

SUPPORTING INFORMATION PARAGRAPH 1.

Experimental methods

1.1. Finite difference time domain (FDTD) simulation

FDTD is a numerical scheme to solve Maxwell's equation in space and time. This is done by discretizing them using a central difference scheme and applying a time marching algorithm¹⁸. To predict the enhancement of the electric near-field in the vicinity of the Ag NPs, we calculated in a representative geometry the electric field that is observed if a plane wave propagates normal to an interface between two infinite half spaces. They consist of TiO₂ and SiO₂, respectively. Directly at the interface but completely buried in the SiO₂, a Ag NPs with a diameter of 40 nm was positioned. The illuminating plane wave with a wavelength of 400 nm was y-polarized. In the propagation direction (z) we have assumed perfectly matched layer to truncate the computational domain²¹. In the two transversal directions (x and y) periodic boundary conditions were chosen. The period in the simulation was set to be 140 nm. Nonetheless, this value will have no influence on the near-field amplitudes as the response is dominated by the LSP resonance of the individual NPs. The refractive indices of TiO₂, SiO₂, and Ag were 3.3, 1.5, and $0.0500 + i\ 2.1051$, respectively.¹⁹ In the FDTD the complex refractive index was taken into account by simulating the time evolution of the polarization in accordance with a Drude type material response. The respective free parameters of the Drude model, the plasma frequency and the damping constant, were determined to match the experimentally available refractive index at the pertinent wavelength. The space was discretized with a resolution of 0.8 nm and the temporal evolution was simulated until steady state was observed.

1.2. Device fabrication procedure.

Silver powder was evaporated onto a SiO₂ substrate to form a 9-nm-thick Ag film. The Ag film on the substrate was heated in N₂ at 800°C for 5 min to form Ag NPs. NDH510-C; Nihon-Soda Co., Ltd. was used for a solution for photocatalytic TiO₂ thin film. NDH510-C is 5wt% Ti(iso-OC₃H₇)₂(AcAc)₂

ethanol solution.²² The TiO₂ solution was spin coated followed by heating at 500°C for 30 min to turn into anatase phase. A 10-W black-fluorescent lamp (FL10BL-B; Matsushita Electric Industrial Co., Ltd.) with a peak emission wavelength at 380 nm was employed as a near UV light source to examine the photocatalytic properties. The intensity of the near UV illumination was 0.5mW/cm². After illumination by near UV light, specimens were kept in darkness for 1 h, because the optical absorption was affected by the electronic excitation.^{23, 24} After these procedures, the optical absorption spectrum was measured again. Optical absorption spectroscopy was performed with Perkin Elmer Lambda-900. SEM and TEM were performed with S4800 Hitachi High-Technologies Co., Ltd. and H-9000NA, Hitachi Co., Ltd., respectively. A specimen for TEM was thinned with 30keV Ga⁺ beam of focused ion beam.

2. Structural appearance and optical response of samples with various thicknesses of the SiO₂ shell

For the evaluation of the photocatalytic activity various samples were fabricated with different thicknesses for the SiO₂ shell. To verify the quality of these devices and to decide whether the layer completely covers the Ag NPs, the surface of samples having a SiO₂ thickness between 5 nm and 30 nm were imaged using a SEM. Results are shown in Fig. S1. White spots that appeared only in Fig. S1 (a), the sample with 5 nm SiO₂ shell thickness, were assigned to Ag with x-ray photoelectron spectroscopy. It implies that a SiO₂ thickness of 5 nm is too thin to cover Ag NPs completely. For all the other thicknesses it can be seen that SiO₂ fully covers the Ag NPs, hence protecting them efficiently from oxidization.

To validate the possibility to shift the LSP resonance as a function of the SiO₂ shell thickness, the absorbance spectra was measured for each of these sample after depositing a 90 nm layer of TiO₂ on them. Results are shown in Fig. S2. In addition, results are shown for a sample covered with SiO₂ only. The LSP peak for the samples with a SiO₂ shell thickness of 5 nm, 10 nm, and 20 nm were located at 440 nm, 420 nm and 415 nm, respectively. Obviously LSP peak position was shifted toward shorter

wavelength with increasing SiO₂ shell thickness as expected. From the calculation as shown in Fig.1, the peaks of LSP with 5nm, 10 nm, and 20 nm thick SiO₂ were estimated at 490nm, 440nm and 410nm. Experimental results in Fig. S2 were close to calculated estimation as shown in Fig.1.

