

# **Bottom-up formation of gold truncated pyramids smaller than 10 nm on SrTiO<sub>3</sub> nanocubes: An application to plasmonic water oxidation**

Kota Kurokawa,<sup>a</sup> Musashi Fujishima,<sup>b</sup> Shin-ichi Naya,<sup>c</sup> Hiroaki Tada<sup>a,b</sup> \*

<sup>a</sup> Graduate School of Science and Engineering, Kindai University, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.

<sup>b</sup> Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.

<sup>c</sup> Environmental Research Laboratory, Kindai University, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan.

\* To whom correspondence should be addressed: TEL: +81-6-6721-2332, FAX: +81-6-6727-2024,

E-mail: [h-tada@apch.kindai.ac.jp](mailto:h-tada@apch.kindai.ac.jp).

## Experimental

### Method

Ishihara sangyo co. kindly gifted us with titanium(IV) oxide (TiO<sub>2</sub>, ST-01, mean particle size = 7 nm, specific surface area of 300 m<sup>2</sup> g<sup>-1</sup>). Lithium hydroxide (LiOH > 98.0%), strontium hydroxide octahydrate (Sr(OH)<sub>2</sub>·8H<sub>2</sub>O > 96.0%), hydrochloric acid (HCl 35-37%), hydrogen tetrachloroaurate(III) tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O > 99%), and urea (CH<sub>4</sub>N<sub>2</sub>O > 99.0%) were purchased from Kanto Chemical co. All chemicals were used as-received without further purification.

### Synthesis of SrTiO<sub>3</sub> NCs

SrTiO<sub>3</sub> nanocubes (SrTiO<sub>3</sub> NCs) was prepared by the reported procedure.<sup>1</sup> LiOH (3.00 g) and Sr(OH)<sub>2</sub>·8H<sub>2</sub>O (2.65 g) were dissolved in H<sub>2</sub>O (25 mL), and the solution was stirred at room temperature for 20 min in 50 mL Teflon-lined stainless-steel autoclave. After adding anatase TiO<sub>2</sub> (0.8 g, ST-01, Ishihara Sangyo) to the solution, the suspension was stirred at room temperature for 1 h. The resulting suspension was heated at 473 K for 24 h, and washed with 1 M HCl aq. and distilled water several times. The particles were dried in vacuo to yield SrTiO<sub>3</sub> NCs.

### Au NP deposition

Au nanoparticles were deposited to SrTiO<sub>3</sub> NCs by the deposition-precipitation method using urea.<sup>2</sup> SrTiO<sub>3</sub> NCs (200 mg) was added to an aqueous solution of HAuCl<sub>4</sub> (4.86 mM, 10 mL) and of urea (292 mg). The suspension was vigorously stirred at 80°C for 18 h, and the resulting particles were corrected by centrifugation. The particles were washed with hot distilled water (323 K) ten times. After drying in vacuo, the particles were calcined at 773 K for 1 h to obtained Au//SrTiO<sub>3</sub> NCs. Au/SrTiO<sub>3</sub> NPs were synthesized by the similar method using SrTiO<sub>3</sub> NPs (Aldrich,  $d < 100$  nm,  $S_{\text{BET}} = 19.8$  m<sup>2</sup> g<sup>-1</sup>).

### Sample characterization

Scanning electron microscopy observation was carried out at an applied voltage of 20 kV (Hitachi SU8230) to determine the mean size of SrTiO<sub>3</sub> NCs. X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (Rigaku SmartLab 3KW) operating with 40 kV and 100 mA. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) observations were carried out by means of JEOL JEM-2100F at an applied voltage of 200 kV. The selected area electron diffraction pattern was obtained by JEOL JEM-2100F. The loading amount of Au was quantified by inductively coupled plasma spectroscopy (iCAP7600D, Thermo Fisher Scientific K. K.). Diffuse reflectance UV-Vis spectra of the samples were recorded by means of a Hitachi U-4000 spectrometer with an integrating sphere at room temperature. The reflectance ( $R_{\infty}$ ) was measured with respect to a reference

of BaSO<sub>4</sub>, and the relative absorption coefficient was calculated by the Kubelka-Munk function [ $F(R_\infty)$ ] expressing the equation  $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$ . Valence band- and wide scan-X-ray photoelectron spectra were measured by means of a Kratos Axis Nova X-ray photoelectron spectrometer using a monochromated Al K $\alpha$  X-ray source (1486.6 eV) at 15 kV and 10 mA. The take-off angle was set to be 90°, and the binding energies ( $E_B$ ) were referenced with respect to the C1s (284.6 eV).

