

Supporting Information

Plasmon-mediated Photothermal Conversion by TiN Nanocubes toward CO Oxidation under Solar Light Illumination

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Preparation procedures for different samples, Characterization techniques

Experimental

Titanium nitride (TiN) Nanocubes (NCs), Silica (SiO₂) Nanospheres (NS) Hexa chloro platinic acid (H₂PtCl₆, ACS reagent, ≥ 99.0%, Sigma Aldrich), Sodium Borohydride (NaBH₄, Sigma Aldrich), Sodium Hydroxide (NaOH, Sigma Aldrich), were used as received.

Deposition of Pt NPs on TiN nanocubes

TiN nanocubes (NC) were synthesized by thermal plasma processing where titanium powder was treated by the plasma of argon and nitrogen.¹ These were purchased from Nisshin Engineering Inc. Deposition of Pt on TiN NC was carried out by chemical reduction method using NaBH₄. An aliquot of 90 mg of TiN NC was added to 10 mL of aqueous solution of H₂PtCl₆ (26.6 mg) and stirred for 30 min at room temperature. To the dark brown solution, NaBH₄ (20 mL, 0.1M) aqueous solution was added dropwise and effervescence were observed with increase of pH up to 9. After 30 min. NaOH (8 mL, 0.2M) was added dropwise. After stirring for one hour the product solution was centrifuged (6000 rpm, 10 min.) and washed thoroughly with water 3-4 times. Finally the powder product was obtained by drying at 80 °C for 3h.

Deposition of Pt NPs on Silica (SiO₂) Nanospheres

To an aqueous solution (20 mL) containing H₂PtCl₆ (26.6 mg), silica nanospheres (NS) were added and stirred for 30 min. The solution was light yellow in colour. NaBH₄ (0.1 M, 20 mL) was added dropwise, an immediate change in colour was observed to black indicating the completion of reduction forming Pt. The solution was centrifuged and washed with water 3-4 times. Product formed was dried at 80 °C for 3 h and further annealed in Ar atmosphere at 300 °C for 3h.

Characterization

Powder X-ray diffractometry (pXRD): The pXRD measurements were performed using Cu K α radiation (λ = 0.15418 nm) with an increment of 0.02 degrees in a range of diffraction angles from 20 to 100 degrees. An obliquely finished Si crystal (non-reflection Si plate) was used as a sample holder to minimize the background.

Hard X-ray photoemission spectroscopy (HAXPES): The HAXPES measurements were performed using X-rays with photon energy of 5.95 keV, at the undulator beam line BL15XU of SPring-8, Japan. Samples for HAXPES measurements were prepared by mixing the sample solution (in THF) with carbon black (Vulcan XC-72, Cabot Co. Ltd.) to avoid charging effects. 10 μ L of the sample was dropped onto carbon substrates (Nilaco Co., Ltd.) and dried under vacuum. The core-level states of the samples were examined at room temperature in UHV using a hemispherical electron energy analyzer (VG SCIENTA R4000). The total energy resolution was set to 240 meV. The binding energy was referenced to the Fermi edge of an Au thin film.

Transmission electron Microscopy: A 200 kV transmission electron microscope (TEM and/or STEM, JEM-2100F, JEOL) was used which was equipped with two aberration correctors (CEOS GmbH) for the image- and probe-forming lens systems and an X-ray energy-dispersive spectrometer (JED-2300T, JEOL) for elemental mapping. The samples for TEM were prepared by dropping an ethanol suspension of the sample powder onto a commercial TEM grid coated with a collodion film. The sample was thoroughly dried in vacuum prior to observation.

Catalytic tests

Thermal CO oxidation

Thermal CO oxidation reaction was performed over the catalyst (10 mg) in a circulating-gas reactor equipped with a gas chromatograph (Shimadzu GC-8A). The catalyst was vacuum-dried in the reactor prior to the reaction. A mixture of CO (6.67 kPa) and O₂ (3.33 kPa) was then circulated through the catalyst at 200 °C. The formation of CO₂ was monitored by a gas chromatography.

Photo-thermal CO oxidation:

The catalyst samples placed in a quartz tube reactor were evacuated, exposed to a solar simulator with a Fresnel lens having the focal length of 150 mm. The position of the solar simulator was adjust so that the focal point illuminated the powder area. . Then mixture of CO (6.67 kPa) and O₂ (3.33 kPa) was circulated through the catalyst (20 mg). The formation of CO₂ was monitored by gas chromatography.

