Supporting information

Photoinduced reversible changes in morphology of plasmonic Ag nanorods on TiO_2 and application to versatile photochromism

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Experimental

Deposition of Ag NRs on TiO_2. A rutile TiO_2(100) single-crystal substrate (10 × 10 × 0.5 mm, Shinkosha) was washed with acetone and ultra-pure water, etched in 20% aqueous HF for 10 min, rinsed with water and dried, followed by annealing at 900 °C for 1 h under atmospheric conditions to obtain an atomically flat surface (step height = 0.46 nm). Biaxially oriented Ag NRs were deposited on the TiO_2 surface by photoelectrochemical reduction of Ag^+ ions under UV light (310 nm, 1 mW cm^{-2}) for 6 min (or 20 min for display of images) in aqueous $AgNO_3$ (3 mM) mixed with equal volume of ethanol (99.5 vol%). The mixture contained acetaldehyde (550 ppm). After the growth, the sample was rinsed thoroughly with ultra-pure water to remove the residual salts and organic molecules. The UV light source was a Hg-Xe lamp (LA-300UV, Hayashi Watch Works) equipped with a bandpass filter (full width at half maximum (fwhm) = 10 nm).

Evaluation of spectral and morphological changes. The prepared sample was irradiated with polarized visible or IR light in N_2 gas at 50-70% RH at room temperature. The light source was a Xe lamp (480-700 nm, Lax-102, Asahi Spectra) or a halogen lamp (800-1300 nm, HA-150UX, Myutron) equipped with a long-pass filter (>460 nm), a bandpass filter (fwhm = 10, 40, 55, 63 and 78 nm for 480-700, 800-1000, 1100, 1200 and 1300 nm, respectively) and a linear polarizer (700-1100 nm, colorPol® VISIR, Codixx).

Extinction spectra were collected by a Jasco V-670 UV/Vis/NIR spectrophotometer. Polarized spectra were collected thorough the polarized filter mounted between the sample and the light source. The longitudinal plasmon mode of polydispersed Ag nanorods, the transverse mode of the nanorods, and less anisotropic Ag nanoparticles are responsible for extinction (Fig. 2a) at >700 nm, 500-700 nm and <500 nm, respectively, as supported by spectral simulation.[2,10] Morphological changes of Ag NRs were observed by AFM (Nanonavi Station/E-sweep, SII Nanotechnology) in a tapping mode (driving frequency = 110–150 kHz, scan rate = 0.4–0.7 Hz) by using a silicon cantilever (SI-DF20, SII Nanotechnology) with a normal spring constant of 15 N m^{-1} and tip radius of curvature of 10 nm. All AFM measurements were performed under atmospheric pressure in the closed chamber filled with dry N_2 gas, which was flowed for 1 h before each measurement. The sample in the chamber was irradiated with light through a glass window in the N_2 gas flow at 50-70% RH following the flow for at least 30 min. After the light irradiation, dry N_2 gas was flowed for more than 1.5 h before the AFM measurement. AFM images were corrected by a Morphology Filter (SII Nanotechnology) in order to eliminate the influence of the tip shape.