### Water oxidation reaction

Au/SrTiO<sub>3</sub> (10 mg) was dispersed into an aqueous solution (10 mL) of AgNO<sub>3</sub> (10 mM) and La<sub>2</sub>O<sub>3</sub> (20 mg). La<sub>2</sub>O<sub>3</sub> was added to maintain pH constant (pH 7.45).<sup>3</sup> After deaeration by Ar bubbling for 0.5 h, visible light was irradiated by using Xe lamp with optical filter ( $\lambda > 400$  nm, Intensity integrated 400-780 nm  $I_{400-780} = 38$  mWcm<sup>-2</sup>) at 298 K. The amount of O<sub>2</sub> evolved was quantified by gas chromatography (Shimadzu. GC-8APT) with a thermal conductivity detector, a Molecular Sieve 5A column ( $\phi$  3.0 mm, 1m), and argon carrier gas. The injection and column temperatures were set at 60°C. To evaluate the external quantum yield ( $\phi_{ex}$ ), monochromatic light was irradiated by using LED lamp with various emission wavelength (365-1450 nm). By assuming four-electron oxidation of H<sub>2</sub>O, the  $\phi_{ex}$  value was calculated as eq 1.

$$\phi_{ex} = 4 \times (\text{molecule number of O}_2 \text{ evolved}) / (\text{incident photon number}) \times 100 \quad (1)$$

### Photodeposition of CoO<sub>x</sub>

Photodeposition of cobalt oxide (CoO<sub>x</sub>) was carried out by the reported procedure.<sup>4</sup> Au/SrTiO<sub>3</sub> NC (20 mg) was dispersed into an aqueous solution (10 mL) of Co(NO<sub>3</sub>)<sub>2</sub> (10 mM) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1 mg). Visible light was irradiated by using Xe lamp with optical filter ( $\lambda > 400$  nm, Intensity integrated 400-780 nm  $I_{400-780} = 38$  mWcm<sup>-2</sup>) at 298 K for 30 min to obtain CoO<sub>x</sub>-Au/SrTiO<sub>3</sub> NC.

### FDTD calculation

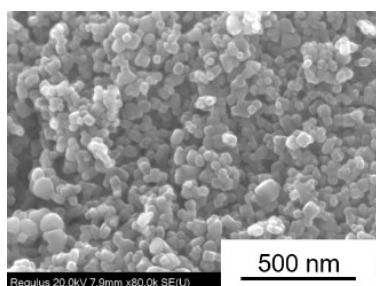
Finite difference time domain (FDTD) simulations were carried out for Au hemisphere (AuHS) and Au truncated pyramid (AuTP) loaded on SrTiO<sub>3</sub> with a FDTD simulation program package (Lumerical Solutions, Inc.). The calculation models were built using particle sizes obtained from TEM observations and complex refractive indices from literatures.<sup>5,6</sup> The light scattering behaviour of the models was simulated using total-field scattered-field (TFSF) source. In the simulation, a  $y$ -polarized plane wave with the wavelength from 300 to 1,100 nm ( $f = 273 \sim 1,000$  THz) was injected to AuHS or AuTP from the  $x$ -axis or  $z$ -axis direction. To enhance the resolution of field mapping images, a mesh override region ( $0.08 \times 0.08 \times 0.08$  nm<sup>3</sup>) was set around particles. The simulation region was set

to be  $566 \times 566 \times 555 \text{ nm}^3$  with perfectly matched layer (PML) absorbing boundary condition. Symmetric and anti-symmetric boundary conditions were used to minimize the computational time.