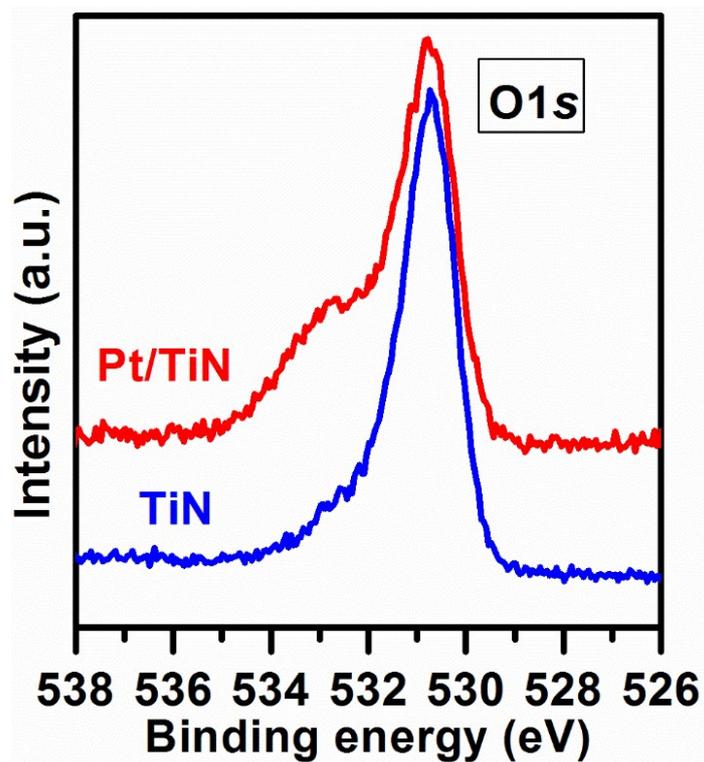


Figure S1. HAXPES spectra for the TiN NC (blue), and Pt/TiN (red) in the O 1s region.

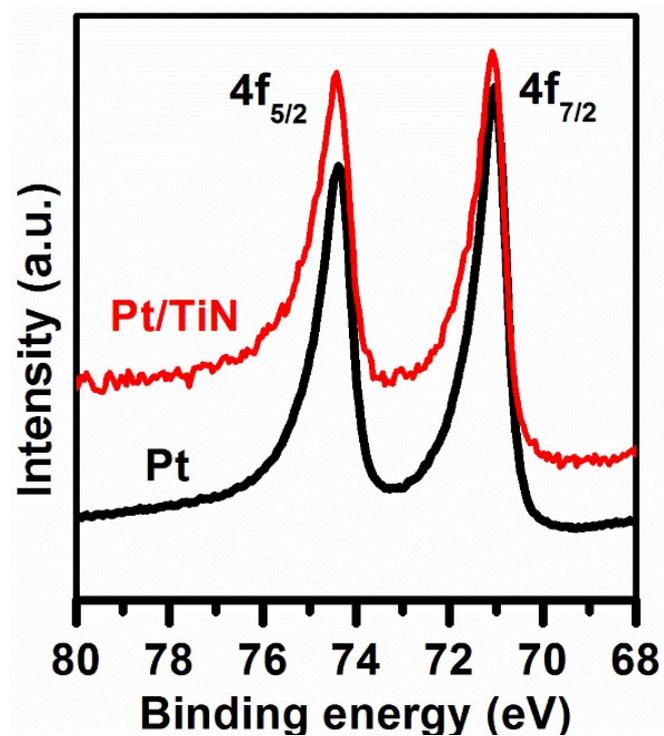


Figure S2. HAXPES spectra for the Pt NPs (black) and Pt/TiN (red) in the Pt 4f region.

