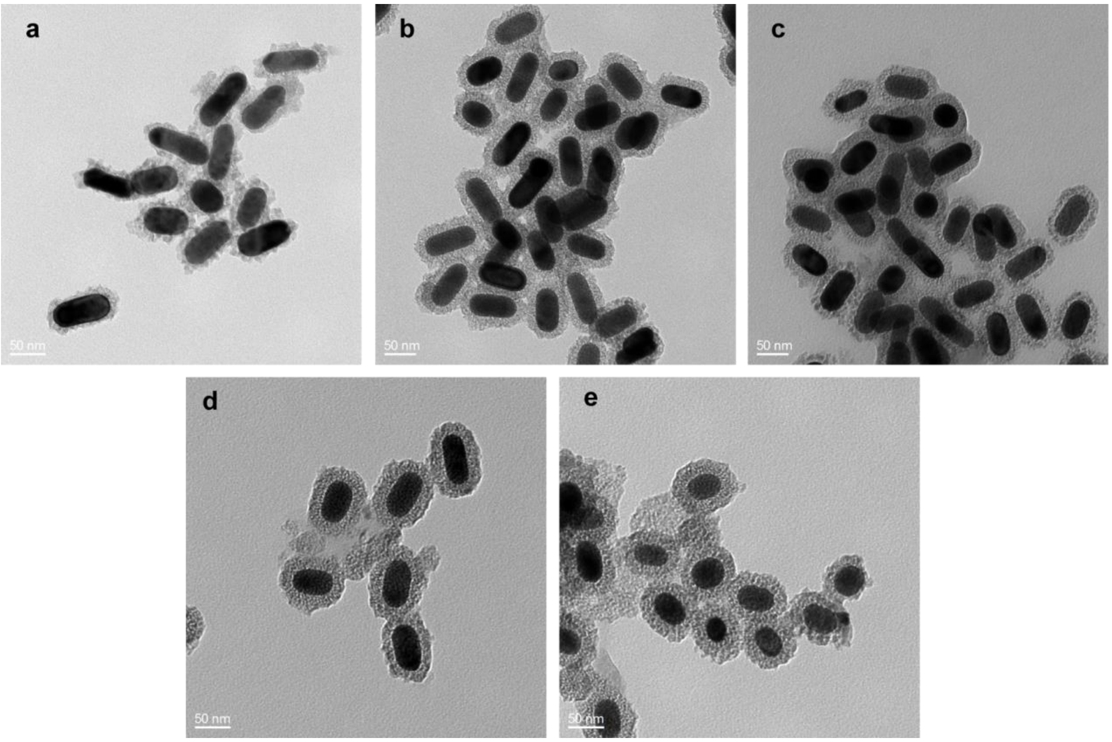

Figure S5. (a−e) TEM images of the AuNR@mTiO$_2$ samples with decreasing AuNR aspect ratios after calcination at 450 ℃ for 2 hr.