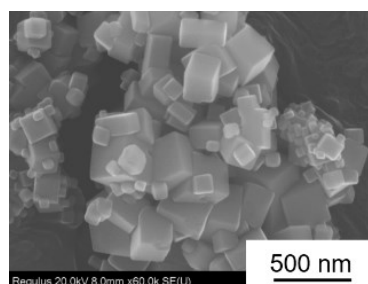
## References

- 1 Z. Zheng, B. Huang, X. Zhang and Y. Dai, *J. Colloid Interface Sci.* 2011, **358**, 68-72.
- 2 R. Zanella, S. Giorgio, C. R. Henry and C. Louis, *J. Phys. Chem. B* 2002, **106**, 7634-7642.
- 3 A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *J. Phys. Chem. A* 2002, **106**, 6750-6753.
- 4 Z. Zheng, N. Murakami, J. Liu, Z. Teng, Q. Zhang, Y. Cao, H. Cheng and T. Ohno, *ChemCatChem* 2020, **12**, 3783-3792.
- 5 D. R. Lide Chief-in-Ed., *Handbook of Chemistry and Physics* 83th Ed., CRC Press, New York, **2002-2003**.
- 6 G. Panomsuwan, O. Takai and N. Saito, *Phys. Status Solidi A* 2013, **210**, 311-319.

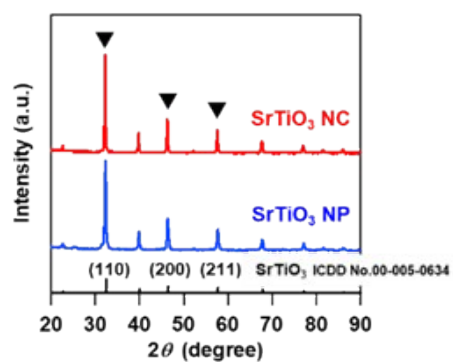
A)



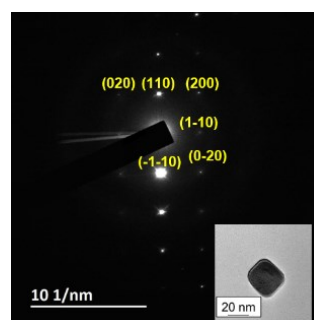
B)



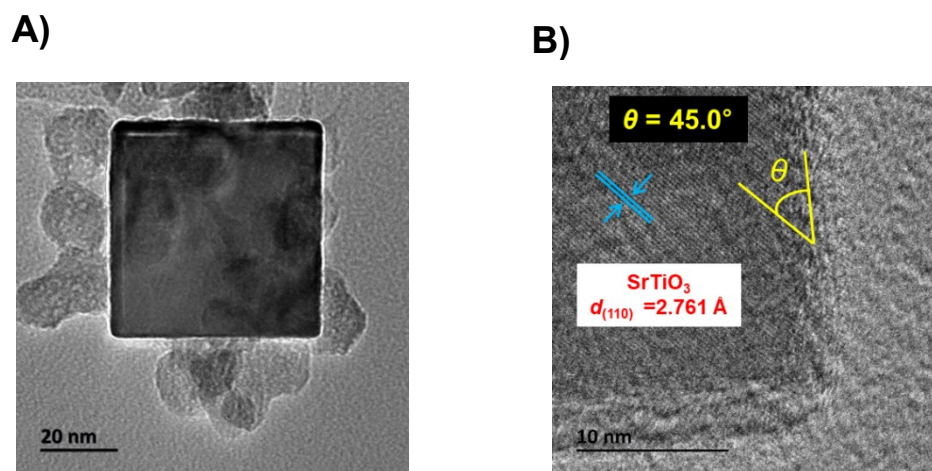
C)