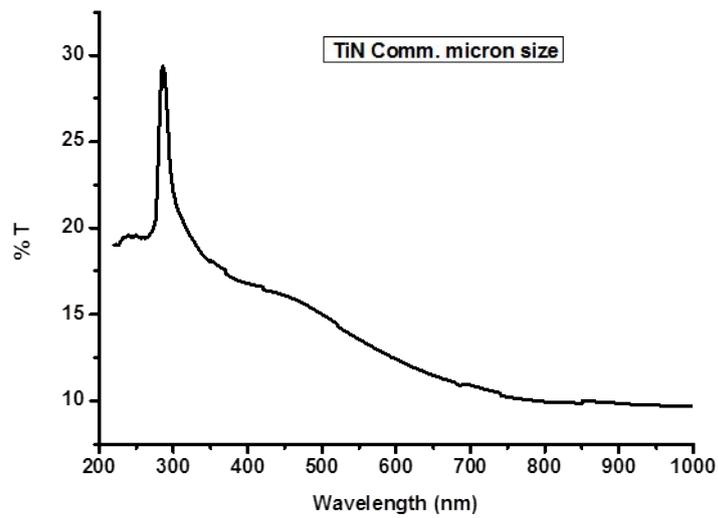


Figure S3. UV-Vis. Absorbance spectrum of the TiN powder (>1 micro m) in pure water at 0.001 vol %. The liquid was put into a transparent plastic cell where the cell thickness was 1 cm. The spectrum is normalized to pure water.

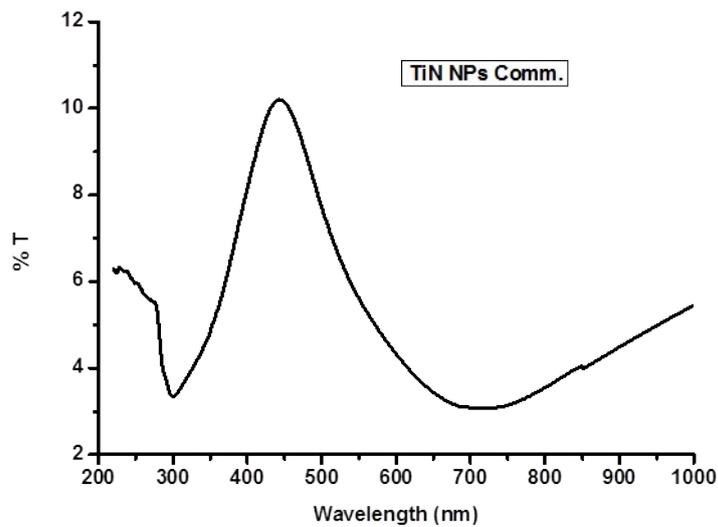


Figure S4. UV-Vis. Absorbance spectrum of the TiN NCs in pure water at 0.001 vol %.

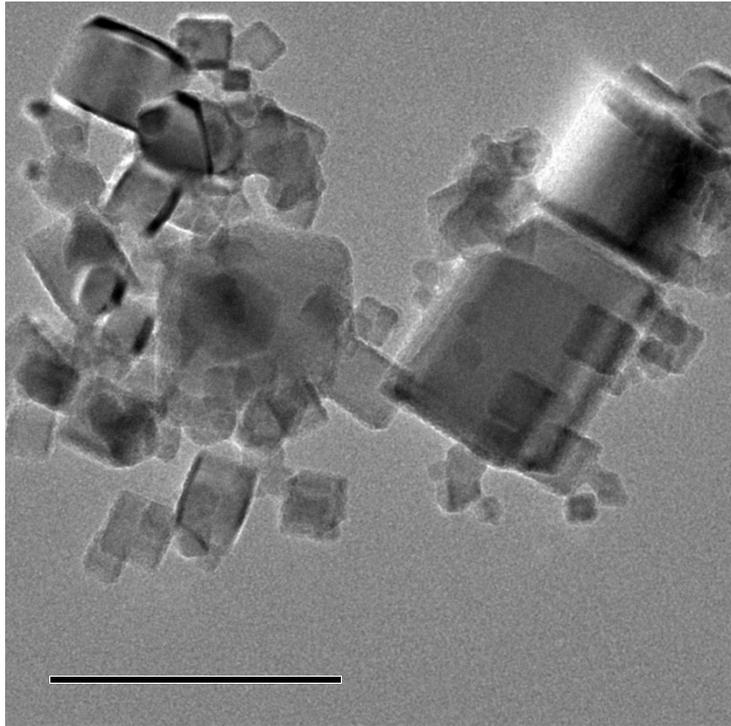


Figure S5. Bright-field TEM image of the TiN nanocubes. The broad distribution in particle size of the TiN nanoparticles is attributed to the high synthesis temperature, which results in large thermal fluctuation in the particle-formation processes.