3. Optical absorption spectra of the decomposition of MB: one of the most popular estimation of photocatalytic ability.

To give an overall impression of the change in absorbance due to MB decomposition by UV light, Fig. S3 shows furthermore the entire absorbance spectra as a function of the time for the sample made of a 20 nm SiO₂ shell thickness. It can be seen that the change in absorbance occurs throughout the entire spectrum. We simply observed one peak due to MB. It means that the electronic excitation of MB could be avoided in our method mentioned in the second part of Methods.

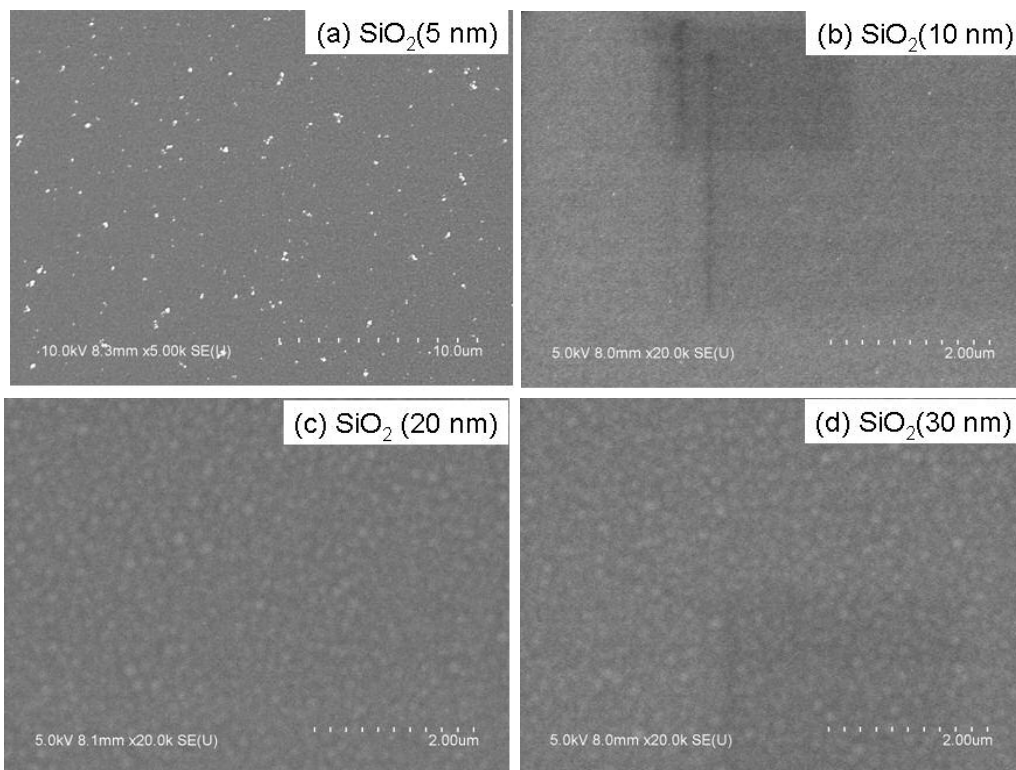


Figure. S1: SEM observations. Ag NPs were deposited on SiO₂ substrates followed by deposition of a SiO₂ layer with a thickness of 5 nm (a), 10 nm (b), 20 nm (c) and 30 nm (d).