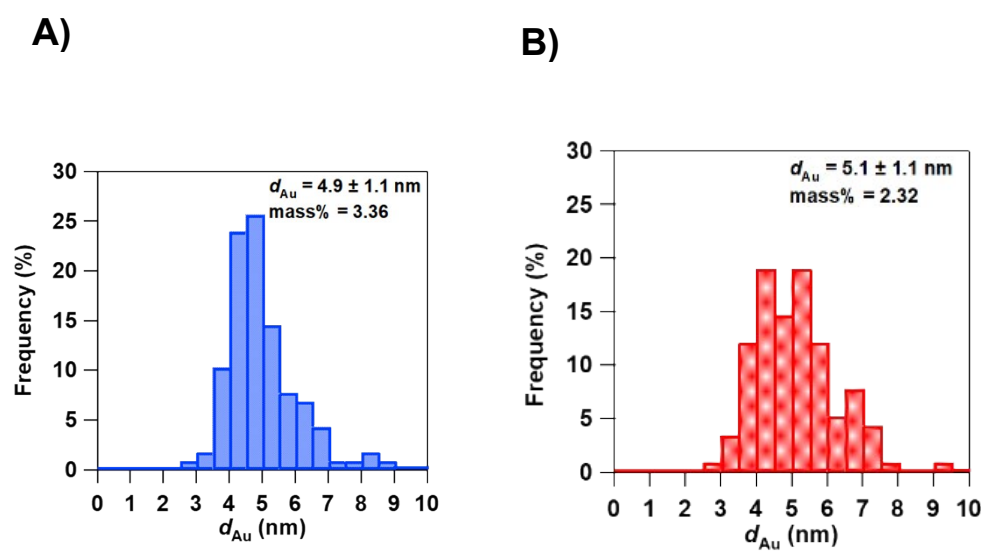
D)



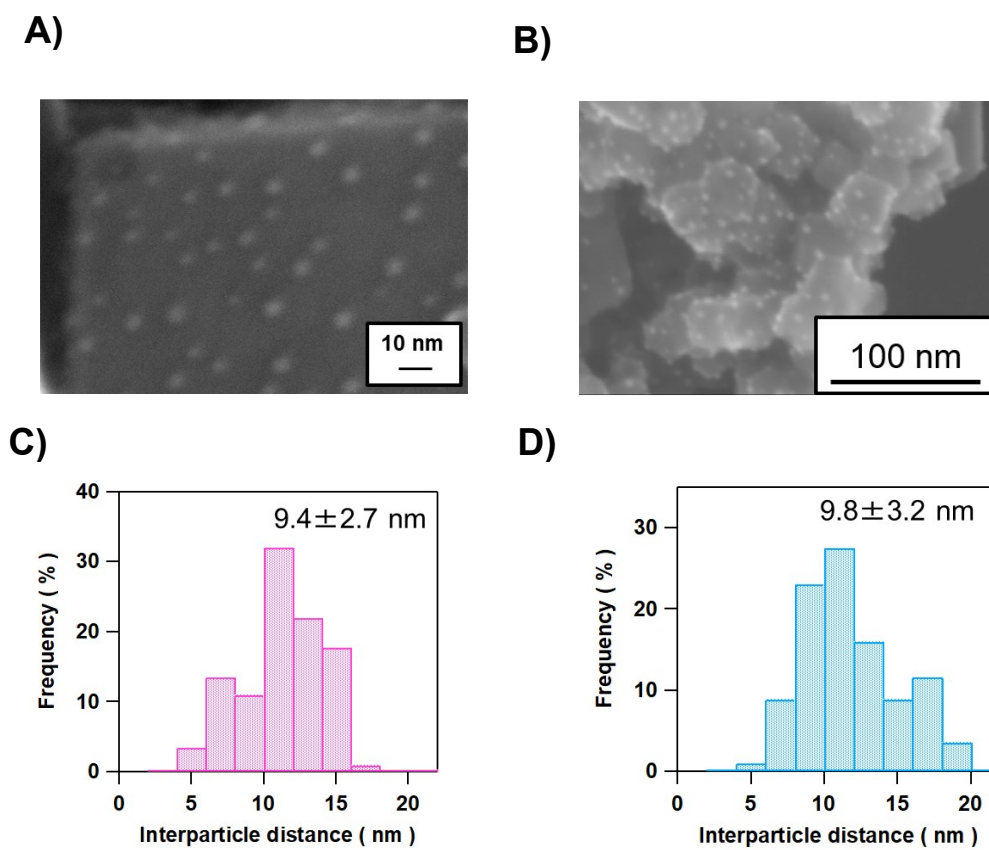
**Figure S1.** TEM images of Aldrich sample (A) and the synthesized sample (B). (C) XRD patterns of the samples (D) Selected area electron diffraction (SAED) pattern for a  $\text{SrTiO}_3$  nanocube.