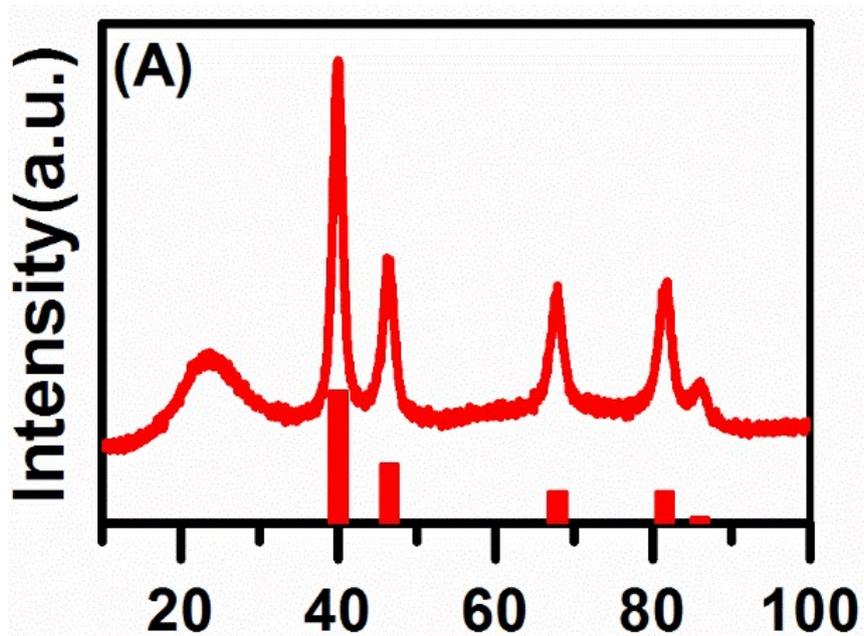


Figure S6. pXRD spectrum of the Pt/SiO₂ and a simulated pattern of Pt (bar charts).

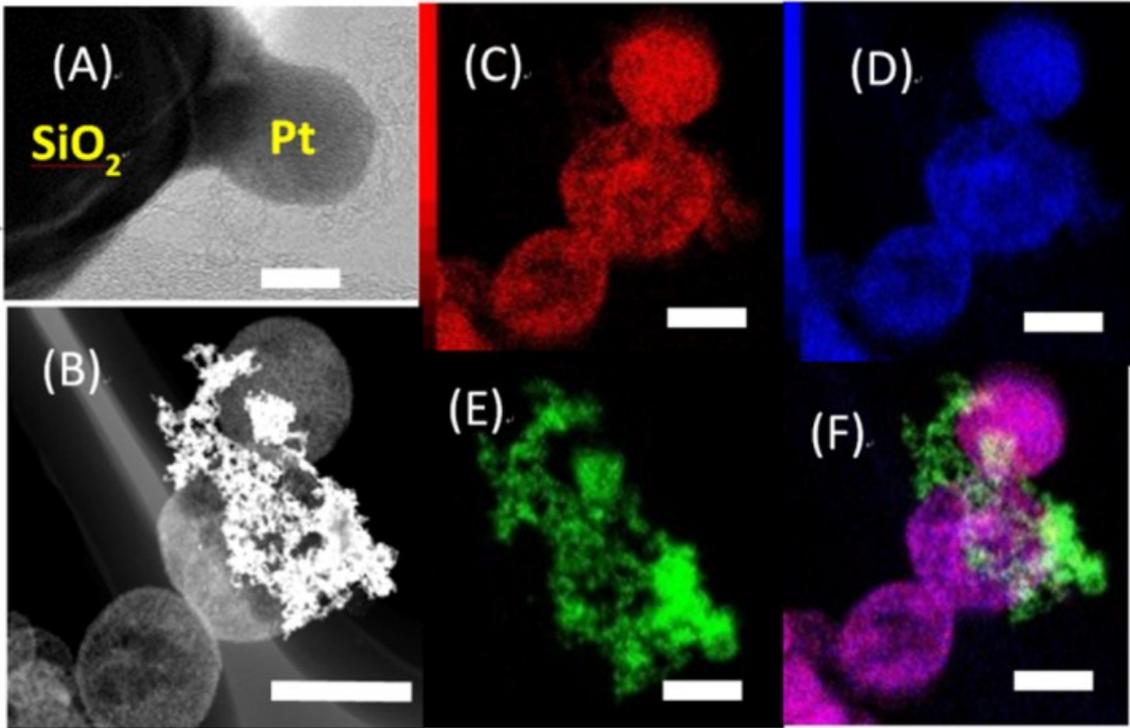


Figure S7. Bright-field TEM image of the Pt/SiO₂ (A). The scale bar corresponds to 5 nm. (B) STEM image and the corresponding compositional mapping images of the Pt/SiO₂ (C-F). (C), (D), (E) and (F) correspond to the Si-, O-, Pt- and merged images, respectively. The scale bars in (C-F) correspond to 50 nm.