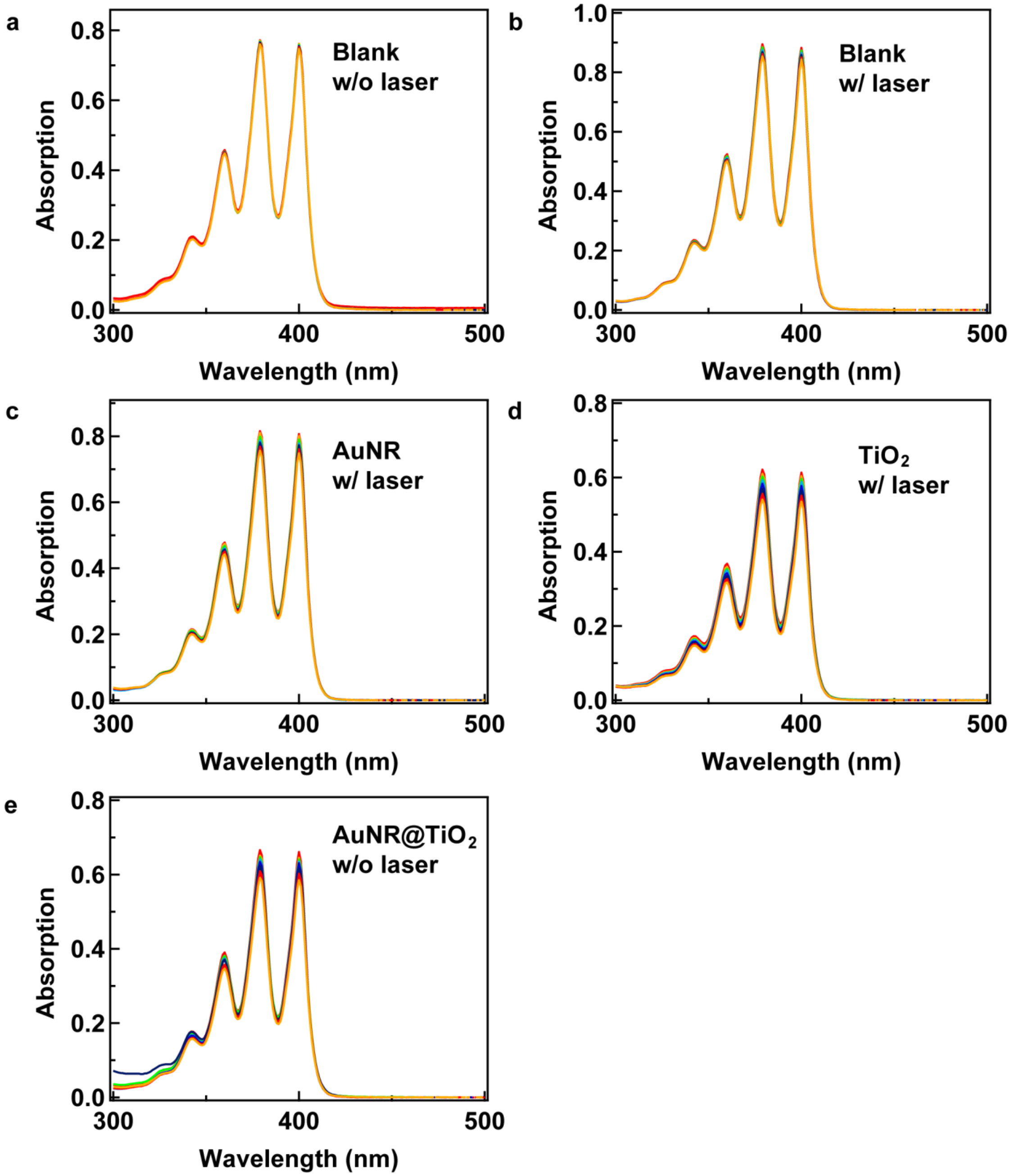

Figure S6. Time evolution of the ABDA absorption spectra of reference samples.

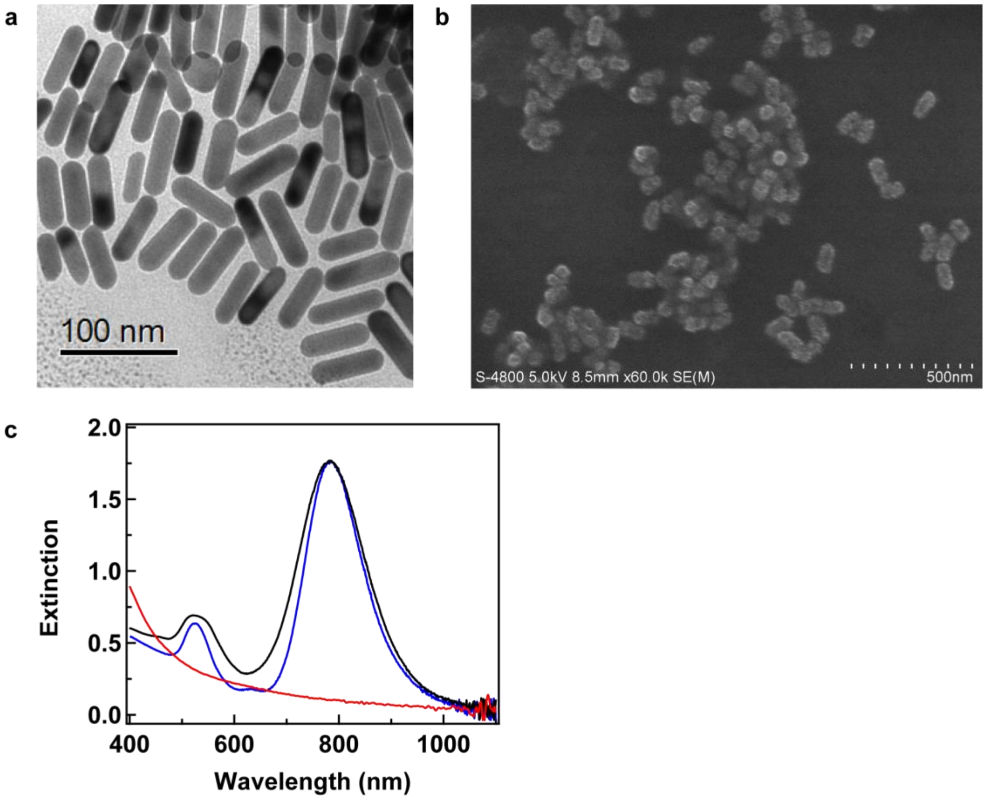

Figure S7. (a) The TEM image of AuNRs with the same ensemble LSPR as the AuNR@TiO_2 nanostructures in Figure 1a. (b) Hollow TiO_2 nanostructures after etching the Au core of the AuNR@TiO_2 nanostructures in Figure 1a. (c) Extinction spectra of the AuNR@TiO_2 nanostructures (black), the AuNRs with the same ensemble LSPR (blue), and the hollow TiO_2 nanostructures (red).