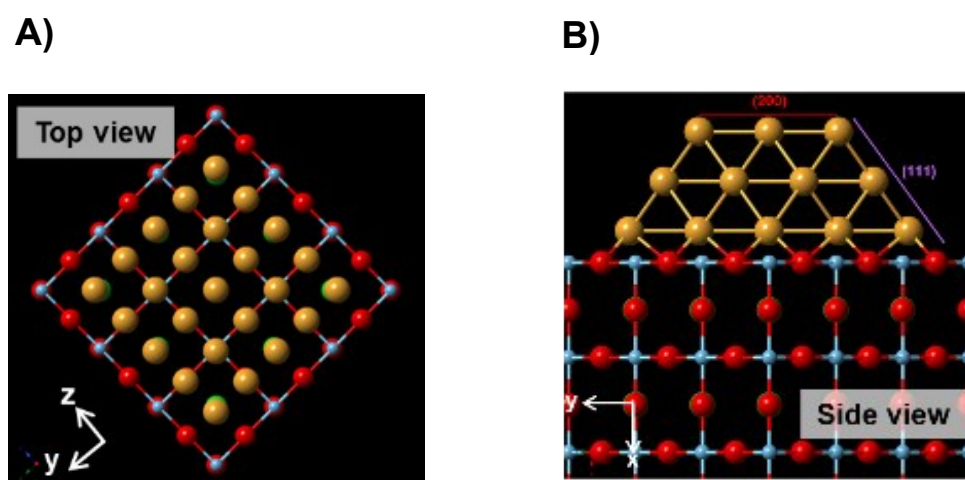
**Figure S2.** TEM (A) and HR-TEM (B) images of SrTiO<sub>3</sub> NCs.



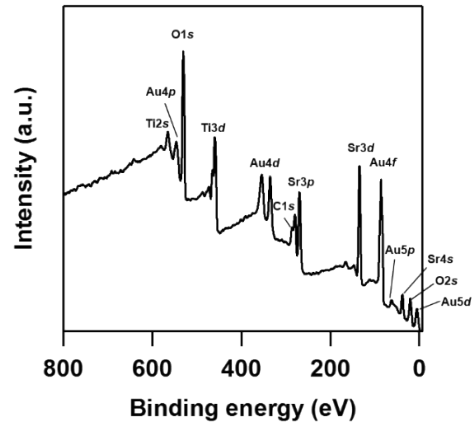
**Figure S3.** Au particle size distribution of Au/SrTiO<sub>3</sub> NPs (A) and Au/SrTiO<sub>3</sub> NCs (B).



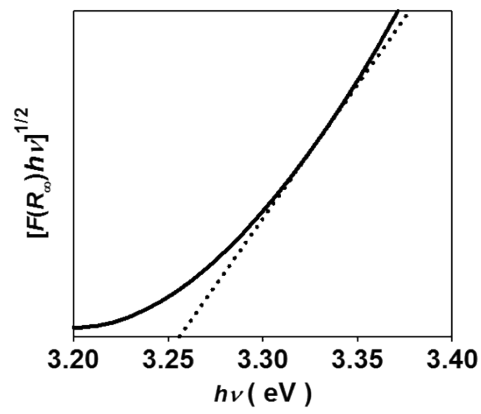
**Figure S4.** SEM image of Au//SrTiO<sub>3</sub> NCs (A) and Au//SrTiO<sub>3</sub> NPs (B). The surface-to-surface interparticle distance between the nearest neighbour Au NPs of Au//SrTiO<sub>3</sub> NCs (C) and Au//SrTiO<sub>3</sub> NPs (D).