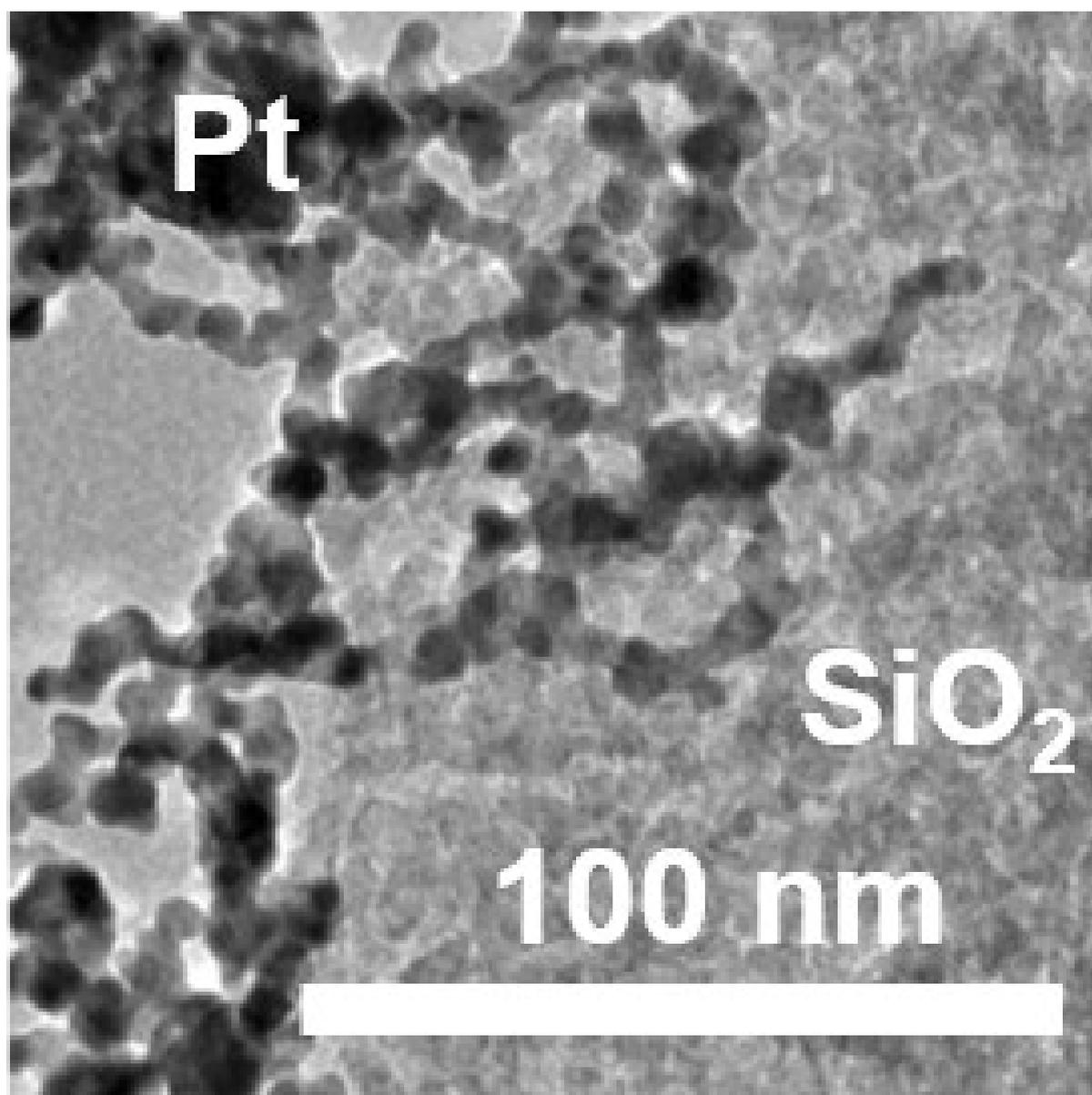


Figure S8. High-resolution transmission electron microscope (HR-TEM) images of the Pt/SiO₂. The Pt nanoparticles were connected to form a network structure.