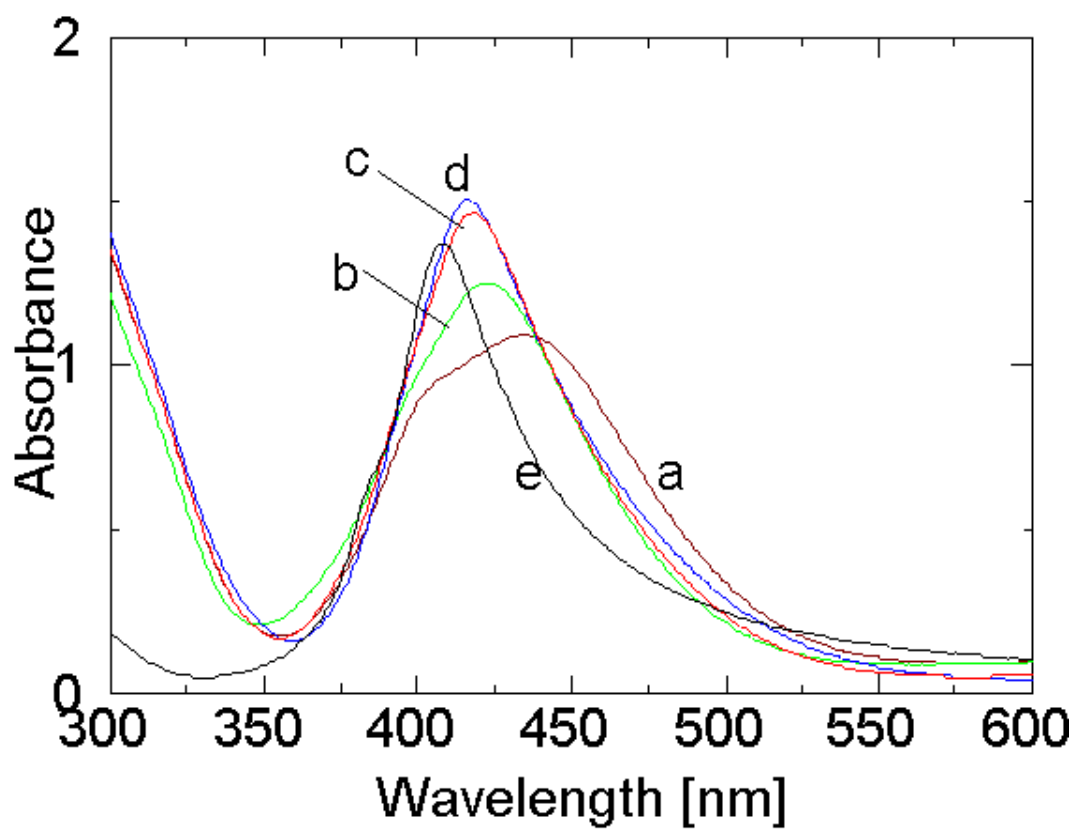


Figure. S2: Optical absorption spectra. SiO₂ was deposited on Ag NPs with thickness of 5 nm (a), 10 nm (b), 20 nm (c) and 30 nm (d) followed by deposition of 90 nm thick TiO₂. Spectrum for SiO₂ deposited on Ag NPs is shown in (e) for comparison.

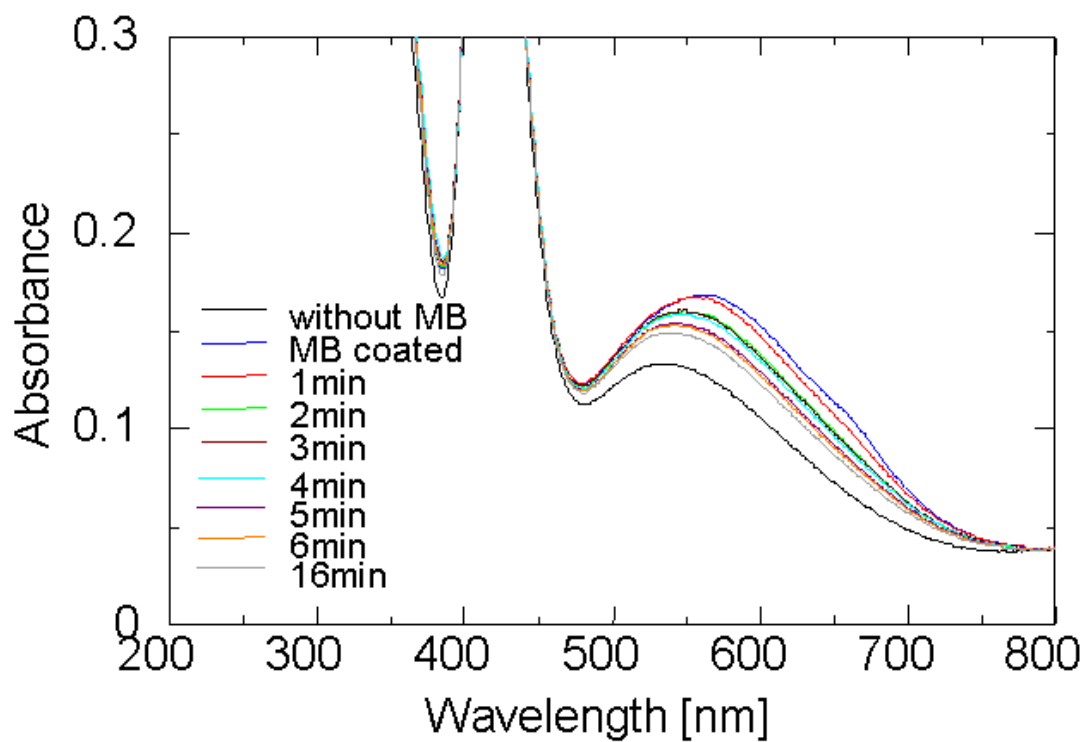


Figure. S3: Spectra before and after MB coating were shown with black and blue lines, respectively. After exposure of near UV for every one minute, optical absorption spectra were measured. Gray line presented the spectrum after 16 min illumination.