**Figure S5.** Top (C) and side view (D) of the interfacial model for Au//SrTiO<sub>3</sub> NC.

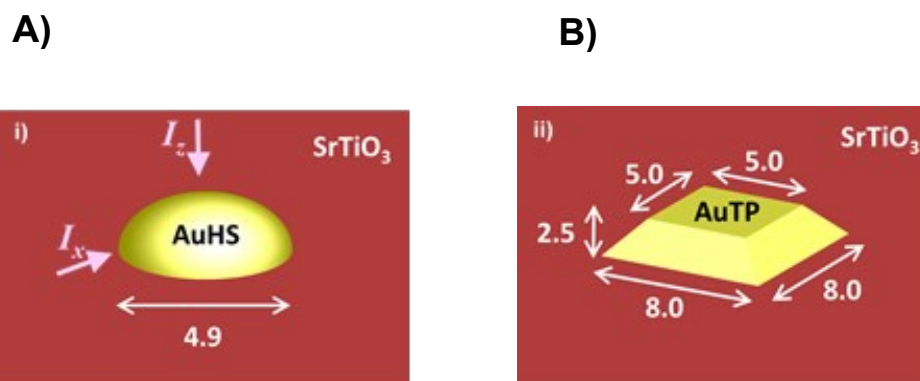


**Figure S6.** Wide-scan XP spectrum of Au//SrTiO<sub>3</sub> NC.

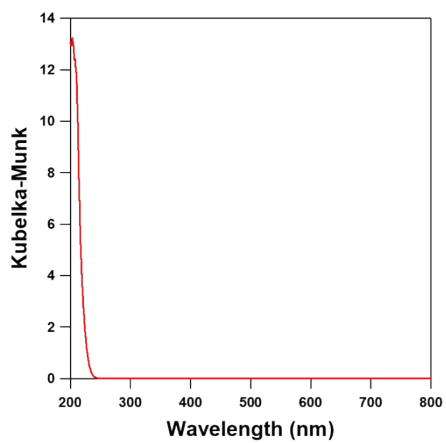


**Figure S7.** Tauc plot for SrTiO<sub>3</sub> NC.

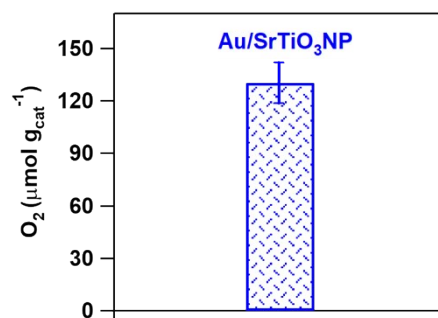




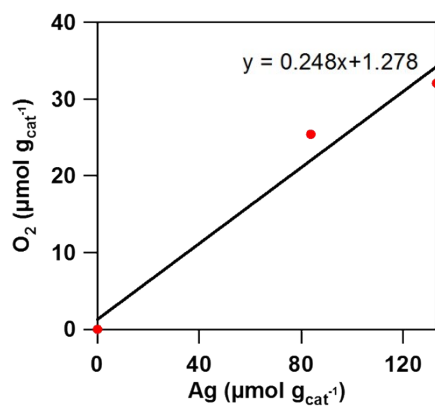
**Figure S8.** Model structures of Au hemisphere (A, AuHS) and Au truncated pyramid (B, AuTP) placed on SrTiO<sub>3</sub> slab for the FDTD simulations. The units for length in (A) and (B) are nanometers (nm).



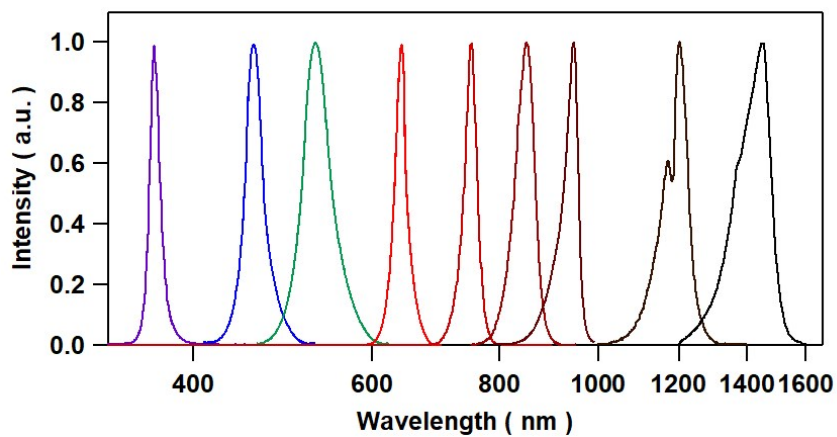
**Figure S9.** Diffuse reflectance UV-Vis-NIR absorption spectrum of La<sub>2</sub>O<sub>3</sub>.