Pt/TiN Before & After Catalysis

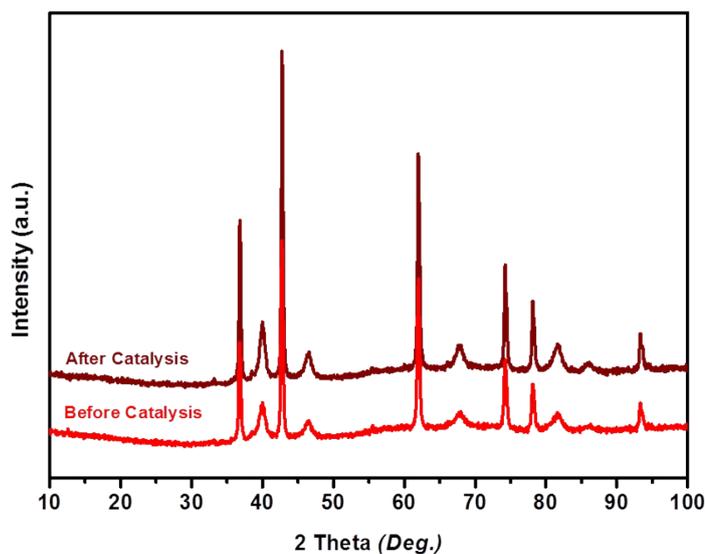


Figure S9. pXRD profile for the Pt/TiN after the photothermal catalysis.

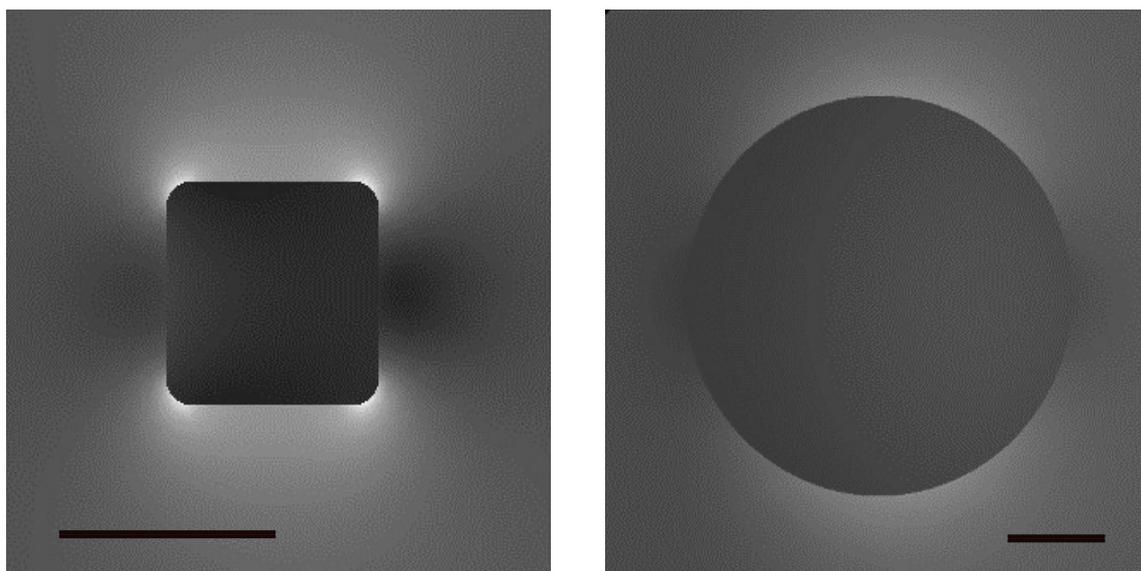


Figure S10. Simulated distribution of electric fields around the TiN NC (A) and SiO₂ NS (B). The scale bars correspond to 50 nm. The wavelength of the electromagnetic field is 550 nm. The electric field is perpendicular to the image.

References :

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- (2) S. Ishii, R. P. Sugavaneshwar, T. Nagao, *J. Phys. Chem. C* **2015**, accepted.

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