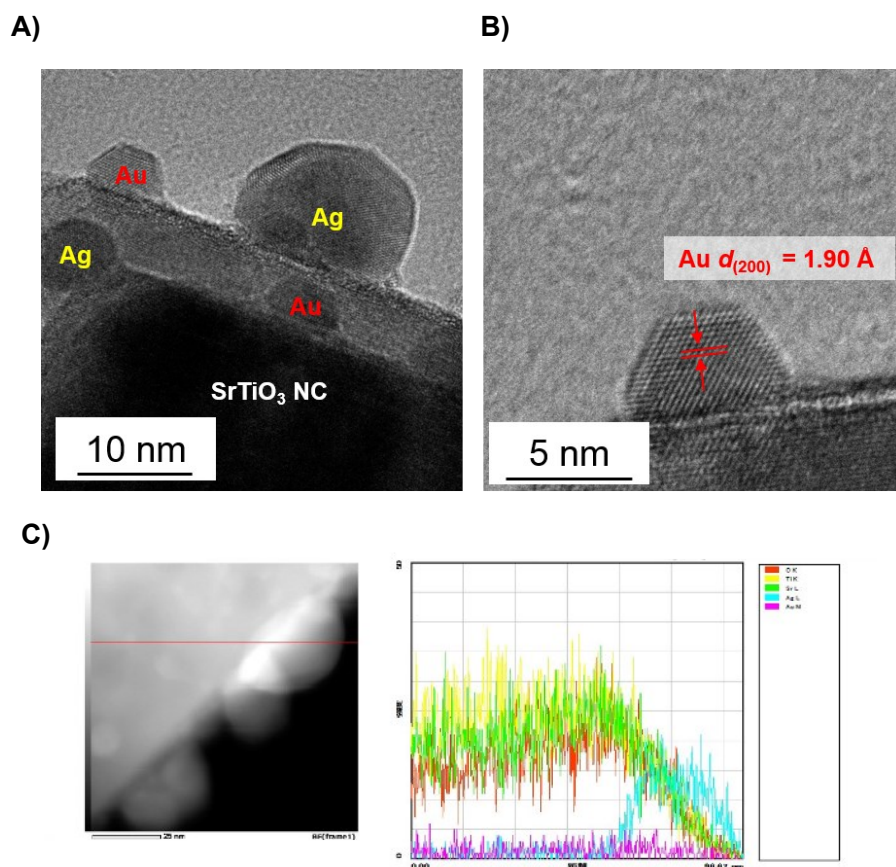
**Figure S10.**  $O_2$  generation from 10 mM aqueous solution of  $AgNO_3$  (10 mL, pH 7.5) containing  $La_2O_3$  (20 mg) under visible-light irradiation ( $\lambda_{\text{ex}} > 400$  nm) in the presence of Au/SrTiO<sub>3</sub> NP for 24 h.



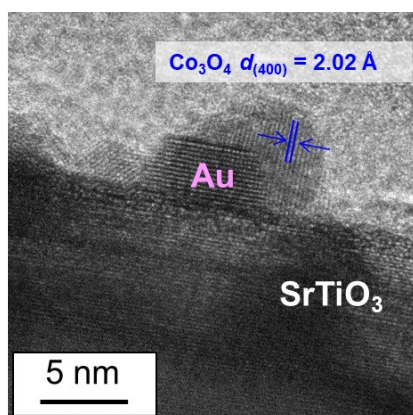
**Figure S11.** Plots of the amount of  $O_2$  generated as a function of the Ag-loading amount on Au/SrTiO<sub>3</sub> NC by the visible light irradiation.



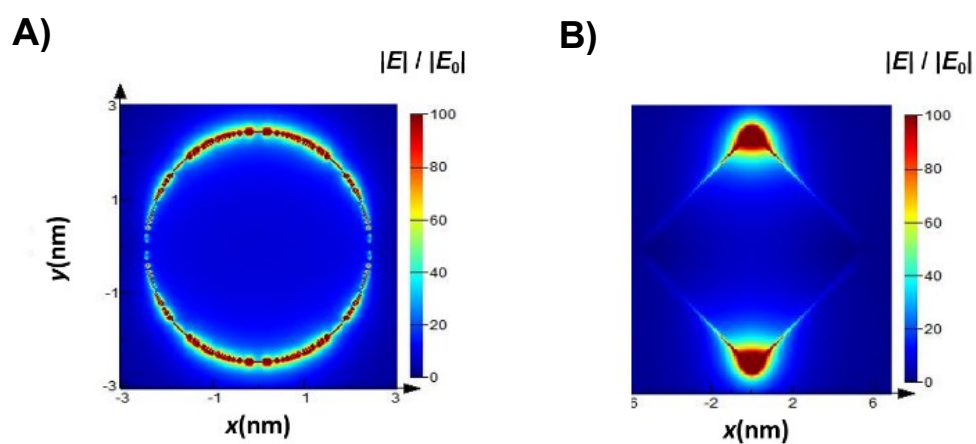
**Figure S12.** Emission spectra of LEDs used for the action spectra of the external quantum yield.



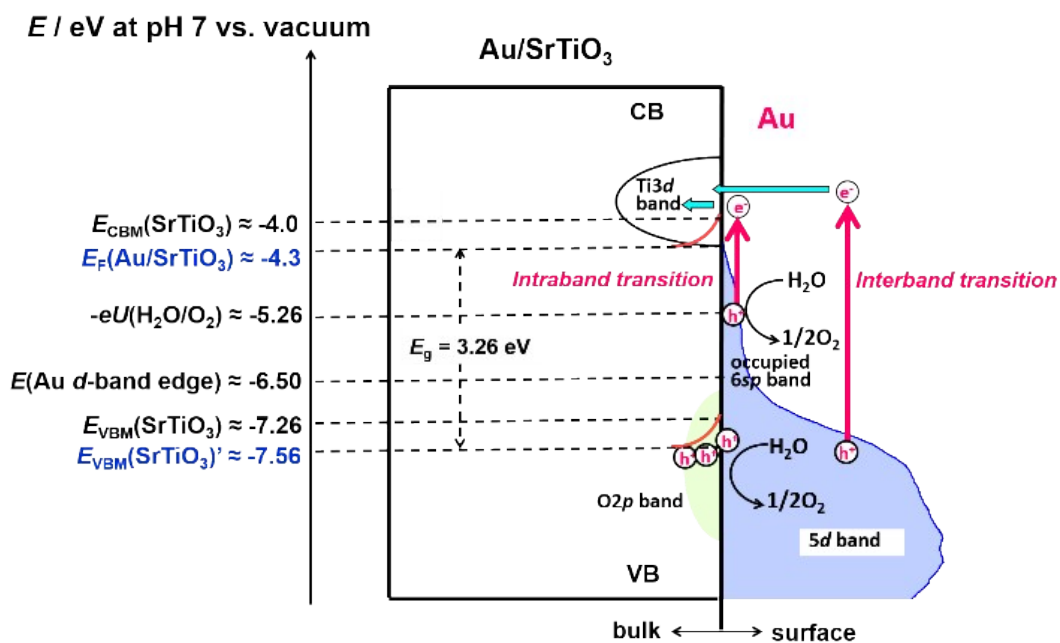
**Figure S13.** TEM (A) and HR-TEM (B) images, and the STEM-EDS line analysis (C) of Ag-photodeposited Au/SrTiO<sub>3</sub> NCs along the red line in the left TEM image.



**Figure S14.** TEM image of  $\text{CoO}_x$ -photodeposited Au// $\text{SrTiO}_3$  NCs.



**Figure S15.** Local electric field images for (C) AuHS ( $I_x$ ) at 666 nm and (D) AuTP ( $I_x$ ) at 824 nm.



**Scheme S1.** Action mechanism of Au//SrTiO<sub>3</sub> NC-photocatalyzed water oxidation reaction, where the energy levels are shown with respect to the vacuum level at pH 7. The band energy of Au NPs in Au//SrTiO<sub>3</sub> NC was obtained by subtracting the valence band XP spectrum of unmodified SrTiO<sub>3</sub> NC from that of Au//SrTiO<sub>3</sub> NC.